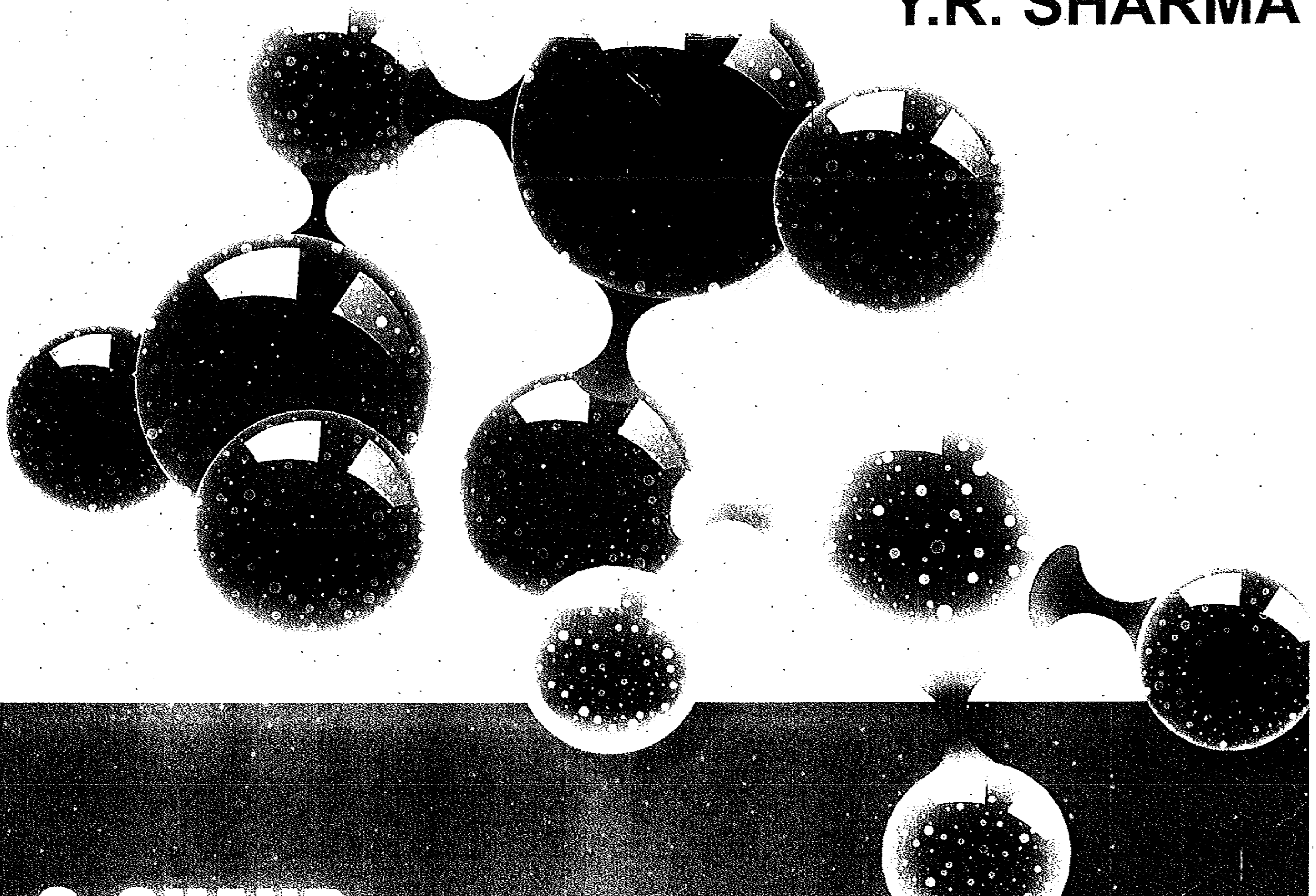
Revised Edition

ELEMENTARY ORGANIC SPECTROSCOPY

PRINCIPLES AND CHEMICAL APPLICATIONS

FOR B.Sc. (HONS.), POSTGRADUATE STUDENTS OF ALL INDIAN UNIVERSITIES AND COMPETITIVE EXAMINATIONS

Y.R. SHARMA

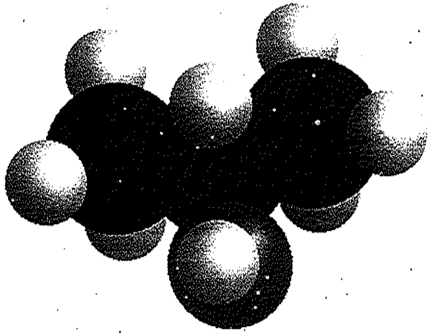


ORGANIC SPECTROSCOPY

PRINCIPLES AND CHEMICAL APPLICATIONS

FOR B.Sc. (HONS.), POSTGRADUATE STUDENTS OF ALL INDIAN UNIVERSITIES AND COMPETITIVE EXAMINATIONS

Y.R. SHARMA
Postgraduate Department of Chemistry,
D.A.V. College, Jalandhar, India.



S. CHAND
PUBLISHING
empowering minds

S. CHAND & COMPANY PVT. LTD.
(AN ISO 9001 : 2008 COMPANY)
RAM NAGAR, NEW DELHI-110055

S.CHAND
PUBLISHING
empowering minds

S. CHAND & COMPANY PVT. LTD.
(An ISO 9001 : 2008 Company)
Head Office: 7361, RAM NAGAR, NEW DELHI - 110 055
Phone: 23672080-81-82, 9899107446, 9911310888 Fax: 91-11-23677446
www.schandpublishing.com; e-mail: helpdesk@schandpublishing.com

Branches
Ahmedabad : Ph: 27541965, 27542369, ahmedabad@schandpublishing.com
Bengaluru : Ph: 22268048, 22354008, bangalore@schandpublishing.com
Bhopal : Ph: 4274723, 4209587, bhopal@schandpublishing.com
Chandigarh : Ph: 2725443, 2725446, chandigarh@schandpublishing.com
Chennai : Ph. 28410027, 28410058, chennai@schandpublishing.com
Coimbatore : Ph: 2323620, 4217136, coimbatore@schandpublishing.com (Marketing Office)
Cuttack : Ph: 2332580; 2332581, cuttack@schandpublishing.com
Dehradun : Ph: 2711101, 2710861, dehradun@schandpublishing.com
Guwahati : Ph: 2738811, 2735640, guwahati@schandpublishing.com
Hyderabad : Ph: 27550194, 27550195, hyderabad@schandpublishing.com
Jaipur : Ph: 2219175, 2219176, jaipur@schandpublishing.com
Jalandhar : Ph: 2401630, 5000630, jalandhar@schandpublishing.com
Kochi : Ph: 2378740, 2378207-08, cochin@schandpublishing.com
Kolkata : Ph: 22367459, 22373914, kolkata@schandpublishing.com
Lucknow : Ph: 4026791, 4065646 lucknow@schandpublishing.com
Mumbai : Ph: 22690881, 22610885, mumbai@schandpublishing.com
Nagpur : Ph: 6451311, 2720523, 2777666, nagpur@schandpublishing.com
Patna : Ph: 2300489, 2302100, patna@schandpublishing.com
Pune : Ph: 64017298, pune@schandpublishing.com
Raipur : Ph: 2443142, raipur@schandpublishing.com (Marketing Office)
Ranchi : Ph: 2361178, ranchi@schandpublishing.com
Siliguri : Ph: 2520750, siliguri@schandpublishing.com (Marketing Office)
Visakhapatnam : Ph: 2782609 visakhapatnam@schandpublishing.com (Marketing Office)

First Edition 1980
Subsequent Editions and Reprints 1984, 86, 89, 90, 92, 93, 94, 95, 96, 97, 99, 2000, 2001, 2002, Fourth Revised and Enlarged (Multicolour) Edition 2007; Reprints 2008, 2009 (Twice), 2010, 2011 (Twice), 2012; Fifth Revised Edition 2013; Reprints 2014, 2015
Reprint 2016

ISBN : 978-81-219-2884-7 Code : 1004C 305

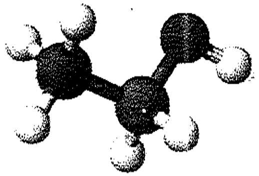
This book is for Sale in India & other SAARC Countries only.

PRINTED IN INDIA

By Vikas Publishing House Pvt. Ltd., Plot 20/4, Site-IV, Industrial Area Sahibabad, Ghaziabad-201010 and Published by S. Chand And Company Pvt. Ltd., 7361, Ram Nagar, New Delhi -110 055.

Dedicated
To
My Father

PREFACE TO THE FIFTH EDITION



The warm reception accorded to the fourth edition of Elementary Organic Spectroscopy and its subsequent reprints has provided me a great deal of encouragement to present the fourth edition of this book. The subject-matter presented in the book is sufficiently comprehensive and the knowledge gained through it will make easy to identify an unknown compound. The massive scope of the subject dictates that all possible visual assistance be available to the students. This has been done by presenting a large number of spectral diagrams which have been added in this edition. Their interpretation serve to reinforce as well as assist the students in learning the subject. This attempt also helps the students to develop an intutive feel in using spectroscopy to solve structural problems. The main features of the present edition are :

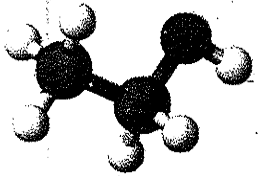
- Multichoice questions are added in each chapter. Some numerical problems are also included where required.
- A chapter on 'Raman Spectroscopy' has been added to meet the demand of a large number of students and teachers. This technique forms a part of curriculum in most of the universities and is dealt here in reasonable detail.
- Each chapter in the text is made more elaborate by induction of suitable material in the form of applications, numerical problems and explanation of new spectra. Important features for each technique, Short Question with Answers, Important problems (Solved) form special features of the fifth edition.
- A number of problems have been given for the students to check their competence.
- Extensive summarises have been placed at the end of each shapter in order to review each topic and highlight the main points.
- Every attempt is made to retain the comprehensive character of the text so as to ensure that it continues to be one volume text for the students studying Organic Chemistry at the Graduate and Postgraduate levels.
- A large number of new figures have been added in the text and all old figures have been redesigned.
- In the ultra-violet spectroscopy, Polycyclic hydrocarbons and their spectra have been discussed and proton nuclear magnetic resonance spectra of carbocations have been given.

I express my gratitude to my colleagues and friends who gave useful suggestions and took keen interest in the revision of the book. Thanks are due to my wife, Mrs. Saroj Sharma for the secretarial assistance which she rendered during the revision of the book. I will welcome suggestions and healthy criticism of the subject-matter and style for the further improvement of this book.

Jalandhar

Y.R. SHARMA
Ph: 0181-2250012
e-mail: sharma_yr1940@ymail.com

PREFACE TO THE FIRST EDITION



Methods based on relationships between structural features and physical properties are now making an ever increasing contribution to organic chemistry, not only in the elucidation of structure, but also in analytical and preoperative work. The advantages of these methods are obvious particularly in the study of tautomeric, conformation and other equilibrium. It is, therefore, not surprising that the growing availability of physical methods has altered both the scope and pace of organic chemistry. Many recent successes in the determination of the structures of complex natural products would have remained out of reach without them and their contribution in widening our understanding of the reactivity of organic compounds can hardly be overestimated. This appreciation of the power of these methods prompted the author to venture on this elementary introduction to the absorption techniques in organic spectroscopy.

The book is written specifically for the undergraduate and it is hoped, that it will render valuable help to the postgraduate students as well. The primary aim of this introductory book is to provide a broad survey of the methods and special care is taken on the application of these methods on selected representative molecules which will give clear insight into the subject. The text will be found to be graded from known to unknown and from very simple to difficult problems. The worked examples and unsolved problems with their answers in the index have been very carefully selected to cover as many as possible of the important aspects of the subject matter in the space available. It is hoped that the book will be warmly received and will prove beneficial to the students and the teachers alike.

I simply fumble for words to express my heavy debt of gratitude towards Dr. O.P. Vig, Professor and Head, Department of Chemistry, Punjab University, Chandigarh, who was gracious enough for sparing time out of his busy schedule to go through the book and then writing foreword to it. It has, of course, enhanced its value and prestige.

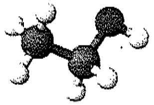
I express my gratitude to my colleagues and friends, who, by their encouragement, interest and advice helped me to write this book. My sincere thanks are particularly due to Dr. I.R. Trehan, Reader in Organic Chemistry, Punjab University, Chandigarh, who took all the pains in reading the whole of the manuscript and gave valuable suggestions. Thanks are also due to Sh. G.D. Sharma, Head of the Post-Graduated Deptt. of Chemistry, D.A.V. College, Jalandhar, Dr. K.D. Sharma, lecturer in Chemistry, Govt. College, Hoshiarpur, and Sh. M.L. Sehgal, lecturer in Chemistry, D.A.V. College, Jalandhar, for making valuable criticisms.

I am grateful to Sh. Shyam Lal Gupta, Managing Director, S. Chand and Company Ltd., New Delhi and Sh. S.K. Moudgil, Branch Manager, Jalandhar, for the interest they took during the preparation of the book.

Finally I thanks my wife, Mrs. Saroj Sharma who inspired me during the preparation of the text. I will welcome any criticism of the subject matter and style for further improvement of this new enterprise.

Y.R. SHARMA

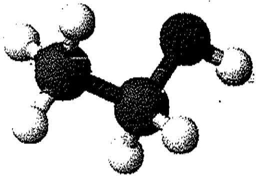
ACKNOWLEDGEMENT



I am extremely grateful to the authorities of Varian Associates, Palo Alto, California (U.S.A.) for their kind permission to reproduce Nuclear magnetic resonance spectra from their catalogues Vol. I and Vol.II. I am also thankful to the Department of Chemistry, Punjab University, Chandigarh for the courtesy shown in scanning some of the spectra for reproduction in the text.

Y.R. SHARMA

CONTENTS

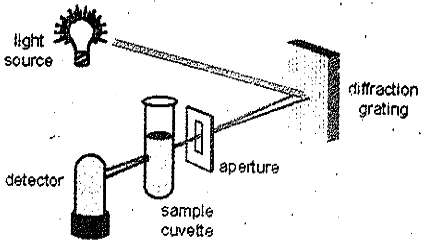


Pages

CHAPTER 1: INTRODUCTION

1.1 Electro-magnetic radiations 1
1.2 Units 3
1.3 Electromagnetic Spectrum and Absorption of Radiations 5
Further Readings 8
Review Questions 8
Multiple Choice Questions 8

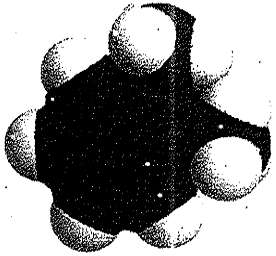
CHAPTER 2: ULTRA-VIOLET AND VISIBLE SPECTROSCOPY



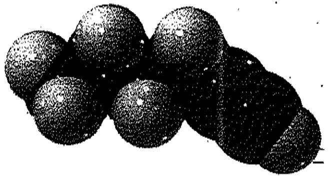
2.1 Introduction 11
2.2 The Absorption Laws 12
2.3 Measurement of Absorption Intensity 16
2.4 Instrumentation 16
2.5 Formation of Absorption Bands 18
2.6 Theory of Electronic Spectroscopy 19
2.7 Types of Electronic Transitions 19
2.8 Transition Probability 22
2.9 The Chromophore Concept 23
2.10 Auxochrome 24
2.11 Absorption and Intensity shifts 25
2.12 Types of Absorption bands 26
2.13 Solvent Effects 27
2.14 Effect of Temperature and Solvent on the Fineness of Absorption Band 29
2.15 Conjugated dienes 30
2.16 Woodward-fieser Rules for Calculating Absorption Maximum in Dienes 33
2.17 Distortion of the Chromophore 37
2.18 Poly-enes and Poly-ynes 38
2.19 Ultra-violet Absorption in α, β-unsaturated Carbonyl Compounds 40
2.20 Woodward-fieser rules for Calculating Absorption Maximum in α, β-unsaturated carbonyl compounds 42
2.21 Compounds with N to O Bonds 47
2.22 Benzene and its Derivatives 47
2.23 Rules for Calculating Absorption Maximum for Derivatives of Acyl-benzenes 48
2.24 Absorption Spectra of Condensed Ring Systems 49
2.25 Heterocyclic Compounds 49
2.26 Steric Hindrance and Coplanarity 51
2.27 Fluorescence and Phosphorescence 52
2.28 Electronic Transitions for Charge Transfer Complexes 53

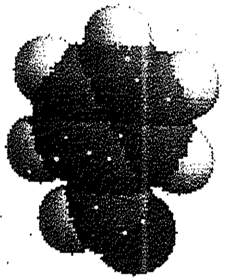
2.29 Study of keto-enol Tautomerism 55
2.30 Applications of ultra-violet Spectroscopy 56
2.31 Important Features in Electronic Spectroscopy 58
2.32 Important Terms and Definitions in Ultraviolet Spectroscopy 63
2.33 Short Questions with Answers 64
Further Readings 68
Review Questions 68
Multiple Choice Question 72

CHAPTER 3: INFRA-RED SPECTROSCOPY



3.1 Introduction 75
3.2 Principle of Infra-red Spectroscopy 76
3.3 Theory—Molecular vibrations 76
3.4 Vibrational Frequency 78
3.5 Number of fundamental vibrations 80
3.6 Selection Rules 83
3.7 Factors Influencing Vibrational Frequencies 84
3.8 Scanning of infra-red Spectrum 90
3.9 Sampling Techniques 91
3.10 Finger Print Region 96
3.11 Spectral Features of Some Classes of Organic Compounds 97
3.11 A Hydrocarbons 98
3.11 A_1 Alkanes and alkyl residues 98
3.11 A_2 Alkenes 100
3.11 A_3 Alkynes 102
3.11 A_4 Cycloalkanes 102
3.11 A_5 Aromatic hydrocarbons 103
3.11 B Halogen compounds 106
3.11 C Alcohols and Phenols 108
3.11 D Ethers 112
3.11 E Carbonyl compounds 114
3.11 E_1 Aldehydes and ketones 114
3.11 F Esters and lactones 123
3.11 G Carboxylic acids 124
3.11 H Acid halides 126
3.11 I Acid anhydrides 127
3.11 J Amides 129
3.11 K Lactams 130
3.11 L Amino acids 132
3.11 M Amines 132
3.11 N Anilides 135
3.11 O Nitro and Nitrite compounds 136
3.11 P Nitriles and related compounds 137
3.11 Q Thiols, Sulphonic acid and Sulphonamides 139



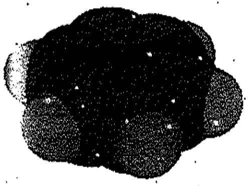


3.11 R Hetroaromatic compounds 140
3.12 Important Features in infra-red Spectroscopy 141
3.13 Applications of infra-red Spectroscopy 144
3.14 Simple Problems on infra-red Spectroscopy 147
3.15 Short questions with Answers 150
3.16 Important tips for Interpreting an infra-red Spectrum 155
3.17 Important Terms and Definitions in infra-red Spectroscopy 157
Further Reading 158
Review Questions 159
Multiple Choice Questions 161

CHAPTER 4: RAMAN SPECTROSCOPY

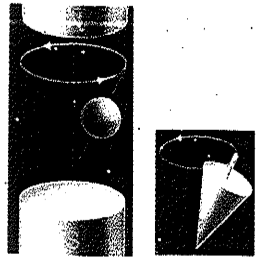
4.1 Introduction 164
4.2 Quantum Theory of Raman Effect 164
4.3 Theory of Raman Spectra (Stoke's and antistoke's lines) 164
4.4 Instrumentation 167
4.5 Conditions for Raman spectroscopy 167
4.6 Equivalence of Beer lambert law of absorption in Raman Scattering 168
4.7 Characteristic Parameters of Raman lines 168
4.8 Raman spectra of diatomic molecules 170
4.9 Rotational-Vibrational Raman Spectra 173
4.10 Vibrational Raman Spectra of Polyatomic Molecules 174
4.11 Rule of Mutual Exclusion Principle 175
4.12 Moment of Inertia of diatomic molecules, and Raman Spectroscopy 175
4.13 Infra-red and Raman Spectra are Complementary 177
4.14 Structure Elucidation by Raman Spectroscopy 178
4.15 Numericals On Raman Spectroscopy 179
4.16 Importance of Raman Spectra 181
4.17 Applications of Raman Spectroscopy 182
4.18 Important Terms and Definitions in Raman Spectroscopy 184
4.19 Short Questions with Answers 185
Further Reading 187
Review Questions 187
Multiple Choice Questions 188

CHAPTER 5: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY



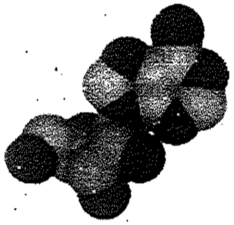
5.1 Introduction 191
5.2 Relaxation Process 194
5.3 Number of Signals 195
5.4 Instrumentation 198
5.5 Positions of Signals (Chemical Shift) 198
5.6 Internal Standards 200
5.7 Shielding and Deshielding Effects* 201

5.8 Factors Influencing Chemical Shift 203
5.9 Solvents Used 207
5.10 Peak Area and Proton Counting 209
5.11 Splitting of the Signals 210
5.12 Spin-spin Coupling 211
5.13 Nmr Absorption by other Nuclei 217
5.14 Calculating the Ratio in the heights of the Signals 219
5.15 Chemical Exchange (Proton Exchange Reactions) 220
5.16 Coupling Constant (J) 222
5.17 Restricted Rotation 231
5.18 Important Tips for Interpreting an Nmr Spectrum 232
5.19 Some Important Nmr Spectra 233
5 20 Double Resonance (Spin Decoupling) 239
5.21 Nuclear Overhauser Effect (N.O.E.) 241
5.22 Nmr Spectrum at more than one Radio-Frequency 242
5.23 Deuterium Exchange Reactions 242
5.24 C13–nmr Spectroscopy 242
5.25 F19– nmr 244
5.26 Nuclear Magnetic Resonance Spectra of Carbocations 244
5.27 Applications of Nmr Spectroscopy 245
5.28 Important Features in Nuclear Magnetic Resonance Spectroscopy 247
5.29 Simple Problems on Nuclear Magnetic Resonance 250
5.30 Short Questions with Answers 256
Further Reading 262
Review Questions 262
Multiple Choice Questions 265



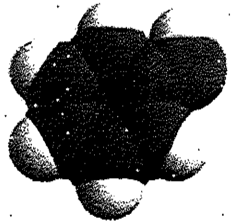
CHAPTER 6: NUMERICAL PROBLEMS ON UV; IR AND NMR

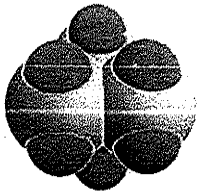
6.1 Double bond and/or Ring equivalents 267
6.2 Problem set with solutions
(Problems 1–30) 269
Problem set I (Unsolved)
(Problems 1–26) 284
Problem set II (Unsolved)
(Problems 27–50) 287

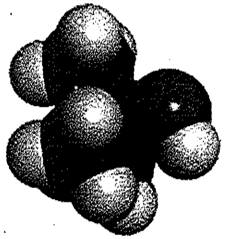


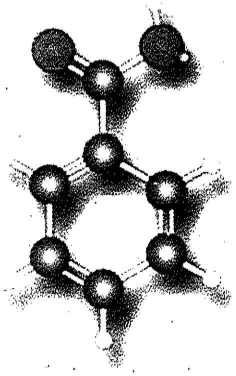
CHAPTER 7: MASS SPECTROMETRY

7.1 Basic Principles 291
7.2 Theory 292
7.3 Instrumentation 292
7.4 Mass Spectrum 295
7.5 Determination of Molecular Formula 297
7.6 McLafferty Rearrangement 298
7.7 Metastable Ions or Peaks 299
7.8 The Nitrogen Rule 301
7.9 General Fragmentation Modes 302
7.10 Important Features of the Mass Spectra of Hydrocarbons 305
7.11 A Alkenes (Olefins) 308
7.11 B Acetylenes (Alkynes) 308
7.11 C Cycloalkanes 309
7.11 D Cycloalkenes and Cycloalkynes 309
7.12 Aromatic Compounds 311
7.13 Alcohols 315
7.14 Phenols 321
7.15 Thiols and Thiophenols 322
7.16 Ethers, Acetals and Ketals 324
7.17 Aliphatic Aldehydes and Ketones 326
7.18 Cyclic ketones 329
7.19 Aliphatic and Aromatic Acids 331
7.20 Esters 332
7.21 Amides 334
7.22 Halogen Compounds 335
6.23 Amines 337
6.24 Nitro Compounds 339
7.25 Aliphatic Nitriles 340
7.26 Important Features in Mass Spectrcscopy 340
7.27 Simple Problems on Mass spectroscopy 343
7.27 Short Questions with Answer 345
Further Reading 350
Review Questions 350
Numerical Problems on Mass Spectrometry 351
Multiple Choice Questions 352
Answers to Problems 354
Subject index 357
Compound index 364







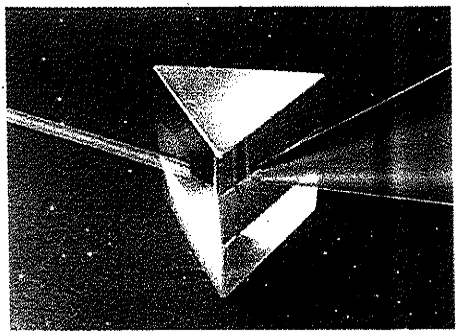


CHAPTER

1

Introduction

1.1 Electromagnetic radiations
1.2 Units
1.3 Electromagnetic Spectrum and Absorption of Radiations



1.1 Electromagnetic Radiations

It was believed that light travels in a straight line. But this concept could not explain some important phenomena like Interference, Refraction, Diffraction etc. To explain these phenomena, light is supposed to travel in waves. Visible light is a form of energy. It can be explained by two complimentary theories, the corpuscular theory and the wave theory. All the properties of light can be explained by considering both the theories.

According to the wave theory, light travels in the form of waves. It was believed that radiant energy is emitted by fluctuation of electric charge and magnetic field. Like light, there are various forms of electromagnetic radiations such as Ultra-violet, Infra-red, X-rays, Radio-waves etc. Some of the important characteristics of electromagnetic radiations are :

(*i*) These are produced by the oscillation of electric charge and magnetic field residing on the atom. The electric and magnetic components are mutually perpendicular to each other and are coplanar (See Fig. 1.1).

(*ii*) These are characterised by their wavelengths or frequencies or wavenumbers.

(*iii*) The energy carried by an electromagnetic radiation is directly proportional to its frequency. The emission or absorption of radiation is quantised and each quantum of radiation is called a **photon**.

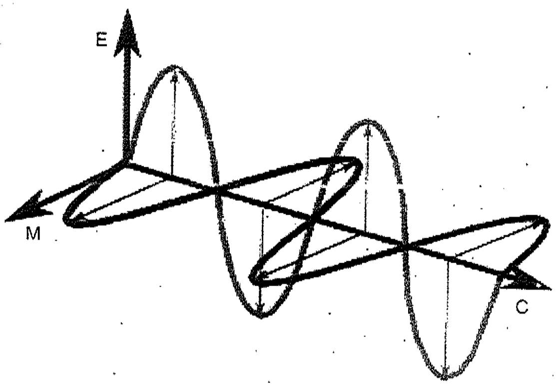
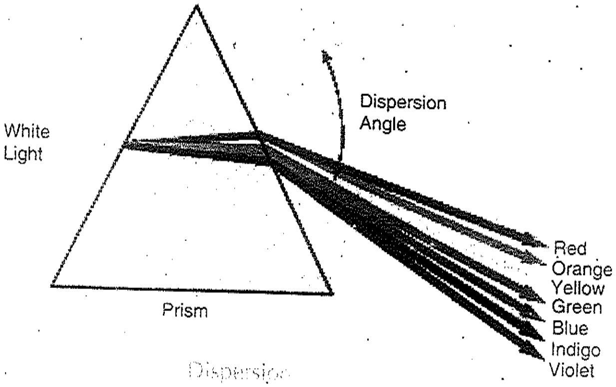


Fig. 1.1. Planes of Electromagnetic waves.

(*iv*) All types of radiations travel with the same velocity and no medium is required for their propagation. They can travel through vacuum.

(*v*) When visible light (a group of electromagnetic radiations) is passed through a prism, it is split up into seven colours which correspond to definite wavelengths. This phenomenon is called **dispersion**. Thus, a group of electromagnetic radiations can be split up into various components for analysis.



Dispersion

The study of spectroscopy* deals with emission as well as absorption spectra. An emission spectrum is produced by the emission of radiant energy by an excited atom. The excitation of atoms can be brought about thermally (by heating the substance strongly) or electrically (by passing electric discharge through the vapours of the substance at a very low pressure). When electric discharge is passed through the vapours of the substance, energy is absorbed and electrons in the ground state are promoted to meta-stable states. When electrons from the meta stable state jump to the lower energy state, then some energy of definite frequency is released as radiation. If this radiation emitted is analysed with the help of a spectroscope, an emission spectrum is observed.

---

* Spectroscopy may be defined as the interaction between the matter and electromagnetic radiations.

If electromagnetic radiations (of certain wavelength range) are passed through the substance under analysis for sometime, then radiations of certain wavelengths are absorbed by the substance. The wavelengths which are absorbed characterise some particular functional groups present in the compound or the compound itself. This dark pattern of lines which correspond to the wavelengths absorbed is called Absorption spectrum. After absorption, the transmitted light is analysed by the spectrometer relative to the incident light of a given frequency. In absorption spectrum, the absorbed energy may heat up the sample or is re-emitted.

1.2 Units

(*a*) **Wavelength.** It is the distance between the two adjacent crests (C—C) or troughs (T—T) in a particular wave. It is denoted by the letter λ (lambda). It can be expressed in Angstrom units or in millimicrons (mμ).

$$1\ \text{Å} = 10^{-8}\ \text{cm}; \qquad 1\ \text{m}\mu = 10^{-7}\ \text{cm}.$$

Visible light constitute waves ranging from 3800Å (violet end) to 7600 Å (Red end). Different colours of light have different values of their wavelengths. Human eye is sensitive only to this small visible range and cannot detect ultraviolet light (λ < 3800 Å) and infra-red radiations (λ > 7600 Å). Ultraviolet light can be detected by photoelectric cell and infra-red light can be detected photographically. In some techniques like ultraviolet and infra-red spectroscopy, the common unit is wavelength.

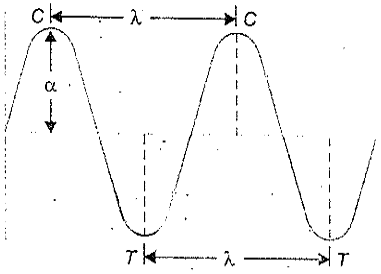


Fig. 1.2. Wave motion.

(*b*) **Wave number.** It is the reciprocal of wavelength and it is expressed in per centimeter. In other words, it is defined as the total number of waves which can pass through a space of one cm. It is expressed as $\bar{\nu}$. It is frequently used in Infra-red technique. If the wavelength of a light radiation is known, the corresponding wave number can be calculated. For example, if the wavelength of a radiation is 2.5 μ*, then the corresponding wave number can be calculated as follows :

$$\lambda = 2.5\ \mu$$
$$= 2.5 \times 10^{-4}\ \text{cm}.$$

∴ Wave number

$$\bar{\nu} = \frac{1}{\lambda \text{ in cm}} = \frac{1}{2.5 \times 10^{-4}\ \text{cm}}$$
$$= 4000\ \text{cm}^{-1}$$

(*c*) **Frequency.** It is defined as the number of waves which can pass through a point in one second. It is expressed as ν (nu) in cycles per second or in Hertz (Hz) where 1 Hz = 1 cycle sec^{-1}

$$\text{Frequency} \propto \frac{1}{\text{Wavelength}}$$

Greater the wavelength, smaller is the frequency.

---

* μ represents micron.

Frequency $\nu = \frac{c}{\lambda}$

where c = Velocity of electromagnetic radiation
$= 2.998 \times 10^{10}$ cm sec^{-1}.

We know that the wavelength range of visible light is 3800 Å – 7600 Å. The corresponding frequency range can be calculated as follows :

(*a*) $\lambda = 3800$ Å
$= 3800 \times 10^{-8}$ cm.

$$\therefore \quad \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10} \text{ cm sec}^{-1}}{3800 \times 10^{-8} \text{ cm}}$$
$$= \mathbf{7.88 \times 10^{14} \ sec^{-1}}$$
$$= 7.88 \times 10^{14} \text{ Hz} = \mathbf{7.88 \times 10^{8} \ MHz}$$

(*b*) When $\lambda = 7600$ Å

$$\nu = \frac{2.998 \times 10^{10} \text{ cm sec}^{-1}}{7600 \times 10^{-8} \text{ cm}}$$
$$\nu = \mathbf{3.94 \times 10^{14} \ sec^{-1}}$$
$$= \mathbf{3.94 \times 10^{8} \ MHz}$$

Thus, the corresponding frequency range of the visible light is 7.88×10^{14} cycles per second to 3.94×10^{14} cycles per second or 7.88×10^{8} MHz to 3.94×10^{8} MHz.

(*d*) **Energy.** Energy of a wave of the particular radiation can also be calculated by applying the relation :

$$E = h\nu = h \cdot \frac{c}{\lambda}$$

Where h = Planck's constant
$= 6.626 \times 10^{-27}$ erg sec.
ν = Frequency of radiation in cycles sec^{-1}
c = Velocity of electromagnetic radiation
λ = Wavelength in centimeters.

The energy of the light radiation can be calculated in ergs which can also be converted into kcal mole^{-1}.

EXAMPLE 1. *Calculate the energy associated with a radiation having wavelength 4000 Å. Give answer in kcal mole^{-1} and also in kilo Joules mole^{-1}.*

SOLUTION.

$$\lambda = 4000 \text{ Å} = 4000 \times 10^{-8} \text{ cm}$$
$$E = h \cdot \frac{c}{\lambda}$$
$$= \frac{6.628 \times 10^{-27} \text{ erg sec} \times 2.998 \times 10^{10} \text{ cm sec}^{-1}}{4000 \times 10^{-8} \text{ cm}}$$
$$= 4.968 \times 10^{-12} \text{ ergs}$$
$$= \frac{4.968 \times 10^{-12} \times 6.023 \times 10^{23}}{4.18 \times 10^{10}} = \mathbf{71.6 \ kcals \ mole^{-1}}$$

Also 1 kcal = 4.184 kJ

$$\therefore \quad E = 71.6 \times 4.134 = \mathbf{299.5 \ kJ \ mole^{-1}}.$$

1.3 Electromagnetic Spectrum and Absorption of Radiations

The arrangement of all types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is known as complete electromagnetic spectrum. The visible spectrum (from violet to red through rainbow colours) represents only a small portion of the electromagnetic spectrum. If we arrange all types of electromagnetic radiations in order of their increasing wavelengths, then the portion above the visible region is called Infra-red while that below it is the ultra-violet region. Infra-red radiations have longer wavelengths and are thus, less energetic. Cosmic rays carry high energy while radiowaves are least energetic. Microwaves have larger wavelengths and are used in telephone transmission.

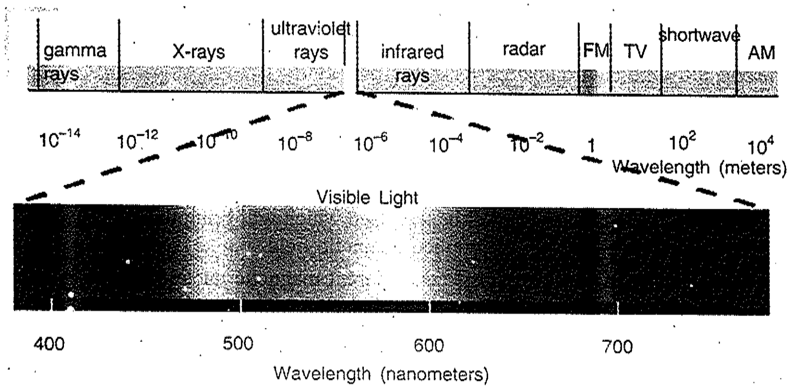


Fig. 1.3. Electromagnetic spectrum.

Although, all types of radiations travel as waves with the same velocity, yet they differ from one another in certain properties.

For example, X-rays can pass through glass and muscle tissues. Radiowaves can pass through air. Visible, Ultraviolet and Infra-red radiations can be bent by reflection or diffraction in a prism and so on.

If some light radiation is passed through a sample of an organic compound, then some of the wavelengths are absorbed while others belonging to that light source remain unaffected. A molecule can only absorb radiation of certain frequency, if there exists within a molecule an energy transition of magnitude, ΔE which is equal to $h\nu$. It is found that when light radiations are passed through an organic compound, then electrons of the component atoms are excited. In addition, the vibrational and the rotational energies of the molecules as a whole are quantised. Thus, any wavelength of light that a particular molecule will absorb will be due to the changes in the electronic, vibrational or rotational energy levels permissible for its atoms. The wavelengths absorbed are measured with the help of a **spectrometer**. If we plot the changes in absorption against wavelengths, we get certain absorption bands which are highly characteristic of a compound and the technique provides an excellent tool to ascertain the molecular structure of an unknown substance.

In an electromagnetic spectrum, we may note that :

(*i*) Visible and ultra-violet radiations cover the wavelength range from 200-800 mμ. The absorption of radiation in this region causes the excitation of π electron in a conjugated or an unconjugated system. In case of a conjugated system, the separation between the ground state and the excited energy level will be less and hence absorption occurs at a longer wave-length. Also carbonyl group of an aldehyde or a ketone absorbs at some characteristic wavelengths. Thus, an ultra-violet or visible spectrum is quite useful for the detection of conjugation, carbonyl group etc. and may not provide any information about the remaining part of the molecule.

(*ii*) The Infra-red radiations which cover the wavelength range from 0.8 to 2.5 μ constitute **near Infra-red region** and that from 15 to 25 μ is called **far Infra-red region**. The most useful region for Infra-red spectroscopy is 2.5 to 15 μ. These radiations are of higher wavelengths and are hence, less energetic. The absorption of radiation by an organic compound in this region causes molecular vibrations. The changes in the vibrational levels are accompanied by the changes in the rotational levels. Thus, certain bands appear which characteristically absorb for the stretching vibrations and are very helpful in structure elucidation. The absorptions at higher wave-length in the infra-red region (Finger print region) are most characteristic of a compound and also help in distinguishing one compound from the other. Although, more useful than ultra-violet technique, it does not reveal fully the environment effects in a molecule.

(*iii*) NMR spectroscopy provides a complete insight into the environment and the arrangement of atoms within a molecule. For this technique, radiations of longest wavelength range, *i.e.*, Radiowaves are useful. A sample under investigation is placed in a strong magnetic field and irradiated with Radiowaves. Depending upon the strength of the magnetic field employed, radiations of definite wavelength (or frequency) will be absorbed which will bring the nuclear magnets into specific orientations with respect to the applied magnetic field.

Due to the different environmental effects, different magnetic nuclei (say protons, N^{15}, C^{13}, F^{19}, P^{31} atoms etc.) will feel the applied magnetic field differently. Hence, absorptions at different field strengths will correspond to different sets of protons or magnetic nuclei. From the Ultra-violet, Infra-red and NMR spectra of an unknown compound, it is possible to determine its structure.

Table 1.1 :

Radiation absorbed	*Effect on the molecule of a substance and information obtained*
(*i*) **Ultra-violet** (190–400 nm) and **visible** (400–800 nm)	Changes in electronic energy levels within the molecule, conjugated unsaturation, conjugation with non-bonding electrons, extent of π-electron system.
(*ii*) **Infra-red** 667 – 4000 cm^{-1}	Changes in the vibrational and rotational movements of the molecule. Detection of almost all functional groups which have specific vibrational frequencies such as $C = O$, $O—H$, NH_2, $C \equiv C$ etc.
(*iii*) **Radio-frequency** Frequency 60-300 MHz	Nuclear magnetic resonance, induces changes in the magnetic properties of certain atomic nuclei, notably that of hydrogen (hydrogen atoms in different environments can be detected, counted and analysed for structure determination.
(*iv*) **Electron beam impact** 70 eV, 6000 kJ mol^{-1}	Ionisation and fragmentation of the molecule into a spectrum of fragment ions (determination of molecular weight and deduction of molecular structure from the fragments obtained)

PRACTICE PROBLEMS

1. Average the following radiations in increasing order of wavelength uv, X-rays, Radio waves, Microwaves, Visible

[**Ans.** X-rays < uv < Visible < Microwaves < Radio waves]

2. In which region of the electromagnetic spectrum do the following frequencies lie;

(*i*) 40 cm^{-1} (*ii*) 90 MHz (*iii*) 12000 cm^{-1} (*iv*) 70000 cm^{-1}

[**Ans.** (*i*) Far-infrared (*ii*) Microwave (*iii*) Visible (*v*) Vacuum ultraviolet]

3. Identify the region in which the following energies lie:

(*i*) 1050 cm^{-1} (*ii*) 700 nm and (*iii*) 300 MHz.

[**Ans.** (*i*) Near infra-red (*ii*) Visible (*iii*) Microwave]

EXAMPLE 2. *(a) Convert a wavelength of 4000 A° into nanometers (nm)*

(b) Convert 90 MHz into cm^{-1}.

(c) The mass of hydrogen atom is 1.6605×10^{-27} kg. What is the reduced mass of hydrogen molecule?

SOLUTION. (*a*) It is known that $1 \text{ nm} = 10^{-9}$ m. or $1\text{m} = 10^{9}$ nm.

Given wavelength, $\lambda = 4000 \text{ A}° = 4000 \times 10^{-8} \text{ cm} = 4000 \times 10^{-10}$ m.

Thus, $4000 \times 10^{-10} \text{ m} \times 10^{9} \text{ nm} = \mathbf{400 \text{ nm}}$

(*b*) Given frequency, $v = 90 \text{ MHz} = 90 \times 10^{6} \text{ Hz} = 90 \times 10^{6}\text{s}^{-1}$.

We know $$v = \frac{c}{\lambda} = c\bar{v}$$

Wave number, $$\bar{v} = \frac{v}{c} = \frac{90\times10^{6}\text{s}^{-1}}{3\times10^{10}\text{cms}^{-1}} = \mathbf{3 \times 10^{-3} \ cm^{-1}}$$

(*c*) Mass of hydrogen atom, $^{m}\text{H} = 1.6605 \times 10^{-27}$ kg (Given)

Reduced mass of hydrogen molecule $$= \frac{m_H \times m_H}{m_H + m_H} = \frac{m^2H}{2mH} = \frac{1}{2}\text{mH}.$$

$$\therefore \text{ Reduced mass of hydrogen molecule} = \mu_{H_2} = \frac{1}{2} \times 1.6605 \times 10^{-27} \text{ kg}$$

$$= \mathbf{8.3025 \times 10^{-28} \ kg.}$$

Moment of Inertia:

The moment of inertia of rigid diatomic rotor is given by the following expression:

$$I = \mu r^2$$

Where I = moment of inertia, μ = reduced mass of rotor and

r = internuclear distance or bond distance in diatomic molecule.

EXAMPLE 3. *What is the moment of inertia of rigid diatomic rotor with bond distance equal to 130 pm and the reduced mass equal to 2×10^{-47} kg.?*

SOLUTION. Given that, internuclear distance, $r = 130 \times 10^{-12}$ m

Reduced mass, $\mu = 2 \times 10^{-47}$ kg

Thus, moment of inertia, $I = \mu r^2 = 2 \times 10^{-47} \text{ kg} \times (130 \times 10^{-12} \text{ m})^2$.

$$= \mathbf{3.38 \times 10^{-67} \ kg \ m^2}$$

EXAMPLE 4. *The moment of inertia of a diatomic molecule of reduced mass 4×10^{-26} kg is 2.5×10^{-45} kg m^2. What is the internuclear distance?*

SOLUTION. Given that, I (moment of inertia) = 2.5×10^{-45} kg m^2

Reduced mass, $\mu = 4 \times 10^{-26}$ kg

Substituting the values in : $I = \mu r^2$

$$2.5 \times 10^{-45} \text{ kg m}^2 = 4 \times 10^{-26} \text{ kg} \times r^2$$

$$\therefore \text{Internuclear distance, } r = \left(\frac{2.5\times10^{-45}\,\text{kg m}^2}{4\times10^{-26}\,\text{kg}}\right)^{1/2} = 2.5 \times 10^{-10} \text{ m}$$

$$= 2.5 \times 10^{-10} \times 10^{12} \text{ pm} = \mathbf{250\ pm}$$

FURTHER READING

1. K.W. Bentley; *Elucidation of Structure by physical and Chemical Methods*, Vol. XI, Part I, Interscience Publishers, New York.
2. W.G. Richards; P.R. Scott; *Structure and Spectra of Atoms*, Wiley Eastern Limited 1978.
3. E.U. Condon and G.H. Shortley; *The Theory of Atomic Spectra*, Cambridge University Press (1963).
4. C.J.Cresswell; O. Runquist and M.M. Campbell; *Spectral Analysis of Organic Compounds*, Burgess, Minneapotis (2nd edition, 1972).

REVIEW QUESTIONS

1. (*a*) What is meant by Electromagnetic radiations ? How do the wavelengths and frequencies of different types of electromagnetic radiations vary ?
   (*b*) Arrange the following radiations in order of their increasing wave-number.
   (*i*) Ultraviolet, X-rays, Visible light, Microwaves, Cosmic rays.
2. (*a*) Describe some important characteristics of Electromagnetic radiations.
   (*b*) Convert the following wavelengths in terms of wave-number in cm^{-1}.
   (*i*) 12.5 μ (*ii*) 285 mm
3. (*a*) Write a note on Electromagnetic spectrum and the absorption of radiations.
   (*b*) Explain Emission and Absorption spectra.
4. (*a*) If the energy difference between the two electronic states is 46.12 kcal mole^{-1}, what will be the frequency of the light emitted when the electron jumps from the higher energy state to the lower energy state ?
   (*b*) The wavelength associated with an ultra-violet radiation is 285 nm. Determine the energy associated with it in kcal mole^{-1}.
5. (*a*) Describe the range of the Electromagnetic radiations useful for ultraviolet and Infra-red spectroscopy.
   (*b*) What is the range of frequencies for visible light ? Express it in wavelengths and also in terms of wave-numbers.

MULTIPLE CHOICE QUESTIONS

1. The electromagnetic radiation in the frequency range $10^{19} - 10^{17}$ Hz belong to
   (*a*) uv spectrum (*b*) X-rays (*c*) I.R. (*d*) visible.
2. The radiation in the wavelength range 400-800 nm corresponds to
   (*a*) ultra-violet (*b*) Infra-red (*c*) visible (*d*) Far IR.

3. Radio frequency radiations are useful in causing transition for
   (*a*) Mass spectrum (*b*) NMR spectra (*c*) Raman spectra (*d*) None
4. The energies of E_1 and E_2 of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths, i.e. λ_1 and λ_2 will be:
   (*a*) $\lambda_1 = \frac{1}{2}\lambda_2$ (*b*) $\lambda_1 = \lambda_2$ (*c*) $\lambda_1 = 2\lambda_2$ (*d*) $\lambda_1 = 4\lambda_2$
5. The ionisation and fragmentation of the molecule into spectrum of fragment ions is caused by
   (*a*) Microwaves (*b*) IR radiations
   (*c*) electron beam impact of 70 eV (*d*) None of these
6. When the frequency of the incident radiation on a metallic plate is doubled, KE of the photoelectrons will be:
   (*a*) doubled (*b*) halved
   (*c*) more than doubled (*d*) increases but less than doubled

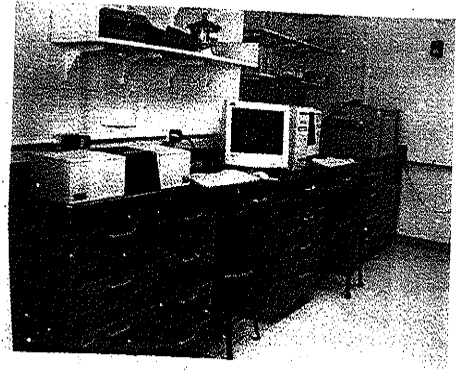
ANSWERS. 1. (*b*) 2. (*c*) 3. (*b*) 4. (*c*) 5. (*c*) 6. (*c*)

CHAPTER

2

Ultra-violet and Visible Spectroscopy

2.1 Introduction
2.2 The Absorption Laws
2.3 Measurement of Absorption Intensity
2.4 Instrumentation
2.5 Formation of Absorption Bands
2.6 Theory of Electronic Spectroscopy
2.7 Types of Electronic Transitions
2.8 Transition Probability
2.9 The Chromophore Concept
2.10 Auxochrome
2.11 Absorption and Intensity Shifts
2.12 Types of Absorption Bands
2.13 Solvent Effects
2.14 Effect of Temperature and Solvent on the Fineness of Absorption Band
2.15 Conjugated Dienes
2.16 Woodward-fieser Rules for Calculating Absorption Maximum in Dienes
2.17 Distortion of the Chromophore
2.18 Poly-enes and Poly-ynes
2.19 Ultra-violet Absorption in α, β-unsaturated Carbonyl Compounds
2.20 Woodward-fieser Rules for Calculating Absorption Maximum in α, β-unsaturated Carbonyl Compounds
2.21 Compounds with N to O Bonds
2.22 Benzene and its Derivatives
2.23 Rules for Calculating Absorption Maximum For Derivatives of Acyl Benzenes
2.24 Absorption Spectra of Condensed Ring Systems
2.25 Heterocyclic Compounds
2.26 Steric Hindrance and Coplanarity
2.27 Fluorescence and Phosphorescence
2.28 Electronic Transitions for Charge-transfer Complexes
2.29 Study of Keto-enol Tautomerism
2.30 Applications of Ultra-violet Spectroscopy
2.31 Important Features in Electronic Spectroscopy
2.32 Important Terms and definitions in Ultraviolet spectroscopy
2.33 Short Questions with Answers



2.1 Introduction

The alternate title for this technique is Electronic Spectroscopy since it involves the promotion of electrons (σ, π, n^* electrons) from the ground state to the higher energy state. It is very useful to measure the number of conjugated double bonds and also aromatic conjugation within the various molecules. It also distinguishes between conjugated and non-conjugated systems; α, β-Unsaturated carbonyl compounds from β, γ-analogues; homoannular and Heteroannular conjugated dienes etc. For visible and ultra-violet spectrum, electronic excitations occur in the range 200-800 mμ and involves the promotion of electrons to the higher energy molecular orbital.

Since the energy levels of a molecule are quantised, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. Clearly, if the substance is exposed to radiation of some different value of frequency, energy will not be absorbed and thus, light or radiation will not suffer any loss in intensity. If radiation of a desired or correct frequency is passed or made to fall on the sample of the substance, energy will be absorbed and electrons will be promoted to the higher energy states. Thus, light radiation on leaving the sample after absorption will be either less intense or its intensity may be completely lost.

Substances absorbing in the visible range will appear coloured to the human eye (For visible range – See Fig. 2.1). The wavelength of particular radiation absorbed can also be expressed in terms of frequency or energy in kcal mole^{-1}.

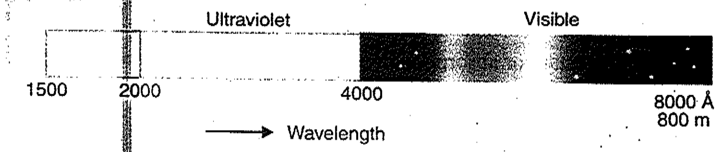


Fig. 2.1. The range of UV-visible Spectra.

$$1\mu = 10^{-4}\ \text{cm}$$
$$1\text{m}\mu = 1\ \text{nm}^{**} = 10^{-7}\ \text{cm} = 10\text{Å}$$

Let us calculate the energy associated with radiations having wavelength 280 mμ.

$$\lambda = 280\ \text{m}\mu = 280 \times 10^{-7}\ \text{cm}$$

We know that
$$E = h\nu$$
$$= h \cdot \frac{c}{\lambda} \qquad (h = 6.62 \times 10^{-27}\ \text{ergs sec.})$$

Avogadro's number $N = 6.023 \times 10^{23}$

4.18×10^7 ergs $= 1$ calorie

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10} \times 6.023 \times 10^{23}}{280 \times 10^{-7} \times 4.18 \times 10^{7} \times 10^{3}}\ \text{kcal mole}^{-1}$$
$$\cong \mathbf{100\ kcal\ mole^{-1}}.$$

Note. It is not advisable to keep the compounds in ultra-violet radiations except for taking the spectrum.

A record of the amount of light absorbed by the sample as a function of the wavelength of light in mμ or nm units is called absorption spectrum which generally consists of absorption bands.

---

* Non-bonding electrons.

** nm means nanometers.

The far ultra-violet region (below 200 mμ) is not much studied due to absorption by oxygen and nitrogen. Moreover, studies in these regions require vacuum instruments.

Problem P_2–1. Calculate the energy associated with radiations having wave-length 400 nm. Calculate the answer in kcals mole^{-1}.

2.2 The Absorption Laws

There are two laws which govern the absorption of light by the molecules. These are :

(*i*) Lambert's law and (*ii*) Beer's law

(*i*) **Lambert's Law** : It states that :

When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

Mathematically, the law is expressed as

$$-\frac{dI}{dx} = kI$$

where I = intensity of radiation after passing through a thickness x, of the medium.

dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, dx of the medium.

$-\frac{dI}{dx}$ = rate of decrease of intensity of radiation with thickness of the absorbing medium.

k = proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let I_0 be the intensity of radiation before entering the absorbing medium ($x = 0$).

Then I, the intensity of radiation after passing through any thickness, say x of the medium can be calculated as :

$$\int_{I_0}^{I}\frac{dI}{I} = -\int_{x=0}^{x=x} k\,dx$$

or

$$ln\frac{I}{I_0} = -kx \quad \text{or} \quad \frac{I}{I_0} = e^{-kx}$$

$$I = I_0 e^{-kx}$$

The intensity of the radiation absorbed, I_{abs} is given by :

$$I_{abs} = I_0 - I = I_0(1 - e^{-kx})$$

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10.

$$I = I_0\,10^{-ax}$$

where a = extinction coefficient of the absorbing medium

$$\left(a = \frac{k}{2.303}\right).$$

Note : For ultraviolet spectrum, the region from 200 mμ to 380 mμ (called quartz region) is considered. The molecular absorption in the *UV–VIS* region depends mainly on the electronic structure of the molecule. Depending upon the presence of a common group, the ultraviolet spectrum of a complex compound and that of a simple compound may be almost identical.

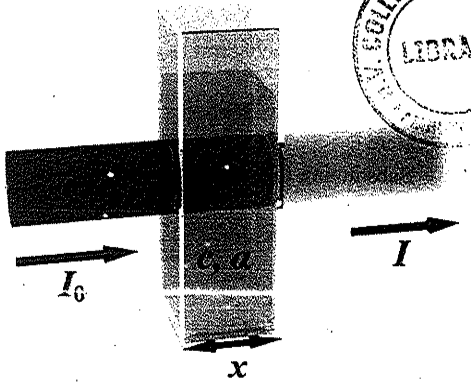
(*ii*) **Beer's Law** : This law states that: *When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.*

Mathematically, this law is stated as

$$-\frac{dI}{dx} = k' Ic$$

where c = conc. of the solution in moles litre^{-1}.

k' = molar absorption coefficient and its value depends upon the nature of the absorbing substance.



The Deeper the Glass, the Darker the view, the lesser of the incident Light that gets through

Suppose I_0 be the intensity of the radiation before entering the absorbing solution. (when $x = 0$), then the intensity of radiation, I after passing through the thickness x, of the medium can be calculated :

$$\int_{I_0}^{I}\frac{dI}{I} = -\int_{x=0}^{x=x} k'\,c\,dx$$

or

$$I = I_0\,e^{-k'cx}$$

The above equation can also be written by changing the nature of logarithm to the base 10.

$$I = I_0 .\, 10^{-a'cx}$$

Here $\frac{k'}{2.303} = a'$ where a' = molar extinction coefficient of the absorbing solution.

Beer's law can also be stated as:

When a monochromatic light is passed through a solution of an absorbing substance, its absorption remains constant when the conc (c) and the thickness of the absorption layer (x) are changed in the inverse ratio.

Alternative expression : On combining the two laws, the Beer-Lambert Law can be formulated as below :

$$\log\frac{I_0}{I} = \in .c.l = A$$

where

I_0 = Intensity of incident light
I = Intensity of transmitted light
c = Concentration of solution in moles litre^{-1}
l = Path length of the sample (usually 1 cm)
$\in$ = Molar extinction coefficient (or molar absorptivity)
A = Absorbance

Limitations of Beer Lambert Law : This law is not obeyed

(*i*) When different forms of the absorbing molecules are in equilibrium as in keto-enol tautomers.

(*ii*) When fluorescent compounds are present.

(*iii*) When solute and solvent form complexes through some sort of association.

EXAMPLE 1. *2.5×10^{-4} M solution of a substance in a 1 cm length cell at λ_{max} 245 nm has absorbance 1.17, Calculate $\in_{max}$ for this transition.*

We know that relation : $\in_{max} = \dfrac{A}{cl}$

Here $A = 1.17,\ c = 2.5 \times 10^{-4}\ M,\ l = 1$ cm

Substituting the values, we get

$$\in_{max} = \frac{1.17}{2.5 \times 10^{-4}\ \text{mol}\ l^{-1} \times 1\ \text{cm}} = \frac{1.17 \times 10^{4} \times 10^{3}}{2.5\ \text{mol. cm}^{-3} \times 1\ \text{cm}}$$

$$= 0.468 \times 10^{7}\ \text{cm}^{2}\ \text{mol}^{-1}$$

EXAMPLE 2. *When a UV light is passed through the given solution, the radiant power is reduced to 50%, calculate the absorbance.*

SOLUTION : Let the radiant power incident light $(I_0) = 2P$

Then the power of emerged beam $(I) = P$

Absorbance can be calculated by applying the relation.

$$A = \log\frac{I_0}{I} = \log\frac{2P}{P} = \log 2 = \mathbf{0.3020}$$

EXAMPLE 3. *When an incident beam of wavelength 3000A° was allowed to pass through 2 mm thick pyrex glass, the intensity of radiation was reduced to one tenth of its incident value. What part of the same beam will be transmitted through 1 mm thick same pyrex glass sheet?*

SOLUTION. First case. According to Lambert's law:

$$\log\frac{I}{I_0} = -k'x. \text{ Here } I = 10\% \text{ of } I_0 \text{ or } \frac{I}{I_0} = \frac{10}{100} = \frac{1}{10}$$

Given $x = 2$ mm $= 0.2$ cm.

Thus, $\log\dfrac{1}{10} = -k'(0.2\ \text{cm})$ or $k' = \dfrac{1}{0.2\,\text{cm}} = 5\ \text{cm}^{-1}$.

Second case. Now $x = 0.1$ cm

Substituting $k' = 5\ \text{cm}^{-1}$ in the expression for lambert's law, we get

$$\log\frac{I}{I_0} = -5\ \text{cm}^{-1} \times 0.1\ \text{cm} = -0.5$$

Taking antilogs, $\dfrac{I}{I_0} = \text{antilog}\ (-0.5) = \text{antilog}\ (\bar{1}.05) = 0.3162$

Thus, $I = 0.3162 \times I_0$

or Intensity of transmitted light = 31.62% of the intensity of incident light

EXAMPLE 4. *When a beam of light (5000A°) was allowed to pass through 4 mm thick glass sheet, the intensity of transmitted light was reduced to 20% of the initial value. What percentage of light of the same radiation will be absorbed by 2 mm thick glass sheet.*

SOLUTION. First case: Given $I_0 = 100,\ I = 20,\ x = 4$ mm $= 0.4$ cm.

Applying Lambert's law: $\log\dfrac{I}{I_0} = -kx$

Substituting the values: $\log\dfrac{20}{100} = -k\ (0.4\ \text{cm})$

or $\log\dfrac{100}{20} = k\ (0.4\ \text{cm})$ or $\log\dfrac{10}{2} = k\ (0.4\ \text{cm})$

Thus, $1 - \log 2 = k\ (0.4\ \text{cm})$ or $k = \dfrac{1 - 0.3010}{0.4\,\text{cm}} = 1.747\ \text{cm}^{-1}$.

Second Case: Given $x = 2$ mm $= 0.2$ cm.

Substituting $k = 1.747\ \text{cm}^{-1}$ in the lambert's law expression

$$\log\frac{I}{I_0} = -kx \quad\text{or}\quad \log\frac{I}{I_0} = -1.747\ \text{cm}^{-1} \times 0.2\ \text{cm} = -0.3494$$

Taking antilogs: $\dfrac{I}{I_0} = \text{antilog}\ (-0.3494) = \text{antilog}\ (\bar{1}.6506) = 0.4473$

Then, $I = 0.4473 \times I_0$

Hence, light absorbed, $I_{abs} = I_0 - I = I_0 - 0.4473\ I_0 = 0.5527\ I_0$

or I_{abs} = 55.27% of the intensity of incident light.

EXAMPLE 5. *A 0.01 M solution of a compound transmits 20% of the radiation in a container with path length equal to 1.5 cm. Calculate the molar extinction coefficient of the compound.*

SOLUTION. Here $\dfrac{I}{I_0} = \dfrac{20}{100} = 0.2$

Where I_0 = Intensity of incident light and I = Intensity of transmitted light.

Also, we know that, absorbance $A = \log\dfrac{I_0}{I} = \in cl.$

Given $\dfrac{I}{I_0} = \dfrac{20}{100} = 0.2$

Substituting the values, $A = -\log\dfrac{I}{I_0} = -\log\ (0.2) = \in \times 0.01\ \text{M} \times 1.5$ cm

or Extinction coefficient, $\in = \dfrac{-\log(0.2)}{0.01\text{M} \times 1.5\,\text{cm}} = \mathbf{46.598\ M^{-1}\ cm^{-1}}$

EXAMPLE 6. *A substance in a cell length 'l' absorbs 20% of the incident light. What fraction of incident light will be absorbed in a cell of length 5l?*

SOLUTION. If I_0 is the intensity of incident light, then the intensity of light absorbed

$$= I_a = \frac{20}{100} I_0.$$

Thus, intensity of transmitted light, $I = I_0 - I_a = I_0 - \dfrac{20 I_0}{100} = \dfrac{80 I_0}{100} = 0.8 I_0$

Thus, $\dfrac{I}{I_0} = 0.8.$ According to Lambert's law, $\ln\dfrac{I}{I_0} = -kx$

Where x = thickness of medium = length of the cell containing the substance = l

In the first case, $\ln\ (0.8) = -k.l$ ...(*i*)

In the second case, $x = 5l$. Thus, $\ln\left(\dfrac{I}{I_0}\right) = -k \times 5l$ ...(*ii*)

From (*i*) and (*ii*)

$$\ln\left(\frac{I}{I_0}\right)\Big/\ln(0.8) = \frac{-k\times 5l}{-k\times l} = 5$$

or $$\ln\left(\frac{I}{I_0}\right) = 5\times\ln(0.8) = \ln(0.8)^5$$

Taking antilogs, the fraction of the transmitted light = $\frac{I}{I_0} = (0.8)^5 = 0.328$

We know that $\frac{I}{I_0} = \frac{I_0 - I_a}{I_0} = 0.328$ or $1 - \frac{I_a}{I_0} = 0.328$

Clearly, the fraction of the incident light absorbed = 1 − 0.328 = **0.672**

EXAMPLE 7. *For a solution of organic ketonic compound ($C_{10}H_{16}O$) in hexane in a 10 cm cell, the absorbance was found to 2.52. What is the concentration of the organic compound? (Given $\in_{max} = 14$).*

SOLUTION. Given that : Absorbance (A) = 2.52

$\in_{max} = 14$, cell length, $l = 10$ cm

Applying the solution: $A = \in.c.l.$

$\therefore$ Concentration, $c = \frac{A}{\in.l} = \frac{2.52}{10\times14} = 1.8\times10^{-2}$ mole L^{-1}

2.3 Measurement of Absorption Intensity

It may be noted that the intensity of absorption is directly proportional to the transition probability. An allowed transition will have ε_{max} value greater than 1000 while those having low transition probability will have its value less than 1000.

Selection Rules : The various electronic transitions which are governed by certain restrictions are called selection rules. These are:

(*i*) The transitions which involve a change in the spin quantum number of an electron during the transition do not occur. Thus, singlet-triplet transitions are forbidden.

(*ii*) The transitions between orbitals of different symmetry do not occur. For example, $n \to \pi^*$ transition is symmetry forbidden.

The wavelength of light corresponding to maximum absorption is written as λ_{max}. It can be directly read from the horizontal axis as shown in Fig. 2.2. The Figure shows the ultra-violet spectrum of vitamin *A* with vertical line showing absorbance *A* which is equal to log I_0/I.

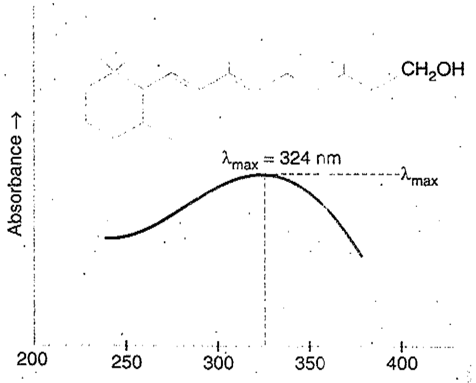


Fig. 2.2. Ultra-violet spectrum of vitamin A.

For vitamin *A*, the absorption maximum (λ_{max}) is observed at 324 nm.

2.4 Instrumentation

A spectrophotometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus, the instrument compares the intensity of the transmitted light with that of the incident light.

The modern ultra-violet–visible spectrometers consist of light source, monochromator, detector, amplifier and the recording devices. The most suitable sources of light are : **Tungsten Filament lamp** and **hydrogen-deuterium discharge lamp** which cover the whole of the UV-visible region. Tungsten filament lamp is particularly rich in red radiations *i.e.*, radiations with wavelength 375 mμ, while the deuterium discharge lamp covers the region below it. The intensity of the deuterium discharge source falls above 360 mμ. The single source is found satisfactory over the entire UV-VIS region. Ordinary spectrometers cover a range 220-800 mμ. Better instruments cover uptó a short wavelength range of 185 mμ. This spectroscopic technique is not useful below 200 mμ (inaccessible region) since oxygen absorbs strongly at 200 mμ and below. To study absorption below 200 mμ, the whole path length is evacuated. The region below 200 mμ is called vacuum ultra-violet region. The low wavelength region can be extended upto 150 mμ by flushing the instrument with nitrogen which absorbs below 150 mμ. Most spectrophotometers are double beam instruments. The primary source of light is divided into two beams of equal intensity. Before dividing it into two beams, the incident radiation is dispersed with the help of a rotating prism. The various wavelengths of a light source are separated with a prism and then selected by slits such that the rotation of the prism causes a series of continuously increasing wavelengths to pass through the slits for recording purposes. The selected beam is monochromatic which is then divided into two beams of equal intensity. Dispersion grating can also be employed to obtain monochromatic beam of light from polychromatic radiation (*UV-VIS* radiation). As the dispersion of a single beam or grating is very small, it is not possible to isolate or collimate very narrow band widths. Thus, light from the first dispersion is passed through a slit and then sent to the second dispersion. After the second dispersion, light passes through the exit slit. The main advantage of the second dispersion is that the band width of the emergent light increases and the light passing through the exit slit is almost monochromatic. Also most of the stray light is suppressed.

One of the beams of selected monochromatic light (See Fig. 2.3) is passed through the sample solution and the other beam of equal intensity is passed through the reference solvent. The solvent as well as the solution of the sample may be contained in cells made of a material which is transparent throughout the region under study. Glass cannot be used since it absorbs strongly in the ultra-violet region. Silica cells can be used. These must be properly stored and their optical surfaces should never be handled. Quartz cells also serve the purpose best. Glass can be used satisfactorily in the visible region. This type of spectrometer is called double beam spectrophotometer. Each absorbance measurement on the solution is accompanied by a simultaneous measurement on the pure solvent.

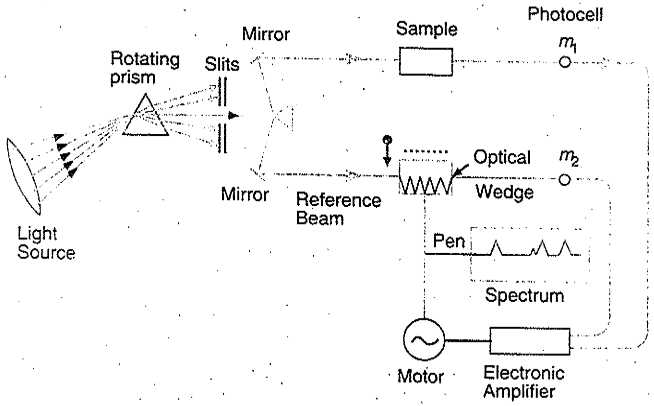


Fig. 2.3. Ultra-violet spectrophotometer.

---

* Clean cells should be used. These are rinsed many times with the solvent. To remove the last trace of the previous sample, the cell may be cleaned with hot nitric acid or with a detergent.

Usually, samples are scanned in dilute solutions. One mg of the compound under investigation (Molecular weight 100-200) is accurately weighed and dissolved in a suitable solvent to make the solution upto 100 ml volume. A little of this solution is taken in a silica cell. The thickness of the solution in the cell should be 1 cm. When the constitution of the absorbing material is unknown, the absorptivity may be sometimes expressed as $E^{1\%}_{1\text{cm}}$. Pure solvent is also taken in an exactly similar cell (Reference cell). These cells are then exposed to the monochromatic beams of equal intensity in the spectrometer. After the beams pass through the sample cell as well as the reference cell, the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. The spectrometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution. Hence, the effects due to the absorption of light by the solvent are minimised. In this way, the absorbance or the transmittance characteristic of the compound alone can be measured. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as absorbance A ($\log_{10} I_0/I$) against wavelength λ (abcissa). The plot is often represented as ε_{max} (Extinction coefficient*) against wavelength.

When the sample absorbs light, its intensity is lowered. Thus, the photoelectric cells P_1 and P_2 will receive an intense beam from the reference cell and a weak beam from the sample cell. This results in the generation of pulsating or alternating currents which flow from the photoelectric cells to the electronic amplifier. The amplifier is coupled to a small servomotor, which in turn, is coupled to a pen recorder. Thus, it records the absorption bands automatically. Actually, the amplifier is coupled to a small servomotor which drives an optical wedge into the reference beam until the photoelectric cell receives light of equal intensities from the sample as well as the reference beams.

2.5 Formation of Absorption Bands

We expect the spectrum to consist of sharp peaks and each peak will correspond to the promotion of electron from one electronic level to another. But, actually sharp peaks are seldom observed and instead, broad absorption bands are recorded. It is due to the fact that the excitation of electrons are also accompanied by the constant vibratory and rotatory motion of the molecules. The vibratory and rotatory modes are also quantised. **A molecule in a particular electronic state is also quantised. Clearly a molecule in a particular electronic state is also accompanied by some vibrational and rotational states.** The differences between two adjacent electronic levels is more as compared to the adjacent rotational levels while the difference between the adjacent vibrational levels has some intermediate value. The electronic excitation is superimposed upon rotational and vibrational levels.

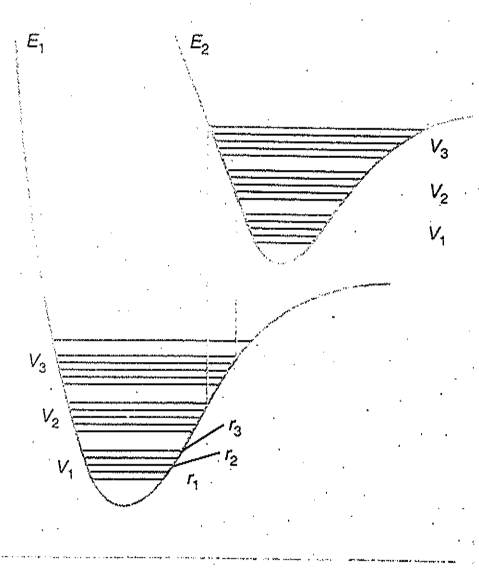


Fig. 2.4. Energy curves for a diatomic molecule.

---

* It is also called molar absorptivity.

Clearly, during promotion, the electron moves from a given vibrational and rotational level within one electronic mode to some other vibrational and rotational level within the next electronic mode. Thus, there will be a large number of possible transitions (close together) responsible for change in electronic. rotational and vibrational levels. Hence, not just one but a large number of wavelengths which are close enough will be absorbed resulting in the formation of bands. In more complex molecules which contain a large number of atoms, the multiplicity of vibrational sub-levels and their closeness results in the discrete bands to coalesce and thus, broad bands are observed.

2.6 Theory of Electronic Spectroscopy

When the molecule absorbs ultraviolet or visible light, its electrons get promoted from the ground state to the higher energy state. In the ground state, the spins of the electrons in each molecular orbital are essentially paired. In the higher energy state, if the spins of the electrons are paired, then it is called an excited singlet state. On the other hand, if the spins of the electrons in the excited state are parallel, it is called an excited triplet state. The triplet state is always lower in energy than the corresponding excited singlet state. Therefore, triplet state is more stable as compared to the excited singlet state. In the triplet excited state, electrons are farther apart in space and thus, electron-electron repulsion is minimised. Normally the absorption of ultraviolet or visible light results in singlet ground state to excited singlet state transition, i.e., excitation proceeds with the retention of spins. An excited singlet state is converted to excited triplet state with the emission of energy as light. The transition from singlet ground state to excited triplet state is symmetry forbidden. The higher energy states are designated as high energy molecular orbitals and also called antibonding orbitals. The highly probable transition due to absorption of quantised energy involves the promotion of one electron from the highest occupied molecular orbital to the lowest available unfilled molecular orbital. In most of the cases, several transitions occur resulting in the formation of several bands.

2.7 Types of Electronic Transitions

According to the molecular orbital theory, when a molecule is excited by the absorption of energy (UV or visible light), its electrons are promoted from a bonding to an antibonding orbital.

(*i*) The antibonding orbital which is associated with the excitation of σ electron is called σ antibonding orbital. So σ to σ* transition takes place when σ (sigma) electron is promoted to antibonding (σ) orbital. It is represented as σ → σ* transition.

(*ii*) When a non-bonding electron (*n*) gets promoted to an antibonding sigma orbital (σ*), then it represents *n* → σ* transition.

(*iii*) Similarly π → π* transition represents the promotion of π electrons to an antibonding π orbital, *i.e.*, π* orbital, (See Fig. 2.5)

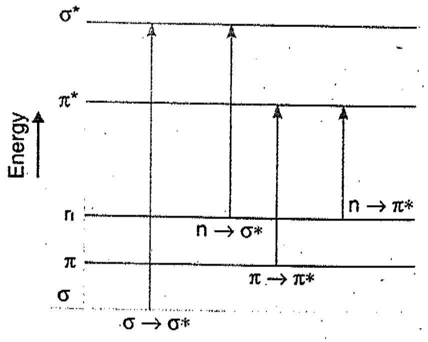


Fig. 2.5. Electronic excitation energies.

---

†called sigma asterisk.

†Unshared pair of electrons.

Similarly, when an *n*-electron (non-bonding) is promoted to antibonding π orbital, it represents $n \rightarrow \pi^*$ transition. The energy required for various transitions obey the following order :

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi - \pi^* > n \rightarrow \pi^*$$

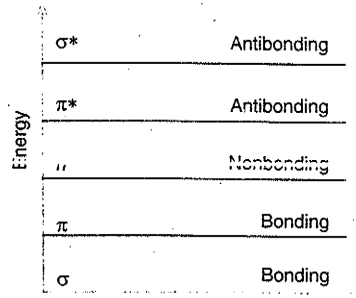
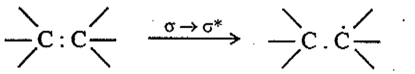


Fig. 2.6. Electronic excitation energies.

Let us now consider the various transitions involved in ultraviolet spectroscopy.

(*a*) **σ → σ* transitions. It is a high energy process since σ bonds are, in general, very strong.** The organic compounds in which all the valence shell electrons are involved in the formation of sigma bonds do not show absorption in the normal ultra-violet region, *i.e.*, 180–400 mμ. For saturated hydrocarbons, like methane, propane etc. absorption occurs near 150 mμ (high energy). Consider σ → σ* transition in a saturated hydrocarbon :



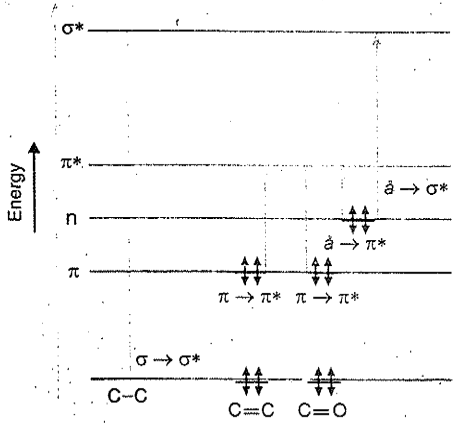


Fig. 2.7. Various transition involved in Electronic spectroscopy.

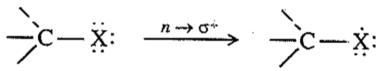
Such a transition requires radiation of very short wavelength (High energy). See Fig. 2.7. The usual spectroscopic technique cannot be used below 200 mμ, since oxygen (present in air) begins to absorb strongly. To study such high energy transitions (below 200 mμ), the entire path length must be evacuated.* Thus, the region below 200 mμ is commonly called vacuum **ultraviolet region**. The excitation of sigma bond electron to σ* (antibonding) level occurs with net retention of electronic spin. It is called excited singlet state which may, in turn, gets converted to excited triplet state. This region is less informative.

---

* Air must be excluded from the instrument so as to avoid absorption due to oxygen.

(*b*) **$n \rightarrow \sigma^*$ transition.** This type of transition takes place in saturated compounds containing one hetero atom with unshared pair of electrons (*n* electrons). Some compounds undergoing this type of transitions are saturated halides, alcohols, ethers, aldehydes, ketones, amines etc. Such transitions require comparatively less energy than that required for σ → σ* transitions. Water absorbs at 167 mμ, methyl alcohol at 174 mμ and methyl chloride absorbs at 169 mμ.

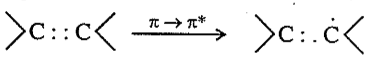
In saturated alkyl halides, the energy required for such a transition decreases with the increase in the size of the halogen atom (or decrease in the electronegativity of the atom).



Let us compare $n \rightarrow \sigma^*$ transition in methyl chloride and methyl iodide. Due to the greater electronegativity of chlorine atom, the *n* electrons on chlorine atom are comparatively difficult to excite*. The absorption maximum for methyl chloride is 172–175mμ whereas that for methyl iodide is 258 mμ as *n* electrons on iodine atom are loosely bound. Since this transition is more probable in case of methyl iodide, its molar extinction coefficient** is also higher compared to methyl chloride.

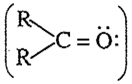
Similarly, amines absorb at higher wavelengths as compared to alcohols and hence the extinction coefficients for amines will be larger. $n \rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus, transition requires greater energy. **Hydrogen bonding shifts the ultra-violet absorptions to shorter wavelengths.** (For details see solvent effects).

(*c*) **π → π* transitions.** This type of transition occurs in the unsaturated centres of the molecule; *i.e.*, in compounds containing double or triple bonds and also in aromatics. The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelength. A π electron of a double bond is excited to π* orbital. For example, alkenes, alkynes, carbonyl compounds, cyanides, azo compounds etc. show π → π* transition. Consider an alkene:



This transition requires still lesser energy as compared to $n \rightarrow \sigma^*$ transition and therefore, absorption occurs at longer wavelengths. Absorption usually occurs within the region of ordinary ultra-violet spectrophotometer. In unconjugated alkenes, absorption bands appear around 170–190 mμ. In carbonyl compounds, the band due to π → π transition appears around 180 mμ and is most intense, *i.e.*, the value of extinction coefficient is high. The introduction of alkyl group to olefinic linkage produces a bathochromic shift of the order of 3 to 5 mμ per alkyl group. The shift depends upon the type of the alkyl group and the stereochemistry about the double bond.

(*d*) **$n \rightarrow \pi^*$ transition.** In this type of transition, an electron of unshared electron pair on hetero atom gets excited to π* antibonding orbital. This type of transition requires least amount of energy out of all the transitions discussed above and hence occurs at longer wavelengths.

Saturated aldehydes  $\left(R_2C=\ddot{O}:\right)$ show both the types of transitions, *i.e.*, low energy $n \rightarrow \pi^*$ and

---

Greater the probability of a particular transition, greater the value of its molar extinction coefficient. ε_{max}.

Shift towards longer wavelength.

high energy $\pi \rightarrow \pi^*$ occuring around 290 mμ and 180 mμ respectively. Absorption occuring at lower wavelength is usually intense. In simple cases, it is quite easy to tell whether the transition is $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ since the extinction coefficient for the former is quite low as compared to that of the latter. The exact electronic structure of the molecules in the excited state (by the absorption of UV or visible light) is not known but the electronic transition involves the redistribution of electrons within the molecule. In carbonyl compounds; a high energy $n \rightarrow \sigma^*$ transition also occurs and is quite intense. Thus, in saturated carbonyl compounds, two types of transitions take place which can be classed as :

(*a*) **High energy transitions**

- (*i*) $n \rightarrow \sigma^*$ (intense)
- (*ii*) $\pi \rightarrow \pi^*$ (intense)

(*b*) **Low energy transition**

$n \rightarrow \pi^*$ (weak)–R*band.

In carbonyl compounds, the shift in the absorption depends upon the polarity of the solvent.

2.8 Transition Probability

It is not always necessary that the excitation of an electron takes place from a bonding orbital or lone pair to an antibonding or nonbonding orbital when a compound is exposed to UV or visible light. It can be shown that

Extinction coefficient

$$\varepsilon_{max} = 0.87 \times 10^{20} . \text{P}a$$

where P = transition probability with values from 0 to 1.

a = Target area of the absorbing system, usually called a chromophore.**

It is found that the values of ε_{max} is about 10^5 when the choromophore has a length of the order of 10 Å or 10^{-7} cm. The chromophore with low transition probability will have ε_{max} value below 1000. Hence, there is a direct relationship between the area of the chromophore and the absorption intensity ε_{max}. In addition, there are some other factors also which govern the transition probability. Depending upon the symmetry and the value of ε_{max}, the transitions*** can be classed as :

(*a*) **Allowed Transitions** (*b*) **Forbidden Transitions**

The transitions with values of (extinction coefficient) ε_{max}, more than 10^4 are usually called allowed transitions. They generally arise due to $\pi \rightarrow \pi^*$ transitions. In Butadiene 1, 3, the absorption at 217 mμ ε_{max} 21,000 is an example of allowed transition.

The forbidden transition is a result of the excitation of one electron from the lone pair present on the heteroatom to an antibonding π^* orbital. $n \rightarrow \pi^*$ transition near 300 mμ in case of carbonyl compounds with ε_{max} value between 10–100, is the result of forbidden transition. The values of ε_{max} for forbidden transition are generally below 10^4. Consider benzophenone. The two types of transitions observed in this case are :

(*i*) 252 mμ ε_{max} 20,000 (allowed)
(*ii*) 325 mμ ε_{max} 180 (forbidden).

Symmetry restrictions in Electronic transitions. The transition (allowed or forbidden) is related with the geometries of the lower and the higher energy molecular orbitals and also on the symmetry of the molecule as a whole. Symmetrical molecules have more restrictions on their electronic transitions than less symmetrical molecules. For example, benzene is a highly symmetrical molecule. Thus, many restrictions apply to the electronic transitions of the benzene molecule and thus, its electronic absorption spectrum is simple. For a totally unsymmetrical molecule, no symmetry restrictions apply to the electronic transitions so that transitions may be observed among all of its molecular orbitals except among filled orbitals. Clearly, for such a substance, a complex electronic absorption spectrum will result.

---

* R-bands (Radikalartig-German).

Between symmetrical and totally unsymmetrical extremes, a large number of organic compounds fall which absorb light in the ultra-violet-visible region. To decide whether the transition is allowed or forbidden for such molecules, it is important to consider

(*i*) the geometry of the molecular orbital in the ground state
(*ii*) the geometry of the molecular orbital in the excited state and
(*iii*) the orientation of the electric dipole of the incident light that might induce the transition.

The transition will be an allowed transition if the above three factors have an appropriate symmetry relationship.

2.9 The Chromophore Concept

All those compounds which absorb light of wavelength between 400-800 mμ appear coloured to the human eye. Exact colour depends upon the wavelength of light absorbed by the compound. Originally, a chromophore was considered any system which is responsible for imparting colour to the compound. Nitro-compounds are generally yellow in colour. Clearly, nitro group is the chromophore which imparts yellow colour. Similarly, aryl conjugated azo group is a chromophore for providing colour to azo dyes. Now, the term chromophore is used in a broader way.

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region.

The absorption occurs irrespective of the fact whether colour is produced or not. Some of the important chromophores are ethylenic, acetylenic, carbonyls, acids, esters, nitrile group etc. A carbonyl group is an important chromophore, although, the absorption of light by an isolated group does not produce any colour in the ultraviolet spectroscopy. There are two types of chromophores :

(*a*) Chromophores in which the group contains π electrons and they undergo $n \rightarrow \pi^*$ transitions. Such chromophores are ethylenes, acetylenes etc.

(*b*) Chromophores which contain both π electrons and n (non-bonding) electrons. Such chromophores undergo two types of transitions *i.e.*, $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. Examples of this type are carbonyls, nitriles, azo compounds, nitro compounds etc.

Note. In compounds of the type $>C-C<$ and $>C-H$ absorption occurs around 150 mμ (vacuum ultraviolet region) as result of $\sigma \rightarrow \sigma^*$ transition.

For compounds containing such atoms as $-\ddot{O}-$, $-\ddot{S}-$, $>\ddot{N}$ absorption occurs around 190 mμ as a result of $n \rightarrow \sigma^*$ transition.

There are no set rules for the identification of a chromophore. The change in position as well as the intensity of absorption depends upon a large number of factors. Following points may be helpful :

(*i*) Spectrum consisting of a band near 300 mμ may contain two or three conjugated units.
(*ii*) Absorption bands near 270–350 mμ with very low intensity, ε_{max} 10–100 are due to $n \rightarrow \pi^*$ transitions of the carbonyl group. See table T_2–1.
(*iii*) Simple conjugated chromophores such as dienes or α, β – Unsaturated ketones have high ε_{max} values, *i.e.*, from 10,000 to 20,000.
(*iv*) The absorption with ε_{max} value between 1000 to 10,000 shows an aromatic system.

Although less intense, it is most characteristic of carbonyl group.

Table T_2—1 Simple Unconjugated Chromophores

Chromophore	*Transition*	*Absorption max (mμ)*	ε_{max}	*Solvent*
C=C	π – π*	~175	~15000	Vapour
		(*i*) ~175	~10000	Hexane
—C≡C—	π – π*	(*ii*) 196	~2000	″
		(*iii*) 220	~150	″
C=O	n → σ*	160	18000	″
	π → π*	180	10000	Hexane
	n → π*	285*	15	
R—NO_2	π – π*	~200	5000	Methanol
		n → π*	~274	15
—C(=O)OH	n → π*	204	60	Methanol
—N=N—	n – π*	338	~5	Ethanol
—$CONH_2$	n → π*	178	9500	Hexane
	n → π*	220	63	Hexane

When aromatic nucleus is substituted with groups which can extend the chromophore, the absorption occurs at still higher values of extinction coefficients.

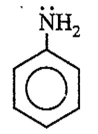
Note. The presence of a compound or a functional group can be confirmed by other spectroscopic techniques.

All compounds with the same functional group will absorb at the same wavelength with nearly the same extinction coefficient if the disturbing factors such as conjugation, substituents etc. are absent. Some of the chromophores with their respective absorption maxima and extinction coefficients are given in Table T_2–1.

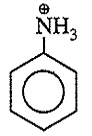
2.10 Auxochrome

An auxochrome can be defined as any group-which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength). The absorption at longer wavelength is due to the combination of a chromophore and an auxochrome to give rise to another chromophore. An auxochromic group is called colour enhancing group. Auxochromic groups do not show characteristic absorption above 200 mμ. Some common auxochromic groups are —OH, —OR, —NH_2, —NHR, —NR_2, —SH etc. The effect of the auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons. Thus, a new chromophore results which has a different value of the absorption maximum as well as the extinction coefficient. For example, benzene shows an absorption maximum at 255 mμ [ε_{max} 203] whereas aniline absorbs at 280 mμ [ε_{max} 1430]. Hence, amino (—NH_2) group is an auxochrome.

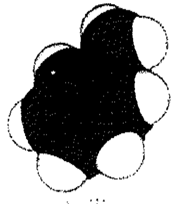
Consider the following :



λ_{max} = 280 nm
(ϵ_{max} = 1430)



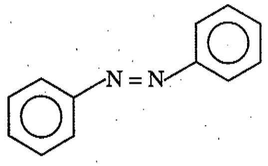
λ_{max} = 254 nm
(ϵ_{max} = 160)



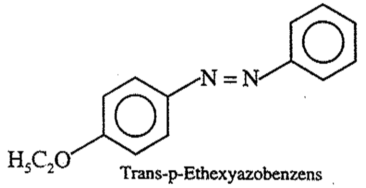
Aniline

In aniline, —$\ddot{N}H_2$ acts as a chromophore. But in anilinium ion, there is no lone pair on nitrogen atom.

Consider trans—Azobenzene and trans-p-ethoxyazobenzene.



Trans-Azobenzene
λ_{max} = 320 nm(ϵ_{max} = 21000)



Trans-p-Ethexyazobenzens
λ_{max} = 385 nm (ϵ_{max} = 42000)

The presence of —OC_2H_5 group (an auxochrome) increases the value of λ_{max} as well as ε_{max}.

Mechanism : All auxochromic groups contain non-bonding electrons. Due to this, there is extension of conjugation of the chromophore by sharing the non-bonding electrons.

$$CH_2{=}CH{-}\ddot{N}(CH_3)_2 \longleftrightarrow :\overset{-}{C}H_2{-}CH{=}\overset{+}{N}(CH_3)_2$$

2.11 Absorption and Intensity Shifts

(*a*) **Bathochromic effect.** It is an effect by virtue of which the absorption maximum is shifted towards longer wavelength due to the presence of an auxochrome or by the change of solvent. (See Fig. 2.8.). Such an absorption shift towards longer wavelength is called Red shift or bathochromic shift. The n → π* transition for carbonyl compounds experiences bathochromic shift when the polarity of the solvent is decreased.

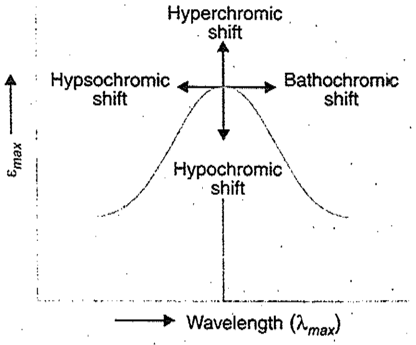
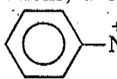


Fig. 2.8. Absorption and intensity shifts.

(*b*) **Hypsochromic shift or effect.** It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength. The absorption shifted towards shorter wavelength is called **Blue shift** or hypsochromic shift.

It may be caused by the removal of conjugation and also by changing the polarity of the solvent. In the case of aniline, absorption maximum occurs at 280 mμ because the pair of electrons on nitrogen atom is in conjugation with the π bond system of the benzene ring. In its acidic solutions, a blue shift is caused and absorption occurs at shorter wavelength (~203 mμ).

In  —$\overset{+}{N}H_3$. ion formed in acidic solution, the electron pair is no longer present and hence conjugation is removed.

(*c*) **Hyperchromic effect.** It is an effect due to which the intensity of absorption maximum increases *i.e.*, ε_{max} increases. For example, the B-band for pyridine at 257 mμ ε_{max} 2750 is shifted to 262 mμ ε_{max} 3560 for 2-methyl pyridine (*i.e.*, the value of ε_{max} increases). The introduction of an auxochrome usually increases intensity of absorption.

(*d*) **Hypochromic effect.** It is defined as an effect due to which the intensity of absorption maximum decreases, *i.e.*, extinction coefficient, ε_{max} decreases. The introduction of group which distorts the geometry of the molecule causes hypochromic effect. For example, biphenyl absorbs at 250 mμ, ε_{max} 19000 whereas 2-methyl biphenyl absorbs at 237 mμ, ε_{max} 10250 [ε_{max} decreases]. It is due to the distortion caused by the methyl group in 2-methyl biphenyl.

2.12 Types of Absorption Bands

Following types of bands originate as a result of the possible transitions in a compound.

(*a*) K* **Bands.** K-bands originate due to π → π* transition from a compound containing a conjugated system. Such type of bands arise in compounds like dienes, polyenes, enones etc. K-bands also appear in an aromatic compound which is substituted by a chromophore. The intensity of K-band, is usually more than 10^4. The K-band absorption due to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent.

Table T_2—2

Compound	*Transition*	(λ_{max} *mμ*)	ε_{max}
Butadiene 1,3	π – π*	217	21,000
Acrolein	π – π*	210	11,500
Styrene	π – π*	214	12,000
Acetophenone	π – π*	240	13,000
2,3 dimethyl Butadiene	π – π*	226	21,400
Pentadiene 1, 3	π – π*	223	22,600

(*b*) R band. Such type of bands originate due to *n* → π* transition of a single chromophoric group and having at least one lone pair of electrons on the hetero atom. R-bands are also called forbidden bands. These are less intense with ε_{max} value below 100.

Table T_2 – 3

Compound	*Transition*	λ_{max} *(mμ)*	ε_{max}
Acetone	*n* → π*	270	15
Acetaldehyde	*n* → π*	293	~12
Acrolein	*n* → π*	315	14
Acetophenone	*n* → π*	319	50
Methyl Vinyl Ketone	*n* → π*	320	~14
Crotonaldehyde	*n* → π*	322	~14

(*c*) B-band. Such type of bands arise due to π → π* transition in aromatic or hetero-aromatic molecules. Benzene shows absorption peaks between 230–270mμ. When a chromophoric group is attached to the benzene ring, the B-bands are observed at longer wave-lengths than the more intense K-bands. For example, K-band appears at 244 mμ, ε_{max} 12000 and B-band at 282 mμ, ε_{max} 450. Out of K, B and R-bands which appear in the spectrum of an aromatic compound, R-band appears at a longer wave-length. For example, in acetophenone R-band (*n* → π*, forbidden) appears at 319 mμ ε_{max} 50 while K and B-bands appear at 240 and 278 mμ respectively. The fine spectrum of B-band in case of

(*i*) substituted aromatic compounds and

(*ii*) by the use of polar solvents

may be missing.

Table T_2—4

Compound	*Transition*	λ_{max}*(mμ)*	ε_{max}
Benzene	π – π*	255	215
Styrene	π – π*	282	450
Toluene	π – π*	262	174
Phenol	π – π*	270	1450
Acetophenone	π – π*	278	1110
Benzaldehyde	π – π*	280	1500
Benzoic acid	π – π*	270	800
Nitro-benzene	π – π*	280	1000
Naphthalene	π – π*	312	289
Quinoline	π – π*	315	2500

(*d*) E-bands. Such bands originate due to the electronic transitions in the benzenoid system of three ethylenic bonds which are in closed cyclic conjugation. These are further characterised as E_1 and E_2-bands. E_1 and E_2 bands of benzene appear at 184 and 204 mμ respectively. E_1 band which appears at lower wave-length is usually more intense than the E_2-band for the same compound which appears at longer wavelength.

Table T_2–5

Compounds	*E_1-band*		*E_2-band*	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}
	(mm)		(mm)	
Benzene	184	50,000	204	79,00
Naphthalene	221	133,000	286	9,300
Anthracene	256	180,000	375	9,000
Pyrrole	234	10,800	288	760
Thiophene	~270	6,300	~294	600
Quinoline	288	40,000	270	3,162

2.13 Solvent Effects

A most suitable solvent is one which does not itself absorb in the region under investigation. A dilute solution of the sample is always prepared for the spectral analysis. Most commonly used solvent is 95% Ethanol. Ethanol is a best solvent as it is cheap and is transparent down to 210 mμ.

Konjugierte-German.

R-band or *n* → π* transition is most characteristic for a carbonyl group of aldehyde or ketone. For aldehydes, it usually appears at higher wavelengths compared to a ketone but at lower value of ε_{max}.

Commercial ethanol should not be used as it contains benzene which absorbs strongly in the ultraviolet region. Some other solvents which are transparent above 210 mμ are n-hexane, methyl alcohol, cyclohexane, acetonitrile, diethyl ether etc. Some solvents with their upper wavelength limit of absorption are given in Table T_2–6.

Table T_2–6

Solvent	Upper wavelength limit (mμ)
Ethanol	210
Hexane	210
Methanol	210
Cyclohexane	210
Diethyl ether	210
Water	205
Benzene	280
Chloroform	245
THF (Tetrahydrofuran)	220
Carbon tetrachloride	265

Hexane and other hydrocarbons can be used as these are less polar and have least interactions with the molecule under investigation. For ultra-violet spectroscopy, ethanol, water and cyclohexane serve the purpose best.

The position and the intensity of absorption maximum is shifted for a particular chromophore by changing the polarity of the solvent. By increasing the polarity of the solvent, compounds like dienes and conjugated hydrocarbons do not experience any appreciable shift. Thus, in general, the absorption maximum for the non-polar compounds is the same in alcohol (polar) as well as in hexane (non-polar). The absorption maximum for the polar compounds is usually shifted with the change in polarity of the solvents. α, β- unsaturated carbonyl compounds show two different shifts.

(*i*) $n \rightarrow \pi^*$ transition (less intense). In such a case, the absorption band moves to shorter wave-length by increasing the polarity of the solvent. In $n \rightarrow \pi^*$ transition, the ground state is more polar as compared to the excited state. The hydrogen bonding with solvent molecules takes place to lesser extent with the carbonyl group in the excited state. For example, absorption maximum of acetone is at 279 mμ in hexane as compared to 264 mμ in water.

(*ii*) $\pi \rightarrow \pi^*$ transition (intense). For such a case, the absorption band moves to longer wavelength by increasing the polarity of the solvent. The dipole interactions with the solvent molecules lower the energy of the excited state more than that of the ground state. Thus, the value of absorption maximum in ethanol will be greater than that observed in hexane.

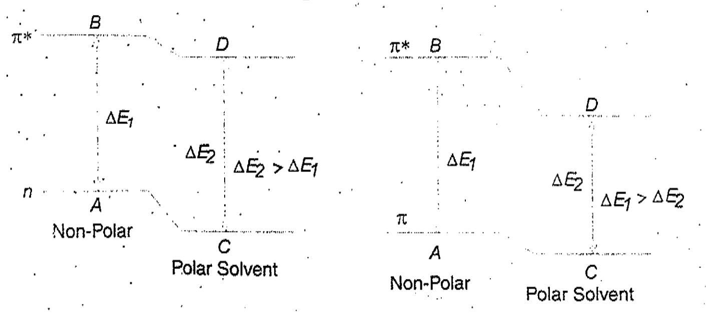


Fig. 2.9. Absorption shift with change in polarity of the solvent.

In short, π^* orbitals are more stabilised by hydrogen bonding with polar solvents like water and alcohol. It is due to greater polarity of π^* orbital compared to π orbital. Thus, small energy will be required for such a transition and absorption shows a red shift.

$n \rightarrow \sigma^*$ transitions are also very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such associations occur due to the presence of nonbonding electrons on the hetero atom and thus, transition requires greater energy.

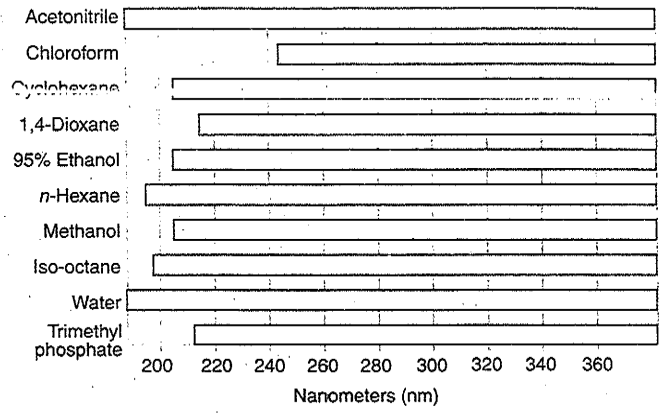


Fig. 2.10. Transparency ranges of useful solvents.

In general, we say that

(*a*) If the group (carbonyl) is more polar in the ground state than in the excited state, then increasing polarity of the solvent stabilises the non-bonding electron in the ground state due to hydrogen bonding. Thus, absorption is shifted to lower wavelength.

(*b*) If the group is more polar in the excited state, then absorption is shifted to longer wavelength with increase in polarity of the solvent which helps in stabilising the non-bonding electrons in the excited state.

It has been found that increase in polarity of the solvent generally shifts $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelengths and $\pi \rightarrow \pi^*$ bands to longer wavelengths.

Following points may also be noted in connection with the effect of solvent polarity on the various types of bands.

(*i*) **K-band.** The K-band absorption due to conjugated'enes' and 'enones' are effected differently by changing the polarity of the solvent. Usually, K-bands due to conjugated dienes are not effected by changing the polarity of the solvent while these bands due to 'enones' show a red shift by increasing the polarity of the solvent.

(*ii*) **R-band.** The absorption shifts to shorter wavelength (blue shift) with the increase in polarity of the solvent.

(*iii*) **B-band.** The position as well as the intensity of the B-band is not shifted by increasing the polarity of the solvent. But in heterocyclic aromatic compounds, a marked hyperchromic shift (increase in ε_{max}) is observed by increasing the polarity of the solvent.

2.14 Effect of Temperature and Solvent on the Fineness of Absorption Band

It is known that the vibrational and the rotational states depend on temperature. As the temperature is decreased, vibrational and the rotational energy state of the molecules are also lowered. Thus, when the absorption of light occurs at a lower temperature, smaller distribution of excited states result. It produces finer structure in the absorption band than what is noticed at higher temperature. Consider the UV spectrum of dodecapentaenoic acid in ether-alcohol solvent at 20 °C and –195 °C.

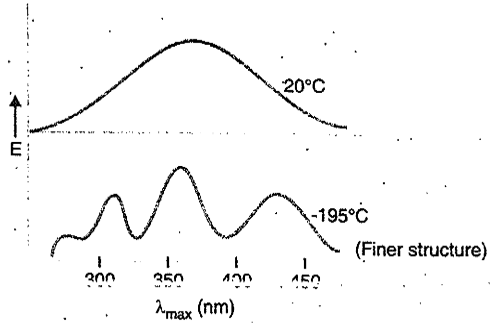


Fig. 2.10(A) Finess of absorption band.

The solvent used also effects the fineness of absorption band in UV spectrum. If the dielectric constant of the solvent is high, there will be stronger solute-solvent interactions. Due to this, vibrational and rotational energy states of molecules increase and thus, the fineness of the absorption band falls.

2.15 Conjugated Dienes

The wavelength of absorption is shifted to higher values (Bathochromic shift), if two or more chromophoric groups are present in conjugation in a molecule. For example, ethylene (one double bond) absorbs at 170 mµ (π → π* transition) while butadiene (two double bonds in conjugation) absorbs at 217 mµ. The bathochromic shift is more pronounced if the double bonds are in conjugation as compared to the isolated double bonds in which there is a little interaction between them. The absorption maximum is usually shifted 15–45 mµ towards higher wavelength in conjugated system (compared to unconjugated) as the electron density is spread over at least four atomic centres. The value of extinction coefficient also increases. In conjugated dienes, π → π* transition results in the formation of a band, called K-band.

Table T_2–7 π → π* transition (K-band)

Compound	$\lambda_{max}(m\mu)$	ε_{max}
Butadiene 1, 3	217	21,000
2,3 dimethyl butadiene	226	21,400
1,3,5, Hexatriene	254	21,400

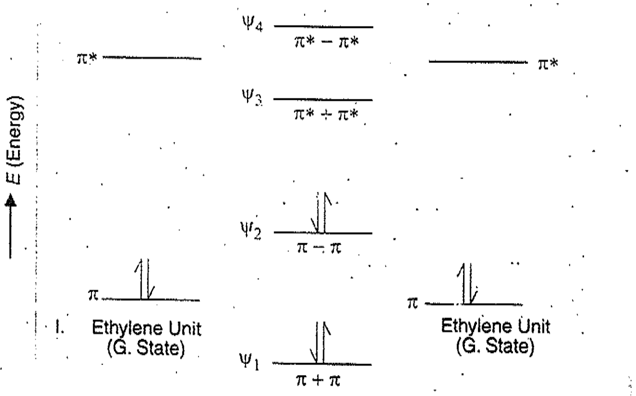


Fig. 2.11. Electronic excitations in conjugated dienes.

When ethylene molecule gets excited, it gives CH_2—CH_2 diradical. The electron cloud is spread on two carbon atoms and the absorption maximum occurs at 170 mµ.

Consider the absorption maximum of butadiene 1,3 (CH_2=CH—CH=CH_2). It consists of two ethylene units. The various excitations are shown in Fig. 2.11.

The two π bonding orbitals, one from each ethylene unit interact or mix up to give rise to two new bonding orbitals.

(*i*) $\pi + \pi = \pi_1$ or ψ_1–having smaller energy.

(*ii*) $\pi - \pi = \pi_2$ or ψ_2–having higher energy.

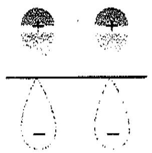


Fig. 2.12. π-bonding orbitals.

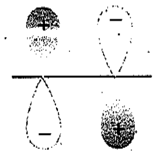


Fig. 2.13. π* antibonding orbitals

The energy of ψ_1 is less than any one of the two combining atomic orbitals.

Also two π* orbitals (antibonding) are formed from two ethylene units which are

(*i*) $\pi^* + \pi^* = \pi_1^* = \psi_3$ having smaller energy.

(*ii*) $\pi^* - \pi^* = \pi_2^* = \psi_4$ having higher energy.

The energies of ψ_3 and ψ_4 are compared with any one of the two (π*) antibonding orbitals.

Thus, ψ_1 can be represented as shown in the Fig. 2.14.

In this case, all the four singly filled atomic orbitals have the same spin of electrons.

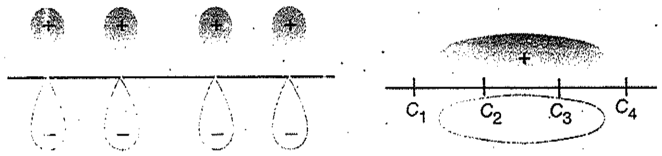


Fig. 2.14. Low energy atomic orbital (ψ_1).

Thus mixing is complete and there is no nodal plane.

$\pi - \pi = \pi_2 = \psi_2$ can be represented as shown in Figure 2.15.

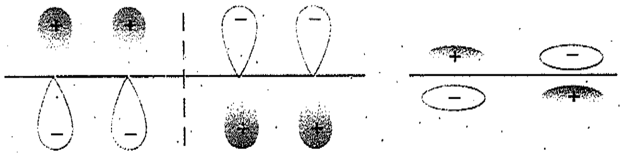


Fig. 2.15. High energy bonding orbital (ψ_2)

In this case, we see one nodal plane.*

Clearly there are double bonds between C_1, C_2 and C_3, C_4 and there is a single bond between C_2 and C_3.

---

* It is defined as an imaginary plane drawn perpendicular to the plane of propagation of the wave where the probability of finding the electron is zero.

$\pi^* + \pi^* = \pi_3^* = \psi_3$ can be represented as shown in Fig. 2.16.

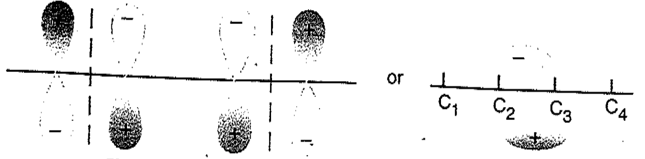


Fig. 2.16. Low energy antibonding orbitals (ψ_3).

In this case, there are two nodal planes and one double bond between C_2 and C_3.

$\pi^* - \pi^* = \pi_4^* = \psi_4$ can be represented as shown in Fig. 2.17.

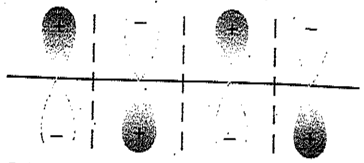


Fig. 2.17. High energy anti-bonding orbital (ψ_4).

This structure corresponds to high energy state since it involves three nodal planes.

Thus, in butadiene, four orbitals are involved. On absorption of energy, electron jumps from π_2 to π_3^*. Since the energy difference between π_2 to π_3^* is less, absorption occurs at higher wavelength. This type of transition is called $\pi \rightarrow \pi^*$ transition. **The net result is that when two double bonds are in conjugation, the energy level of higher occupied molecular orbital (HOMO) is raised and that of the lowest unoccupied molecular (antibonding) orbital (LUMO) is lowered. (See figure 2.17).**

Now this absorption corresponds to the transition *y* (low energy or higher wavelength). Similarly, when dissimilar chromophores are in conjugation, absorption occurs at longer wavelength as compared to the isolated chromophores. In general longer the conjugated system, smaller will be the energy needed to cause $\pi \rightarrow \pi^*$ transition and therefore, absorption occurs at still longer wavelength. In a long conjugated system like carotene, absorption occurs in the visible region (higher wavelength region).

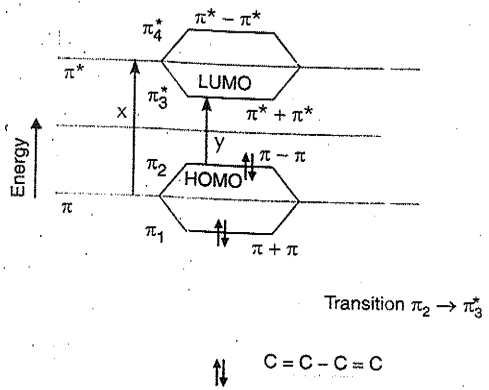


Fig. 2.18. Electronic transition in conjugated diene.

The values of absorption maximum (λ_{max}) as well as extinction coefficient for conjugated and unconjugated alkenes can be compared from their spectra shown in Fig. 2.19.

The values of λ_{max} and ε_{max} are more for conjugated diene as compared to those for an unconjugated alkene. A bathochromic as well as hyperchromic effect are observed when the spectrum of conjugated triene is compared to that of conjugated diene.

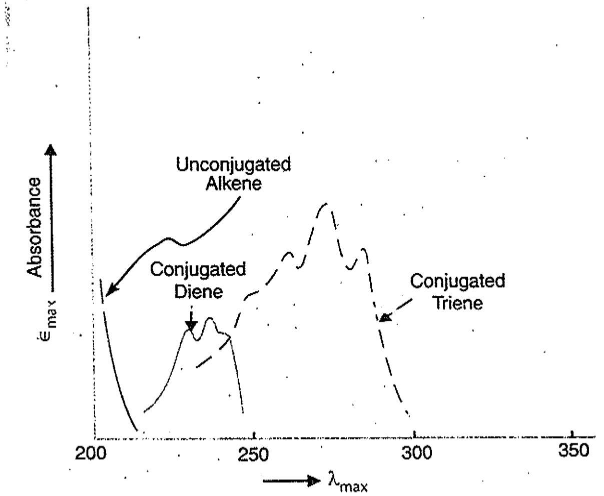


Fig. 2.19. Absorption in conjugated and un-conjugated systems.

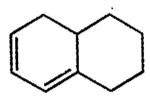
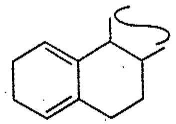
It is important to note that greater the number of conjugated double bonds, greater is the bathochromic shift. With continuous increase in conjugation, the absorption may even shift to the visible region. As the conjugation increases, the energy gap between HOMO and LUMO decreases, (See Fig. 2.18). In case of β-carotene which contain eleven double bonds, the absorption bands appear at (*i*) λ_{max} 478 nm (ε_{max} 139000) and (*ii*) λ_{max} 452 nm (ε_{max} 122000).

2.16 Woodward-fieser Rules for Calculating Absorption Maximum in Dienes

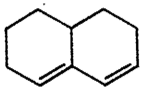
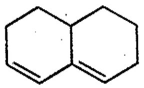
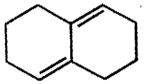
Longer the conjugated system, greater is the wave-length of absorption maximum. The intensity of absorption [ε_{max}] also increases with the increase in the length of the chromophore (see Fig. 2.19). The conjugated polyene system appears coloured to the naked eye if there are more than five double bonds in conjugation and absorption occurs around or above 400 mμ (visible region). The presence of alkyl group on the double bond also causes bathochromic shift. Various types of double bonds in conjugation are described below :

(*a*) **Alicyclic dienes or dienes contained in an open chain system,** *i.e.*, where basic unit is butadiene system.

(*b*) **Homo-annular conjugated double bonds** are the conjugated double bonds present in the same ring. It is also called **Homodiene.** Some examples of this type are :

(*c*) **Hetero-annular conjugated double bonds** are the conjugated double bonds which are not present in the same ring. Some examples of this type are :

$\pi^* + \pi^* = \pi_3^* = \psi_3$ can be represented as shown in Fig. 2.16.

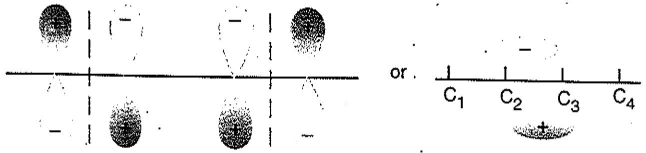


Fig. 2.16. Low energy antibonding orbitals (ψ_3).

In this case, there are two nodal planes and one double bond between C_2 and C_3.
$\pi^* - \pi^* = \pi_4^* = \psi_4$ can be represented as shown in Fig. 2.17.

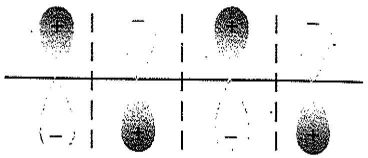


Fig. 2.17. High energy anti-bonding orbital (ψ_4).

This structure corresponds to high energy state since it involves three nodal planes.

Thus, in butadiene, four orbitals are involved. On absorption of energy, electron jumps from π_2 to π_3^*. Since the energy difference between π_2 to π_3^* is less, absorption occurs at higher wavelength. This type of transition is called $\pi \rightarrow \pi^*$ transition. **The net result is that when two double bonds are in conjugation, the energy level of higher occupied molecular orbital (HOMO) is raised and that of the lowest unoccupied molecular (antibonding) orbital (LUMO) is lowered. (See figure 2.17).**

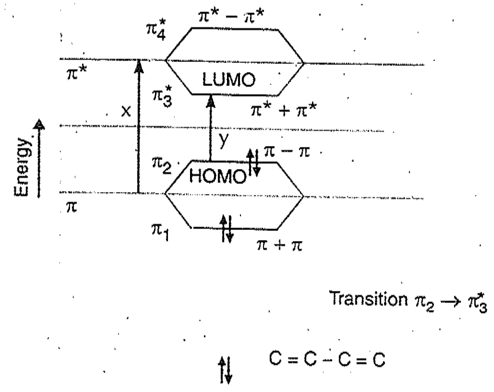


Fig. 2.18. Electronic transition in conjugated diene.

Now this absorption corresponds to the transition y (low energy or higher wavelength). Similarly, when dissimilar chromophores are in conjugation, absorption occurs at longer wavelength as compared to the isolated chromophores. In general longer the conjugated system, smaller will be the energy needed to cause $\pi \rightarrow \pi^*$ transition and therefore, absorption occurs at still longer wavelength. In a long conjugated system like carotene, absorption occurs in the visible region (higher wavelength region).

The values of absorption maximum (λ_{max}) as well as extinction coefficient for conjugated and unconjugated alkenes can be compared from their spectra shown in Fig. 2.19.

The values of λ_{max} and ε_{max} are more for conjugated diene as compared to those for an unconjugated alkene. A bathochromic as well as hyperchromic effect are observed when the spectrum of conjugated triene is compared to that of conjugated diene.

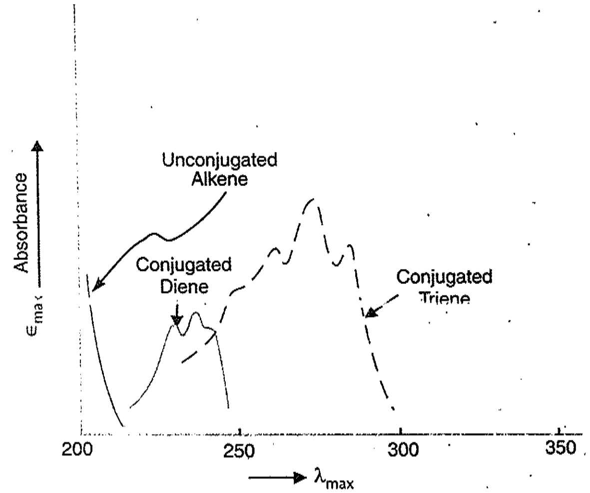


Fig. 2.19. Absorption in conjugated and un-conjugated systems.

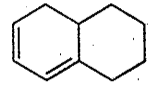
It is important to note that greater the number of conjugated double bonds, greater is the bathochromic shift. With continuous increase in conjugation, the absorption may even shift to the visible region. As the conjugation increases, the energy gap between HOMO and LUMO decreases, (See Fig. 2.18). In case of β-carotene which contain eleven double bonds, the absorption bands appear at (*i*) λ_{max} 478 nm (ε_{max} 139000) and (*ii*) λ_{max} 452 nm (ε_{max} 122000).

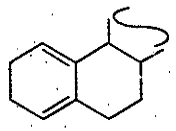
2.16 Woodward-fieser Rules for Calculating Absorption Maximum in Dienes

Longer the conjugated system, greater is the wave-length of absorption maximum. The intensity of absorption [ε_{max}] also increases with the increase in the length of the chromophore (see Fig. 2.19). The conjugated polyene system appears coloured to the naked eye if there are more than five double bonds in conjugation and absorption occurs around or above 400 mμ (visible region). The presence of alkyl group on the double bond also causes bathochromic shift. Various types of double bonds in conjugation are described below :

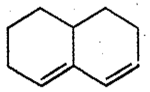
(*a*) **Alicyclic dienes or dienes contained in an open chain system,** *i.e.*, where basic unit is butadiene system.

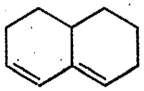
(*b*) **Homo-annular conjugated double bonds** are the conjugated double bonds present in the same ring. It is also called **Homodiene.** Some examples of this type are :

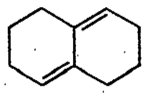




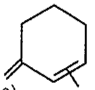
(*c*) **Hetero-annular conjugated double bonds** are the conjugated double bonds which are not present in the same ring. Some examples of this type are :

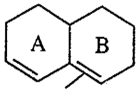




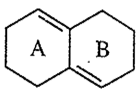


(*d*) **Exocyclic and Endocyclic conjugated double bonds :** Exocyclic double bond is a double bond, part of the conjugated system, formed by any carbon atom of any ring but present outside the ring. Endocyclic double bond is present inside the ring. Such double bonds are shown in the following examples :





(Exocyclic double bond to ring A)



(Contain two exocyclic, double bonds)

Woodward formulated certain empirical rules for calculating the λ_{max} in case of dienes. These rules were later modified by Fieser in 1948. According to these rules, each type of diene has a certain fixed basic value and the value of absorption maximum (λ_{max}) depends upon :

(*i*) The number of alkyl substituents or ring residues on the double bond.

(*ii*) The number of double bonds which extend conjugation and

(*iii*) The presence of polar group such as —Cl, —Br, —OR, —SR etc.

Ring residue is a C–C bond, not a part of the conjugated system but attached to any one of the carbon atoms of the conjugated polyene system.

The various rules for calculating the absorption maximum in case of dienes and trienes are summarised in the Table T_2–8.

Table T_2–8

Solvent–Ethanol ***Transition involved—π → π****	
Parent value for Butadiene system or a cyclic conjugated diene	217 mμ
Acyclic Triene	245 mμ
Homoannular conjugated diene	253 mμ
Heteroannular conjugated diene	215 mμ
Increment for each substituent	
Alkyl substituent or ring residue	5 mμ
Exocyclic double bond	5 mμ
Double bond extending conjugation	30 mμ
Auxochrome	
—OR	+ 6 mμ
—SR	+ 30 mμ
—Cl*, —Br*	+ 5 mμ
—NR_2	+ 60 mμ
$OCOCH_3$	0 mμ

Some examples illustrating the above rules are as follows :

EXAMPLE 1. *Calculate the absorption maximum in the ultra-violet spectrum of 2, 4- Hexadiene.*

Wavelength of absorption maximum.

In case of a cyclic diene or diene contained in an open chain, 17 mμ are added in the basic value for chlorine as well as for bromine atom.

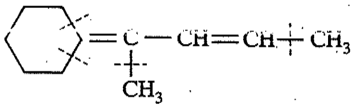
SOLUTION. The basic unit in 2, 4. hexadiene is butadiene. There are two alkyl substituents (one on each double bond) on it. Thus,

$(CH_3—CH{=}CH—CH{=}CH—CH_3)$

Basic value = 217 mμ
2-alkyl substituents (2 × 5) = 10 mμ
Calculated value = 227 mμ

The observed value is also found to be 227 mμ.

EXAMPLE 2. *Calculate the absorption maximum in the UV spectrum of*



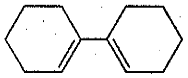
It is a butadiene system. There are two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exo-cyclic double bond.

The value of absorption maximum is calculated as follows :

Basic value = 217 mμ
2-alkyl substituents (2 × 5) = 10 mμ
2-Ring residues (2 × 5) = 10 mμ
1-Exocyclic double bond = 5 mμ
Calculated value = **242 mμ**

The observed value is also found to be 242 mμ.

EXAMPLE 3. *Calculate* λ_{max} *for*

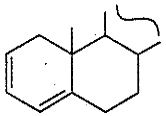


It is an example of heteroannular diene and there are four ring residues on the double bonds. Thus,

Basic value = 215 mμ
Four Ring residues (4 × 5) = 20 mμ
Calculated value = **235 mμ**

The observed value is also found to be 234 mμ,.

EXAMPLE 4. *Calculate the absorption maximum for the compound*



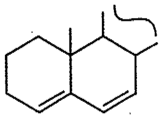
in ethanol.

SOLUTION. It is an example of homoannular conjugated diene and there are three ring residues on it. Moreover, it contains an exocyclic double bond in it. Thus,

Basic value = 253 mμ
3-Ring residues (3 × 5) = 15 mμ
1-exocyclic double bond = 5 mμ
Calculated value = **273 mμ**
Observed value = **274 mμ**

The calculated value and the observed value of absorption for a particular compound can differ by 5 mμ.

EXAMPLE 5. *Calculate the absorption maximum for the compound*



SOLUTION. It is an example of heteroannular diene and there are three ring residues in it. Moreover, it contains one exocyclic double bond in it. Thus,

Basic value	= 215 mμ
3-Ring residues	= 15 mμ
1-exocyclic double bond	= 5 mμ
Calculated value	= **235 mμ**

The observed value of absorption maximum in the ultra-violet spectrum of this compound is also found to be 235 mμ.

Note—**Important.** In case, both homoannular and heteroannular conjugated diene systems are present in the same compound, then calculations are based on longer wave-length, *i.e.*, for homoannular conjugated diene system (253 mμ).

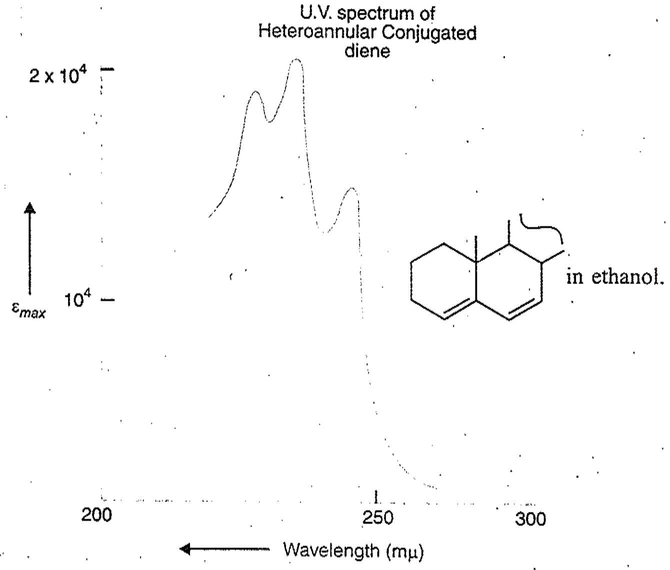
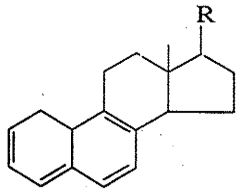


Fig. 2.20. UV spectrum of heteroannular conjugated diene.

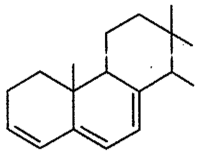
EXAMPLE 6. *Calculate the value of absorption maximum for the compound*



SOLUTION. It is a homodiene system. There are five ring residues on the double bonds, one exocyclic bond and also two double bonds which extend conjugation.

Basic value		=	253 mμ
2-double bonds extending conjugation	2 × 30 =		60 mμ
5-Ring residues	5 × 5 =		25 mμ
1-Exocyclic double bond	1 × 5 =		5 mμ
Calculated value		=	**343 mμ**
Observed value		=	345 mμ

EXAMPLE 7. *Calculate λ_{max} for the compound.*



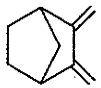
SOLUTION. It is a homoannular conjugated diene system. It contains four ring residues; two exocyclic double bonds and one double bond which extend conjugation. Thus, λ_{max} for this compound is calculated as:

Basic value		=	253 mμ
4-Ring residues	(4 × 5) =		20 mμ
2-exocyclic double bonds	(2 × 5) =		10 mμ
1-double bond extending conjugation		=	30 mμ
Calculated value		=	**313 mμ**
Observed value		=	312 mμ

Bicyclic Compounds

If a diene system is present in a bicyclic compound, then due to the strain in the bicyclic compound, 15 mμ is added as the ring strain correction in the calculated value of absorption maximum.

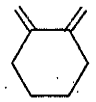
EXAMPLE 8. *Calculate the absorption maximum in the ultraviolet spectrum of 2, 3 dimethylene bicyclo [2, 2, 1] heptane.*



SOLUTION. The value of absorption maximum for this compound is calculated as :

Basic value		=	217 mμ
2-Ring residues	(2 × 5) =		10 mμ
2-Exocyclic double bonds		=	10 mμ
1-bicyclic system (strain correction)		=	15 mμ
Calculated value		=	**252 mμ**
Observed value		=	254 mμ

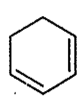
2.17 Distortion of the Chromophore



Distortion of the chromophore may lead to red or blue shift depending upon the nature of distortion. The following compound whose structure is given is expected to show absorption maximum at 237 mμ but distortion of chromophore causes it to absorb at 220 mμ. The blue shift is due to the loss of conjugation as the structure is no longer coplanar (double bonds do not remain coplanar).

The change of ring size in case of simple homoannular conjugated diene leads to departure from the predicted value of 263 mμ as follows :

For cyclohexadiene, the absorption maximum can be calculated as



Basic Value = 253 mμ $\left[\begin{array}{c}\text{Homoannular}\\ \text{conjugated diene}\end{array}\right]$

2-Ring residues = 10 mμ

Calculated value = **263 mμ.**

But, the absorption maximum for

(*i*) Cyclopentadiene occurs at 238.5 mμ; ε_{max} 3400

(*ii*) Cycloheptadiene occurs at 248 mμ; ε_{max} 7500.

The cause for the blue shift is distortion in chromophoric system which no longer remains coplanar.

2.18 POLY-enes and POLY-ynes

With the increase in the number of double bonds in conjugation, the values of absorption maximum as well as intensity increase. Note the values of absorption maximum as well as extinction coefficients in case of —(CH=CH)$_n$–where $n \geq 3$ are given below :

		λ_{max}	ε_{max}
(*i*) when	$n = 3$	275 mμ	30,000
(*ii*)	$n = 4$	310 mμ	76,500
(*iii*)	$n = 5$	342 mμ	122,000 etc.

Thus, as the number of double bonds in conjugation increases, the value of absorption maximum also increases but does not increase proportionally as expected. It is probably due to the variation in bond length between double and single bonds. Let us consider the cyanine dye analogue.

$$Me_2\overset{+}{N} = CH—(CH = CH)_n— \ddot{N}\ Me_2 \leftrightarrow Me_2\ \ddot{N}—(CH{=}CH)_n—CH{=}\overset{+}{N}Me_2$$

In this case, resonance leads to uniform bond length and bond order along the polyene chain. As there is no change in bond length in the polyene chain, calculations give values which are very close to observed ones.

Note. It is important to note that the change from trans to cis configuration at one or more double bonds lower the wavelength as well as the intensity of absorption.

In case of acetylenic compounds, weak bands are observed (low intensity bands) at high wave-lengths and high intensity bands occur at lower wave-lengths. Consider the absorption bands in case of —(—C≡C—)$_n$—where $n \geq 3$.

		λ_{max}	ε_{max}
(*i*) When	$n = 3$	(*i*) 207 mμ	135,000
		(*ii*) 306 mμ	120
(*ii*)	$n = 4$	(*i*) 234 mμ	281,000
		(*ii*) 354 mμ	105

The ultraviolet spectrum of penta-yne is shown in the Fig. 2.21.

In Penta-yne, the absorption occurs at 260 mμ ε_{max} 352,000 and also a band at 394 mμ ε_{max} 120 which need a mention.

The absorption spectrum of a typical poly-yne and a typical poly-eneyne is shown in Fig. 2.22. The intensity and absorption maximum (λ_{max}) values increase with increasing conjugation and substitution. It helps in elucidating the structure of some unknown closely related compounds.

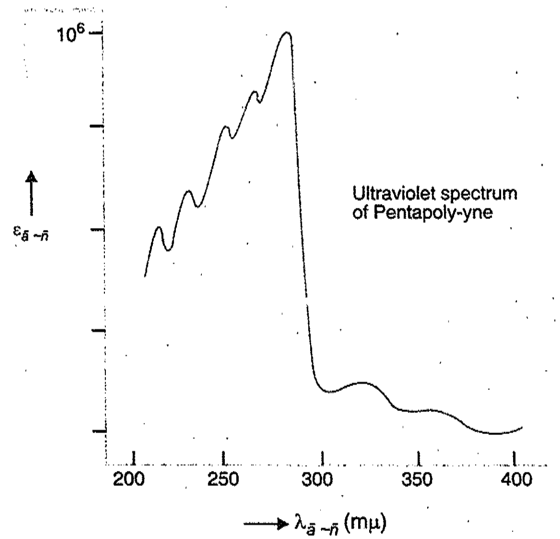


Fig. 2.21. UV Spectrum of pentapoly-yne.

Note. If a conjugated polyene contains more than four double bonds, then Fieser-Kuhn rules are used. According to this approach, both λ_{max} and ε_{max} are related to the number of conjugated double bonds as well as other structural units by the following equations.

$$\lambda_{max} = 114 \times 5\ M + n\ (48.0 - 1.7n) - 16.5\ R_{endo} - 10\ R_{exo}$$

$$\varepsilon_{max} = (1.74 \times 10^4)n$$

where
n = no. of conjugated double bonds.
M = no. of alkyl or alkyl like substituents on the conjugated system.
R_{endo} = no. of rings with endocyclic double bonds in the conjugated system.
R_{exo} = no. of rings with exocyclic double bonds.

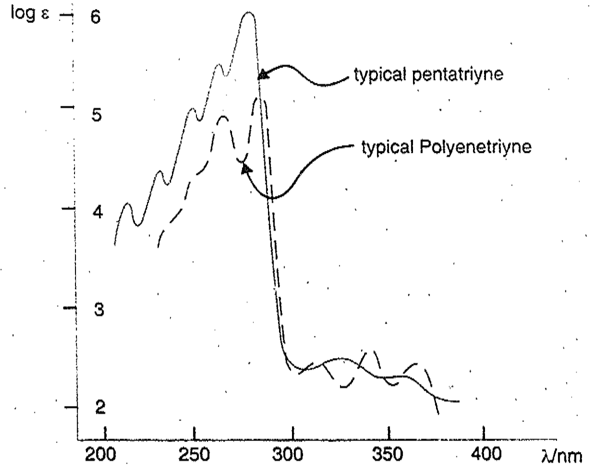
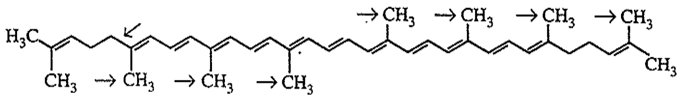


Fig. 2.22. Electronic absorption spectra typical of Poly-yne and Polyeneyne Chromophores.

Consider the case of Lycopene :



(Lycopene)

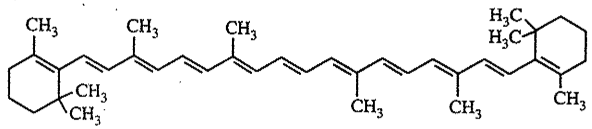
In this compound, only eleven double bonds are in conjugation. Thus, $n = 11$. In addition to this, there are eight substituents (methyl groups and chain residues). Thus, M = 8. As there is no ring system, there are neither exo nor endocyclic double bonds in this conjugated system. λ_{max} can be calculated as under :

$$\lambda_{max} = 114 + 5(8) + 11\,[48.0 - 1.7(11)] - 0 - 0 = 476 \text{ nm}$$

The observed value of λ_{max} is found to be 476 nm (hexane)

$$\varepsilon_{max} \text{ (calculated)} = 19.1 \times 10^4.$$

Similarly, λ_{max} can be calculated for β-carotene.



The calculated value of λ_{max} is found to be 453.3 nm and ε_{max} 19.1 × 10^4.

2.19 Ultra-violet Absorption in α, β-unsaturated Carbonyl Compounds

For a carbonyl group, two types of transitions occur.

(i) $>C{=}\ddot{O}: \xrightarrow{\pi \to \pi^*} >\dot{C}\text{: }\ddot{O}:$

(ii) $>C{=}\ddot{O}: \xrightarrow{n \to \pi^*} >C{=}\dot{O}$

The first transition involves the promotion of one of the π electrons to an antibonding π* orbital (π → π*). It is very intense and corresponds to shorter wavelength. The second transition (n → π*) involves the promotion of one of the non-bonding paired electron to π_3^* orbital. It is less intense and corresponds to longer wave-length. It is called R-band. (See Fig. 2.23).

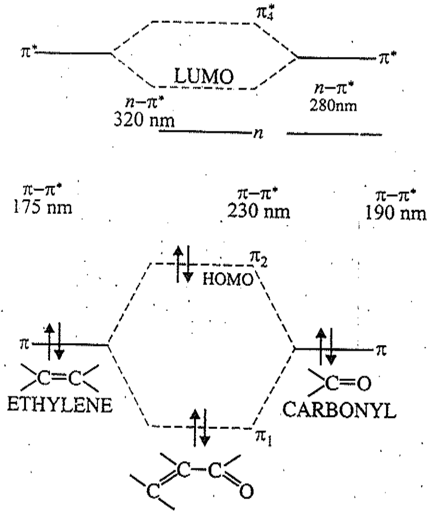


Fig. 2.23. UV transitions in α, β-unsaturated carbonyl compounds.

In α, β-unsaturated carbonyl compounds, the double bond and the carbonyl group are in conjugation. The spectra for such compounds are simple summation of ethylene and carbonyl chromophores. A bathochromic shift is observed if two chromophoric groups are conjugated as π electron cloud is spread over at least four carbon atoms. There is a π → π* transition due to ethylene unit which is in conjugation with carbonyl group.

In α, β-unsaturated carbonyl compounds where ethylene and carbonyl groups are conjugated, both π → π* and n → π* transitions show bathochromic shifts. The various transitions involved are shown above in Fig. 2.23. From the energy level diagram, it is clear that π_2 (HOMO) energy level is higher than either of the π levels of C=C and C=O. The π_3^* (LUMO) energy level is lower than that of π* level of C = C and C = O chromophores. Since the energy difference between (HOMO) and (LUMO) is less, the π → π_3* transition shows bathochromic effect. Similarly, n → π* transition (R-band) also shows bathochromic shift.

n → π* transition in aldehydes and ketones. Aldehydes and ketones show a weak forbidden band in the range 275 to 300 mμ due to the excitation of an oxygen lone electron to π* orbital. Aldehydes and highly substituted ketones absorb at upper end of the range. Polar substituents on α-carbon atom in axial or equitorial position raise or lower the extremes of this range respectively. When the carbonyl group is substituted by an auxochrome as in an ester, amide etc. the π* orbital is raised while n level of lone pair is hardly altered. Due to this, the n → π* transition in these compounds is shifted to lower wave-length range (200—215 mμ). Clearly, a weak band at 275 to 300 mμ [ε_{max} 10–100] is a positive identification of aldehydic or ketonic carbonyl group.

α, β--unsaturated carbonyl compounds show slightly stronger n → π* band or series of bands in the 300–350 mμ range. The positions as well as the intensity of n → π* bands are influenced by the transannular* interactions and also by the solvent.

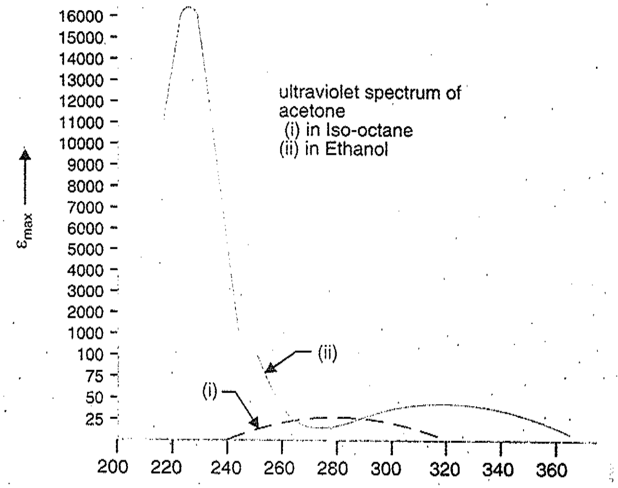


Fig. 2.24. UV spectrum of acetone in (i) Iso-octane (ii) Ethanol.

Axially substituted isomers absorb at longer wavelength than equitorially substituted isomers.

α, β-unsaturated acids, esters show bathochromic shift but absorb at comparatively shorter

---

* Trans-annular interaction arises due to the presence of apparently non-conjugated C=O and C=C groups in a compound.

wavelengths. α, β-unsaturated amides have been shown to absorb at lower values than the corresponding acids. The absorption occurs usually in the inaccessible region. It is important to note that the positions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition in carbonyl compounds vary with the nature of the solvent used. (See Fig. 2.24).

By increasing the polarity of the solvent, $\pi \rightarrow \pi^*$ transition experiences a red shift while $n \rightarrow \pi^*$ transition undergoes a blue shift. The changing polarity of the solvent brings about a change in the energy difference between the levels involved in the transitions. The shift is due to the change in the stability of the ground or the excited electronic states. The absorption due to $n \rightarrow \pi^*$ transition experiences a blue shift as the degree of hydrogen bonding between the carbonyl group and the solvent increases by increasing the polarity of the solvent. In other words, the energy of n electrons is strongly lowered by hydrogen bonding and thus, greater energy is required for promoting n electrons of π^* level.

A comparison in the ultra-violet spectra of un-conjugated carbonyl compounds (see Fig. 2.25) reveals that the value of absorption maximum for carbonyl group experiences a bathochromic as well as hyperchromic effects in conjugated carbonyl compound as compared to an un-conjugated carbonyl compound.

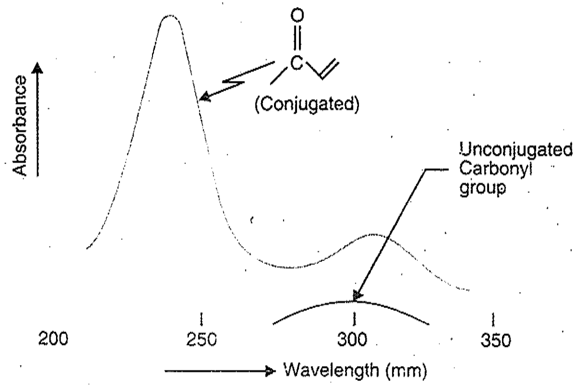


Fig. 2.25. UV Absorption spectra for conjugated and unconjugated carbonyl compounds.

2.20 Woodward-fieser Rules for Calculating Abscrption Maximum in α, β-unsaturated Carbonyl Compounds

Woodward and Fieser framed certain empirical rules for estimating the absorption maximum for α, β-unsaturated carbonyl compounds. The rules were later modified by Scott and are as follows :

(*a*) The basic value of α, β-unsaturated ketone is taken as 215 mμ. The α, β-unsaturated ketone may be acyclic or six membered.

For a compound, = CH—COX, basic value is 215 mμ, if X is an alkyl group.

If X=H, basic value becomes 207 mμ. The basic value is 193 mμ if X is OH or OR.

(*b*) If the double bond and the carbonyl group are contained in a five membered ring (cyclopentenone), then for such an α, β-unsaturated ketone, the basic value becomes 202 mμ. The ε_{max} for such compounds are generally above 10,000.

The structural increments for estimating λ_{max} for a given α, β-unsaturated carbonyl compound are as follows :

(*i*)	For each exocyclic double bond	+ 5 mμ
(*ii*)	For each double bond endocyclic in five or seven membered ring except cyclo-pent-2 enone	+ 5 mμ
(*iii*)	For each alkyl substituent or ring residue at the	
	α-position	+ 10 mμ
	β-position	+ 12 mμ
	γ- or δ- or higher position	+ 18 mμ
(*iv*)	For each double bond extending conjugation	+ 30 mμ
(*v*)	For a homoannular conjugated diene.	+ 39 mμ

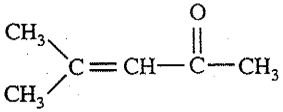
(*vi*) Increments for various auxochromes in the various α-, β-, γ- etc. positions are given in the following Table T_2–9.

Table T_2–9

Chromophore	*Increment in nm (or mμ) for position w.r.t. the carbonyl group*			
	α-	*β-*	*γ-*	*δ- or higher*
—OH	+ 35	+ 30	—	+ 50
—OAc	+ 6	+ 6	+6	+ 6
—Cl	+ 15	+ 12	—	—
—Br	+ 25	+ 35	—	—
—OR	+ 35	+ 30	17	31
—SR	—	+ 85	—	—
—NR_2	—	+ 95	—	—

Making use of the above rules, the absorption maximum for the various α, β-unsaturated compounds can be estimated.

EXAMPLE 1. *Calculate λ_{max} (Ethanol) for the given structure :*



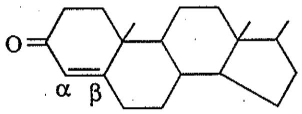
$$(CH_3)_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

SOUTION. The basic value for acyclic α, β-unsaturated ketone is 215 mμ. In this structure, we see two β-alkyl substituents. The value of absorption maximum is thus calculated as :

Basic value	=	215 mμ
2β–alkyl substituents (2 × 12)	=	24 mμ
Calculated value	=	**239 mμ**

The observed value is found to be 237mμ ε_{max} 12,500.

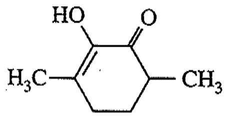
EXAMPLE 2. *Calculate λ_{max} for the given structure.*



Basic value = 215 mμ
23-ring residues (2 × 12) = 24 mμ
1 exocyclic double bond = 5 mμ
Calculated value = **244 mμ**

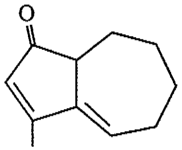
The observed value is found to be 241 mμ.

EXAMPLE 3. *Calculate λ_{max} for the given structure.*



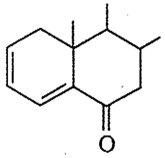
SOLUTION. Basic value = 215 mμ
CH substitution at
α position = 25 mμ
23-substituents (one alkyl and one ring residue) = 24 mμ
Calculated value = **274 mμ**
Observed value = 275 mμ

EXAMPLE 4. *Calculate λ_{max} for the following structure.*



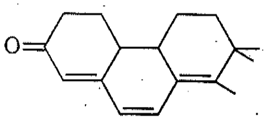
SOLUTION. It is an α, β-unsaturated cyclopentenone system.
Basic value = 202 mμ
1 β-alkyl substitution = 12 mμ
1 exocyclic double bond = 5 mμ
1 double bond extending conjugation = 30 mμ
1 γ-ring residue = 18 mμ
1 δ-ring residue = 18 mμ
Calculated value = **285 mμ**
Observed value = 287 mμ

EXAMPLE 5. *Calculate λ_{max} for the given structure*



SOLUTION. Basic value = 215 mμ
α-ring residue = 10 mμ
δ-ring residue = 18 mμ
1 exocyclic double bond = 5 mμ
Homoannular conjugated diene = 39 mμ
1 double bond extending conjugation = 30 mμ
Calculated value = **317 mμ**
Observed value = 319 mμ

EXAMPLE 6. *Calculate λ_{max} for the given structure*



SOLUTION. Basic value = 215 mμ
1 β-ring residue = 12 mμ
1 (δ + 1) ring residue = 18 mμ
2 (δ + 2) ring residues (2 × 18) = 36 mμ
2 double bonds extending conjugation (2 × 30) = 60 mμ
2 exocyclic double bonds (2 × 5) = 10 mμ
Calculated value = **351 mμ**
Observed value = 354 mμ

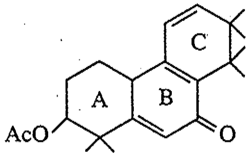
It may be noted that the value of absorption maximum is shifted due to the change in the polarity of the solvent, *i.e.*, absorption maximum is solvent dependent. More polar solvents will experience hydrogen bonding with the carbonyl group and $n \rightarrow \pi^*$ transition will experience blue shift. Sovent corrections may be noted as follows :

Hexane = + 11 mμ
Dioxane = + 7 mμ
Methanol = 0 mμ
Water = − 8 mμ
Chloroform = − 1 mμ

After making the necessary solvent corrections, the value of absorption maximum is obtained in ethanol.

In case there is a cross conjugation in a compound, *i.e.*, the carbonyl group has α, β-unsaturation on either side; then the value of absorption maximum is estimated by considering the most highly substituted conjugated system. Consider the following example.

In ring B, the carbonyl group is conjugated on either side but conjugated system is highly substituted towards ring C. Thus, the value of absorption maximum is calculated as follows :



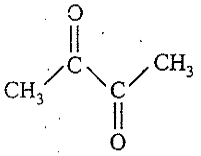
Basic value = 215 mμ
1 α-ring residue = 10 mμ
1 β-ring residue = 12 mμ
1 δ-ring residue = 18 mμ
1 double bond extending conjugation = 30 mμ
Homoannular conjugation diene = 39 mμ
Calculated value = **324 mμ**
Observed value = 327 mμ

For such compounds, the value of the extinction coefficient is usually high.

Quinones. In quinones, weak $n \rightarrow \pi^*$ transitions are responsible for imparting colour to some simple quinones. The absorption values in π-quinone are :

(*i*)	242 mμ	ε_{max}	24,000
(*ii*)	281 mμ	ε_{max}	400
(*iii*)	434 mμ	ε_{max}	20

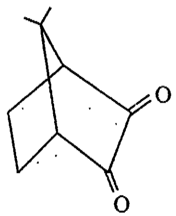
α-Diketones and α-keto Aldehydes. Acyclic α-diketones such as biacetyl, exist in the S-trans conformation (with a dihedral angle, 180°). The spectrum of biacetyl shows the normal weak R-band at 275 nm and weak band near 450 nm. The second band (at 450 nm) is formed as a result of interaction between the carbonyl groups.



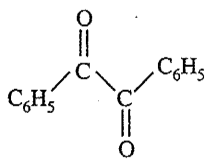
$\lambda_{max} = 450$ nm
$\epsilon_{max} = 10$

The position of the long wave length band of α-diketones incapable of enolisation reflects the effect of coplanarity upon resonance and thus depends upon the dihedral angle between the carbonyl groups.

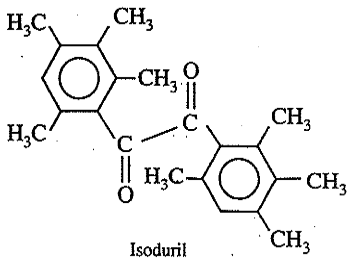
Consider the following:



Camphoquinone
(I)
Dihedral angle 0-10°
$\lambda_{max} = 488$ nm
$\varepsilon_{max} = 17$

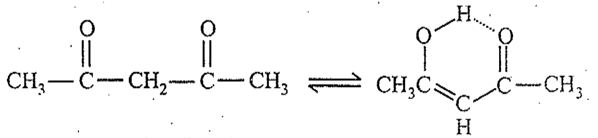


Benzil
(II)
Dihedral angle = 90°
$\lambda_{max} = 370$ nm
$\varepsilon_{max} = 40$



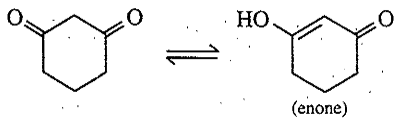
Isoduril
(III)
Dihedral angle = 180°

β-Diketones. The ultraviolet spectra of β-diketones depend on the degree of enolisation. The possibility of intra-molecular hydrogen bonding stabilises the enolic form in acetylacetone. The enolic species exists to the extent of 15% in aqueous solution. In the vapour phase or in solution in non-polar solvents it exists to the extent of 91-92%. The absorption depends directly on the concentration of the enol tautomer.



λ_{max} (in H_2O) = 274 nm, $\varepsilon_{max} = 2050$
λ_{max} (in Iso-octane) = 272 nm, $\varepsilon_{max} = 12000$

Cyclic β-diketones such as cyclohexane dione exists almost exclusively in the enolic form even in polar solvents. The enolic structures show strong absorption in the 230-260 nm region due to $\pi - \pi^*$ transition in the S-trans enone system.



The formation of the enolate ion, in alkaline solution, shifts the strong absorption band into the 270-300 nm region.

2.21 Compounds With *N* To *O* Bonds

Four groups, *viz.*, nitro, nitroso, nitrates and nitrites contain multiple nitrogen to oxygen linkages. These structures show weak absorption in the near ultraviolet region resulting from $n \rightarrow \pi^*$ transition. The sulphur atom in sulphones has no lone pair electrons and the lone pairs of electrons associated with the oxygen atom appear to be tightly bound. Saturated sulphoxides absorb near 220 nm with intensities of the order of 1500.

Table T_2-10

Compound	*n → π* transition (R-band)*		*Solvent*
	λ_{max}	ε_{max}	
Nitromethane	275 nm	15	Heptane
2-Methyl-2 nitropropane	280.5	23	Heptane
Nitrosobutane	300	100	Ether
	665	20	
Octyl nitrate	270	15	Pentane
n-Butyl nitrite	218	1050	Ethanol

2.22 Benzene and Its Derivatives

The B-band at 254 mμ in ultraviolet spectrum of benzene shows a great deal of fine structure in the vapour phase. The fineness of the structure diminishes if we scan it in hexane solution and is almost completely destroyed in ethanol solution (See Fig. 2.26). In hexane solution, benzene shows absorptions at 184 mμ. ε_{max} 60,000; 204 mμ ε_{max} 7400 and 254 mμ ε_{max} 204. The band at 254 mμ is the result of forbidden transitions in highly symmetrical benzene molecule. Benzene shows a series of low intensity bands between 230 and 270 mμ.

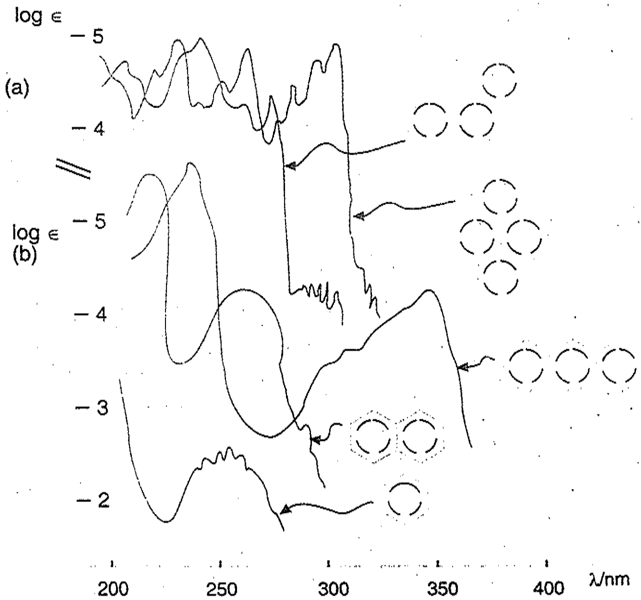
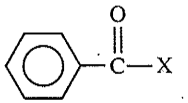


Fig.2.26. Electronic absorption spectra of typical polynuclear aromatic hydrocarbons (in hexane).

It has been noted that absorption maximum for poly-nuclear aromatic hydrocarbons moves to longer wavelength. Comparing the ultra-violet spectrum of benzene with naphthalene, we see that the value of absorption maximum as well as extinction coefficient are more for naphthalene as compared to those of benzene. Naphthalene absorbs at 480 mμ ε_{max} 11000 while anthracene absorbs at still higher value. Pentacene absorbs at 580 mμ ε_{max} 12600 and appears blue.

2.23 Rules for Calculating Absorption Maximum for Derivatives of Acyl Benzenes

Like Woodward Fieser rules, Scott devised a set of rules for calculating the absorption maximum for the derivatives of acyl benzenes. These rules help in estimating the position of absorption maximum in ethanol in a number of monosubstituted aromatic ketones, aldehydes, acids and esters.

For a compound of the type 

(i) the basic value is 246 mμ if X is an alkyl group or alicyclic residue.

(ii) If X is hydrogen atom, the basic value becomes 250 mμ and

(iii) the basic value is 230 mμ if X is OH or OR. The structural increments in mμ for further substitution on the aromatic ring in the ortho, meta and para positions are given in the Table T_2–11.

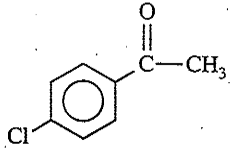
Table T_2–11

Auxochrome	*Increment in mμ* *Position of the Substituent*		
	Ortho	*Meta*	*Para*
Alkyl	+ 3	+ 3	+ 10
OH, OR	+ 7	+ 7	+ 25
Cl	0	0	+ 10
Br	+ 2	+ 2	+ 15
NH_2	+ 13	+ 13	+ 58
NHAc	+ 20	+ 20	+ 45
NR_2	+ 20	+ 20	+ 85
O^-	+ 11	+ 20	+ 75

Note. It is important to note that the effect of the para substituent is more pronounced for the bathochromic shift.

EXAMPLE 1. *Calculate the absorption maximum in ethanol for p-chloroacetophenone.*

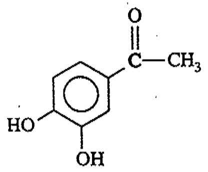
SOLUTION. In this case, X is an alkyl group and thus the basic value is 246 mμ.



Basic value = 246 mμ
Cl-substitution at para position = 10 mμ
Calculated value = 256 mμ

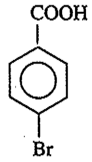
The observed value is found to be 254 mm.

EXAMPLE 2. *Calculate the absorption maximum for the following compound.*



SOLUTION. Basic value = 246 mμ
OH substitution at meta = 7 mμ
OH substitution at para = 25 mμ
Calculated value = **278 mμ**
Observed value = 281 mμ

EXAMPLE 3. *Calculate the absorption maximum for the following compound.*



SOLUTION. Basic value = 230 mμ
Br substitution at para = 15 mμ
Calculated value = **245 mμ**
Observed value = 245 mμ

In disubstituted benzenes,

(a) When electronically complementary groups such as —NH_2 and —NO_2 are substituted para to each other, there is a pronounced bathochromic shift in the main absorption band compared to the effect of either substituent considered separately. For example, p-nitroaniline absorbs at 375 mμ ε_{max} 16000. It is due to the extension of the chromophore from the electron donating group to the electron withdrawing group through the benzene ring.

(b) When the two groups in the para positions are not complimentary or are ortho or meta to each other, then the absorption spectrum is close to that of the separate non-interacting chromophores. For example, *m*-dinitrobenzene absorbs at 200 mμ ε_{max} 13000.

2.24 Absorption Spectra of Condensed Ring Systems

The range of absorption maximum for polycyclic hydrocarbons is very great and spectra are usually complicated (See Fig. 2.26, page 47). Such spectra are useful as finger prints. Moreover, the relatively non-polar substituents have a very small effect on the shape and position of the absorption peak of parent hydrocarbon. Identification of polycyclic hydrocarbon is usually done by comparison.

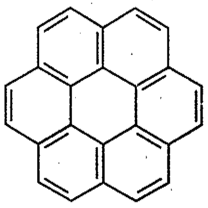
The condensed systems are classified into

(a) **Cata-condensed system.** In cata-condensed system, no carbon atom belongs to more than two rings. Benzene, naphthalene etc. are the examples.

(i) *Linear cata-condensed compounds.* These are Naphthalene, Anthracene etc.

(ii) *Bent cata-condensed compounds.* These include phenanthrene type molecules.

The spectra of cata-condensed hydrocarbons resemble benzene. Bathochromic shift is observed with the increase in the number of rings in the structure. For example, benzene absorbs at 254 mμ ε_{max} 204. Naphthalene absorbs at 312 mμ ε_{max} 289, while pentacene absorbs in the visible region.



Coronene

(b) **Peri-condensed system.** In peri-condensed systems, a carbon atom belongs to more than two rings. An example is **coronene.**

Peri-condensed rings show absorptions at longer wave-lengths as compared to cata-condensed structures.

Coronene shows absorptions at 305 mμ, 342 mμ and 428 mμ.

2.25 Heterocyclic Compounds

The ultra-violet spectrum of five-membered heterocyclic aromatic compounds can be compared with cyclopentadiene. It has been observed that in these compounds, a forbidden band (R-band) due to $n \rightarrow \pi^*$ transition is also observed with very low value of ε_{max}. For example, in furan, we observe a band at 252 mμ ε_{max} 10,000. The chromophoric or auxochromic substitution brings about bathochromic as well as hyperchromic shift.

Table T_2–12

Compound	λ_{max} *(mμ)*	*Intensity* ε_{max}
Furan	200	10,000
	252	1
2-Nitro furan	225	3,400
	315	8,100
Pyrrole	183	–
	211	15,000
Pyrrole 2-aldehyde	252	5,000
	290	16,500
Thiophene	231	7,100
2-Bromothiophene	236	9,100

In six-membered heterocyclic compounds, the ultra-violet spectrum of pyridine can be distinguished from that of benzene as its B-band is more intense than that of benzene. Moreover, B-band in pyridine shows a marked increase in intensity with the increase in polarity of the solvent (UV spectrum of pyridine is shown in Fig. 2.27). On the other hand, this band for benzene is little effected in position as well as intensity. The presence of substitution in pyridine usually brings hyperchromic effect. For example, the B-band for pyridine at 275 mμ ε_{max} 2750 is shifted to 262 mμ ε_{max} 3560 for 2 methyl pyridine and to 263 mμ ε_{max} 3650 for 2-chloro-pyridine.

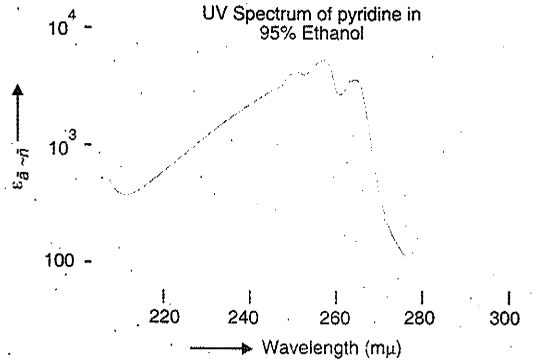
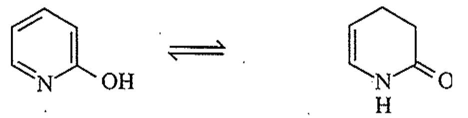


Fig. 2.27. UV spectrum of pyridine in 95% ethanol.

In some cases, like hydroxy pyridines, hypochromic shifts are also observed. Sometimes, a change in pH brings about a marked change in the absorption maximum of the substance which is clearly due to the change in the chromophore. The change in chromophore is explained as the shifting of equilibrium to one of the tautomeric forms with the change in pH. Thus, a substance existing in tautomeric forms can be carefully diagnosed for the preference of one form over the other by this technique. For example, 2-hydroxy pyridine and Pyridone-2 exist in tautomeric equilibrium.



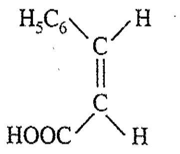
2 Hydroxy Pyridine ⇌ Pyridone-2

The spectra of these compounds were shown to favour pyridone-2 which is an α, β-unsaturated ketone. Clearly, the equilibrium is shifted towards right.

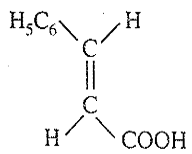
Steric Hindrance and Coplanarity

Woodward rules give reliable results only for those compounds in which there is no strain around the chromophore. We know that in the case of extended conjugation, the position of absorption depends upon the length of the conjugated system. Longer the conjugated system, higher will be the absorption maximum and larger will be the value of the extinction coefficient. If, in a structure, the π electron system is prevented from achieving coplanarity, there is a marked shift in the absorption maximum and extinction coefficient. The departure in the value of absorption maximum calculated from the empirical rules is due to steric crowding which distorts the geometry of the chromophore. Thus, the conjugation is reduced by reduction in the π orbital overlap. Consider the cases of biphenyl and substituted biphenyl. The $\pi \rightarrow \pi^*$ transition for diphenyl which readily achieves coplanarity absorbs at 250 mμ ε_{max} 19,000 but in 2-methyl diphenyl, $\pi \rightarrow \pi^*$ transition undergoes blue shift and diminished intensity as the two rings remain no longer coplanar. The absorption maximum for 2-methyl diphenyl is 237 mμ ε_{max} 10250. Also nitro benzene absorbs at 252 mμ ε_{max} 8620 while orthonitro-toluene absorbs at 250 mμ ε_{max} 5950 due to reduction in coplanarity.

If the compound containing alkene chromophore is capable of existing as geometrical isomers, the trans-isomer is found to absorb at longer wave-length with higher value of extinction coefficient as compared to cis-isomer. It is due to more effective π orbital overlap possible in the trans-isomer which, thus, achieves coplanarity of π electron system more readily. Consider the case of cinnamic acid. It exists in two isomers :



(Cis)



(Trans)

Due to greater crowding in cis-form (both bulky groups are on the same side), the geometry of the alkene chromophore is distorted and departure from coplanarity results. Thus, $\pi \rightarrow \pi^*$ transition in cis-cinnamic acid takes place at lower wave-length with lower extinction coefficient.

(i) Trans-cinnamic acid absorbs at 272 mμ ε_{max} 15900.

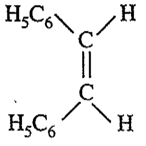
(*ii*) Cis-cinnamic acid absorbs at 268 mμ ε_{max} 10700.

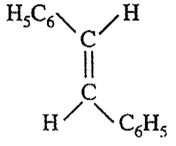
Slight steric hindrance to coplanarity about a single bond has a very little effect on the position and intensity of the absorption maximum. If the steric hindrance to coplanarity about a single bond is more, then, there is a marked decrease in intensity and may accompany a red or blue shift. The absorption maximum of 2, 5 dimethyl-*p*-nitro aniline occurs at 385 mμ ε_{max} 4840 showing a red shift and marked decrease in intensity as compared to *p*-nitroaniline which absorbs at 375 mμ ε_{max} 16000. A blue shift is observed in case of 2, 4, 6 trimethyl acetophenone which absorbs at 242 mμ ε_{max} 3200 as compared to *p*-methyl acetophenone at 252 mμ ε_{max} 15000. Out of cis-and

---

It is due to hydrogen bonding through the lone pair of electrons on nitrogen in pyridine with solvent molecules.

trans-stilbenes, a distortion in coplanarity in cis-stilbene is due to steric hindrance. This results in lowering the value of absorption maximum at lower extinction coefficient. Thus, a band which appears at 295 mμ ε_{max} 25000 in trans-stilbene has a value 283 mμ ε_{max} 12300 in cis-stilbene.


(Cis-stilbene)


(Trans-stilbene)

In some cases, steric hindrance to coplanarity about the double bond raises the ground state energy level but leaves the excited state relatively unchanged. This results in a bathochromic shift from the expected value.

2.27 Fluorescence and Phosphorescence

Fluorescence is the light of comparatively longer wavelength emitted from a molecule after it has absorbed light of different and short wavelength.

Anthracene is a colourless substance and its electronic absorption spectrum lies in the ultra-violet region. But it is found that pure samples of anthracene when viewed in the ultra-violet light give off a blue-visible light. This light is called **fluorescence.** The emission of light or fluorescence stops atonce when the irradiating light is removed. On the other hand, the phenomenon of phosphorescence is said to occur when the substance continues to emit the radiation of longer wavelength even when the irradiating light is removed. To study the phenomenon of fluorescence and phosphorescence, let us study the one electron excitation process (see Fig. 2.28).

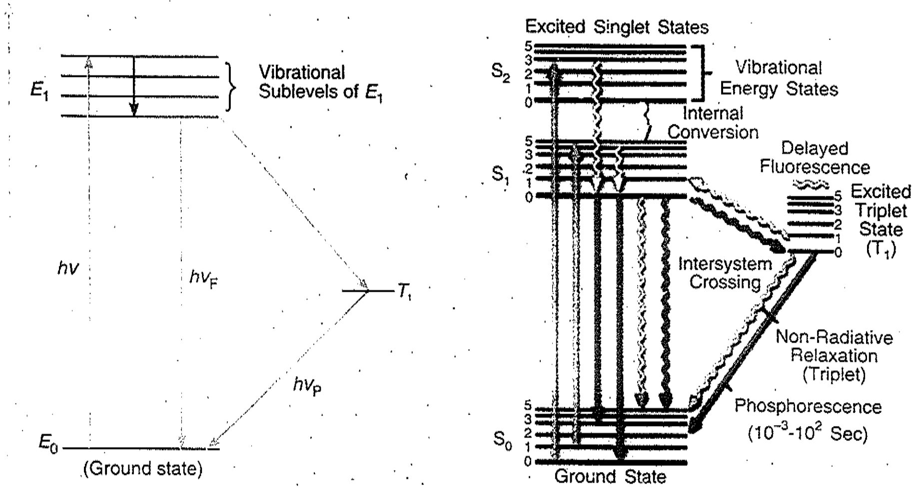
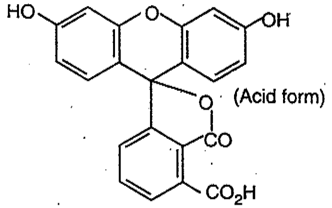


Fig. 2.28. Mechanism of Fluorescence and Phosphorescence.

When the molecule in the ground state absorbs light ($h\nu$), its one electron gets promoted from the ground state molecular orbital to one of the vibrational sub-levels of the first excited state molecular orbital (E_1) or to the higher excited states E_2, E_3 etc. When the electron returns from E_1 to E_0, it emits radiation which is of longer wavelength or lower energy than $h\nu$. It is called $h\nu_f$, called **fluorescent radiation.**

In another mode, the energy may be lost from E_1 to T_1 and then from T_1 to the ground state, E_0. The main difference between E_1 and T_1 is the electron spin orientation. The spins of the two electrons must be anti-parallel which originally occupy the ground state molecular orbital. The original promotion of electron to first excited state E_1, followed by its return to the lowest vibrational sub-level E_1 does not change the spin of the electron. But the transition from E_1 to T_1 level does change the spin. Energy states containing only spin paired electrons are called singlet states while those with parallel spin electrons are called triplet states. In the excited triplet state, electrons are farther apart in space and thus, electron-electron repulsion is minimised. Thus, triplet states are more stable than singlet states and are longer lived. Thus, this state may survive after the irradiating light is removed. After this, electron jumps to E_0 state by emitting the radiation of energy $h\nu_p$. It is called **phosphorescent radiation.**

The fluorescent spectrum for anthracene consists of four maxima with λ_{max} 380, 400, 420 and 450 nm. Important uses of the fluorescence phenomenon are shown by the molecules of fluorescein and optical brightner derivative of 4, 4′ diaminostilbene.



Fluorescein

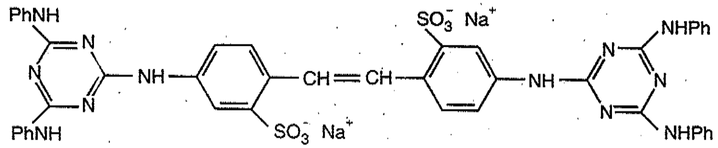


Fig. 2.29. An Optical Brightner.

The intense green fluorescence of aqueous fluorescein solution makes it an excellent material for leak detection and an excellent marker for sea rescue operations etc. The property of fluorescence is applied in polymer chemistry to detect and identify plasticizers and in the study of impurities. Biological applications include the study of the *three dimensional tertiary* structure of proteins by measuring the proximity of known fluorescent groups within the protein. These fluorescent groups are generally aromatic amino-acids. Phosphorescence seen at night in the sea is due to several species of marine micro-organism which when agitated by an oar splash undergo an enzymatic alarm reaction which liberates energy in the form of green light. This phenomenon is called **Bioluminescence.**

2.28 Electronic Transitions for Charge-transfer Complexes

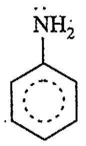
Iodine imparts violet colour in hexane while it is brown in benzene. When aniline is dissolved in chloroform and tetracyanoethylene (colourless) is added to it, a deep blue solution results. These colour shifts are due to the formation of complexes between the pairs of molecules. As a result, two new molecular orbitals are formed which undergo new electronic transition.

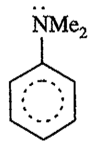
The formation of these complexes involves the transfer of electronic charge from an electron rich molecule* to an electron deficient molecule with molecular orbitals of suitable energy and symmetry. These complexes are called charge transfer complexes.

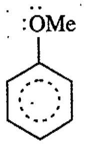
---

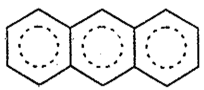
* Electron rich molecule is Lewis base donor.

Some charge transfer donors are :

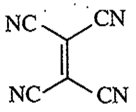

Aniline

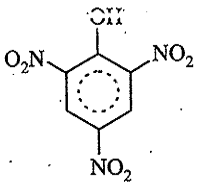

N,N-Dimethyl Aniline


Anisole


Anthracene

Some charge transfer acceptors are :


Tetra Cyano Ethylene


Picric Acid

$AlCl_3$ Aluminium Chloride

I_2 Iodine

The filled π-orbitals (A) in the donor molecule overlap with depleted orbitals (B) in the acceptor molecule. Due to this, two new molecular orbitals are formed. These are (*i*) the low energy molecular orbital (occupied) in the ground state (A_1) (*ii*) the upper molecular orbital (B_1). The transitions from A_1 to B_1 result in the formation of new absorption bands. (See Fig. 2.30)

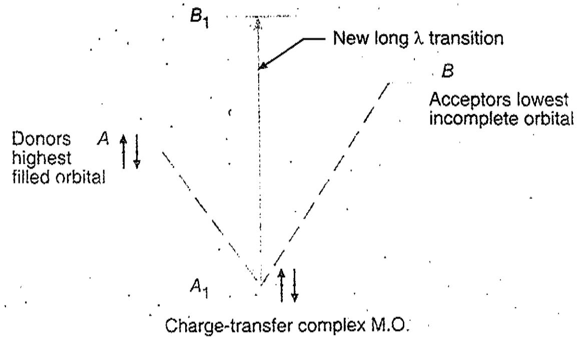
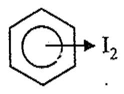
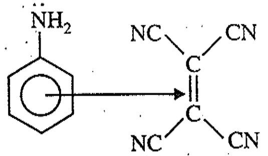
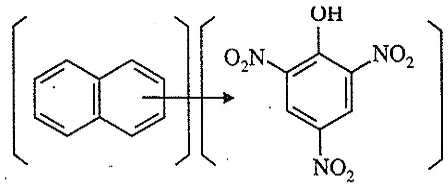


Fig. 2.30. Electronic transitions for charge-transfer complexes. Donor and acceptor orbitals combine to form two new orbitals (A and B) for the complex. New electronic transitions for long λ are then possible between A and B.

Some charge transfer complexes are shown below:


Benzene-Iodine Complex

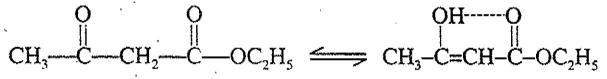

Aniline-tetracyanoethylene Complex


Naphthalene-Picric Acid Complex

In the benzene-iodine complex, λ_{max} for benzene is 255 nm but for molecular iodine in hexane, the absorption occurs in the visible region around 500 nm. This charge transfer complex has an intense additional band around 300 nm but this tails into the visible region and modifies the violet colour of molecular iodine to brown. The λ_{max} value for aniline is 280 nm and that for tetracyanoethylene is at 300 nm. But the complex of aniline with tetracyanoethylene absorbs in the visible region at 610 nm.

2.29 Study of Keto-enol tautomerism

Carbonyl compounds containing α-hydrogen exist as keto-enol tautomers. β-ketones and β-ketoesters exist as tautomeric mixtures. Their UV spectra show absorption bands which are characteristic of both keto and enol forms. Due to **enol** form, a strong $\pi \rightarrow \pi^*$ bands is observed and also a weak $n \rightarrow \pi^*$ band for the **keto** group. Consider the case of ethylacetoacetate ($CH_3COCH_2COOC_2H_5$) in ethanol. A strong band ($\pi \rightarrow \pi^*$) at 245 nm (ε_{max} 18000) is observed and a weak band ($n \rightarrow \pi^*$) is observed at 275 nm (ε_{max} 20) due to keto form.



Ethyl acetoacetate (keto form 92.5%) λ_{max} = 275 nm ε_{max} 20.

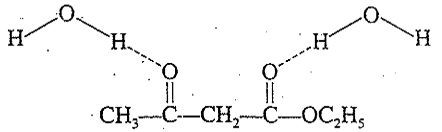
Ethyl acetoacetate (Enolic form 7.5%) λ_{max} = 245 nm ε_{max} 18000.

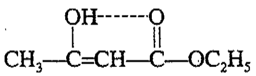
In the same way consider Acetonylacetone

Acetonylacetone (keto form 16%)

Acetonylacetone (Enolic form 84%) λ_{max} = 273 nm ε_{max}10500.

From above we see that ethylacetoacetate exists predominantly in keto form in ethanol whereas acetonylacetone exists predominantly in the enolic form. It is known that in solvents like water, C_2H_5OH etc. (Polar protic solvents), ketonic form predominates due to stabilisation by hydrogen bonding. Also in non-polar solvents (like Hexane), hydrogen bonding is not possible and the enolic form predominates by intramolecular hydrogen bonding.


Intermolecular H-bonding (keto form)


Intermolecular H-bonding (Enatic form)

As the polarity of the solvent increases, the percentage of enolic form decreases. Thus, by using solvents of different polarities and measuring corresponding λ_{max} values, the relative amounts of keto and enol forms can be found. Therefore, the value of equilibrium constant can also be found.

2.30 Applications of Ultra-violet Spectroscopy

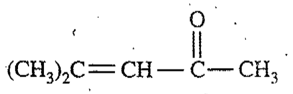
Ultra-violet spectroscopy has been mainly applied for the detection of functional groups (chromophore), the extent of conjugation, detection of polynuclear compounds by comparison etc. Some important applications of ultraviolet spectroscopy are as follows :

(*a*) **Detection of functional groups.** The technique is applied to detect the presence or absence of the chromophore. The absence of a band at a particular wavelength may be regarded as an evidence for the absence of a particular group in the compound. A little information can be drawn from the UV spectrum if the molecule is very complicated. If the spectrum is transparent above 200 mμ, it shows the absence of (*i*) conjugation (*ii*) a carbonyl group (aldehydes and ketones) (*iii*) benzene or aromatic compounds and also (*iv*) bromo or iodo atoms. An isolated double bond or some other atoms or groups may be present. It means that no definite conclusions can be drawn if the molecule absorbs below 200 mμ.

(*b*) **Extent of conjugation.** The extent of conjugation in polyenes R—(CH=CH)$_n$—R can be estimated. Addition in unsaturation with the increase in the number of double bonds (increase in the value of *n*) shifts the absorption to longer wavelength. It is found that the absorption occurs in the visible region, *i.e.*, at about 420 mμ, if *n* = 8 in the above polyene. Such an alkene appears coloured to the human eye.

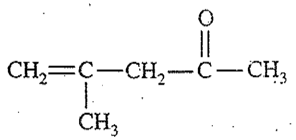
(*c*) **Distinction in conjugated and non-conjugated compounds.** It also distinguishes between a conjugated and a non-conjugated compound. The following isomers can be readily distinguished since one is conjugated and the other is not.

(*i*)



$$(CH_3)_2C{=}CH{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3$$

(*ii*)



$$CH_2{=}\underset{\underset{\large CH_3}{|}}{C}{-}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3$$

The forbidden $n \rightarrow \pi^*$ band for the carbonyl group in the compound (*i*) will appear at longer wave-length compared to that for the compound (*ii*).

The alkyl substitution in an alkene causes a bathochromic shift. The technique is not much useful for the identification of individual alkenes.

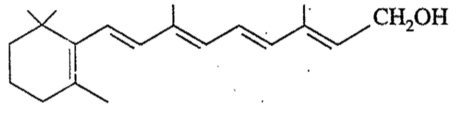
(*d*) **Identification of an unknown compound.** An unknown compound can be identified by comparing its spectrum with the known spectra. If the two spectra coincide, the two compounds must be identical. If the two spectra do not coincide, then the expected structure is different from the known compound.

(*e*) **Examination of Polynuclear hydrocarbons.** Benzene and Polynuclear hydrocarbons have characteristic spectra in the ultra-violet and visible-region. Thus, the identification of the polynuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compounds. The presence of substituents on the ring, generally, shifts the absorption maximum to longer wavelength.

(*f*) **Elucidation of the structure of vitamins A and K.** It is useful for the elucidation of the structures of vitamins K$_1$ and K$_2$ and also those of A$_1$ and A$_2$. The ultraviolet spectra of vitamins

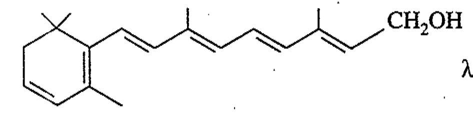
K$_1$ and K$_2$ are due to the presence of the same chromophore, *i.e.*, 2, 3 dimethyl naphtha-quinone. The absorption maxima of this compound are 243, 249, 260, 269 and 330 mμ.

The elucidation of the structures of vitamins A$_1$ and A$_2$ are possible by this technique. Vitamin A$_1$ absorbs at 325 mμ and absorption maxima for Vitamin A$_2$ appear at 287 and 351 mμ. The absorption maxima appear at longer wavelength for vitamin A$_2$ due to the presence of additional ethylenic bond.



λ_{max} = 325 mμ

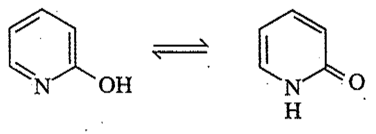
Vitamin A$_1$



λ_{max} = 325 mμ
and
351 mμ

Vitamin A$_2$

(*g*) **Preference over two Tautomeric forms.** If a molecule exists in two tautomeric forms, preference of one over the other can be detected by ultra-violet spectroscopy. Consider 2-hydroxy pyridine which exists in equilibrium with its tautomeric form, pyridone-2.

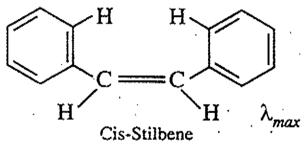


2 Hydroxy Pyridine Pyridone-2

The spectra of these two compounds were found to favour pyridone-2 which is an α, β-unsaturated ketone and clearly, the equilibrium is shifted towards the right, *i.e.*, Pyridone-2.

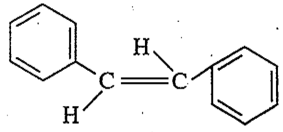
(*h*) **Identification of a compound in different solvents.** Sometimes, the structure of the compound changes with the change in the solvent. Chloral hydrate shows an absorption maximum at 290 mμ in hexane while the absorption disappears in the aqueous solution. Clearly, the compound contains a carbonyl group in hexane solution and its structure is $CCl_3.CHO.H_2O$ whereas in aqueous solution it is present as $CCl_3.CH(OH)_2$.

(*i*) **Determination of configurations of Geometrical isomers.** The results of absorption show that cis-alkenes absorb at different wavelengths as compared to their corresponding trans-isomers. The distinction becomes possible when one of the isomers is forced to be non-coplanar by steric hindrance. Thus, cis forms suffer distortion and absorption occurs at lower wavelength.



λ_{max} = 283 mμ

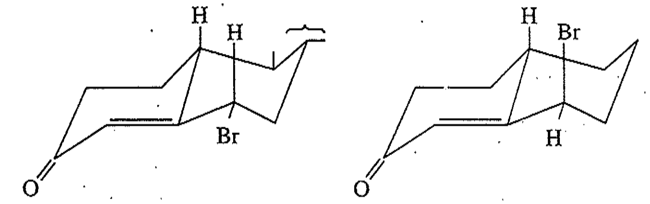
Cis-Stilbene



λ_{max} = 295.5 mμ

Trans-Stilbene

(*j*) **Distinguishes between Equitorial and Axial Conformations.** This technique also distinguishes between equitorial and axial conformations. Consider the following conformations.

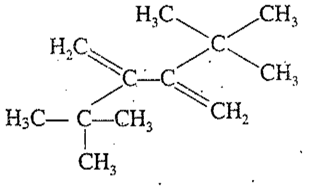


The $n \rightarrow \pi^*$ (R-band) which appears at longer wavelength in α, β-unsaturated ketones is influenced by the presence of polar group in the γ-position. It has been noted that the effect of an axial substituent to displace the R-band to longer wavelength is greater compared to that observed in its equitorial isomer.

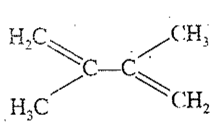
(*k*) **Determination of strength of hydrogen bonding.** Solvents like water, C_2H_5OH etc form hydrogen bonds with the *n*-electrons of carbonyl oxygen. Due to this, the energy of *n*-electrons in the ground state is lowered depending upon the strength of hydrogen bonds. Thus, $n \rightarrow \pi^*$ transition of carbonyl compounds is shifted towards shorter wavelength. Hence, by measuring the λ_{max} of a carbonyl compound in a non-polar and polar protic solvent, the strength of hydrogen bond can be determined. Consider $n \rightarrow \pi^*$ transition of acetone in hexane (at 279 nm) and that in water at 264.5 nm. The blue shift by 14.5 nm corresponds to an energy of 5 kcal mol^{-1}. Clearly, the strength of hydrogen bond between water and acetone is 5 kcal mol^{-1}. It is in fair agreement with the known strength of hydrogen bonds.

(*l*) **Hindered Rotation and Conformational Analysis.** This technique is employed to study hindered rotation in sterically hindered dienes and also in o-substituted diphenyls.

Sterically hindered dienes. Any deviation from coplanarity of double bonds will result in the reduction of π-orbital overlap and thus λ_{max} shifts to lower values of λ_{max} and ε_{max}. Consider the case of 2, 3-di-tertbutyl-1, 3-butadiene. In this case, there is little conjugation between two double bonds due to bulky tert-butyl groups. It shows absorption at lower wavelength (λ_{max} = 180 nm) compared to 2, 3-dimethyl-1, 3-butadiene (λ_{max} = 225 nm) in which there is no deviation from coplanarity.



2,3-Di-tert-butyl-1,3-butadicue
λ_{max} = 180 nm



2.3-Dimethyl-1,3-butadiene
λ_{max} = 225 nm

2.31 Important Features in Electronic Spectroscopy

1. **Electronic Transition.** The study of energy levels of electrons in a molecule can be made through electronic transitions. Consider a molecule *AB*. If it absorbs energy enough to excite an electron, it will definitely affect the bond strength of the molecule. The effect will cause

(*i*) Change in equilibrium bond distance and

(*ii*) Change in the dissociation energy, *D*.

Now it is essential to know the region of electromagnetic spectrum in which electronic spectra appear and other transitions associated with the electronic transitions. We know that the energy of electromagnetic radiation is given by : $E = h\nu$. Here, ν is the frequency of radiation and *h* is planck's constant. When a molecule absorbs radiation of frequency, ν, the electron undergoes excitation from a lower to the higher energy level. The difference between the ground state and the excited state is given by :

$$E_{excited} - E_{ground} = h\nu$$

It is found that this energy difference is of the order of 5 eV which corresponds to wavelength equal to 2500 A°.

This wavelength (2500 A°) corresponds to ultra-violet region of electromagnetic radiation. As the wavelength range of **UV** radiation starts at the blue end of visible light (~ 4000 Å) and ends at 2000 Å, the ultra-violet region is divided into two spectral regions.

(*i*) The region between 2000 Å to 4000 Å is called near ultra-violet or simply **ultra-violet region** and

(*ii*) the region below 2000 Å (1000-2000 Å) is called **Far vacuum *uv* region.**

It is found that short wavelength region of the visible and the near *uv* region of the electromagnetic radiation cause electronic transition in the molecule and produce electronic spectra. Hence, the ultra-violet spectroscopy is called Electronic Spectroscopy.

A molecule usually contains two or more atoms and can exist in a number of energy levels. An electronic transition is accompanied by a number of vibrational and rotational transitions. Clearly, an electronic spectrum is made up of a number of lines due to simultaneous changes in the vibrational and rotational energies. According to **Born-oppenheimer approximation**, the total energy of the molecule is given by :

$$E_{Total} = E_{Trans} + E_{vib} + E_{Rot} + E_{Ele}$$

Also the change in energy (Δ*E*) of molecule due to absorption of radiation is given by :

$$\Delta E = \Delta E_{Trans} + \Delta E_{vib} + \Delta E_{Rot} + \Delta E_{Ele}$$

Neglecting change in translational energy, the magnitude of the change in energies has the order:

$$\Delta E_{Ele} > \Delta E_{vib} > \Delta E_{Rot}$$

Since the molecular spectra consists of a number of closely spaced lines in the form of a band, the electronic spectra are often called **band spectra**. It is different from the line spectra obtained in the case of atoms. The frequency (in cm^{-1}) of the electronic transition is given by :

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{(\Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot})\ \text{cm}^{-1}}{hc}$$

we must know that ΔE_{vib} and ΔE_{Rot} have a number of values depending upon their respective quantum numbers. Clearly, the number of possible lines for a given change in electronic level is large. **Hence, the electronic band spectra are complex.** Considering the magnitude of electronic, vibrational and rotational energy changes, it is found that spectra of electronic transition consists of:

(*i*) Vibrational coarse structure and (*ii*) Rotational fine structure

Each electronic level has its characteristic potential energy diagram. The position of the minimum in the potential energy curve shows the changes in the bond distance and the dissociation energy of the molecule. The transition from one curve to another curve occurs so quickly that atoms do not get a chance to move appreciably by the time, it takes place. As a result of this, the transition tends to take place vertically upward or downward. This result is called **Franck Condon Principle.** We know that a molecule has highly probable nuclear separation *r* in both ground and the excited states. As ψ^2 is a measure of probability, it leaves a position at a distance *r* at which magnitude of vibrational wave function $|\psi_{vib}|$ is high and goes to the levels for which $|\psi_{vib}|$ is high at the same value of *r*. Other transitions are less probable. Clearly, the probability of transition is given by how much the ψ functions with same magnitude would overlap.

2. Franck Condon Principle. According to this principle, "*An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.*"

This principle is true to the first approximation since the electrons move so much faster than the nuclei that during the electronic transition, the nuclei do not change their positions. Hence, an electronic transition may be represented by a vertical line on the plot of potential energy versus internuclear distance.

Consider a diatomic molecule. Two potential energy curves are shown in Fig. 2.31 for the molecule in the ground electronic state (E_0) and the first electronic state (E_1). Since the bonding in the excited state is weaker than in the ground state, the minimum in the potential energy curve for the excited state occurs at a slightly greater internuclear distance than the corresponding minimum in the ground electronic state. Quantum mechanically, it is known that the molecule is in the centre of the ground vibrational level of the ground electronic state.

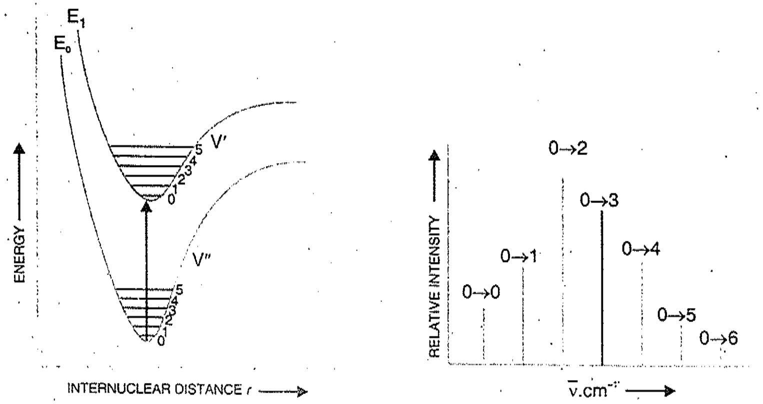


Fig. 2.31. Electronic transition in diatomic molecule.

When an electron falls on the molecule the most probable electronic transition (according to Franck Candon Principle) takes place from, $V'' = 0$ to $V' = 2$ (*i.e.* 0→2). Transitions to other vibrational levels of the excited electronic state occur with lower probabilities so that their relative intensities are smaller than the intensity of the O→2 transition. (See Fig. 2.32).

Now consider a slightly different case of a diatomic molecule. It has potential energy curve (E_0) in the ground state and two potential energy curves E_1 and E_2 in the excited state. We see that potential energy curve E_2 does not have a minimum. (Fig. 2.32).

The equilibrium internuclear distance is larger in E_1 than in E_0 as the bond is weaker in the excited state. The transition state indicated by arrow **a** (as per Franck Condon Principle) has maximum intensity. Other possible transitions are from the first excited vibrational level of the ground electronic state. They are shown by $\boldsymbol{b_1}$ and $\boldsymbol{b_2}$. The transition b_1 ends in the lowest vibrational level of the first electronic state where the molecule is still held firmly. But the transition b_2 promotes the molecule to a point where the energy is far above the potential energy plateau of state E_1 at large distance with the result that the molecule dissociates. It may be noted that the molecule will also dissociate if it is excited to a level below the plateau in E_1 but above point c where the P.E. curves for E_1 and E_2 cross. At an internuclear distance w.r.t. point *c*, the molecule may undergo a crossover from one state to the other without energy change and continue to dissociate in two parts.

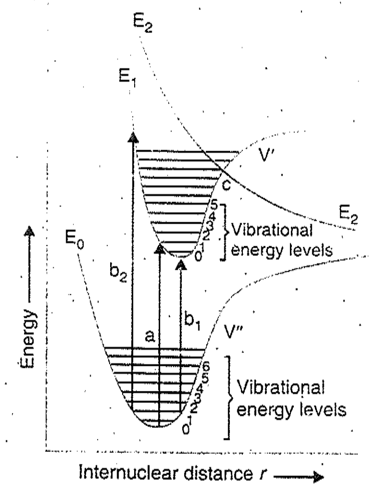


Fig. 2.32. Potential energy curves for the ground state, two excited states of a diatomic molecule. The curve crosses the curve E_1.

In molecule like H_2, N_2 etc. (homonuclear), the highest occupied molecular orbital (HOMO) in the ground state is a bonding molecular orbital and the lowest unoccupied molecular orbital (LUMO) is an antibonding molecular orbital. On absorption of energy, the electron undergoes a transition from HOMO to LUMO. It occurs in the lower end of the UV region. In case of Oxygen molecule which carries two unpaired electrons and is in the triplet state, the transition occurs from the triplet ground state to the triplet excited state.

The electronic spectra of polyatomic molecules are more complex. The rotational and the vibrational fine structure of electronic spectra can be observed in the gaseous state of small molecules. In solution the rotational energy levels are not well defined. Also the vibrational transitions are broad.

3. Excited state and the Ground state: In a photochemical process, the absorption of a quantum of energy promotes the electron from the ground state energy level to the higher level. As the energy levels of a molecule are quantised, the amount of energy required to raise an electron in a given molecule from one level to the higher one is a fixed quantity. The light in the frequency equivalent to this energy will be able to cause excitation. If light of another frequency is sent through the sample, no absorption will be caused and it passes without any loss of intensity. On the other hand, if light of exact frequency in passed through the sample, then light leaves the sample with diminished intensity and also excitation of electron in caused. A spectrophotometer is an instrument which compares the intensity of transmitted light with that of the incident light.

Absorption position are usually expressed in wavelength units. If a compound absorbs in the visible region, it appears coloured and possesses a colour complimentary to that which is absorbed. For example, a compound absorbing in the violet region is yellow in colour, *i.e.*, yellow is the complimentary colour of violet colour.

Table T_2–13:

Wavelength absorbed, (Å)	*Absorbed colour*	*Observed complimentary colour*
4000–4500	Violet	Yellow
4500 -5000	Blue	Orange
5000 -5500	Green	Red
5500 -6000	Yellow	Violet
6000 -6500	Orange	Blue
6500 -7000	Red	Green

From these considerations, it appears that an electronic spectrum should consist of one or more sharp peaks, each corresponding to the transfer of an electron from one electronic level to another. But under ordinary conditions, peaks are seldom sharp and instead, broad absorption bands are recorded. It is due to the fact the excitation of electrons are also accompanied by the constant vibratory and rotatory motion of the molecules. The vibratory and the rotatory modes are also quantised. Clearly, a molecule in a particular electronic state is also accompanied by some vibrational and rotational states. The difference between two adjacent electronic levels is more as compared to the adjacent rotational levels while the difference between the adjacent vibrational levels has same intermediate value. The electronic excitation is superimposed upon rotational and vibrational levels. Clearly, during promotion, the electron moves from a given vibrational and rotational level within one electronic mode to some other vibrational and rotational level within the next electronic mode.

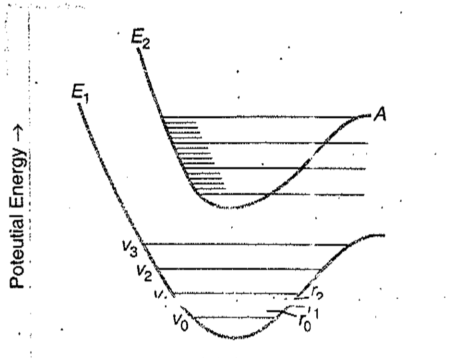
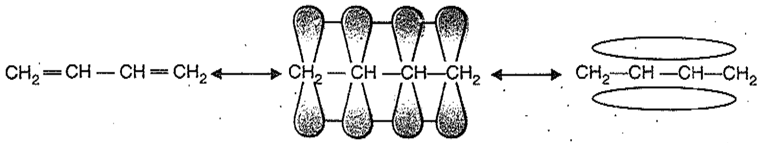


Fig. 2.33. Energy levels of diatomic molecules.

Thus, there will be a large number of possible transitions (closed together) responsible for change in electronic, rotational and vibrational level. Hence, not one but a large number of wave lengths which are close enough will be absorbed resulting in the formation of bands. In more complex molecules which contain a large number of atoms, the multiplicity of the vibrational sublevels and their closeness results in the discrete bands to coalesce and thus, broad bands are observed.

4. **Electronic transitions of Polyethenes using free electron model:** In conjugated diene such as 1, 3-butadiene, the π-electrons are completely delocalised on four carbon atoms.



Similarly, in 1, 3, 5-Hexatriene, the π-electron cloud is spread on six carbon atoms. Such systems are treated in terms of '**Free electron model**' and it is found that the absorption bands shift to longer wavelengths as the extent of conjugation increases. Clearly, in the compound, C_6H_5—$(CH = CH)_n$-C_6H_5, the π → π* transition lies in the UV region when $n = 1$ or 2. As n increases, the electronic transition shifts to the visible region (See Fig. 2.34).

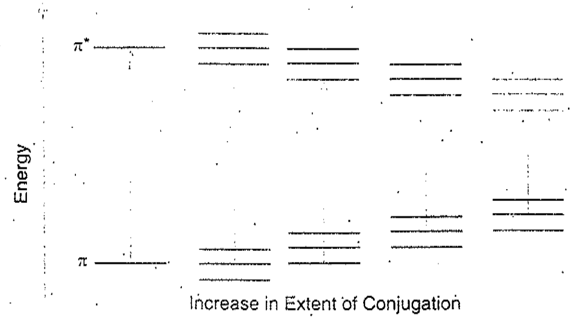


Fig. 2.34. Diagram shows that wavelength of absorption varies directly to the extent of conjugation.

The intensity of the electronic band is determined by the extent of overlap of the wave functions in the ground and excited states. As there is poor overlap of wave functions of the ground and excited states in the $n \rightarrow \pi^*$ transition and there is considerable overlap of the corresponding wave functions in the $\pi \rightarrow \pi^*$ transitions, we say that $n \rightarrow \pi^*$ transitions are less intense than $\pi \rightarrow \pi^*$ transitions. In the strongly acidic medium, the $n \rightarrow \pi^*$ band disappears due to protonation of lone pair of electrons. The protonation of a functional group introduces prominent changes in the spectra. The $n \rightarrow \pi^*$ transitions are changed by the solvent effects in cases where lone pair of electrons on nitrogen and oxygen containing systems interact with the solvent.

2.32 Important Terms and definitions in Ultraviolet spectroscopy

1. **Electronic spectroscopy.** Its range is
   (*i*) UV : 200 – 400 nm and
   (*ii*) Visible : 400 – 800 nm

2. **Principle:** When UV or visible radiation is passed through a substance under examination, absorption of energy results in the promotion of electron from the ground electronic state to the excited electronic state. During the process of absorption, a large number of photon-molecule collisions are possible but only those collisions will cause absorption of energy in which the energy of photon matches the energy difference between the ground and the excited electronic state of the molecule. The absorption of energy is quantised. In ultra-violet and visible spectroscopy, electronic transitions take place.

3. **Far UV and Near UV region:** The UV region extending from 100–200 nm is called far UV region while that from 200–400 nm in near UV region. At 200 nm or below, Oxygen absorbs strongly. Thus, measurement in this region is carried by flushing the instrument with N_2. Also at 150 nm or below, N_2 starts absorbing. Hence, the region below 150 nm is studied only by using evacuated instruments. The region below 150 nm is called vacuum region.

4. **Lambert's law:** When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

5. **Beer's law:** When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.

6. **Beer-Lambert's law:** According the Beer-Lambert's law:

$$\log \frac{I_0}{I} = \epsilon c l = A.$$

Where A = absorbance or optical density. ∈ = Molar extinction coefficient, ∈ is the property of the molecule undergoing transition. Its value depends upon the probability of transition and the size of the absorbing chromophore. Its values vary from $0 - 10^6$. High intensity absorptions have values, above 10^4 while low intensity absorptions have values below 10^3. Values between $0–10^3$ are due to forbidden transitions.

7. **Bands and not sharp peaks:** The UV spectra of organic compounds consists of bands and not sharp peaks. The reason is that each electronic transition is accompanied by the changes in vibrational and rotational levels. As a result, the absorption spectrum in the vapour phase consists of a large number of closely spaced peaks but if the spectrum of solution is taken, then the fine structure turns into bands. It may be due to solvent-solute interactions.

8. **Hydrogen bonding:** shifts the ultra violet absorptions to shorter wavelengths of high frequencies.

9. **Chromophore:** It is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultra-violet or the visible region.

10. **Auxochrome:** It is any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength).

11. Bathochromic effect: It is an effect due to which the absorption maximum is shifted towards longer wavelength due to the presence of auxochrome or by the change of solvent. Increase in conjugation causes bathochromic shift.

12. Hypsochromic shift or effect: Due to this, absorption maximum is shifted to shorter wavelength. It is due to reduction in conjugation or change in the polarity of solvent.

13. A good solvent in U.V.: Spectroscopy is one which is low priced and is transparent down to 210 nm. Polar bonds like carbonyl are effected by solvent polarity. With increase in solvent polarity, $n \rightarrow \pi^*$ transitions undergo blue shift while $\pi \rightarrow \pi^*$ transitions undergo red shift.

14. In ultra-violet spectrum: Sharp peaks are seldom observed but instead broad bands are observed. The reason is that vibrational and rotational effects are superimposed on the electronic transitions.

2.33 Short Questions with Answers

1. Define the term 'spectroscopy'.

Ans. Spectroscopy involves the interaction between electromagnetic radiation and the substance under investigation.

2. Why is absorption and not emission spectroscopy used to study the spectra of organic compounds?

Ans. Emission spectroscopy cannot be used since the emission of radiation from an organic compound requires very high temperature. Organic compounds are low melting and thus, generally decompose at high temperatures.

3. What is the effect of ultra-violet or visible light on the organic compound?

Ans. When the substance under investigation is subjected to the action of UV or visible radiation, then it causes changes in the electronic energy levels within the molecule.

4. What do you mean by absorption of radiation in a spectrum or a record?

Ans. Absorption of radiation at a particular wavelength leads to decrease in the percent transmission to appear in the spectrum as a dip, called a peak or an absorption band.

5. What do you mean by a spectrum or record of the spectrum?

Ans. The spectrum of a compound represents a graph of either wavelength or frequency continuously changing over a small portion of the electromagnetic spectrum versus either percent transmission or absorbance.

6. Define Absorbance.

Ans. Absorbance is a measure of the absorption of radiation by a sample.

$$A = \log\left(\frac{\text{original intensity}}{\text{Intensity}}\right) = \log\frac{I_0}{I} = \in cl.$$

7. What is the effect of hydrogen bonding on ultra-violet absorption?

Ans. Hydrogen bonding shifts the ultra-violet absorptions to shorter wave lengths.

8. What do you mean by a good solvent in UV spectroscopy and what is its effect on absorption maximum?

Ans. A good solvent in ultra-violet or visible spectroscopy is one which is low priced and is transparent down 210 nm. Polar bonds like carbonyl are affected by solvent polarity. With increase in solvent polarity, $n \rightarrow \pi^*$ transitions undergo blue shift (towards short wave length) while $\pi \rightarrow \pi^*$ transition undergo red shift.

9. Tell whether a molecule can undergo more than one electronic shift.

Ans. Depending upon the wavelength of light used, a molecule can undergo all the possible electronic transitions. For example, acetaldehyde (CH_3CHO) can undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions.

10. What happens to the excited molecule when radiation is cut off?

Ans. In that case, the excited molecule gives off energy and returns to the ground state. The process is called deactivation. The excited molecule may undergo a chemical change depending upon the nature of the molecule. Cis-trans isomerisation is an example of the type.

11. For the detection of aldehydes and ketones, which transition is more authentic, $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$.

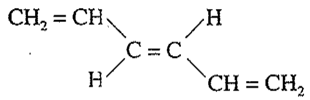
Ans. $n \rightarrow \pi^*$ with low value of extinction coefficient ($\in_{max}$).

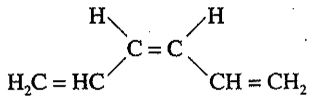
12. Describe the shift in absorption ($n \rightarrow \pi^*$) when a more polar solvent is used.

Ans. When a more polar solvent is used, the excitation of n electrons to π^* orbital requires more energy. Thus, the shift is towards shorter wavelength.

13. How will you distinguish between cis and trans-1, 3, 5-Hexatriene.

Ans. The structure of hexatrienes are:


(Trans)


(Cis)

cis-isomer absorbs at lower wavelength, because the bulky groups on the same side cause repulsive interactions resulting in the reduction in conjugation.

14. Which spin state is observed at the instant of excitation?

Ans. Excitation occurs very rapidly ($<10^{-13} s$) and thus, there is no time for the excited electron to change its spin (Franck Condon Principle). Clearly, singlet ground state (S_0), gives singlet excited state (S_1).

15. For which isomer, $\pi \rightarrow \pi^*$ transition occurs at high wavelength and higher extinction coefficient: cis-stilbene or trans-stilbene.

Ans. Trans-stilbene absorbs at higher wavelength. The reason is that coplanarity is needed for the most effective overlap of π-orbitals and thus, increased ease of $\pi \rightarrow \pi^*$ transition. It is possible in case of trans-isomer.

16. What structural features may produce bathochromic or hypsochromic effect in an organic compound?

Ans. A bathochromic or red shift is caused by the change of solvent or the presence of an auxochrome. A hypsochromic (or blue) shift is caused by the change of solvent or by the structural changes such as reduction in conjugation.

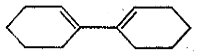
17. Aniline absorbs at 280 nm ($\in_{max}$ 8600) but in acidic solution, the main absorption band is seen at 203 nm ($\in_{max}$ 7500) which is comparable to benzene. Explain.

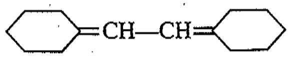
Ans. In the acidic medium, aniline is converted to anilinium ion. Thus, due to removal of conjugation of lone pair of electrons on nitrogen atom of aniline with π-bond system of benzene, the hypsochromic shift takes place.

18. Which out of benzene (colourless) or quinone (yellow) has more easily promoted electrons?

Ans. Quinone.

19. Why the λ_{max} for the diene (I) is observed at lower nm than II?


(I)


(II)

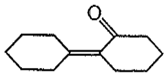
Ans. In both the dienes, there are four ring residues as substituents. In diene (II), the two double bonds are exocyclic. Thus, λ_{max} for II will be higher by 2 × 5 nm or 10 nm.

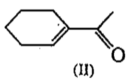
20. Which of the following compounds would be suitable or unsuitable as a solvent for use in recording UV spectra of organic compounds?

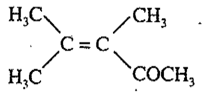
(*a*) Cyclohexane (*b*) Iodoethane (*c*) benzene (*d*) diethyl ether.

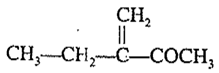
Ans. Cyclohexane or diethyl ether do not absorb above 200 nm and hence can be used as solvents. But benzene and iodoethane absorb above 200 nm and thus, cannot be used as solvents.

21. Following four ketones are filled in four bottles and their labels are removed. Measurement of ultra-violet spectra of the contents of four bottles give λ_{max} 221, 249, 237 and 258 nm. Assign structures to the appropriate λ......


(I)


(II)


(III)


$CH_3—CH_2—\overset{\overset{\large CH_2}{||}}{C}—COCH_3$

(IV)

Ans. (*i*) **For compound I**

$$\begin{aligned} \text{Basic value} &= 215 \text{ nm}\\ \text{one } \alpha\text{-ring residue} &= 10 \text{ nm}\\ \text{two } \beta\text{-ring residue} &= 24 \text{ nm}\\ \text{exocyclic DB to two rings} &= \underline{10 \text{ nm}}\\ \lambda_{max} &= 259 \text{ nm} \end{aligned}$$

(*ii*) **For compound II**

$$\begin{aligned} \text{Basic value} &= 215 \text{ nm}\\ \text{one } \alpha\text{-alkyl} &= 10 \text{ nm}\\ \text{one } \beta\text{-ring residue} &= \underline{12 \text{ nm}}\\ \lambda_{max} &= 237 \text{ nm} \end{aligned}$$

(*iii*) **For compound III**

$$\begin{aligned} \text{Basic value} &= 215 \text{ nm}\\ \text{one } \alpha\text{-alkyl} &= 10 \text{ nm}\\ \text{two } \beta\text{-alkyls} &= \underline{24 \text{ nm}}\\ \lambda_{max} &= 249 \text{ nm} \end{aligned}$$

(*ii*) For compound IV

$$\begin{aligned} \text{Basic value} &= 215 \text{ nm}\\ \text{one } \alpha\text{-alkyl} &= \underline{10 \text{ nm}}\\ \lambda_{max} &= 225 \text{ nm} \end{aligned}$$

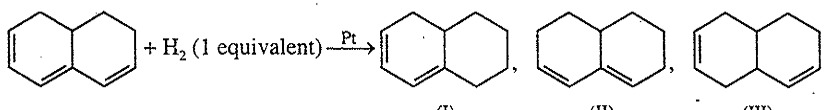
22. Calculate the concentration in μg ml^{-1} of a solution of organic compound (mol mass 211.2) in 0.11 M HCl giving an absorption at its λ_{max} 281 nm of 0.612 in 4 cm cell. The molar absorptivity at 281 mm is 5372.

Ans. We know the relation: $A = \epsilon c.l.$

Substituting the values, we get

$$\begin{aligned} 0.612 &= 5372 \times c \times 4\\ c &= \frac{0.612}{5372 \times 4} = 0.0000\ 2848 \text{ mol } l^{-1}\\ &= 0.00002848 \times 211.2 = 0.002848 \text{ gm } l^{-1}\\ &= 2.848 \ \mu\text{g ml}^{-1}. \end{aligned}$$

23. The following triene on partial hydrogenation gives three products, which are separated by chromatography. How can you identify the products by the application of woodward-fesher rules.



(I) (II) (III)

Ans. (*i*) **For compound I**

$$\begin{aligned} \text{Basic value} &= 253 \text{ nm}\\ \text{3 Ring residue} &= 15 \text{ nm}\\ \text{1 exocyclic DB} &= \underline{5 \text{ nm}}\\ \lambda_{max} &= 273 \text{ nm} \end{aligned}$$

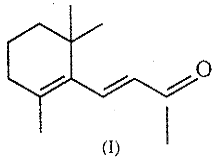
(*ii*) **For compound II**

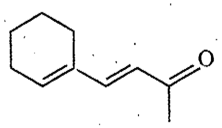
$$\begin{aligned} \text{Basic value} &= 214 \text{ nm}\\ \text{3 Ring residue} &= 15 \text{ nm}\\ \text{1 exocyclic DB} &= \underline{5 \text{ nm}}\\ \lambda_{max} &= 234 \text{ nm} \end{aligned}$$

(*ii*) **For compound III**

As the compound is not conjugated, λ_{max} occurs below 200 nm.

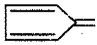
24. How will you identify the following compounds from the given spectral data. λ_{max} 296 nm, ϵ_{max} 10700 and λ_{max} 281 nm, ϵ_{max} 20800?


(I)


(II)

Ans. We see that the compound with λ_{max} 296 nm has half intensity as compared to the other compound. The decrease in intensity is due to steric hindrance by methyl group and its effect on the absorption of conjugated system. Thus, the compound I has decreased intensity.

25. Benzene is colourless but its isomer, fulvene is yellow. How will you explain it?

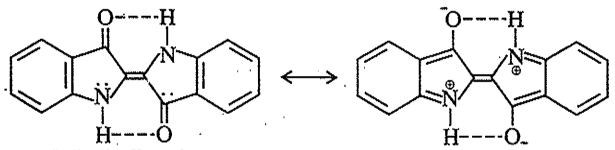
Ans. The formula of fulvene is $=CH_2$. It is an isomer of benzene (C_6H_6). Resonance stabilises the ground state of benzene compared to its excited state whereas fulvene is stabilised in the excited state. Thus, the electronic excitation energy required for fulvene is lower than that for benzene. As a result of this, fulvene absorbs at higher wavelength which makes it yellow in colour. Benzene absorbs at lower wavelength and is colourless.

26. o-Nitroacetanilide is deep yellow but para-nitro acetanilide is yellow. Why is the colour of 'o'-isomer deeper?

Ans. The ortho isomer exhibits intramolecular hydrogen bonding whereas the para Isomer shows intermolecular hydrogen bonding. Internal or intramolecular hydrogen bonding stabilises the excited state of a molecule to the greater extent than the intermolecular hydrogen bond. Clearly, the electronic excitation energy required for o-isomer is smaller and thus, absorption occurs at longer wavelength and result in deepening of the colour.

27. Why is Indigotin dark blue in colour?

Ans. The trans form of indigotin can be written as in the following resonating structures.



Indigolin (Trans form)
(I) (II)

The resonating structure II is more stable in the excited state. Also the internal hydrogen bonding gives further stability in the excited state. Thus, the transition from HOMO to LUMO is very low. As a result λ_{max} for the electronic transition is high and indigotin shows dark blue colour.

FURTHER READING

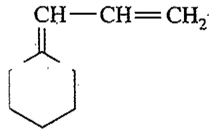
1. *A.I. Scott, Interpretation of the ultra-violet spectra of natural products.* Pergamon, Oxford 1964. It is an authoritative work on Wood-ward rules *etc.*
2. C. Nordling, *Angew, Chem. int.* Ed. II (1972), 83 (Review of E.S.C.A.).
3. C.N.R. Rao, *Ultraviolet and visible spectroscopy. Chemical applications.* Plenum Press, 1975.
4. I. Fleming and D.H. William, *Spectroscopic methods in organic chemistry.* Mc-Graw Hill, 1973.
5. Nachod and Zuckkerman, Determination of organic structure by physical methods. Academic press—(Five volumes).
6. UV Atlas of organic compounds, Butterworths, London, 1965. (A collection of the spectra of about 1,000 compounds).
7. Ultra-violet reference spectra, Sadtler Research laboratories, 3314–20 spring garden st, Philadelphia, Pa.
8. B.M. Trost, *Problems in spectroscopy : Organic structure determination by NMR, UV & visible and mass spectra,* Benjamin, 1967.

REVIEW QUESTIONS

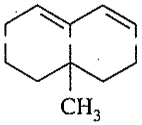
1. (*a*) Define Electronic spectroscopy. What is its absorption range? Write the relationship between wavelength, frequency and wave number.
   (*b*) Calculate the energy associated with the radiations having wave number 3×10^4 per cm.
2. (*a*) What are absorption laws? How is an ultraviolet spectrum plotted ?
   (*b*) Explain quantisation of energy.
   (*c*) Write a short note on Electromagnetic spectrum.
3. Describe briefly how an ultraviolet spectrum can be scanned for a pure organic compound? Why are absorption bands formed instead of sharp lines in the spectrum?
4. (*a*) Detail the chemistry of electronic spectroscopy. Give the various types of transitions involved in this technique with one example in each case.
   (*b*) Explain the effect of polar solvents on (*i*) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.
5. (*a*) Define the following terms :
   (*i*) Bathochromic shift (*ii*) Hypsochromic shift
   (*iii*). A Chromophore (*iv*) Hyperchromic effect.

   (*b*) On what factors do (*i*) and (*ii*) depend?
6. (*a*) Explain transition probability.
   (*b*) Describe the various types of absorption bands which arise as a result of the electronic transitions. Discuss the effect of solvent polarity on K and R-bands.
7. (*a*) Define the term 'chromophore'. How will you detect the presence of carbonyl group in aldehydes and ketones?
   (*b*) Following the Woodward-Fieser rules, calculate the absorption maximum for each of the following compounds :

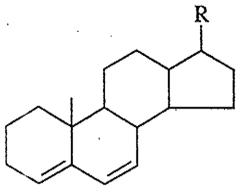
(*i*)



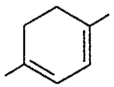
(*ii*)



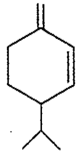
(*iii*)



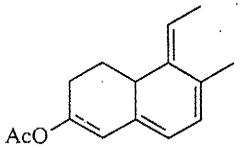
(*iv*)



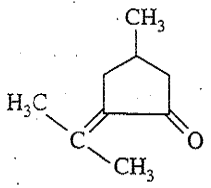
(*v*)



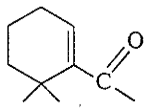
(*vi*)



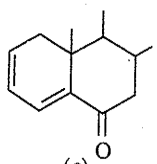
8. Discuss the various types of electronic transitions and explain the effect of the polarity of the solvent on each type of transition.
9. "A conjugated diene absorbs at a higher wavelength with higher value of extinction coefficient as compared to a diene in which double bonds are isolated." Comment on this statement with examples giving the chemistry involved.
10. Describe the Woodward-Fieser rules for calculating the absorption maximum in dienes. Do these rules obey strictly on all dienes? If not why ?
11. Explain the various applications of the ultra-violet spectroscopy.
12. What type of transitions are observed in α, β-unsaturated carbonyl compounds? How absorption maximum and intensity are shifted when carbonyl group is not conjugated? Discuss the effect of solvent polarity on R-band.
13. Following Woodward-Fieser-Scott rules, it has been found that the following compounds have absorption maxima at (*i*) 237 mμ (*ii*) 317 mμ (*iii*) 259 mμ end (*vi*) 285 mμ. Explain which is which ?



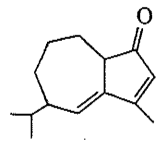
(*a*)



(*b*)



(c)



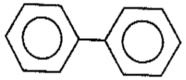
(d)

14. Aniline absorbs at 280 nm (ε_{max} 8600), however, in acidic solution, the main absorption band is seen at 203 nm. Explain.

Hint. In acidic medium, the lone pair on nitrogen is no longer present and hence conjugation is removed.

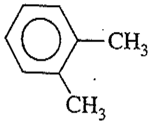
15. The position of absorption of acetone shifts in different solvents. 279 nm (hexane), 272 nm (ethanol) and 264.5 nm (water). Explain.

16. Biphenyl shows the following UV absorption data. In its 2, 2,-dimethyl derivative, however, the absorption pattern becomes almost similar to o-xylene. Explain.



(Biphenyl)

λ_{max} 252 ε_{max} 19000



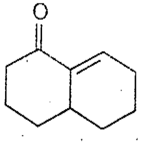
o-Xylene

λ_{max} 262 nm ε_{max} 270

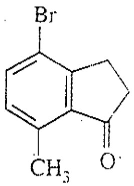
Hint. The angle of twist is very small in biphenyl. Thus, conjugation between the rings is not affected. It has thus, planar conformation. Thus, it shows a very intense absorption band at 252 nm. Also biphenyl derivatives with bulky substituents in the ortho positions are more stable in twisted conformations than in the planar conformation. Clearly, there is loss of conjugation in the twist conformation of 2, 2-dimethyl biphenyl. Structurally, it is like that of o-xylene. Therefore o-xylene absorbs at comparatively lower wavelength than that of the expected value."

17. How will you distinguish between K-band and R-band which arise due to the electronic excitations in the carbonyl group of ketones? Do you expect any shift in their positions of absorption maxima and intensity by using a more polar solvent?

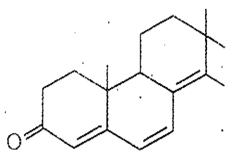
18. Applying Woodward-Fieser rules, calculate the values of absorption maxima for the following compounds :



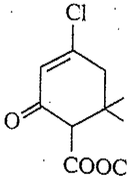
(i)



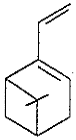
(ii)



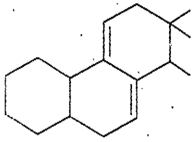
(iii)



(iv)



(v)



(vi)

19. Mark the correct statements out of the following :
    - (i) Acetone absorbs at 280 mμ ε_{max} 16,000.
    - (ii) Ethylene absorbs at 165 mμ ε_{max} 10,000.
    - (iii) Butadiene absorbs at 217 mμ ε_{max} 21,000.
    - (iv) Benzene shows a K-band at 254 mμ ε_{max} 60,000.
    - (v) The absorption corresponding to R-band in acetophenone shows a bathochromic shift if the polarity of the solvent is increased."
    - (vi) The K-band in conjugated diene experiences a blue shift if the polarity of the solvent is increased.
    - (vii) Hexadiene 1, 3, shows a B-band near 230 mμ.
    - (viii) Methyl vinyl ketone shows K, B and R-bands.
    - (ix) The R-band in case of acetaldehyde appears at higher wavelength as compared to that of acetone.
    - (x) B-bands for hetero-aromatic compounds shift to longer wavelengths if the polarity of the solvent is increased.

    Justify your answer in each case.

20. (a) The UV spectrum of acetone shows two peaks at

λ_{max} = 280 nm ε_{max} 15.

and λ_{max} = 1900 nm ε_{max} 100.

   - (i) identify the electronic transition for each.
   - (ii) which one of these is more intense ?

(b) Why is methanol a good solvent for UV but not for IR determination?

21. (a) How will you detect $>C=C-C=C<$ by UV spectroscopy ?

(b) Write why absorption bands are formed in ultra-violet spectrum instead of sharp peaks ?

22. Write a detailed account of the various types of transitions involved in the ultra-violet spectrum. What is the effect of hydrogen bonding on UV absorption ?

23. "Increase in polarity of the solvent shifts $\pi \rightarrow \pi^*$ band to longer wavelength but $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelength." Comment on the statement.

24. (a) Write notes on K-band and R-band.

(b) Which solvents are generally used in ultra-violet spectroscopy and why ?

25. The wavelength as well as the extinction coefficient increases with the increase in conjugation in the compound. Justify the statement.

26. (a) Describe the Woodward-Fieser rules for calculating absorption maximum in dienes.

(b) Write a note on B-band.

27. Identify the type of transition in each of the following compounds:

(i) Ethanal = 290 nm ε_{max} 17.
(ii) Acetic anhydride = 227 nm ε_{max} 44.
(iii) Pentadiene 1, 3 = 224 nm ε_{max} 22650.
(iv) Crotonaldehyde = 214 nm ε_{max} 15850.
(v) Styrene = 282 nm ε_{max} 450

28. Write a note on symmetry restrictions in electronic transitions.

29. What do you know of electronic transitions as applied to

(a) Fluorescence and Phosphorescene

(b) Charge-transfer complexes.

MULTIPLE CHOICE QUESTIONS

1. The energy required for various transitions follow the order:

(*a*) $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi - \pi^* > n \rightarrow \pi^*$

(*b*) $\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$

(*c*) $\pi \rightarrow \pi^* > n \rightarrow \pi^* > \sigma \rightarrow \sigma^* > n \rightarrow \sigma^*$

(*d*) $n \rightarrow \pi^* > \sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^*$.

2. Hydrogen bonding in organic compounds shifts the ultraviolet absorptions to:

(*a*) shorter frequencies (*b*) shorter wavelength

(*c*) remain unchanged (*d*) none of these

3. The value of extinciton coefficient increases with

(*a*) increase in conjugation (*b*) addition of chromophore

(*c*) both of these

4. An auxochrome is one which is

(*a*) colour enhancing

(*b*) a group or atom with lone pairs of electrons

(*c*) extending conjugation

(*d*) all of these

5. In a carbonyl compound (aldehyde or ketone)

(*a*) $n \rightarrow \pi^*$ transition is less intense

(*b*) $\pi \rightarrow \pi^*$ transition is less intense

(*c*) $n \rightarrow \pi^*$ transition is more intense

(*d*) None is correct

6. In a carbonyl compound, the increase in polarity of a solvent shifts the following transitions to shorter wavelength

(*a*) $n \rightarrow \pi^*$ (*b*) $\pi \rightarrow \pi^*$ (*c*) $n \rightarrow \sigma^*$ (*d*) $\sigma \rightarrow \sigma^*$

7. In conjugated dienes, the $\pi \rightarrow \pi^*$ transition occurs at longer wavelength. The reason is that as the conjugation extends, the distance between HOMO and LUMO:

(*a*) decreases (*b*) increases

(*c*) first increases and then decreases (*d*) not certain

8. Certain alkenes show cis-trans Isomerism. For example, cis and trans cinnamic acid show absorptions in UV radiation. Out of these, cis-isomer absorbs at _____ and transition is _____.

(*a*) lower wavelength than trans (*b*) higher wavelength than trans

(*c*) $\pi \rightarrow \pi^*$ (*d*) $n \rightarrow \pi^*$

9. Ultra violet spectroscopy is useful for the detection of —

(*a*) functional group (*b*) extent of conjugation

(*c*) geometrical isomers (*d*) all of these

10. The effect of the ultraviolet radiation on organic compound is to cause

(*a*) bond vibrations in the molecule (*b*) rotation in the molecule

(*c*) electronic transitions (*d*) all of these

11. When a flew drops of an acid is added to arylamine, absorption occurs at lower wave length. The reason is:

(*a*) increase in conjugation (*b*) reduction in conjugation

(*c*) acid decomposes the compound (*d*) compound remains insoluble

12. The structural increment of 5 nm for estimating λ_{max} for α, β-unsaturated carbonyl compound is given for:

(*a*) exocyclic double bond (*b*) alkyl substituent

(*c*) ring residue (*d*) all of these

13. Applying woodward Fieser rules, the basic value of 215 nm is given to:

(*a*) acyclic ketone (*b*) six membered cyclic ketone

(*c*) α, β-unsaturated aldehyde (*d*) α, β-unsaturated ester

14. While studying keto-enol tautomerism, the extinction coefficient is much higher for:

(*a*) ketonic form (*b*) enolic form (*c*) not sure.

15. o-Nitroacetanilide is deep yellow whereas para-nitroacetanilide is yellow. The reason is:

(*a*) ortho-shows intramolecular hydrogen bonding

(*b*) intramolecular hydrogen bonding stablises the excited state

(*c*) excitation energy required for other isomer is smaller.

(*d*) all of these.

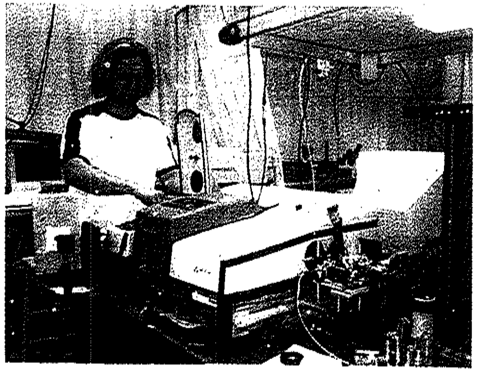
ANSWERS. 1. (*a*) 2. (*b*) 3. (*c*) 4. (*d*) 5. (*a*) 6. (*a*) (*c*) 7. (*a*) **8.** (*a*, *c*) **9.** (*d*) **10.** (*c*) **11.** (*b*) **12.** (*d*) 13. (*a*, *b*) **14.** (*b*) **15.** (*d*)

CHAPTER

3

Infra-red Spectroscopy

3.1 Introduction
3.2 Principle of infra-red spectroscopy
3.3 Theory—Molecular Vibrations
3.4 Vibrational Frequency
3.5 Number of Fundamental Vibrations
3.6 Selection Rules (Active and Forbidden Vibrations)
3.7 Factors Influencing Vibrational Frequencies
3.8 Scanning of Infra-red Spectrum (Instrumentation)
3.9 Sampling Techniques
3.10 Finger Print Region
3.11 Spectral Features of Some classes of organic Compounds
3.11 A1 Alkanes and Alkyl residues
3.11 A2 Alkenes
3.11 A3 Alkynes
3.11 A4 Cycloalkanes
3.11 A5 Aromatic Hydrocarbons
3.11 B Halogen Compounds
3.11 C Alcohols and Phenols
3.11 D Ethers
3.11 E Carbonyl compounds
3.11 E1 Aldehydes and Ketones
3.11 F Esters and Lactones
3.11 G Carboxylic Acids
3.11 H Acid Halides
3.11 I Acid Anhydrides
3.11 J Amides
3.11 K Lactams
3.11 L Amino Acids
3.11 M Amines
3.11 N Anilides (R-NHCOR')
3.11 O Nitro and Nitrite Compounds
3.11 P Nitriles and Related Compounds
3.11 Q Thiols or Mercaptans, Sulphonic acids and sulphonamides
3.11 R Heteroaromatic Compounds
3.12 Important Features in Infra-red Spectroscopy
3.13 Applications of infra-red spectroscopy



3.1 Introduction

Infra-red spectrum is an important record which gives sufficient information about the structure of a compound. Unlike ultraviolet spectrum which comprises of relatively few peaks, this technique provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of Infra-red radiations (quantised) causes the various bands in a molecule to stretch and bend with respect to one another. The most important region for an organic chemist is 2.5 μ to 15 μ in which molecular vibrations can be detected and measured in an infra-red spectrum and in a Raman spectrum. The ordinary infra-red region extends from 2.5 μ to 15 μ. The region from 0.8 μ to 2.5 μ is called **Near infra-red** and that from 15 μ to 200 μ is called **Far IR Region.**

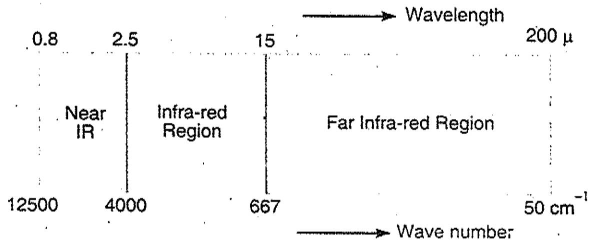


Fig. 3.1. Infra-red region.

The absorption of Infra-red radiations can be expressed either in terms of wavelength (λ) or in wave number ($\bar{\nu}$). Mostly infra-red spectra of organic compounds are plotted as percentage transmittance against wave number. The relationship between wavelength and wave number is as follows:

$$\text{Wave number} = \frac{1}{\text{wavelength in centimetres}}$$

$$\text{If wavelength } (\lambda) \text{ is } 2.5\ \mu = 2.5 \times 10^{-4}\ \text{cm, then}$$

$$\text{Wave number } (\bar{\nu}) = \frac{1}{2.5 \times 10^{-4}\ \text{cm}}$$

$$= 4000\ \text{cm}^{-1} \qquad \left[\bar{\nu} = \frac{1}{\lambda \text{ in cm}}\right]$$

The wavelength 15 μ corresponds to wave number equal to 667 cm^{-1}. Thus, in terms of wave number, the ordinary infra-red region covers 4000 cm^{-1} to 667 cm^{-1}.

Band intensity is either expressed in terms of absorbance (A) or Transmittance (T).

$$A = \log_{10}(1/T)$$

This technique can be employed to establish the identity of two compounds or to determine the structure of a new compound. In revealing the structure of a new compound, it is quite useful

---

μ represents microns. $1\ \mu = 10^{-4}$ cm

$$\text{Wave number in cm}^{-1} = \frac{10000}{\text{wavelength in microns}}$$

to predict the presence of certain functional groups which absorb at definite frequencies. For example, the hydroxyl group in a compound absorbs at 3600-3200 cm^{-1}; carbonyl group of ketones gives a strong band at 1710 cm^{-1}. The shift in the absorption position helps in predicting the factors which cause this shift. Some of the factors which shift the absorption band for a particular group from its characteristic frequency (or wave number) are inductive effect, conjugation, angle of strain, hydrogen bonding etc. It is, thus, a very reliable technique for disclosing the identity of a compound.

3.2 Principle of Infra-red Spectroscopy

The absorption of Infra-red radiations causes an excitation of molecule from a lower to the higher vibrational level. We know that each vibrational level is associated with a number of closely spaced rotational levels. Clearly, the Infra-red spectra is considered as **vibrational-rotational spectra.** All the bonds in a molecule are not capable of absorbing infra-red energy but only those bonds which are accompanied by **a change in dipole moment** will absorb in the infra-red region. Such vibrational transitions which are accompanied by a change in the dipole-moment of the molecule are called infra-red active transitions. Thus, these are responsible for absorption of energy in the Infra-red region. On the other hand, the vibrational transitions which are not accompanied by a change in dipole-moment of the molecule are not directly observed and these are Infra-red inactive. For example, vibrational transitions of C = O, N—H, O—H etc. bands are accompanied by a change in dipole-moment and thus, absorb strongly in the Infra-red region. But transitions in Carbon-Carbon bonds in symmetrical alkenes and alkynes are not accompanied by the change in dipole-moment and hence do not absorb in the infra-red region. It is important to note that since the absorption in infra-red region is quantised, a molecule of the organic compound will show a number of peaks in the infra-red region.

3.3 Theory—Molecular Vibrations

Absorption in the infra-red region is due to the changes in the vibrational and rotational levels (see Fig. 3.2). When radiations with frequency range less than 100 cm^{-1} are absorbed, molecular rotation takes place in the substance. As this absorption is quantised, discrete lines are formed in the spectrum due to molecular rotation. Molecular vibrations are set in, when more energetic radiation in the region 10^4 to 10^2 cm^{-1} are passed through the sample of the substance. The absorption causing molecular vibration is also quantised. Clearly, a single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appear as vibrational-rotational bands. In the Infra-red spectroscopy (Region 2.5 μ – 15 μ), the absorbed energy brings about predominant changes in the vibrational energy which depends upon:

(*i*) Masses of the atoms present in a molecule,

(*ii*) Strength of the bonds, and

(*iii*) The arrangement of atoms within the molecule.

It has been found that no two compounds except the enantiomers can have similar Infra-red spectra.

It may be noted that the atoms in a molecule are not held rigidly. The molecule may be visualised as consisting of balls of different sizes tied with springs of varying strengths. Here balls and springs correspond to atoms and chemical bonds respectively. When Infra-red light is passed through the sample, the vibrational and the rotational energies of the molecules are increased. Two kinds of fundamental vibrations are:

(*a*) **Stretching.** In this type of vibrations, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

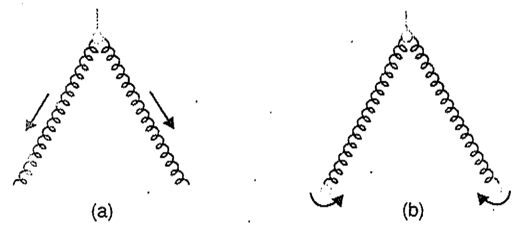


Fig. 3.2. Types of vibrations : (*a*) Stretching, (*b*) Bending.

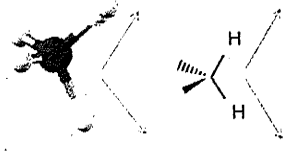
(*b*) **Bending.** In this type of vibrations, the positions of the atoms change with respect to the original bond axis. We know that more energy is required to stretch a spring than that required to bend it. Thus, we can safely say that stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorptions of the same bond.

The various stretching and bending vibrations of a bond occur at certain quantised frequencies. When Infra-red radiation is passed through the substance, energy is absorbed and the amplitude of that vibration is increased. From the excited state, the molecule returns to the ground state by the release of extra energy by rotational, collision or translational processes. As a result, the temperature of the sample under investigation increases.

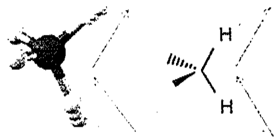
Types of stretching vibrations. There are two types of stretching vibrations:

(*i*) **Symmetric stretching.** In this type, the movement of the atoms with respect to a particular atom in a molecule is in the same direction.

(*ii*) **Asymmetric stretching.** In these vibrations, one atom approaches the central atom while the other departs from it.



Symmetric stretching



A symmetric stretching

Fig. 3.3. Types of stretching vibrations.

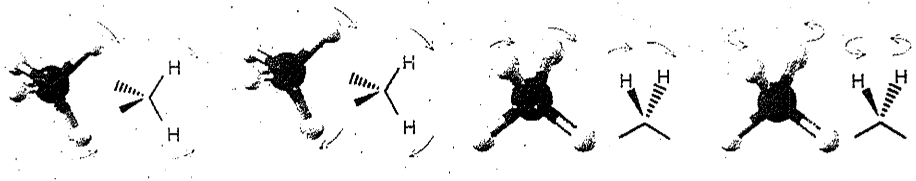
Types of bending vibrations. (*Deformations*). Bending vibrations are of four types:

(*i*) **Scissoring.** In this type, two-atoms approach each other.

(*ii*) **Rocking.** In this type, the movement of the atoms takes place in the same direction.

(*iii*) **Wagging.** Two atoms move 'up and down' the plane with respect to the central atom.

(*iv*) **Twisting.** In this type, one of the atoms moves up the plane while the other moves down the plane with respect to the central atoms.



Scissoring Rocking Wagging Twisting

Fig. 3.4. Types of bending vibrations. (*a*) Scissoring, (*b*) Rocking, (*c*) Wagging, (*d*) Twisting

Note. Bending vibrations require lesser energy and hence occur at higher wavelengths or lower numbers than stretching vibrations.

3.4 Vibrational Frequency

The value of the stretching vibrational frequency of a bond can be calculated fairly accurately by the application of **Hooke's law** which may be represented as:

$$\frac{\nu}{c} = \bar{\nu} = \frac{1}{2\pi c}\left[\frac{k}{\frac{m_1 m_2}{m_1+m_2}}\right]^{1/2}$$

$$= \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass.

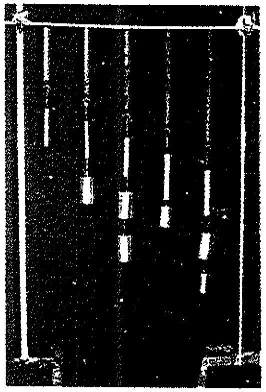
m_1 and m_2 are the masses of the atoms concerned in grams in a particular bond.

k = Force constant of the bond and relates to the strength of the bond. For a single bond, it is approximately 5×10^5 gm sec^{-2}. It becomes double and triple for the double and triple bonds respectively.

c = Velocity of the radiation = 2.998×10^{10} cm sec^{-1}

Thus, the value of vibrational frequency or wave number depends upon:

(*i*) Bond strength, and (*ii*) Reduced mass.



Clearly, if the bond strength increases or the reduced mass decreases, the value of the vibrational frequency increases.

Let us calculate the approximate frequency of C—H stretching vibration from the following data:

k = 5×10^5 gm sec^{-2}

Mass of carbon atom (m_1) = 20×10^{-24} gm

Mass of hydrogen atom (m_2) = 1.6×10^{-24} gm

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\frac{m_1 m_2}{m_1+m_2}}}$$

$$= \frac{7}{2\times 22}\left(\frac{5\times10^5 \text{ gm sec}^{-2}}{\frac{20\times10^{-24}\text{ gm}\times 1.6\times10^{-24}\text{ gm}}{(20+1.6)10^{-24}\text{ gm}}}\right)^{1/2}$$

$$= 9.3 \times 10^{13} \text{ sec}^{-1}$$

This value of frequency can be converted into wave number as follows:

$$\bar{\nu} = \frac{\nu}{c} = \frac{9.3\times10^{13}\text{ sec}^{-1}}{3.0\times10^{8}\text{ m sec}^{-1}} = 3.1 \times 10^5 \text{ m}^{-1} = \mathbf{3100\ cm^{-1}}$$

C = C stretching is expected to absorb at higher frequency than C—C stretching. It is due to the higher bond strength (value of k) of the double bond compared to the single bond. Similarly, O—H stretching absorbs at higher frequency compared to C—C bond. It can be explained on the basis of the smaller value of reduced mass for O—H compared with C—C bond. We can expect O—H to absorb at higher frequency as compared to F—H. But this is not true. Actually, F—H absorbs at the higher frequency. This can be explained due to the higher electronegativity of fluorine compared to that of oxygen.

EXAMPLE 1. *Calculate the wave number of stretching vibration of a carbon-carbon double bond. Give force constant ($k = 10 \times 10^5$ dynes cm^{-1})*

SOLUTION. Atomic mass of carbon = 12 amu

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1+m_2} = \frac{12\times12}{12+12} = 6\ amu = \frac{6}{6.02\times10^{23}}\text{gm} = 9.97 \times 10^{-24}\text{gm}$$

$$\text{Wave number } \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} = \frac{1}{2\times3.142\times3\times10^{10}\text{cm s}^{-1}}\sqrt{\frac{10\times10^{5}\text{ gm sec}^{-2}}{\frac{6\text{ gm}}{6.02\times10^{23}}}}$$

$$= \frac{1}{18.852\times10^{10}\text{cm s}^{-1}}\times\sqrt{10.03\times10^{28}} = 0.1680\times10^4\text{cm}^{-1}$$

$$= \mathbf{1680\ cm^{-1}}.$$

EXAMPLE 2. *The reduced mass of a diatomic molecule is 2.5×10^{-26} kg and its vibrational frequency is 2900 cm^{-1}. Calculate the force constant.*

SOLUTION. Given reduced mass, $\mu = 2.5 \times 10^{-26}$ kg

vibrational frequency, $\bar{\nu}$ = 2900 cm^{-1}.

Applying the relation $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ or force constant, $k = 4\pi^2c^2\cdot\mu\cdot\bar{\nu}^2$

or $k = 4 \times (3.142)^2\ (3 \times 10^8 \text{ ms}^{-1})^2\ (2900 \times 10^2 \text{ m}^{-1})^2\ (2.5 \times 10^{-26} \text{ kg})$

= **7476.4 Nm^{-1}** [1N = 1 kg ms^{-2}]

EXAMPLE 3. *The force constant for carbon monoxide molecule is 1840 Nm^{-1}. Calculate the vibrational frequency (in cm^{-1}). Given atomic masses are: $^{12}C = 19.9 \times 10^{-27}$ kg; $^{16}O = 26.6 \times 10^{-27}$ kg.*

SOLUTION. We know that fundamental vibrational frequency (ν) is expressed as:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}. \text{ Given } k = 1840 \text{ Nm}^{-1}$$

$$\text{Reduced mass} = \mu_{CO} = \frac{m_C\times m_O}{(m_C+m_O)} = \frac{19.9\times10^{-27}\text{kg}\times26.6\times10^{-27}\text{kg}}{(19.9\times10^{-27}+26.6\times10^{-27})\text{kg}}$$

$$= 1.138 \times 10^{-26} \text{ kg.}$$

$$\text{The relation is : } \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\text{Substituting the values: } \bar{\nu} = \frac{1}{2\times3.142\times3\times10^{8}\text{ms}^{-1}}\sqrt{\frac{1840\text{ kg s}^{-2}}{1.138\times10^{-26}\text{kg}}} = 2.132 \times 10^5\text{m}^{-1}$$

$$\text{or} \quad \bar{\nu} = 2.132 \times 10^5 \times 10^{-2} \text{ cm}^{-1} = \mathbf{2132\ cm^{-1}}.$$

EXAMPLE 4. *The force constant of HF is listed at 880 Nm^{-1}. At what wave number is the fundamental v = 0 → v = 1 vibrational absorption expected?*

SOLUTION. We know the relation: $\bar{v} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$

Assuming vibrations to be simple harmonic,

$$\bar{v} = \frac{1}{2\times 3.142\times 3\times 10^{8}\,\text{ms}^{-1}} \times \sqrt{\frac{800\text{Nm}^{-1}(\text{or kg s}^{-2})(1+19)\times 6.02\times 10^{23}}{1\times 19\times 10^{-3}\,\text{kg}}}$$

$$= 396071.8 \text{ m}^{-1} = \mathbf{3960.7 \text{ cm}^{-1}}$$

3.5 Number of Fundamental Vibrations

The Infra-red light is absorbed when the oscillating dipole-moment interacts with the oscillating electric vector of an Infra-red beam. For this interaction or absorption to occur, it is important that the dipole-moment at one extreme of the vibration must be different from the dipole-moment at the other extreme of the vibration in a molecule. For Infra-red absorption, the vibrations should not be centro-symmetric. Only those vibrations are Infra-red active which are not centro-symmetric. As most of the functional groups in organic chemistry are not centro-symmetric, this technique is most informative to organic chemists. The symmetry properties of a molecule in a solid can be different from those of an isolated molecule.

The Infra-red spectrum of a molecule results due to the transitions between two different vibrational energy levels. The vibrational motion resembles the motion observed for a ball attached to a spring, i.e., harmonic oscillator. A chemical bond can be visualised as two balls attached to a spring. But it differs from this system since in Infra-red certain vibrational energy levels only are allowed in molecules. The vibrational energy of a chemical bond is quantised and can have the value.

$$E_{vib} = \left(V+\frac{1}{2}\right)h\nu$$

where V is the number of the vibrational level and can have the values 0, 1, 2, 3........

h = Planck's constant

and ν = vibrational frequency of the bond.

It is already known that

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\frac{m_1 m_2}{m_1+m_2}}}$$

The energy difference between the two vibrational energy levels can be written as

$$\Delta E_{vib} = h\nu$$

At ordinary temperature, where molecules are in their lowest vibrational energy levels, the potential energy diagram approximates that of a harmonic oscillator. But at higher temperatures, the deviations do occur (see Fig. 3.5).

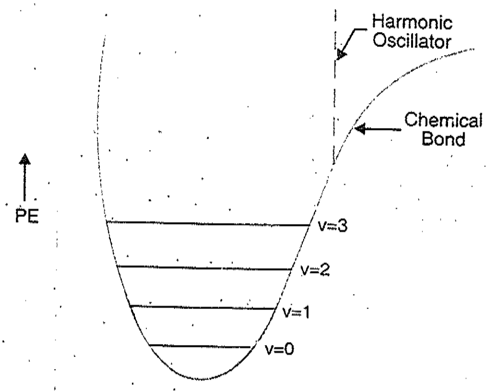


Fig. 3.5. Potential Energy diagram.

Absorption of radiation with energy equal to the difference between two vibrational energy levels (ΔE_{vib}) will cause a vibrational transition to occur. Radiation with energy sufficient to cause vibrational transition is found in the Infra-red region of the electromagnetic spectrum.

Transitions from the ground state ($V = 0$) to the first excited state ($V = 1$) absorb light strongly and give rise to intense bands called the Fundamental bands. The energy difference (ΔE_{vib}) between the lowest possible energy level of a bond and the next higher energy level is given as:

$$\begin{aligned}\Delta E_{vib} &= E_{vib(V=1)} - E_{vib(V=0)}\\ &= \left(1+\frac{1}{2}\right)h\nu - \left(0+\frac{1}{2}\right)h\nu\\ &= \frac{3}{2}h\nu - \frac{1}{2}h\nu = h\nu\end{aligned}$$

This gives the frequency of a fundamental band. Transitions from the ground state ($V = 0$) to the second excited state ($V = 2$) with the absorption of Infra-red radiation give rise to weak bands, called overtones.

Assuming that all the vibrational bands are equally spaced (in fact, these are not), the energy of the first overtone is given by

$$\begin{aligned}\Delta E_{vib} &= E_{vib(V=2)} - E_{vib(V=0)}\\ &= \left(2+\frac{1}{2}\right)h\nu - \left(0+\frac{1}{2}\right)h\nu\\ &= 2\,h\nu\end{aligned}$$

Polyatomic molecules may exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the **degrees of freedom** in a molecule. The number of degrees of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three cartesian co-ordinates (X, Y, Z) necessary to describe its position relative to other atoms in a molecule. An isolated atom which is considered as a point mass has only translational degrees of freedom. It cannot have vibrational and rotational degrees of freedom. When atoms combine to form a molecule, no degrees of freedom are lost, *i.e.*, the total number of degrees of freedom of a molecule will be equal to $3n$ where n is the number of atoms in a molecule. A molecule which is of finite dimensions will, thus, be made up of rotational, vibrational and translational degrees of freedom. So,

$3n$ degrees of freedom = Translational + Rotational + Vibrational.

Rotational degrees of freedom result from the rotation of a molecule about an axis through the centre of gravity. Since we are concerned only with the number of fundamental vibrational modes of a molecule, so we calculate only the number of vibrational degrees of freedom of a molecule. Since only three co-ordinates are necessary to locate a molecule in space, we say that a **molecule has always three translational degrees of freedom.**

In case of linear molecule, there are only two degrees of rotation. It is due to the fact that the rotation of such a molecule about its axis of linearity does not bring about any change in the position of the atoms while rotation about the other two axes changes the position of the atoms. Thus, for a linear molecule of n atoms.

Total degrees of freedom = $3n$
Translational degrees of freedom = 3
Rotational degrees of freedom = 2
∴ Vibrational degrees of freedom = $3n - 3 - 2 = \mathbf{3n - 5}$

Each vibrational degree of freedom corresponds to the fundamental mode of vibration and each fundamental mode corresponds to a band. Hence, theoretically there will be $3n - 5$ possible fundamental bands for the linear molecules.

In a linear molecule of carbon dioxide (CO_2), the number of vibrational degrees of freedom can be calculated as follows:

Number of atoms (n) $= 3$
Total degrees of freedom $= 3n = 3 \times 3 = 9$
Translational $= 3$
Rotational $= 2$
$\therefore$ Vibrational degrees of freedom $= 9 - 3 - 2 = 4$

Hence, for carbon dioxide molecule, the theoretical number of fundamental bands should be equal to four.

In the case of non-linear molecule, there are three degrees of rotation as the rotation about all the three axes (*X, Y, Z*) will result in a change in the position of the atoms. So, for a non-linear molecule of n atoms, the vibrational degrees of freedom can be calculated as follows:

Total degrees of freedom $= 3n$
Translational degrees of freedom $= 3$
Rotational degrees of freedom $= 3$
$\therefore$ Vibrational degrees of freedom $= 3n - 3 - 3 = \mathbf{3n - 6}$

Thus, in a non-linear molecule, C_6H_6, the number of vibrational degrees of freedom can be calculated as follows:

Number of atoms (n) $= 12$
Total degrees of freedom $= 3 \times 12 = 36$
Translational $= 3$
Rotational $= 3$
$\therefore$ Vibrational degrees of freedom $= 36 - 3 - 3 = \mathbf{30}$

So, theoretically there should be 30 fundamental bands in the Infra-red spectrum of benzene.

It has been observed that the theoretical number of fundamental vibrations are seldom obtained. It is because of the following reasons:

(*i*) Fundamental vibrations that fall outside the region under investigation, *i.e.*, 2.5 to 15 μ.

(*ii*) Fundamental vibrations that are too weak to be observed as bands.

(*iii*) Fundamental vibrations that are so close that they overlap, *i.e.*, degenerate vibrations.

(*iv*) Certain vibrational bands do not appear for want of the required change in the dipole-moment in a molecule.

(*v*) There may appear some additional bands called combination bands, difference bands and overtones. Thus, due to these, a large number of bands will be observed as compared to the theoretical number. If there are two fundamental bands at x and y, then the additional bands can be expected at:

  (*i*) $2x$, $2y$ (Overtones)
  (*ii*) $x + y$, $x + 2y$, $2x + y$ etc. (Combination bands)
  (*iii*) $(x - y)$, $(x - 2y)$, $(2y - x)$ etc. (Difference bands)

It may be noted that these additional bands are usually 10-100 times less intense as compared to the fundamental bands.

EXAMPLE 5. *Predict the number of fundamental vibrational modes in the following molecules.*

(*i*) H_2S (*ii*) C_2H_2

SOLUTION. (*i*) H_2S molecule. This a non-linear molecule. Thus, the number of normal mades of vibration $= (3n - 6)$.

Where n = Total number of atoms in the molecule. Here $n = 3$.
Number of normal modes of vibrations in $H_2S = 3 \times 3 - 6 = \mathbf{3}$
(*ii*) $HC \equiv CH$. Acetylene is a linear molecule
Here $n = 4$
$\therefore$ Number of normal modes of vibrations $= (3n - 5) = 3 \times 4 - 5 = 7$

Note. Absorptions due to bending vibrations occur at frequencies below 1500 cm^{-1}. These are not very useful for structural information as confusion of one with the other may occur. Moreover, bands are obscured due to overtones and combination bands. The region below 1500 cm^{-1} is called **Finger print region.** This region is important for comparing the identity of the two compounds and also for the detection of certain functional groups like esters, ethers, type of disubstitution on the benzene ring etc.

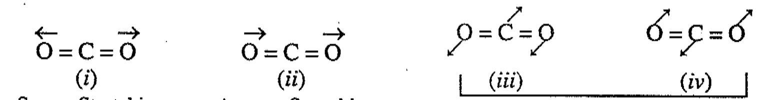
3.6 Selection Rules (Active and Forbidden Vibrations)

Infra-red light is absorbed only when a change in dipole character of the molecule takes place. Complete symmetry about a bond eliminates some absorption bands. Clearly, some of the fundamental vibrations are Infra-red active and some are not. It is governed by the selection rules which are explained below:

(*i*) If a molecule has a centre of symmetry, then the vibrations are centrosymmetric and are **inactive** in the Infra-red but are active in the Raman.

(*ii*) The vibrations which are not centrosymmetric are active in Infra-red but inactive in Raman.

Since in most of the organic compoun, the functional groups are not centrosymmetric. Infra-red spectroscopy is most informative. Consider various vibrations in case of carbon dioxide.



Symm Stretching
DM = 0. IR inactive

Asymm Stretching
ν = 2350 cm^{-1}
IR inactive

Bending vibrations
ν = 667 cm^{-1}

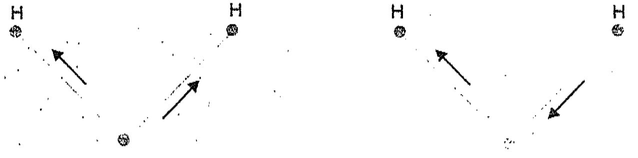
The above vibrations are all fundamental vibrations of carbon dioxide. Since (*i*) does not give rise to any change in dipole-moment, it is infra-red inactive. Asymmetric stretching causes, a net change in dipole-moment and thus is infra-red active and absorbs at 2350 cm^{-1} vibrations (*iii*) and (*iv*) are said to be degenerate. The bending of bonds in the molecule are identical but occur in perpendicular planes and thus appear in the same position (ν = 667 cm^{-1}) in the spectrum. Thus the spectrum of carbon dioxide consists of two bands (*i*) 2350 cm^{-1} due to asymmetric stretching and (*ii*) 667 cm^{-1} due to bending vibrations.

Intensity and position of Infra-red absorption bands. The intensity of a fundamental absorption depends upon the difference between the dipole moments of the molecule in the ground state and the vibrational excited state. Greater the difference, more is the intensity of absorption. In case, there is no change in the dipole moment, then the vibrational mode is said to be Infra-red inactive. Since the intensity of absorption band in infra-red spectroscopy cannot be measured with greater accuracy, it is sufficient to know whether the absorption is strong, medium or weak. If the most intense peak is assigned an intensity of 100%, then the relative intensities of other peaks can be estimated. Frequency of absorption is generally expressed in terms of wave number (cm^{-1}) as wave number is directly proportional to frequency as well as energy.

3.7 Factors Influencing Vibrational Frequencies

We know that the probable frequency or wave-number of absorption can be calculated by the application of Hooke's law. It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. The difference arises from the fact that vibration of each group is influenced by the structure of the molecule in the immediate neighbourhood of the bond. If a particular vibration is absolutely free from any influence, then the Infra-red spectrum would tell us whether a certain group is/or is not present in the molecule. Moreover, the value of absorption frequency is also shifted since the force constant of a bond changes with its electronic structure. There are many factors which are responsible for vibrational shifts and one factor cannot be isolated from another. Frequency shifts also take place on working with the same substance in different states (solids, liquids or vapours). In the vapour state, a substance, usually absorbs at higher frequency as compared to that when it is in the liquid and solid states. Following are some of the factors responsible for shifting the vibrational frequencies from their normal values:

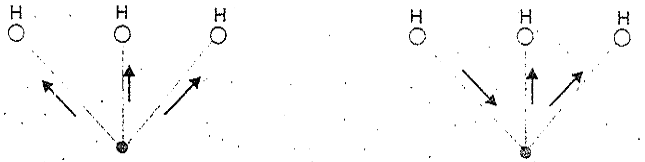
1. **Coupled Vibrations and Fermi Resonance.** We expect one stretching absorption frequency for an isolated C—H bond but in the case of methylene (—CH_2—) group, two absorptions occur which correspond to symmetric and asymmetric vibrations as follows:



(a) Symmetric (b) Asymmetric

Fig. 3.6. Stretching vibrations in methylene group.

In such cases, asymmetric vibrations always occur at higher wave number compared with the symmetric vibrations. These are called coupled vibrations since these vibrations occur at different frequencies than that required for an isolated C—H stretching. Similarly, coupled vibrations of —CH_3 group take place at different frequencies compared to —CH_2— group. For methyl group, symmetric vibrations are as follows:



(a) Symmetric (b) Asymmetric

Fig. 3.7. Types of stretching vibrations in methyl group.

Sometimes, it happens that two different vibrational levels have nearly the same energy. If such vibrations belong to the same species (as in the case of —CH_2— group or —CH_3 group), then a mutual perturbation of energy may occur, resulting in the shift of one towards lower frequency and the other towards higher frequency. It is also accompanied by a substantial increase in the intensity of the respective bands.

Acid anhydrides show two C=O stretching absorptions between 1850-1800 and 1790-1745 cm^{-1} with a difference of about 65 cm^{-1}. This can be explained due to the symmetric and asymmetric stretching. In Infra-red spectrum, absorption bands are spread over a wide range of frequencies. It may happen that the energy of an overtone level chances to coincide with the fundamental mode of different vibration. A type of resonance occurs as in the case of coupled pendulums. This type of resonance is called **Fermi Resonance.** This can be explained by saying that a molecule transfers its energy from fundamental to overtone and back again. Quantum mechanically, resonance pushes the two levels apart and mixes their character so that each level becomes partly fundamental and partly overtone in character. Thus, this type of resonance gives rise to a pair of transitions of equal intensity.

This phenomenon was first observed by Enrico Fermi in the case of carbon dioxide. Carbon dioxide molecule (Triatomic) is linear and four fundamental vibrations are expected for it. Out of these, symmetric stretching vibration is Infra-red inactive since it produces no change in the dipole-moment **(D.M.)** of the molecule.

(a) (b)

Fig. 3.8. (a) Symmetric stretching, (b) Asymmetric stretching.

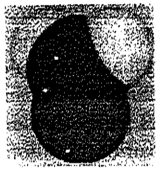
For symmetric stretching, Raman spectrum shows a strong band at 1337 cm^{-1}. The two bending vibrations are equivalent and absorb at the same frequency of 667.3 cm^{-1}. The overtone of this is 1334.6 cm^{-1} (2 × 667.3) which is very close to 1337 cm^{-1}. Thus, Fermi Resonance takes place resulting in the shift of first level towards higher frequency. The mutual perturbation of 1337 cm^{-1} (Fundamental) and 1334.6 cm^{-1} (Overtone) gives rise to two bands at 1285.5 cm^{-1} and 1388.3 cm^{-1} having intensity ratio of 1 : 0.9.

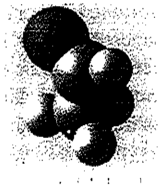
Another example of Fermi Resonance is given by aldehydes in which C—H stretching absorption usually appears as a doublet (~2820 cm^{-1} and ~2720 cm^{-1}) due to the interaction between C—H stretching (fundamental) and the overtone of C—H deformation (bending). Fermi Resonance is also shown by the spectrum of *n*-butyl vinyl ether. In this case, the overtone of the fundamental vibration at 810 cm^{-1} chances to coincide with the band at 1640 cm^{-1}. The mixing of the two bands (Fundamental and Overtone) in accordance with Fermi Resonance gives two bands of almost equal intensity at 1640 cm^{-1} and 1630 cm^{-1}.

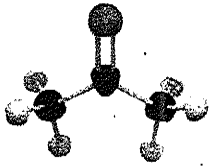
Similarly, Fermi Resonance is required to explain the doublet in case of certain lactones and cycloketones. In cyclopentanone, the absorption due to carbonyl group occurs at 1746 cm^{-1} and 1750 cm^{-1}. This splitting can be explained by Fermi Resonance. In large molecules, Fermi Resonance is observed only when the normal vibrations and the overtones are in the same area of the molecule and also if certain symmetrical conditions are fulfilled (Two bands should be of the same symmetry).

2. **Electronic Effects.** Changes in the absorption frequencies for a particular group take place when the substituents in the neighbourhood of that particular group are changed. The frequency shifts are due to the electronic effects which include *Inductive effect, Mesomeric effects, Field effects* etc. These effects cannot be isolated from one another and the contribution of one of them can only be estimated approximately. Under the influence of these effects, the force constant or the bond strength changes and its absorption frequency shifts from the normal value. The introduction of alkyl group causes +I effect which results in the lengthening or the weakening of the bond and hence the force constant is lowered and wave number of absorption decreases. Let us compare the wave numbers of ν (C=O) absorptions for the following compounds:

(*i*) Formaldehyde (HCHO)	1750 cm^{-1}
(*ii*) Acetaldehyde (CH_3CHO)	1745 cm^{-1}
(*iii*) Acetone (CH_3COCH_3)	1715 cm^{-1}







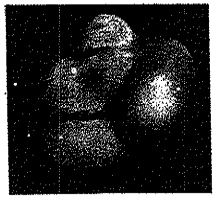
Note. Aldehydes absorb at higher wave number than ketones.

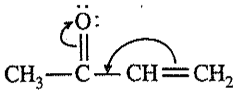
The introduction of an electronegative atom or group causes–I effect which results in the bond order to increase. Thus, the force constant increases and hence the wave number of absorption rises. Now, let us consider the wave numbers of absorptions in the following compounds:

(*i*) Acetone (CH_3COCH_3)	1715 cm^{-1}
(*ii*) Chloroacetone (CH_3COCH_2Cl)	1725 cm^{-1}
(*iii*) Dichloroacetone ($CH_3COCHCl_2$)	1740 cm^{-1}
(*iv*) Tetrachloroacetone ($Cl_2CH—CO—CHCl_2$)	1750, 1778 cm^{-1}

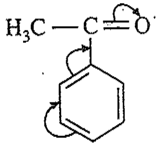
In most of the cases, mesomeric effect works alongwith inductive effect and cannot be ignored. Conjugation lowers the absorption frequency of C═O stretching whether the conjugation is due to α, β-unsaturation or due to an aromatic ring. In some cases, inductive effect dominates over mesomeric effect while reverse holds for other cases. *Mesomeric effect* causes lengthening or the weakening of a bond leading in the lowering of absorption frequency. Consider the following compounds:

In these two cases, –I effect is dominated by mesomeric effect and thus, the absorption frequency falls.

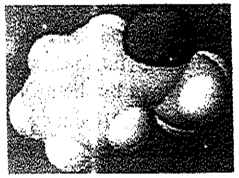




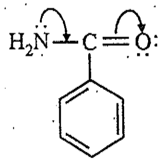
Methyl Vinyl Ketone
ν C = O 1706 cm^{-1}



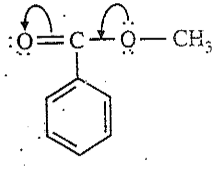
Acetophenone
ν C = O 1693 cm^{-1}



In some cases, where the lone pair of electrons present on an atom is in conjugation with the double bond of a group, say carbonyl group, the mobility of the lone pair of electrons matters. Let us compare the absorption frequencies of ν (C═O) stretching in amides and esters.



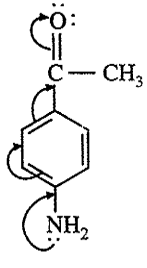
Benzamide
ν C = O 1693 cm^{-1}



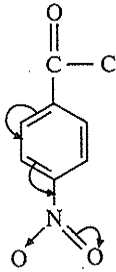
Methyl benzoate
ν C = O 1730 cm^{-1}

As nitrogen atom is less electronegative than oxygen atom, the electron pair on nitrogen atom in amide is more labile and participates more in conjugation. Due to this greater degree of conjugation, the C═O absorption frequency is much less in amides as compared to that in esters.

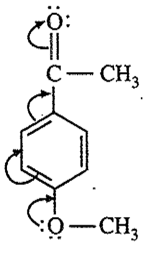
Let us compare the absorption frequencies of the following compounds:



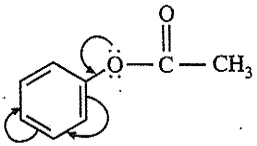
I
p-Amino
Acetophenone
ν C═O 1677 cm^{-1}



II
p-Nitro
Acetophenone
ν C═O 1700 cm^{-1}



III
p-Methoxy
Acetophenone
ν C═O 1684 cm^{-1}

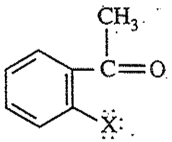


IV
Phenyl Acetate
ν C═O 1770 cm^{-1}

Due to the low electronegativity of nitrogen atom, the lone pair of electrons participates more in conjugation in compound I as compared to that in compound III. Thus, in compound I, ν (C═O) absorption occurs at lower wave number compared to that in compound III. In compounds II and IV, inductive effect dominates over mesomeric effect and hence absorption takes place at comparatively higher frequencies.

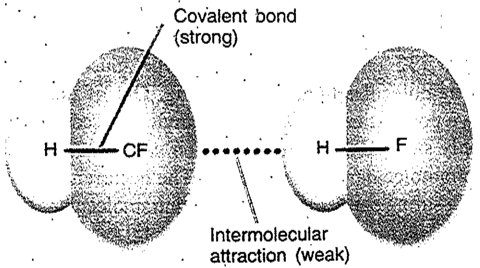
It is important to note that only inductive effect is considered when the compound is meta substituted.

In para substitution, both inductive and mesomeric effects become important and the domination of one over the other will decide the wave number of absorption. In ortho substitution, inductive effect, mesomeric effect alongwith steric effect are considered. In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is called **Field effect**. Consider ortho haloacetophenone.



The non-bonding electrons present on oxygen atom and halogen atom cause electrostatic repulsions. This causes a change in the state of hybridisation of C═O group and also makes it to go out of the plane of the double bond. Thus, the conjugation is diminished and absorption occurs at a higher wave number. Thus, for such ortho substituted compounds, cis absorbs (field effect) at a higher frequency as compared to the trans isomer.

3. Hydrogen bonding. Hydrogen bonding brings about remarkable downward frequency shifts. Stronger the hydrogen bonding, greater is the absorption shift towards lower wave number than the normal value. Two types of hydrogen bonds can be readily distinguished in Infra-red technique. Generally, intermolecular hydrogen bonds give rise to broad bands whereas bands arising from intramolecular hydrogen bonds are sharp and well defined. Intermolecular hydrogen



Intermolecular Hydrogen bonding

bonds are **concentration dependent**. On dilution, the intensities of such bands are independent of concentration. The absorption frequency difference between free and associated molecule is smaller in case of intramolecular hydrogen bonding than that in intermolecular association.

Hydrogen bonding in O—H and N—H compounds deserve special attention. Mostly non-associating solvents like carbon disulphide, chloroform, carbon tetrachloride are used because some solvents like benzene, acetone etc., influence O—H and N—H compounds to a considerable extent. As nitrogen atom is less electronegative than an oxygen atom, hydrogen bonding in amines is weaker than that in alcohols and thus, the frequency shifts in amines are less dramatic. For example, amines show N—H stretching at 3500 cm^{-1} in dilute solutions while in condensed phase specra, absorption occurs at 3300 cm^{-1}.

In aliphatic alcohols, a sharp band appears at 3650 cm^{-1} in dilute solutions due to free O—H group while a broad band is noticed at 3350 cm^{-1} due to hydrogen bonded O—H group. Alcohols are strongly hydrogen bonded in condensed phases. These are usually associated as dimers and polymers which result in the broadening of bands at lower absorption frequencies. In vapour state or in inert solvents, molecules exist in free state and absorbs strongly at 3650 cm^{-1}. Alcohols can be written in the following resonating structures.

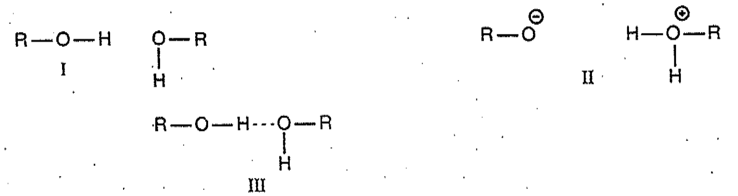


Fig. 3.9. Resonating structures of alcohols.

Structure III is the hybrid of structures I and II. This results in the lengthening of the original O—H group. The electrostatic force of attraction with which hydrogen atom of one molecule is attracted by the oxygen atom of another molecule makes it easier to pull hydrogen away from the oxygen atom. Thus, small energy will be required to stretch such a bond (O—H) and hence absorption occurs at a lower wave number.

Intramolecular hydrogen bonding can be observed in dilute solutions of di- and polyhydroxy compounds in carbon tetrachloride where no intermolecular hydrogen bonds are formed. Under these conditions, it was observed that a number of cyclic and acyclic diols have two bands and others have a single band in the O—H stretching mode region.

The spectrum of glycol in dilute carbon tetrachloride shows two νO—H bands at 3644 cm^{-1} and 3612 cm^{-1}. The band at 3644 cm^{-1} is due to free O—H and that at 3612 cm^{-1} is due to O—H···O bonding. As the absorption shift (32 cm^{-1}) is small, the type must be intramolecular hydrogen bonding. Out of the two possible conformations of ethylene glycols, only staggered syn conformation can form an intramolecular hydrogen bond. The occurrence of a strong band arising from the intramolecular

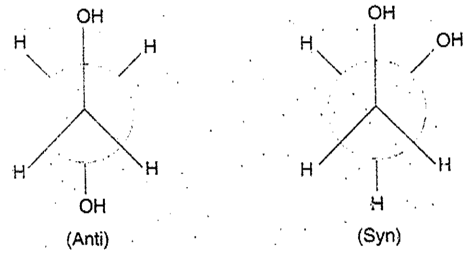


Fig. 3.10. Anti and Syn conformations of Ethylene glycol.

The band due to free O—H group is usually less intense while that due to bonded O—H group is broad and sharp.

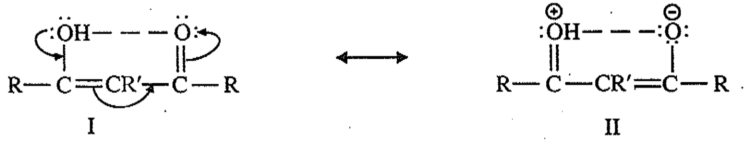
hydrogen bond shows that the molecule exists in staggered-syn conformation.

The energy of the hydrogen bond compensates for excess energy (5 kcal $mole^{-1}$) due to steric and dipolar repulsions of the two O—H groups. The small frequency shift ($\Delta v = 32\ cm^{-1}$) shows that hydrogen bonding is weak.

At higher concentrations, the I.R spectra of diols show a third band arising from the intermolecular hydrogen bonding of the hydroxy group. This new band shows all the characteristics observed in monohydric alcohols, *i.e.*, the bands formed are strong and broad. The intermolecular association of diols results in a larger shift of νO—H than intramolecular hydrogen bonding does. If the free νO—H in diols is 3626 cm^{-1}, then intermolecularly bonded O—H abosrbs at 3477 cm^{-1}.

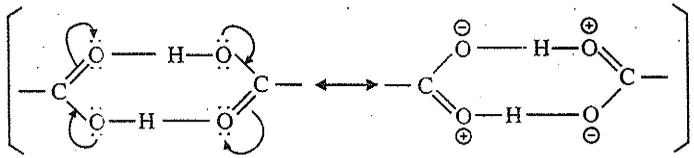
Note. In aromatic amines, differences between intramolecularly associated and free N—H bond absorption frequencies are small and difficult to observe.

In enols and chelates, hydrogen bonding is exceptionally strong and absorptions due to O—H stretching occurs at very low values. As these bonds are not broken easily on dilution by an inert solvent, free O—H stretching may not be seen at low concentrations. It is due to the fact that the bonded structure is stabilised by resonance. Consider acetyl acetone:



The O—H group involved in chelation gives rise to broad absorptions between 3000 and 2500 cm^{-1}. The νCO absorption in the enolic form occurs at 1630 cm^{-1} and that in the keto form at 1725 cm^{-1}. From the intensities of the two peaks, it is possible to determine the quantities of the enolic and the ketonic forms.

Mostly the acids exist as dimers and bridges formed are stabilised by resonance.



The formation of bridges lowers the force constants and thus νC=O and νO—H decreases. The larger decrease in the frequency in these dimers indicates the exceptional strengths of hydrogen bonds.

The carboxylic acid dimers display very broad band at 3000-2500 cm^{-1} due to O—H stretching. In vapour phase, νC=O absorption occurs at 1770 cm^{-1} in acetic acid and in the liquid state, absorption band appears at 1739 cm^{-1}. Infra-red spectrum of benzoic acid shows a broad band at 3000-2500 cm^{-1} due to O—H stretching. Pi (π) cloud interactions are also noted when acidic hydrogen interacts with lewis bases (Nucleophiles) such as alkenes and benzene. For example, the frequency of O—H stretching in phenols is lowered by 40-100 cm^{-1} when spectrum is taken in benzene solution as compared to that in carbon tetrachloride solution. Due to this interaction, lengthening and hence weakening of O—H bond occurs.

4. **Bond angles.** It has been found that the highest νC=O frequencies arise in the strained cyclobutanones. This can be explained in terms of bond angles strain. The C—CO—C bond angle is reduced below the normal angle of 120° and this leads to increased *s*-character in the C=O bond. Greater *s*-character causes shortening of C=O bond and thus C=O str occurs at higher frequency.

In case the bond angle is pushed outwards above 120°, the opposite effect operates. Due to this reason, di-tert-butyl ketone absorbs at 1697 cm^{-1} (low) as a result of C=O str.

It is also assumed that there is no change in the C=O force constant and it is an increased rigidity in the C—CO—C bond system as the ring size decreases. In such cases, C=O str couple more effectively with C—C str leading to higher C=O str frequencies.

3.8 Scanning of Infra-red Spectrum (Instrumentation)

The most important source of Infra-red light for scanning the spectrum of an organic compound is **Nernst glower** which consists of a rod of the sintered mixture of the oxides of Zirconium, Yttrium and Erbium. The rod is electrically heated to 1500°C to produce Infra-red radiations.

A rod of silicon carbide (Globar) can also be electrically heated to produce Infra-red radiations. To obtain monochromatic light, optical prisms or gratings can be used. For prism material, glass or quartz cannot be used since they absorb strongly through most of the Infra-red region. Sodium chloride or certain alkali metal halides are commonly used as cell containers or for prism materials as these are transparent to most of the Infra-red region under consideration. Sodium chloride is hygroscopic and is, therefore, protected from the condensation of moisture by working at suitable temperature. Gratings give better resolution than do prisms at high temperatures.

Light from the source is split into two beams. One of the beams is passed through the sample under examination and is called the sample beam. The other beam is called the reference beam. When the beam passes through the sample, it becomes less intense due to the absorption of certain frequencies. Now, there will be a difference in the intensities of the two beams. Let I_0 be the intensity of the reference beam and I be the intensity of the beam after interaction with the sample respectively.

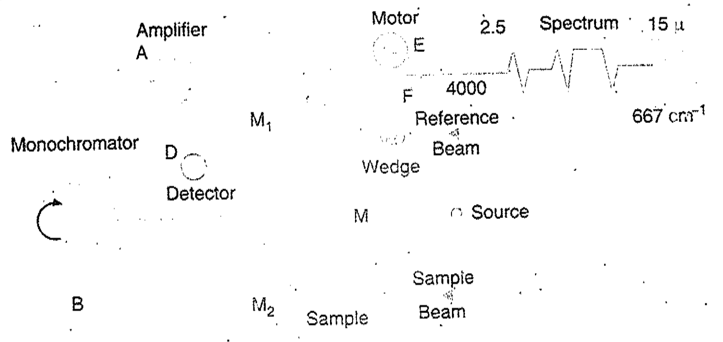


Fig. 3.11. Infra-red Spectrometer.

The absorbance of the sample at a particular frequency can be calculated as:

$$A = \log (I_0/I)$$

Also transmittance, $T = I/I_0$

or $A = \log (1/T)$

Intensities of the bands can be recorded as a linear function T against the corresponding wave-number. Intensities of the two beams are converted into and measured as electrical energies with the help of detector thermopile. For this we proceed as follows:

---

[*] It works on the thermopile principle—when two ends of the metal wire are attached with the two ends of another metal wire, then a difference in temperature between the two ends causes a current to flow in the wires. The intensity of radiation falling on the thermopile produces a current.

The two beams (Sample and Reference) are made to fall on a segmented mirror M (chopper) with the help of two mirrors M_1 and M_2. The chopper (M) which rotates at a definite speed reflects the sample and the reference beams to a monochromator grating (B). As the grating rotates slowly, it sends individual frequencies to detector thermopile[*] (D) which converts Infra-red energy into electrical energy. It is then amplified with the help of amplifier (A). Due to the difference in intensities of the two beams, alternating currents start flowing from the detector thermopile to the amplifier. The amplifier is coupled to a small motor (E) which drives an optical wedge (F). The movement of the wedge is in turn coupled to a pen recorder which draws absorption bands on the calibrated chart. The movement of the wedge continues till the detector receives light of equal intensity from the sample and the reference beams. Calibration can be carried out using spectrum of Polystyrene.

Sampling Techniques

Various techniques can be employed for placing the sample in the path of the Infra-red beam depending upon whether the sample is a gas, a liquid or a solid. The intermolecular forces of attraction are most operative in solids and least in case of gases. Thus, the sample of the same substance shows shifts in the frequencies of absorption as we pass from the solid to the gaseous state. In some cases, additional bands are also observed with the change in the state of the sample. Hence, it is always important to mention the state of the sample on the spectrum which is scanned for its correct interpretation.

(*a*) Solids. Solids for the Infra-red spectrum may be examined as an alkali halide mixture. Alkali metal halides, usually sodium chloride, which is transparent throughout the Infra-red region is commonly used for the purpose. Potassium bromide also serves the purpose well. The substance under investigation should be absolutely dry as water absorbs strongly at about 3710 cm^{-1} and also near 1630 cm^{-1}. The sample (solid substance) is ground with KBr and is made into a disc after drying and then pressing it under elevated temperature at high pressures. Also a blank disc is prepared with pure potassium bormide which may be placed in the path of the reference beam. It is often advisable to carry out grinding under Infra-red lamp to avoid condensation of atmospheric moisture. Grinding is usually done in agate mortar and pestle. Discs obtained from poorly ground mixture scatter more light than they disperse. The particle size of the ground mixture should be less than 2$m\mu$ to avoid scattering. Potassium bromide is transparent to the Infra-red region (2.5μ – 15μ) and thus, a complete spectrum can be scanned by mixing 1-2% of the solid sample with it and then grinding it to the desired particle size.

The spectrum of the solid can also be conveniently determined as a mull or a paste. Some commonly used mulling reagents are (*i*) nujol (*ii*) Hexachlorobutadiene (*iii*) chloro fluoro carbon oil etc. The most commonly used mulling reagent is nujol which is a mixture of liquid paraffinic hydrocarbons with high molecular weights. When nujol is used as a mulling reagent [Spectrum shown in figures 3.12 (*a*) and 3.12 (*b*)] absorptions due to C—H stretching at 3030-2860 cm^{-1} and those for C—H bending at about 1460 cm^{-1} and 1374 cm^{-1} are observed. Clearly, no information about the sample can be recorded from these regions of absorptions. The regions of absorptions due to nujol can be studied only by taking another spectrum of the sample using hexachlorobutadiene as the mulling reagent. A solid film can also be deposited over the alkali metal halide (NaCl or KBr) disc by putting a drop of the solution of the sample (sample dissolved in a volatile solvent) on the disc and then evaporating the solvent. Polymers, fats and waxy materials show excellent spectra in this way. Solid samples can also be examined in solutions. A polystyrene film is commonly used for calibration of wave numbers. For this, calibration is done using the bands at 3026, 3002, 2924, 1602, 1495 and 906 cm^{-1}.

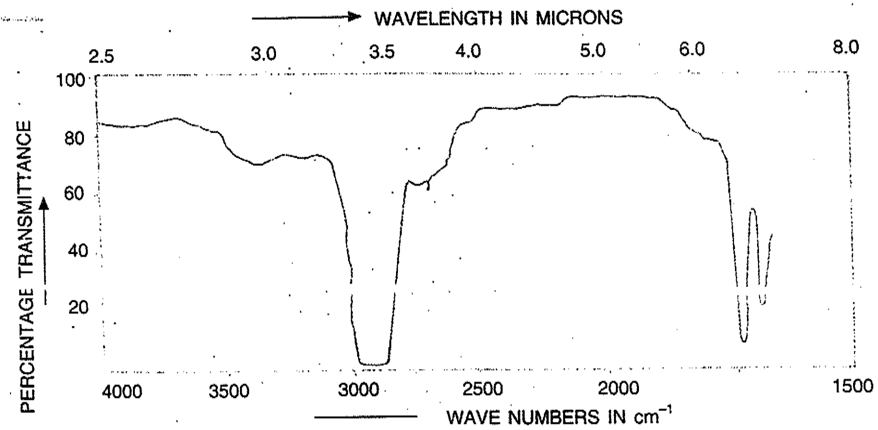


Fig. 3.12. (*a*) Infra-red spectrum of Nujole (higher).

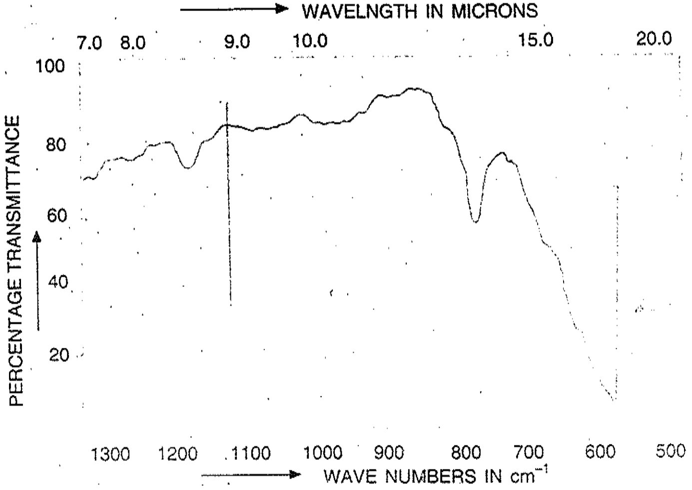


Fig. 3.12. (*b*) Infra-red spectrum of Nujole (lower).

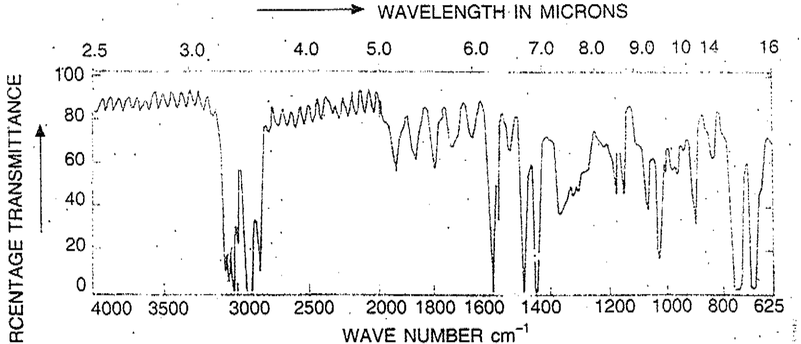


Fig. 3.12. (*c*). Polystyrene-wavelength v/s Percent transmittance.

(*b*) **Liquids :** The simplest technique consists of sampling a liquid in a thin film (0.1 to 0.3 mm) squeezed between two sodium chloride plates, *i.e.*, plates made of the material transparent to Infra-red light. For samples that contain water, plates may be constructed with calcium fluoride. A drop of the liquid sample is placed on the top of the sodium chloride plate and another sodium chloride plate is placed on it. The pair of sodium chloride plates enclosing the liquid film is then placed in the path of the sample beam. Similarly, a drop of the low melting substance can be likewise placed between two plates for spectral analysis.

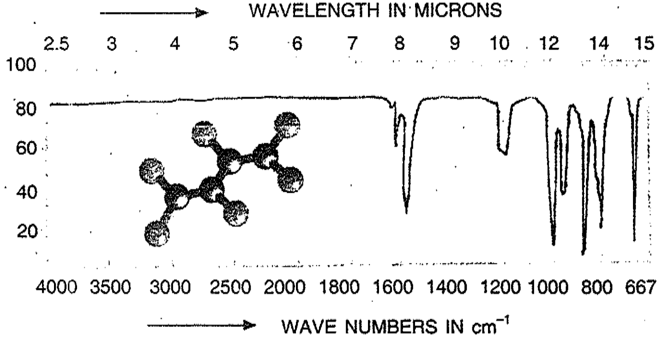


Fig. 3.13. Infra-red spectrum of Hexachlorobuta-diene-1.3.

(*c*) **Gases :** The gaseous sample is introduced into a 'gas cell'. The walls of the cell are made of sodium chloride. Sodium chloride windows allow the cell to be placed directly in the path of the sample beam. The gas cell is usually 10 cm long. Very few organic compounds can be examined as gases. The low frequency rotational changes in the gaseous phase often split the high frequency vibrational bands.

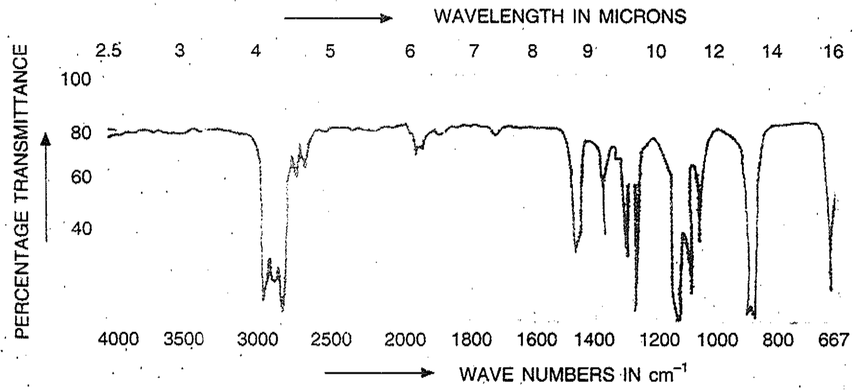


Fig. 3.14. Infra-red spectrum of 1, 4 Dioxane.

(*d*) **Solutions :** It is most convenient to determine the spectrum in solutions. Excellent solvents are those which have poor absorptions of their own. Unlike ultraviolet spectroscopy, too many solvents cannot be used in this technique. In Infra-red technique, all solvents do absorb in one region or the other. Some important solvents which may be used are:

(*i*) Chloroform, (*ii*) Carbon tetrachloride, (*iii*) Carbon disulphide etc.

Water cannot be used as a solvent as it absorbs in several regions of the infra-red spectrum.

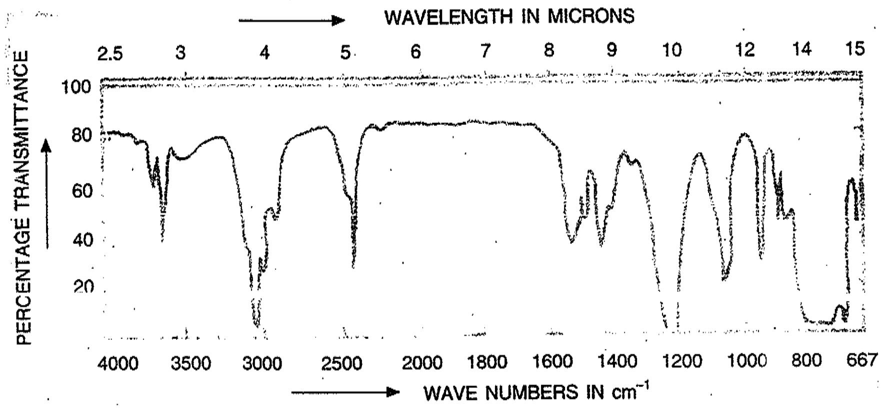


Fig. 3.15. Infra-red spectrum of Chloroform.

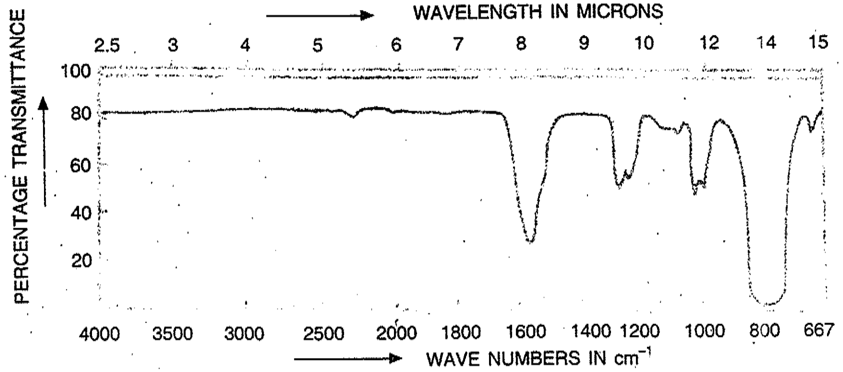


Fig. 3.16. Infra-red spectrum of Carbon tetrachloride.

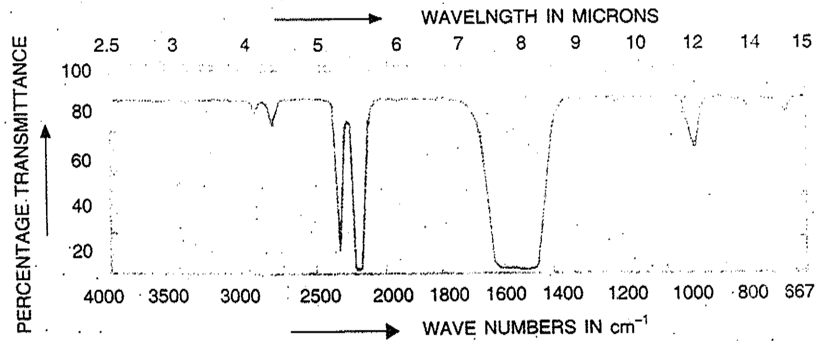


Fig. 3.17. Infra-red spectrum of Carbon disulphide.

The sample under analysis is dissolved in a solvent. Its 1-5% solution is placed in a solution cell consisting of transparent windows (made of alkali metal halide). A second cell containing the pure solvent is placed in the path of the reference beam to cancel out solvent interferences. In fact solvents do absorb in one region or the other. Hence, for correct analysis, two spectra should be run by dissolving the sample in two different solvents whose absorption regions are complimentary (see spectra for $CHCl_3$, CCl_4 and CS_2). It may also be noted that for careful analysis, the path length of the reference cell should be less than that of the solution cell for exact compensation (the mass of the solvent in the reference as well as in sample cell should be the same). Usually, determination of spectra of the substance in chloroform as well as in carbon disulphide provides complete information about the structure of the substance in solution. From the spectra of the various pure solvents, it is observed that chloroform gives many absorptions of its own as it is a less symmetric molecule. But, due to its better solvent properties, it is commonly used.

Infrared spectra of the substance taken at different concentrations also help in detecting the effect on Infra-red absorptions due to hydrogen bonding or intermolecular associations. In dilute solutions, the effects due to intermolecular associations are minimised. Consider the case of alcohols. Free O—H group shows a sharp band due to O—H stretching at 3610 cm^{-1} but this absorption becomes broad at about 3300 cm^{-1} when hydroxyl group is in polymeric association. The value of absorption frequency depends upon the strength of hydrogen bonding. Stronger the hydrogen bonding, lower is the stretching frequency of absorption. It may be noted that stretching frequencies are lowered and bending frequencies are raised* as a result of hydrogen bonding.

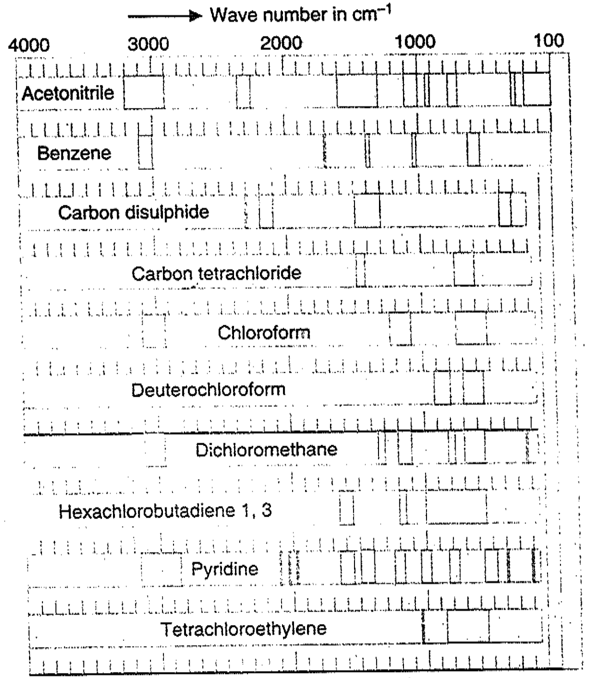


Fig. 3.18. Regions of absorption for various solvents in infra-red spectroscopy.

---

* It involves the change in coplanarity which is comparatively difficult to achieve and requires greater energy.

* N—H bending vibrations(an exception) occurs above 1600 cm^{-1}. For example, N—H bending in $—NH_2$ group occurs between 1650-1500 cm^{-1} (*m*).

3.10 Finger Print Region

One of the important functions of Infra-red spectroscopy is to determine the identity of two compounds. Two identical compounds have exactly the same spectra when run in the same medium under similar conditions. The region below 1500 cm^{-1} is rich in many absorptions which are caused by bending vibrations and those resulting from the stretching vibrations of C—C, C—O and C—N bonds. In a spectrum, the number of bonding vibrations is usually more than the number of stretching vibrations. The said region is usually rich in absorption bands and shoulders. It is called **Finger print region.*** Some molecules containing the same functional group show similar absorptions above 1500 cm^{-1} but their spectra differ in finger print region. The identity of an unknown compound can also be revealed by comparing its Infra-red spectrum with a set of spectra of known compounds under identical conditions. The identity of Infra-red spectra of two compounds is much more characteristic than the comparison of their many physical properties. It is not possible to distinguish between two enantiomers even if their spectra are run with the same machine under exactly identical conditions such as sampling, scan speed etc. Also it is not possible to distinguish the Infra-red spectra of straight chain alkanes containing 30 carbon atoms or more and it becomes necessary to make distinction with the help of their mass spectra. Finger print region can be subdivided into three regions as follows:

(*i*) 1500 – 1350 cm^{-1}

(*ii*) 1350 – 1000 cm^{-1} and

(*iii*) Below 1000 cm^{-1}.

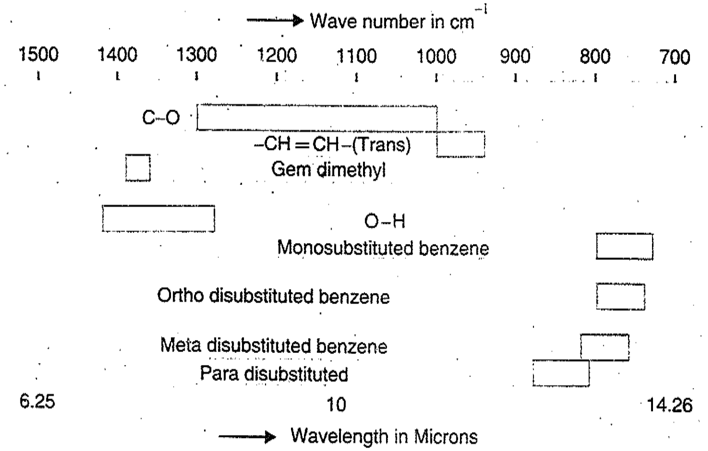
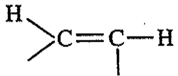


Fig. 3.19. Characteristic absorptions in the Finger print region.

Some characteristic absorptions in each of the above regions are described below:

(*i*) **Region: 1500-1350 cm^{-1}.** The appearance of a doublet near 1380 cm^{-1} (m) and 1365 cm^{-1} (s) shows the presence of tertiary butyl group in the compound. Gemdimethyl shows a medium band near 1380 cm^{-1}. Out of the two strong bands for the nitro compound, one appears in the finger print region, near 1350 cm^{-1}.

(*ii*) **Region: 1350-1000 cm^{-1}.** All classes of compounds viz. alcohols, esters, lactones, acid anhydrides show characteristic absorptions (strong bands) in this region due to C—O stretching. Primary alcohols form two strong bands at 1350-1260 cm^{-1} and near 1050 cm^{-1}. Phenols absorb near 1200 cm^{-1}. Esters show two strong bands between 1380-1050 cm^{-1}. Absorption in the region 1150-1070 cm^{-1} is most characteristic of ethers, *i.e.*, C—O stretching in C—O—C group.

(*iii*) **Region: below 1000 cm^{-1}.**  $>C=C(-)-H$ deformation at ~700 cm^{-1} (s) and that at 970-960 cm^{-1} (s) distinguishes between cis and trans alkenes. The higher value indicates that the hydrogen atoms in the alkene are trans with respect to each other.

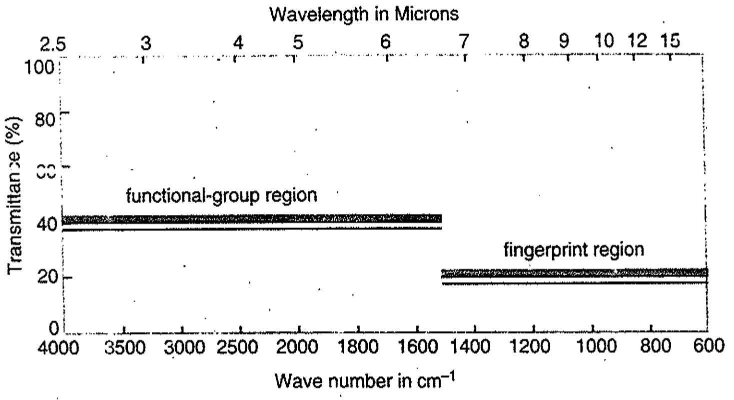


Fig. 3.20. Functional group and finger print regions.

The presence of mono substitution and also disubstitution at ortho, meta and para positions in benzene are detected by most characteristic absorptions in this region. A band in the region 750-700 cm^{-1} shows mono substituted benzene.

3.11 Spectral Features of Some Classes of Organic Compounds

Infra-red spectrum of a compound provides more information than is normally available from the electronic spectra. In this technique, almost all groups absorb characteristically within a definite range. The shift in the position of absorption for a particular group may change (within the range) with the changes in the structure of the molecule.

Impurities in a compound can be detected from the nature of the bands which no longer remain sharp and well defined. If the spectrum contains a strong absorption band between 1900-1600 cm^{-1}, the presence of carbonyl group $\left(>C=O\right)$ in a compound is suspected. The position of the peak or the band not only tells the presence of a particular group but also reveals a good deal about the environments affecting the group. Further study of the spectrum reveals whether it is aldehydic, ketonic, ester, amide etc. Aldehydes can be recognised from its characteristic C—H stretching; esters from C—O stretching and amides show absorptions for N—H stretching and N—H bending absorptions in addition to νC=O in the said range.

Presence of conjugation with carbonyl group can be detected as it shifts νC=O stretching to the lower wave number. The absorption values for certain groups such as C=O, O—H are also important in detecting hydrogen bonding. In case of hydrogen bonding, the wave number of absorption is shifted downwards for both the donor as well as the acceptor group. It can also make distinction between intermolecular hydrogen bonding and intra-molecular hydrogen bonding; the absorption position due to the latter being independent of the change in concentration.

Due to the different positions of absorptions, it is also possible to know the axial and the equitorial positions of certain groups in a cyclic structure.

The force constants responsible for the absorption peaks can be used to calculate bond distances and bond angles in some simple cases. When the Infra-red spectrum of an unknown compound is scanned, a large number of questions come to our mind viz.

(*i*) Which group/groups can be present in the compound?

(*ii*) What environments are influencing it?

(*iii*) What type is the carbon skeleton in the compound?

(*iv*) Is the compound aromatic? If so, what type of substitution?

Some of the important families giving characteristic absorptions and the environmental effects on them are discussed below:

3.11 A Hydrocarbons

These compounds are made up of carbon and hydrogen only. Hydrocarbons may be saturated and unsaturated aliphatics; cyclics or aromatics.

3.11 A_1 Alkanes and alkyl residues

The alkane residues are detected from C—H stretching and C—H deformation absorptions. As C—H does not take part in hydrogen bonding, its absorption position is little effected by chemical environments. Since most of the organic compounds possess alkanes residue, C—H absorption bands in a spectrum are of little diagnostic value. Commonly two C—H stretching absorption bands appear just below 3000 cm^{-1}; one for symmetrical and the other for asymmetrical vibrational frequencies. The group of bands corresponding to C—H def. is characteristic of alkyl group provided it is not under some electrical influence.

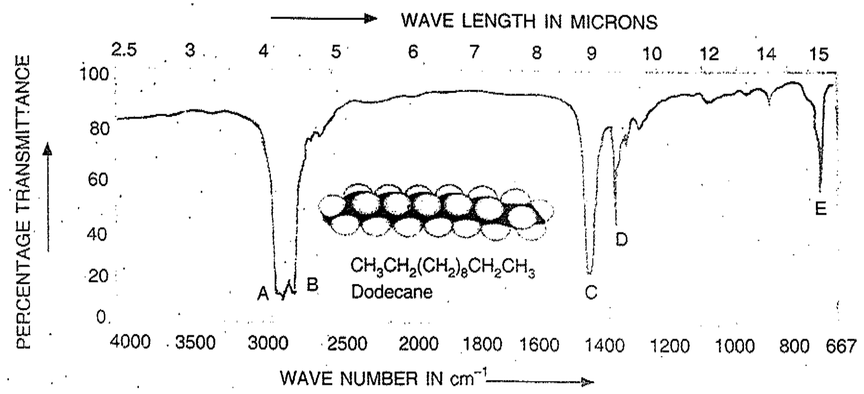


Fig. 3.21. Infra-red spectrum of Dodecane.

Courtesy: Sadtler Research Laboratories, Philadalphia

Positions of some characteristic absorptions

A = 2962 cm^{-1}; C—H Str

B = 2872 cm^{-1}; C—H Str in CH_3

C = 1465 cm^{-1}; C—H_{def}

D = 1450 cm^{-1}; C—H def in CH_2

E = 772 cm^{-1}; CH_2 (Rocking)

Positions of some characteristic absorptions

A = 2941 cm^{-1}; C—H Str.

B = 2880 cm^{-1}; C—H Str. in methyl/methylene

C = 1450 cm^{-1}; C—H def.

D = 1372 cm^{-1}; C—H def. in CH_3

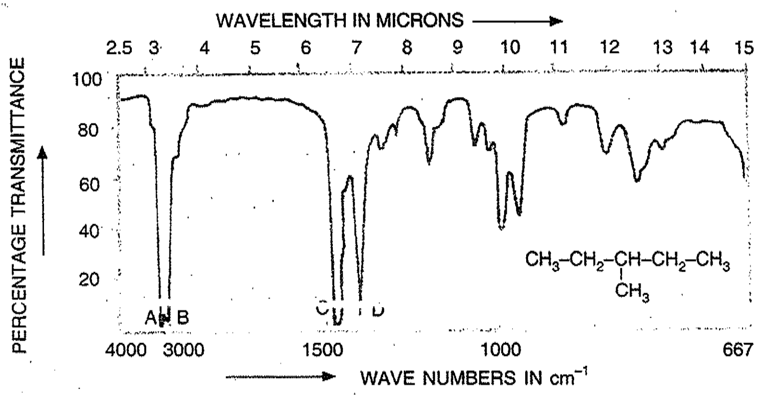


Fig. 3.22. Infra-red spectrum of 3-methyl pentane.

The various C—H bending vibrations in alkanes appear in the region 1485-1340 cm^{-1}. Vibrational absorptions for C—H bonds are much different from C—C bonds due to the large mass differences. C—C linkages are less characteristic and appear as weak bands in the region 1300-800 cm^{-1}. Spectra of isoalkanes differ from those of *n*-alkanes in the region 1500-700 cm^{-1}.

In gem dimethyl [—$C(CH_3)_2$], a doublet appears at about 1380 cm^{-1}. An absorption band in the range of 1395-1385 cm^{-1} appears for —$C(CH_3)_2$ group. For aldehydes (—CHO), two weak C—H str absorptions appear between 2900-2820 cm^{-1} and 2775 – 2700 cm^{-1}.

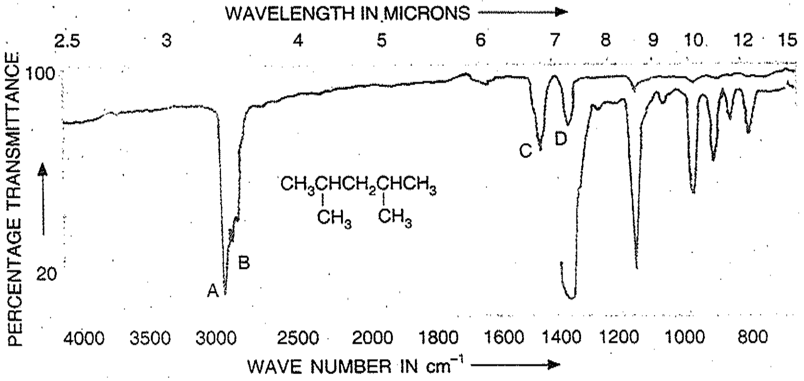


Fig. 3.23. Infra-red spectrum of 2, 4-dimethyl pentane.

Courtesy: Sadtler Research Laboratories, Philadalphia.

Positions of some characteristic absorptions

A = 2962 cm^{-1} C—H str

B = 2872 cm^{-1} C—H str in CH_3, CH_2

C = 1465 cm^{-1} C—H def

D = 1375 cm^{-1} C—H def (gem dimethyl)

For molecules containing —OCH_3, -$N(CH_3)$, O—CH_2—O etc., C—H str absorption appears below 3000 cm^{-1}.

---

* str. stands for stretching.

Table T_3—1. Alkanes

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
C—H	C—H str C—H def	2960-2850 (*m, s*) 1485-1340 (*w*)
C—C	C—C str	1300-800 (*w*)
—CH_2—	C—H def	1485-1440 (*m*)
—CH_3	C—H def	1470-1430 (*m*)
—$C(CH_3)_2$ Gem dimethyl	C—H def	~1380 (*m*) doublet
—$C(CH_3)_3$ Tert.Butyl	C—H def	~ 1365 (*s*) 1395-1385 (*m*)

3.11 A_2 Alkenes

In alkenes (olefines), C—H str absorption band appears in the region 3100-3000 cm^{-1}. Conjugation of double bond with an aromatic ring shows C=C str near 1625 cm^{-1}.

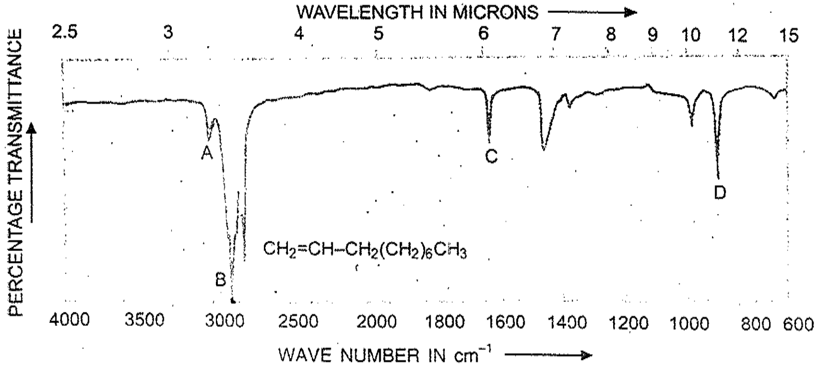


Fig. 3.24. Infra-red spectrum of 1-Decene.

Courtesy: Sadtler Research Laboratories, Philadalphia.

Positions of some characteristic absorptions

(*i*) A	=	3049 cm^{-1}	C—H str in olefins
B	=	2960 – 2850	C—H str in CH_3, CH_2
C	=	1645 cm^{-1}	C=C str
D	=	986 cm^{-1}	C—H def out of plane
E	=	720 cm^{-1}	Methylene rocking

For trans alkenes, C—H def comes around 970 cm^{-1} and for the corresponding cis isomer, it appears at about 700 cm^{-1} (not much identified). This helps in distinguishing cis and trans alkenes. Conjugated dienes which form a symmetrical molecule as butadiene (CH_2=CH—CH=CH_2) shows one band near 1600 cm^{-1} (C=C stretching). Similar absorptions for molecules without centre of symmetry as 1, 3 Pentadiene appear in the region 1650–1600 cm^{-1}. Cumulative double bonds such as C=C=C shows strong absorption band around 2000-1900 cm^{-1}. For a symmetrical alkene, $>C=C<$, absorption is Raman active due to molecular symmetry.

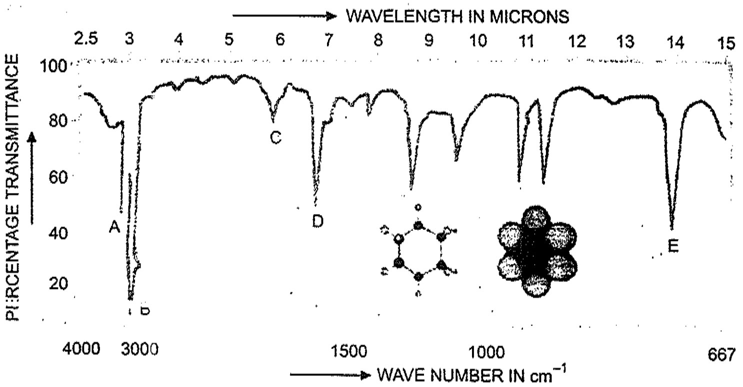


Fig. 3.25. Infra-red spectrum of Cyclohexene.

Positions of some characteristic absorptions

A	=	3033 cm^{-1}	=C—H str
B	=	2940 cm^{-1}	C—H str in CH_2
C	=	1640 cm^{-1}	C=C str
D	=	1435 cm^{-1}	C—H def in CH_2
E	=	721 cm^{-1}	C—H def. (cis isomer).

Table T_3—2.

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
Alkenes	$>C=C-H$ str	3100-3000 (*m*)
Monosubstituted	C—H str C—H def	3090-3075 (*m*) 3040-3010 (*m*) 700 (*s*) 915-905 (*s*)
Disubstituted (Trans)	C—H str C—H def C=C str	3040-3010 (*m*) 970-960 (*s*) ~1675 (*m*)
Disubstituted (cis)	C—H str C—H def C=C str	3040-3010 (*m*) ~700 (*s*) ~1660 (*m*)
Trisubstituted	C—H str C—H def C=C str	3040-3010 (*m*) 850-790 (*s*) ~1670 (*m*)
Tetra substituted	C=C str	~1670 (*m*)
Disubstituted (gem)	C—H str C—H def C=C str	3095-3075 (*m*) 895-875 (*s*) ~1670 (*m*)
Non-conjugated diene	C=C str	1650-1600 (*v*)
Conjugated diene	C=C str	~1600 (*w*) ~1650 (*w*)

3.11 A_3 Alkynes

In acetylenes, a strong band for —C≡C—H str appears at about 3300 cm^{-1} and a weak C≡C str occurs at about 2200 cm^{-1}. For mono-substituted acetylenes, C—H stretching appears at about 3300 cm^{-1}. This band is strong and narrow and can be distinguished from the hydrogen bonded O—H and N—H stretching occurring in the same region. C—H bending for acetylenes and mono-substituted acetylenes occur at 650-610 cm^{-1}.

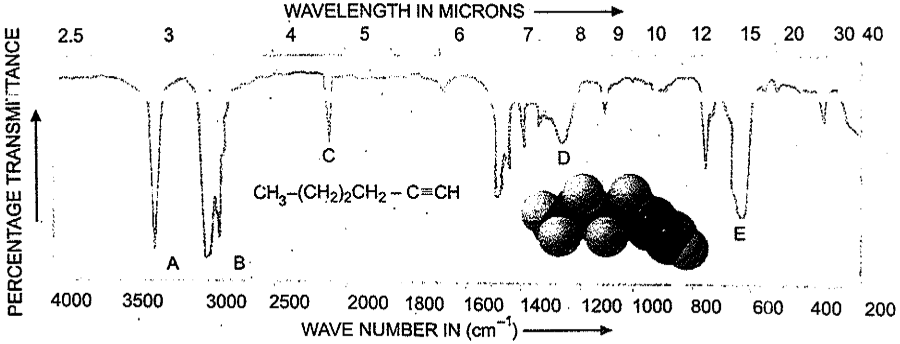


Fig. 3.26. Infra-red spectrum of 1-Hexyne.

Courtesy: Sadtler Research Laboratories, Philadalphia.

Positions of some characteristic absorptions

A	= 3268 cm^{-1}	≡C—H str
B	= 2940-2860	C—H str in CH_3, CH_2
C	= 2110 cm^{-1}	C≡C str
D	= 1247 cm^{-1}	≡C—H def (overtone)
E	= 630 cm^{-1}	≡C—H def (Fundamental)

Cycloalkanes

In cycloalkanes, the value of C—H str increases with the increasing angle of strain in the ring. The asymmetric CH_2 stretching vibrations for cyclopropane is between 3100-2919 cm^{-1} and that for cyclohexane is 2950 cm^{-1}. With increasing strain in the ring, C—H bending also shows an increase. For example, C—H bending in cyclopentane is at 1455 cm^{-1} while that in cyclohexane is at 1442 cm^{-1}.

Table T_3—3. Alkynes and Cycloalkanes

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
Alkyne	C≡C—H str	~ 3300 (*s*)
	C—H def	650-610 (*s*)
Monosubstituted	C—H def	650-610 (*s*)
	C≡C str	2140-2100 (*m*)
Disubstituted	C≡C str	2260-2200 (w)
Allene C=C=C	C=C str	2000-1900 (*m*)
Cycloalkanes	C—H str*	3100-2920 (*m*)

---

* Its value changes with the change in the angle of strain in the ring. The C—H str. absorption for cyclo-propane occurs at a higher wave number as compared to that in cyclohexane.

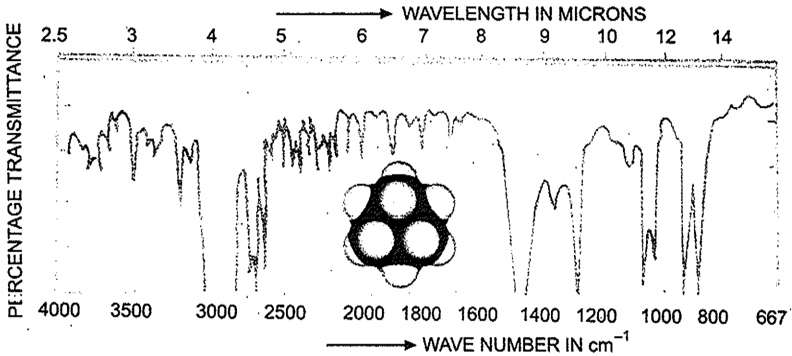


Fig. 3.27. Infra-red spectrum of cyclohexane.

Note. Such a spectrum (cyclohexane) is important as a finger print and can be used for comparison.

Aromatic Hydrocarbons

In aromatic hydrocarbons, a variable C—H stretching absorption occurs in the region 3050-3000 cm^{-1}; C=C str at 1650-1450 cm^{-1} and C—H def vibrations at 900-700 cm^{-1}. For aromatic compounds, the most characteristic C=C stretching bands are at 1600 cm^{-1}, 1580 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1} (*m*). If there is no absorption in this region, it is a fair proof that the compound is not aromatic. Monosubstituted benzene can be easily recognised by bands at 710-690 cm^{-1} (*s*) and at 770-730 cm^{-1} (*s*). Metasubstituted benzene usually shows two bands (*i*) 710-690 cm^{-1} (*m*) and (*ii*) 800-750 cm^{-1} (*m*). Ortho and para substituted benzenes show one band each at 770-735 cm^{-1} (*v, s*) and at 840-800 cm^{-1} (*m*) respectively.

Table T_3—4.

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
Aromatic	Ar—H str	3050-3000 (*v*)
hydrocarbons	C=C str	~1600 (*v*)
		~1580 (*v*)
		~1500 (*m*)
		~1450 (*m*)
	C—H def	900-700 (*m*)
Monosubstituted	C—H def	(*i*) 710-690 (*s*)
		(*ii*) 770-730 (*s*)
Disubstituted (meta)	C—H def	(*i*) 710-690 (*m*)
		(*ii*) 800-750 (*m*)
Disubstituted (ortho)	C—C def	770-735 (*v, s*)
Disubstituted (para)	C—H def	840-800 (*m*)

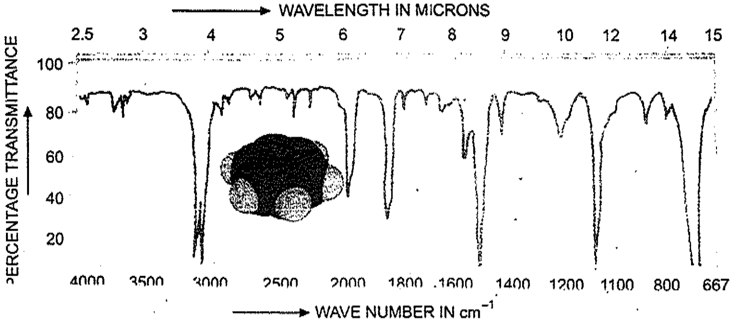


Fig. 3.28. Infra-red spectrum of Benzene.

Exercise. Mark the various bands in the Infra-red spectrum which are most characteristic of benzene.

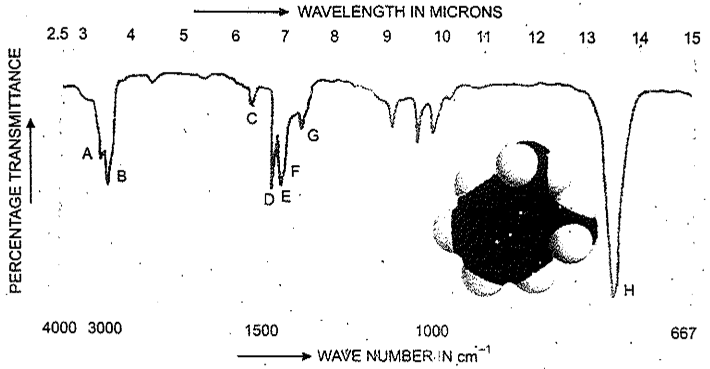


Fig. 3.29. Infra-red spectrum of ortho-Xylene.

Positions of some characteristic absorptions

A = 3020 cm^{-1}; =C—H str in olefins/aromatics
B = 2941 cm^{-1}; C—H str
C, D, E, F = 1606, 1495, 1460, 1450 cm^{-1}; C=C str in aromatic nuclei.
G = 1375 cm^{-1}; C—H def in methyl
H = 745 cm^{-1}; ortho-disubstituted benzenes

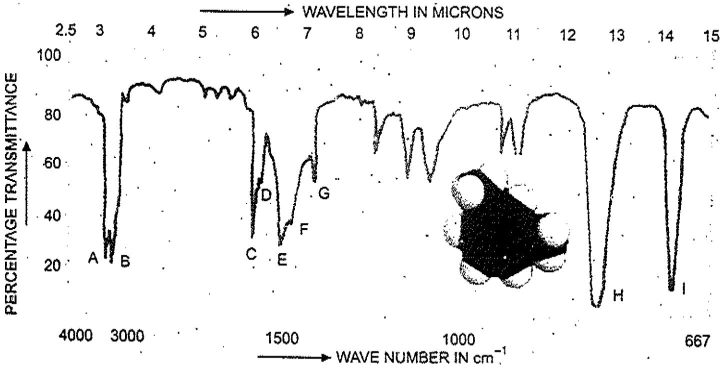


Fig. 3.30. Infra-red spectrum of meta-Xylene.

Positions of some characteristic absorptions

A = 3030 cm^{-1}; C—H str in olefines/aromatics
B = 2940 cm^{-1}; C—H str
C, D, E, F = 1610, 1585, 1492, 1455 cm^{-1}; C=C str in aromatic nuclei.
G = 1370 cm^{-1}; C—H def in methyl
H and I = 770 cm^{-1}; meta-disubstituted benzene

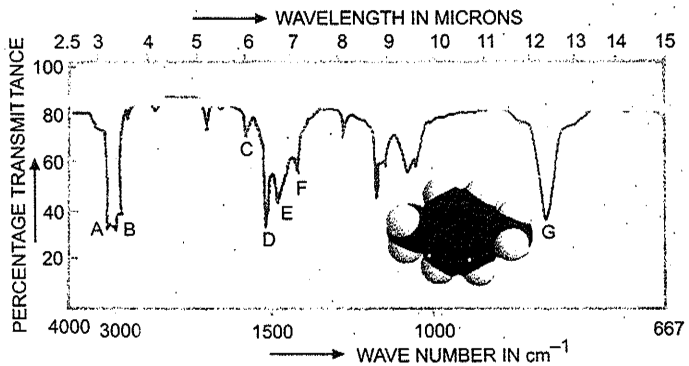


Fig. 3.31. Infra-red spectrum of para- Xylene.

Positions of some characteristic absorptions

A = 3030 cm^{-1}; =C—H str in olefins/aromatics
B = 2940 cm^{-1}; C—H str in methyl
C, D, E = 1624, 1510, 1450 cm^{-1}; C=C str in aromatic nuclei
F = 1370 cm^{-1}; C—H def
G = 802 cm^{-1}; Para-disubstituted benzene

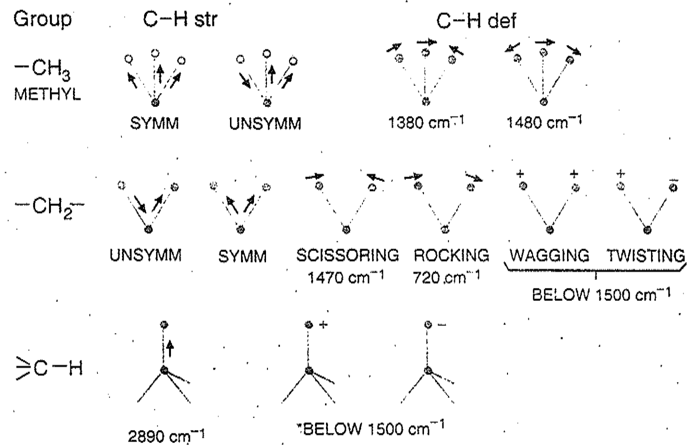
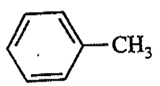


Fig. 3.32. Representation of C—H str and C—H def vibration for —CH_3, —CH_2— and C—H groups.

---

* (+) and (–) signs indicate vibrations perpendicular to the plane of the paper.

EXAMPLE 6. *Write the various infra-red bands in the case of toluene.*



SOLUTION. Some of its important Infra-red bands are :

(*i*) Ar—H str ~3030 cm^{-1}

(*ii*) C—H str in CH_3— 2850-2960 cm^{-1}

(*iii*) C = C str ~1600 cm^{-1}, ~1580 cm^{-1}, ~1460 cm^{-1}

(*iv*) C—H bending for monosubstituted benzene = 730 – 770 cm^{-1}.

EXAMPLE 7. *Describe the various infra-red bands in case of 1-Hexyne.*

SOLUTION. The structure of 1-Hexyne is

$$H_3C—CH_2—CH_2—CH_2—C{\equiv}CH$$

Some of its important absorption bands in Infra-red spectroscopy are :

(*i*) ≡ C—H str	~ 3300 cm^{-1}
(*ii*) C—H str in CH_2 and CH_3	~ 2860 – 2950 cm^{-1}
(*iii*) C ≡ C str	~ 2100 cm^{-1}
(*iv*) C—H bending	~ 1465 cm^{-1}

EXAMPLE 8. *Describe the various characteristic absorption bands in case of 2-Hexene in the Infra-red spectroscopy.*

SOLUTION. The structure of 2-Hexene is

$$H_3C—CH_2—CH_2—CH = CH—CH_3$$

Some of its important characteristic absorption bands are :

(*i*) C—H str in alkenes	~ 3050 cm^{-1}
(*ii*) C—H str in CH_2 and CH_3	~ 2860 – 2950 cm^{-1}
(*iii*) C = C str	~ 1680 cm^{-1}
(*iv*) C—H bending	~ 1460 cm^{-1}
(*v*) —CH = CH_2 (for cis, trans)	700 – 970 cm^{-1}

PROBLEM P_3–1. An Infra-red spectrum of a hydrocarbon containing 10 per cent hydrogen gave two bands (*i*) 3295 cm^{-1} and (*ii*) 625 cm^{-1} alongwith a weak absorption band near 2130 cm^{-1}. What is the probable structure of the compound ?

PROBLEM P_3–2. The Infra-red spectrum of the hydrocarbon containing 14.3 per cent hydrogen gave the following absorption bands :

(*i*) 3.32-3.29 μ (*m*), (*ii*) 10.40 μ (*s*) and (*iii*) 5.96 μ (*m*). What is the probable structure of the compound? Also tell the geometry of this compound.

[illegible] Halogen Compounds

In the halogen compounds, the C—H stretching shifts to higher wave number due to the –I effect of the halogen atom. Due to the –I (inductive) effect of halogen, C—H part of the molecule becomes rich in s-component and hence force constant increases. Greater the electronegativity of the halogen atom, greater is the value of C—H stretching. C—X bonds show lower values of absorption frequencies as compared to C—H bond due to the decreased force constant and increase in the reduced mass. C—X str (X = Cl, Br, I) absorption lies between 800-500 cm^{-1} while in the case of C—F bond, stretching vibrations occur in the region 1400-1000 cm^{-1}.

Bromides and chlorides are best detected by their mass spectra. The asymmetric C—H stretching vibrations of —CH_3 group in CH_3X occur above 3000 cm^{-1} which is also the region for aromatic and unsaturated compounds.

C—H stretching shifts to higher frequencies in dihalogen and trihalogen derivatives. The detection of halogen by this technique is not reliable as most of the absorptions occur below 650 cm^{-1}.

Table T_3—5. Halogen Compounds

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
C—Cl	C—Cl str	800-600 (s)
C—Br	C—Br str	600-500 (s)
C—I	C—I str	~ 500 (s)
C—F	C—F str	1400-1000 (s)

The Infra-red spectrum of chlorobenzene is shown below :

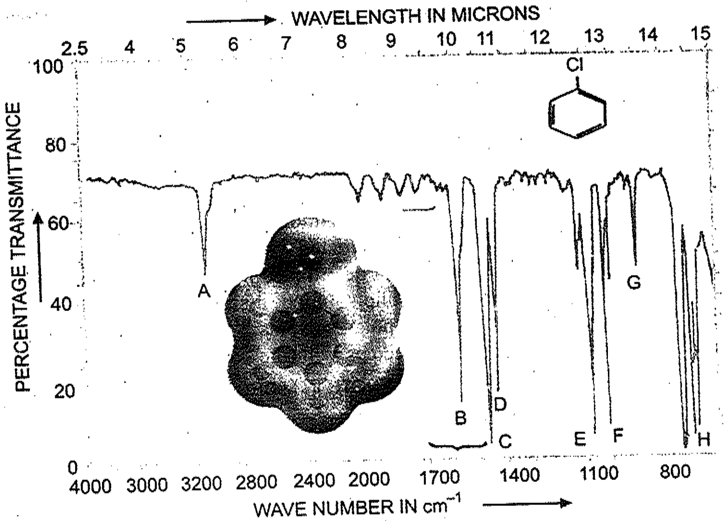


Fig. 3.33. Infra-red spectrum of chlorobenzene.

Positions of some characteristic absorptions

A = 3072 cm^{-1}	C—H str (Aromatic)
B = 1584 cm^{-1}	C═C str
C = 1478 cm^{-1}	C═C str
D = 1446	C═C str of benzene
G and H 735 cm^{-1}, 702 cm^{-1}	C—Cl str

The infra-red spectrum of 2-Bromopropane is shown below :

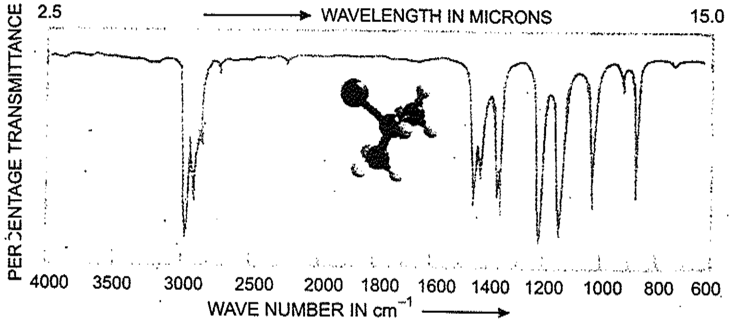


Fig. 3.34. Infra-red spectrum of 2-Bromopropane.

EXERCISE: (Write characteristic absorption peaks of 2-Bromopropane yourself)

In this spectrum, C—H bending vibration of a methyl group is seen as a doublet as two methyl groups are present on the same carbon atom.

3.11 C Alcohols And Phenols

Alcohols and phenols exhibit an excellent property of hydrogen bonding. Due to this reason, O—H stretching bands for such compounds are normally recorded in dilute solutions of the sample in non-associating solvents. A variable sharp band appears in the region 3700-3500 cm^{-1}, when a spectrum of a dilute solution of alcohol in carbon tetrachloride is scanned. Because of its high intensity, the O—H absorption band can be differentiated from the overtones and the combination bands of this region. Spectra for alcohols are best determined in the vapour phase. If the spectrum is taken with increased concentration of alcoholic solution, a sharp band disappears and a broad band at lower frequency appears instead. In polar solvents, O—H str. appears at lower wave number due to the association of alcohol molecules with the solvent molecules.

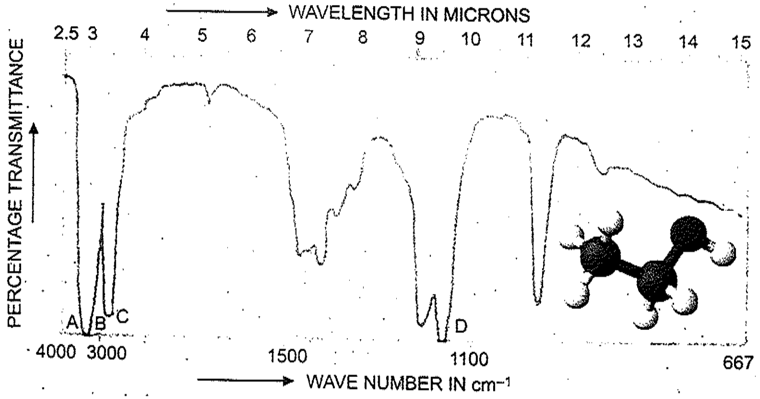


Fig. 3.35. Infra-red spectrum of Ethanol as a film.

Positions of some characteristic absorptions

A = 3330 cm^{-1}	O—H str (hydrogen bonded)
B = 2996 cm^{-1}	C—H str
C = 2924 cm^{-1}	C—H str
D = 1050 cm^{-1}	C—O str (for primary alcohols)

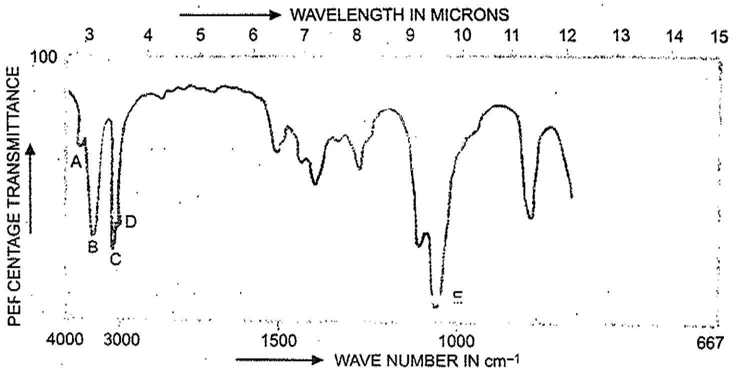


Fig. 3.36. Infra-red spectrum of Ethanol in carbon tetrachloride.

EXERCISE. Mark the various bands in the Infra-red spectrum which are most characteristic of ethanol.

Primary, secondary and tertiary alcohols can be frequently classified from the bands for the coupling vibrations, *i.e.*, C—O str and O—H bending. Primary alcohols show a strong band near 1050 cm^{-1} and secondary alcohols near 1100 cm^{-1} in addition to another strong band at 1350-1260 cm^{-1}. Tertiary alcohols can be distinguished due to the appearance of strong band at 1200 cm^{-1} and another at 1410-1310 cm^{-1}. The strong absorption observed in the spectra of hydroxy derivatives between 1250-1000 cm^{-1} was assigned to a characteristic absorption of $>\!\!C-OH$ group.

The frequency range (3640-3600 cm^{-1}) decreases alongwith band intensities in the order, primary > secondary > tertiary. It can be expected on the basis of +I effect. In concentrated solution or in the solid state, the O—H str absorption band becomes broader and sharper and occurs at lower wave number. **Thus, the absorption maximum for O—H stretching depends upon concentration, nature of the solvent and temperature.** In case, an alcohol is branched heavily in the α-position, the absorption band corresponds to the free O—H group. In intermolecular hydrogen bonded molecules, absorption shifts are concentration dependent. The O—H stretching absorption band appears at 3570-3450 cm^{-1} in compounds which show intramolecular hydrogen bonding. For such molecules, there is no absorption shift on diluting the sample. For chelate molecules such as mono-carboxylic acids existing as dimers, hydrogen bonded structure is stabilised by resonance. Thus, O—H str absorption appears as a broad band between 3000-2500 cm^{-1}.

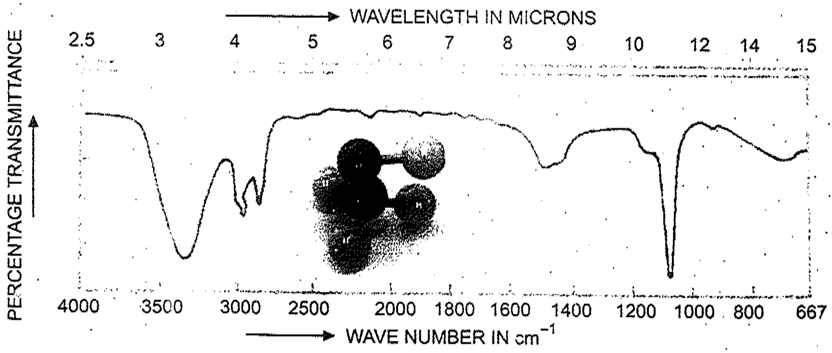


Fig. 3.37. Infra-red spectrum of Methanol.

EXERCISE. Mark some characteristic absorption bands in the Infra-red spectrum of methanol.

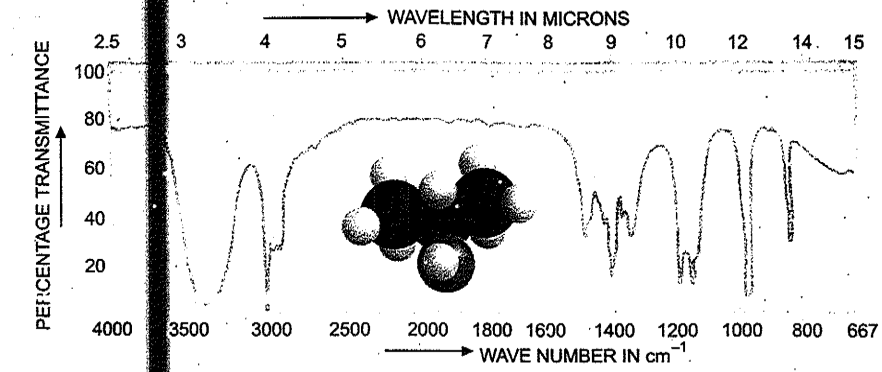


Fig. 3.38. Infra-red spectrum of Propan-2-ol.

EXERCISE. Mark some characteristic absorption bands in the Infra-red spectrum of propan-2-ol.

The axial or the equitorial position of the O—H group in cyclohexanols can also be detected. The frequency of the axial hydroxyl group is higher than that of the equitorial. This can be explained by repulsion between the groups in the 1, 3 positions of the cyclohexane ring, hindering the vibration of the oxygen atom responsible for the increase in force constant of the O—H bond. It may be noted that in equitorial O—H groups, the motions are less restrained. Consider the case of 1, 2, cyclohexane diols (chair form). In cis-form, one of the two OH groups is axial and the other is equitorial while in the trans-form, both are either axial or equitorial. In trans 1, 2 cyclohexane diol, the distance OH........O calculated for axial conformation (*a*, *a*) is about 3.3 Å and for equitorial conformation, (*e*, *e*), it is 2.34 Å. The spectra for trans 1, 3, cyclohexane diol shows a band for bonded OH at 3602 cm^{-1}. Clearly, the molecule exists in equitorial conformation which is energetically more favoured.

EXERCISE. Mark some characteristic absorption bands in the Infra-red spectrum of 2-methyl cyclohexanol.

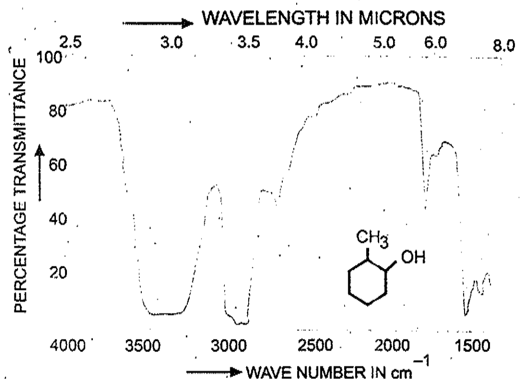


Fig. 3.39. Infra-red spectrum of 2 methyl

In phenols, the frequency of the free O—H str lies near 3600 cm^{-1}. In addition to the usual band for O—H str, phenols show characteristic strong C—O str band near 1200 cm^{-1} and another at 1410-1300 cm^{-1}. Phenols form intermolecular hydrogen bonds more readily than alcohols. Hydroxyl group in the associated form absorbs at 3500-3300 cm^{-1}. As in alcohols, the value of frequency shift in phenols provides information as regards the strength of the hydrogen bonds and also the type of association. It was shown that in concentrated solutions, meta and para substituted monoalkyl phenols form polymeric associations and absorption occurs near 3322 cm^{-1} (bonded region). *The strength of the hydrogen bond is not influenced by the nature or the volume of the substituents in these positions* (*e.g.*, substituent group may be methyl or the tertiary butyl). Compared with alcohols, phenol can be classified as sterically hindered, partially hindered and normal. If the phenol is substituted in the ortho positions, it is said to be sterically hindered and we cannot expect absorption in the bonded region. Thus, the spectrum for such a compound shows a strong band corresponding to free hydroxyl group near 3640 cm^{-1}. If a single alkyl group is present in the ortho position in phenol, the absorption shows a slight downward shift. Spectra of ortho substituted phenols (capable of forming hydrogen bonds with —OH group), show a free OH band alongwith another band arising from intramolecularly bonded O—H group. In such a case, bonded O—H band has a lower frequency of absorption. Di and poly hydroxylic phenols with adjacent O—H groups form intramolecular hydrogen bonds. Catechol in dilute solution shows two bands at 3610 cm^{-1} (due to free O—H group) and another at 3570 cm^{-1} (due to intramolecularly bonded O—H group).

---

* Absorption shifts to higher wave-number on dilution.

** No absorption shift on dilution.

Table T$_3$—6.

Group	Type of Vibrations	Region in cm^{-1} and intensity
Alcohols		
Free O—H group	O—H str	3700-3500 (*v*, *sh*)
Intermolecular hydrogen bonded OH* (Polymeric association)	O—H str	3400-3200 (*v*, *b*)
Intramolecular hydrogen bonded OH**	O—H str	3570-3450 (*v*, *sh*)
Chelate compounds	O—H str	3000-2500 (*w*, *b*)
Primary alcohols	C—O str	(*i*) 1350-1260 (*s*) (*ii*) ~1050 (*s*)
Secondary alcohols	C—O str	(*i*) 1350-1260 (*s*) (*ii*) ~ 1100 (*s*)
Tertiary alcohols	C—O str	(*i*) 1400-1310 (*s*) (*ii*) ~ 1150 (*s*)
Cis-1, 2 cyclohexanediol	O—H str	(*i*) 3626 (free) (*ii*) 3600 (bonded)
Phenols	C—O str	(*i*) ~1200 (*s*) (*ii*) 1410-1300 (*s*)

PROBLEM P$_3$-3. An organic compound (Molecular weight = 108) gave the following peaks in its Infra-red spectrum :

3401 cm^{-1} (*s*, *b*); 3077 cm^{-1} (*w*), 2899 cm^{-1}, 1499 cm^{-1} (*w*, *sh*) and 1456 cm^{-1}, (*m*, *sh*). With alkaline potassium permanganate, it is oxidised to an acid. It gives a negative test with ferric chloride solution.

The infra-red spectrum of Phenol is given below :

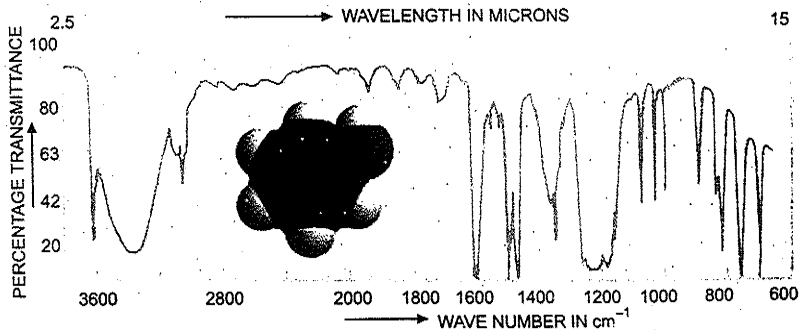


Fig. 3.40. Infra-red spectrum of Phenol. (Courtesy : Research laboratories, Division of Bio-Rad Laboratories).

EXERCISE. Explain some important characteristic absorptions in the above spectrum.

The Infra-red spectrum of Benzyl alcohol is shown below :

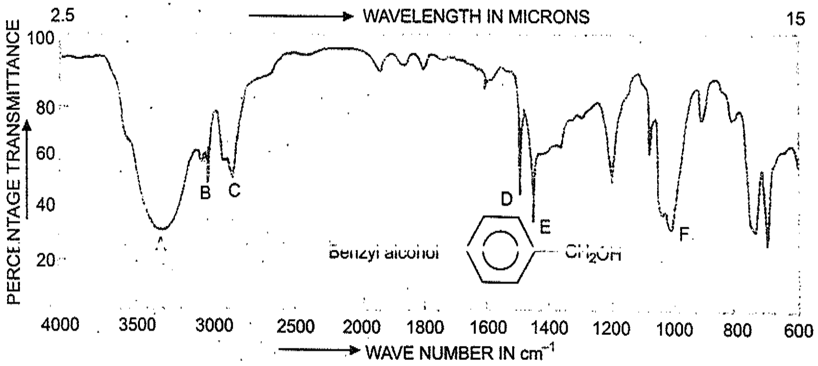


Fig. 3.41. Infrared spectrum of Benzyl alcohol. (Courtesy : Sadtler Research Laboratories)

Positions of some characteristic absorptions

A = 3330 cm^{-1}	O—H str	(broad, H-bonding)
B = 3100 – 3000 cm^{-1}	C—H str	(Aromatic)
C = 2980 – 2840 cm^{-1}	C—H str	(in methylene)
D, E = 1580, 1460 cm^{-1}	C $\overset{\cdots}{=}$ C str	(Aromatic)
F = 1017 cm^{-1}	C—O str	(1°–alcohol)

The Infra-red spectrum of *p*-cresol is given below :

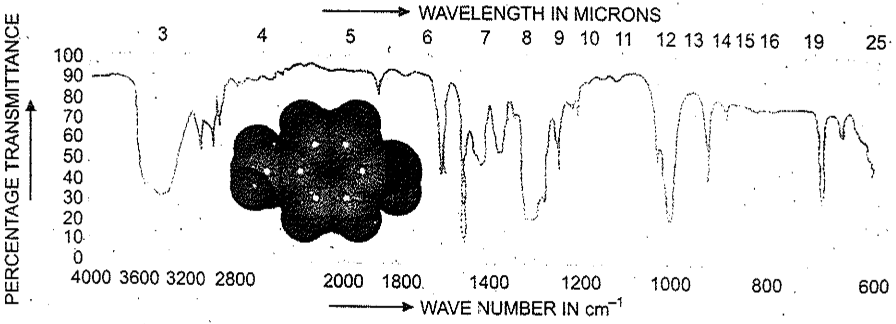


Fig. 3.42. Infra-red spectrum of p-cresol (liquid-neat)

EXERCISE. Mark some important characteristic absorptions in the above spectrum.

3.11.D Ethers

Ethers are derivatives of alcohols and show characteristic C—O—C bands. Since the masses of C—C and C—O are comparable, their force constants are quite close. But due to the large difference in their dipole-moments, the C—O bonds are stronger as compared to C—C bonds. Ethers show only one characteristic band in the region 1300-1050 cm^{-1}. The identification of ether in an unknown compound is difficult in presence of another oxygenated compound because many other strong bands appear in the same region. Saturated aliphatic ethers show a strong band in the region 1150-1070 cm^{-1} for asymmetric C—O—C stretching and another at 940 cm^{-1} for symmetrical stretching. The C—O—C absorption spectrum of higher members lie in the broader region 1250-1070 cm^{-1}. Keto ethers and esters are difficult to distinguish since both are identified for the values of C = O stretching and C—O stretching.

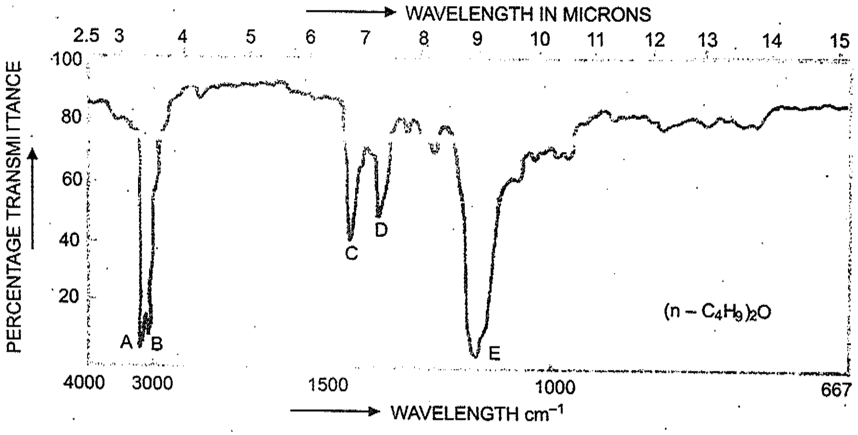
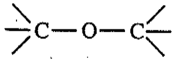
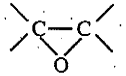


Fig. 3.43. Infra-red spectrum of di-*n*-butyl ether.

Positions of some characteristic absorptions

A = 2960 cm^{-1}	C—H str in methyl
B = 2880 cm^{-1}	C—H str
C = 1462 cm^{-1}	C—H def methyl/methylene.
D = 1372 cm^{-1}	C—H def in methyl.
E = 1124 cm^{-1}	C—O str in C—O—C group

Table T$_3$—7.

Group	*Type of vibrations*	*Region in cm^{-1} and intensity*
	C—O str	1150-1070 (s)
C—O—CH$_3$	C—H str	2850-2810 (m)
	C—O str	~ 1250 (s) ~ 910 (s) ~ 800 (s)
C=C—O—C	C—O str	1070-1020 (s) 1270-1200 (s)

The Infra-red spectrum of Phenetole is given below :

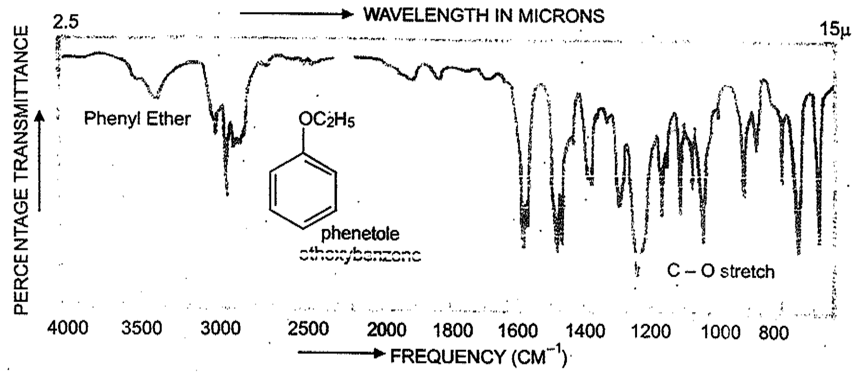


Fig. 3.44. Infra-red spectrum of Phenetole. (*Courtesy* : Sadtler Research Laboratories).

Mark some important characteristic absorptions in the above spectrum.

3.11 E Carbonyl Compounds

The appearance of a strong band in the spectrum between 1650-1950 cm^{-1} shows the presence of a carbonyl group in the compound. It is due to C=O str and is the most representative type of vibration localised in an individual bond. After detecting the carbonyl group, the next step is to examine other peaks in the spectrum for the determination of the exact functional group viz., aldehyde, ketone, ester, amide, quinone etc. Greater the number of peaks in the spectrum, easier becomes the detection. The frequency of absorption due to the carbonyl group depends mainly on the force constant which in turn depends upon inductive effect, conjugative effect, field effect and steric effects. All these effects operate simultaneously. A carbonyl compound can be written in the following two forms :

I II

If R$_1$ and R$_2$ are electron repelling groups, the structure II is favoured, the force constant (also bond order) is lowered and absorption occurs at lower wave number. If R$_1$ or/and R$_2$ is/are electron withdrawing group/groups, then under its/their influence, the structure I is favoured. Clearly, the force constant for structure I is more and hence absorption occurs at higher wave number. The position of absorption is also sensitive to unsaturation. C=O stretching for α, β-unsaturated ketones occurs at a lower frequency as compared to its saturated analogue. Aryl ketones show C=O stretching absorption at a lower wave number as compared to aliphatic ketones. The position of C=O stretching absorption also depends upon the ring size. The wave number of absorption is raised with the decrease in the size of the ring.

3.11 E$_1$ Aldehydes and Ketones

Due to the large +I effect operating in ketones as compared to that in aldehydes, the latter usually absorb at higher wave number as compared to the former. The C=O stretching absorption for formaldehyde (HCHO), acetaldehyde (CH_3CHO) and acetone (CH_3COCH_3) are 1750, 1745 and 1718 cm^{-1} respectively. Aldehydes can be easily distinguished from ketones due to the presence of two weak C—H str (asymm. and symm.) absorption bands—one near 2820 cm^{-1} and the other near 2720 cm^{-1}.

Usually, the band at higher wave number is not observed if there is another C—H str due to some other part of the molecule. Ketones exist in equilibrium with their enolic forms. The enolic form can be detected by a broad band in the bonded O—H region and another at a very low C=O stretching frequency. Lower the value of the carbonyl frequency, greater is the enolic content in equilibrium. In case of some electron withdrawing groups which also cause α, β-unsaturation, viz., alkenyl, alkynyl, aryl etc., the conjugative effect dominates over inductive effect and the result is the net decrease in the wave number of carbonyl absorption.

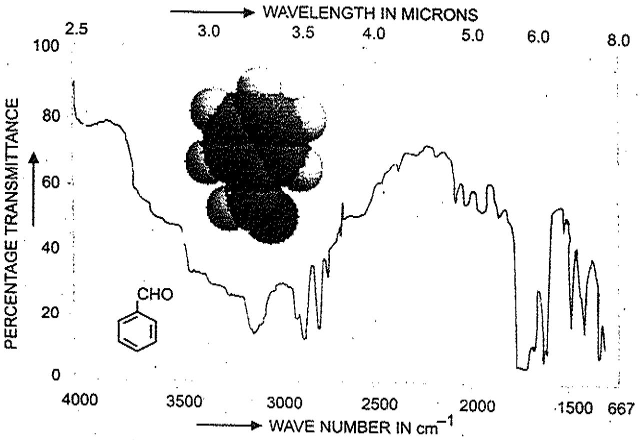
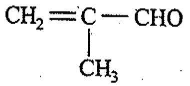


Fig. 3.45. Infra-red spectrum of Benzaldehyde (higher).

EXERCISE. Mark some characteristic absorptions in the Infra-red spectrum of Benzaldehyde.

EXAMPLE. *Compare the νCO stretching absorption in the following compounds:*

CH_3CHO $CH_2{=}CH{-}CHO$



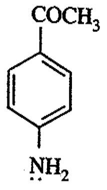
$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CHO$

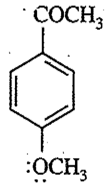
(I) 1745 cm^{-1} (II) 1723 cm^{-1} (III) 1702 cm^{-1}

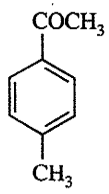
In II, conjugative effect dominates over—I effect and absorption occurs at a low wave number. In III, both conjugative and + I effect (due CH_3 group) operate in the same direction and help in still lowering the wave number of absorption.

In cyclic ketones, νC=O absorption increases as the size of the ring decreases (ring strain increases). Cyclopropanone shows carbonyl absorption at 1855 cm^{-1}. Cyclobutanone at 1788 cm^{-1} and cyclopentanone at 1746 cm^{-1}. Cyclohexanone absorbs at almost the same wave number at which acyclic saturated ketones absorb. A rise in νC=O with decrease in the ring size is due to the changes in the state of hybridisation in small rings. As the ring size decreases, the ring bonds become enriched in *p*-component and C=O bond acquires greater s-character. Hence, force constant for C=O bond increases and also the wave number of absorption rises. With α, β-unsaturation, the said absorption frequency is lowered by about 30 cm^{-1}. Consider the spectra of cyclohexanone and 2-cyclopentenone. Due to α, β-unsaturation in 2-cyclopentenone, the downward shift corresponding to cyclopentenone is to the extent of nearly 30 cm^{-1} and both absorb at nearly the same wave number.

The νC=O absorption for aryl ketones is lower than that in alkyl ketones reaching a minimum value in *p*-N, N-dimethyl amino benzophenone. In aryl alkyl ketone, the +I effect due to alkyl group has an additional effect besides conjugation of C=O with the ring. νC=O absorption for these compounds occur near 1690 cm^{-1}. For ortho and para substituted ketones, inductive as well as conjugative effects play a significant role. In meta substituted compounds, frequency shifts are due to inductive effect only. Consider the νC=O absorption in the following compounds.


(I)
1677 cm^{-1}


(II)
1684 cm^{-1}


(III)
1693 cm^{-1}

In (I) and (II) the lone pair of electrons on nitrogen and oxygen atom are involved in conjugation with the ring. The electron pair on nitrogen atom is more labile and is more readily available for conjugation with the ring. These groups (NH$_2$, —OCH$_3$) facilitate conjugation by the electron release and hence νC = O absorption occurs at a lower wave number. In III, methyl group in the para position causes +I effect and brings down the absorption to occur at 1693 cm^{-1}.

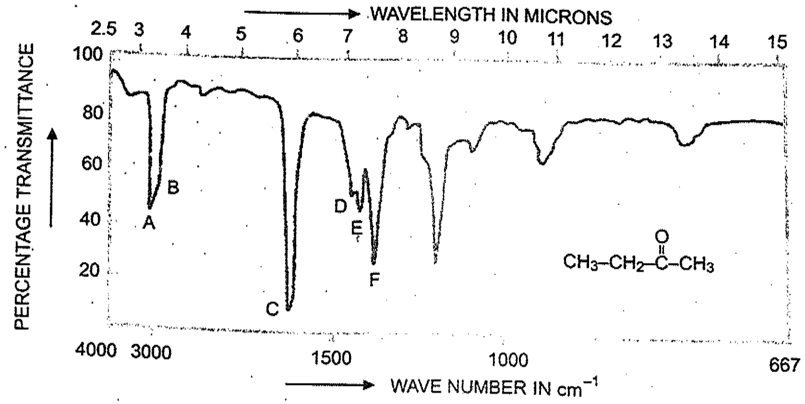


Fig. 3.46. Infra-red spectrum of Ethyl methyl ketone.

Positions of some characteristic absorptions

A = 3002 cm^{-1}	C—H str in methyl/methylene.
B = 2940 cm^{-1}	C—H str
C = 1715 cm^{-1}	C = O str
D = 1450 cm^{-1}	C—H def in methyl/methylene
E = 1406 cm^{-1}	C—H def in —CH$_2$
F = 1360 cm^{-1}	C—H def in —CH$_3$.

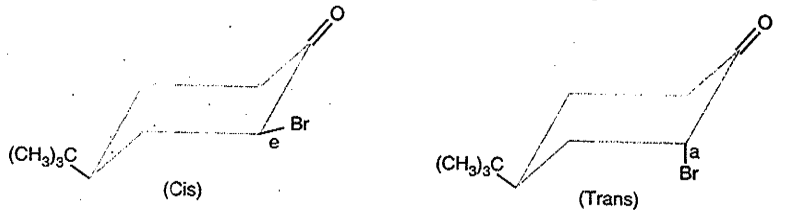
In α-chloro and α-bromo ketones, the νC = O absorption is about 20 cm^{-1} higher than the corresponding non-halogenated compound. The electro-negative halogen atom changes the electron distribution in C = O group by –I effect and field effect.

Field effect is the electrostatic effect which is transmitted through space.

Note the νC = O absorption in the following compounds taken in the liquid phase.

CH_3COCH_3	CH_3COCH_2Cl	$CH_3COCHCl_2$
1715 cm^{-1}	1725 cm^{-1}	1740 cm^{-1}

The spectra of α-halogenated cyclic ketones are particularly interesting in establishing the configuration of the halogen atom. In α-halogeno-cyclohexanone, the equitorial halogen atom is practically eclipsed by the carbonyl group which has a trigonal geometry. If halogen atom is axial, then it must be in the staggered position relative to the carbonyl oxygen atom. In a conformation in which halogen atom is equitorial, the almost parallel dipole of C—X and C = O bonds result in the rise of νC = O absorption by 20 cm^{-1} whereas no shift in the νC = O absorption is caused when halogen is in the axial position. Consider the spectra of cis and trans 2-bromo-4-tert butyl cyclohexanone. The bulky tert butyl group must be in the equitorial position.



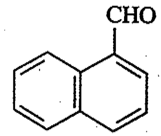
(Cis) (a)

(Trans) (b)

Fig. 3.46 (a). 2-Bromo-4-tert. butyl Cyclohexanone.

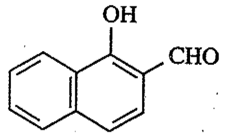
When bromine atom is equitorial, it (form *a*) becomes cis and νC = O absorption is raised by about 20 cm^{-1}. When bromine atom is axial (form *b*), the configuration is trans which does not show any νC = O shift from the normal value.

νC = O 1700 cm^{-1}, lowering is due to conjugation of C=O with the ring.



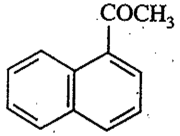
(*i*)

νC = O 1651 cm^{-1}, lowering is due to conjugation as well as intramolecular hydrogen bonding.



(*ii*)

νC = O 1685 cm^{-1}, lowering is due to conjugation of C = O with the ring.

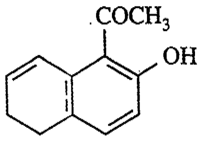


(*iii*)

Field effect is the electrostatic effect which is transmitted through space.

Normal value of νC = C absorption is more for aldehydes as compared to the corresponding ketones.

X is a halogen atom.



(*iv*)

νC = O 1625 cm^{-1}, lowering is due to conjugation as well as intramolecular hydrogen bonding.

In hydroxy aldehydes and ketones, intramolecular hydrogen bonding lowers the νC = O and νO—H absorptions. In saturated hydroxy ketones, the intra-molecular hydrogen bonds give a strong O—H band in the region 3400-3200 cm^{-1}. Note the νCO absorptions in the compound (Fig. 3.47).

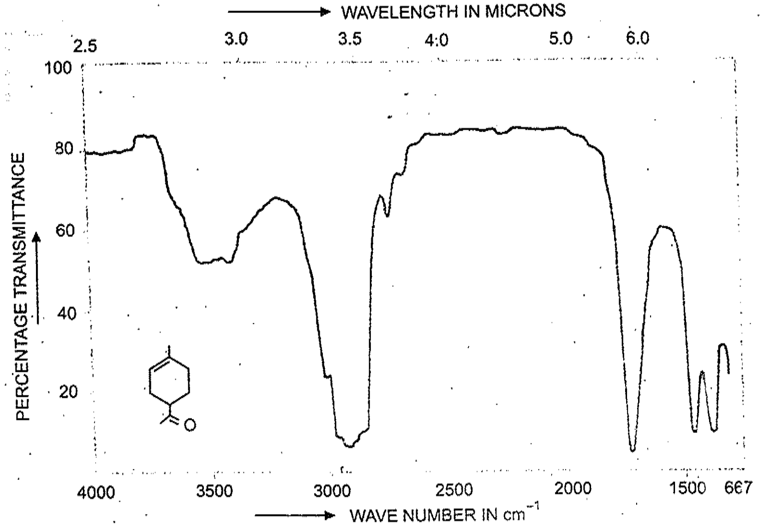
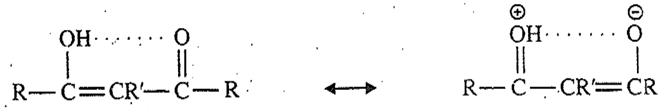


Fig. 3.47. Infra-red spectrum of 1-acetyl-4 methylcyclo-hex 3-ene.

EXERCISE. Mark some characteristic absorptions in the Infra-red spectrum of 1-acetyl-4 methyl cyclohex - 3e.

We know that β-diketones exist as a mixture of ketonic and enolic forms in equilibrium with each other. The enolic form is stabilised by resonance.



For enolic form, νC = O absorption band appears in the region 1640-1580 cm^{-1} which is much lower than that for conjugated ketones. This much lowering is due to the intra-molecular hydrogen bonding stabilised by resonance. Acetyl acetone absorbs in the ketonic form at 1725 cm^{-1} and in the enolic form at 1630 cm^{-1}. Quantitative studies of these forms are possible from the peak intensities.

Quinones are a special case of α, β-unsaturated ketones. For this class of compounds, characteristic frequencies of absorption due to C = O stretching and C = C stretching lie in the region 1695 to 1587 cm^{-1}. *p*-quinones with two carbonyl groups in the same ring absorb in the range 1680-1660 cm^{-1}. Presence of electron repelling groups (+I effect) lowers the frequency of absorption while the presence of electron attracting group (–I effect) increases the force constant and hence raises the wavenumber of absorption.

EXAMPLE 9. *Distinguish between the following two isomers of the molecular formula,* C_3H_6O

(*i*) CH_3CH_2CHO (*ii*) CH_3COCH_3

SOLUTION.

CH_3CH_2CHO

(*i*) νC = O str 1740-1720 cm^{-1},

(*ii*) νC—H str ~2720 cm^{-1} (For CHO)

(*iii*) νC—H str ~3000 cm^{-1}

CH_3COCH_3

(*i*) νC = O str ~ 1715 cm^{-1}

(*ii*) νC—H str 2960-2850 cm^{-1}

PROBLEM P_3–4

Molecular formula—C_3H_6O

(*i*) UV: λ_{max} 292 *nm*, ε_{max} 21.

(*ii*) I.R. (*i*) 2720 cm^{-1} (*w*) (*ii*) 1738 cm^{-1} (*s*)

Determine the structure of the compound.

Table T_3—8. Aldehydes and ketones

Group	*Types of vibration*	*Region in cm^{-1} and intensity*
Saturated aldehydes	C = O str	1740-1720 (*s*)
HCHO	C = O str	1750 (*s*)
CH_3CHO	C = O str	1745 (*s*)
α, β-Unsaturated (aliphatic)	C = O str	1705-1680 (*s*)
Aryl aldehyde	C = O str	1715-1690 (*s*)
All aldehydes	C—H str	(*i*) 2900-2820 (*w*) (*ii*) 2770-2700 (*w*) (*iii*) 1640-1550 (s)
Saturated ketones	C = O str	1725-1700 (*s*)
α, β-Unsaturated ketones	C = O str	1685-1665 (*s*)
Cyclopropanone	C = O str	~ 1855 (*s*)
Cyclobutanone	C = O str	~ 1788 (*s*)
Cyclopentanone	C = O str	~1746 (*s*)
Cyclohexanone	C = O str	1725-1705 (*s*)
α, β-Unsaturated (Five membered)	C = O str	1725-1710 (*s*)
α, β-Unsaturated (Six membered)	C = O str	1680-1665 (*s*)
Aryl ketones	C = O str	1670-1660 (*s*)
Diaryl ketones	C = O str	1700-1680 (*s*)
β-diketones	C = O str	(*i*) ~ 1725 (*s*) ketonic (*ii*) 1640-1580 cm^{-1} (enolic)
p-quinones	C = O str	1680-1660 (*s*)
Hydroxy aldehydes and ketones in which hydrogen bonding is possible	C = O str	~ 1630 (*s*)

For aldehydes, two C—H str bands may be noted; especially the one which appears at a lower wave number.

* νO—H absorption gives a broad band near 3400-3200 cm^{-1}.

** νC = O absorption is sufficiently lower since intramolecular hydrogen bonded structure is stabilised by resonance.

Note the various regions of absorptions for C—H, ≡ C—H, = C—H, N—H, and O—H stretching frequencies in Fig. 3.48.

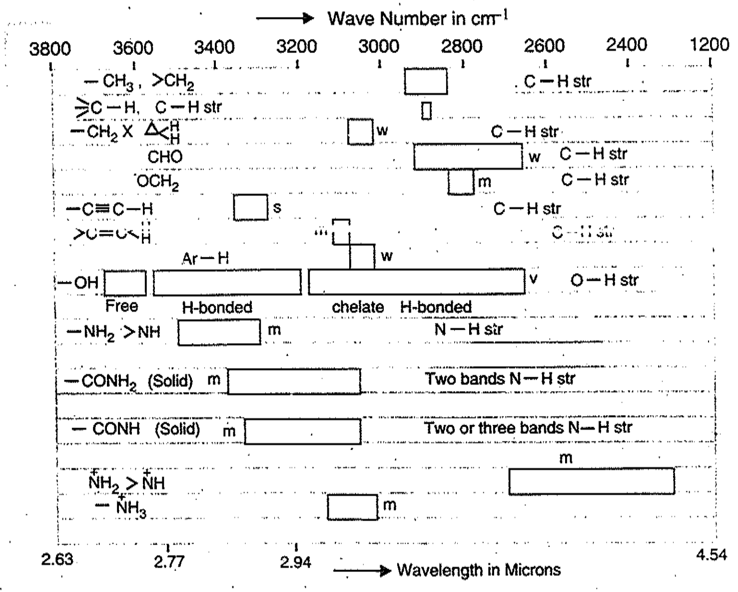


Fig. 3.48. Regions of absorptions for single bond hydrogen stretching frequencies.

Note the various regions of absorptions for C=C, C≡C, C≡N, C=C stretching frequencies and also N—H bending frequencies in Fig. 3.49.

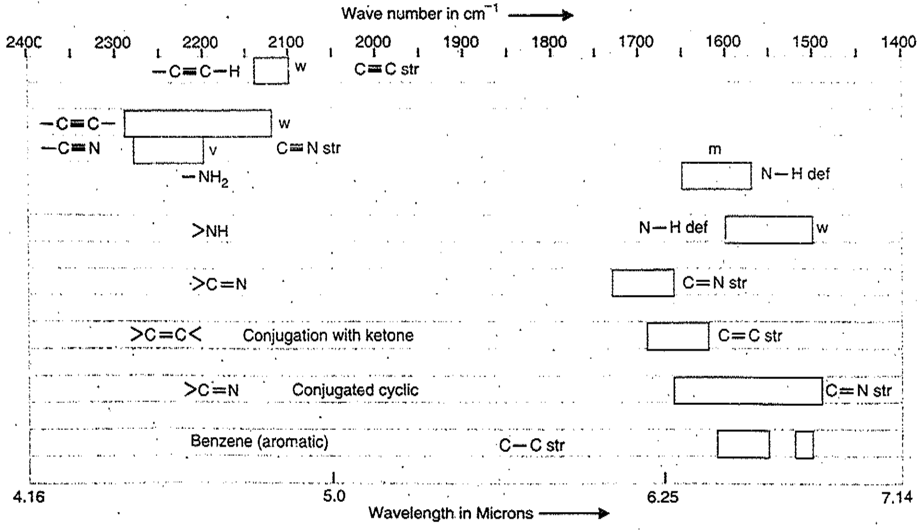


Fig. 3.49. Regions of absorption for (*i*) stretching frequencies of double and triple bonds and (*ii*) N—H bending frequencies.

Write important regions of absorption for:

(*i*) ≡ C—H str for acetylenic compounds

(*ii*) C—H str in aldehydes

(*iii*) O—H str for free and bonded alcohols

(*iv*) O—H str for carboxylic acids

(*v*) N—H str for primary and secondary amines/amides

Write important regions of absorption for.

(*i*) C=C str when the double bond is in conjugation with the carbonyl group.

(*ii*) C=C str in aromatic compounds,

(*iii*) C≡C str in acetylenes,

(*iv*) C≡N str in nitriles,

(*v*) N—H def (bending) in case of primary and secondary amines and amides.

Note the various regions of absorption for C = O stretching frequencies in Fig. 3.50.

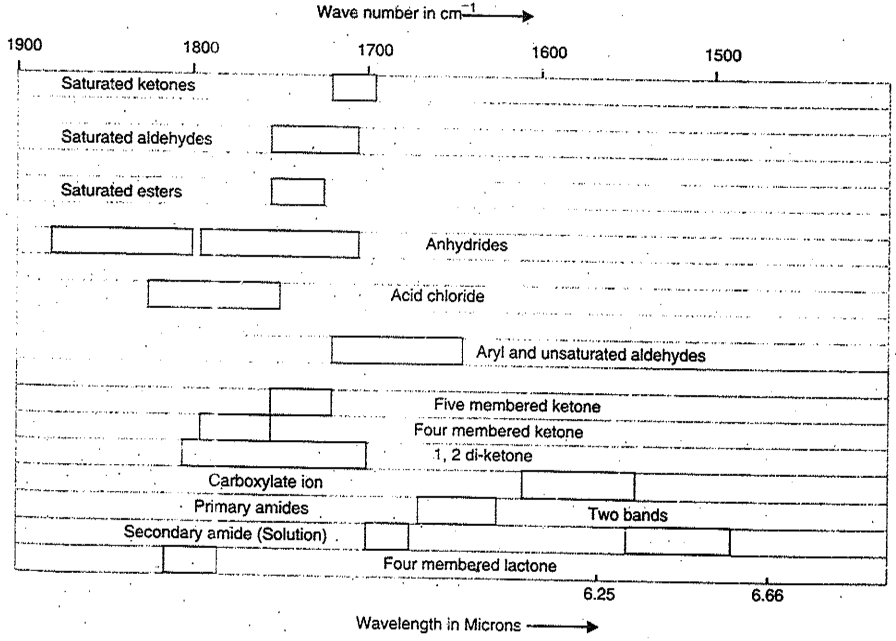


Fig. 3.50. Regions of absorption for the stretching frequencies of carbonyl group.

Write important regions of absorption for:

(*i*) C = O str. in anhydrides (two bands are observed; one is usually intense and the other is medium).

(*ii*) C = O str in esters (the presence of an ester is confirmed by C—O str in the finger print region).

(*iii*) C = O str in aldehydes (saturated and unsaturated). The presence is confirmed by C—H str at about 2720 cm^{-1}.

(*iv*) C = O str in amides (primary and secondary). The presence is confirmed if there is absorption in the N—H str region.

Infra-red spectra of some more carbonyl compounds

(*i*) **Butanal:** The Infra-red spectrum of Butanal is given below:

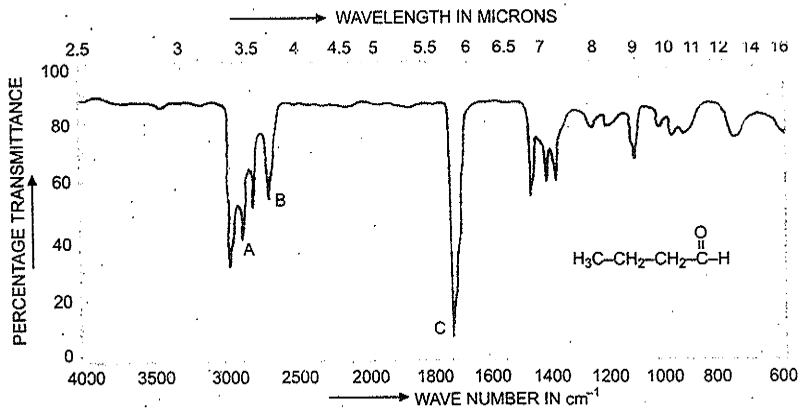


Fig. 3.51. Infra-red spectrum of Butanal.

Positions of some charactristic absorptions.

A = 2820 cm^{-1} C — H str (in methyl)
B = 2715 cm^{-1} C — H str (characteristic of aldehydes)
C = 1720 cm^{-1} C = O str (due to aldehydes)

(*ii*) **Hexan-2-one:** The Infra-red spectrum of Hexan-2-one is given below:

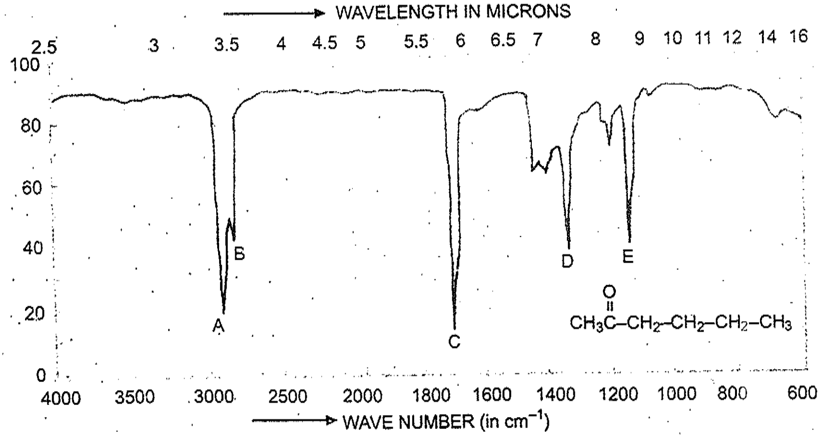


Fig. 3.52. Infra-red spectrum of Hexan-2-one.

Mark some important absorption positions characteristic of Hexan-2-one.

3.11 F. Esters And Lactones

An ester can be recognised if there are two strong bands owing to C = O str. and C—O str in an Infra-red spectrum. Esters show the νC = O absorption at 1750-1735 cm^{-1}. The position of νC = O absorption is sensitive to ring and unsaturation due to conjugation. The presence of one more oxygen atom in esters R—COOR′ compared to ketones RCOR′ raises the wave number of absorption due to –I effect. The carbonyl absorption for aryl esters or α, β-unsaturated esters is shifted to lower wave number. The carbonyl absorption occurs at higher wave number if the carbonyl group of an ester is present in the five membered ring.

The νC = O absorption for lactone is raised to higher wave number with the decrease in the size of the ring. β-lactones show a strong band near 1820 cm^{-1}. γ and δ-lactones absorb at comparatively lower wave numbers. α, β-unsaturation in lactones brings down the νC = O absorption. β-keto esters exist as an equilibrium mixture of keto and enol forms. The ketonic form shows C = O stretching at 1724 cm^{-1} while absorption band for hydrogen bonded C = O group (stabilised by resonance) occurs at 1650 cm^{-1}.

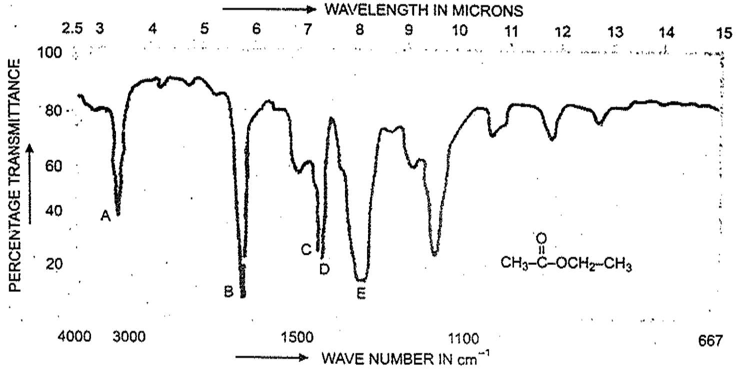


Fig. 3.53. Infra-red spectrum of Ethyl acetate.

Positions of some characteristic absorptions

A = 3002 cm^{-1}; C—H str in methyl/methylene.
B = 1742 cm^{-1}; C = O str (in esters)
C and D 1450 and 1370 cm^{-1}; C—H def
E = 1240 cm^{-1}; C—O str in esters.

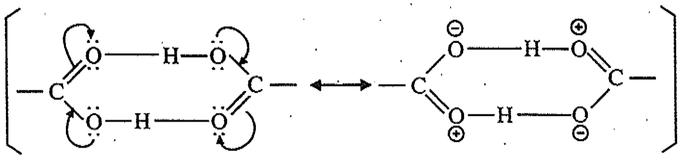
Table T_3—9.

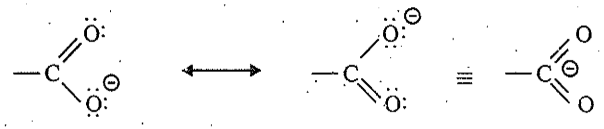
Group	*Type of vibration*	*Region in cm^{-1} and intensity*
Saturated Esters	C = O str	1750-1735 (*s*)
α, β-Unsaturated esters	C = O str	1730-1715 (*s*)
Aryl esters	C = O str	1730-1715 (*s*)
β-lactones	C = O str	~ 1820 (*s*)
γ-lactones	C = O str	1780-1760 (*s*)
δ-lactones	C = O str	1750-1735 (*s*)
α, β-Unsaturated γ-lactones	C = O str	1760-1740 (*s*)
α, β-Unsaturated δ-lactones	C = O str	1730-1715 (*s*)
β-Ketonic esters	C = O str	(*i*) 1725 (*s*) ketonic (*ii*) ~ 1650 (*s*) enolic

Usually all classes of esters show two strong bands in the region 1340-1050 due to C—O stretching. With α, β-unsaturation, the wave number of absorption shifts downwards by 20 cm^{-1} compared to saturated lactone.

3.11 G Carboxylic Acids

Carboxylic group (—COOH) is the easiest functional group to detect by Infra-red spectroscopy since this group can be considered as being formed from C = O and O—H units. The absorption of O—H stretching appears as a broad band near 3000-2500 cm^{-1}. The νC = O stretching absorption in aliphatic acids occurs at 1725-1700 cm^{-1}. An acid (—COOH) is formed from an aldehyde (—CHO) on replacing a hydrogen atom by an OH group. Due to the –I effect of OH group, νC = O absorption for acids should occur at higher wave number as compared to aldehydes. But actually it is not so. νC = O absorption for acids is lowered due to internal conjugation (lone pair on oxygen in conjugation with C = O) working in opposite direction, α, β-unsaturated acids or aryl acids show carbonyl absorption at a lower wave number. Some of the acids *viz.*, acetic acid, benzoic acid, exist as dimers due to hydrogen bonding. Formation of bridge lowers the force constants and thus, νC = O and νO—H absorption occur at lower wave numbers. As the hydrogen bonded structure is stabilised by resonance, the O—H stretching occurs as a broad band in the region 3000-2500 cm^{-1}. If the acid is converted into its soluble salt, then in the carboxylate anion formed, both the C = O bonds become exactly equivalent as shown below:





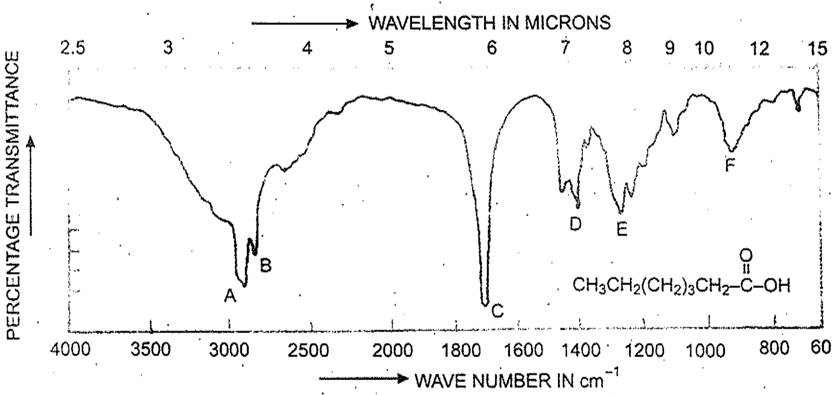
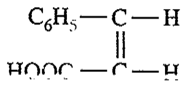


Fig. 3.54. Infra-red spectrum of Heptanoic acid. *Courtesy:* Sadtler Research Laboratories. Philadalphia.

Positions of some characterstic absorptions

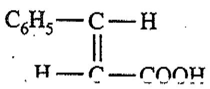
A = 3300 – 2500 cm^{-1}	Broad O—H str
B = 2950 – 2850 cm^{-1}	C—H str (superimposed upon O—H str)
C = 1715 cm^{-1}	C = O str. Normal dimeric carboxylic acid
D = 1408 cm^{-1}	C—O—H in-plane band
E = 1280 cm^{-1}	C—O str
F = 930 cm^{-1}	O–H def (out-of plane)

As the internal conjugation is prevalent in carboxylate anion, the force constant for C = O is less in it as compared to that in case of an acid. Hence νC = O absorption occurs at a higher wave-number for an acid as compared to that in carboxylate anion. In cis-trans isomers of an acid, small differences in νC = O absorptions are observed. But in case of cis/trans cinnamic acid, Maleic acid-Fumaric acid etc., νC = O absorption differences are larger.



$$\begin{array}{c} C_6H_5—C—H \\ \| \\ HOOC—C—H \end{array}$$

Cis-cinnamic acid
1705 cm^{-1}

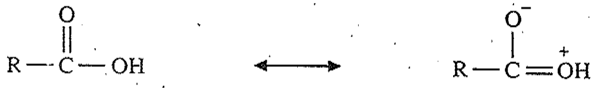


$$\begin{array}{c} C_6H_5—C—H \\ \| \\ H—C—COOH \end{array}$$

Trans-cinnamic acid
1680 cm^{-1}

Cis-cinnamic acid absorbs at a higher wave number. It is partially explained due to the steric effect caused by the bulky groups on the same side of the double bond. Due to repulsive interactions, the C = O part of —COOH group goes out of the plane of the double bond. Thus, conjugation diminishes and hence νC = O absorption occurs at a higher wave number. Similar explanation can be given for maleic acid (cis) which absorbs at 1705 cm^{-1} as compared to fumaric acid (trans) at 1680 cm^{-1}.

Note. νC = O absorptions of acids existing as dimers are very sensitive to dilution. In very dilute solutions, the absorption caused by νO—H stretching is observed near 3570 cm^{-1} while that from the dimeric form appears in the region 3000-2500 cm^{-1}. This broad band also appears for the acids which do not exist as dimers. It is explained by writing the resonating structures of the acid.



$$\underset{(i)}{R—\overset{\overset{\displaystyle O}{\|}}{C}—OH} \longleftrightarrow \underset{(ii)}{R—\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{O}H}$$

The +ve charge on the oxygen atom reduces the bond order in O—H group and hence absorption occurs at a lower wave number.

Infra-red spectrum of Propanoic acid is given below:

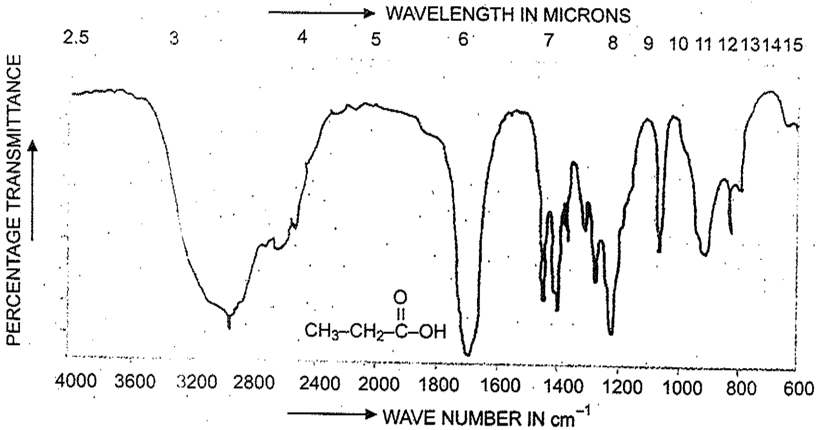


Fig. 3.55. Infra-red spectrum of Propanoic acid.

Exercise : Mark some important characteristic absorption positions in cm^{-1} in the above spectrum.

3.11 H Acid Halides

In acid halides (RCOX), the presence of electro-negative atom displays –I effect which increases the force constant of the carbonyl group and hence its wave number of absorption increases. In halogenated acids, –I effect is more pronounced when halogen is present in the α-position. When halogen atom is in a more remote position, the νC = O absorption returns to normal.

$BrCH_2COOH$	νC = O str	1730 cm^{-1} (*s*)
$ClCH_2COOH$	νC = O str	1736 cm^{-1} (*s*)
$Cl_2CHCOOH$	νC = O str	1751 cm^{-1} (*s*)
F_3CCOOH	νC = O str	1776 cm^{-1} (*s*)
$BrCH_2CH_2CH_2COOH$	νC = O str	1725 cm^{-1} (*s*)

(Br is in more remote position)

Infra-red spectum of Benzoyl Chloride is shown below:

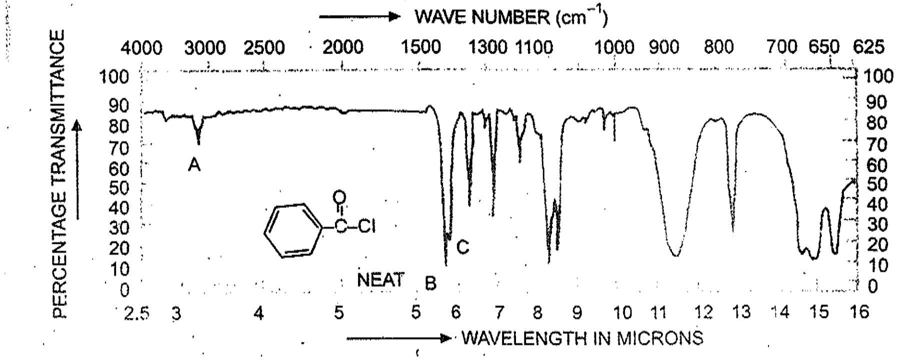


Fig. 3.56. Infra-red spectrum of Benzoyl chloride. *Courtesy* : Sadtler Research Laboratories, Philadalphia.

Positions of some characteristic absorptions

A = 3080 cm^{-1}	C—H str aromatic
B = 1790 cm^{-1}	C = O str (raised due to electronegative Cl-atom)
C = 1745 cm^{-1}	Fermi resonance band (C = O str and overtone of 875 cm^{-1} band)

In parahalobenzoic acid, –I and +E effects cancel each other (work in opposite directions) and thus, frequency of absorption returns to normal. For *m*-halobenzoic acid, the νC = O is higher than that for benzoic acid due to the absence of conjugation.

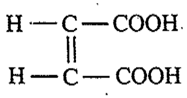
Table T_3—10. Carboxylic Acids and Acid Halides

Group	*Type of vibration*	*Region in cm^{-1} andintensity*
Saturated aliphatic acids	C = O str	1725-1700 (*s*)
α, β-unsaturated acids	C = O str	1715-1694 (*s*)
Carboxylate anion (in soluble salts)	C = O str	1610-1550 (*s*)
Aryl carboxylic acids	C = O str	1700-1680 (*s*)
Carboxylic acids	O—H str (bonded)	3000-2500 (*w, b*) most characteristic of an acid
Acyl fluorides	C = O str	~ 1850 (*s*)
Acyl chlorides	C = O str	~ 1795 (*s*)
Acyl bromides	C = O str	~ 1790 (*s*)
RCOCl (Vapour state)	C = O str	~ 1821 (*s*)
RCOF (Vapour state)	C = O str	~ 1872 (*s*)
$F_3.C.COR$	C = O str	~ 1901 (*s*)
COF_2	C = O str	~ 1928 (*s*)

Note. The frequency of absorption is sensitive to both –I effect and the mass effect of the halogen atom.

EXAMPLE 10. *How will you distinguish between Maleic acid and Fumeric acid?*

SOLUTION.



$$\begin{matrix} H-C-COOH \\ \| \\ H-C-COOH \end{matrix}$$

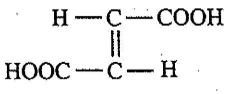
(Maleic acid)

(*i*) νC = O 1702 cm^{-1} (*s*)

The absorption at higher wave number is due to diminished conjugation.

(*ii*) νC—H str ~3000 cm^{-1}

(*iii*) νC = C str 1650 cm^{-1}



$$\begin{matrix} H-C-COOH \\ \| \\ HOOC-C-H \end{matrix}$$

(Fumeric acid)

(*i*) νC = O 1680 cm^{-1} (*s*)

(*ii*) νC—H str ~3000 cm^{-1}

(*iii*) νC = C str 1600 cm^{-1}

3.11 I Acid Anhydrides

An acid anhydride can be easily detected due to the appearance of two frequency bands in the region 1850-1750 cm^{-1}. The doublet appears because of the coupled vibrations of two C = C groups. The high frequency band is assigned to symmetrical vibrations and lower frequency band to asymmetric vibrations. The splitting of the band is due to **Fermi Resonance**. In acyclic anhydrides of saturated carboxylic acids, the two bands appear at (*i*) 1850-1800 cm^{-1} and (*ii*) 1790-1740 cm^{-1}. The absorption at higher wave number is more intense. In the α, β-unsaturated anhydrides, the higher absorption band shifts downward by 20-40 cm^{-1} while the second band due to asymmetric vibrations maintains its position. Symmetric vibrations towards lower frequencies take place in aromatic anhydrides. In cyclic anhydrides, both the bands shift towards higher frequencies.

Positions of some characteristic absorptions

A = 2980 cm^{-1}	C—H str in methyl
B = 2890 cm^{-1}	C—H str
C and D = 1820 and 1748 cm^{-1}	C = O str in acyclic anhydrides
E, F, G = 1460, 1406, 1380 cm^{-1}	C—H def in methyl
H = 1035 cm^{-1}	C—O str in acyclic anhydrides

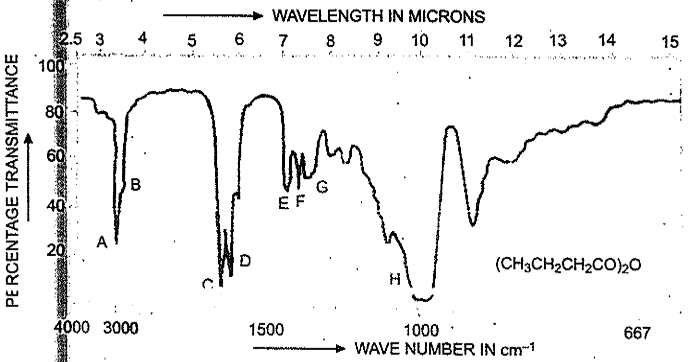


Fig. 3.57. Infra-red spectrum of n-Butyric anhydride.

Table T_3—11. Acid Anhydrides

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
Saturated (acyclic compounds)	C = O str	1850-1800 (*s*) 1790-1740 (*s*)
Aryl or α, β-unsaturated (acyclic)	C = O str	1830-1780 (s) 1770-1725 (*s*)
Five membered ring (cyclic)	C = O str	1870-1820 (*s*) 1800-1750 (*s*)
Five membered α, β unsaturated	C = O str	1850-1800 (*s*) 1820-1780 (*s*)

Note 1. Acid anhydrides are always characterised by two high frequency bands usually separated by about 60 cm^{-1}.

Note 2. α, β-unsaturation lowers the νC = O absorption by about 20 cm^{-1}.

Note 3. All classes of anhydrides show two bands in the region 1300-1050 cm^{-1} due to C—O stretching.

The Infra-red spectrum of Benzoic anhydride is given below:

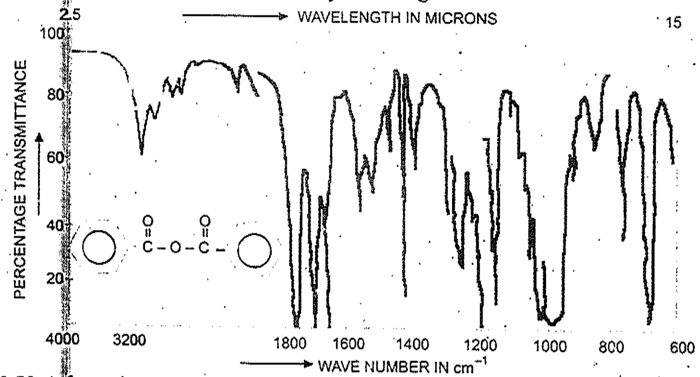


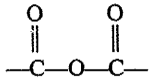
Fig. 3.58. Infra-red spectrum of benzoic anhydride *Countesy* : Sadtler Research laboratories.

Exercise : Mark some important characteristic absorption positions in the above spectrum.

The high frequency band is more intense in acyclic anhydride but in cyclic anhydrides, low frequency band is more intense.

Hint :

(*i*) Permanent absorptions (C = O str) due to symmetric and asymmetric vibrations. The higher frequency band is more intense.

(*ii*) Strong absorption between 1200-1000 cm^{-1} due to  $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$ unit in anhydrides.

(*iii*) The moderate intensity band and strong absorption band show asymmetric and symmetric C—H in plane bending vibrations of methyl group.

3.11 J Amides

The presence of nitrogen atom has –I effect but a lone pair of electrons present on nitrogen atom is involved in conjugation which tend to decrease C = O force constant. This effect is more pronounced in amides due to the greater mobility of electron pair on nitrogen atom (less electronegative) and hence, its greater participation in conjugation. The νC = O absorption in amides takes place at lower wave number. In addition to the νC = O absorption, amides can be recognised by N—H stretching and N—H def bands. Primary amides in dilute solutions show two bands (N—H str) near 3400 cm^{-1} and 3500 cm^{-1}. These two bands arise due to symmetrical and asymmetrical N—H stretching. Secondary amides give only one band while tertiary amides do not show any band in the region 3500-3100 cm^{-1}. In tertiary amides which do not contain N—H group, νC = O absorption does not show any marked shift due to dilution. Since hydrogen bonding is absent in tertiary amides, its spectra in the solid and in solution form are almost the same.

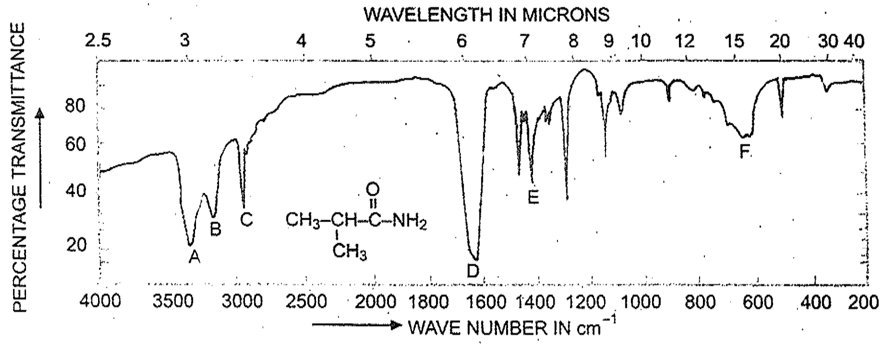


Fig. 3.59. Infra-red spectrum of 2-Methyl propanamide.
Courtesy : Sadtler Research Laboratories – Philadalphia.

Positions of some characteristic absorptions

A = 3350 cm^{-1}	N—H str coupled, primary amide, hydrogen bonded—asymmetric
B = 3170 cm^{-1}	N—H str symmetric
C = 2960 cm^{-1}	C—H str aliphatic
D = 1640 cm^{-1}	C = O str of amide
E = 1425 cm^{-1}	C—N str
F = 700-600 cm^{-1}	N—H def (out of plane band)

3.11 K Lactams

Cyclic amides of the amino acids are called Lactams. The νC = O absorptions in lactams depend upon the ring size. The νC = O absorption is higher in γ-lactams due to the greater ring strain as compared to that in δ-lactams. The value of νC = O absorption is raised further in β-lactams. β-lactams in dilute solution absorb at 1760-1730 cm^{-1} whereas γ- and δ-lactams absorb at ~ 1700 cm^{-1} and ~1680 cm^{-1} respectively.

Note. The values of absorption for lactams are measured in dilute solution as these are shifted with the change in concentration.

β-lactams have been extensively studied in connection with the structure of **Penicillin**. In penicillin, the νC = O absorption occurs at 1760 cm^{-1}.

In cyclic imides the νC = O absorptions are very sensitive to ring size and α, β-unsaturation. The νC = O absorption is raised with the decrease in the size of the ring while, α, β-unsaturation brings down the wave number of absorption.

Table T_3—12.

Group	*Type ofvibrations*	*Region in cm^{-1} and intensity*
Primary amides (dilute solution)	C = O str N—H str N—H str (hydrogen bonded) N—H def	~1690 (*s*) ~3500 (*m*) ~3400 (*m*) ~3350 (*m*) ~3180 (*m*) 1620-1590 (*s*)
Secondary amides (dilute solution)	C = O str N—H str N—H str (hydrogen bonded) N—H def	~1700-1670 (*s*) ~3425 (*m*) 3330-3140 (*m*) 1550-1510 (*s*)
Tertiary amides	C = O str	1670-1630 (*s*)
β-lactams	C = O str	1760-1730 (*s*)
γ-lactams	C = O str	~ 1700 (*s*)
δ-lactams	C = O str	~ 1680 (*s*)
Imides* (acyclic)	C = O str	~ 1710 (*s*) ~ 1700 (*s*)
Imides (Five membered cyclic)	C = O str	~ 1700 (*s*) ~ 1770 (*s*)
Imides (Six membered cyclic)	C = O str	~ 1700 (*s*) ~ 1710 (*s*)

Note 1. **Important :** If the spectra of amides are scanned with concentrated solutions or with the solid samples, νC = O absorption is lowered by about 40 cm^{-1} from the normal values.

Note 2. The respective value of νC = O absorptions are raised, if the lactam is fused with another ring. The spectra for lactams are scanned in dilute solutions.

The Infra-red spectrum of Benzamide is given below:

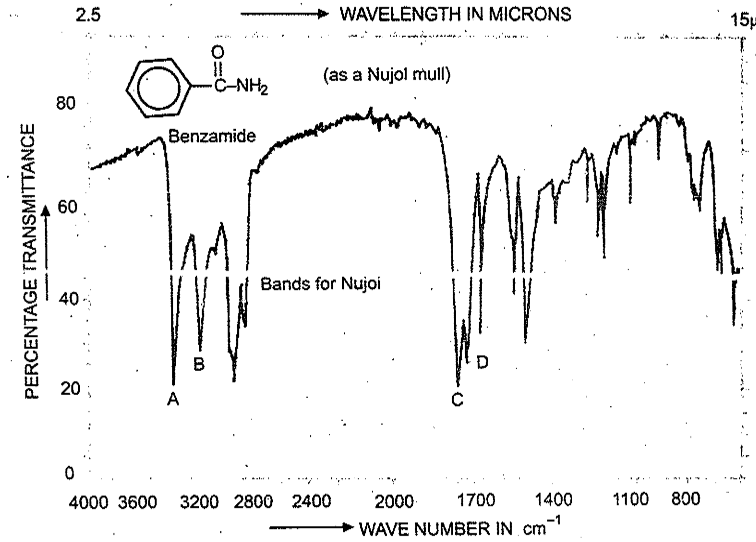


Fig. 3.60. Infra-red spectrum of Benzamide *Courtesy* : Sadtler Research Laboratories.

Positions of some characteristic absorptions

A = 3370 cm^{-1}	N—H str (due to asymmetric stretching vibrations)
B = 3170 cm^{-1}	N—H str (due to symmetric stretching)
C = 1660 cm^{-1}	C = O (*s*) (lower value due to conjugation with one pair on nitrogen atom)
D = 1631 cm^{-1}	N—H bending (in amide)

PROBLEM : The Infra-red spectrum of Butanamide is given below. Mark some characteristic absorption positions in it in terms of wave number (cm^{-1})

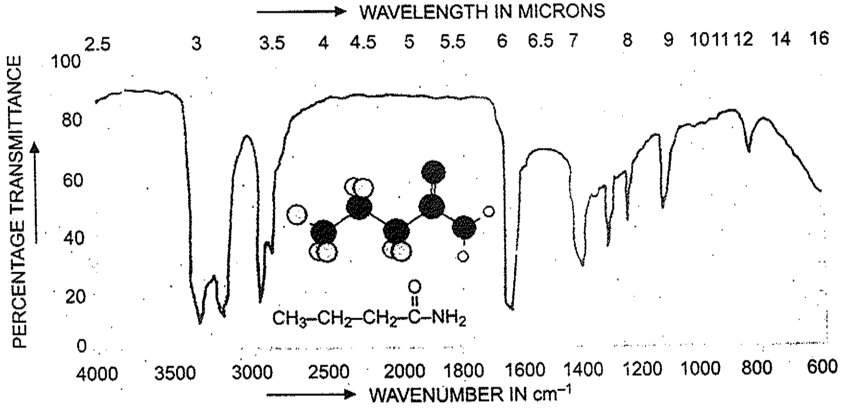


Fig. 3.61. Infra-red spectrum of Butanamide.

---

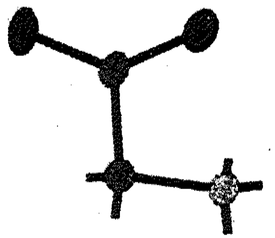
* Imides are generally characterised by two strong bands.

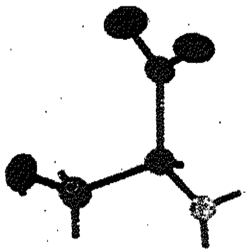
3.11 L Amino Acids

All amino acids exist as **Zwitter ions** at the isoelectric points due to the internal neutralisation of the acidic and the basic group in the molecule.

$$NH_2CH_2COOH \rightleftharpoons \overset{+}{N}H_3CH_2COO^-$$

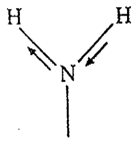
Due to the insolubility of amino acids in common solvents, Infra-red spectrum of amino acids are usually taken in the solid state. In the aqueous solution or in the solid state, its presence can be detected by the absorption of $\overset{+}{N}H_3$ and COO^- groups. Amino acids in the form of Zwitter ions do not show N—H stretching at 3200 cm^{-1} but show a broad band between 3130 cm^{-1} and 3030 cm^{-1} assigned to asymmetric stretching of $\overset{+}{N}H_3$ group. Absorption depends upon the structure of amino acids. Hydrochlorides of amino acids containing $\overset{+}{N}H_3$ group absorb between 3145 and 3050 cm^{-1}. In Zwitter ions, two vibrational modes of the carboxylate ion are readily identified between 1600-1410 cm^{-1}. The asymmetric vibrational band at 1600-1560 cm^{-1} is broad and strong. In hydrochlorides of amino acids, the $\nu C = O$ absorptions are shifted to higher frequencies. In the hydrochloride of α-amino acid, C = O stretching occurs at 1754-1724 cm^{-1}. This higher frequency absorption is due to the –I effect of $\overset{+}{N}H_3$ group. When $\overset{+}{N}H_3$ group is present in the more remote position, *e.g.*, in δ-amino valeric acid, $\nu C = O$ stretching returns to 1710 cm^{-1}. N—H deformation bands occur near 1600 cm^{-1}.



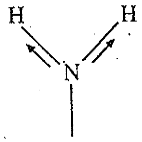


3.11 M Amines

Amines are the alkyl derivatives of ammonia. These can be recognised by absorption due to N—H str in the region 3500-3300 cm^{-1}. The position of absorption depends upon the degree of hydrogen bonding. Primary amines show two sharp bands; secondary amines give only one band while tertiary amines do not absorb in the said N—H str region. N—H and O—H groups have some common properties and their absorptions due to these groups are superimposed making their identification difficult. Since nitrogen atom is less electronegative than oxygen atom, the N—H...N hydrogen bonds are weaker as compared to O—H...O bonds and hence frequency shifts due to hydrogen bonding in amines are smaller. νN—H absorptions occur at lower frequencies compared to νO—H frequencies. The dilute solution of primary amine in an inert solvent give two sharp bands due to asymmetric and symmetric stretching vibrations between 3500-3300 cm^{-1}.



Asymmetric
(High Frequency)



Symmetric
(Low Frequency)

The Infrared spectrum of aniline is shown below:

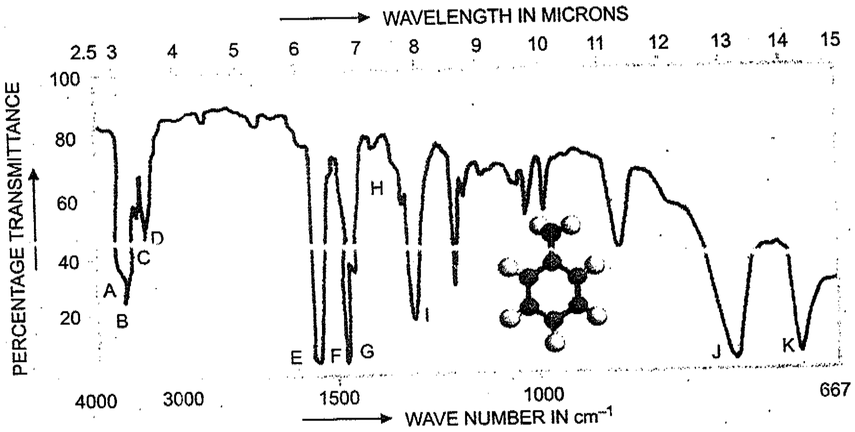


Fig. 3.62. Infra-red spectrum of Aniline.

Positions of some characteristic absorptions

A and B 3450 and 3390 cm^{-1};	N–H str in primary amines
C 3226 cm^{-1};	N—H str (hydrogen bonded).
D 3030 cm^{-1};	=C—H str in olefins/aromatics.
E, F and G 1620, ~1602, 1499 cm^{-1};	C=C str in aromatic nuclei.
H and I 1306, 1275 cm^{-1};	C—N str in primary aromatic amines.
J and K 754 and 696 cm^{-1};	characteristic of monosubstituted benzene.

νN—H stretching absorptions for aromatic amines are comparatively higher than those of aliphatic amines. This behaviour is different from other groups conjugated with the ring. For aromatic amines, lower νN—H absorption values are expected due to —I and +E effects. In phenols, similar electronic effects (—I and +E) produce a decrease in the force constant and thus, phenols absorb at a lower frequency as compared to alcohols but it is not so in amines since electronic effect is shielded by hybridisation effect. In aliphatic amines, the nitrogen atom has pyramidal configuration (almost sp^3) and force constant is influenced by the adjacent atoms or groups in the same way as in alcohols. In aromatic amines, the nitrogen atom is partially rehybridised towards sp^2 due to conjugation. This increases the *s*-character in N—H bond and thus, due to the formation of a stronger bond, the $\nu C = O$ absorption rises.

Aliphatic amines are more sensitive to hydrogen bonding than aromatic amines since they are stronger bases. The νN—H absorption is usually broad unless spectrum is scanned in dilute solutions. It has been noted that in aliphatic and aromatic amines, the νNH_2 symmetric absorption band is more intense than the asymmetric band. The N—H stretching band depends upon the state of the amines. Samples in the solid form show N—H stretching at lower wave number due to greater degree of hydrogen bonding. In amines, the shift due to hydrogen bonding does not exceed 100 cm^{-1}. The N—H bending vibration for primary amines occur at higher wave number as compared to secondary amines. The N—H def, vibrations for amino salts appear as strong bands at 1600—1575 cm^{-1} and also near 1500 cm^{-1}. The C—N vibrations for aliphatic amines appears as weak bands at ~1410 cm^{-1} and also at 1220–1020 cm^{-1}.

Table T$_3$—13. Amines and Amino Acids

Group	Type of vibration	Region in cm^{-1} and intensity
Amines		
Primary	N—H str (symm. and asym)	3500—3300 (*m*)
Secondary	N—H str	3500—3300 (*m*) (For indole and pyrrole, it is sharp)
Amino acids		
$\overset{+}{(NH_3)}$	N—H str	3130–3030 (*m*)
$\overset{+}{>NH_2}$	N—H def	~ 1600 (*s*)
$\overset{+}{>NH_2}$	N—H str	2700–2250 (*m*)

The Infra-red spectrum of 1-propanamine is shown below:

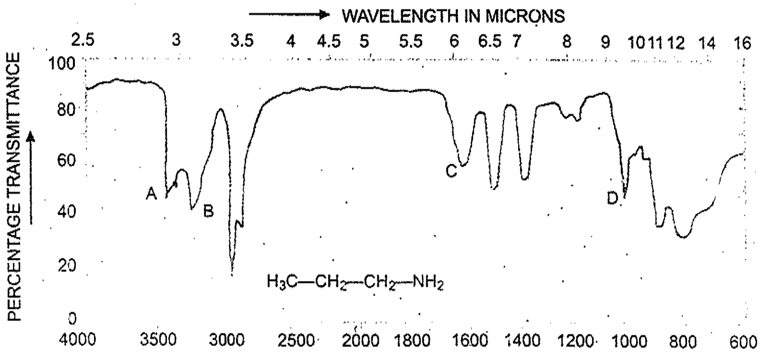


Fig. 3.63. Infra-red spectrum of 1-Propanamine.

Positions of some characteristic absorptions.

A = 3400 cm^{-1};	N—H str (in amines)
B = 3300 cm^{-1};	N—H str
C = 1590 cm^{-1};	N—H bending
D = 1070 cm^{-1};	C—N stretching.

PROBLEM : The Infra-red spectrum of diethylamine is given below. Mark some characteristic absorptions positions in it in terms of wave number.

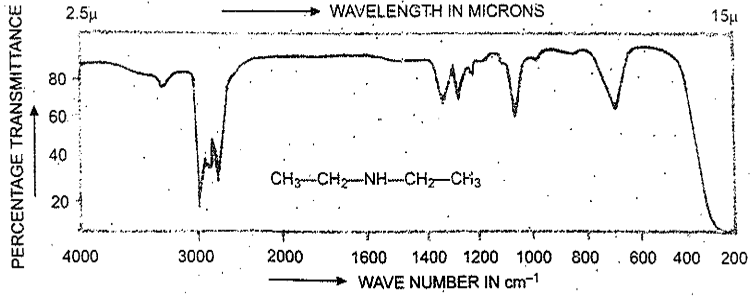


Fig. 3.64. infra-red spectrum of Diethylamine.

EXERCISE : The Infra-red spectrum of *p*-toluidine is given below. Mark some important characteristic absorption positions in it in terms of wave number.

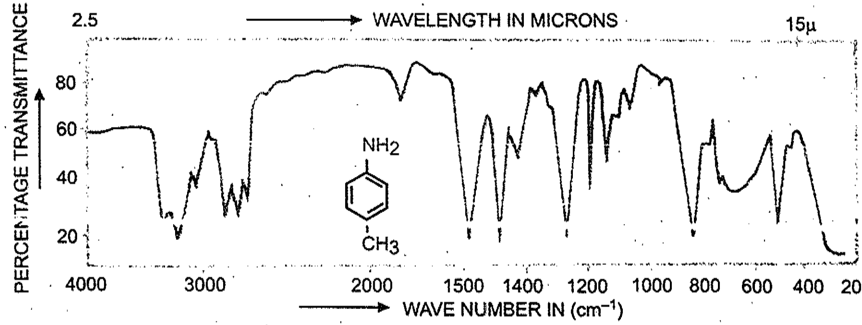


Fig. 3.65. Infra-red spectrum of *p*-Toluidine.

3.11 N Anilides (R-NHCOR′)

Anilides (RNHCOR′) are the acyl derivatives of amines where R and R′ may be alkyls or aryl or both. . In anilides, multiple bands of medium to weak intensity at 3300-3100 cm^{-1} indicate N—H stretching. Absorption near 3060 cm^{-1} indicate C—H stretching. The bands at 2980 and near 2800 cm^{-1} represent asymmetric and symmetric stretching of methyl group. A strong frequency band also appears due to C = O str at relatively lower wave number as lone pair on nitrogen atom is in conjugation with the carbonyl group. Some bending vibrations also appear near 700-750 cm^{-1} in case of aromatic compounds.

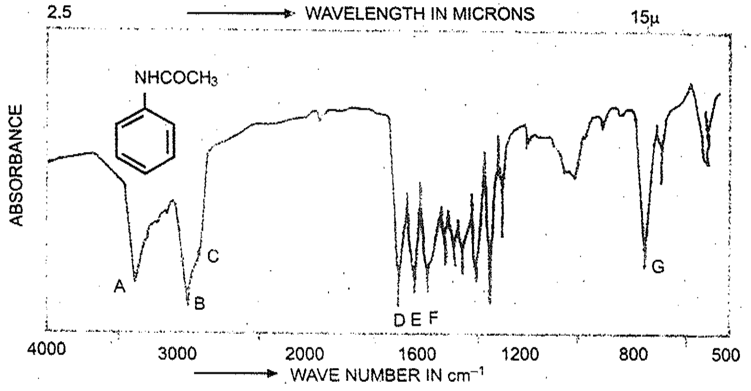


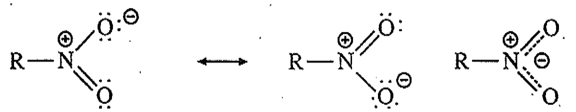
Fig. 3.66. Infra-red spectrum of Acetanilide.

Positions of some characteristic absorptions.

A = ~3300 cm^{-1}	N—H stretching
B = 3060 cm^{-1}	C—H stretching
C = 2980 cm^{-1}	C—H stretching (due to methyl group)
D = 1670 cm^{-1}	C = O str (lowering due to conjugation with lone pair on N-atom)
E, F = 1600, 1500 cm^{-1}	C—C str (due to aromatic ring)
G = 700 cm^{-1}	C—C bending (out of plane vibration).

3.11 O (a) Nitro and Nitrite Compounds

(*a*) **Nitro Compounds :** The electron diffraction method and X-ray analysis have shown that the two oxygen atoms are equidistant from the nitrogen atom (1.22 Å) and also π electrons are equally distributed between the two N—O bonds by isovalent conjugation. The uniform p electron distribution in the nitro group can be expressed as follows:



The vibrational behaviour of the nitro group also supports this structure. The presence of nitro group in a compound is characterised by the presence of two strong bands in its Infra-red spectrum which arise from the symmetrical and asymmetrical stretching modes which occur in the region (*i*) 1620–1535 cm^{-1} and (*ii*) 1375–1275 cm^{-1}. Bands arising from deformation modes are difficult to distinguish from other bands occurring in the low frequency region. Primary derivatives ($RCH_2—NO_2$) absorb at higher frequency as compared to secondary (R_2CHNO_2). Tertiary nitro compounds ($R_3C.NO_2$) absorb at still lower frequency.

Aromatic compounds show two strong bands (*i*) 1570–1500 cm^{-1} and (*ii*) 1370–1300 cm^{-1}. Nitrites (—O—N = O) can be readily recognised from the two strong bands in the regions (*i*) 1680–1650 cm^{-1} and (*ii*) 1625–1605 cm^{-1}.

Table T_3—14.

Group	*Type of vibration*	*Region in cm^{-1} and intensity*
C—NO_2	N = O str	1620—1535 (*s*) 1375—1275 (*s*)
Ar—NO_2	N = O str	1570—1500 (*s*) 1370—1300 (*s*)
—O—N = O	N = O str	1680—1650 (*s*) 1625—1605 (*s*)
O—NO_2	N = O str	1650—1600 (*s*) 1270—1250 (*s*)

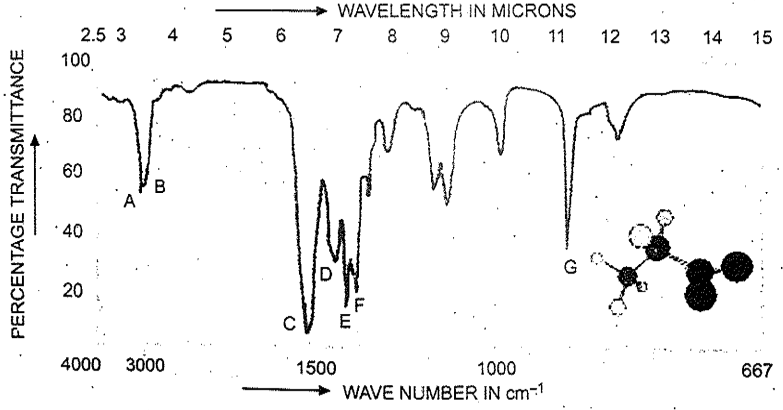


Fig. 3.67. Infra-red spectrum of Nitroethane as a film.

Positions of some characteristic absorptions

A and B 3003 and 2940 cm^{-1};	C—H str in CH_3
C and E 1562 and 1394 cm^{-1};	Characteristic of nitro group
D = 1440 cm^{-1}	C—H def in methyl
F = 1362 cm^{-1}	C—H def
G = 875 cm^{-1}	C—N str

The regions of adsorption for primary, secondary and tertiary nitro-compounds are described in Table T_3–15.

Table T_3—15.

Compound	*νNO_2 (asym)*	*νNO_2 (Symm.)*
CH_3NO_2	1567 cm^{-1} (*s*)	1380 cm^{-1} (*s*)
R_2CHNO_2	~1550 cm^{-1} (*s*)	~ 1360 cm^{-1} (*s*)
$R_3.C.NO_2$	~1536 cm^{-1} (*s*)	~ 1350 cm^{-1} (*s*)

PROBLEM : The Infra-red spectrum of Nitrobenzene is given below. Mark some important characteristic absorptions in it in terms of wave number (cm^{-1})

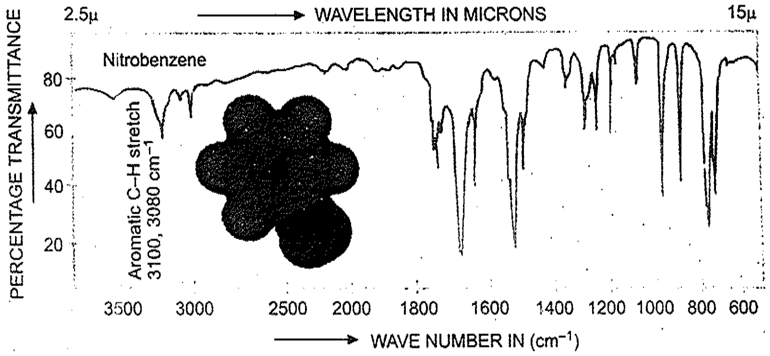


Fig. 3.68. Infra-red spectrum of Nitrobenzene.

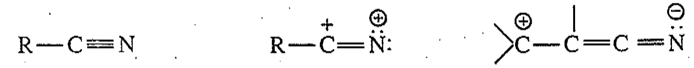
(*b*) Alkylnitrites (R—O—N = O). Organic nitrites are characterised by the following absorption bands

(*i*) Strong absorption bands appear in the regions 1680-1650 cm^{-1} and 1625-1610 cm^{-1} due to N = O stretching vibrations in the trans and cis-isomers respectively. Also the corresponding N—O stretching absorptions occur in the region 815-750 cm^{-1} and 850-810 cm^{-1}. Overtones of N = O appear as medium intensity bands in the region 3360-3220 cm^{-1}.

(*ii*) Nitrites form two strong bands near 690-615 cm^{-1} and 625-565 cm^{-1} due to O = N = O bending vibrations.

3.11 P Nitriles and Related Compounds

Nitriles are the functional derivatives of the carboxylic acids containing C ≡ N group. Various equivalent structures of cyanides can be written as



$R—C{\equiv}N \qquad R—\overset{+}{C}{=}\overset{\oplus}{\ddot{N}}{:} \qquad >\overset{\oplus}{C}—\overset{|}{C}{=}C{=}\overset{\ominus}{\ddot{N}}$

(*a*) (*b*) (*c*)

The electronegative nitrogen atom makes the carbon atom more positive and the polar—CN group has —I effect on the adjacent bond. The infra-red spectra of various cyanides (nitriles) have shown that the predominant form is (*a*) with a triple bond between carbon and nitrogen atoms. Thus, the infra-red absorption occurs in the triple bond region between 2280–2200 cm^{-1}. The shift in $\nu C \equiv N$ stretching absorption depends upon the electronic effect of atoms of groups attached to $C \equiv N$ group.

In aliphatic nitriles, the intensity of $\nu C \equiv N$ stretching band is low.

$CH_3—C \equiv N$	2280 cm^{-1}
$CH_3—CH_2—C \equiv N$	2257 cm^{-1}

The decrease in the wave number of absorption is due to +I effect of the alkyl group/groups attached to $C \equiv N$ group. In α, β-unsaturated nitriles, conjugation of electrons of the double bond with C≡N group lowers the force constant and hence the wave number of absorption is also lowered.

Conjugative effect dominates and $\nu C \equiv N$ stretching occurs at a lower wave number if a group exerting –I and +E effects is attached with the $C \equiv N$ group.

For example, acrylonitrile shows $\nu C \equiv N$ stretching at 2231 cm^{-1}.

In aromatic nitriles, the $\nu C \equiv N$ stretching decreases by about 20 cm^{-1} but band intensity increases as compared to the saturated compounds.

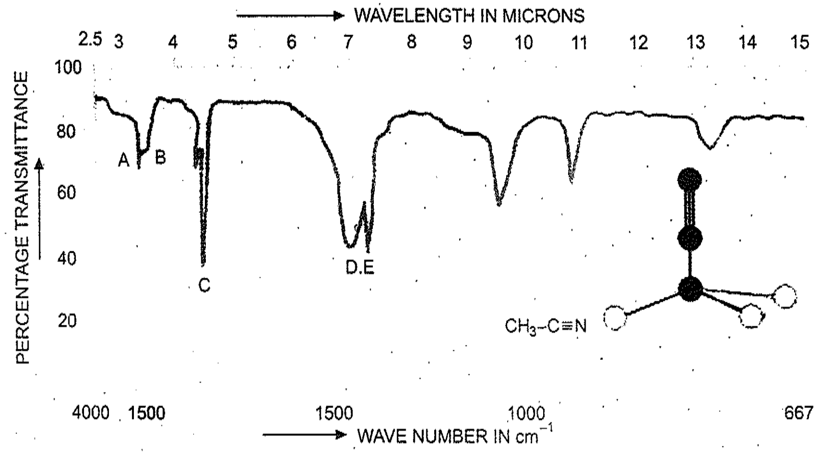


Fig. 3.69. Infra-red spectrum of Methyl cyanide.

Positions of some **characteristic absorptions**

A = 3002 cm^{-1}	C—H str in CH_3	
B = 2940 cm^{-1}	C—H str	
D = 1440 cm^{-1}	C—H def in CH_3	
E = 1370 cm^{-1}	C—H def	
C = 2256 cm^{-1}	$C \equiv N$ str in alkyl cyanides	
Alkyl nitrile	$\nu C \equiv N$	~2250 cm^{-1}
Benzonitrile	$\nu C \equiv N$	~2230 cm^{-1}

EXERCISE : The Infra-red spectrum of Benzonitrile (Phenylcyanide) is given below. Mark some important characteristic absorptions in it in terms of wave number.

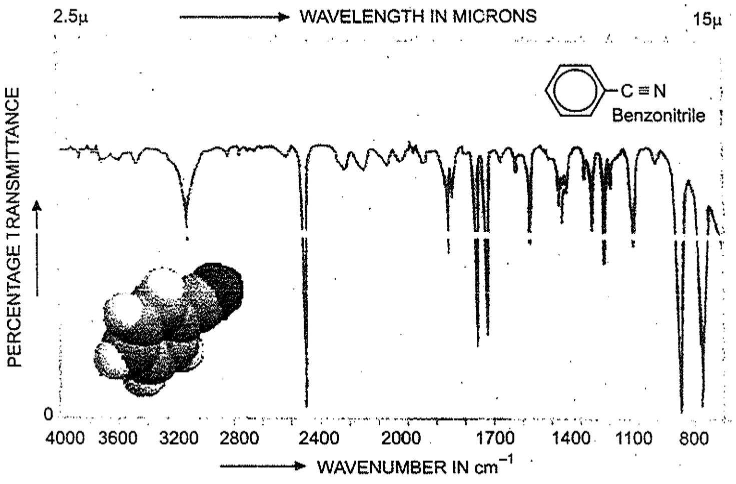


Fig. 3.70. Infra-red spectrum of Benzonitrile
(*Courtesy* : Sadtler Research Laboratories)

Isocyanides show an absorption band in the region 2200-2075 cm^{-1}.

Isocyanates absorb in the region 2275–2250 cm^{-1}.

In the case of azo compounds (—N = N—), the N = N stretching vibrations occur in the region 1630–1570 cm^{-1}. In case of diamides, azides etc., absorption in the Infra-red spectrum occurs in the region 2160–2120 cm^{-1}.

3.11 Q Thiols or Mercaptans, Sulphonic acids and sulphonamides

(*a*) Thiols: When Oxygen is replaced by a sulphur atom in alcohol, the compound formed is called alkyl thiol or mercaptan. In this type of compound, the characteristic absorptions belong to S—H stretching and C—S stretching. Mercaptans and thiophenols absorb as a weak band in the region 2590-2540 cm^{-1}. In such compounds, hydrogen bonding is much weaker and as a result the shift to lower frequency is not so marked. The C—S stretching appears as a weak band in the region 800-600 cm^{-1}.

(*b*) **Sulphonic acids (RSO_2OH).** Anhydrous sulphonic acid show the following characteristic absorption bands.

The O—H stretching vibration appears at 2900 cm^{-1} as a broad intense band alongwith a small band near 2400 cm^{-1}. Asymmetric and symmetric stretching vibrations appear as strong bands in the region 1352-1342 cm^{-1} and 1165-1150 cm^{-1} respectively. In sulphonic acids, S—O stretching absorption of medium intensity appears in the region 910-895 cm^{-1}.

(c) **Sulphonamides ($-SO_2NH_2$).** The characteristic absorption bands in case of sulphonamides are due to N—H stretching, S—N stretching alongwith SO_2 stretching vibrations and N—H in plane bending vibration. The N—H asymmetric and symmetric vibrations appear near 3330 and 3260 cm^{-1} respectively in primary sulphonamide. In case of secondary sulphonamide, a single band appears in the region 3300-3260 cm^{-1} due to N—H stretching. Asymmetric and symmetric SO_2 stretching vibrations appear as strong bands near 1370-1330 cm^{-1} and 1180-1150 cm^{-1} respectively. The characteristic S—N stretching absorption appears at 910-900 cm^{-1}.

3.11 R Heteroaromatic Compounds

Heteroaromatics such as pyridine, furan, thiophene etc. show C—H str bands in the region 3077–3000 cm^{-1}. Such compounds containing N—H group shows N—H str absorption in the region 3500–3220 cm^{-1}. In this region of absorption, the exact position depends upon the degree of hydrogen bonding and hence upon the physical state of the sample or the polarity of the solvent. Pyrrole and Indole in dilute solution in non-polar solvents show a sharp band near 3495 cm^{-1}.

Ring stretching vibrations occur in the general region between 1600–1300 cm^{-1}. The absorption involves stretching and contraction of all the bonds in the ring and interaction between these stretching modes, Pyridine shows four absorption bands in this region. In this respect, it closely resembles a monosubstituted benzene.

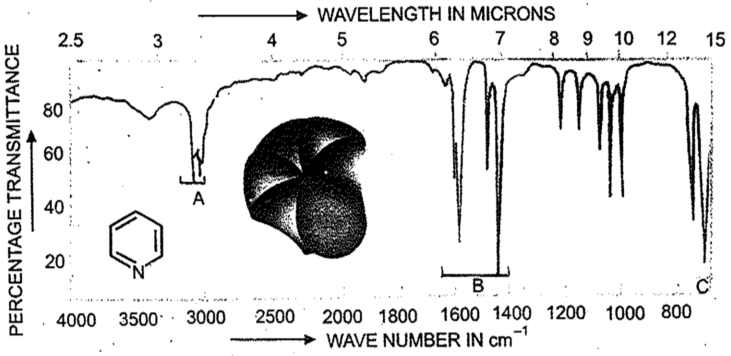


Fig. 3.71. Infra-red spectrum of Pyridine.
Courtesy : Sadtler Research Laboratories, Philadalphia.

Positions of some characteristic absorptions

A = 3080–3010 cm^{-1}	C—H str aromatic
B = 1600–1430	C = C and C = N str (in Ring)
C = 748, 703 cm^{-1}	C—H def out of plane

EXAMPLE 11 *An organic compound (A) with molecular formula, C_3H_9N shows the following peaks in the Infra-red spectrum;*

(*i*) 3012 cm^{-1} (*m*) (*ii*) 3423 cm^{-1} (*s*)

(*iii*) 3236 cm^{-1} (*m*) and (*iv*) 1615 cm^{-1} (*m*)

When the compound A is treated with nitrous acid, we get a compound B which shows a strong peak at 3430 cm^{-1}. What are A and B and explain the reactions involved?

SOLUTION. (*i*) The two bands at 3423 cm^{-1} and 3236 cm^{-1} are due to asymmetrical and symmetrical N—H str. Clearly, the compound contains —NH_2 group.

(*ii*) The band at 3012 cm^{-1} is due to C—H str.

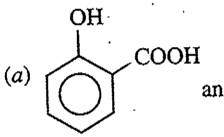
(*iii*) The band at 1615 cm^{-1} is due to N—H bending.

The probable structure of (A) consistant with the given molecular formula and data is $CH_3CH_2CH_2NH_2$. When it is treated with nitrous acid, —NH_2 is converted into OH group which forms a strong peak at 3430 cm^{-1}. The reaction involved is written as:

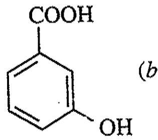
$$\underset{n\text{-Propyl amine}}{CH_3CH_2CH_2NH_2} + HONO \longrightarrow \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} + N_2 + H_2O$$

EXAMPLE 12. *How will you differentiate between the following pairs of compounds using Infra-red spectra:*

(*a*)



and



(*b*) (*i*) CH_3CH_2CHO and (*ii*) $CH_2{=}CH—CH_2OH$

SOLUTION. (*a*) o-hydroxy benzoic acid (salicylic acid) and *m*-hydroxy benzoic acid shows a similar broad band due to O—H str in —COOH between 3000—2500 cm^{-1}.

Difference. (*i*) In salicylic acid, intramolecular hydrogen bonding takes place. Therefore, the O—H str shifts to some lower wave number. As it is intramolecular. change in concentration does not cause any shift in O—H str absorption. In case of m-hydroxy benzoic acid, νO—H str occurs at a still lower value due to intermolecular hydrogen bonding. Moreover, the absorption band will be broad and position of absorption shifts with dilution.

(*i*) o-hydroxy benzoic acid shows one band at 735—770 cm^{-1} while *m*-hydroxy benzoic acid shows two bands at 690–710 cm^{-1} and 730–770 cm^{-1}.

(*i*) Propanal (CH_3CH_2CHO) shows characteristic absorption bands at
  - (*i*) 1720–1740 cm^{-1} due to νC—H str
  - (*ii*) νC—H str in aldehyde ~ 2720 cm^{-1}
  - (*iii*) C—C str at 1400—1000 cm^{-1}

(*ii*) CH_2= CH—CH_2OH shows characteristic absorption at

(*i*) νO—H str	3300–3600 cm^{-1}
(*ii*) νC = C str	1650 cm^{-1}

EXAMPLE 13. *How would the Infra-red spectrum of $C_6H_5CH_2NH_2$ and CH_3—CO—$N(CH_3)_2$ differ?*

(*a*) Benzylamine shows the following characteristic absorptions.

(*i*) νC—H str	~3100–3040 cm^{-1}
(*ii*) νC = C str (in aromatics)	~ 1600 cm^{-1}, ~ 1500 cm^{-1}, ~ 1460 cm^{-1}
(*iii*) νN—H str	~3250–3500 cm^{-1}

(*b*) N,N-Dimethyl acatamide shows bands at

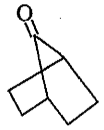
νC = O str	1675 cm^{-1} (*s*)
νC—H str	~3300 cm^{-1}

3.12 Important Features in Infra-red Spectroscopy

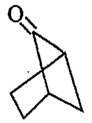
1. Ring Strain in cycloalkanones and Carbonyl Stretching frequency.

It is found that the C = O str frequency increases with the decrease in the ring size of a cycloalkanone. For unstrained acyclic ketone, the C = O str occurs at 1717 cm^{-1}. For the compounds with rings smaller than $n = 6$, the angle θ is less than 109° 28′ (normal tetrahedral angle) and this causes strain and change C = O str frequency. *It is found that the angle* (θ) *is inversely proportional to* νC = *O str*. The reason for this is the increased interaction between the carbonyl double bond and the associated neighbouring single bonds. With decrease in ring size, the said interaction increases which offers resistance to the motion of carbonyl carbon during stretching vibration. This increases the force constant and hence the frequency of absorption is raised.

In case of highly strained bridged ketones, the C = O str absorption occurs around 1800 cm^{-1}. Examples are 7-keto-bicyclo [2, 2, 1] heptane and 6-keto-bicyclo [2, 2, 1] hexane.



7-keto-bicyclo
(2, 2,1) heptane



6-keto-bicyclo
(2, 2,1) hexane

2. Resonance splitting : It has been found that when each of the two bonds oscillates with a common atom having nearly the same individual frequency, they interact very strongly. Due to this, the resulting frequencies are displaced from their original positions, depending upon the relative phasing and coupling of two oscillators. For example, in allene ($CH_2 = C = CH_2$), because of the common atom, the coupling between the two C = C stretching vibrations will be in the single bond (1070 cm^{-1}) and triple bond region (1980 cm^{-1}) respectively.

3. Group Frequencies : Group frequencies are usually independent of the structure of the molecule as a whole with a few exceptions. The vibrations of light atoms in terminal groups (*e.g.* CH_3, OH, $>C=O$, $C \equiv N$) are of high frequency whereas those of heavy atoms (C—Cl, C—Br etc) are of low frequency. Their absorption frequencies being highly characteristic can be used for analysis. The isolated multiple bonds ($>C=C<$, $—C \equiv C—$) have frequencies which are highly characteristic. When two such groups occur together in a molecule, resonance occurs and the group frequencies are shifted considerably from their expected values. For example, isolated carbonyl in ketone and $>C=C<$ bond have group frequencies of 1715 cm^{-1} and 1650 cm^{-1} respectively. But when their grouping occurs *i.e* $>C=\overset{|}{C}-\overset{|}{C}=O$, their separate frequencies are shifted and also the intensity of $>C=C<$ absorption increases and becomes comparable to strong C = O str band. Also closer coupling of the two groups as in ketene $>C=C=O$ give rise to absorption at about 2100 cm^{-1} and 1100 cm^{-1} which are very far removed from their characteristic frequencies of separate groups.

It is known that —OH stretching frequency of alcohols is dependent on the degree of hydrogen bonding which lengthens or weakens the O–H bond. In case hydrogen bond is formed between the OH group and carbonyl group, the absorption frequency of C = O str gets lowered to a small extent. The shifts in group frequency position caused by resonance or intermolecular effects are in themselves highly characteristic and can be employed for structure elucidation.

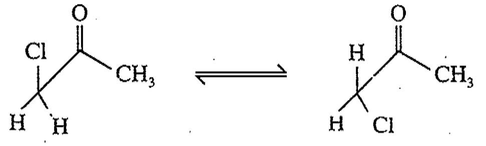
Physical state also causes a shift in the frequency of absorption particularly when the molecule is polar. More condensed phase of the substance gives a lower frequency band. The trend could be written as :

$$\nu_{gas} > \nu_{liquid} > \nu_{solid}.$$

In a relatively polar molecule like HCl, there is a shift of about 100 cm^{-1} in passing from vapour to liquid and a further decrease of 20 cm^{-1} on solidification. Incase of non-polar CO_2, negligible shifts are recorded from gaseous to liquid and a lowering of about 60 cm^{-1} on solidification.

4. Field Effects : If a polar group is oriented properly relative to carbonyl group, then it exerts inductive effect as well as the field effect on the stretching frequency of the carbonyl group. The C = O str frequency for α–haloketone is raised compared to parent ketone. The shift in absorption frequency increases with increase in dipole moment of the C—X bond. It is due to the electrostatic interaction between two similarly oriented dipoles and occurs when C—X and C = O bonds are approximately, coplanar. In molecules like α–haloketo steroids, the halogen atom is equitorial to the near carbonyl group and thus, field effect is caused which raises the frequency by 15 cm^{-1} in C = O str.

Consider α–chloroketones which exhibit two C = O str absorptions due to rotational isomerism.



Field effect
$\nu C=O$ 1745 cm^{-1}

(Normal)
(No field effect) $\nu C=O$ 1725 cm^{-1}

When the chlorine atom is near the carbonyl oxygen, repulsion betweent the negative field and the bonding electrons raises the value of force constant and hence frequency of absorption is also raised. Field effect is also termed as dipolar interaction through space.

5. Effect of Adsorption on Force Constant : Adsorption is a surface phenomenon. The adsorption of a molecule on the surface of adsorbent restricts the rotational movements of the adsorbate. As a result, it affects its vibrational movements also. It, thus effects the particular vibrational frequency and the value of adsorption frequency can be utilised to get an estimate of the strength of the bond with the adsorbent. The vibrational frequency of a diatomic molecule taken as simple harmonic oscillator is given by :

$$\bar{\nu} = 1303.16\sqrt{\frac{k}{\mu n}}$$

The adsorption of the molecule on the surface of adsorbent changes vibrational frequency. From this, the value of force constant (k) can be calculated. In case the value of k decreases, it means the weakening of bond that holds the absorbate on the surface of the adsorbent.

EXAMPLE 11. *A certain diatomic gas (A = B) is known to have force constant (k) equal to 16.83 millidynes /A°. When the molecule is adsorbed on the surface of a metal, the A = B stretching bond is observed at 2025 cm^{-1}. Show that the C = O bond strength is weakened as a result of adsorption on metal surface. (At. mass A = 12, B = 16).*

SOLUTION. Given that $\bar{\nu} \equiv 2025\ cm^{-1}$.

$$\mu_m = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 16}{12 + 16} = \frac{192}{28} = 6.857\ amu.$$

The molar force constant, k for A = B is :

$$\bar{\nu} = 1303.16\sqrt{k/\mu_m}$$

or
$$k = \frac{(2025)^2 \times 6.857}{(1303.16)^2} = 16.55 \text{ millidynes/A°}$$

Since the value of force constant decreases, we say that the strength of A = B decreases due to adsorption on the surface of the metal.

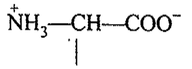
6. Specific heat of Adsorption from group frequency shift : The physical adsorption of a substance on the surface of adsorbent say silica causes a frequency shift of the surface OH groups. It is found that the frequency shift varies linearly with the specific heat of adsorption of adsorbate. Thus, this method is valuable to calculate the heat of adsorption of adsorbate on the dehydroxylated silica surface (ΔH_{ad}). The corresponding heat of adsorption on hydroxylated silica surface, ΔH_h is known.

$$\Delta Q_{(adsorbed)} = \Delta H_{ad} - \Delta H_h$$

3.13 Applications of infra-red spectrcscopy

1. **Identification of an Organic Compound :** The identity of an organic compound can be established from its finger print region (1400–900 cm^{-1}). The identity of an organic compound is confirmed if its finger print region exactly matches with the known spectrum of that compound. It may be noted that the compounds containing the same functional groups may have similar absorptions above 1500 cm^{-1} but they differ considerably in finger print regions.

2. **Structure determination :** This technique helps to establish the structure of an unknown compound. All major functional groups absorb at their characteristic wave numbers. The shift due to environmental effects may also be looked into. From the data available due to absorption frequencies, the probable structure can be predicted. If some chemical data is available, it can lead to the confirmation of the structure. It is known that the infra-red spectra of amino-acids exhibit bands for ionised carboxylic acids and amine salts (–$\overset{+}{N}H_3$). No band for free —NH$_2$ and —COOH groups is observed. Clearly, amino acids exist as zwitter ions as below :



$$\overset{+}{N}H_3—\underset{|}{CH}—COO^-$$

Similarly, from the I R bands of sulphanilic acid, it is said that the compound contains $\overset{+}{N}H_3$ and $SO_3^{\ominus}$ and not free groups as —NH$_2$ and SO$_3$H.

3. **Qualitative analysis of functional groups :** The presence or the absence of absorption bands help in predicting the presence of certain functional groups in the compound. The presence of oxygen reveals that the group may be —OH, C = O, COOR, —COOH, anhydride etc. But an absorption band between 3600-3200 cm^{-1} limits the possibilities. The band in this region may be due to —O—Hst. This region also speak of absorption in case of —NH$_2$, —NH groups. In case of —NH$_2$, two absorption bands appear in the above region. NH group give only one bond. Its distinction from O—H str can be made from the extent of hydrogen bonding which is stronger in —OH compounds and causes more lowering in wave number.

4. **Distinction between two types of hydrogen bonding :** This technique is quite valuable to distinguish between the types of hydrogen bonding. It is known that in hydrogen bonding, the electron cloud transfers from a hydrogen atom to the neighbouring electronegative atom. The condition is that the *s*-orbital of proton should effectively overlap the *p*-orbital of the acceptor group. It may be noted that the strength of hydrogen bond is maximum when the proton donor group and the axis of lone pair orbital are collinear and varies inversely to the distance between X and Y (where X is H or hydrogen containing group and Y is oxygen, nitrogen or halogen atom).

The molecules of the substance which contain active hydrogen grouping (say —OH, —COOH etc) undergo self association. For example, the hydroxy compounds in the solid or liquid state exist as polymeric aggregates. The absorption in aggregate form occurs at lower frequencies and bands formed are relatively broad. But when such a substance is dissolved in non-polar solvent, such as CCl$_4$, the aggregates or Polymers break in dimers and monomers. Due to this, the O—H str. absorption shifts to higher frequencies and the peaks become sharp. Further this technique helps to distinguish between intra molecular and intermolecular hydrogen bonding. For example, o—Nitro phenol exhibits intramolecular hydrogen bonding whereas *p*-Nitro phenol exhibits intermolecular hydrogen bonding. Intramolecular hydrogen bonded compound does not show any shift in absorption on dilution whereas intermolecular H-bonded does.

5. **Quantitative analysis :** It helps to make a quantitative estimation of an organic mixture. The estimation of the components of a mixture can be done by :

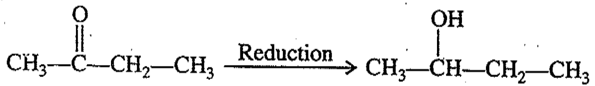
(*i*) measuring the intensities of absorption bands characteristic of each component

(*ii*) knowing the optical density of the absorption band for a pure component.

It is known that commercial xylene exists as a mixture of three isomers, viz-ortho, meta and para-xylenes. The separation of the mixture cannot be easily done. However, the percentage composition of the mixture can be determined by taking the IR spectrum of the mixture. Bands are formed at (*i*) 740 cm^{-1} for ortho isomer, (*ii*) 880 cm^{-1} for meta isomer and (*iii*) 830 cm^{-1} for the para isomer. Mixtures of known composition are recorded and the working curves are drawn for the above bands for ortho, meta and para-isomers.

From the optical density values for commercial xylene, the percentage composition of each isomer can be calculated from the working curves.

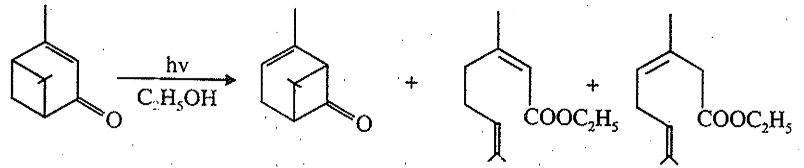
6. **Study of a Chemical reaction.** This technique is quite useful for studying chemical reactions. Consider the reduction of a saturated aliphatic ketone to form secondary alcohol. Ketone forms a strong band at about 1710 cm^{-1}. When it is subjected to reduction, it forms Butan-2-ol which



$$CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_3 \xrightarrow{\text{Reduction}} CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—CH_3$$

Butan-2-one Butan-2-ol

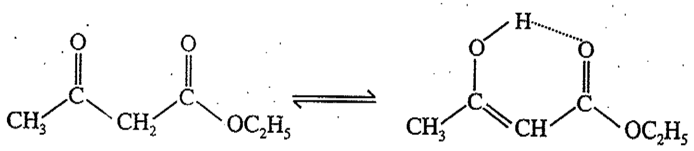
absorbs at 3300 cm^{-1} due to O-Hstr. The progress of reaction can be studied from time to time and the reduction will be complete when a strong band due to C = Ostr will be missing and only a band due to O—H str is present. Infra-red spectroscopy is also used to predict the products formed in a photochemical reactions. When verbenone is irradiated in ethanol solution, the uv absorption maximum due to verbenone disappears and Infra-red spectrum of crude verbenone appears at 1787, 1740, 1715 and 1685 cm^{-1}. When the crude verbenone is subjected to chromatographic separation, we get chrysanthenone, Ethyl geranate and Ethyl-3, 7-dimethylocta-3, 6-dienoate. The photochemical reaction can be shown below.



Verbenone Chrysanthenone Ethyl geranate Ethyl -3, 7-dimethyl octa-3, 6-dienoate

$\nu C = O$ str 1685 cm^{-1} $\nu C = O$ str 1787 cm^{-1} $\nu C = O$ str 1715 cm^{-1} $\nu C = O$str 1740 cm^{-1}

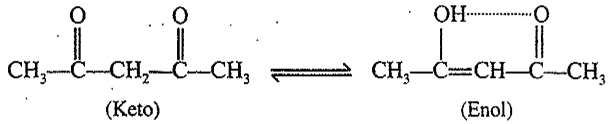
7. **Study of Keto-enol tautomerism :** Diketones and ketoesters exhibit keto-enol tautomerism provided they have α-H atom in them. The infra-red spectrum of such a compound contain bands due to C = O, O—H and C = C bonds. Consider ethyl acetoacetic ester. It exists in keto-enol isomers in equilibrium.



$\nu C = O$str 1733, 1710 cm^{-1}(s)

$\nu O = H$str ~ 3300 cm^{-1}(b)
$\nu C = O$str 1645 cm^{-1}(s)

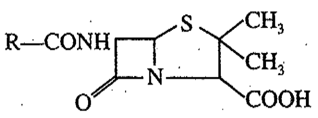
The lowering of νC = O str absorption in the enolic form is due to intra-molecular hydrogen bonding which is stabilised by Resonance. The appearance of the above bands clearly confirm keto-enol tantomerism in acetoacetic ester. Similar absorption bands are also noted in case of β-diketones.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

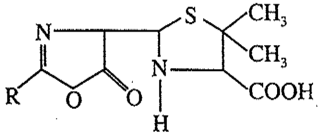
(Keto) (Enol)

8. Study of complex molecules : This technique is also useful to establish the structure of complex molecules. For example, following two structures of Penicillin were proposed on the basis of IR spectral studies.



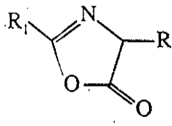
I

β-Lactam structure



II

Oxazolone structure

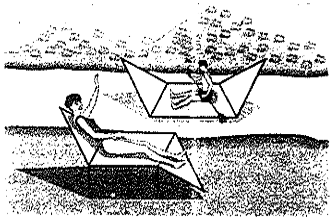


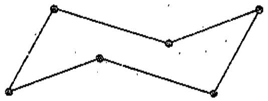
The infra-red spectra of oxazolones of the type (shown) show two characteristic bands (*i*) 1825 cm^{-1} due to νC = O str and (*ii*) νC = N str due to 1675 cm^{-1}. It is found that no such band appears in the spectrum of Penicillin. Thus, the oxazolone structure for Penicillin is ruled out.

νC = O str 1825 cm^{-1}
νC = O str 1675 cm^{-1}

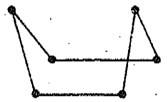
It is known that β-lactams do not absorb near 1770 cm^{-1} where as β-lactams fused to thiazolidine ring exhibits a band at 1770 cm^{-1}. Since Penicillin gives a strong band at 1770 cm^{-1}, the β-lactam structure of Penicillin is confirmed.

9. Conformational Analysis : (*a*) This technique is quite useful in determining the relative stability of various conformations of cyclic compounds. Cyclohexane exists in both chair and boat forms. Their relative stability is determined as below.





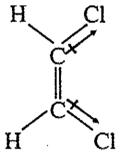
Chair
I



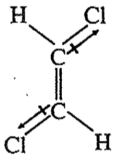
Boat
II

As per the selection rules, there are 18 Infra-red active C—C str and CH_2 rocking and twisting vibrations possible for boat forms II. On the other hand, there are only five for the chair form I. The spectral examination of cyclohexane in the region 1350-700 cm^{-1} reveals five bands are expected for chair form. This shows the greater stability of chair conformation over boat conformation. (*b*) By infra-red spectroscopy, axial and equitorial substituents in cyclohexane can also be distinguished. It has been found that an equitorial substituent usually absorbs at a higher frequency than does the same substituent at the axial position. The higher absorption frequency of C—X bond (X = Cl, Br, OH etc) in the equitorial position is due to less steric interaction of C—X bond with adjacent hydrogen atoms.

10. Geometrical Isomerism. It is known that a vibration is infra-red active only if it causes a change in dipole-moment of the molecule. Also the intensity of absorption depends upon the change in the dipole moment. This technique clearly makes a distinction between cis and trans isomers. Consider 1, 2-dichloro ethene. Its geometrical isomers are :



μ = 1.85 D



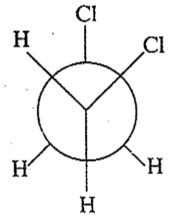
μ = 0

For most of the vibrations, the change in the dipole-moment occurs in the cis isomer. On the other hand, trans isomer is non-polar with dipole moment equal to zero.

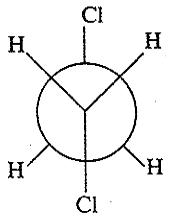
Accordingly the C = C str absorption peak at 1580 cm^{-1} is not observed in case of trans-isomer since the vibration in it does not produce any change in the dipole moment. On the other hand, this peak (1580 cm^{-1}) appears due to C = C str in cis isomer.

In the same way, it is observed that in methyl acetylene ($CH_3C \equiv CH$), the vibration due to C ≡ C str is infra-red active whereas in dimethyl acetylene ($CH_3C \equiv C—CH_3$), the vibration is infra-red inactive.

11. Rotational Isomerism : Infra-red spectroscopy helps in the detection of Gauche (skew) and staggered conformations. The two conformations of 1, 2-dichloro ethane can be shown below :



I
Gauche
1235 cm^{-1} (CH_2 rocking)



I
Staggered (Trans)
1291 cm^{-1} (CH_2 rocking)

Two bands at 1291 cm^{-1} and 1235 cm^{-1} appear in the spectrum of 1, 2-dichloroethane. The staggered (trans) form predominates at lower temperature whereas gauche form dominates at higher temperature. The relative intensities of the bands depend upon temperature. The rocking vibration band at 1291 cm^{-1} becomes less intense as the temperature is raised. From the relative intensities of the bands, their relative abundance at a particular temperature can be estimated.

12. Detection of Impurity in a compound. Infra-red spectroscopy is also useful in the detection of impurity in a compound by comparing its spectrum with the spectrum of the authentic sample of the compound. Moreover, a pure sample always consists of sharp peaks and bands while impure sample will consist of poor bands and also some additional bands.

3.14 Simple Problems on infra-red Spectroscopy

1. *An organic compound with molecular mass C_8H_{18} shows the following characteristic absorption bonds :*

(*i*) 2925 cm^{-1} (st), (*ii*) 1465 cm^{-1}, (*iii*) 1380 cm^{-1} and (*iv*) 720 cm^{-1}.

Determine the structure of the compound.

Ans. From the positions of the absorption bands, it is clear that the compound is a saturated hydrocarbon. A band at 2925 cm^{-1} shows C—H stretching whereas that at 1465 cm^{-1} is due to C—H bending for methyl and methylene. Absorption position of 1380 cm^{-1} is due to

C–H bending for methyl. Absorption at 720 cm^{-1} due to rocking motion for methylene Hence the organic compound is *n*-octane ($CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$).

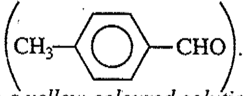
2. *An organic liquid with molecular formula C_7H_8 burns with a sooty flame. It shows the following absorption bands in its Infra-red spectrum : (i) 3060 cm^{-1} (ii) 3040 cm^{-1} (iii) 2918, 2870 cm^{-1} (iv) 1500, 1450 cm^{-1} (v) 750 cm^{-1}. Deduce the structure of the compound.*

Ans. Since the compound burns with a sooty flame, it appears to be aromatic. The absorption at 3060 cm^{-1} is due to C—H str aromatic. Also a band at 3040 cm^{-1} is due to C—H stretching (aromatic). Two absorption positions due to C—H str for methyl group appear at 2918 cm^{-1} and at 2870 cm^{-1}. The aromatic ring is further confirmed as two absorption bands appear at 1500 cm^{-1} and 1450 cm^{-1} due to C═C stretching. The aromatic compound is mono substituted due to the appearance of a band at 750 cm^{-1}. Hence, the probable organic aromatic compound is toluene.

3. *The analytical data and the molecular mass determination gave C_8H_8O as the molecular formula of the compound. The compound burns with a sooty flame and gave an oxime with hydroxylamine hydrochloride. Following absorption bands appear in its Infra-red spectrum : (i) 2825 cm^{-1}, (ii) 2717 cm^{-1}, (iii) 3060 cm^{-1} and (iv) 1700 cm^{-1} (s) and 830 cm^{-1}. Deduce the structure of the compound.*

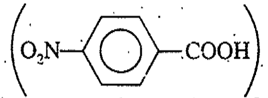
Ans. The organic compound is aromatic as it burns with a Sooty Flame. It also contains an aldehydic group as it forms an oxime with hydroxyl-amine hydrochloride.

Two bands at 2825 cm^{-1} and 2717 cm^{-1} are due to C—H str which are most characteristic of an aldehydic group. A band at 3060 cm^{-1} is due to C—H stretching in aromatic compounds. Benzene ring in it must be disubstituted as an absorption peak is formed at 830 cm^{-1}. Thus, C_6H_4— and CHO are the parts of the molecule. Clearly, CH_3 is left. Thus, the organic compound under investigation is *p*-Tolualdehyde

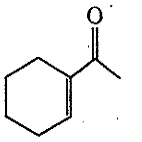


4. *An organic compound dissolves in sodium hydroxide to form a yellow coloured solution. It gives brisk effervescence with sodium bicarbonate solution. Its infra-red spectrum exhibits the following absorption bands : (i) 3060-3110 cm^{-1}, (ii) 3000-2520 cm^{-1} (b), (iii) 1602, 1510, 1450 cm^{-1} and (iv) 1620, 1375 cm^{-1} (s) and 830 cm^{-1}.*

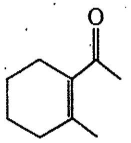
Ans. Organic compound which dissolves in sodium hydroxide producing yellow coloured solution should contain —NO_2 group in it. The efferrescence with sodium bicarbonate shows that it contains a —COOH group in it. The presence of —COOH group is further confirmed from a broad band at 3000-2500 cm^{-1}. The absorption bands at 1602, 1510 and 1450 cm^{-1} are most characteristic of C═C stretching in aromatics. The presence of nitro group is revealed from the two bands at 1620 and 1375 cm^{-1}. The absorption position at 830 cm^{-1} shows that the compound is disubstituted. Hence, the most likely structure of the compound is *p*-Nitrobenzoic acid.



5. *Which of the following two compounds will show νC = O stretching absorption band at a higher wave number ? Give suitable reason for your answer.*



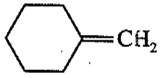
and



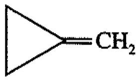
(i) (ii)

Ans. Compound (*ii*) will absorb (due to νC = O str) at a sightly higher wave number as compared to compound (*i*). It is due to steric hindrance. The effect occurs when the carbonyl group is forced slightly out of the plane of the double bond and due to this *p*-orbital overlap is reduced.

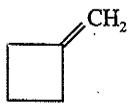
6. *Arrange the following compounds in order of their increasing wave number of absorption due to C=C stretching*



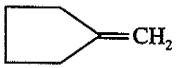
(*i*)



(*ii*)



(*iii*)



(*iv*)

Assign reason for your answer.

Ans. The exocyclic olefinic double bonds show an increase in C=C stretching frequency as the size of the ring decreases. Thus, with the increase in ring strain, C=C str requires more energy and wave number of absorption is raised. The wave number of absorption has the order :

(*i*) < (*iv*) < (*iii*) < (*ii*)

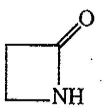
7. *An organic compound with molecular formula C_8H_6 decolourises bromine in carbon tetrachloride and gives a white precipitate with ammonical silver nitrate solution. Give the probable structure of the compound. Its infra-red spectrum gives a band at 2150-2200 cm^{-1} and the region near 3300 cm^{-1} is transparent.*

Ans. The compound appears to be unsaturated as it decolourises bromine in carbon tetra chloride. It cannot be ethylenic as it gives, white precipitate with ammonical silver nitrate solution. The presence of C ≡ C is further confirmed due to an absorption band at 2150-2200 cm^{-1}. Hence, the compound can be $C_6H_5—C≡CH$.

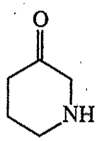
8. *How will you distinguish between : (i) p—$CH_3CO—C_6H_4—OCH_3$ and (ii) $CH_3CO—C_6H_4—NO_2$?*

Ans. Methoxy group in the para position causes +M effect in *p*-methoxy acetophenone. Due to this, the force constant of C = O bond is decreased which results in the lowering of wave number of absorption. On the other hand, the —NO_2 group causes —M effect and raises the bond order of C = O bond resulting in the absorption at higher wave number.

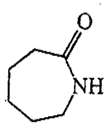
9. *Arrange the following compounds (Lactams) in order of their decreasing wave number of absorption :*



(*i*)



(*ii*)



(*iii*)

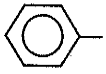
Ans. In cyclic amides or Lactams, the ring strain increases the C=O stretching frequency. We know that the smaller rings are more strained than the bigger rings. With the decrease in ring size, the force constant of C=O bond increases and hence the absorption position is raised. Hence, the decreasing order is :

(*i*) > (*ii*) > (*iii*)

10. *An aromatic organic compound decolourises bromine in carbon tetra-chloride and exhibits the following absorption position.*

(*i*) 3090 cm^{-1} (*ii*) 3040 and 3000 cm^{-1} (*iii*) 2820 and 2750 cm^{-1} (*iv*) 1685 cm^{-1}(s) (*v*) 1630 cm^{-1} (*vi*) 1580 and 1450 cm^{-1} (*vii*) 750 cm^{-1}.

Ans. Absorption bands at 1580 and 1450 cm^{-1} confirms the presence of aromatic ring. A peak at 750 cm^{-1} shows that the ring is monosubstituted. A strong band at 1685 cm^{-1} shows the presence of carbonyl group. The carbonyl group is aldehydic as two characteristic peaks appear at 2820 cm^{-1}. Further the compound certains C=C due to the presence of a band at 1630 cm^{-1}. (also confirmed by the decolourisation of bromine) Thus, the structural units in the compound under investigation are : C_6H_5, C = C, CHO. Hence, the probable structure of the compound is :

$C_6H_5CH{=}CH{-}CHO$ or —CH=CH—CHO. (Cinnamaldehyde)

3.15 Short Questions with Answers

1. **What is the range of infra-red radiations ?**

Ans. The range of infra-red radiations is 2.5 μ–15 μ *i.e.*, 4000 cm^{-1} to 667 cm^{-1}.

2. **What happens when a substance is irradiated with infrared radiations ?**

Ans. When a substance is exposed to infra-red radiations, the various bonds in a molecule stretch and bend with respect to one another. The absorption of radiations between 1500 cm^{-1}-4000 cm^{-1} cause the bonds to stretch and the bands formed due to these absorptions are most characteristic of different functional groups. The absorption of radiations below 1500 cm^{-1} cause bending of bonds.

3. **Can you distinguish a pair of enantiomers by infra-red spectroscopy ?**

Ans. No. The enantiomers of an optically active substance cannot be distinguished by this technique.

4. **Name the various types of bending vibrations.**

Ans. These are Scissoring, Rocking, Wagging and twisting. For such vibrations, energy required is below 1500 cm^{-1}.

5. **What is Hooke's law ?**

Ans. Hooke's law helps to calculate approximately the value of stretching vibrational frequency of a bond. According to this law,

$$\bar{\nu}\text{ (wave no.)} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass.

$$\mu = \sqrt{\frac{m_1 m_2}{m_1 + m_2}}$$

6. **Compared to the number of bonds in a molecule, there are generally more number of peaks in the infra-red spectrum. Explain.**

Ans. In addition to the number of peaks / bands characteristic of different bonds in a molecule, the other peaks may be due to overtones, combination bands, difference bands etc. For example, if x cm^{-1} and y cm^{-1} are the frequencies of fundamental bands, then peaks of low intensity also appear at $2x$, $2y$, $(x + y)$, $(x - y)$ cm^{-1} etc.

7. **How inductive effect brings about a change in the position of absorption for a particular bond ?**

Ans. The presence of electron releasing groups. (+I effect) such as alkyl groups brings about a downward shift in wave number of absorption. For example, Acetaldehyde (CH_3CHO) gives C = O str band at 1745 cm^{-1} whereas acetone (CH_3COCH_3) due to additional methyl group absorbs at 1715 cm^{-1} due to C = O str. Similarly, the presence of —I groups (F, Cl, —NO_2 etc) raise the wave number of absorption from the normal value. For example, C = O str for acetone is at 1715 cm^{-1} whereas those for chloroacetone and dichloroacetone are at 1725 cm^{-1} and 1740 cm^{-1} respectively.

8. **How hydrogen bonding change the position of absorption in the Infra-red spectroscopy ?**

Ans. Hydrogen bonding brings about a remarkable downward shift in the wave number of absorption. For example, alcohol in the vapour state (Isolated molecule) shows O—H str at about 3600 cm^{-1} whereas that in the associated form gives a broad absorption band at 3200 cm^{-1}. Stronger the hydrogen bonding, more broadening of the band occurs at much lower wave number.

9. **Can you distinguish the type of hydrogen bonding by Infra-red spectroscopy ?**

Ans. Yes, It can be easily done by taking the infra-red spectra of the given compound at two different concentrations. If there is a shift in the absorption position of a particular peak or band, then the type of hydrogen bonding in the substance is intermolecular otherwise it is intra molecular. Intra-molecular hydrogen bonding in a substance does not depend upon the concentration of the solution.

10. **Discuss the positions of absorption of a particular band in a substance in all the three states.**

Ans. In the vapour state, the absorption band for stretching of a particular bond occurs at the highest wave number compared to that when the substance is in the liquid state which in turn occurs at higher wave number than when the same substance is in the solid state.

11. **Linear molecules have (3*n*-5) vibrational degrees of freedom whereas non-linear molecules have (3*n*-6) vibrational degrees of freedom. Explain.**

Ans. In non-linear molecules, three degrees of freedom describe rotation and another three describe translational. The remaining (3*n*-6) are the vibrational degrees of freedom. But in linear molecules, there are only two degrees of rotation.

12. **Infra-red spectroscopy is the best technique to establish the identity of organic compounds. Explain.**

Ans. In this technique, when a substance is exposed to infra-red radiations, almost all types of bonds in a molecule show absorption bands at characteristic wave numbers. Most characteristic stretching absorption bands appear above 1500 cm^{-1}.

13. **Some of the fundamental vibrations are infra-red active while others are not. Explain.**

Ans. Infra-red light is absorbed only when a molecule of the substance under examination undergoes a net change of dipole-moment. Total symmetry about a bond eliminates certain bonds and thus the number of bands which appear does not agree with the number of fundamental vibrations. Clearly, some of the fundamental vibrations in infra-red are active and some are inactive.

14. **What happens to O-H str position when 10 ml of carbon tetrachloride is added to 2 ml of ethyl alcohol ?**

Ans. Ethyl alcohol exhibits intermolecular hydrogen bonding and due to this, absorption band occurs at 3200 cm^{-1}. When carbon tetrachloride is added it, there is decrease in hydrogen bonding and thus, the absorption position is raised.

15. **What do you mean by Finger print region ?**

Ans. The region below 1500 cm^{-1} is rich in many absorptions which are caused by bending vibrations. In the spectrum, the number of bending vibrations is usually more than the number of stretching vibrations. This region is called Finger print region. Some substances containing the same functional group show similar absorption above 1500 cm^{-1} but their absorption positions differ in the finger print region. Such compounds can be easily distinguished by comparing their finger print regions.

16. In acetylene, —C ≡ C—H str appears at about 3300 cm^{-1}. How will you distinguish it from an O—H str in alcohol ?

Ans. In alcohols, the O—H str absorption band appears between 3200-3600 cm^{-1}. ≡ C—H str at 3300 cm^{-1} can be easily distinguished because O—H str band at this position will be broader and will change with change in concentration of solution. ≡ C—H str position will be a sharp peak and is concentration independent.

17. How will you show that the compound under investigation is not aromatic ? Use Infra-red technique.

Ans. The absence of bands due to C══C str at 1600 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1} shows that the given compound is not aromatic.

18. How will you distinguish between CH_3CH_2CHO and CH_3COCH_3 ?

Ans. For propanal, in addition to νC = O str at 1720 cm^{-1}, there will be a peak at C—H str at ~2720 cm^{-1}. The peak at ~2720 cm^{-1} is most characteristic of an aldehyde and it will be missing in case of an aldehyde.

19. The C—H str vibration in chloroform occurs at 3000 cm^{-1}. Calculate the C—D str frequency in deutero chloroform.

Ans. The wave number for fundamental vibration can be calculated by using the expression:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

For C—H str and C—D str; k is supposed to be the same. The ratio of their reduced masses (μ) can be calculated as under :

(*i*) For C—H ; $$\mu_r = \frac{m_1 m_2}{m_1 + m_2} = \frac{12\times1}{12+1} = \frac{12}{13} = 0.92$$

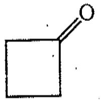
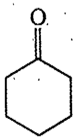
(*ii*) For C—D ; $$\mu = \frac{12\times2}{12+2} = \frac{24}{14} = 1.71$$

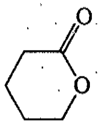
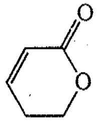
For calculating the wave number of absorption (C—D), we write

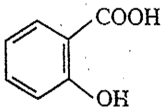
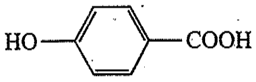
$$\frac{\bar{V}_D}{\bar{V}_H} = \sqrt{\frac{\mu_H}{\mu_D}} = \sqrt{\frac{0.92}{1.71}} = 0.73$$

Thus, the C—D str absorption band will appear at 3000 × 0.73 = **2190 cm^{-1}**.

20. How will you distinguish between the following pairs on the basis of Infra-red spectroscopy ?

(*i*)  and 

(*ii*)  and 

(*iii*)  and 

Ans. (*i*) In cyclic ketones, νC = O str absorption increases as the size of the ring decreases (ring strain increases). Thus, cyclobutanone shows carbonyl absorption at higher wave number (nearly 1788 cm^{-1}) whereas cyclohexanone absorbs at almost the same wavenumber at which saturated ketones absorb.

(*ii*) The νC = O absorption in case of conjugated cyclic ketone absorbs at lower wave number as compared to the other. The absorption bands are sharp in both the cases.

(*iii*) In *o*-Hydroxy benzoic acid (salicyclic acid), we see intramolecular hydrogen bonding. The absorption band due to O—H str appears as a broad bond at nearly 3300 cm^{-1} and is concentration independent. But in *p*-hydroxybenzoic acid, the association is due to intermolecular hydrogen bonding. Absorption occurs at about 3000 cm^{-1} as a broad band. The position of absorption is raised as the solution is diluted by adding a non-aqueous solvent such as carbon tetrachloride.

21. Which of the following diatomic molecules do not absorb in the Infra-red region.

HCl, ClBr, N_2, H_2, O_2

Ans. N_2, H_2 and O_2 are homodiatomic molecules. Their molecular vibrations are not accompanied by any change in dipole moment and hence they do not absorb in IR region.

22. Why is methanol a good solvent for UV but not for IR spectroscopy ?

Ans. The reason is that methanol (CH_3OH) does not absorb in UV, *i.e.* it is transparent above 200 *m*μ. But is absorbs strongly in the infra-red region (4000 cm^{-1} to 667 cm^{-1}).

23. What is the effect of hybridisation of carbon on the stretching frequency of C—H bonds ?

Ans. With the increase in s-character of hybridised carbon, the force constant (k) for C—H bond increases and hence the value of stretching frequency increases.

$\overset{sp^3}{C}$—H str (2950–2850 cm^{-1}) $=\overset{sp^2}{C}$—H str (3000–3100 cm^{-1}) $\equiv\overset{sp}{C}$—H (3300 cm^{-1})

24. *cis*-1, 2-dichloroethene is Infra-red active while trans-1, 2-dichloroethene is IR inactive. Explain.

Ans. When the compound under examination is exposed to IR radiations, *cis*-1, 2-dichloroethene undergoes a net change in dipolemoment and hence absorbs in IR. Thus, it is IR active. On the other hand, trans-1, 2-dichloroethene is symmetrical and does not show any change in dipole-moment. Hence, it is IR inactive.

25. How will you note the progress of the oxidation of 2-Propanol to Propanone in Infra-red spectroscopy ?

Ans. 2-Propanol shows a strong band at 3400-3200 cm^{-1} due to O—H str. On the other hand, propanone shows a strong band at 1715 cm^{-1} due to C = O str. As oxidation of 2-propanol takes place, the intensity of O—H band decreases while that of C = O str increases. On complete oxidation, the band at 3400 cm^{-1}-3200 cm^{-1} will be missing and an intense band at 1715 cm^{-1} will appear.

26. How will you distinguish between *cis* and *trans*-cinnamic acid ?

Ans. *cis*-Cinnamic acid absorbs at a higher wave number as compared to its trans-isomer. It is partially explained due to the steric effect caused by the bulky groups on the same side of the double bond. Due to repulsive interactions, the C = O part of —COOH group goes out of the plane of the double bond. Thus, conjugation diminishes and hence νC = O absorption occurs at a higher wave number.

27. Can you detect an anhydride by Infra-red spectroscopy ?

Ans. Yes. An anhydride can be detected by the formation of two bands which appear at :

(*i*) 1850-1800 cm^{-1} and (*ii*) 1790-1740 cm^{-1}. The presence of unsaturation causes lowering in absorption positions by 20-40 cm^{-1}.

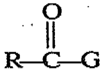
28. How will you distinguish between CH_3CONH_2 and $CH_3CH_2NH_2$?

Ans. In case of a acetamide, a strong absorption band appears near 1600 cm^{-1} which will be missing in ethylamine.

29. Infra-red absorption due to carbonyl stretching occurs at higher frequencies than stretching of C = C bond. Explain.

Ans. This is explained in terms of π-bond of the C = O bond, which is considerably stronger than the π-bond in C = C bond.

30. An acyl group is readily detected from the infra-red spectroscopy since the C = O stretching frequency varies with the functional group, *i.e.* with G. From the following trends in the strong carbonyl stretching absorption peak in the 1700 cm^{-1} region, identify a particular acid derivative in each case :



$$R-\overset{\overset{\large O}{\|}}{C}-G$$

(*i*) 1700-1815 cm^{-1},

(*ii*) 1740-1790 cm^{-1} and 1800-1850 cm^{-1} (two bands),

(*iii*) 1720-1750 cm^{-1} and (*iv*)1630-1690 cm^{-1}

Ans. (*i*) Must be acid chloride

(*ii*) The two absorption bands at the given positions show that the compound is an anhydride.

(*iii*) The absorption position at 1720-1750 cm^{-1} shows that the compound is an ester.

(*iv*) The absorption position at a much lower wave number is clearly due to C = O str in an amide. The lowering is due to the fact that the lone pair on N-atom is in conjugation with the carbonyl group.

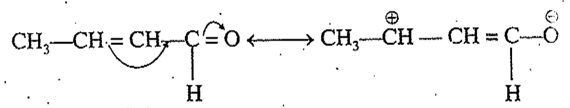
31. The C—H frequency of is a compound observed at 2910 cm^{-1}. Predict the corresponding C—D stretching frequency whose hydrogen is replaced by deuterium.

Ans. $\nu C{-}H = \sqrt{2} \cdot \nu C{-}D$

$$\therefore \quad \nu C{-}D = \frac{\nu C-H}{\sqrt{2}} = \frac{2910}{1.414} = 2058\ cm^{-1}.$$

32. An aliphatic aldehyde containing unconjugated double bond shows C = C and C = O stretching at ~1645 cm^{-1} and 1720-1740 cm^{-1} respectively. Explain why crotonaldehyde shows the corresponding absorptions at 1700 cm^{-1} and 1630 cm^{-1}.

Ans. In crotonaldehyde, C=C is in conjugation with C=O and can be written in the resonating structure as below :



Due to resonance the frequencies of absorption due to C = O str as well as C = C str get lowered.

33. What do you mean by Fundamental vibrations and overtones ?

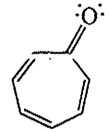
Ans. The fundamental vibrations correspond (in quantum treatment) to the first vibrational transition from the zeroth vibrational level *i.e* $v_0 \rightarrow v_1$. The term overtone is used for any multiple of the given fundamental frequency. Thus, the transition from $v_0 \rightarrow v_2$ and $v_0 \rightarrow v_3$ are the first and the second overtones of the fundamental.

34. How will you explain that the carbonyl stretching frequency of an aldehyde is slightly higher than that of the corresponding methyl ketone ?

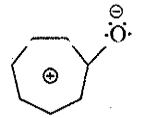
Ans. In case of methyl ketone (CH_3—CO—), the electron donating group is methyl which leads to more single bond character in carbonyl and hence νC = O stretching is lowered.

35. The carbonyl stretching frequency in 2, 4, 6-cycloheptatrienone is exceptionaly low. Explain.

Ans. The exceptional low value of νC = O str in 2, 4, 6-cycloheptatrienone is due to the conjugation effect. The cyclohepta trienyl cation (II) which is tropylium cation



I



II

contains 6 π electron cloud and its structure is stable. As a result of strong resonance contribution, the νC = O str frequency is quite low.

36. Saturated aliphatic monocarboxylic acid, show carbonyl stretching near 1755 cm^{-1} whereas the saturated aliphatic ketones absorb near 1720 cm^{-1}. Explain.

Ans. In monocarboxylic acid, the carbonyl group is bound to oxygen atom. Now two opposing effect strongly influence the carbonyl frequency. These effects are inductive effect and mesomeric effect. Out of these, inductive effect dominates and thus absorption frequency in case of carboxylic acid is more.

3.16 Important Tips for Interpreting an Infra-red Spectrum

Following are some useful tips for interpreting an infra-red spectrum.

(*i*) Always place more reliance upon the negative evidence. The absence of a band in a particular region is a sure indication of the absence of group/groups absorbing in that region. For example if there is no absorption in the region 1900–1600 cm^{-1}, the carbonyl group $\left(>C{=}O \right)$ must be absent in the compound.

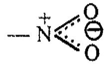
(*ii*) Always start from the higher frequency end of the spectrum. Mostly stretching vibrations occur in the region above 1500 cm^{-1} and are most informative. The region 1500–1000 cm^{-1} may be used for confirming esters, alcohols, ethers etc.

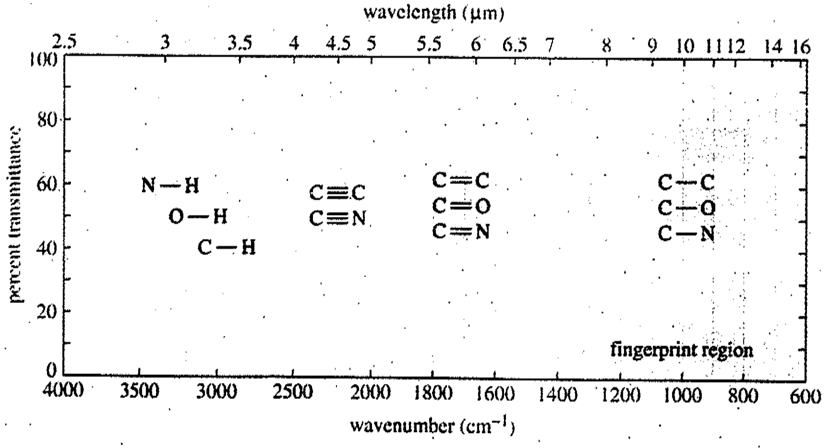
(*iii*) To distinguish between intermolecular and intramolecular hydrogen bonding, the spectra of the sample are scanned at two different concentrations. Various solvents may be used to study association effects.

(*iv*) For easy detection of the various groups present in the compound, the infra-red region (4000 to 667 cm^{-1}) may be visualised as consisting of the following portions:

Table T_3—15.

Type of Vibration	*Class of Compound*	*Frequency (cm^{-1})*	*Intensity*
C – H Str	(*i*) Alkanes	2960-2850	(s)
C – H Str	(*ii*) Alkenes	3100-3010	(s)
C – H Str	(*iii*) Alkynes	~ 3300	(s)
C – H Str	(*iv*) Aromatics	3150-3020	(s)
C – H Str	(*v*) Aldehydes	~ 2820, 2775-2720	(w) (w)

C = C Str	(*i*) Alkenes	1675-1600	(m, w)
C ⩦ C Str	(*ii*) Aromatics	1600-1450	(m, w)
C ≡ C Str	(*iii*) Alkynes	2260-2100	s
C = O Str	(*i*) Aldehydes	1740-1720	(s)
C = O Str	(*ii*) Ketones	1725-1705	(s)
C = O Str	(*iii*) Carboxylic acids	1725-1700	(s)
C = O Str	(*iv*) Esters	1750-1730	(s)
C = O Str	(*v*) Amide	1680-1630	(s)
C = O Str	(*vi*) Anhydrides	1850-1800 1790-1740	(s) (s)
C = O Str	(*vii*) Acid chlorides	~ 1790	(s)
O – H Str	(*i*) Alcohols and Phenols (dilute Solution)	3650–3580	(sharp, v)
O – H Str	(*ii*) Alcohols, Phenols (Hydrogen bonded)	3550-3200	(b, s)
O – H Str	(*iii*) Carboxylic acids	2700-2500	(b)
N – H Str	(*i*) 1°-amines, amides (Free) (Two bands)	~ 3500	(m)
N – H Str	(*ii*) 1°-amines, amides (H-bonded)	~ 3400	(m)
N – H Str	(*iii*) 2°-amines, amides Free-(one band)	3500-3300	(m)
N – H Str	(*iv*) 2°-amines, amides (Hydrogen bonded)	3310-3140	(m)
C ≡ N Str	Nitriles	2260-2220	(m)
 $-\overset{+}{N}(=O)O^{-}$ (Str)	Nitro compounds		
	(*i*) Asymmetric	1620-1535	(s)
	(*ii*) Symmetric	1375-1275	(v)



(*a*) 3600–3200 cm^{-1}. The appearance of the bands in this region shows the presence of —OH, —NH_2, NH group in the compound. The position, intensity and the breadth of the bands tell whether the group is free, intramolecularly bonded or exhibit intermolecular hydrogen bonding. ≡ C—H str also shows a medium band near 3300 cm^{-1}.

(*b*) 3200–3000 cm^{-1}. Absorptions due to C—H str and Ar—H stretching occur in this region. The sharp bands of weak to medium intensities are observed.

(*c*) 3000–2500 cm^{-1}. The absorptions due to C—H stretching from methyl or methylene groups occur in this region. The asymmetric C—H stretching occurs at slightly higher wave number as compared to that of symmetric C—H str. A very broad band between 3000—2500 cm^{-1} is most characteristic of acids (—COOH group). Two weak bands, one at 2720 cm^{-1} and the other near 2820 cm^{-1} are most characteristic of C—H stretching in aldehydes. The higher frequency band is seldom observed.

(*d*) 2300—2100 cm^{-1}. This is the region in which alkynes, cyanides, cyanates, isocyanates absorb. The bands observed are weak and variable. —C≡C stretching occurs between 2140–2100 cm^{-1}. —C ≡ N stretching shows a variable band between 2260–2200 cm^{-1}. Isocyantes show a strong band between 2280–2250 cm^{-1}.

(*e*) 1900–1650 cm^{-1}. Strong bands due to C = O stretching occur in this region.

Anhydrides show two strong bands in the region 1850–1740 cm^{-1}. Esters, aldehydes, ketones, lactones, carboxylic acids, amides show strong bands due to C=O stretching in this region. Imides are also recognised by two strong bands (doublet) in the region around 1700 cm^{-1}. Following points regarding C = O stretching may be helpful.

(*i*) α, β-unsaturation lowers the frequency of absorption by 15–40 cm^{-1}. But in amides, a small absorption shift towards lower frequency is observed.

(*ii*) Increase in the ring strain in case of cyclic ketones raises νC = O absorption.

(*iii*) Hydrogen bonding to the carbonyl compound lowers νC = O absorption by 40–60 cm^{-1}.

(*f*) 1600–1000 cm^{-1}. This region is very important for identifying nitro compounds and also confirming the presence of ethers, esters, primary, secondary and tertiary alcohols. The appearance of strong bands due to C—O stretching at 1300–1050 indicates (*i*) an ester provided C = O stretching is observed in the region 1750–1735 cm^{-1} and (*ii*) an alochol if O–H stretching free and/or bonded occurs between 3600–3200 cm^{-1}. Ethers show a strong band in the region 1150–1070 cm^{-1} due to C—O stretching in —C—O—C—. This region also helps to identify C—H str in aromatic compounds. For aromatic rings, medium bands around 1600 cm^{-1}, 1580 cm^{-1} and 1500 cm^{-1} are observed.

(*g*) Below 1000 cm^{-1}. This region is very useful in identifying the type of substitution on the aromatic ring:

(*i*) a strong band at 770–730 cm^{-1} (*s*) shows monosubstitution.

(*ii*) ortho and para disubstituted compounds show one band each. The latter absorbs at a higher wavenumber.

(*iii*) Meta-disubstituted compounds are usually recognised by two medium bands in the region 850–710 cm^{-1}.

3.17 Important Terms and Definitions in Infra-red Spectroscopy

1. **Infra-red region.** For structure elucidation, the Infra-red region is from 4000–667 cm^{-1}. Out of this, the high frequency region (4000–1300 cm^{-1}) is the functional group region and that from 1300–667 cm^{-1} is the finger print region.
2. **Infra-red spectrum.** I.R. spectrum of a compound represents its energy absorption pattern in the infra-red region. It is obtained by plotting percent absorbance/transmittance of the

infrared radiation as a function of wave number over a particular range.

3. **Fundamental vibrations and overtones.** The fundamental vibrations correspond in the quantum treatment to the first vibrational transition from the zeroth vibrational level to the first ($\nu_0 \rightarrow \nu_1$). The term overtone is used to apply to a multiple of fundamental frequency. The transition $\nu_0 \rightarrow \nu_2$ and $\nu_0 \rightarrow \nu_3$ are the first and the second overtones of the second overtones of the fundamental and require radiation of twice or three times of its frequency.
4. **Infra-red active compounds.** Infra-red radiation is absorbed when the molecule undergoes a net change in the dipole-moment. Total symmetry about a bond eliminates certain absorption bands. Thus, the number of absorption bands does not exactly coincide with the number of fundamental vibrations. Clearly, some of the fundamental vibrations are infra-red active whereas others are not.
5. For the detection of functional groups, the functional group region is most important and for the comparison of compounds containing the same functional group, fingereprint region is useful.
6. The presence of electron donating group and conjugation lower the wave number of absorption while the presence of electron attracting groups raise the wave number of absorption.
7. Hydrogen bonding lower the wave number of absorption. Lowering in wave number and broadening of band are significant in case of intermolecular hydrogen bonding. Inter molecular hydrogen bonding is concentration dependent while intramolecular hydrogen bonding is not.
8. For the detection of C ≡ C and C ≡ N groups, the absorption for ≡C—H str may also be observed, if any.
9. The axial and equitorial positions of —OH group can be distinguished in Infra-red. The frequency of the axial hydroxyl group is higher than that of the equitorial.
10. The detection of C=O str in aldehydes can only be confirmed if there is a pair of absorption bands between 2720–2820 cm^{-1}.
11. For Alkynes, ≡C—H str near 3300 cm^{-1} may not be confused with O–H str as its position is uneffected by dilution.
12. For primary amines and primary amides, two free N–H bands appear near 3500, 3400 cm^{-1} and near 3350, 3150 cm^{-1}, hydrogen bonded bands appear.

    For secondary amines and amides, one free band appear near 3400 cm^{-1} and for bonded structure, the band appears at 3320–3140 cm^{-1}.
13. In case of acids, the O—H str absorption band is very broad and appears between 3000–2500 cm^{-1}.
14. In case of acid anhydrides, a doublet appears because of coupled vibrations of two C = O groups. The high frequency band is assigned to symmetrical vibrations and lower frequency band to asymmetric vibrations.
15. Two different compounds cannot have the same Infra-red spectrum. But the Infra-red spectrum of enantiomers is the same.

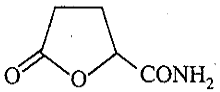
FURTHER READING

1. C.N.R. Rao, Chemical applications of Infra-red spectroscopy. Academic Press, New York (1963).
2. Nachod and Zuckkerman, Determination of organic structure by physical methods. Academic Press (Five Volumes).

3. Margareta Avram and Mateescu, Infra-red spectroscopy (Applications in organic chemistry)—Wiley Interscience 1972.
4. L.J. Bellamy, The Infra-red spectra of complex molecules, 2nd ed. Methuen, London, 1958.
5. N. Luff, D.M.S., Working Atlas in Infra-red, Butterworths, London (1970) (very valuable collection grouped according to functional class etc.).
6. S.K. Freeman, Applications of Laser and Raman spectroscopy, Wiley, London (1973).
7. J.R. Dyer, Applications of absorption spectroscopy of organic compounds, Prentice Hall, Eaglewood Cliffs, N.J. 1965.
8. Nakanishi, Koji Infra-red absorption spectroscopy—Practical, San Francisco, Holden Day
9. E.L. Eliel, Stereo-chemistry of carbon compounds, New York McGraw Hill.
10. R.M. Silverstein and G.C. Bassler, Spectrometric identification of organic compounds, Wiley, New York (1964).
11. Scheinmann F, Ed. An introduction of spectroscopic methods for the identification of organic compounds. Pergamon Press, New York (1970).
12. James, W. Cooper, Spectroscopic techniques for Organic Chemists, Wiley Interscience 1980.

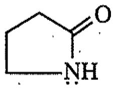
REVIEW QUESTIONS

1. Define Infra-red spectroscopy. Describe the various molecular vibrations in the technique. What is the major requirement for Infra-red absorption ?
2. (*a*) What are the factors which influence the positions of absorption frequencies from their normal value?
   (*b*) Write a note on Fermi Resonance.
3. (*a*) How will you distinguish an aliphatic aldehyde from an aliphatic ketone?
   (*b*) Describe the effect of intermolecular and intramolecular hydrogen bonding on the position of absorption frequency of a compound. Give an example.
4. Write the expected infra-red peaks for the following compounds :
   (*i*) Acetophenone (*ii*) Benzamide
   (*iii*) Acetic anhydride (*iv*) Dimethyl cyclopropanone
   (*v*) Methyl benzoate (*vi*) 2-Formyl cyclohexanone
   (*vii*) Salicylaldehyde and (*viii*)



5. Explain the electronic factors which influence the absorption frequency
6. (a) How will you distinguish between an aliphatic and an aromatic compound?
   (*b*) Explain why does maleic acid absorb at a higher frequency as compared to fumaric acid?
   (*c*) Write the effect of ring size on carbonyl absorption in case of cycloketones.
7. (*a*) Write a short note on finger print region.
   (*b*) Briefly describe the scanning of an Infra-red spectrum of an organic compound.
8. (*a*) What do you mean by coupled vibrations and how do they arise?
   (*b*) Distinguish between the following pairs of compounds with the help of infra-red technique.
      (*i*) Ethanol and Dimethyl ether
      (*ii*) Propanal and Propanone
      (*iii*) cis and trans cinnamic acid
      (*iv*) Ethanol from Ethyl amine

9. (*a*) Arrange the following compounds in order of increasing wave number of carbonyl absorption in the intra-red spectrum :
   (*i*) Acetophenone, *p*-nitroacetophenone, *p*-amino acetophenone.
   (*ii*) Cyclohexenone, Butanone,
   (*iii*)

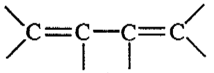


(b) Write the expected I.R. peaks for the following compounds :
   (*i*) *p*-nitrophenol
   (*ii*) *p*-nitrobenzoic acid
   (*iii*) acetic anhydride

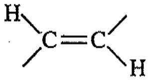
(c) An organic compound (A) with molecular formula C_3H_7NO gives absorption peaks in the regions 3413 (*m*), 3236 (*m*), 3030–2899 (*m*), 1667 (*s*), 1634 (*s*) and 1460 cm^{-1} (*s*). Give its probable structure.

10. How will you detect the following types of compounds by infra-red spectroscopy?

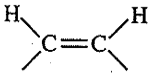
(*a*)



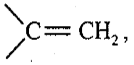
(*b*)

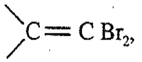


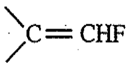
and



11. (*a*) List the types of vibrations which may occur in CH_2=CH–CH_2Br.
(*b*) Arrange the following sets of double bonds in order of increasing stretching frequencies:







(*c*) Ethyl acetate absorbs at 1735 cm^{-1}. At which wave number phenyl acetate is expected to absorb?

12. (*a*) The infra-red* spectrum of methyl salicylate shows peaks at 3300, 1700, 3050, 1540, 1590 and 2990 cm^{-1}. Attribute these peaks to the following structures:
   (*i*) CH_3
   (*ii*) C = O
   (*iii*) OH group on ring.
   (*iv*) aromatic ring.
(*b*) Why is methanol a good solvent for UV and not for IR determination?

13. What do you mean by the number of fundamental vibrations ? How will you detect the type of hydrogen bonding involved in a particular compound by intra-red spectrum ?

14. Discuss in detail the various factors which influence the vibrational frequency of a particular group. Give examples.

15. (*a*) What are the various solvents which are generally used in infra-red technique? How the change in polarity of the solvent affect the position of absorption?
(*b*) Which groups do you detect on the basis of the following data : 2841 (*w*), 2755 (*w*), 1686 (*s*), 1605, 1460 cm^{-1} (*w*).

16. Discuss at least three types of groups for which the study of finger print region is most essential.

17. How will you distinguish the following pairs of compounds with the help of Infra-red spectrum?
   (*i*) CH_3CH_2OH and CH_3—O—CH_3
   (*ii*) CH_3CH_2CHO and CH_3—CO—CH_3
   (*iii*) Maleic and fumaric acid

18. Discuss the inductive and the mesomeric effects influencing the carbonyl absorption frequency. Give examples.

19. How will you detect the presence of
   (*a*) Cyclic and acyclic anhydride
   (*b*) Primary and secondary amides
   (*c*) Conjugated and unconjugated nitro-compound in an organic compound?

20. Discuss the following statements:
   (*i*) Hydrogen bonding raises the wave-length of absorption.
   (*ii*) The presence of –I effect raises the wave-number of absorption.
   (*iii*) Conjugation raises the wavelength of absorption of a particular group.

21. Explain giving reasons why
   (*i*) the νC = O frequency of absorption for β-lactone is higher as compared to γ-lactone.
   (*ii*) α, β-unsaturated ester absorbs at a higher wave length as compared to a saturated analogue.
   (*iii*) A compound in the vapour state absorbs for a particular bond (stretching frequency) at a higher wave number as compared to that when it is in the solid state?

22. Describe some characteristic absorption bands with their probable region and intensity for the following functional groups:
   (*i*) Aldehydes
   (*ii*) Esters
   (*iii*) Anhydrides
   (*iv*) amides
   (*v*) Ethers
   (*vi*) meta-disubstituted benzenes

23. Discuss the various types of stretching and bending vibrations which arise in aromatic compounds in their Infra-red spectrum.

24. Discuss all types of stretching and bending vibrations with their probable values and respective intensities for the following compounds:
   (*i*) Salicylic acid
   (*ii*) Benzamide
   (*iii*) Acetyl acetone (both in keto and enol forms)
   (*iv*) Phthalimide
   (*v*) Benzoic anhydride
   (*vi*) Camphor
   (*vii*) Crotonic acid (Trans)
   (*viii*) Benzanilide

25. How will you classify the following types of compounds with the help of Infra-red spectroscopy?
   (*i*) Primary, secondary and tertiary alcohols
   (*ii*) Axial and equitorial O—H group
   (*iii*) Alkane nitrile and Benzonitrile
   (*iv*) Four and five membered cyclic ketones
   (*v*) Mono and disubstituted benzene.

MULTIPLE CHOICE QUESTIONS

Choose the correct answer:

1. Vibrational transition exists in
   (*a*) Infra-red (*b*) microwave (*c*) radio wave region of the spectrum
2. The total number of normal modes of vibration of a linear molecule consisting of N atoms is given by:
   (*a*) $(3N - 6)$ (*b*) $(3N - 5)$ (*c*) $(3N - 7)$
3. For a pure rotational spectrum, the selection rule is
   (*a*) $\Delta J = +1$ (*b*) $\Delta J = \pm 2$
   (*c*) $\Delta J = 0$, provided the molecule has permanent dipolemoment.

4. The IR band spectra show the changes in vibrational and rotational energies of a molecule subject to selection rule:
(*a*) $\Delta v = 0, \Delta J = \pm1$ (*b*) $\Delta v = \pm1, \Delta J = \pm1$
(*c*) $\Delta v = \pm1, \Delta J = \pm2$

5. For a linear molecule such as HCL, the number of modes of vibration are:
(*a*) zero (*b*) 1 (*c*) 2 (*d*) 3

6. For a non-linear molecule like H_2O, the number of vibrational modes are:
(*a*) 3 (*b*) 4 (*c*) 5 (*d*) 6

7. For CO_2 molecule, number of modes of vibration are:
(*a*) 3 (*b*) 5 (*c*) 4 (*d*) 6

8. The unit of force constant in CGS unit is:
(*a*) dyne cm^2 (*b*) Joule cm^{-1} (*c*) dyne cm^{-1} (*d*) None

9. The factor (s) on which the wave number of absorption depends in infra-red spectroscopy is/are:
(*a*) Inductive effect (*b*) Field effect (*c*) Hydrogen bonding (*d*) all of these

10. For a same organic compound in all the three states, the absorption frequency has the least value when the compound is in:
(*a*) liquid state (*b*) solid state
(*c*) Vapour state (*d*) same in all the three states

11. In infra-red spectroscopy, the pair of isomers, which cannot be distinguished is / are:
(*a*) cis-trans/isomers (*b*) functional isomers
(*c*) enantiomers (*d*) Position isomers

12. The cycloalkanones, the frequency of absorption for carbonyl group ie $vc = 0$ increases with
(*a*) increase in size of the ring (*b*) decrease in size of the ring
(*c*) decrease in bond angle. (*d*) None of these

13. Primary amide (say $RCONH_2$) shows two absorption bands between 3400-3500 cm^{-1}. On treatment with P_2O_5, the compound formed absorbs at
(*a*) 3500 cm^{-1} (*b*) 1650 cm^{-1} (*c*) 2256 cm^{-1} (*d*) 3250 cm^{-1}

14. The absence of absorption bands near 1600, 1580 and 1500 cm^{-1} is a sure proof for the absence of:
(*a*) aromatic ring (*b*) Carbonyl group
(*c*) –OH group (*d*) Secondary amino group.

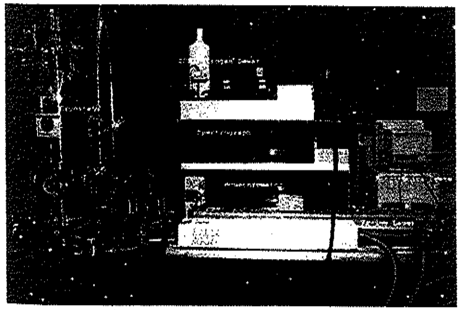
15. The type of hydrogen bonding in organic compounds can be distinguished by taking the spectra after dilution with:
(*a*) water (*b*) methyl alcohol
(*c*) Carbon tetrachloride (*d*) acetone.

ANSWERS. 1. (*a*) 2. (*b*) 3. (*a*) 4. (*b*) 5. (*b*) 6. (*a*) 7. (*c*) 8. (*c*) 9. (*d*)
10. (*b*) 11. (*c*) 12. (*b*, *c*) 13. (*c*) 14. (*a*) 15. (*c*)

CHAPTER

4

Raman Spectroscopy



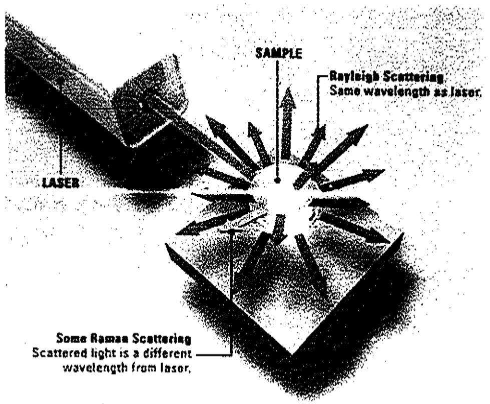
4.1 Introduction
4.2 Quantum theory of Raman Effect
4.3 Theory of Raman spectra- Stoke's and anti-stoke's lines
4.4 Instrumentation
4.5 Conditions for Raman spectroscopy
4.6 Equivalence of Beer Lambert law of absorption in Raman Scattering
4.7 Characteristic Parameters of Raman lines
4.8 Raman spectra of diatomic molecules
4.9 Rotational-Vibrational Raman Spectra
4.10 Vibrational Raman Spectra of Polyatomic Molecules
4.11 Rule of Mutual Exclusion Principle
4.12 Moment of Inertia of diatomic molecules and Raman Spectroscopy
4.13 Infra-red and Raman Spectra are Complementary
4.14 Structure elucidation of Raman Spectroscopy
4.15 Numericals on Raman Spectroscopy
4.16 Importance of Raman Spectra
4.17 Applications of Raman Spectroscopy
4.18 Important terms and Definitions in Raman Spectroscopy
4.19 Short Questions with Answers

4.1 Introduction

When a substance (in any state) is irradiated with a monochromatic light of definite frequency (ν), the light scattered at right angles to the incident light contains lines of

(*i*) incident frequency and

(*ii*) also of lower frequency.



Sometimes lines of higher frequency are also obtained. Thus, certain discrete frequencies above and below that of the incident beam will be scattered. It is called **Raman Scattering.**

The lines with lower frequency are called **Stoke's lines.** Also the lines with higher frequency are called **Antistoke's lines.** The line with the same frequency as that of the incident light is called **Rayleigh line.** It is observed that the difference between the frequency of the incident light and that of a particular scattered line is constant and depends only upon the nature of the substance which is irradiated. It is completely independent of the frequency of the incident light. If ν_O is the frequency of the incident light and ν_R is the frequency of a particular scattered line, then:

$$\Delta\nu \text{ (Difference)} = \nu_o - \nu_R$$

This difference is called **Raman frequency** or **Raman shift.**

It may be noted that Raman frequencies for a particular substance are characteristic of that substance. The various observations made by Raman are called Raman effect. Also the spectrum obtained is called **Raman spectrum.**

Quantum theory of Raman Effect

Raman Scattering can be easily understood in terms of quantum theory of radiation. Photons (each of energy $h\nu$) can be imagined to undergo collisions with molecules. In case the collision is perfectly elastic, they will get deflected unchanged. A detector collects energy at right angles to the incident beam and thus receives photons of energy $h\nu$. It may happen that energy is exchanged between the incident photon and the molecule during collision. Such collisions are called inelastic collisions. The molecule of the substance can lose or gain energy according to the quantum laws. Thus, ΔE (energy change) is the difference in energy between two of its allowed states. Clearly, ΔE represents a change in the vibrational and/or rotational energy of the molecule. In case the molecule gains energy (ΔE), the photon will be scattered with energy, $h\nu - \Delta E$ and the equivalent radiation will have a frequency $\nu - \Delta E/h$. Also if a molecule of the substance loses energy (ΔE), then the scattered frequency with be $\nu + \Delta E/h$. Radiation scattered with a frequency lower than that of incident beam is called stoke's radiation and that with higher frequency is called antistokes, radiation. Since the stoke's radiation is accompanied by an increase in molecular energy, it is generally more intense than antistoke', radiation.

Theory of Raman Spectra (Stoke's and antistoke's lines)

When a beam of monochromatic light is passed through liquid or gas (Called Scatterer), a small fraction of it is scattered due to collisions between molecules of the scatterer and photons of light. It is explained by assuming that a complex is formed between a molecule and a photon during very short interval (~ 10^{-15} sec) of collision. This complex has energy lower than the excited molecular electronic state. In other words, we can say that photon has energy $h\nu$, insufficient

to cause a transition of the molecule from the ground electronic state with low vibrational and rotational states to a higher electronic state as shown in Fig *4.1.* Two cases may arise depending upon whether a collision between a photon and a molecule in its ground state is elastic or inelastic in nature.

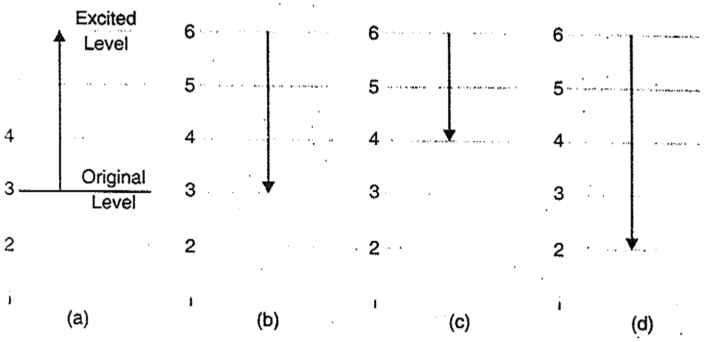


Fig. 4.1. (a) Energy absorbed by the molecule and Rayleigh Scattering (b) Formation of Stoke's and (c) Formation of anti-stoke's lines

Case 1. If the collision is elastic, the complex will dissociate to give the photon and molecule of the same energy which it had before collision. This is equivalent to saying that the molecule merely deviates the photon without absorbing its energy or the collision merely induces forced oscillations in the molecule. This leads to the appearance of unmodified lines (or unmodified frequency of light) in the scattered beam and this explains **Rayleigh scattering.**

Case 2. **If the collision is inelastic,** there will be exchange or transfer of energy between the scattering molecule and the incident photon. Two different cases may arise here:

(*i*) The molecule is in lower vibrational and rotational level before collision and is present in any one of higher rotational-vibrational state of the same level (as allowed by selection rules) after excitation and emission of photon. Thus, the molecule absorbs or gains energy equal to the difference in the two energy levels involved. Because this energy is supplied by photon of incident light, the frequency of emitted photon is less. (Fig *4.1.* (*b*)).

(*ii*) Before the collision, the molecule is present in one of the excited vibrational and rotational energy state but after emission of photon, it occupies one of lower vibrational energy state of the same level according to selection rule. Since the molecule imparts some of its intrinsic energy to the incident photon, the emitted photon has higher energy (or frequency) than the incident photon (Fig *4.1.* (*c*)).

These two cases of inelastic collision between photon and a molecule constitute Raman scattering. As such inelastic scattering was observed by C.V. Raman in 1928. The frequency of this scattered light or emitted photon which is either higher or lower than that of the incident photon is called **Raman frequency** (ν_R).

Treating the scattering phenomenon as a collision between the photon and the molecule with the final result that the molecule is shifted from energy a level with energy ε' to another level with energy ε'' and applying the law of conservation of energy, we may write :

Total energy before collision = Total energy after collision

$$\varepsilon' + \frac{1}{2}mv'^2 + h\nu_0 = \varepsilon'' + \frac{1}{2}mv''^2 + h\nu_R$$

Where
ν_0 = frequency of incident photon.
ν_R = frequency of scattered photon
v' = velocity of molecule before impact
v'' = velocity of molecule after impact
ε' = Intrinsic energy of molecule before impact

ε'' = Intrinsic energy of molecule after impact.

As collision does not cause any appreciable change of temperature and further if temperature is kept constant during the experiment, we have :

$$\frac{1}{2}mv'^2 = \frac{1}{2}mv''^2$$

Therefore $\varepsilon' + h\nu_0 = \varepsilon'' + h\nu_R$ ...(ii) ($\because \nu_0$ = Frequency of incident light)

or $h(\nu_R - \nu_0) = \varepsilon' - \varepsilon''$ ...(iii)

or $\nu_R = \nu_0 + \frac{\varepsilon' - \varepsilon''}{h}$ ...(iv)

(*i*) If $\varepsilon' = \varepsilon''$, $\nu_R = \nu_0$ Which explains Rayleigh scattering (unmodified line)

(*ii*) If $\varepsilon'' > \varepsilon'$, $\nu_R < \nu_0$ *ie;* the frequency of scattering lines is less than that of the incident light. This gives **stoke's line** of Raman spectra.

(*iii*) If $\varepsilon'' < \varepsilon'$, $\nu_R > \nu_0$, which corresponds to **antistoke's line** of Raman spectra where frequency of scattering light is more than that of incident light.

If the quantum principle is applied to the change of intrinsic energy of molecule, we have

$\varepsilon'' - \varepsilon'$ or $\varepsilon' - \varepsilon'' = h\nu_m$ (Whether final level is lower or higher than initial one)

Where 'ν_m' is the characteristic frequency of the molecule.

Hence, equation (*iv*) becomes :

$$\nu_R = \nu_0 \pm \nu_m \quad ...(v)$$

The difference in the frequencies of Rayleigh (ν_o) and Rawan (ν_R) lines is called **'Raman shift'**

$$\text{Raman shift} = \Delta\nu = [\nu_R - \nu_0] \quad ...(vi)$$

The Raman shift is independent of the frequency of incident light *i.e.,* incident light may be at any frequency. However, Raman spectra is studied with visible or ultra-violet light. The equation (*iv*) shows that the Raman shift is a measure of difference in the energy of two involved levels of the molecule as is, therefore, characteristic of the molecule. The equation (*v*) shows that Raman lines are symmetrically situated on either side of the parent line corresponding to the frequency of Rayleigh line (ν_o) (*i*) with stoke's lines on the lower side of (ν_o) and antistoke's lines on the higher side of ν_o. **Stoke's lines are more intense than antistoke's lines**. The reason is that **stokes lines** are caused by molecules of lower energy level which is more populated and have more intensity of absorption. Antistokes lines are caused by molecules of higher energy level which are less populated and hence less intense. Ordinarily, less than one part in 10^6 of incident light undergoes inelastic scattering. So, Raman lines in the spectrum are very weak as campared to Rayleigh line of scattering. Therefore, long exposures are required with conventional light source. However, the use of laser a powerful monochro-matic source has considerably reduced the time and solved this problem. The most commonly used laser is He-Ne source with the wavelength of incident light as 3628A°.

Effect of Temperature on Raman lines : At room temperature, the number of molecules possessing low energy is more. Duete this, stoke's transitions will take place more frequently than antistoke's transitions. Duete this, stoke's lines are more intense But when the temperature is raised, the kinetic energy of the molecule increases and more number of molecules are raised to higher energy state. Thus, the antistokes lines will gradually increase their intensity also increases and they become prominent.

4.4 Instrumentation

It is known that Raman scattering is much weaker than Rayleigh scattering in which there is no chemical shift. The reason is that the interactions which produce Raman scattering are of higher order. Thus, most experiments require an intense source which is as monochromatic as possible. A laser with a narrow line width is usually used and the collected light must be carefully filtered to avoid the potentially overwhelming Rayleigh signal. The laser beam from Argon-ion laser is filtered for monochromaticity and directed by a system of mirrors to a focussing lens.

The beam is focused onto the sample. The scattered light which passes back through the same lens is then passed through a second lens into the first stage of the spectrometer. The spectrometer itself is separated into two stages (See Fig. *4.2.*). The first stage is called a mono-chromator and is used a filter. Its structure is basically two diffraction gratings, separated by a slit, with input and output focussing mirrors.

The incomming signals from the collecting lenses is focussed on the first grating, (G_1) which separates the different wavelength. The spread out light is then passed through a slit. Since light of different wavelengths is now travelling in different directions, the slit width can be tuned to reject wavelengths outside of a user defined range. The light which makes it through the slit is then refocused on the second grating (G_2). The grating is oriented such that the dispersion pattern is the mirror image of that from the first grating. Finally, the light is refocussed and sent out to the second stage. In the second stage, the filtered light is focussed on the final grating (G_3). The dispersed light is then analysed as a function of position, which corresponds to wave lengths. The signal as a function of position is read by the system detector. Here the detector is a multichannel charge-coupled device (CCD) array in which different positions (wave lengths) are read simultaneously. Wavelength and intensity information are read. It is Raman spectrum.

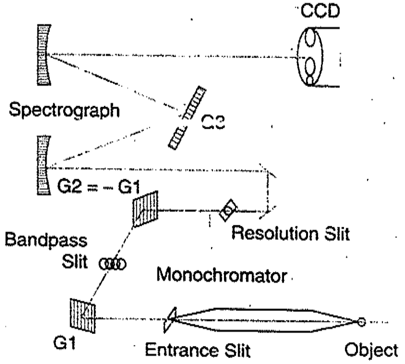


Fig. 4.2. Instrumentation–Raman Spectrophotometer.

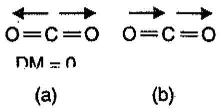
Conditions for Raman spectroscopy

The Raman spectroscopy involves the study of vibrational-rotational energy changes in molecules by means of scattering of light. Raman spectra occurs as a result of oscillation of a dipole-moment induced in a molecule by the oscillating electric field of an incident wave. As the induced dipolemoment is directly proportional to the polarisability of the molecule, the molecule must possess anisotropic polarisability which should change during molecular rotation or vibration for vibrational or rotational-vibrational Raman spectra. Anisotropic polarisability depends upon the orientation of the molecule and is explained as follows :

In the presence of an electric field, the electron cloud of an atom or molecule is distorted or polarised. In the case of an atom, the polarisability is isotropic because the same distortion is induced whatever the direction of the applied field. In case of a molecule, the extent of distortion (or polarisability) may change with the direction of field.

For centrosymmetric molecule like diatomics such as H_2,O_2,N_2 etc and linear molecules like CO_2 which possess a centre of symmetry, the vibration which are IR active are Raman active. This is in accordance to **'Mutual Exclusion Rule**. Consider the case of hydrogen molecule. According to the (3n – 6) or (3n – 5) rule, the molecule will have one fundamental vibrational frequency. It is shown as ← H – H →. As hydrogen atoms have the same phase, they will vibrate in phase in opposite directions with the same amplitude. The motion as → H – H → is ruled out since it leads to net translational motion and hence, a change in the centre of mass of the molecule. It is clearly not vibratory motion. Also ← H – H → is not accompanied by a change in the dipole-moment. Thus, hydrogen and also such homonuclear diatomic molecules do not show IR spectra. On the basis of mutual exclusion rule, the IR inactive fundamental will be **Raman active**.

In short, the molecule which shows a net change in dipole-moment are IR active. Carbon monoxide, Iodiono chloride (I-Cl) which show a change in the dipole-moment are IR active but hydrogen (H_2), nitrogen (N_2), chlorine (Cl_2) and other symmetrical diatomics are not IR active but instead are Raman active. Vibrational modes which are IR inactive may give rise to observable bands in the Raman spectra. Consider the case of carbon dioxide molecule. It is a linear molecule and four fundamental vibrations are expected for it. Out of these, symmetric streching vibration is infra-red in active since it produces no change in the dipolemoment of the molecule.



For symmetric stretching, **Raman spectrum** shows a strong band at 1337 cm^{-1}. The other two bending vibrations are equivalent and absorb at the same frequency of 667.3 cm^{-1}. The overtone of this is 1334.6 cm^{-1} (= 2 × 667.3 cm^{-1}) which is very close to 1337 cm^{-1}. Thus, fermi resonance takes place resulting in the shift of first level towards higher frequency. The mutual pertubation of 1337 cm^{-1} (Fumdamental) and 1334.5 cm^{-1} (overtone) gives rise to two bonds at 1285.5cm^{-1} and 1388.3 cm^{-1} having intensity ratio of 1 : 0.9.

Out of cis and trans, 1, 2-dichloroethene, trans-isomer shows no change in the dipole-moment. Thus C = C Str in trans-isomer is not IR active but is **Raman active**.

4.6 Equivalence of Beer lambert law of absorption in Raman Scattering

Consider that a single molecular species is exposed to radiation of intensity, I_o (ω cm^{-2}). The intensity of the scattered radiation (I_s) at a single Raman frequency is expressed as :

$$I_s = \sigma I_o (\omega)$$

where σ has the dimensions of cm^2.

Clearly, for N molecules, the total intensity of scattered radiations is

$$I_s = N \sigma I_o (\omega) \quad ...(i)$$

Let
ΔN = the number of molecules per ml.
A = area of cross-section illuminated in cm^2.
Δx = path length of the illuminated volume in cm.

Then,

$$N = \Delta N . A . \Delta x \quad ...(ii)$$

Combining (*i*) and (*ii*), we get

$$I_s = (\sigma \Delta N) (A I_o) (\Delta x) = k I \Delta x \quad ...(iii)$$

Here $I = AI_o$ and $k = \sigma \Delta N$ (loss factor in cm^{-1})

Relation (*iii*) is equivalent to Beer law for loss of energy from the exciting beam due to Raman scattering into a given Raman band.

4.7 Characteristic Parameters of Raman lines

Normal Raman Scattering is also called First order Raman Scattering. Raman scattering occurs when the intensity of incident radiation corresponds to that of the source. Normal Raman scattering is linear as the induced dipole moment varies linearly with the electric field of incident radiation. The important parameters include the (*i*) frequency shift (*ii*) the degree of polarisation (*iii*) the intensity and (*iv*) the width and the shape of the Raman lines.

(*i*) Frequency shifts of Raman lines. It may be noted that the frequency shifts of Raman lines from Rayleigh lines vary from 4000 cm^{-1} to a few wave numbers and are independent of the incident radiation. Frequency shifts (Δν) increase with increase in temperature.

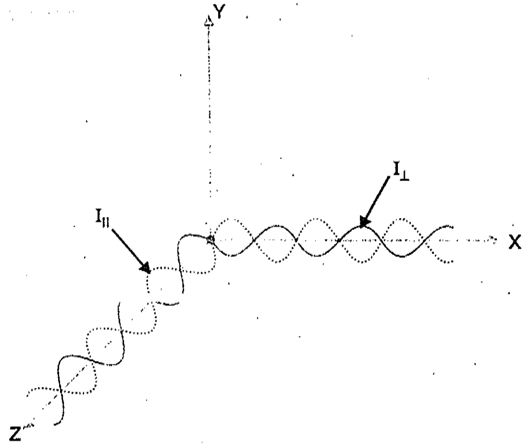


Fig. 4.3. Plane ‖ and Plane ⊥ to plane of polarisation of incident radiation.

(*ii*) Degree of Polarisation. The scattered radiation is partially polarised irrespective of the polarisation of incident radiation. The degree of polarisation of scattered radiation depends upon the structure and also the symmetry of the vibrational motion. The degree of polarisation helps to determine the phase changes in liquid crystals and solids when these substances are heated. When a beam of radiation is incident on a molecule with isotopic polarisability, it scatters. The scattered radiation may be perpendicular to the direction of incident radiation. The scattered radiation may be polarised in a plane-parallel and perpendicular to the plane of polarisation of incident radiation (See Fig. 4.3).

The plane of vibration or displacement is always perpendicular to the plane of polarisation of radiation. The degree of depolarisation is expressed as :

$$\rho = \frac{I_{\|}}{I_{\perp}}$$

where $I_{\|}$ = intensity of scattered radiation polarised in parallel plane.
$I_{\perp}$ = intensity of scattered radiation in perpendicular plane.

The above ratio is called the degree of depolarisation.

When the polarisability of the molecule remains isotopic during vibration, then ρ = 0. But when the polarisability of the molecule is anisotropic during vibrational motion, then ρ ≠ 0. Now the scattered radiation will be polarised in the parallel and perpendicular planes. The study of depolarisation of Raman lines helps in the assignment of vibrations and also in the analysis of molecular structure.

It is important to note that totally symmetrical vibrations cannot lead to depolarisation of radiation. It is found that non-symmetric vibrations give rise to intense Raman lines and symmetric vibrations appear as weak lines and sometimes are not even observed.

(*iii*) Intensity of Raman lines. As per **Placzek's theory**, the intensity of Raman line varies directly as $(\nu_o - \nu_{vib})^4$ except in the vicinity of Raman resonance scattering. Thus, it is clear that Raman lines depend upon the frequency of incident radiation. Stoke's lines are relatively stronger than antistoke's lines. The reason is that at room temperature, the higher levels are thinly populated than the lower levels. The intensity ratio of stoke's and antistoke's lines is expressed in terms of Maxwell-Boltzmann law :

$$\frac{I_a}{I_s} = e^{-\Delta E/kT}$$

where I_a and I_s are the intensities of antistoke's and stoke's lines respectively, k = Boltzmann constant.

For correct determination of the above ratio, which is $(\nu_o - \nu_{vib})^4$ for the stokes' lines and $(\nu_o + \nu_{vib})^4$ for antistokes' lines should be taken in account. With the increase in temperature, the antistoke's lines grow in number.

(*iv*) **Width and Shape of Raman lines.** The Raman lines are narrow in gases, liquids and crystals but in amorphous substances the lines are broad and diffuse. With increase in temperature, the width of the Raman lines increases.

Width of Raman line $\propto \sqrt{T}$ where T = temperature in Kelvin.

The reason for the increase in width is the anharmonicity of vibrations. In case of liquids, a continuum, called Raman wing appear on both sides of the Rayleigh lines. It shows continuous decreasing intensity. The reason for the Raman wing is that, in liquids, the vibrational motion is hindered. The intensity and width of Raman wing vary from liquid to liquid and depends upon the anisotropy of the molecules of the liquid.

4.8 Raman spectra of diatomic molecules

This technique is employed to find the vibrational, rotational, rotational-vibrational spectra and also the rotational and vibrational constants of homonuclear (H_2, N_2, O_2 etc) as well as of heteronuclear (HCl, NO, CO etc) diatomic molecules.

Pure Rotational Raman spectra of diatomic molecules (Selection rules for pure rotational spectra). Following are the selection rules for pure rotational spectra:

(*i*) For transition probability of Raman effect, $\Delta\alpha \neq 0$.

where $\Delta\alpha$ = change of polarizability along the internuclear axis.

(*ii*) The selection rules for the pure rotational Raman spectra of diatomic molecules are :

$$\Delta J = 0, \pm 2$$

Clearly, the selection rule, $\Delta J = 0$ corresponds to Rayleigh Scattering and selection rule $\Delta J = 2$ form Raman lines.

Energy of rotational level ($\bar{\nu}$ = wave number) with quantum number J is given by :

$$\bar{\nu} = BJ(J+1) \qquad \ldots(i)$$

When transition takes place from lower rotational level with quantum number J to a higher rotational level with quantum number, J′, the energy absorbed in terms of wave number is given by

$$\Delta\bar{\nu} = BJ'(J'+1) - BJ(J+1) \qquad \ldots(ii)$$

For the selection rule, $\Delta J = +2$ *i.e.*, $J' - J = 2$, we get

$$\Delta\bar{\nu} = B(J+2)(J+3) - BJ(J+1)$$

$$\Delta\bar{\nu} = B(4J+6) \text{ where } J = 0, 1, 2, 3 \qquad \ldots(iii)$$

Again for the selection rule, $\Delta J = -2$ *i.e.* $J' - J = -2$, we get

$$\Delta\bar{\nu} = BJ'(J'+1) - B(J'+2)(J'+3)$$

$$\Delta\bar{\nu} = -B(4J'+6) \text{ where } J' = 0, 1, 2 \qquad \ldots(iv)$$

Combining the results of (*iii*) and (*iv*), the wave numbers of the lines obtained will be given by

$$\bar{\nu} = \bar{\nu}_i \pm \Delta\bar{\nu} \text{ or } \bar{\nu} = \bar{\nu}_i + B(4J+6) \qquad \ldots(v)$$

where $J = 0, 1, 2, 3$

Here $\bar{\nu}_i$ tells the wave number of the Rayleigh line. Plus sign gives lines with higher wave numbers and are called *antistoke's lines*. Minus sign gives lines with lower wave numbers and are called *stoke's lines*.

An harmonicity refers to deviations from harmonic behaviour. Harmonic vibrations are characterised by a restoring force which in turn is proportional to the displacement. At very small amplitudes, vibrations of atomic nuclei in molecues are harmonic. At very large amplitudes when dissociation of bond approaches, these vibrations are anharmonic (confirmed by band spectra).

From equation (*v*), we see that for $J = 0$, $\bar{\nu} = \bar{\nu}_i = 6B$. It means that the first stoke's and antistokes' line will be at a separation of $6B$ from the Rayleigh line. Now putting J = 1, 2, 3..., the separation between any two adjacent stoke's lines or antistoke's lines will be $4B$. Hence, the pure rotational Raman spectrum expected for a diatomic molecule is shown in Fig. 4.4.

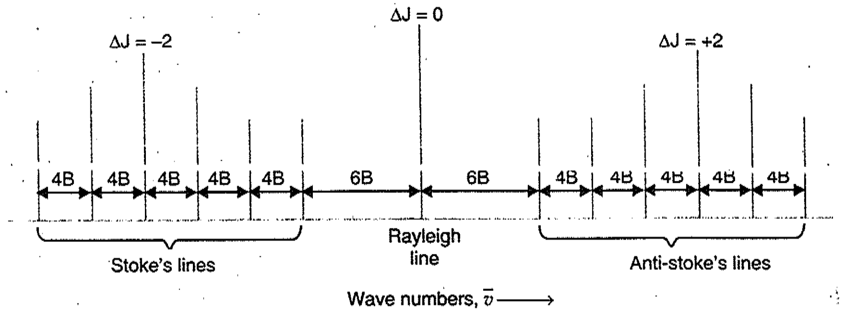


Fig 4.4. Pure Rotational Spectrum for diatomic molecule.

Pure vibrational Raman spectra of Diatomic molecules

The selection rules for pure vibrational spectra are :

(*i*) $\Delta\alpha \neq o$. It means that Raman spectrum is due to change in the polarizability along the internuclear axis.

(*ii*) The second selection rule is :

$$\Delta V = \pm 1, \pm 2, \pm 3, \ldots$$

It is identical with infra-red vibrational spectra

The transition between two vibrational levels is given by

$$E_V = hc\, w_e \left(V + \frac{1}{2}\right) - hc\, w_e x_e \left(V + \frac{1}{2}\right)^2$$

If V' and V'' are the vibrational quantum numbers for the lower and the upper states respectively, then

$$E_{V'} = hc\, w_e \left(V' + \frac{1}{2}\right) - hc\, w_e x_e \left(V' + \frac{1}{2}\right)^2 \qquad \ldots(i)$$

Also $$E_{V''} = hc\, w_e \left(V'' + \frac{1}{2}\right) - hc\, w_e x_e \left(V'' + \frac{1}{2}\right)^2 \qquad \ldots(ii)$$

From (*i*) and (*ii*)

$$\frac{E_{V''} - E_{V'}}{hc} = w_e (V'' - V') - w_e x_e (V'' - V')(V' + V'' + 1) = V_o - V_R \qquad \ldots(iii)$$

where ν_o = Rayleigh frequency

ν_R = Raman frequency

$$\frac{\Delta E}{hc} = w_e (V'' - V') - w_e x_e (V'' - V')(V' + V'' + 1) \qquad \ldots(iv)$$

∴ From (*iii*) and (*iv*) $V_R = V_o - [w_e (V'' - V') - w_e x_e (V'' - V')(V' + V'' + 1)]$ ...(*v*)

Applying the selection rules, we get

(*a*) For $\Delta V = +1$

$$\nu_R = \nu_o - [w_e - 2w_e x_e (V' + 1)]$$

---

* w_e = equilibrium vibrational frequency

x_e = anharmonicity constant

or $$\nu_s = \nu_o - [w_e - 2w_e x_e (V' + 1)] \quad ...(vi)$$

ν_s = Scattering frequency

We know that $\nu_o - \nu_s = \bar{V}_{\text{vib}}$

Thus, $$\bar{V}_{\text{vib}} = w_e - 2w_e x_e (V' + 1) \quad ...(vii)$$

Also for transition from ground state to first excited state, *i.e.* 0 → 1, $V' = 0$

As a result, $$\bar{V}_{\text{vib}} = w_e(1 - 2x_e) \quad ...(viii)$$

For transition 1 → 2

$$\bar{V}_{\text{vib}} = w_e(1 - 4x_e)$$ It is called the first hot band

Similarly, for $\Delta V = -1$

$$\bar{V}_{\text{vib}} = -w_e(1 - 2x_e) \quad ...(ix)$$

Hence the frequency of the first line in the vibrational Raman spectrum of diatomic molecules will be observed at

$$\bar{V}_{\text{vib}} = \pm w_e(1 - 2x_e) \quad ...(x)$$

It shows that the fundamental vibrational line lies on both sides of the excitation line at a space of $w_e(1 - 2x_e)$. It is true in case of solids and liquids which have no rotational fine structures.

(*b*) For $$\Delta V = \pm 2$$

$$\bar{V}_{\text{vib}} = \pm 2\, w_e(1 - 3x_e) \quad ...(xi)$$

and also for $$\Delta V = \pm 3,$$

$$\bar{V}_{\text{vib}} = 3\, w_e\, (1 - 4x_e) \quad ...(xii)$$

From this, it is clear that the fundamental, first, second... overtones exist at $w_e\,(1 - 2x_e)$, $2w_e\,(1 - 3x_e)$, $3w_e(1 - 4x_e)$ respectively on both sides of the central line.

The Raman frequency shifts also conform to fundamental and its overtones in the infra-red spectrum of diatomic molecules. The spacing between the consecutive lines decreases as ΔV decreases. It is due to anharmonic nature at the diatomic vibrator. In case the diatomic vibrator behave as a harmonic oscillator, the vibrational lines are observed of frequencies w_e, $2w_e$, $3w_e$ and the spacing between the lines is w_e. Also the intensity of these lines decreases sharply in the order.

$$I_{\Delta V(\pm 1)} >> I_{\Delta V(\pm 2)} >> I_{\Delta V(\pm 3)}$$

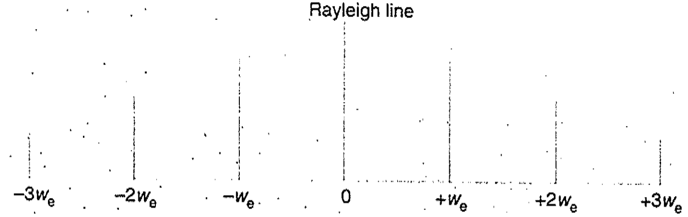


Fig. 4.5. Schematic vibrational Raman spectrum of diatomic harmonic vibrator.

From the position of stoke's or antistoke's lines and the Rayleigh line, the vibrational frequency and the force constant of a diatomic molecule can be predicted.

When HCl^{35} is irradiated with 4358 Å (Hg line), the stokes' line is observed at 20057 cm^{-1}. The vibrational frequency of HCl is

$$\bar{V}_{\text{vib}} = V_o - V_s = \frac{1}{4358\times10^{-8}} - 20057 \text{ cm}^{-1}$$
$$= 22946 - 20057 = 2889 \text{ cm}^{-1}$$

Also we know $$\bar{V}_{vib}\ (\text{cm}^{-1}) = 1303.16\sqrt{\frac{k\ (\text{millidynes/Å})}{\mu\ (\text{amu})}}$$

$$\mu \text{ (Reduced mass) for HCl} = \frac{m_1 m_2}{m_1 + m_2} = \frac{1\times35}{1+35} = \frac{35}{36} \text{ amu.}$$

Thus, $$2889 = 1303.16\sqrt{\frac{k}{35/36}}$$

or $$k \text{ (Force constant)} = \sqrt{\frac{2889\times2889\times35}{1303.16\times1303.16\times36}} = 4.77 \text{ millidynes/Å}$$

4.9 Rotational-Vibrational Raman Spectra

We know that the selection rule for the molecule to give rotational-vibrational Raman spectrum is that the polarisation of the molecule must change as the molecule vibrates. In diatomic molecules (homonuclear and heteronuclear) we see that as the molecule vibrates, the control of the nuclei over the electrons changes and thus, there is a change in polarisability. As a result of this, both types of diatomic molecules give rotational-vibrational Raman spectra *i.e.*, they are vibrational Raman active. It is the main advantage of Raman spectra over infra-red spectra because homonuclear diatomic molecules do not give pure vibrational or rotational spectra as they do not possess permanent dipole moment. It may be noted that diatomic gaseous molecules give rotational-vibrational Raman spectra which are governed by the selection rules:

$$\Delta V = \pm 1 \text{ and } \Delta J = 0, \pm 2.$$

But it is found that at room temperature, many of the molecules are in the lowest vibrational level ($V = 0$). Clearly, the fundamental or significant vibrational transition is from $V = 0$ to $V = 1$. Restricting to this vibrational transition only, the results obtained are given below:

(*i*) For $\Delta J = 0$, $\Delta\bar{V} = w_e(1 - 2x_e)$. It is called Q-branch.

(*ii*) For $\Delta J = +2$, $\Delta\bar{V} = w_e(1 - 2x_e) + B(4J + 6)$. It is called S-branch.

(*iii*) For $\Delta J = -2$, $\Delta\bar{V} = w_e(1 - 2x_e) - B(4J' + 6)$. It is called O-branch. It may be noted that w_e (Vibrational quantum number)

$$= \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \mu^{-1}.$$

If $\Delta\bar{V}_{(Q)}$, $\Delta\bar{V}_{(S)}$ and $\Delta\bar{V}_{(O)}$ represent values for Q, S and O-branch respectively and the wave number of exciting radiation be V_i, the wave numbers of stokes' lines will be described as:

$$\bar{V}_Q = \bar{V}_i - \Delta\bar{V}_{(Q)}$$
$$\bar{V}_S = \bar{V}_i - \Delta\bar{V}_{(S)}$$

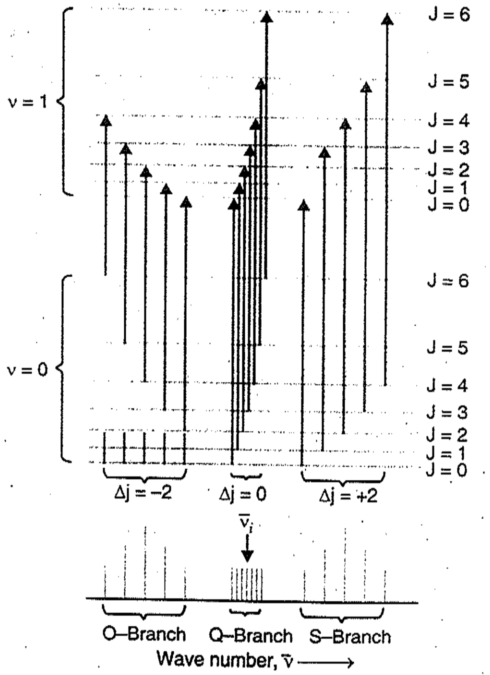


Fig. 4.6. Rotation-vibration Raman spectrum of a diatomic molecule.

$$\bar{V}_O = \bar{V}_i - \Delta\bar{V}_{(O)}$$

$\Delta V = +1$ represents stokes' line whereas antistokes' lines are those for which $\Delta V = -1$. It may be noted that antistokes' lines are usually weak because very few molecules are in the excited vibrational state initially. The vibrational transitions which accompany vibrational transition from $V = 0$ to $V = 1$ and the rotational-vibrational Raman spectra obtained is shown in Fig. 4.5.

4.10 Vibrational Raman Spectra of Polyatomic Molecules

We have seen that Raman spectra are generally simpler as compared to infra-red spectra. The reason is that only very few combination and overtones appear in Raman spectra. Like vibrational Infra-red spectra, the vibrational Raman spectra for polyatomic molecules are more complicated than diatomic molecules. The basic features of the spectra can be understood by extending the treatment of the Raman vibrational spectra of diatomic to polyatomic molecules.

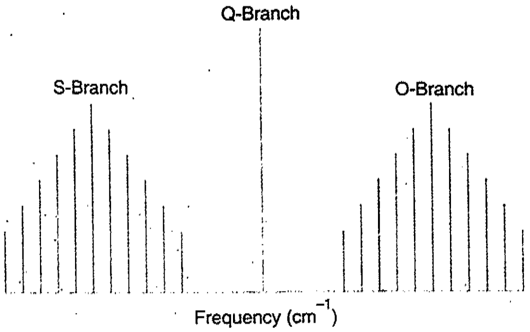


Fig. 4.7. Theoretical rotational-vibrational spectrum of diatomic molecules.

The vibrational-rotational band of oxygen is shown below (Fig. 4.8).

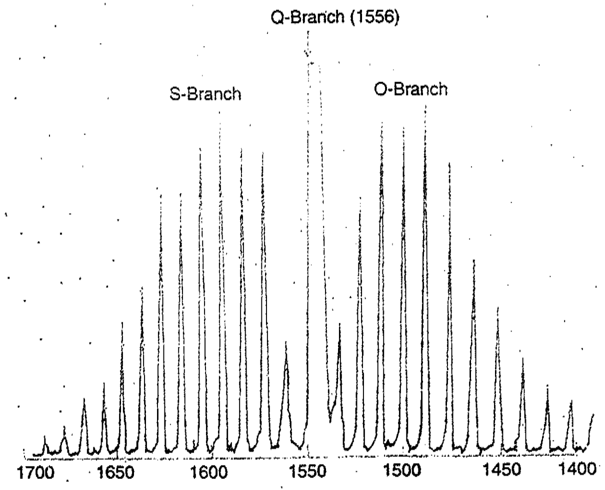


Fig. 4.8. Rotation-vibration Raman spectrum of oxygen.

For polyatomic molecules, we need to know the number of fundamental modes of vibrations and their symmetry to know the Raman activity. All the molecules which have a centre of symmetry (say CO_2) exhibit the principle of mutual exclusion. According to the principle, *"All vibrations of a molecule, with centre of symmetry, which are Raman active are Infra-red in unit active and vice versa".*

In other words, no fundamental frequency can appear in both Raman and Infra-red spectra. Consider the case of carbon dioxide. In carbon dioxide (*i*) a symmetric stretching (2349 cm^{-1}) and bending (667 cm^{-1}) vibrations are infra-red active whereas, (*ii*) symmetric stretching (1330 cm^{-1}) is Raman active.

In simple words, we say that symmetrical vibrations give rise to Raman scattering while antisymmetrical vibrations give strong Infra-red absorptions.

4.11 Rule of Mutual Exclusion Principle

According to this principle, if a molecule has centre of symmetry (*e.g.*, centrosymmetric molecules like H_2, CO_2, C_2H_2 etc.), the Raman active vibrations are infra-red inactive and vice versa. The molecule for which, centre of symmetry is absent can simultaneously be IR as well as Raman active. Clearly, the stretching vibrations of homonuclear diatomic molecules (like H_2, O_2, N_2 etc.) which are IR inactive are Raman active. Hence, we say that infra-red and Raman spectra are complimentary to each other.

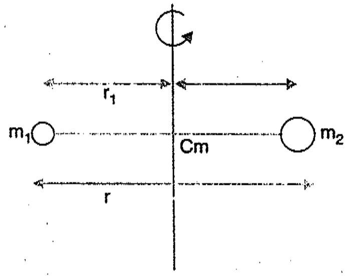


Fig. 4.9.

Also consider the case of carbon disulphide (S = C = S). It is a centrosymmetric molecule. According to the rule of mutual exclusion principle, all vibrations in it are Raman active and Infra-red inactive. Also the structure of nitrous oxide (N_2O) is N—N—O and not N—O—N. In this case, the vibrations are simultaneously IR as well as Raman active. It shows that N_2O has a linear structure and is not centrosymmetric like CO_2. In the same way, we say that SO_2 (bent structure) has no centre of symmetry and vibrations in it are simultaneously IR and Raman active.

4.12 Moment of Inertia of diatomic molecules, and Raman Spectroscopy

Consider a diatomic molecule the masses of whose nuclei are m_1 and m_2. Let r_1 and r_2 be the distances of the respective nuclei from the centre of mass, C_m of the molecule such that the bond length :

$$r = r_1 + r_2 \quad \text{...}(i)$$

Taking the bonds about C_m, we get

$$m_1 r_1 = m_2 r_2 \quad \text{...}(ii)$$

From (*i*) and (*ii*)

$$r_1 = \frac{m_2 r}{m_1 + m_2} \text{ and}$$

$$r_2 = \frac{m_1 r}{m_1 + m_2} \quad \text{....}(iii)$$

The general expression for the moment of inertia of a diatomic molecule is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{...}(iv)$$

In diatomics, the moment of inertia about molecular axis is zero since all the masses concentrate on this axis, ie, for this this particular rotation in diatomics since $r = 0$, hence $I = 0$

Substituting the value of r_1 and r_2 from (*iii*) in equation (*iv*), we get

$$I = m_1 \frac{m_2^2 r^2}{(m_1+m_2)^2} + \frac{m_2 . m_1^2 r^2}{(m_1+m_2)^2}$$

or $$I = \frac{m_1 m_2 . r^2}{m_1+m_2}\left[\frac{m_2}{(m_1+m_2)} + \frac{m_1}{(m_1+m_2)}\right] = \frac{m_1 m_2}{m_1+m_2} . r^2$$

or Moment of Inertia, $I = \mu_m . r_2$ (where μ_m = Reduced mass)

We know that $$V_R = V_o + \frac{E_{V'} - E_{V''}}{h}$$

where $E_{V'}$ = Energy of initial level of molecule

$E_{V''}$ = Energy of final level of molecule.

Rotational energy of molecule is expressed as $BJ(J + 1)$

where J = rotational quantum number of a molecular level.

$$B = \frac{h^2}{8\pi^2 I} = \text{rotational constant in energy units.}$$

where I = moment of inertia

The selection rule for pure rotational Raman spectra in homonuclear diatomic molecule is: ΔJ = 0, +2, provided the molecule has anisotropic (non-spherical) polarisability.

Here ΔJ = 0 corresponds to Rayleigh scattering line.

ΔJ = +2 for Stoke's lines and ΔJ = –2 for antistoke's lines.

(*a*) **For stokes' lines.** The allowed transitions are from initial level (J) to final level $(J + 2)$ for $\Delta J = \pm 2$ where $J = 0, 1, 2, ...$

$$\therefore \quad E_{V'} - E_{V''} = E_J - E_{J+2} = BJ(J+1) - B(J+2)(J+2+1)$$
$$= B(-4J-6) = -2B(2J+3)$$

$$\therefore \quad V_R = V_o + \left[\frac{-2B(2J+3)}{h}\right]$$

Dividing the above expression by c (velocity of light), we get

$$\bar{V}_R = \bar{V}_o - \frac{2B}{hc}(2J+3) \quad \text{or} \quad \bar{V}_R = \bar{\nu}_o - 2\bar{B}(2J+3) \qquad ...(i)$$

where $J = 0, 1, 2...$ and $\bar{B} = \frac{h}{8\pi^2 Ic}$ (rotational constant in wave number)

The relation (*i*) gives the frequency (in wave number) of stokes' line in Raman spectra. It shows that the frequency, $\bar{\nu}_R$ is less than the Rayleigh scattering frequency $(\bar{\nu}_o)$.

(*b*) **For antistoke's lines.** The allowed transitions, $(\Delta J = -2)$ of the molecule are from initial level (J) to final level $(J - 2)$ for $J = 2, 3, 4, ...$

Therefore, $$E_{V'} - E_{V''} = E_J - E_{J-2}$$
$$= BJ(J+1) - B(J-2)(J-2+1) = B(4J-2)$$
$$= 2B(2J-1)$$

$$\therefore \quad V_R = V_o + \frac{2B(2J-1)}{h} \quad \text{or} \quad \bar{V}_R = \bar{V}_o + 2\bar{B}(2J-1) \qquad ...(ii)$$

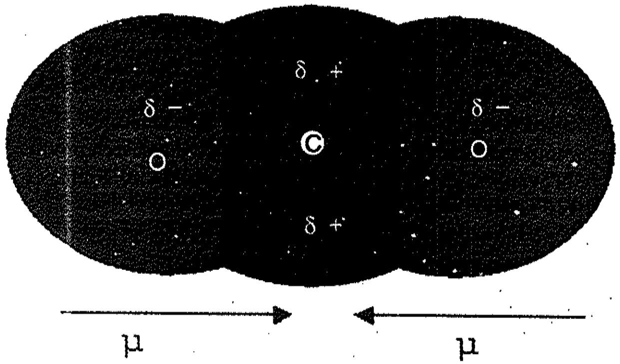
where $J = 2, 3, 4.$

From the relation (*ii*), we see that frequency $\bar{\nu}_R$ (in wave number) for antistokes' line in Raman spectra is more than that of Rayleigh scattering line. It is also clear from the relations (*i*) and (*ii*) that the first stokes' or antistokes' line will be at a separation of $6\bar{B}$ from Rayleigh line while remaining lines will be at a constant spacing of $4\bar{B}$.

Rotational Raman spectra resembles far infra-red spectra whereas rotation-vibrational Raman spectra generally resembles near infra-red spectra with a difference that constant spacing between spectral lines is $4\bar{B}$. This fact may be used to find the moment of inertia and band distance in diatomic molecules.

Infra-red and Raman Spectra are Complementary

For the infra-red spectrum to occur, the molecule must show a change in the dipole moment. For the Raman spectra, there must be a change in the polarisability of the molecule. As these two requirements are somewhat different, lines may be formed in one of the spectra or in both. The symmetrical stretching of the molecule which are usually missing in the infra-red appear prominently in Raman spectra. On the other hand, asymmetric vibrations show opposite behaviour. Thus, we say that vibrational modes which are inactive in Infra-red are somewhat active in Raman spectra. Consider the case of carbon dioxide molecule.



(*i*) $\overset{\leftarrow}{O} = C = \vec{O}$ Symm. Stretching — IR inactive (No change in dipole moment); Raman active (Appreciable change in polarisability)

(*ii*) $O = \vec{C} = \vec{O}$ Asymm. Stretching — IR active (Appreciable change in dipole moment); Raman inactive (No change in polarisability)

(*iii*) $\overset{+}{O} = \overset{-}{C} = \overset{+}{O}$ Out of phase bending — IR active; Raman inactive (Both are degenerate)

In case of small molecules, the less symmetric vibrations often produce intense IR bands whereas more symmetric vibrations produce strong Raman bands.

Table T_4-1.

Infra-red spectra	*Raman spectra*
1. It is due to absorption of a radiation by the vibrating molecules.	1. It is due to the scattering of radiation by vibrating molecules.
2. The dipole moment of the molecule changes.	2. The polarisability of the molecule changes.
3. The intensity of IR absorption band depends upon the magnitude of the change in dipole moment of the molecule.	3. The intensity of Raman line depends upon the magnitude of the change of polarisability of the molecule.
4. Water cannot be used as it is opaque to IR.	4. Water can be used as solvent.
5. Dilute solutions are generally used.	5. Concentrated solutions are used to increase the intensity of Raman lines.
6. Optical systems are made up of special crystals like NaBr, CaF_2, etc.	6. Optical systems are made up of glass or quartz.

4.14 Structure Elucidation by Raman Spectroscopy

Raman spectroscopy is of great value for molecular vibrations that are inactive in the infrared due to molecular symmetry. For centro-symmetric molecules like H_2, CO_2, C_2H_2 ete, the vibrations which are IR inactive are Raman active **In fact, Raman spectroscopy supplements infra-red spectroscopy.** It is an important tool for solving some intricate research problems concerning the structure elucidation of compounds. Some important applications of Raman spectra in structure elucidation are:

(*i*) Structure of centro-symmetric molecules. Carbon dioxide is a centro-symmetric molecule with linear structure (O = C = O). One expects two fundamental modes in the infra-red and one in the Raman. Actually, it is confirmed experimentally. (*i*) 1337 cm^{-1} (Raman active) and (*ii*) 667 cm^{-1} (*iii*) 2349 cm^{-1} which are infrared active. The structure is said to be centrosymmetric when the vibration is infrared active and Raman inactive and vice versa.

(*ii*) Structure of N_2O. If N_2O is symmetrical like CO_2, one should expect similar behaviour as seen in carbon dioxide. If it is unsymmetrical as N – N – O, then vibration should be active both in infrared as well as Raman.

Actually, additional fundamental vibration is observed both in IR and Raman spectroscopy. This shows that the structure of N_2O is N – N – O.

(*iii*) Structure of water. For water to have bent structure, the fundamental vibrations v_1, v_2 and v_3 should be active both in Raman as well as in IR. Since, it is experimantally true, water has a bent structure.

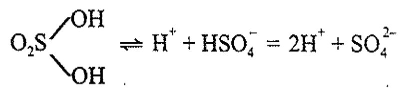
(*iv*) Structure of Mercurous salts. The Raman spectrum of the aqueous solution of mercurous salt shows a line which is absent in the spectra of other metal nitrates. The two shows Hg – Hg covalant bond in Hg^{2+} molecules.

(*v*) Structure of Chloro Complexes of Mercury. The Raman Spectrum of a solution of $HgCl_2$ and NH_4Cl mixed in the ratio of 1 : 2 shows a strong line at 269 cm^{-1}. This compares with a strong line at 273cm^{-1} for solid ammonium tetrachlor mercurate (*II*) showing the formation of $HgCl_4^{2-}$ in solution.

(*vi*) Hydrogen cyanide. Raman spectrum for hydrogen cyanide shows two lines at 2062 cm^{-1}. It can be attributed to two Isomers in dynamic equilibrium.

(*vii*) **Sulphuric acid.** Raman frequency of 25% sulphuric acid matches with that shown by $KHSO_4$ but on dilution, the Raman frequency corresponds to that of K_2SO_4. It shows the existence of HSO_4^- ion.

Thus,



$$O_2S(OH)_2 \rightleftharpoons H^+ + HSO_4^- = 2H^+ + SO_4^{2-}$$

(*viii*) **In Organic Compounds.** In addition, Raman spectroscopy helps in revealing the molecular structure of organic compounds. Raman spectrum provides information about the following fact.

(*a*) The structure of simple organic compounds.
(*b*) Shows the presence or absence of specific linkages in a molecule.
(c) Studying of Isomers.
(*d*) Preseure of impurities in the dyes.
(e) Classification of compounds.

It has been found that Raman lines usually lie in the region 500-350 cm^{-1}.

(*ix*) **Geometrical Isomers.** It is known that cis and trans Isomers of 1, 2-dichloroethylene exist in equilibrium proportions. Out of these, trans configuration has centre of symmetry. Thus, the coincident frequencies observed in IR and Raman spectra of the sample can be assigned to cis-configuration. In this way, the analysis of cis and trans Isomers can be carried out.

Note. Raman spectroscopy also uses visible and ultra-violet radiations rather than IR radiations. Clearly, the walls of the sample cell and the other units of the optical system can be made of glass or quartz rather than of special material which are transparent to IR radiations. Also experiment can be conducted conveniently with aqueous media as water is more transparent in the visible and UV regions than in IR region. Raman spectroscopy can be utilised for the investigation of biological systems such as proteins is aqueous solutions.

4.15 Numericals On Raman Spectroscopy

EXAMPLE 1 *A sample was excited by the 4358 Å line of mercury. A Raman line was observed at 4447 Å. Calculate the Raman shift (in cm^{-1})*

SOLUTION. Given that $\bar{v}_o$ (Frequency of incident photon)

$$= \frac{1}{\lambda} = \frac{1}{4358 \times 10^{-8}\ cm} = 22946\ cm^{-1}$$

Also $\bar{v}_R$ (Frequency of scattered photon giving Raman line)

$$= \frac{1}{\lambda_R} = \frac{1}{4447 \times 10^{-8}\ cm} = 22487\ cm^{-1}$$

Hence, the Raman shift $\Delta\bar{V} = \bar{V}_o - \bar{V}_R = (22946 - 22487)\ cm^{-1} = 459\ cm^{-1}$

$$\Delta\bar{V} = 459\ cm^{-1}$$

We see that $\bar{V}_R < \bar{V}_O$. We can say that it is *stoke's line.*

EXAMPLE 2 *Using radiation of wavelength 4 × 10^3 Å, the first stoke's line appears at a spacing of 350 cm^{-1} from the Rayleigh line. Calculate the frequency of the first antistoke's line in wave number.*

SOLUTION. We know that $\bar{V}$ (Stoke's line) = $\bar{V}_o - \bar{V}_R$

Also $\bar{V}$ (antistokes' line) = $\bar{V}_o - \bar{V}_R$

Given that, $\Delta\bar{V}_R$ is the Raman frequency. It is equal to the change in the frequency of incident photon.

Thus, $\Delta\bar{V}_R = 350 \text{ cm}^{-1}$

$$\bar{V}_o \text{ (incident)} = \frac{1}{\lambda} = \frac{1}{4\times10^3 \text{ Å}} = \frac{1}{4\times10^{-5}\text{cm}} = 2.5 \times 10^{+4} \text{ cm}$$

$$= 25000 \text{ cm}^{-1}$$

Hence, we write, $\bar{V}$ (stoke's lines) $= 25000 - 350 = 24650 \text{ cm}^{-1}$

Also $\bar{V}$ (antistoke's lines) $= 25000 + 350 = \mathbf{25350 \ cm^{-1}}$

EXAMPLE. 3. *Acetylene shows two C–H stretching vibrations, a symmetrical one at 3374 cm^{-1} $(\overleftarrow{H-C}\equiv\overrightarrow{C-H})$ and an unsymmetrical one at 3287 cm^{-1} $(\overrightarrow{H-C}\equiv\overrightarrow{C-H})$*

(*i*) *Which of these vibrations will be Raman active and why?*

(*ii*) *Calculate the Raman wavelength for a 4358 Å exciting line.*

(*iii*) *Calculate the IR active frequency.*

SOLUTION. (*i*) The second vibration (3287 cm^{-1}) is asymmetric. In this case, there is change in the dipole moment during the course of vibration. Thus, it will be IR active. The molecule has a centre of symmetry. Applying the law of mutual exclusion principle, Raman active vibrations are IR inactive. Thus, 3374 cm^{-1} vibration is Raman active. It is the fundamental vibration.

(*ii*) Raman wavelength for 4348 Å excited line is obtained as below:

$$\bar{V}_R \text{ (Raman wave number)} = \bar{V} \text{ (excited)} - \bar{V}_o \text{ (Fundamental)}$$

$$\therefore \quad \bar{V} \text{ (excited)} = \frac{1}{\lambda} = \frac{1}{4358\times10^{-8}} = 22946 \text{ cm}^{-1}$$

Also $\bar{V}_o$ (Fundamental) $= 3374 \text{ cm}^{-1}$

Thus, Raman wave number,

(*a*) $\bar{V}_1 = 22946 + 3374 = 26320 \text{ cm}^{-1}$ (*b*) $\bar{V}_2 = 22946 - 3374 = 19572 \text{ cm}^{-1}$

The corresponding Raman wavelengths are :

(*a*) $\frac{1}{26320}\times10^8 = 3799.4$ Å (*b*) $\frac{1}{19572}\times10^8 = 5109.3$ Å.

(*iii*) IR active frequency $(\nu) = \bar{V} \times c = (3287 \text{ cm}^{-1})(3 \times 10^{10} \text{ cm s}^{-1})$

$$= \mathbf{9.861 \times 10^{13} \ s^{-1}}.$$

EXAMPLE. 4 *The rotational spectrum of HCl has lines 21.1 cm^{-1} apart. Calculate the moment of inertia and bond length in HCl and show that the spacing and the observed spacing are in agreement with each other.*

(H = 1.008 amu, Cl = 34.98 amu, $h = 6.626 \times 10^{-34}$ *Js*, c = 2.998×10^8 ms^{-1}, 6.024×10^{26} amu = 1 kg, internuclear distance, $r_o = 0.1275$ nm).

SOLUTION. Moment of Inertia, $I = \mu r_0^2$ ...(*i*)

$$\mu = \frac{m_1 m_2}{m_1+m_2} = \frac{1.008\times34.98}{1.008+34.98} = 0.984 \text{ amu.}$$

Given 6.024×10^{26} amu = 1 kg; Thus 1 amu $= \frac{1}{6.024\cdot10^{26}} = 1.662 \times 10^{-27}$

$$\therefore \quad \mu = 0.984 \times 1.662 \times 10^{-27} \text{ kg} = 1.627 \times 10^{-27} \text{ kg.}$$

Substituting the value in (*i*), we get

$$I = \mu r_0^2 = 1.627 \times 10^{-27} \text{ kg } (1.275 \times 10^{-10} \text{ m})^2$$

$$= 2.645 \times 10^{-47} \text{ kg m}^2.$$

Also rotational constant, $B = \frac{h}{8\pi^2 I.C} \text{ m}^{-1}$

$$= \frac{6.626\times10^{-34}}{8\times(3.142)^2(2.645\times10^{-47})\times(2.998\times10^{-8})} = 1058 \text{ m}^{-1}$$

$$\Delta\bar{V} = 2B = 2 \times 1058 = 2116 \text{ m}^{-1} = 21.16 \text{ cm}^{-1}.$$

Hence, we say that the calculated and the observed values of $\Delta\bar{V}$ are in good agreement with each other.

EXAMPLE.5. *The Infra-red spectrum of a triatomic molecule, AB$_2$, shows two fundamental vibrational frequencies while its Raman spectra shows an additional frequency not found in its spectrum. Deduce the structure of AB$_2$.*

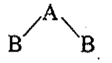
The possible structures of AB$_2$ are :

B—A—B

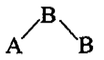
(*i*) linear

B—B—A

(*ii*) Linear



(*iii*) non-linear



(*iv*) non-linear

Let us calculate the fundamental vibrational frequencies of each. Structures (*i*), (*ii*), (*iii*) and (*iv*) have number of vibrational frequencies as 4 (3n–5), 4 (3n–5), 3 (3n–6), 3 (3n–6) respectively. However, all the frequencies of each of the structure (*ii*), (*iii*) and (*iv*) are IR active because all are accompanied by change in the depole-moment of the molecule. The fact rules out these structures because it does not agree with the given data. The structure (*i*) is the correct structure, since its symmetrical bending and asymmetrical stretching modes are IR active while symmetrical stretching is Raman active.

Example 1. *The fundamental frequency of a molecule is 8.67 × 10^{13} s^{-1}. Calculate the corresponding Raman lines if the molecules is irradiated with 435.8 mm wave length.*

[Ans. 498.6 nm (stoke's), 387 nm (antistoke's)

Example 2. *The IR spectra of a molecule of the type AB$_2$ shows three fundamental vibrational frequencies one of which is doubly degenerate. The Raman spectra of the molecule shows the same three frequencies. Predict the structure of AB$_2$ molecule.* **[Ans.** Linear. A—B—B**]**

Example 3. *On irradiation of CCl$_4$, with the 435.8 nm mercury line, one of the Raman lines appears at 460 nm. Calculate (i) the Raman frequency of CCl$_4$ in wave number (cm^{-1}) (v) the wavelength in micrometers (µm) in the IR region at which the absorption would be expected.*

[Ans. (*i*) 1207 cm^{-1} k(*ii*) 8.3 µm)

4.16 Importance of Raman Spectra

The following facts explain the importance of Raman spectra:

(*i*) All linear diatomic molecules (Homo or Heteronuclear) are rotationally Raman active. But spherical top molecules like CH$_4$, SF$_6$ are not Raman active.

(*ii*) It has an advantage over Infra-red spectroscopy since the intensity of Raman line depends upon a change in the polarisability of a molecule on vibration and not on the change in dipole moment. In case of carbon dioxide, the totally symmetric vibration is Raman active but is not seen in IR as it is not accompanied by any change in the dipole moment. Thus, we say that in some cases where rotational and vibrational bands are not seen in IR, the Raman spectra give useful information.

(*iii*) All Raman lines do not have their corresponding IR bands and vice versa. *If the same lines in both IR and Raman spectra are obtained, the molecule has no centre of symmetry.*

(*iv*) Raman spectra can be obtained for a compound in all the three states but infra-red spectrum is quite diffused in the liquid and the solid state of matter and is not useful.

(*v*) Raman spectral lines are independent of the frequency of incident radiation. Thus, it can be easily studied in the visible spectral region. But IR spectrum is obtained in more difficult range of infra-red radiation.

(*vi*) Raman spectrum is not interfered by the presence of mixture or water in the sample. On the other hand, infra-red spectrum is affected by the presence of water.

(*vii*) Raman spectrum is employed for the quantitative analysis of the mixtures. In the quantitative analysis, the height of the Raman peak varies linearly with the concentration of the sample.

4.17 Applications of Raman Spectroscopy

Raman spectroscopy is a simpler technique and has many advantages over infra-red spectroscopy. It is a valuable method for directly detecting the frequencies of Infra-red inactive vibrations. It helps in studying the structures of molecules and also the structural changes which occur due to association, dissociation and solvation. This technique is also useful is studying the kinetics of Fast reactions. It is quite significant in biological studies since interferences, due to the presence of water are insignificant. Some of the important applications of Raman spectroscopy are:

1. **Elucidation of Molecular Structure.** It helps in finding the structures of molecules and complex ions from the activity and depolarisation ratios of the Raman bands. The elucidation of structure by the activity selection criterion is also possible. For example, XY_3 systems can either be trigonal or pyramidal. Out of the six modes of vibrations, only four are observable since two fundamental modes are doubly degenerate. Four observable modes of vibration of SO_3 are at 1332, 1068, 530 and 653 cm^{-1}. The bands at 1332, 1068 and 530 cm^{-1} are Raman active only. Due to this, SO_3 has a planar or trigonal structure.

In case of ammonia (NH_3), four observable modes of vibration are 3337, 950, 3414 and 1628 cm^{-1}. Only two bands appear in the spectrum of 3337 and 950 cm^{-1}. The reason that the two bands (at 3414 and 1628 cm^{-1}) in the Raman spectrum are not observed is that the structure of ammonia is not full symmetry. Thus, the structure of ammonia is pyramidal.

2. **Nature of the chemical bond.** In the tetrahedral complexes, *viz.*, $ZnCl_4^{-2}$ (275 cm^{-1}), $CdCl_4^{2-}$ (260 cm^{-1}), SO_4^{2-} (982 cm^{-1}) and octahedral complexes, *viz.*, SF_6 (775 cm^{-1}), UF_6 (66 cm^{-1}), we see totally symmetric vibrations. Thus, such ions or molecules are *Raman active* only. The force constant for M–L bond can be calculated by using the equation:

$$\nu_{M-L} = 1303.16\sqrt{\frac{k}{\mu_m}}$$

The high values of force constants for SO_4^{2-} (6.04); PO_4^{3-} (5.46) show the presence of $d\pi$–$p\pi$ bond between the central atom and oxygen atom in addition of σ-bond.

3. **Study of Ionic equilibria.** Consider the following equilibria

$$HX + H_2O \underset{}{\overset{k}{\rightleftharpoons}} H_3O^+ + X^-$$

where *k* is dissociation constant of the acid.

It is found that the scattering intensity is directly proportional to the concentration of the scattering species. Thus,

$$I_{X^-} \propto [X^-]$$

Also
$$I_{HX} \propto [HX]$$

$$\therefore \quad K_{HX} = \frac{I_{X^-}}{I_{HX}} = \frac{[X^-]}{[HX]} \qquad \ldots(i)$$

The value of *k* can be found by simply monitoring the scattering intensities of the vibrational bands of X^- and HX respectively.

Similarly, consider the following equilibria

$$H_2X + H_2O \rightleftharpoons H_3O^+ + HX^-$$

$$K_{H_2X} = \frac{I_{HX^-}}{I_{H_2X}} = \frac{[HX^-]}{[H_2X]} \qquad \ldots(ii)$$

and
$$HX^- + H_2O \rightleftharpoons H_3O^+ + X^{2-}$$

$$K_{HX^-} = \frac{I_{X^{2-}}}{I_{HX^-}} = \frac{[X^{2-}]}{[HX^-]}$$

Thus, Raman spectra give a proof of the existence of unionised ions in the aqueous solutions of nitric acid and sulphuric acids of moderate concentrations.

4. **Study of Hydrogen bonded Equilibria.** Consider the following equilibria:

$$A-H + B \overset{k}{\rightleftharpoons} A-H \cdots B \qquad \text{where A or B = O, N, F}$$

Due to hydrogen bonding, A–H stretching frequency will show a change in absorption. Thus, by measuring the scattered intensity of the free A–H and hydrogen bonded A–H bands as a function of concentration of B, the value of equilibrium constant K can be determined by using the following expression.

$$K = \frac{[A\text{–}H\cdots B]}{[A\text{–}H][B]} \qquad \ldots(i)$$

Two non-equivalent configurations of o-chlorophenol in solution of carbon tetrachloride is shown below:

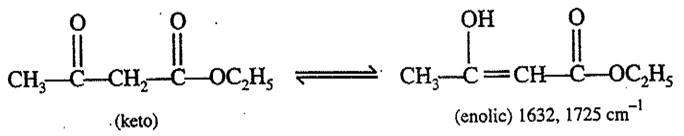
(trans) (cis)

Out of these forms, cis form is stabilised by hydrogen bonding. As a result, two bands corresponding to free OH (trans) and O–H hydrogen bonded (cis) appear in the Raman spectrum. The hydrogen bond equilibrium constant, K can be determined by the expression

$$K = \frac{I_{(cis)}}{I_{(trans)}}$$

The intensity ratio for the first IR overtones of OH stretching band at 6910 cm^{-1} (for cis) and at 7050 cm^{-1} (for trans) is found to be equal to 10.

5. **Mechanism of tautomerism.** All carbonyl compounds containing an α-hydrogen atom exists as keto and enol tautomers. The existence of tautomeric forms is confirmed by Raman spectroscopy. Consider ethyl acetoacetic ester. In this compound, two Raman lines appear at 1632 and 1725 cm^{-1}. These two lines are characteristic of ethylenic bond. It shows the existence of enolic form in it.

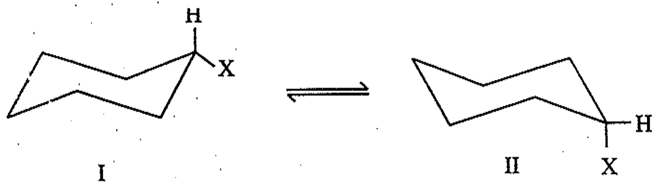


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

(keto) (enolic) 1632, 1725 cm^{-1}

These two lines are absent in ethyl dimethyl acetoacetate. The reason is that this compound does not contain α-H atom and hence, ethylenic bond (C = C) is absent in it.

6. **Conformational equilibria.** Consider the following conformational equilibrium in monosubstituted cyclohexane.



(X = F, Cl, Br, I, OH)

I II

The frequencies of the Raman bands due to C–X depends upon the fact whether X is equitorial or axial. They differ in steric interactions with adjacent protons. It is found that:

$$\nu_{C-X(e)} > \nu_{C-X(a)}$$

It is also known that intensity of Raman line is directly proportional to the amount of the scattering species. Thus,

$$I_{(e)} \propto C_e \qquad \text{and also } I_{(a)} \propto C_{(a)}$$

$$K = \frac{I_e}{I_a} = \frac{C_e}{C_a}$$

Hence, by monitoring the intensities of ν_{C-X} bands corresponding to two conformations, the value of conformational equilibrium constant (K) can be determined.

Important Terms and Definitions in Raman Spectroscopy

1. **Raman spectroscopy.** It involves the study of vibrational-rotational energy changes in molecules by means of scattering of light.

2. **Polarisability.** It is dipole moment induced by the unit electric field.

3. **Rayleigh scattering.** It is defined as the scattering of radiation without any change in frequency.

4. **Raman scattering.** The scattering of radiations with certain discrete frequencies above and below that of the incident beam is called Raman scattering.

5. **Stoke's lines.** When the scattering of radiation produce lines with lower frequency compared to that of the incident beam, then these are called stoke's lines.

6. **Antistoke's, lines.** When the scattering of radiation produce lines with higher frequency compared to that of the incident beam, then, these lines are antistoke's lines.

7. **Raman shift.** It is the difference between the frequency of the incident light and that of the particular scattered light. It depends only on the nature of the substance employed and not on the frequency of the incident light.

8. **Intensity of Raman lines.** The intensity of Raman lines depends upon the concentration of the substance. More the concentration, more is the intensity of Raman lines. It depends upon the magnitude of the change of polarisability of the molecule.

9. **Selection Rule for Raman spectrum.** For transition probability of Raman effect, the molecule must show a change of polarisability along the internuclear axis.

10. **Rule of Mutual Exclusion Principle.** In a molecule which has a centre of symmetry, the Raman active vibrations are infra-red inactive and vice-versa. A linear molecule in which centre of symmetry is absent can simultaneously be IR as well as Raman active.

Short Questions with Answers

1. **Briefly explain Raman scattering.**

Ans. If a monochromatic radiation is passed through a substance, a small amount of radiation energy is scattered. The scattered energy consists of radiation of incident frequency (called Rayleigh scattering) and also of discrete frequencies above and below the incident beam, called Raman scattering.

2. **Define stoke's and antistoke's radiation.**

Ans. Radiation scattered with a frequency lower than that of the incident beam is called stoke's radiation and that with higher frequency is called antistokes' radiation. Stoke's radiation is generally more intense than antistokes' radiation.

3. **What do you understand by molecular polarisation ?**

Ans. When a molecule is put into a static electric field, it suffers some distortion. The positively charged nuclei get attracted towards the negative pole of the field and the electrons to the positive pole. The separation of charge centres causes an induced electric dipole moment to be set in the molecule. Such a molecule is thus, said to be polarised.

4. **What is the condition for the substance to be Raman active ?**

Ans. For the substance to be Raman active, a molecular rotation or vibration must cause some change in a component of the molecular polarisability. A change in polarisability is reflected by the change in either the magnitude or the direction of the polarisability ellipsoid.

On the contrary, a substance is IR active if the molecular motion in it produce a change in the electric dipole of the molecule.

5. **What are S-branch lines in Raman spectroscopy ?**

Ans. If a molecule gains rotational energy from the photon during collision, we have a series of S-branch lines to the low wave number side of the exciting line (Stoke's lines). But if the molecule loses energy to the photon, the S-branch lines appear on the high wave number side (antistoke's lines).

6. **What do you say about Raman spectrum in case of molecules like H_2, O_2 and CO_2?**

Ans. Molecules as H_2, O_2, CO_2 etc have centre of symmetry. For such molecules, the effects of nuclear spin will be observed in the Raman and infra-red. Thus, for O_2 and CO_2 (since the spin of oxygen is zero), every alternate rotational level is absent. In case of O_2, every level with even J values is missing and thus every transition labelled $J = 0, 2, 4, ...$ is also missing in the spectrum. In the case of H_2, and other molecules composed of nuclei with non-zero spin, the spectral lines show an alternation of intensity.

7. **Can you decide about Raman activity if the molecule has little or no symmetry.**

Ans. If a molecule has little or no symmetry, it is quite easy to decide whether its vibrational modes will be Raman active or inactive. It is usually correct to assume that all its modes are Raman active. But when the molecule has considerable symmetry, it is not always easy to decide whether or not the polarisability changes during the vibration.

8. **Explain in brief the Rule of mutual exclusion.**

Ans. The rule states that if a molecule has a centre of symmetry, then Raman active radiations are infra-red inactive and vice versa. If there is no centre of symmetry, then some vibrations may be both Raman as well as infra-red active.

9. **Write a few lines about the Raman spectrum of chloroform.**

Ans. Raman lines appear at 262, 366, 668, 761, 1216 and 3019 cm^{-1} on the low frequency (stoke's) side of the exciting line while the line at 262 cm^{-1} in the frequency (antistoke's) side is included for a comparison of its intensity.

10. **Explain intensity of Raman lines.**

Ans. The intensity of Raman line, IR is directly proportional to $(V_o - V_{vib})^4$. The intensity of Raman lines depends upon the frequency of incident radiation. Stoke's lines are usually stronger than the antistoke's lines. The reason is that at room temperature, the higher levels are thinly populated than the lower levels.

11. **Describe the effect of temperature on Raman lines.**

Ans. At room temperature, the number of molecules possessing low energy is more. Due to this stokes' transitions will take place more frequently than antistoke's transitions. Due to this, stokes' lines are more intense. But when the temperature is raised, the kinetic energy of the molecule increases and more number of molecules are raised to the higher energy state. Due to this, antistoke's lines will gradually increase. Intensity also increases and they become prominent.

12. **What is the cause of Raman effect ?**

Ans. Raman spectra is due to the oscillation of a dipole moment induced in a molecule by the oscillating electric field of the incident light wave, Fig. 4.10. As the induced dipole moment is directly proportional to the polarisability of the molecule, the molecule must possess anisotropic polarisability which should change during molecular rotation or vibration for rotation or rotational-vibrational Raman spectra.

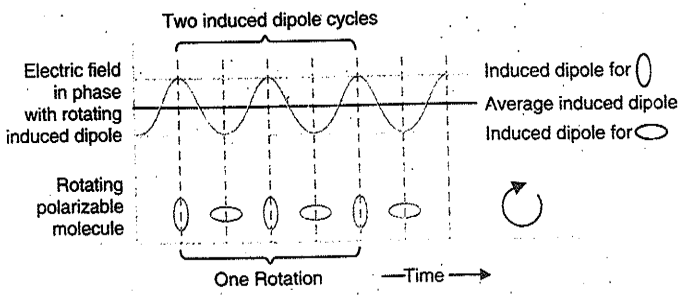


Fig. 4.10. Variation of polarisability of rotating with the oscillating electric field of radiations.

In the presence of electric field, the electron cloud of the atom or molecule is distorted or polarised. In the case of an atom, the polarisability is isotropic because the same distortion is introduced whatever is the direction of applied field. In case of a molecule, the extent of distortion (or polarisability) may change with the direction of the field. For example, hydrogen molecule is more distorted if the electric field is applied in the direction of bond.

13. **Write two advantages of Raman spectroscopy over infra-red spectroscopy.**

Ans. 1. Raman spectral lines are independent of the frequency of incident radiations. Hence, it can be easily studied in the visible region whereas IR spectrum is obtained in the range 4000–667 cm^{-1}.

2. Raman spectrum is not interfered by the presence of moisture or water in the sample whereas IR spectrum is affected by the presence of water in the sample.

3. Raman spectra can be obtained clearly in the gaseous, liquid and solid state of the compound.

14. **How will you distinguish Raman effect with Fluorescence ?**

Ans. In Raman effect, the molecule does not absorb the incident photon for the excitation of electron to well-defined electronic state. The electron wave function is perturbed by the photon for a period of 10^{-15} s, a value which may be compared to the half life of about 10^{-8} s for the fluorescent effect. The difference becomes more clear by the fact that fluorescence may be quenched but Raman effect cannot. The spacing between the bands in the fluorescent spectrum is equal to the difference in energy between the vibrational levels of the ground state whereas the spacing between the bands of absorption spectrum is equal to the difference in the energy between vibrational levels of the ground state.

Raman and infra-red spectra give a picture of molecule which is more instantaneous because the period of molecular vibration is in the order of 10^{-12} – 10^{-14}s which is extremely small. On the other hand, in the NMR technique at room temperature, the time on average spans a period long enough for interconversion of different conformational isomers.

FURTHER READING

1. **Carey, P.R.** Biochemical applications of Raman and Resonance Raman spectroscopies. Academic Press, 1982.
2. **William, D.H. and I. Fleming.** Spectroscopic methods in organic chemistry 4th ed. McGraw-Hill, 1989.
3. **Grasselli, J.G., M.K., Snavely and B.J. Bulkin.** Chemical applications of Raman spectroscopy, Wiley, 1981.
4. **Herzberg, G.** Molecular structure and Molecular spectra vol. 2, Infra-red and Raman spectra of Polyatomic molecules, Van Nostrand, 1945.
5. **Hendra, P.C. Jones and G. Warnes.** FT Raman spectroscopy, Ellis Horwood, 1991.

REVIEW QUESTIONS

1. (*a*) What is meant by the term Polarisability?
   (*b*) State the selection rules for Raman scattering.
2. What is Raman spectra? What is the criterion for a molecule to be Raman active?
3. What are Rayleigh. Stoke's and antistoke's lines?
4. Explain the cause of Raman effect. Give its importance.
5. What are stoke's and antistoke's line? Explain.
6. What do you understand by P, Q and R branches in vibrational-rotational band?
7. What type of molecule, exhibit vibrational-rotational spectra and why?
8. (*a*) Discuss briefly the quantum theory of Raman effect.
   (*b*) Explain why N_2 is Raman active?
9. What is Raman effect? How does Raman effect help in the calculation of moment of inertia and the bond length?
10. (*a*) State the selection rules for rotation Raman transitions. Derive expression for stokes' and antistokes' lines.
    (*b*) What type of compounds exhibit Raman spectra?
11. (*a*) Describe briefly the applications of pure rotational spectra.
    (*b*) Write a short note on Raman spectroscopy.
12. (*a*) Describe the occurrence of stoke's lines, antistoke's lines and Rayleigh lines in the above type of spectroscopy.

How do their intensities vary in pure Raman rotational spectra?

(*b*) Why are molecules which are not IR active show the type of spectrum ?

13. A substance shows Raman line at 4567 Å when the exciting line 4358 Å is used. At what positions stoke's and antistoke's lines for the same substance will be observed when the position of Rayleigh line is 4047 Å ?
14. The Rayleigh line in the Raman experiment is 4358 Å and the spectrum shows the stokes' line at 6433 Å. Find the wavelength of the antistoke's line.
15. The centre of vibrational band of oxygen lies at 1556 cm^{-1} while that of HCl vapour at 2886 cm^{-1}. Calculate the relative intensities of stoke's and antistoke's lines for both the cases.
16. (*a*) Rotational intensities of transitions occurring in a molecule are different. Comment.
    (*b*) Show that the energy difference between two adjacent lines in the rotational spectrum of a rigid diatomic molecule is constant.
17. (*a*) What do you know about Raman effect? What is its cause? Discuss a theory to explain the frequency due to Rayleigh, Stoke's and antistokes' lines in the vibration-rotation Raman spectrum.
    (*b*) What are the advantages of Raman spectroscopy over IR spectroscopy ?
18. When acetylene is irradiated with 4358 Å line of mercury, a Raman line attributed to symmetrical stretching vibration is observed at 4768 Å. Compute the fundamental frequency for the said vibration.
19. (*a*) What are the rotational selection rules and their basis and the uses? Explain.
    (*b*) Describe the effect of temperature on rotation spectra.
    (*c*) Explain factors affecting the intensity of spectral lines.
20. (*a*) Explain Raman effect. What information does it give regarding the structure of the molecule.
    (*b*) What are the advantages of Raman spectroscopy over Infra-red spectroscopy.
21. The fluorine molecules were excited by 4047 Å and 4358 Å Hg lines. The stokes' lines are observed at 4199 Å and 4534 Å respectively. Compute the ground state vibrational frequency of F_2 and its force constant also.
22. (*a*) What is Raman spectrum? Name the different types of lines present in it and explain the reasons for observing these lines.
    (*b*) What is the difference between pure rotational spectra and vibrational-rotational spectrum. In which regions, are these observed?
23. (*a*) Which of the following will show rotational spectra and why?
    HCl, CO_2, C_6H_6 and CO.
    (*b*) How do you explain stoke's lines and antistoke's lines in the Raman spectra?

MULTIPLE CHOICE QUESTIONS

Choose the correct answer:

1. For Raman spectra, the molecule must have
   (*a*) anisotropic polarisability (*b*) isotropic polarisability
   (*c*) oscillating dipolomoment
2. The selection rule of stokes line in the rotational Raman spectrum of a molecule is:
   (*a*) $\Delta J = -2$ (*b*) $\Delta J = +2$ (*c*) $\Delta J = 0$ (*d*) $\Delta J = +1$
3. The cause of Raman spectrum of a molecule is:
   (*a*) Change of polarisability of the molecule
   (*b*) no effect on polarisability of the molecule
   (*c*) none.
4. Which of the following are microwave active?
   (*a*) HCl (*b*) CO_2 (*c*) H_2 (*d*) O_2

5. The molecule which is I.R. inactive but Raman active is:
   (*a*) HCl (*b*) SO_2 (*c*) N_2 (*d*) Protein
6. Raman effect is
   (*a*) absorption of light (*b*) emission of light
   (*c*) inelastic scattering of light (*d*) elastic scattering of light.
7. Raman spectra differs from Infra-red spectra as it shows:
   (*a*) scattering of radiation by vibrating molecules
   (*b*) Polarisability of the molecule changes
   (*c*) Water can be used as solvent
   (*d*) All of these.
8. Stokes lines are more intense than antistoke's lines because stokes' lines are caused by molecule of:
   (*a*) lower energy level (*b*) more populated molecules
   (*c*) higher energy are more populated (*d*) None of these
9. In case same lines are obtained both in infra-red and Raman spectra, then the molecule should
   (*a*) be centrosymmetric (*b*) has no centre of symmetry
   (*c*) have high value of dipolomoment (*d*) low value of dipolomoment
10. Raman spectrum of a compound is not disturbed by
    (*a*) frequency of incident radiation (*b*) the presence of water
    (*c*) absence of polarisability (*d*) None of these
11. For quantitative analysis of the mixtures, the height of the Raman peak varies:
    (*a*) inversely with concentration of the sample
    (*b*) linearly with concentration of the sample
    (*c*) with magnitude of dipolemoment of the molecule
    (*d*) None of these
12. Rotational Raman spectra of a compound resembles
    (*a*) Infra-red spectra (*b*) Ultra-violet spectra
    (*c*) near infra-red spectra (*d*) far infra-red spectra.

ANSWERS. 1. (*a*) 2. (*b*) 3. (*a*) 4. (*a*) 5. (*c*) 6. (*c*)
7. (*d*) 8. (*a*, *b*) 9. (*b*) 10. (*a*, *b*) 11. (*b*) 12. (*c*)

CHAPTER

5

Nuclear Magnetic Resonance Spectroscopy

5.1 Introduction
5.2 Relaxation Process
5.3 Number of Signals
5.4 Instrumentation
5.5 Positions of Signals (Chemical Shift)
5.6 Internal Standards
5.7 Shielding and Deshielding Effects
5.8 Factors Influencing Chemical Shift
5.9 Solvents Used
5.10 Peak area and Proton Counting
5.11 Splitting of the Signals
5.12 Spin-spin Coupling
5.13 NMR Absorption by other Nuclei
5.14 Calculating the Ratio in the Heights of the Signals
5.15 Chemical Exchange (Proton Exchange Reactions
5.16 Coupling Constant (J)
5.17 Restricted Rotation
5.18 Important tips for Interpreting an Nmr Spectrum
5.19 Some Important Nmr Spectra
5.20 Double Resonance* (Spin Decoupling)
5.21 Nuclear Overhauser Effect (N.O.E.)
5.22 NMR Spectrum at More than One Radio-frequency
5.23 Deuterium Exchange Reactions
5.24 C^{13}–NMR Spectroscopy
5.25 F^{19}– NMR
5.26 Nuclear Magnetic Resonance Spectra of Carbocations
5.27 Applications of NMR Spectroscopy
5.28 Important Features in Nuclear Magnetic Resonance Spectroscopy
5.29 Simple Problems on Nuclear Magnetic Resonance
5.30 Short Questions with Answers

5.1 Introduction

The nucleus of a hydrogen atom (proton) behaves as a spinning bar magnet because it possesses both electric and magnetic spin. Like any other spinning charged body, the nucleus of hydrogen atom also generates a magnetic field (see Fig. 5.1).

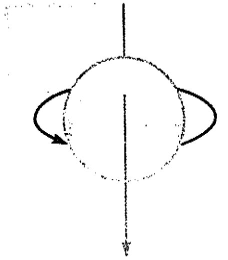
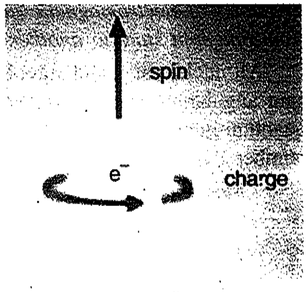


Fig. 5.1. Spinning charge in nucleus generates magnetic dipole



Nuclear magnetic resonance involves the interaction between an oscillating magnetic field of electromagnetic radiation and the magnetic energy of the hydrogen nucleus or some other type of nuclei when these are placed in an external static magnetic field.

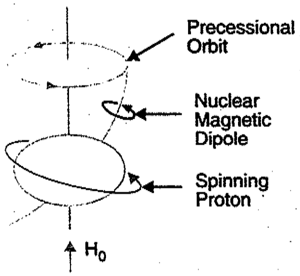
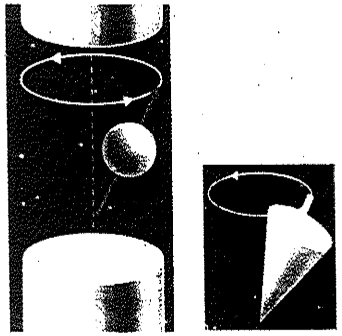


Fig. 5.2. Proton precessing in magnetic field H_0.

The sample absorbs electromagnetic radiations in radiowave region at different frequencies since absorption depends upon the type of protons or certain nuclei contained in the sample. Consider a spinning top. It also performs a slower waltz like motion, in which the spinning axis of the top moves slowly around the vertical. This is **precessional motion** and the top is said to be precessing around the vertical axis of earth's gravitational field. The precession arises from the interaction of spin with earth's gravity acting vertically downwards. It is called **Gyroscopic motion.** Let us consider a peculiarity of a small magnet spinning in an external field. It has been found that the proton (tiny magnet) precesses about the axis of the external magnetic field in the same manner in which a spinning gyroscope precesses under the influence of gravity. (see Fig. 5.2).



It has been found that

$$\omega = \gamma H_0 \quad \ldots(i)$$

where ω = angular precessional velocity
H_0 = applied field in gauss:
γ = Gyromagnetic ratio = $\frac{2\pi\mu}{hI}$
Here μ = magnetic moment of the spinning bar magnet.
I = spin quantum number of the spinning magnet.
h = Planck's constant

According to the fundamental NMR equation which correlates electromagnetic frequencies with the magnetic field, we say that

$$\gamma H_0 = 2\pi\nu \quad \ldots(ii)$$

Here ν is frequency of electromagnetic radiation

From (*i*) and (*ii*)

Angular precessional velocity $\omega = 2\pi\nu$

The value of this frequency (ν) inserted is called **Precessional frequency.**

The precessional frequency may be defined as the number of revolutions per second made by the magnetic moment vector of the nucleus around the external field H_0. Alternatively, the precessional frequency of the spinning bar megnet (nucleus) may be defined as equal to the *frequency of electromagnetic radiations in megacyles per second necessary to induce a transition from one spin state to another.*

All nuclei carry a charge. So, they will possess spin angular momentum. The moment of the spin angular momentum is quantised, *i.e.*, only those nuclei which have a finite value of spin quantum number ($I > 0$) will precess along the axis of rotation. It is known that the spin quantum number I is associated with mass number and atomic number of the nuclei.

Mass number	*Atomic number*	*Spin quantum number I*
odd	odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ...$
even	even	0
even	odd	1, 2, 3, ...

The circulation of the nuclear charge generates a magnetic moment along the axis. The intrinsic magnitude of the generated dipole is expressed in terms of magnetic moment μ.

If a proton is placed in a magnetic field, then it starts precessing at a certain frequency in the radiowave region and thus, will be capable of taking up one of the two orientations* with respect to the axis of the external field.

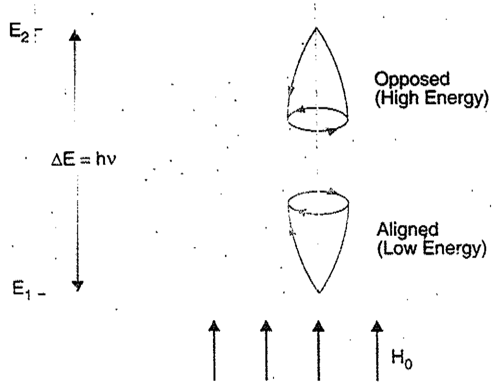
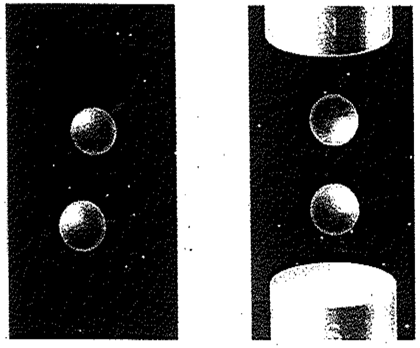
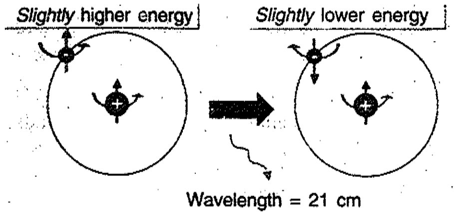


Fig. 5.3. Energy level of a proton.



(*i*) Alignment with the field and

(*ii*) Alignment against the field.



If a proton is precessing in the aligned orientation, it can pass into the opposed orientation by absorbing energy. From the high energy opposed orientation, it comes back to the low energy aligned orientation (more stable) by losing energy. The transition from one energy state to the other is called **flipping** of the proton. The transition between the two energy states can be brought about by the absorption of a quantum of electromagnetic radiation in the radiowave region with energy $h\nu$.

The energy required to bring about the transition ($\Delta E = h\nu$) or to flip the proton depends upon the strength of the external field. Stronger the field, greater will be the tendency of the nuclear magnet to remain lined up with it and higher will be the frequency of the radiation needed to flip the proton to the higher energy state.

We know that $$\nu = \frac{\gamma H_0}{2\pi}$$

where

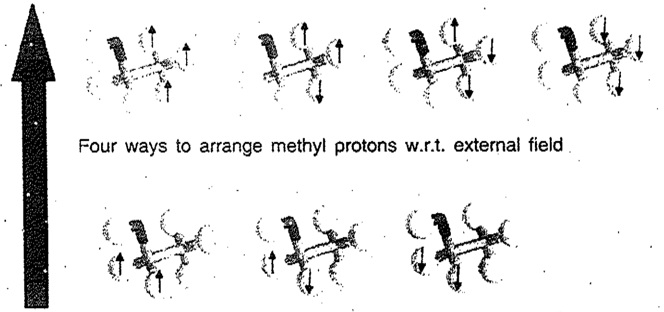
ν = Frequency in cycles per sec or Hz.

H_0 = Strength of the magnetic field in gauss.

γ = Nuclear constant or Gyromagnetic ratio and is equal to 26750 for the proton.

In a field of 14092 gauss, the energy required to cause flipping corresponds to electromagnetic radiation of frequency 60 million cycles per second or 60 MHz (Radiowave region). This energy is much lower than that possessed by infra-red radiation. If we irradiate the precessing nuclei with a beam of electromagnetic radiation of desired frequency, then the low energy nuclei will absorb it and move to higher energy state. The precessing proton will absorb energy from the radio-frequency source only if the precessing frequency is the same as the frequency of the radio frequency beam, *i.e.*, when the quantum energy ($h\nu$) of electromagnetic radiation matches up the energy difference between the two energy states at the field strength H_0. When this occurs, the nucleus and the radio-frequency beam are said to be in resonance. Hence, the term nuclear magnetic resonance.

This technique consists of exposing the protons (placing the substance) in an organic molecule to a powerful field. The protons* will precess at different frequencies. Now, we irradiate these precessing protons with steadily changing frequencies (for promoting or flipping protons from the low energy state to high energy state) and observe the frequency/frequencies at which absorptions** occur. It is generally more convenient to keep the radio-frequency constant and the strength of the magnetic field is constantly varied. At some value of the field strength, the energy required to flip the protons matches the energy of the radiation. Absorption occurs and a signal is observed. Such a spectrum is called **Nuclear magnetic resonance spectrum**.



Four ways to arrange methyl protons w.r.t. external field

Three ways to arrange methyene protons w.r.t. external field

NMR Spectrum Splitting

---

* The number of orientations taken up by a spinning nucleus is given by $2I + 1$. For proton, $I = 1/2$. Thus, a proton can have ($2 \times 1/2 + 1 = 2$) two orientations with respect to the axis of the external field.

* Different sets of protons.

** In the absence of such process, all the nuclei in the lower energy state will be raised to the higher energy state. Thus, no more energy is absorbed and nuclear magnetic resonance will not occur.

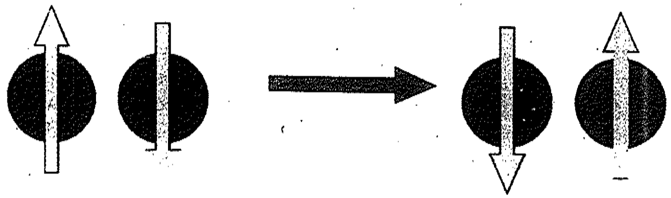
It may be noted that all protons do not absorb at the same applied field but absorption depends upon the magnetic field which a particular proton feels. Clearly, the effective field strength is different for different sets of protons as one set of protons will have slightly different environment from any other set of protons. Thus, at a given radio-frequency, different protons (different sets of equivalent protons) will require slightly different applied field strengths to produce the same effective field strength which causes absorption. In the *nmr* spectrum, we measure applied field strengths for each set of protons and the absorption peaks are plotted. The number of signals at different applied field strengths is equal to the different sets of equivalent protons.

5.2 Relaxation Process

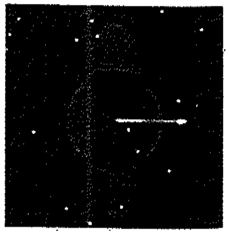
Relaxation processes involve some non-radiative transitions by which a nucleus in an upper transition state returns to the lower spin state. Three kinds of relaxation processes are :

(*i*) Spin-spin relaxation
(*ii*) Spin-lattice relaxation
(*iii*) Quadrupole relaxation

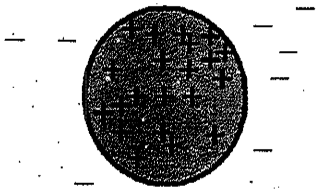
(*i*) **Spin-spin Relaxation.** It is due to the mutual exchange of spins by two precessing nuclei which are in close proximity to each other. We know that each precessing nucleus is associated with a magnetic vector component rotating in a plane perpendicular to the field. If this small rotating magnetic field is the same as is required to induce a transition in the neighbouring proton, then mutual exchange of spin takes place. In other words, it involves the transfer of energy from one nucleus to the other. There is no net loss of energy. The spread of energy among the nuclei concerned results in line broadening which makes *nmr* spectra of solids comparatively more interesting.



(*ii*) Spin-lattice Relaxation (**Longitudinal relaxation**). It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice. The energy is transferred to the components of the lattice as the additional translational, vibrational and rotational energy. The total energy of the system remains the same. An efficient relaxation process involves a short time and results in the broadening of absorption peaks. Smaller the time of the excited state, greater is the line width. This mechanism is not effective in solids. This process keeps the excess of nuclei in the lower energy state which is a necessary condition for nuclear magnetic resonance phenomenon.



Spin-lattice Relaxation



Quadroupole moment

(*iii*) **Quadrupole Relaxation.** It is a prominent relaxation process for nuclei having $I > \frac{1}{2}$. The nuclei (such as ^{14}N, ^{17}O, ^{11}B, etc) due to anisotropic interaction between non-spherical, electrically quadrupole nuclei and the electric field gradients at the nucleus caused by electric environments possess an asymmetric positive charge distribution on the nuclei. Hence, these nuclei exhibit electric quadrupole moments and relax rapidly as display very broad signals. This process of deactivation of nuclei is called electric quadrupole relaxation. In case of chlorine, bromine and iodine, this mechanism is very fast and these nuclei became practically non-magnetic for the purpose of high resolution nuclear magnetic resonance spectroscopy. But for nitrogen (N^{14}) and deuterium (H^2), quadrupole relaxation is less effective and their resonance lines are observed more easily.

Note : The broadening of a signal is directly proportional to the life time of the absorbing nuclei in the excited state. More efficient the relaxation process, more broader is the resonance band. Thus, for maximum resolution :

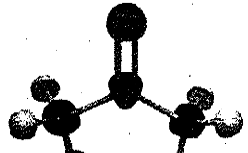
(*i*) the spin-spin relaxation process is efficient in solids and viscous liquids. Clearly, for better resolution, use of solids viscous samples should be avoided otherwise broad signals result.

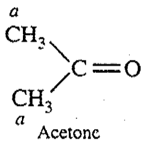
(*ii*) paramagnetic impurities like oxygen and other magnetic ions and materials should be removed from the sample.

5.3 Number of Signals

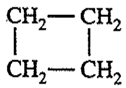
The number of signals in the *nmr* spectrum tell the number of different sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons. **It may be noted that magnetically equivalent protons are chemically equivalent protons.** *Let us find the various sets of equivalent protons (signals) in the following types of compounds:*

(*a*)

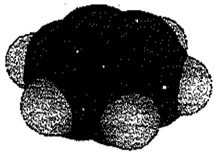


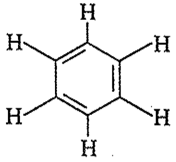


Acetone
(one signal)

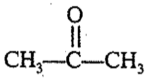


Cyclobutane
(one signal)



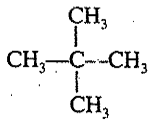


Benzene
(one signal)



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Acetone
(one signal)



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

Tetramethyl methane
(one signal)

In acetone, all the six protons are in exactly similar environment. Therefore, only one signal is observed. Similarly, we see only one signal for cyclobutane.

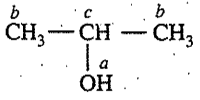
(*b*) Some compounds showing more than one signal are as follows:

(*i*) $\overset{b}{CH_3}-\overset{a}{OH}$
2 *nmr* signals

(*ii*) $\overset{c}{CH_3}-\overset{b}{CH_2}-\overset{a}{NH_2}$
3 *nmr* signals

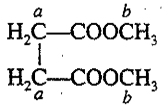
(*iii*) $\overset{c}{CH_3}-\overset{b}{CH_2}\overset{a}{CH_2Cl}$
3 *nmr* signals

(*iv*)



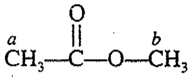
$\overset{b}{CH_3}-\underset{\underset{\overset{a}{OH}}{|}}{\overset{c}{CH}}-\overset{b}{CH_3}$

3 *nmr* signals



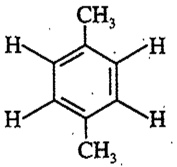
$\begin{array}{l}\overset{a}{H_2C}-\overset{b}{COOCH_3}\\ \ |\\ \underset{a}{H_2C}-\underset{b}{COOCH_3}\end{array}$

(Two signals)



$\overset{a}{CH_3}-\overset{\overset{O}{\|}}{C}-O-\overset{b}{CH_3}$

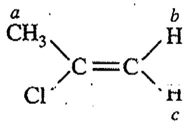
Methyl acetate
(Two signals)



p-xylene
(Two signals)

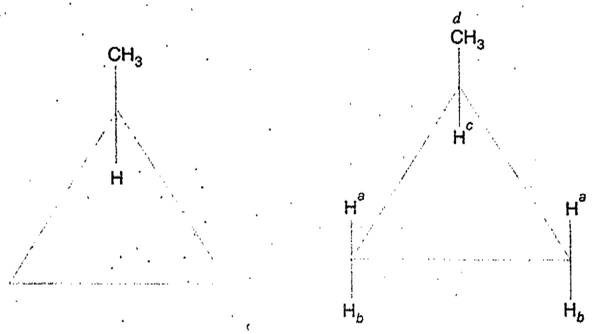
(*c*) Strictly speaking, chemically equivalent protons must also be stereo-chemically equivalent, *i.e.*, a particular set of protons are said to be chemically equivalent only if they remain in exactly similar environment when the stereo-chemical formula of the molecule under consideration is written.

Consider the case of 2-chloropropene, $CH_3—C(Cl) = CH_2$. From this structure, one can expect two sets of equivalent protons (Two peaks). But stereo-chemical formula reveals three sets of protons in it.



H^b and H^c are not in exactly similar environment.

Now consider methyl cyclopropane. For this compound, one can expect three sets of protons. But actually four signals are observed as is clear from the following stereo-chemical formula [Fig. 5.4 (*a*)].

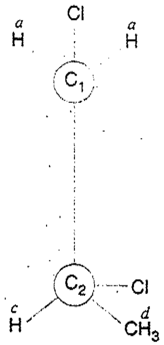


4 *nmr* signals

Methyl cyclopropane

Fig. 5.4 (*a*). Number of signals in Methyl cyclopropane.

Consider 1, 2-dichloropropane $\overset{3}{C}H_3—\overset{2}{C}H(Cl)—\overset{1}{C}H_2Cl$. For this compound one can expect three signals. But actually, four signals are observed as two hydrogen atoms attached with C_1 are not in exactly similar environment. Rotation around C—C single bond in this molecule cannot bring similar environment for the said hydrogen atoms.

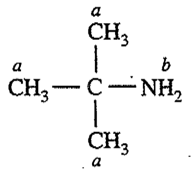


1, 2 – dichloropropane

Fig. 5.4 (b). Four signals in 1, 2-dichloropropane.

Let us note the number of *nmr* signals for the following compounds:

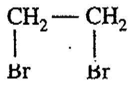
(*i*)



$$\overset{a}{CH_3}—\underset{\underset{a}{CH_3}}{\overset{\overset{a}{CH_3}}{C}}—\overset{b}{NH_2}$$

Tert-butylamine (2 *nmr* signals)

(*ii*)



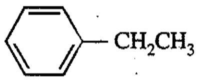
$$\underset{Br}{CH_2}—\underset{Br}{CH_2}$$

1, 2-dibromoethane (1 *nmr* signal)

(*iii*) CH_3CHBr_2 (2 *nmr* signals)

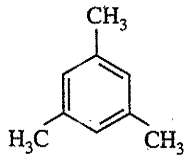
1,1-dibromoethane

(*iv*)



(Ethyl benzene) (3 *nmr* signals)

(*v*)



Mesitylene (2 *nmr* signals)

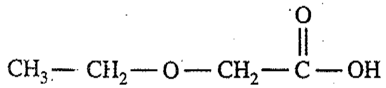
(*vi*) $CH_3—CH_2—O—CH_2—CH_3$ (2 *nmr* signals)

Diethyl ether

(*vii*) CH_3CH_2CHO (3 *nmr* signals)

Propanal

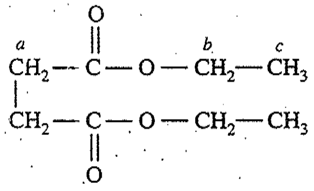
(*viii*)



$$CH_3—CH_2—O—CH_2—\overset{\overset{O}{\|}}{C}—OH$$

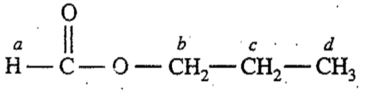
Ethoxy acetic acid (4 *nmr* signals)

(*ix*)



Diethyl succinate (3 *nmr* signals)

(*x*)



$$\overset{a}{H}—\overset{\overset{O}{\|}}{C}—O—\overset{b}{CH_2}—\overset{c}{CH_2}—\overset{d}{CH_3}$$

n– Propyl formate (4 *nmr* signals)

Note. *nmr* does not distinguish between mirror images or enantiomers.

5.4 Instrumentation

Nuclear Magnetic Resonance spectrophotometer makes use of a magnet, a radio-frequency, a detector and an amplifier. The detection system is used to note that energy is being transferred from the radio-frequency beam to the nucleus.

The sample under investigation is taken in a glass tube which is placed between the pole faces of a magnet. A radio-frequency source ($\nu = 60$ mega cycles sec^{-1}) is made to fall on the sample. It can be done by feeding energy (Radio-frequency source) into a coil wound round the sample tube. A signal is detected if the nuclei in the sample resonates with the source, *i.e.*, ΔE, energy required to flip the proton is the same as that of the source. Energy is transferred from the source via nuclei to the detector coil. The output from the detector can be fed to a cathode ray oscillograph or to a strip chart recorder after amplication etc.

Protons being in different electronic environments in a molecule cannot resonate at exactly 60 mega cycles sec^{-1}. For practical purposes, radio-frequency source is held steady at the said frequency and field strength is varied by placing small electromagnet to the pole faces of the main magnet. By increasing the current flowing through these electromagnets, the total field strength is increased.

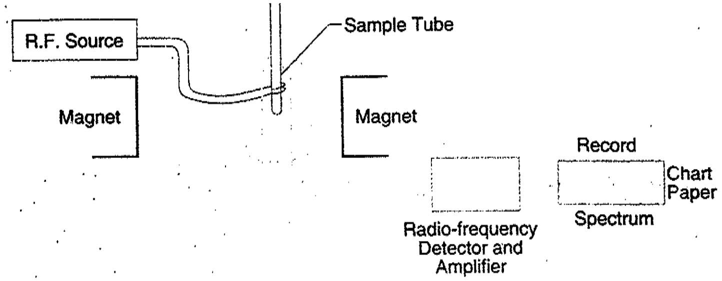


Fig. 5.5. Nuclear magnetic resonance spectrophotometer.

As the field strength increases, the precessional frequency of each proton increases until resonance with the radio-frequency source takes place. As a proton (or a set of equivalent protons) comes to resonance, the signal from the detector produces a peak on the chart paper. The *nmr* spectrum consists of series of peaks that correspond to different applied field strengths. Each peak means a set of protons.

Positions of Signals (Chemical Shift)

The number of signals in an *nmr* spectrum tells the number of the sets of equivalent protons in a molecule.

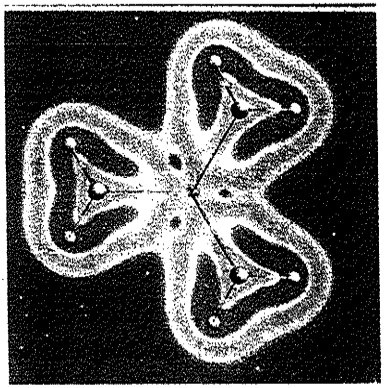
The positions of the signals in the spectrum help us to know the nature of protons *viz.*, aromatic, aliphatic, acetylenic, vinylic, adjacent to some electron attracting or electron releasing group etc. Each of these types of protons will have different electronic environments and thus, they absorb at different applied field strengths. It is important to note that it is the electronic environment which tells where a proton shows absorption in the spectrum.

When a molecule is placed in a magnetic field, its electrons are caused to circulate and thus, they produce secondary magnetic fields *i.e.*, induced magnetic field. Rotation of electrons about the proton itself generates a field in such a way that at the proton, it opposes the applied field. Thus, the field felt by the proton, is diminished and the proton is said to be **shielded.** Rotation of electrons (specially π electrons) about the nearby nuclei generates a field that can either oppose or reinforce the applied field at the proton. If the induced field opposes the applied field, then proton is said to be shielded. But if the induced field reinforces the applied field, the proton feels a higher field strength and thus, such a proton is said to be **deshielded.** Shielding shifts the absorption upfield and deshielding shifts the absorption downfield to get an effective field strength necessary for absorption.

---

* At a steady external field, different sets of protons will absorb or come to resonance at different values of the radio-frequencies.

Such shifts (compared with a standard reference) in the positions of *nmr* absorptions which arise due to the shielding or deshielding of protons by the electrons are called *chemical shifts*. For measuring chemical shifts of various protons in a molecule, the signal for tetramethyl silane (TMS) is taken as a reference. Due to the low electronegativity of silicon, the shielding of equivalent protons in tetramethyl silane is greater than most of the organic compounds. Therefore, *nmr* signal for tetramethyl silane is taken as a reference and chemical shifts for different kinds of protons are measured relative to it. Clearly, the *nmr* signal for a particular proton in a molecule will appear at different field strengths compared to a signal from TMS., *This difference in the absorption position of the proton with respect to TMS signal is called chemical shift* (δ-value). It is not measured in gauss but is measured in equivalent frequency units which is then divided by the frequency of the spectrometer used. This gives the value of δ (delta). Protons with the same chemical shift are called equivalent protons. Non-equivalent protons have different chemical shifts. δ (Delta) or τ (Tau) scales are commonly used. In majority of organic compounds, protons resonate at a lower field than the protons of tetramethyl silane (TMS). Thus assigning delta (δ) value for TMS equal to zero, a scale can be defined in which most proton resonances are of the same sign. Any proton or set of protons which absorb at a field lower than TMS is given a positive value for δ, Tetramethyl silane is the most convenient reference and has the following characteristics:



[illegible] Silane

(*i*) It is miscible with almost all organic substances.
(*ii*) It is highly volatile (low boiling) and is readily removed from the system.
(*iii*) It does not take part in intermolecular associations with the sample.

The values of δ for a substance with respect to TMS can be obtained by measuring $\nu_S—\nu_{TMS}$

where ν_S = Resonance frequency of the sample
ν_{TMS} = Resonance frequency of TMS

Keeping the radio-frequency constant, an *nmr* signal for a particular set of proton in the sample will appear at different field strength than the signal obtained from TMS. Thus, the value for $\nu_S—\nu_{TMS}$ can be expressed in the corresponding field strength in gauss. Since, the operating frequency of the instrument is directly proportional to the strength of the magnetic field, we can define δ as

$$\delta = \frac{\nu_{\text{samples}} - \nu_{\text{reference}}}{\text{operating frequency in megacycles (per sec.)}}$$

$$= \frac{\Delta\nu}{\text{operating frequency in megacycles (per sec.)}}$$

where Δν is the frequency shift. The value of δ is expressed in parts per million (ppm). Most chemical shifts have δ values between 0 and 10. In the τ scale, signal for the standard reference, TMS is taken as 10 ppm. It has been found that signals for fluorine resonances (absorptions due to fluorine nuclei) do not appear in this range but are observed downfield by about 50 ppm or even more.

The two scales are related by the expression

$$\tau = 10 - \delta$$

NMR signal is usually plotted with magnetic field strength increasing to the right. Thus, the signal for TMS (highly shielded) appears at the extreme right of spectrum with $\delta = 0$ ppm. **Greater the deshielding of protons, larger will be the value of δ.** For most of the organic compounds, signals appear downfield to the left of TMS signal. The value of chemical shifts for protons in different environments are:

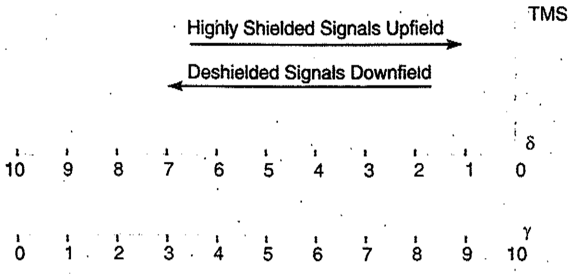


Fig. 5.6. Chemical shift

If the observed shift from TMS is 250 Hz and the operating frequency of the instrument is 100 MHz, then the chemical shift in terms of δ is given by the expression :

$$\delta = \frac{250 \text{ Hz}}{100 \times 10^6 \text{ Hz}} = 2.5 \times 10^{-6}$$

The frequency ratio is then multiplied by 10^6 and the resulting value is chemical shift which is expressed as parts per million (10^{-6}) of the operating frequency.

$$\delta(\text{Chemical shift}) = \frac{\nu_s - \nu_{TMS} \text{ (in Hz)}}{\text{Operating frequency of instrument}} \times 10^6 \text{ ppm}$$

$$= 2.5 \times 10^{-6} \times 10^6 = \mathbf{2.5 \text{ ppm.}}$$

It is important to note that chemical shift is independent of the operating frequency of the instrument but depends upon the solvent. Thus, it becomes essential that the value of chemical shift is reported alongwith solvent used for running the spectrum.

Internal Standards

Reference materials which are commonly employed as internal standards are :

1. Tetramethyl Silane (TMS). It is generally employed as internal standard for measuring the position of ^1H, ^{13}C and ^{29}Si in NMR spectroscopy. It is due to the following facts :

(*i*) It is chemically inert and miscible with a large range of solvents.

(*ii*) Its twelve protons are all magnetically equivalent.

(*iii*) It is highly volatile and can be easily removed to get back the sample.

(*iv*) It does not take part in intermolecular associations with the sample.

(*v*) Its resonance position is far away from absorptions due to protons in most organic molecules. Thus, assigning TMS = 0 (δ), a scale can be deviced in which most of the proton resonances are of the same sign.

2. Sodium salt of 3-(trimethyl silyl) propane sulphonate. It is a water soluble campound. It is used as internal standard for running PMR spectra of water soluble substances in deuterium oxide (D_2O) solvent.

The chemical shifts for various types of protons with TMS as standard reference is given in Table T_5–1.

Table T_5–1. Chemical shift for various types of protons.

Types of protons			*Chemical shift in ppm*	
			δ	τ
(*i*)	Cyclo-propane	$\overset{CH_2}{H_2C—CH_2}$	0.2*	9.8
(*ii*)	Primary hydrogens	$R—CH_3$	0.9	9.1
(*iii*)	Vinylic	C = C—**H**	4.6–5.8	5.4–4.2
(*iv*)	Acetylenic	C ≡ C—**H**	2–3.5	8–6.5
(*v*)	Aromatic	Ar—**H**	6–9.0	4–1.0
(*vi*)	Fluorides	**H**—C—F	4–4.5	6–5.5
(*vii*)	Chlorides	HC—Cl	3–4	7–6
(*viii*)	Alcohols	**H**—C—OH	3.4–4	6.6–6
(*ix*)	Ethers	**H**—C—OR	3.3–4	6.7–6
(*x*)	Esters	**H**—C—COOR	2–2.2	8–7.8
(*xi*)	Acids	H—C—COOH	2–2.5	8–7.5
(*xii*)	Aldehydic	RCHO	9–10	1–0
(*xiii*)	Hydroxy	R—OH	1–5.5	9 – 4.5
(*xiv*)	Phenolic	Ar—OH	4–12	6 to –2
(*xv*)	Enolic	C=C—OH	15–17	–5 to –7
(*v*)	Carboxylic	RCOOH	10.5–12	–0.5 to –2

Shielding and Deshielding Effects*

Hydrogen nuclei in a molecule are surrounded by the electronic charge which shields the nucleus from the influence of the applied field. Thus, to overcome the shielding effect and to bring the protons to resonance, greater external field is required. Clearly, greater the electron density around the proton, greater will be the induced secondary magnetic field (Local diamagnetic effect) which opposes the applied field and thus, greater external field will cause proton absorption. The extent of shielding is represented in terms of shielding parameter α. When absorption occurs, the field H felt by the proton is represented as:

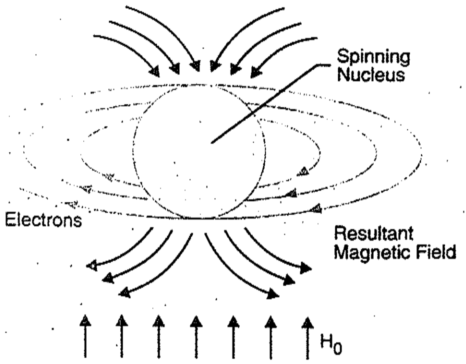


Fig. 5.7. Diamagnetic shielding about the nucleus.

$$H = H_0(1 - \alpha) \quad ...(1)$$

where H_0 is the applied field strength. Clearly the field felt by the proton does not correspond to the applied field.

---

* Slightly less shielded than TMS.

Greater the value of α, greater will be the value of applied field strength which has to be applied to get the effective field required for absorption and vice versa.

$$\text{Also} \qquad \nu = \frac{\gamma H}{2\pi} \quad ...(2)$$

$$\text{From 1 and 2,} \qquad \nu = \frac{\gamma H_0(1-\alpha)}{2\pi}$$

From this relation, it is clear that the protons with different electronic environments or with different shielding parameter can be brought into resonance in two ways:

(*i*) The strength of the external field is kept steady and the radio-frequency is constantly varied.

(*ii*) The radio-frequency is kept steady and the strength of the applied field is constantly varied.

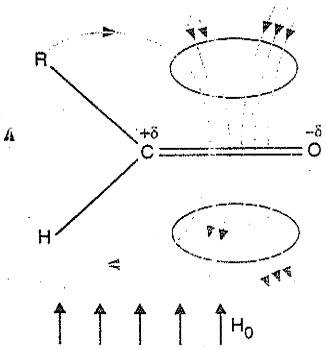
Clearly, at constant radio-frequency, shielding shifts the absorption upfield in the molecules where there is a spherical distribution of electrons around the proton. It is called **positive shielding**.

Presence of the electronegative atoms or groups cause reduction in electron density around the proton (deshielding) and thus, absorption is shifted downfield (τ decreases). Hence, we say that if local diamagnetic currents were responsible, then the value of proton absorption should depend upon the electronegativities of the attached atoms or groups. But there are some other factors viz., the diamagnetic and the paramagnetic effects from the neighbouring atoms and also the effects from the interatomic currents which results in the proton absorption shift.

It has been found that the absorption depends upon the manner in which the π electrons circulate under the influence of the applied field. In case of ethene oriented at right angles to the direction of the applied field, the induced magnetic field (due to the circulation of π electrons) is diamagnetic (opposes external field) around the carbon atoms and is paramagnetic (in the direction of the applied field) in the region of protons. Thus, protons feel more magnetic field (Deshielding) and hence absorption occurs at low field. Similarly, aldehydic protons appear at low field.

In the case of acetylene, the protons experience a diamagnetic shielding effect. The induced magnetic field at the protons is diamagnetic but paramagnetic at the carbon atoms. Thus, protons are said to be shielded (feel smaller field) and hence absorption occurs upfield (τ value increases).

In case of olefins, acetylenes, aldehydes, ketones, acids, esters, nitriles etc., if the proton is present in the positive region, it will be shielded and absorption occurs upfield. On the other hand, if the proton lies in the negative region, its absorption is downfield. In the case of benzene and other aromatic compounds, strong diamagnetic currents are induced (in the loops of the π electrons) by the applied field. This causes paramagnetic shielding at the aromatic protons and thus, absorption occurs downfield. On the other hand, any group which is present above or below the plane of the aromatic nucleus will be shielded and absorption for such a proton occurs upfield. Ring current effect as is seen in benzene and other aromatic compounds is absent in saturated hydrocarbons.



Deshielding of aldehydic proton

Fig. 5.8. Deshielding of aldehydic proton.

$H = K\nu$

Where K is constant and is called the magnetic susceptibility of the absorbing nucleus.

Anisotropic effect.

In saturated cyclic hydrocarbons, diamagnetic currents are induced as a result of the circulating bond electrons. This effect is weaker relative to that in aromatic nuclei (mobility of electrons). Although weak, yet it is responsible to distinguish between the axial and the equitorial protons in cyclohexane. Axial protons are comparatively shielded and such protons absorb 0.5 ppm upfield as compared to those of equitorial protons.

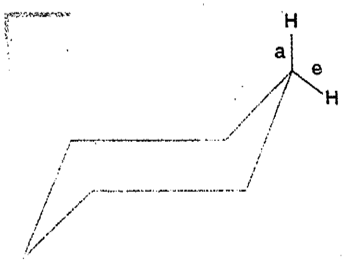
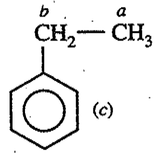


Fig. 5.9. Cyclohexane.

The deshielding effect due to a particular group decreases as its distance from the absorbing proton increases.



(A)

$$\overset{c}{CH_3}—\overset{b}{CH_2}—\overset{a}{CH_2Cl}$$

(B)

Due to the decreasing deshielding influence, the τ values of absorption decrease in the following order:

Compound A	Compound B
$a > b > c$	$c > b > a$

For saturated molecules, the diamagnetic contribution is most important and the absorption positions of the protons depend upon the electronegativities of the attached atoms or groups. The deshielding effect due to an electronegative atom falls with distance and there is a little effect on the position of absorption of protons which are three bonds away. In unsaturated compounds, paramagnetic effects become important. In addition to the distance, the effect depend upon the relative orientation of the protons with respect to the groups present in the molecule.

5.8 Factors Influencing Chemical Shift

Following are the factors which influence the chemical shift:

(*a*) Inductive effect

(*b*) van der Waal's deshielding

(*c*) Anisotropic effects

(*d*) Hydrogen bonding

(*a*) **Inductive effect.** A proton is said to be deshielded if it is attached with an electronegative atom or group. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will also be more. Consider the following compounds:

(*i*) $\overset{b}{CH_3}\overset{a}{CH_2}F$ (*ii*) $\overset{b}{CH_3}—\overset{a}{CH_2}—Cl$

Two signals are expected for each of the two compounds. Deshielding for protons '*a*' in compound (*i*) is more than that for similar protons in compound (*ii*).

As the distance from the electronegative atom increases, the deshielding effect due to it diminishes. Protons '*b*' are comparatively less deshielded and hence will resonate at comparatively lower value of δ.

Table T_5—1. Tau Value for CH_3-protons

Compound	*τ value*
CH_3F	5.75
CH_3Cl	6.90
CH_3Br	7.36

Why deshielding ? Hydrogen nuclei in a molecule are surrounded by electronic charge and shields the nucleus slightly from the influence of the applied field. Thus, to bring this proton to resonance, the applied field must be increased to overcome the shielding effect. In a magnetic field, the electrons around the proton are induced to circulate and thus, generate induced magnetic field which opposes the applied field. Greater the electron density circulating around the proton, greater is the induced magnetic field (opposing the external field) and greater will be the applied field required to overcome the shielding effect. On the other hand, electronegative atoms or groups withdraw electron density around the proton and thus, causes deshielding (reverse of shielding). Due to deshielding, smaller value of applied field will be needed to bring the proton to resonance.

Greater the electronegativity of the atom or group, greater will be the deshielding effect on a proton.

Greater the distance of the electronegative atom or group from a particular proton, smaller is the deshielding effect on it. In TMS, four electron releasing groups (—CH_3 groups) cause powerful shielding effect and hence TMS proton (all equivalent) resonate at high field.

Protons adjacent to $—\overset{+}{N}\langle$ are very strongly deshielded while those near $\rangle\overset{=}{C}—$ are powerfully shielded.

(b) Van der Waal's deshielding. In overcrowded molecules, it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate at slightly higher value of δ than expected in the absence of this effect.

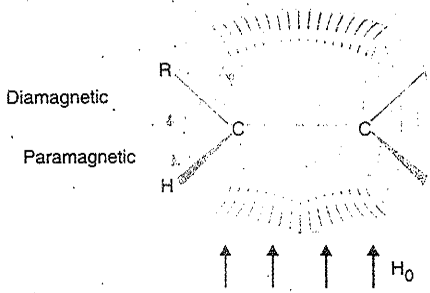


Fig. 5.10. Deshielding of Ethylenic protons.

(c) Anisotropic effects (Space effect). The deshielding effect on protons attached to C=C is higher than that can be accounted for by the inductive effect alone. Aldehydic and aromatic protons are much more deshielded. Alkyne protons appear at relatively low value of δ. The values of δ (chemical shift) in each case can be justified by explaining the manner in which the π electrons circulate under the influence of the applied field. Consider an alkene. It is so oriented that the plane of the double bond is at right angles to the applied field. Induced circulation of π electrons generates induced magnetic field which is diamagnetic around carbon atom and paramagnetic in the region of the alkene protons. Thus the protons will feel greater field strength and hence resonance occurs at lower applied field.

Alkynes. In alkynes, electronic circulation around triple bond takes place in such a way that the protons experience diamagnetic shielding effect. When the axis of the alkyne group lies parallel to the direction of the applied field, the π electrons are induced to circulate around the axis in such a way that the induced field opposes the applied field. Thus, protons feel smaller field strength (shielding) and hence resonance occurs at higher applied field (low δ value).

Benzene. In case of benzene, loops of π electrons are delocalised cylindrically over the aromatic ring. These loops of electrons are induced to circulate in the presence of the applied field producing ring current. The induced current is diamagnetic (opposing the applied field) in the centre of the ring and is paramagnetic outside the ring. Thus, the aromatic protons (around the periphery of the ring) experience a magnetic field greater in magnitude than the applied field. Such protons are said to be deshielded and hence, smaller applied field (higher value of δ) will be required to bring them to resonance. It may be noted that the protons held above and below the plane of the ring resonate at low δ value. In a molecule of toluene, the methyl protons resonate at 2.34 δ whereas a methyl group attached to an acyclic alkene appears at 1.95 δ. It can be explained by the greater deshielding influence of the ring current in an aromatic compound as compared to the deshielding influence caused by conjugated alkene group. From the NMR spectrum, we can thus, decide whether a particular compound has substantial aromatic character in it or not.

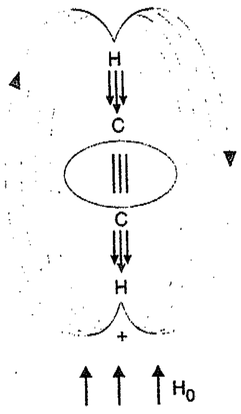


Fig. 5.11. Shielding of acetylene protons.

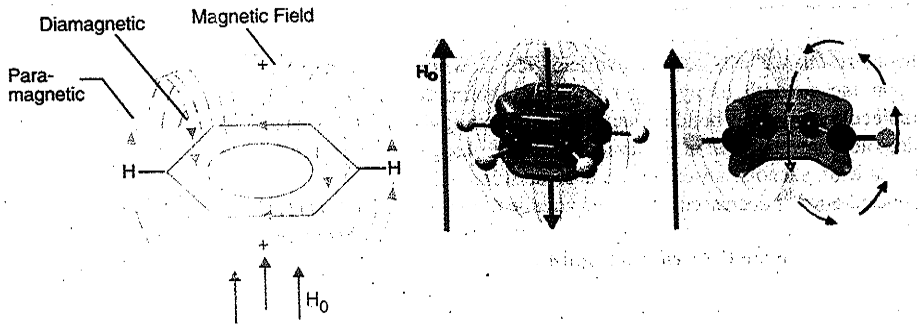
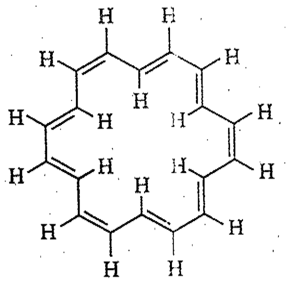


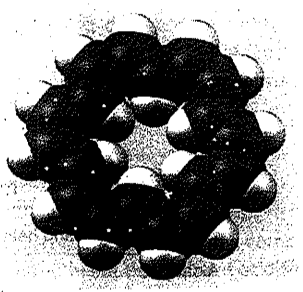
Fig. 5.12. Ring current effects in Benzene.

An excellent example of shielding and deshielding by ring currents is given by some of the annulenes. The protons outside the ring of [18] annulenes are strongly deshielded and those inside the ring are strongly shielded.

Compared to the anisotropic effects of circulating π-electrons, the sigma electrons of C—C bond produce a small effect. The axis of C—C bond is the axis of the deshielding cone.



[18] Annulene



[18] Annulene

The above figure accounts for the deshielding effect of successive alkyl substituents on the proton attached to a carbon atom. Thus, the protons absorb downfield in the order, RCH_3, R_2CH_2, R_3CH. Also an equitorial proton is found to absorb further downfield by 0.7–0.1 ppm than the axial

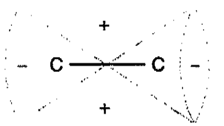


Fig. 5.13. Shielding (+) and deshielding (–) zones of C–C.

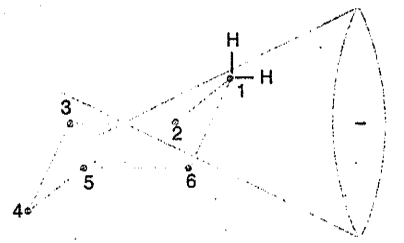
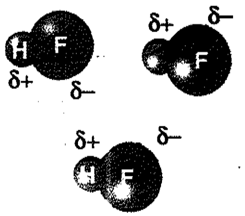


Fig. 5.14. Deshielding of equitorial proton of a rigid six membered ring.

proton on the same carbon atom in a rigid six membered ring. The axial and equitorial protons on C_1 are oriented in the same way with respect to C_1—C_2 and C_1—C_6 but the equitorial proton is within the deshielding cone of C_2—C_3 and C_5—C_6 bands.

(*d*) **Hydrogen bonding.** It has been found that a hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a low field in comparison to the one which does not. The hydrogen bonded proton being attached to a highly electronegative atom will have smaller electron density around it. Being less shielded, the field felt by such a proton will be more and hence resonance will occur downfield. The downfield shift depends upon the strength of hydrogen bonding. Intermolecular and intramolecular hydrogen bonding can be easily distinguished as the latter does not show any shift in absorption due to the change in concentration. In case of phenols, absorption occurs between—2 to 6τ. But if the concentration is decreased, *i.e.*, if the volume of the solvent, say, carbon tetrachloride is increased, then the absorption for OH proton occurs upfield. In case the OH group on benzene is intramolecularly bonded with some other group in the ortho position, the absorption for OH proton may occur even at the negative tau value. For example, the OH proton in salicylic acid absorbs at —0.6τ. Enols show strong intra-molecular hydrogen bonding which is further stabilised by resonance. Due to this, a great deshielding effect is caused and absorption for such a proton occurs at the negative tau value (10.5–12δ). It is due to the fact that acids exist as dimers as a result of hydrogen bonding. A signal for carboxylic acid proton in ethoxy acetic acid appears at –0.95τ (10.95δ).



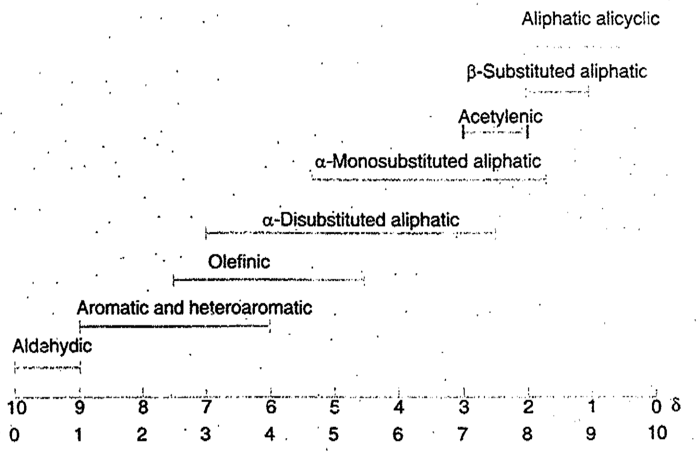


Fig. 5.15. General regions of chemical shifts.

The regions of absorption for protons attached to the unsaturated linkage are shown below:

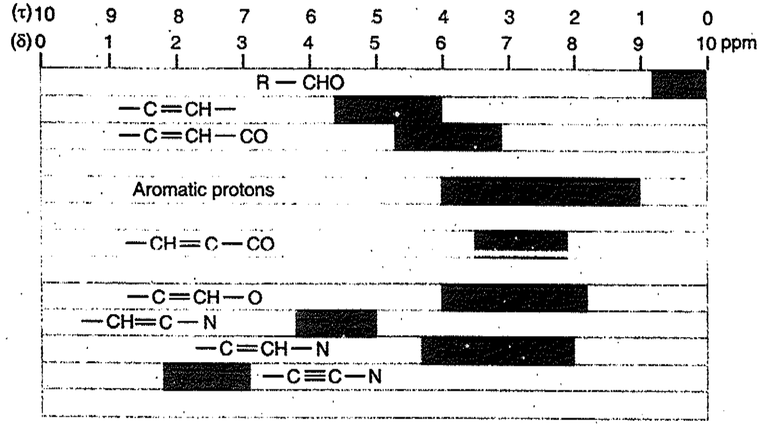
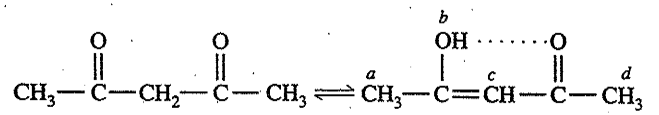


Fig. 5.16. Regions of absorption for protons attached to the unsaturated linkage.

Consider a diketone, say acetyl acetone. It exists in the following equilibrium:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons \overset{a}{CH_3}-\overset{\overset{\overset{b}{OH}\cdots\cdots}{|}}{C}=\overset{c}{CH}-\overset{\overset{O}{\|}}{C}-\overset{d}{CH_3}$$

(ketonic) (enolic)

In the enolic form, the compound is found to show absorptions at

(*i*) a = 8.02τ 1.98δ
(*ii*) b = – 4.9τ 14.9δ
(*iii*) c = 4.5τ 5.5δ
(*iv*) d = 8.02τ 1.98δ

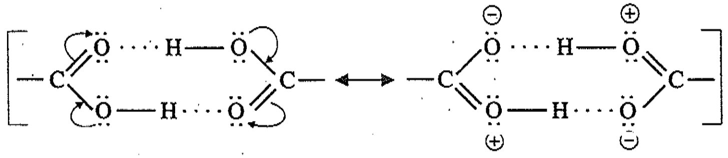
Similarly, amines show hydrogen bonding and thus, absorptions in them occur downfield. Since intermolecular hydrogen bonding is concentration dependent, the concerned proton absorption shifts upfield by decreasing the concentration. With decreasing concentration, the extent of hydrogen bonding falls and thus, the paramagnetic effect is also diminished.

5.9 Solvents Used

A substance free of proton should be used as a solvent, *i.e.*, which does not give absorption of its own in NMR spectrum. Moreover, the solvent should be capable of dissolving at least 10% of the substance under investigation. Following solvents are commonly used in NMR spectroscopy:

(*i*) Carbon tetrachloride—CCl_4
(*ii*) Carbon disulphide—CS_2
(*iii*) Deuterochloroform—$CDCl_3$
(*iv*) Hexachloroacetone—$(CCl_3)_2CO$ etc.

These solvents differ considerably as regards their polarity. Clearly, *nmr* spectrum of a compound measured in one solvent may be slightly different from that measured in another solvent of different polarity. Hence, it is important to mention the solvent used in an *nmr* spectrum. Hydrogen bonding also affects the value of δ in this technique. As hydrogen bonding involves electron cloud transfer from hydrogen atom to a neighbouring electronegative atom (O, N, S etc.), the hydrogen atom experiences a net deshielding effect. At higher concentrations of —OH, —NH compounds (strong intermolecular hydrogen bonding), deshielding of proton is greater and signal appears at higher δ value than that at low concentration. With increase in temperature, the extent of hydrogen bonding falls. Thus, signal in *nmr* appears at smaller δ value at high temperature. Carboxylic acids exist as dimers (by hydrogen bonding) which are resonance stabilised. Thus, in carboxylic acid, signal for carboxylic –OH appear between 10.5 to 12 δ.



For a compound showing intramolecular hydrogen bonding, the concerned δ value remains unchanged even if the solution is diluted.

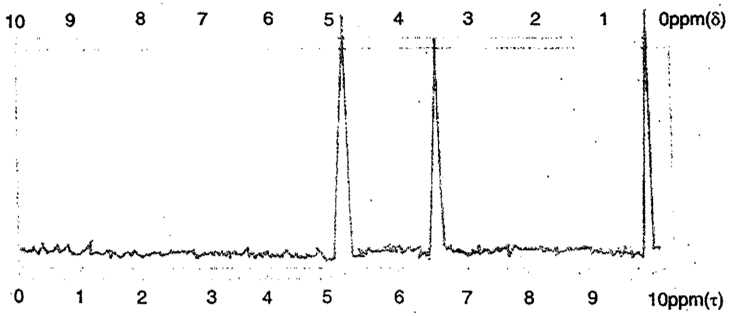


Fig. 5.17. NMR spectrum of Deutero-methane.

Trifluoro acetic acid is a very useful solvent as its proton absorbs at a very low field (δ = 11.2) and hence, does not interfere with most of the spectra. It is especially useful for the *nmr* spectrum of amines. The protons of the substituted aliphatic and aromatic ammonium ion absorbs in the range 0.5—2.9τ (aromatic at low field).

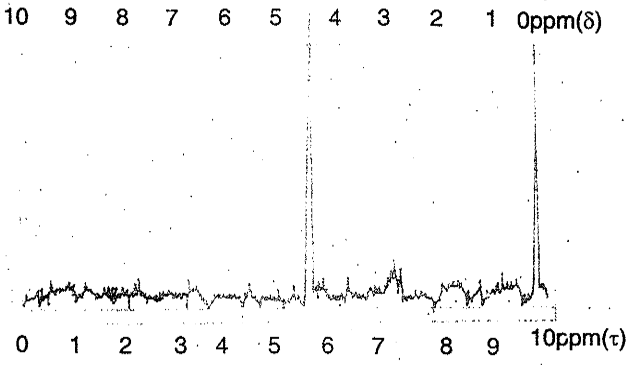


Fig. 5.18. NMR spectrum of Deuterium oxide.

Dimethyl sulphoxide (DMSO) [highly polar solvent] can be used in *nmr* spectroscopy. Some important characteristics of solvents used in this technique are:

(*i*) It should be chemically inert and magnetically isotropic,

(*ii*) It should be devoid of hydrogen atom, and

(*iii*) It should dissolve the sample to a reasonable extent.

Some other solvents which require some corrections of the order of 0.5 ppm or more in the tau values obtained for the various samples are:

(*i*) Pyridine	(*ii*) Benzene
(*iii*) Dioxane	(*iv*) Acetonitrile
(*v*) Trichloro aceto-nitrile	(*vi*) Dimethyl formamide

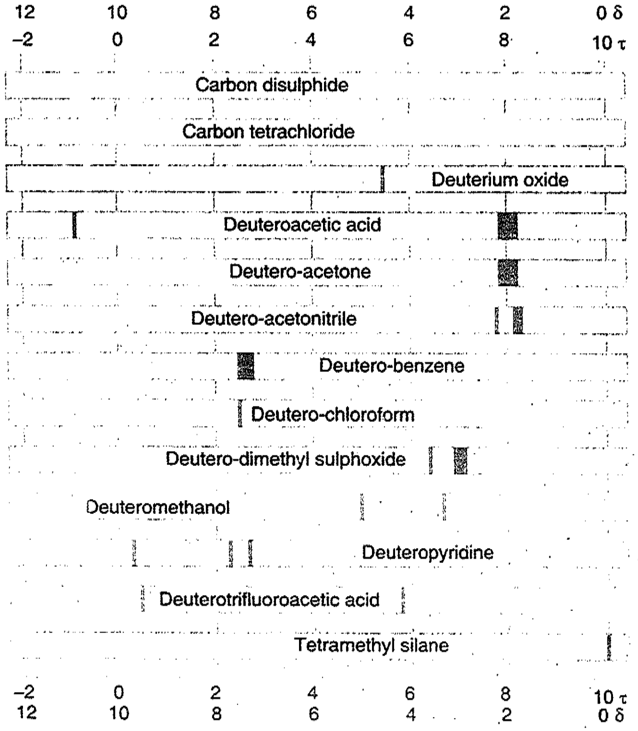


Fig. 5.19. Regions in which weak signals appear due to the presence of minor impurities in the solvent.

It has been found that the NMR spectrum of even completely deuterated solvent does show one or more peaks. It is due to the presence of minor impurities in the solvent. (See the spectra of some deuterated solvents, page 5.19).

5.10 Peak Area and Proton Counting

In an *nmr* spectrum, various peaks represent equivalent sets of protons. The size or the area of each peak tells the number of protons in each set present in the compound under investigation. The area under an *nmr* signal is directly proportional to the number of protons giving rise to signal. For flipping over of a proton, a quantum of energy is absorbed in the same effective magnetic field. Greater the number of protons that flip over at a particular frequency, greater will be the energy absorbed and greater is the area under the absorption peak. Squares under each peak are simply counted and from this, the ratio between various kinds of protons is found out. These ratios are then converted into whole numbers. These whole numbers (or some multiple of them) tell the number of protons represented by the various *nmr* signals.

Consider the spectrum of toluene. It shows two types of protons as is clear from the two signals. If the number of squares under each signal are counted, it will be found that the areas under the two peaks have the ratio 5 : 3. Thus, in toluene, five protons are of one kind and three protons are of another kind. Hence, we say that the *nmr* spectrum of toluene represents two kinds of protons which are in the ratio 5 : 3.

(*i*) Five proton signal (downfield due to deshielding) and

(*ii*) Three proton signal (upfield).

Note. Important. The students are advised to draw small squares in the *nmr* spectrum of a compound like the squares in a graph paper. The number of squares under each signal are carefully counted and then the said ratio is found out.

Integration. It is a process by which relative areas under spectral peaks are measured. These areas are proportional to the number of equivalent protons giving the signal. The NMR instrument draws an horizontal line in case there is no signal. On receiving a signal, the line ascends and levels off as the signal ends. The relative distance from plateau to plateau gives, the relative area. Hence, the integration process tells the relative number of protons. Consider the PMR spectrum of

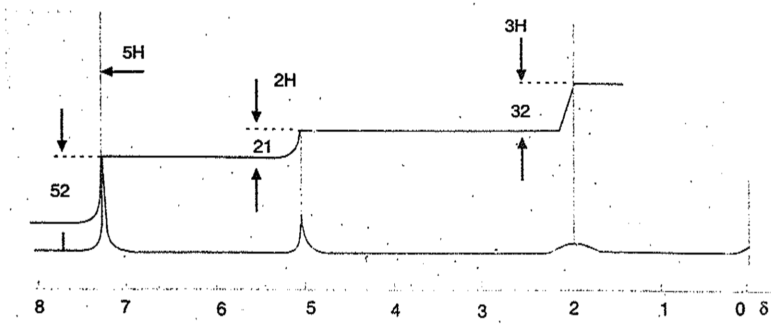


Fig. 5.20. Integrated PMR spectrum of benzyl acetate.

Benzylacetate ($\overset{a}{C}H_3COO\overset{b}{C}H_2\overset{c}{C}_6H_5$). It is found that the three types of protons give three signals in the integral ratio 52 : 21 : 32 or 5 : 2 : 3.

5.11 Splitting of the Signals

It is already pointed out that each signal in an *nmr* spectrum represents one kind or one set of protons in a molecule. It is found that in certain molecules, a single peak (singlet) is not observed, but instead, a multiplet (group of peaks) is observed. Consider a molecule of $\overset{a}{C}H_3\overset{b}{C}H_2Br$, ethyl bromide. This molecule has two kinds of protons in it and thus, two signals are expected in its *nmr* spectrum. It has been observed that for each kind of protons, we do not get singlets but a group of peaks are observed. For '*a*' kind of protons (CH_3), a triplet, *i.e.*, a group of three peaks is observed and a quartet (group of four peaks) is noticed for '*b*' kind of protons (—CH_2—). (See Fig. 5.21)

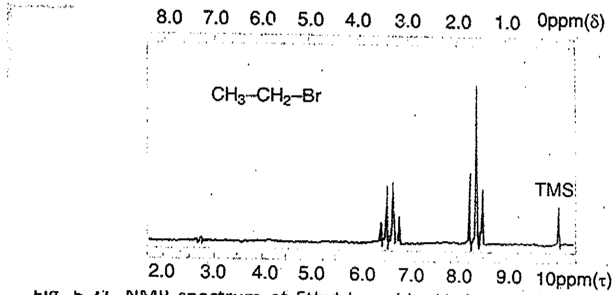


Fig. 5.21. NMR spectrum of Ethyl bromide. Varian catalogue spectrum No. 10.

Signals and their absorption positions

(*i*) a three proton triplet	8.35τ
(*ii*) a two proton quartet	6.6 τ

Similarly, in the *nmr* spectrum of 1 : 1 : 2 trichloroethane ($Cl_2\overset{b}{C}H$ □ $\overset{a}{C}H_2Cl$), two signals are observed. For '*a*' kind of protons, a doublet (a group of two lines) is observed while a triplet (a group of three lines) is noticed for '*b*' kind of protons.

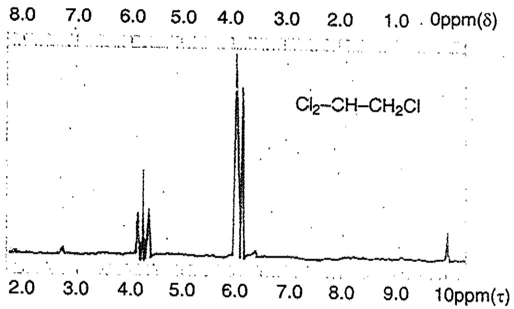


Fig. 5.22. NMR spectrum of 1 : 1 : 2 trichloro ethane. Varian catalogue spectrum No. 2

Signals and their absorption positions

(*i*) a two proton doublet	6.05τ
(*ii*) a one proton triplet	4.2τ

Now we are to study the origin of multiplet (group of peaks) for a particular kind of protons. The splitting of an *nmr* signal is due to spin-spin coupling.

5.12 Spin-spin Coupling*

To understand it properly, consider a molecule of ethyl bromide (CH_3CH_2 Br). The spin of two protons (—CH_2—) can couple with the adjacent methyl group (— CH_3) in three different ways relative to the external field. The three different ways of alignment are:

(*i*) ↑↑ (Reinforcing)

(*ii*) ↓↑ ↑↓ (Not effecting)

(*iii*) ↓↓ (Opposing)

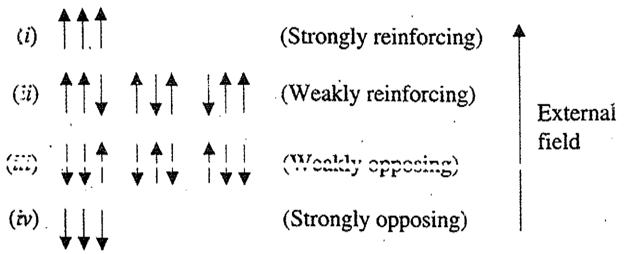
↑ External field

---

* Chemically equivalent protons do not show spin-spin coupling due to interactions among themselves.

Thus, a triplet of peaks results with the intensity ratio of 1 : 2 : 1 which corresponds to the distribution ratio of alignment.

Similarly, the spin of three protons (CH_3—) can couple with the adjacent methylene group (—CH_2—) in four different ways relative to the external field.



Thus, quartet of peaks results with an intensity ratio of 1 : 3 : 3 : 1 which corresponds to the distribution ratio of all the alignments. The relative intensities of the individual lines of a multiplet correspond to the numerical coefficient of the lines in the binomial expression:

$$(1 + x)^n = 1 + x \text{ if } n = 1$$

If $n = 2$, then $(1 + x)^2 = 1 + 2x + x^2$. Thus, the lines of the triplet have relative intensities 1 : 2 : 1.

If $n = 3$, then $(1 + x)^3 = 1 + 3x^2 + 3x + x^3$. Thus, the lines of the quartet formed due to the influence of three equivalent protons will have relative intensities 1 : 3 : 3 : 1.

Similarly, the lines of the pentet (quintet) formed will have relative intensities 1 : 4 : 6 : 4 : 1.

Hence, **the splitting of a signal is due to the different environment of the absorbing proton not with respect to electrons but with respect to the nearby protons** (Protons attached to the adjacent carbon atom). Let us consider the case of 1 : 1 : 2 trichloro-ethane $Cl\overset{a}{C}H_2–\overset{b}{C}HCl_2$.

This compound has two types of protons in it. The mutual magnetic influence between the protons '*a*' and '*b*' is not transmitted through space but through the electrons in the intervening bonds. The nuclear spin of protons '*a*' first couples with the electron spin of C—H_a bonding electrons and these in turn couple with C—C bonding electrons and then with C—H_b bonding electrons. Thus, the coupling is eventually transmitted to the spin of H_b nucleus. The magnetic field that the proton '*a*' feels at a particular instant is slightly increased or decreased by the spin of the neighbouring proton '*b*'. The field felt by proton '*a*' is increased if the proton '*b*' happens to be aligned at that instant with the applied field. If the proton '*b*' is aligned against the applied field, then at that instant, the field felt by the proton '*a*' will be slightly decreased. Thus, absorption by protons '*a*' is shifted slightly downfield for half the molecules and slightly upfield for other half of the molecules. Thus, the signal for '*a*' kind of protons is split into two peaks, *i.e.*, into doublet with equal peak intensities.

Splitting by proton '*b*'

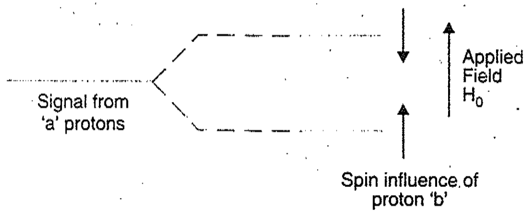


Fig. 5.23. Signal is split into a doublet.

Thus, coupling with proton '*b*' (one proton) gives 1 : 1 doublet.

Splitting by Proton 'a'

Now let us see, how the signal from '*b*' proton is effected by '*a*' kind of proton (Two protons). These two protons can be aligned with the applied field in three different ways and will consequently influence the proton '*b*'.

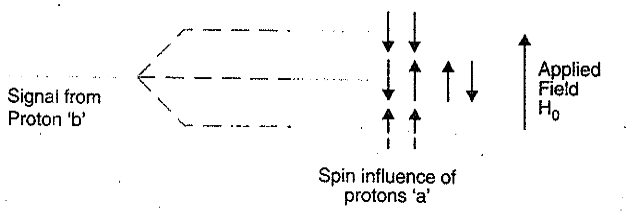


Fig. 5.24. Signal is split into a triplet.

Thus, a signal for '*b*' proton will be split up into three peaks (Triplet) which are equally spaced with peak intensities 1 : 2 : 1. It is called one proton triplet. Thus, in the above compound, we observe 1 : 1 doublet which corresponds to '*a*' protons (—CH_2—) and 1 : 2 : 1 triplet which represents '*b*' proton. (—$CHCl_2$). The total area under the doublet is twice as large as the total area under the triplet which shows that the number of protons representing doublet is twice as many as the number of protons which represent a triplet. From this, we see that a single proton '*b*' is split into a triplet (group of three peaks) under the influence of two equivalent protons '*a*'. Similarly, a signal for two equivalent protons '*a*' is split into a doublet under the influence of the neighbouring proton '*b*'. Thus, in general, we say that a set of *n* equivalent protons splits up a signal (due to neighbouring protons) into a group of $(n + 1)$ peaks (multiplet).

Let us consider another example $\overset{a}{C}H_3–\overset{b}{C}HBr_2$. In this compound (Ethylidene dibromide), we see two sets of equivalent protons '*a*' and '*b*'. The signal due to equivalent protons '*a*' will be under the influence of neighbouring proton '*b*'. The spin of proton '*b*' may be aligned with or against the applied field. Due to the two possibilities of spin of the single proton '*b*', the absorption by three equivalent protons '*a*' will be slightly downfield due to half of the molecule and slightly upfield due to the other half of the molecule. Thus, the signal for three equivalent protons (— CH_3) will be split up into a doublet.

Similarly, the signal for proton '*b*' will be under the influence of three equivalent protons '*a*' whose spin possibilities with respect to the applied field can be described as under.

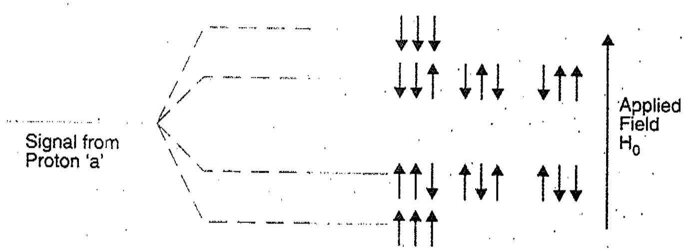


Fig. 5.25. Signal is split into a quartet.

Clearly, the signal for proton '*b*' is split into a quartet (group of four peaks) which are in the intensity ratio of 1 : 3 : 3 : 1.

Note. Important. Neighbouring protons means protons attached with the adjacent carbon atom.

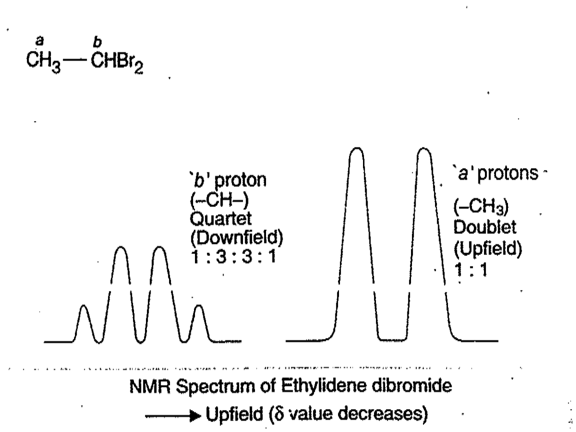


Fig. 5.26. NMR spectrum of 1, 1-Dibromoethane.

The *nmr* spectrum of Ethylidene dibromide is shown in the Fig. 5.26. The peak area under the doublet will be thrice as much as the total area under the quartet. It is due to the fact that the doublet is due to the absorption of thrice as many protons as the quartet. Hence, for '*b*' proton, different energy states are produced and it comes to resonance four times forming a quartet.

The peak intensities for quintets, sextets etc. can be similarly found out. It is important to remember that no splitting is caused if

(*i*) all the protons in a molecule are equivalent. For example, in case of cyclobutane, benzene etc., we observe a singlet as all the protons in each of the above compounds are exactly equivalent.

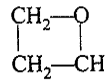
(*ii*) a set of equivalent protons do not have another set of protons attached with the adjacent carbon atom. For example, in the *nmr* spectrum of butanone-2 ($\overset{c}{C}H_3\overset{b}{C}H_2—CO—\overset{a}{C}H_3$), a singlet appears for protons '*a*' since there is no hydrogen atom attached with the adjacent carbon atom. The peak intensities of the various multiplets can be described as under:

Peak area ratio	Signai
1	Singlet
1 : 1	Doublet
1 : 2 : 1	Triplet
1 : 3 : 3 : 1	Quartet
1 : 4 : 6 : 4 : 1	Quintet
1 : 5 : 10 : 10 : 5 : 1	Sextet

Fig. 5.27. Peak intensities of various multiplets.

It is important to note that the peak area depends upon the number of the absorbing protons and the multiplicity of a signal depends upon the number of the neighbouring protons. Let us consider a few examples :

(*a*) In the spectrum of

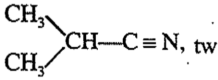


, two signals are observed.

(*i*) A four proton triplet
Downfield
Area = 2

(*ii*) A two proton quintet
Upfield
Area = 1

(*b*) In the spectrum of



$(CH_3)_2CH—C\equiv N$, two signals are observed.

(*i*) A one proton septet
Downfield
Area = 1

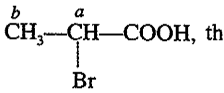
(*ii*) A six proton doublet
Upfield
Area = 6

(*c*) In the *nmr* spectrum of Butanone-2, $\overset{a}{C}H_3—CO—\overset{b}{C}H_2—\overset{c}{C}H_3$ three signals are observed. '*a*' protons appear as a singlet and the multiplicities of protons '*b*' and '*c*' are:

(*i*) A two proton quartet
(—CH_2—)
Downfield
Area = 2

(ii) A three proton
triplet (—CH_3)
Upfield
Area = 3

(*d*) In the spectrum of α-bromopropanoic acid



$\overset{b}{C}H_3—\overset{a}{C}H(Br)—COOH$, three signals are observed.

The carboxylic proton will appear as a singlet at a δ value between 10.5 to 12. The multiplicity of other signals for protons '*a*' and '*b*' are:

(*i*) A one proton quartet
Downfield
Area = 1

(*ii*) Three proton doublet
Upfield
Area = 3

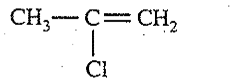
From the above examples, it is clear that the chemical shifts for various protons are exactly in accordance with the factors on which the values of chemical shifts depend. The presence of electronegative atoms or groups near the proton, bring the absorption downfield and the effect diminishes with the increasing distance of the said atom or group from the concerned proton.

Important note. Spin-spin coupling takes place between non-equivalent neighbouring (on adjacent carbon atom) protons. Non-equivalent protons are those which have different chemical shifts.

Problem. Which of the compounds will have multiplets in their spectra ?

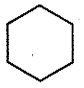
(*i*) $(CH_3)_2 \cdot C{=}CH_2$
2-methyl propene

(*ii*)



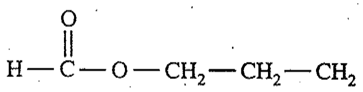
$CH_3—C(Cl){=}CH_2$
2-chloropropene

(*iii*)



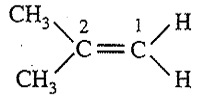
Cyclohexane

(*iv*)



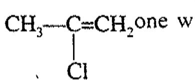
$H—C(=O)—O—CH_2—CH_2—CH_2$
n-Propyl formate

Solution. (*i*) 2–methyl propene can be written as



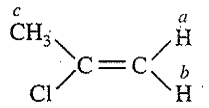
In this compound, we have two sets of equivalent protons and thus, two signals will be observed in its *nmr* spectrum. None of the two signals will split as adjacent carbon atoms do not carry protons with different chemical shift. No hydrogen atom is attached with C_2.

(*ii*) In 2-chloropropene



$CH_3—\underset{Cl}{\underset{|}{C}}=CH_2$

one will expect two signals but actually three signals are observed which correspond to three non-equivalent protons as follows:



The H^a and H^b also cause splitting of signals and each appears as a doublet.

(*iii*) In cyclohexane, only one signal is observed and no splitting is possible as all the protons are in exactly similar environment.

(*iv*) In propyl formate, $\overset{a}{H}—CO—O—\overset{b}{CH_2}\overset{c}{CH_2}\overset{d}{CH_3}$ four signals are observed in *nmr* spectrum. One will be a singlet due to proton '*a*'. The multiplicity of other signals are:

Protons '*b*' will be a two proton triplet; Protons '*d*' will appear as a three proton triplet and protons '*c*' will appear as a sextet as these two protons are under the influence of five protons attached with adjacent carbon atoms.

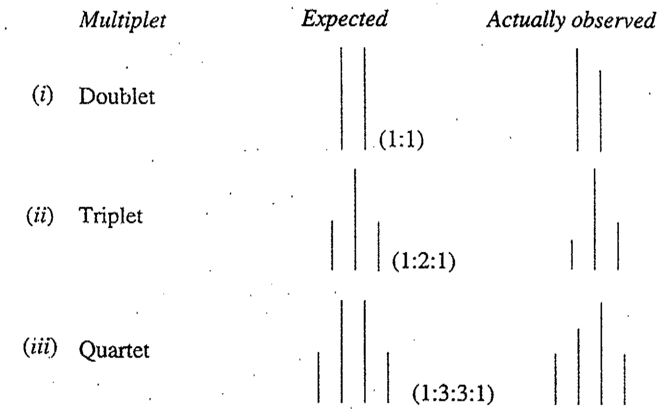
Now let us consider the spectrum of 1, 1, 2 tri-chloroethane $Cl_2\overset{b}{C}H—\overset{a}{C}H_2Cl$. Its *nmr* spectrum consists of a one proton triplet and a two proton doublet whose peak areas are respectively 1 : 2. Each multiplet is recognised from the even spacings within it and also from its symmetrical intensity pattern. Consider its triplet. The three peaks are evenly spaced and areas under each of the three peaks are in the ratio 1 : 2 : 1.

Similarly, in the doublet of this compound, the two peaks are separated by the same distance and the area under each peak is in the ratio 1 : 1. The distance between the centres of two adjacent peaks in a particular multiplet is shown by the value of J and is called **coupling constant**.

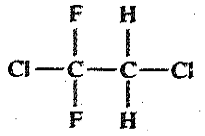
We note that the separation of peaks in a triplet is exactly the same as that observed in the doublet. From this, we derive an important conclusion that spin-spin coupling is a reciprocal affair, *i.e.*, the effect of '*a*' kind of protons on '*b*' protons is exactly the same as the effect of '*b*' proton on '*a*' type of protons in 1, 1, 2 trichloroethane.

But, things are not so simple. It has been noted that the heights of the peaks in a particular multiplet are not always symmetrical. For example, in a doublet, the intensity ratio should be 1 : 1, but sometimes, it is not exactly so. Same is the case with a triplet and other multiplets. In certain spectra, the various multiplets differ from the expected ones as shown on next page.

Thus, we see that the peaks in a particular multiplet are not in the expected intensity ratio *i.e.*, the various multiplets do not show the symmetry, we expect for them. This departure from the symmetrical pattern is due to the fact that the separation between the two signals is not very large relative to the separation of peaks within a particular multiplet. If the separation between the signals (multiplets) is very large, *i.e.*, when the chemical shift is much larger than the coupling constant, we can expect perfectly symmetrical multiplets.



Note. The mass number as well as the atomic number of fluorine being odd, its nucleus also has magnetic properties of the same kind as those of the proton. It also shows absorption, although at different frequency field strength as compared to proton. Fluorine atoms (nuclei) can couple with each other as well as with proton and thus, the splitting of signal can be observed. Consider a compound.



1 : 1 difluoro 1, 2 dicholoro ethane

The coupling of two equivalent protons with fluorine nuclei gives a triplet in the spectrum. It looks rather surprising, how a single triplet (one multiplet only) can appear in the spectrum since most commonly, it originates from a set of equivalent protons when these are under the influence of two equivalent neighbouring protons with different chemical shift.

Exercise. Why is not another triplet due to two fluorine atoms observed ?

Note. See *nmr* absorption by other nuclei.

5.13 NMR Absorption by other Nuclei

The nucleus of an isotope whose spin quantum number I is greater than zero shows absorption in the nmr spectroscopy. The *nmr* spectroscopy studied for the absorption of most abundant natural isotope of hydrogen, H^1 is called proton magnetic resonance (PMR) spectroscopy. The numerical value of I is related to the mass number and the atomic number of the concerned isotope. Such nuclei are said to be magnetic and assume only a discrete set of orientations. Some nuclei of this type are:

Isotope	*Spin quantum number I*
H^1	$\frac{1}{2}$
H^2	1
B^{10}	3
C^{13}	$\frac{1}{2}$
N^{14}	1

F^{19}	$\frac{1}{2}$
P^{31}	$\frac{1}{2}$
Cl^{35}	$\frac{1}{2}$
Br^{79}	$\frac{3}{2}$
I^{127}	$\frac{5}{2}$

The nuclei of some isotopes viz. C^{12}, O^{16} etc., for which I = 0 are non-magnetic and hence cannot cause such orientations. Thus, such nuclei are not capable of causing absorption in the *nmr* spectroscopy.

The spin quantum number I indicates the number of orientations (2I + 1) that a nucleus may assume in a magnetic field. For *nmr* spectroscopy of other nuclei, no modification compared with H^1 nmr spectrometer is needed except for the appropriate radio-frequency source. In a magnetic field of 14092 gauss, the *nmr* frequency in mega cycles is different for different nuclei. Out of the halogens (F, Cl, Br, I), protons can couple only with fluorine atom present on the same or on the adjacent carbon atom. It is due to the fact that a very large electric quadrupole moment of the halogen atoms (Cl, Br, I) effectively cause spin decoupling of adjacent protons. In F^{19} *nmr* spectroscopy, chemical shifts are usually measured in *ppm* relative to $CFCl_3$ taken as the internal standard. Coupling with H^1 and F^{19} is quite strong. Fluorine attached with benzene also couples with the nuclear protons. Consider the spectrum of CH_3CHFCl. Normally, in the H^1 *nmr* spectrum, CH_3CH—should form a doublet (3H) and a quartet (1H). But due to the presence of fluorine atom, each line of doublet is further split into two and the signal is, therefore, a double doublet. Similarly, each line of a quartet (for —CH—) is further split into two due to coupling with fluorine atom and the signal is, therefore, a doublet of quartets.

Also a signal for one fluorine nucleus appears as a doublet of quartet since it is under the influence of —CH— (attached with the same carbon atom) and —CH_3 protons under different environments. This absorption range in fluoro compounds is 200 ppm with large values of coupling constants. Thus, in the normal PMR spectrum (scale 0—10 ppm), the signal for fluorine absorption will be missing. Hence, for the above compound, only two signals are observed.

(*i*) *A three proton double doublet at 7.2τ.* The methyl group appears as a double doublet (4 lines). In this signal $J_{H,H}$ is 6 cps while J_{HF} is 22 cps.

(*ii*) *A one proton double quartet at 2.7τ.* The values of coupling constants in this signal will be

$$J_{H,H} = 6 \text{ cps and } J_{HF} \simeq 50 \text{ cps}$$

It is clear that fluorine resonances are well separated and do not appear in the normal range from 0 – 10 ppm. Moreover, the values of coupling constants in the absorptions for the fluorine nuclei are very high as compared to those observed in H^1 *nmr* signals. For example, geminal F—F coupling ranges from 40 – 370 cps while vicinal F — F couplings have values of J between 0 – 40 cps. Trans fluorine show coupling constant (J) between 106 – 150 cps while in cis, the value is between 0 – 58 cps. In the case of nitrogen (N^{14}), the electric quadrupole can effectively provide the vectors necessary for excited protons to relax. Clearly, the splitting of the nitrogen nucleus by a proton is not resolved. NMR spectrum of other nuclei provide structural information just as PMR does. Generally, very broad bands are observed compared with proton spectrum. Double resonance technique can be used to remove broadening of absorption.

5.14 Calculating the Ratio in the heights of the Signals

It has been noted that due to spin-spin coupling, each signal is split up into a multiplet. The ratio in the heights of the lines in a multiplet can be easily calculated. Consider ethyl alcohol CH_3CH_2OH.

Due to the deshielding effect of oxygen atom, the signal for OH proton will be downfield. Next comes a signal for methylene (—CH_2—) which appears as a quartet while a signal for methyl protons appears as a triplet and will be upfield. Ordinarily, the mutual coupling between —OH and —CH_2— does not take place. It is due to the fact that the proton on oxygen atom is rapidly exchanging, i.e., it does not stay in the same environment long enough for its coupling with —CH_2— protons to be detected and hence —OH proton is seen as a singlet. Thus, in ethyl alcohol, CH_3CH_2OH, we see

(*i*) Singlet 1 H (for hydroxyl proton)
(H = 1 peak height 1 unit)

(*ii*) Triplet 3H

Intensity 1 : 2 : 1 $\quad$ 1 unit = $\frac{3}{4}$ = 0.75

Thus, peak heights will be in the ratio 0.75 : 1.5 : 0.75

(*iii*) Quartet 2H

Intensity 1 : 3 : 3 : 1 $\quad$ 1 unit = $\frac{2}{8}$ = 0.25

The peak heights will be in the ratio of

0.25 : 0.75 : 0.75 : 0.25

After those calculations, the heights of the various peaks can be represented as:

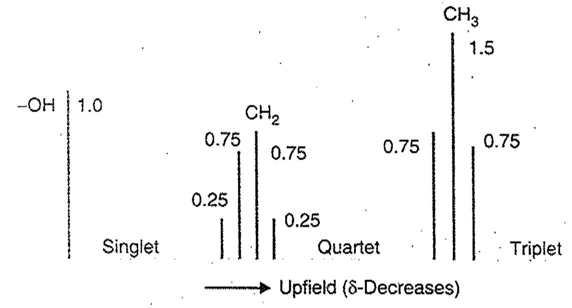
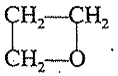


Fig. 5.28. Peak heights.

Similarly, consider the spectrum of  . The spectrum consists of

(*i*) Triplet 4H

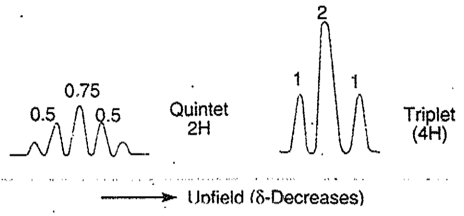
Intensity ratio 1 : 2 : 1 $\quad$ 1 unit = $\frac{4}{4}$ = 1

The peak heights will be in the ratio 1 : 2 : 1.

(*ii*) Quintet 2H

Intensity ratio 1 : 4 : 6 : 4 : 1 $\quad$ 1 unit = $\frac{1}{16}$ = 0.125

The peak heights of the quintet will be in the ratio 0.125 : 0.5 : 0.75 : 0.5 : 0.125. The end peaks in the quintet will be almost insignificant.



The NMR spectrum of this compound can be represented as follows:

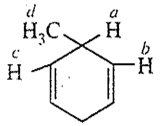
Splitting of signals in other cases

If the protons responsible for spin-spin coupling are not in exactly similar environment, the number of lines for a particular multiplet will be equal to $(n + 1)(n' + 1)(n'' + 1)$ where n, n', and n'' are the number of protons in different environments. A few examples are listed below:

(*a*) Consider a compound 1 : 1 dibromo 3 : 3 dichloropropane. $\mathbf{Br_2\overset{a}{C}H—\overset{b}{C}H_2—\overset{c}{C}HCl_2}$. In this compound, we see three sets of protons. Protons '*a*' and '*c*' are non-equivalent (with different chemical shifts) and thus, will influence the methylene (—CH$_2$— *i.e.*, protons '*b*') protons differently. Thus, the signal for —CH$_2$— protons appears as a multiplet and consists of $(n + 1)(n' + 1) = (1 + 1)(1 + 1) = 4$ lines where n and n' are the number of protons of the kinds '*a*' and '*c*'.

(*b*) Consider a compound 1 bromo, 3 chloropropane. $BrCH_2—CH_2—CH_2Cl$. The signal for the central methylene (—CH$_2$—) protons will clearly be a multiplet consisting of $(n + 1)(n' + 1) = (2 + 1)(2 + 1) = 9$ peaks where n and n' are the number of protons '*a*' and '*c*' respectively. The central —CH$_2$— protons being under the influence of two kinds of protons (two in each set) with different chemical shifts. Thus, for central methylene, asymmetrical pattern results.

(*c*) Consider the spectrum of methyl cyclohexadiene.



In this compound, proton '*a*' is under the influence of three sets of protons with different chemical environments. These protons are '*b*', '*c*' and '*d*'. Thus, the signal for proton '*a*' is expected to be a complicated pattern consisting of $(n + 1)(n' + 1)(n'' + 1)$ line *i.e.*, $(1 + 1)(1 + 1)(3 + 1) = 16$ lines.

5.15 Chemical Exchange (Proton Exchange Reactions)

In a molecule, if a proton shuttles between two magnetic environments at a rate which is much faster in comparison with the *nmr* transition times, then the resonance observed for that proton will be simply that of the average effective field in the two environments. Thus, only one resonance will be observed, although, the proton will shuttle in two different magnetic environments. We know that the —OH proton in water has different chemical shifts as compared to that of the —OH proton in acetic acid. But, strange enough, we see only one signal in the *nmr* spectrum of acetic acid in water at an average position (in between the two parent positions) according to the following formula:

$$N_a\delta_a + N_b\delta_b$$

where
N_a = mole fraction of the proton a.
N_b = mole fraction of the proton b.
δ_a = chemical shift of unexchanged proton '*a*'.
δ_b = chemical shift of unexchanged proton '*b*'.

This clearly shows that the rate at which the —OH proton exchanges between water and acetic acid is much faster than the nuclear transition time.

The phenomenon of chemical exchange can be explained by considering the *nmr* spectrum of anhydrous ethanol and also the spectrum of ethanol containing small quantities of water.

In the case of pure anhydrous ethanol $\overset{a}{C}H_3.\overset{b}{C}H_2—\overset{c}{O}H$, three signals are observed.

(*i*) a triplet for —CH$_3$ protons at 8.82τ due to coupling with —CH$_2$— protons.

(*ii*) a multiplet consisting of eight lines for —CH$_2$— protons at 6.38τ. The —CH$_2$— protons are under the influence of two kinds of protons in different chemical environments. Thus, the multiplet consists of $(n + 1)(n' + 1) = (3 + 1)(1 + 1) = 8$ lines.

(*iii*) a triplet for —OH proton at 4.72τ. The OH proton appears as a triplet because of coupling to —CH$_2$— protons.

Now if we scan the spectrum of ethyl alcohol containing water, the OH signal appears as a singlet and its coupling with adjacent —CH$_2$— does not take place.

It can be explained by saying that the proton exchange becomes faster as the water content is increased. The exchange of OH protons among ethanol molecules in presence of water or at high temperature or in acidic medium is normally so rapid that a particular proton does not reside on a particular oxygen atom long enough for the nuclear coupling to be observed.

$$ROH^* + HOH = R—OH + HOH^*$$

Similarly, absorption due to —CH$_2$— protons will not be split by OH proton due to rapid chemical exchange. Rapid chemical exchange causes **spin decoupling**, because the spin values get averaged. The proton exchange does not occur.

(*i*) if the sample is pure,

(*ii*) if the sample is recorded at a low temperature, or

(*iii*) if the sample is dissolved in a highly polar solvent like dimethyl sulphoxide (strong solvation effect).

Low temperature and solution of the polar sample in a highly polar solvent are some of the factors which reduce the chemical exchange and hence, coupling of —OH proton with the neighbouring proton does take place.

Proton exchange also occurs rapidly in some other compounds in which hydrogen is attached with nitrogen, sulphur and oxygen (carboxylic acids, thiols, amines etc.) and hence no coupling is observed between the protons of these functional groups with the protons on the adjacent carbon atoms.

We have seen that when alcohol contains some quantity of water, a singlet is observed for the hydroxyl proton. **The position of the singlet peak for the OH proton is slightly shifted depending upon the water content in alcohol and hence, it helps in the quantitative analysis of ethanol-water; acetic acid-water mixtures.**

The spin decoupling can usually be observed at

(*i*) high temperature and

(*ii*) by using highly polar solvents for the polar samples.

The spectrum of methanol (CH$_3$OH) at very low temperature (– 40 °C) shows **a quartet for** hydroxyl proton and a doublet for methyl protons. This shows that the chemical exchange is very slow at –40 °C as compared to the *nmr* transition time. But, if the temperature is raised to + 31 °C, multiplets for CH_3 and —OH protons collapse to two sharp singlets. This shows that the rate of chemical exchange becomes faster than the *nmr* transition time.

Note. A proton undergoing chemical exchange does not show spin-spin coupling.

5.16 Coupling Constant (J)

The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant. The value of the coupling constant is independent of the external field. It is measured in Hertz (Hz) or in cps (cycles per second). It is denoted by the letter J. If we work the spectrum of a particular compound at different radio-frequencies, the separation of signals due to different chemical shifts change but the separation of two adjacent peaks in a multiplet remains always constant. In other words, we say that the value of J (separation of adjacent peaks in the multiplet) remains the same whatever the applied field. From the value of coupling constant, one can distinguish between the two singlets and one doublet and also a quartet from two doublets. It can be done by simply recording the spectrum at two different radio-frequencies. If the separation (in Hz) between the lines (value of J) does not change, then the signal is a doublet. On the other hand, if the separation between the lines increases with increasing frequency, then the signal in fact, will be two singlets. The value of 'J' generally lies between 0 and 20 Hz. Same explanation can be given to distinguish a quartet from the doublets.

Now let us consider a compound, $>\overset{b}{\text{CH}}\text{—}\overset{a}{\text{CH}_2}\text{—}$. In this compound two signals are expected in the *nmr* spectrum. Under the influence of two equivalent protons '*a*', the signal for proton '*b*' will appear as a triplet. The distance between any two adjacent peaks in a multiplet will be exactly the same. The triplet formed due to spin-spin coupling is shown as:

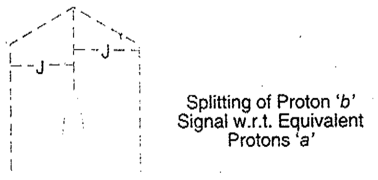


Fig. 5.29. A triplet

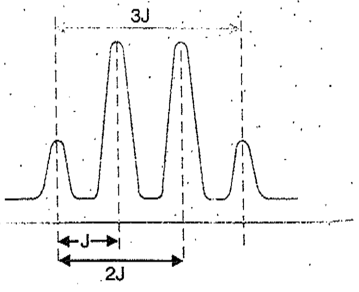


Fig. 5.29 (*a*). A quartet.

Similarly, consider a compound, $>\overset{b}{\text{CH}}\text{—}\overset{a}{\text{CH}_3}\text{—}$. In the *nmr* spectrum of this compound, proton '*b*' is under the influence of three equivalent protons '*a*'. Thus, due to spin-spin coupling, the signal for proton '*b*' will appear as a quartet with intensity ratio 1 : 3 : 3 : 1. The quartet for '*b*' can be represented as in Fig. 5.29 (*a*).

From the constant value of 'J', we say that the multiplets formed are of symmetrical nature. It has been noted that the departure from the symmetrical nature of the multiplet results when the absorption positions (chemical shifts) of the interacting groups are close enough.

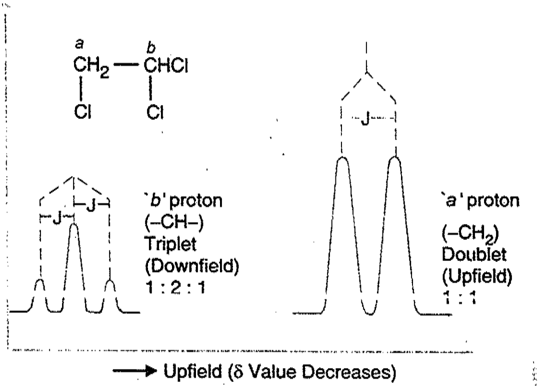
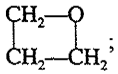


Fig. 5.30. NMR Spectrum of 1, 1, 2–Trichloroethane.

In the *nmr* spectrum of 1, 2, 2– trichloroethane (see Fig. 5.30) two multiplets are observed. The value J in each of its multiplets is found to be constant.

Following are some of the compounds which have constant value of J in each of their multiplets.

(*a*) In the spectrum of  ; a low field triplet (4H) and an upfield quintet (2H) are observed. The value of J (peak separation) in the triplet as well as in the quintet is found to be the same, *i.e.*, 7.1 cps.

(*b*) In the spectrum of Isopropyl cyanide; a doublet (6H) and a septet (1H) are formed. The value of 'J' in each of these multiplets formed is the same, *i.e.* 6.7 cps.

(*c*) Consider the spectrum Butanone—2. In this case, two multiplets are formed.

(*i*) A low field quartet (2H) and (*ii*) an upfield triplet (3H). The value of J in each of these multiplets observed is the same and is equal to 7.3 cps.

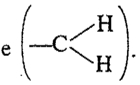
Similarly, a large number of examples can be quoted in which the value of 'J' remains the same for any two multiplets of a compound in which a signal for one kind of protons is split under the influence of another kind of protons and vice versa. But if a signal is split due to the influence of two different sets of protons (protons with different chemical shifts), then the peak separations in the multiplet observed will not be equidistant.

Consider an example of propyl iodide $\overset{c}{\text{CH}_3}\text{—}\overset{b}{\text{CH}_2}\text{—}\overset{a}{\text{CH}_2}\text{I}$. The signal for '*b*' kind of protons are under the influence of protons '*a*' as well as protons '*c*'. The examination of the expanded spectrum of propyl iodide reveals, that J_{ab} = 6.8 cps and J_{bc} = 7.3 cps. From these values of the coupling constants, the multiplet pattern of '*b*' protons can be found out. Under the influence of five adjacent protons, the signal for $\text{—}\overset{b}{\text{CH}_2}\text{—}$ protons will be split into a sextet. If J_{ab} were equal to J_{bc}, a symmetrical sextet would have been observed. Since the values of J are close enough, the signal for $\text{—}\overset{b}{\text{CH}_2}\text{—}$ protons (multiple) will resemble a sextet.

On the other hand, consider the spectrum of pure ethyl alcohol $\overset{c}{\text{CH}_3}\overset{b}{\text{CH}_2}\overset{a}{\text{OH}}$. '*b*' protons are under the influence of '*a*' protons (OH proton) and also the '*c*' protons. The examination of the expanded spectrum of ethyl alcohol reveals that J_{ab} = 5.0 cps and J_{bc} = 7.2 cps. Since the values of coupling constants in methylene multiplet are much different (assuming the symmetry of multiplets), we do not observe a quintet normally expected for '*b*' protons in pure ethyl alcohol.

Actually, a group of eight lines are observed in its multiplet. Quintet would have been formed if J_{ab} were equal to J_{bc}.

It may be clearly noted that the value of coupling constant depends partly on the number of covalent bonds through which protons may interact and also upon the structural relationships between the coupled protons. Various types of coupling may be noted:

(*a*) **Geminal coupling.** In the case of geminal protons (protons attached on the same carbon having different chemical environment) of a saturated compound, the value of J depends upon the bond angle  $\left(-C\begin{smallmatrix}H\\H\end{smallmatrix}\right)$. J can have any sign.

Geminal protons are separated by two bonds. If these protons are in different environments, then the coupling is usually strong. When the bond angle is 105°, J is approximately –25 cps. J becomes nearly –12 cps when the bond angle increases to 109°. With the bond angle widened to 125°, the value of J increases to zero. If the bond angle is wider than 125°, we observe small positive values for the coupling constants. A plot showing the relationship between the values of J versus the bond angle is shown as under :

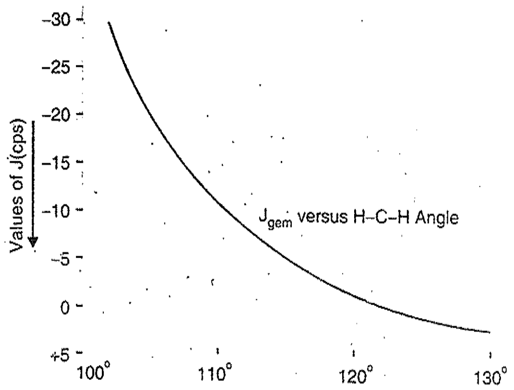


Fig. 5.31. Geminal Coupling Constants.

A few characteristics of geminal coupling constant (J_{gem}) may be noted :

(*i*) The value of coupling constant increases with the increase in bond angle (increases in *s*-character) J_{gem} is –12.4 cps for methane whereas, it is +2.5 cps for ethylene.

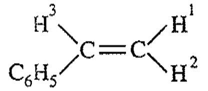
(*ii*) The increase in electronegativity of the atom or group, which withdraws sigma electrons, increases the value of coupling constant. For example, the value of coupling constant for methyl chloride is – 10.8 cps whereas it is – 9.4 cps for methyl fluoride.

(*iii*) The value of J decreases if an electronegative substituent withdraws electrons from the π bonds. For example, J_{gem} is +2.3 cps for ethene whereas it is – 3.3 cps for vinyl fluoride. The values of geminal coupling constants for some compounds are as follows:

Compound	J_{gem}
Methane	– 12.4 cps
Methyl chloride	– 10.8 cps
Methyl fluoride	– 9.4 cps
Ethene	+ 2.5 cps
Formaldehyde	+ 41.0 cps.

Exercise. The value of coupling constant for formaldehyde is + 41 cps while that for ethylene is + 2.5 cps. Comment.

Geminal coupling constants for olefins, are quite small. For mono-substituted olefins $J_{trans} > J_{cis} > J_{gem}$. For isomeric olefins, it is found that the value of coupling constant for gem cis protons is two-third of the value of gem trans protons. Consider the case of styrene:



$J_{cis}(H^1, H^3) = 10.6$ cps

$J_{trans}(H^2, H^3) = 17.4$ cps

$J_{gem}(H^1, H^2) = -1.4$ cps

(*b*) **Vicinal coupling.** For vicinal protons, the value of coupling constant varies with the dihedral angle. **Vicinal protons are the protons which are separated by three bonds.** A plot for the values of J versus the dihedral angle for vicinal protons is shown as under.

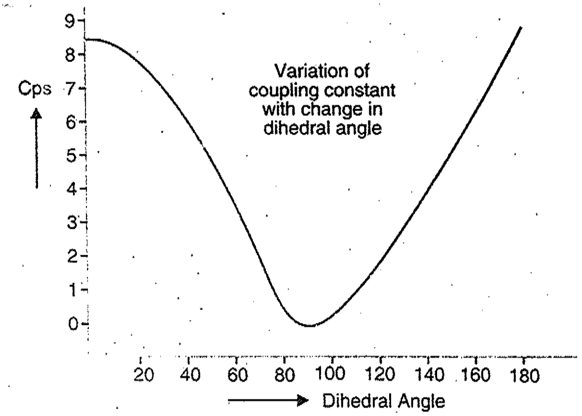
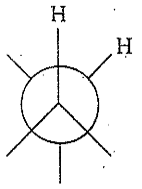


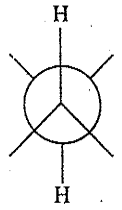
Fig. 5.32. Variation of coupling constant with dehedral angle.

When the dihedral angle is 0° or 180°, we observe largest values for the coupling constants. The value of 'J' is slightly negative when the dihedral angle is 90°.

Consider the gauche and the anti-conformations of a compound.



(Gauche)

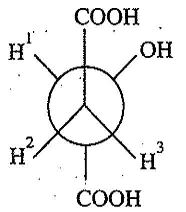


(Anti)

In a signal (multiplet) for gauche proton, the value of J varies from 2 to 4 cps and that for anti-protons, the coupling constant varies from 5 to 12 cps.

In the case of cyclopentanes, where the dihedral angle in cis protons is zero, the value of J is expected to be 8 cps whereas it is nearly zero when the dihedral angle in trans is 90°. It has been observed that in cyclohexanes, the absorption due to axial and equitorial protons are different. For axial-axial interactions, when the dihedral angle is nearly 180°, the coupling constant is approximately 8 cps whereas for axial-axial and equitorial-equitorial interactions when the dihedral angle is 60°, the coupling constant is nearly 2 cps. Thus, from the value of the coupling constant, it is possible to determine the configuration of a particular system.

We know that the various conformations of a compound interconvert rapidly into one another. But at much lower temperatures, it is found that the rate of interconversion of conformational isomers may be so slow that the spectrum of each may be observed. Let us consider the following conformation of malic acid.



The values of 'J' as a result of the various types of interacting nuclei are given as

J (H^1, H^2) [Vicinal-gauche] = 4.4 cps
J (H^1, H^3) [Vicinal-anti] = 7.1 cps
J (H^2, H^3) [Gem] = 17.0 cps

Some important conclusions in connection with the values of vicinal coupling constants are as follows:

(*i*) The values of coupling constants are always positive.
(*ii*) In olefinic compounds J_{trans} is more than J_{cis}.
(*iii*) The values of coupling constants can be approximately calculated from the dihedral angle θ.
(*i*) $J = 8.5 \cos^2 \theta - 0.28$ (θ varies from 0 to 90°)
(*ii*) $J = 9.5 \cos^2 \theta - 0.28$ (θ varies from 90° – 180°)

The values of vicinal coupling constants for a few compounds are listed below :

(*i*) Propane (Ganche) = 7.2 cps
(*ii*) Propane (Anti) = 6.5 cps
(*iii*) Dibromoethane = 3.4 cps (Gauche)
= 15.1 cps (Anti)

Note. Out of the halogens (F, Cl, Br, I), protons can only couple with fluorine atom present on the same or the adjacent atom. A very large electric quadrupole of the halogen atom (Cl, Br, I) effectively cause spin decoupling of the adjacent proton.

(*c*) **Long-range coupling.** Usually no coupling is observed if the distance between the two absorbing nuclei is more than three covalent bonds. But in unsaturated compounds or in fluoro compounds, appreciable coupling is observed with the help of high resolution spectrometers even if the concerned nuclei are three bonds apart. It is called **long-range coupling.**

In π bond system, appreciable couplings are frequently observed between protons separated by even four or five bonds. The effects of the nuclear spin are transmitted from C—H bond (σ bond) by coupling of the resulting electron spin on carbon atom with π electrons. In 2, 4 dichlorobenzaldehyde, long range coupling takes place between the aldehydic proton and a ring proton.

The values of long range coupling constants in compounds which involve σ – π coupling are as follows:

(*i*) $\mathbf{CH_3}$—CH = CH_2 = – 1.7 cps
(*ii*) $\mathbf{H_2}$C = C—$\mathbf{CH_2}$—CH_3 = – 2.3 cps
(*iii*) $\mathbf{CH_3}$—C = C(CH_3)—COOH = – 1.2 cps

Table T$_5$ – 2. Coupling constants due to geminal and vicinal coupling.

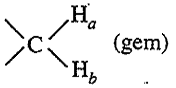
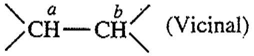
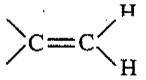
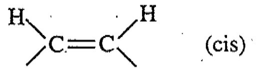
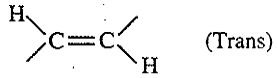
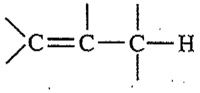
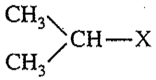
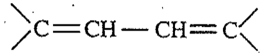
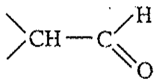
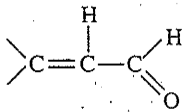
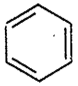
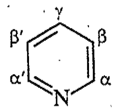
Function	*Jcps*
	0–25. Depending upon the electronegativities of the attached groups and bond angle. It can have any sign.
	2–9. Depends upon the dihedral angle. It is always positive.
	0.5 – 3.0.
	7 – 12.
	13 – 18.
	4 – 10.
CH_3—CH_2—X	6.5 – 7.5.
	5.5 – 7.0.
	9 – 13.
H—C≡C—H	9.1.
	1 – 3.
	6 – 8.
	(*i*) ortho = 6 – 9. (*ii*) meta = 1 – 3. (*iii*) para = 0 – 1.
	αβ = 4.9 – 5.7 αβ′ = 0.7 – 1.1 αα′ = 0.2 – 0.5 αγ = 1.6 – 2.6 ββ′ = 1.4 – 1.9 βγ = 7.2 – 8.5

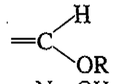
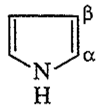
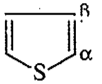
Table T_5 – 3 Tau values for the CH_3 protons when attached with different groups.

TMS *sp^3*	**10.00**
C — CH_3	9.1
CH_3 — CH = CH_2	8.3
CH_3—CH=N—	8.0
CH_3—C≡	8.0
CH_3—COOR(—COOAr)	8.0
CH_3—C ≡ N	8.0
CH_3CONH_2(—$CONR_2$)	8.0
CH_3COOH	7.7
CH_3COR	7.9
CH_3NH_2 (—NR_2)	7.9
CH_3I	7.9
CH_3CHO	7.8
CH_3Ar	7.7
CH_3Br	7.4
CH_3NHCOR (—NRCOR)	7.1
CH_3Cl	7.0
CH_3OR	6.7
CH_3NR_3	6.7
CH_3OH	6.6
$CH_3O.COR$	6.4
CH_3OAr	6.3
$CH_3O.COAr$	6.1
CH_3NO_2	5.7

Note. A slight fall in the tau (τ) values are observed for —CH_2— protons (in RCH_2—) when above-mentioned groups are attached with RCH_2—group. Thus —CH_3 protons absorb at slightly higher field as compared to —CH_2— protons and —CH_2— protons (in RCH_2—) absorb at slightly higher field as compared to —CH— proton (RR′CH— compounds).

R and R′ are alkyl groups.

Table T_5–4. [illegible]

Function	*Tau value*
ROH	6—9.5
ArOH	5.5 (Due to hydrogen bonding. τ values may be lowered to about one) chelated OH absorb at negative tau (off the scale)
RCOOH	—0.5 to – 2
RNH_2, RNHR	2 to 5 (lines are usually broad)
$ArNH_2$	4.5 to 7
$RCONH_2$, RCONHR′	1.5 to 5 (Broad, may not be observed)
RSH	8.0 to 9.
 $=C\begin{smallmatrix}H\\OR\end{smallmatrix}$	3.2
= N—OH	0 to – 2
	(*i*) α = 3.5 (*ii*) β = 3.9
	(*i*) α = 2.8 (*ii*) β = 2.9

For enols, the tau values are negative (off the scale) and lines are broadened.

Benzene protons absorb at 2.73τ and shift in the absorption position of benzene protons due to the presence of substituents on the ring are mentioned in Table T_5–5.

Table T_5 – 5. Shift in the absorption position of Benzene protons.

Substituents	*Position of the Substituent group*		
	ortho	*meta*	*para*
—CH_3	+ 0.15	+ 0.1	+ 0.1
—COOH,—COOR	– 0.8	– 0.15	– 0.2
—CN	– 0.3	– 0.3	– 0.3
—$CONH_2$	– 0.5	– 0.2	– 0.2
—COR	– 0.6	0.3	0.3
—SR	– 0.1	+ 0.1	+ 0.2
—NH_2	+ 0.8	+ 0.15	+ 0.4
—$N(CH_3)_2$	+ 0.5	+ 0.2	+ 0.5
–I	– 0.3	+ 0.2	+ 0.1
—CHO	– 0.7	– 0.2	– 0.4
–Br	0	0	0
–NHCOR	– 0.4	+ 0.2	+ 0.3
—Cl	0	0	0
—$\overset{+}{N}H_3$	– 0.4	– 0.2	– 0.2
OR	+ 0.2	+ 0.2	+ 0.2
OH	+ 0.4	+ 0.4	+ 0.4
—OCOR	– 0.2	+ 0.1	+ 0.2
—NO_2	– 0.1	– 0.3	– 0.4
—SO_3H, —SO_2NH_2	– 0.4	– 0.1	– 0.1

Note 1. The absorption positions of these groups mentioned in various tables are concentration dependent and are shifted to higher tau values (upfield) in more dilute solutions.

Note 2. A slight shift in the positions of absorption is also noted by the change in the nature of the solvent.

Given below are the actual tau values for the different sets of protons in the following compounds. From this, the shielding and the deshielding effects due to various groups can be readily assessed. Tau values for various sets of protons are taken in comparison with that for the protons of tetramethyl silane (TMS) taken as 10 ppm.

Table T_5 – 6. [illegible]

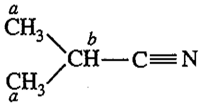
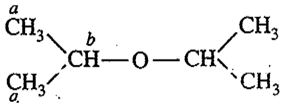
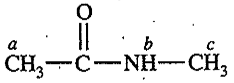
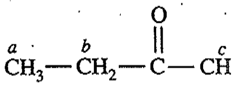
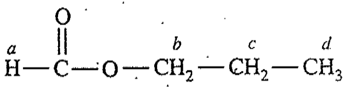
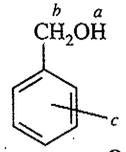
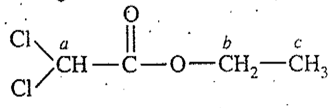
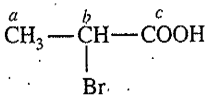
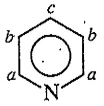
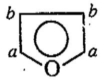
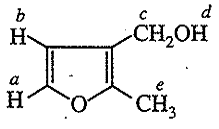
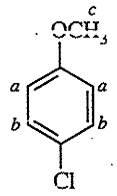
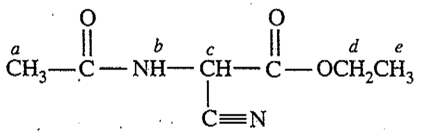
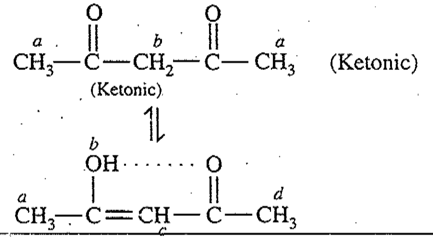
	Compound	Tau values
(i)		$a = 8.67$ $b = 7.28$
(ii)		$a = 8.95$ $b = 6.44$
(iii)	$\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{CH_2}-I$	$a = 8.98$ $b = 8.14$ $c = 6.83$
(iv)	 $\overset{a}{CH_3}-\overset{\overset{O}{\|}}{C}-\overset{b}{NH}-\overset{c}{CH_3}$	$a = 8.08$ $b = 1.87$ $c = 7.30$
(v)	 $\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{\overset{O}{\|}}{C}-\overset{c}{CH_3}$	$a = 8.93$ $b = 7.52$ $c = 7.88$
(vi)	$\overset{a}{CH_3}-\overset{b}{CH_2}\overset{c}{OH}$	$a = 8.93$ $b = 6.38$ $c = 4.72$
(vii)	 $\overset{a}{H}-\overset{\overset{O}{\|}}{C}-O-\overset{b}{CH_2}-\overset{c}{CH_2}-\overset{d}{CH_3}$	$a = 1.93$ $b = 5.88$ $c = 8.33$ $d = 9.05$
(viii)		$a = 5.40$ $b = 6.14$ $c = 2.74$
(ix)		$a = 6.05$ $b = 5.65$ $c = 8.62$
(x)	 $\overset{a}{CH_3}-\underset{Br}{\overset{b}{CH}}-\overset{c}{COOH}$	$a = 8.17$ $b = 5.48$ $c = -1.93$
(xi)		$a = 1.44$ $b = 2.82$ $c = 2.44$
(xii)		$a = 2.66$ $b = 3.71$

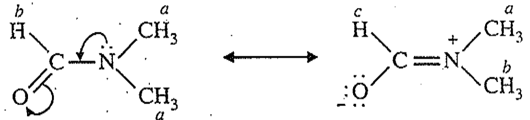
Table T_5–7. Tau values for different sets of protons in some more complicated structures.

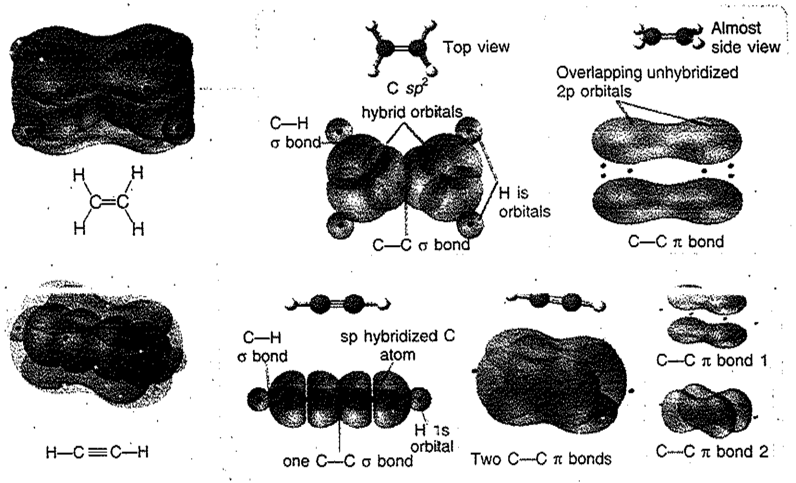
	Compound	Tau values
(i)	 (Spectrum in D_2O)	$a = 2.89$ $b = 3.82$ $c = 5.80$ $d = 5.77$ $e = 7.87$
(ii)	 (Spectrum in D_2O)	$a = 3.33$ $b = 2.88$ $c = 6.35$
(iii)	 $\overset{a}{CH_3}-\overset{\overset{O}{\|}}{C}-\overset{b}{NH}-\underset{C\equiv N}{\overset{c}{CH}}-\overset{\overset{O}{\|}}{C}-\overset{d}{OCH_2}\overset{e}{CH_3}$	$a = 7.90$ $b = 3.23$ $c = 4.47$ $d = 5.61$ $e = 8.62$
(iv)	 (Ketonic)	$a = 7.86$ $b = 6.35$ $a = 8.03$ $b = -4.3$ (enolic) $c = 4.4$ $d = 7.87$

5.17 Restricted Rotation

The isomers which arise due to rotation about single bond are called conformational isomers or conformers. The presence of conformations in a solution cannot be detected by the *nmr* spectroscopy. But at temperatures much below room temperature, the rate of interconversion of rotational isomers is usually diminished and *nmr* absorption resulting from each may be observed.

The presence of double bond (a sigma and a π bond) in a compound restricts rotation and results in the formation of cis and trans isomers. Cis and trans isomers are the distinct compounds with different properties and different *nmr* spectra. In a compound, where a double bond may originate in its equivalent resonating structure, the rate of rotation about the given bond becomes intermediate between free rotation about unhindered single bond in one structure and hindered rotation about the double bond in the other structure. Consider the spectrum of N, N-dimethyl formamide at room temperature.


(I) (II)



Thus, the *nmr* spectrum for such a compound usually consists of a superimposition of spectra resulting from two or more rotational isomers present at equilibrium. Some amides, oximes, nitroso amines etc. show restricted rotation. The spectrum for N, N-dimethyl formamide shows two non-equivalent methyl groups which absorb at different field strengths. The two signals observed (doublets) for methyl groups are as a result of coupling with the formyl proton. For each doublet, we observe a different value of coupling constant. Proton absorption for one methyl doublet is at 7.21τ and that for the other methyl doublet is at 7.06τ. The value of coupling constant for methyl signal appearing at 7.21τ is found to be higher. Clearly, its position is predicted as trans with respect to the formyl proton. At elevated temperatures, the rapid rotation between C—N makes both the methyls magnetically equivalent and only one signal is observed for both the methyl groups.

5.18 Important Tips for Interpreting an NMR Spectrum

(*a*) Following points regarding the value of chemical shift may be useful :

(*i*) Tau value of methyl, methylene and methyne protons have the order:

Methyl > Methylene > Methyne

(*ii*) Tau value depends upon the nature of the substituent on the carbon atom bearing the proton. Greater the electronegativity of the substituent, lower is the value of tau.

(*iii*) The value of tau depends upon the type of the hybrid orbital holding the proton.

$$sp^3 > sp > sp^2$$

(*iv*) The tau value for aromatic protons is always less than 4 ppm. The value depends upon the degree and the nature of substitution.

(*v*) Tau values for the aldehydic protons are generally lower, *i.e.*, 0.8 ppm or lower.

(*vi*) Tau value of protons in a cyclic compound is always higher than that of any other proton. The set of protons in cyclopropane has the maximum tau value.

(*vii*) The chemical shift of the protons in O—H group and also in —NH_2 group depend upon temperature, solvent, concentration and the neighbouring groups. For example, the alcoholic (—OH) proton gives a singlet at 4.5 – 9.0τ, the phenolic OH absorbs at – 2 to 6τ. If C = O group is present in the ortho positions in phenol, then due to intramolecular hydrogen bonding, absorption occurs even at negative values of tau. The OH proton in the enolic form absorbs at – 4 to – 5τ.

(*viii*) The absorption due to —COOH group appears at – 0.5 to – 2.0τ. (10.5 – 12 δ).

(*b*) The number of signals in an *nmr* spectrum tells the number of sets of the protons in different chemical environments.

(*c*) It also tells the number of equivalent protons causing the splitting of a signal.

Let us consider a few cases :

(*i*) In a spectrum, two signals, say, singlets are observed. This spectrum can be interpreted by saying that there are two kinds of protons and the two carbon atoms carrying the two sets of protons are not the adjacent carbon atoms otherwise splitting of signals would have taken place.

(*ii*) The spectrum consisting of one doublet and one triplet must be due to the molecule having —CH_2—CH— as its part.

(*iii*) Formation of two triplets must be due to two methylene groups whose protons are in different environments.

$$X—CH_2—CH_2—Y$$

(*iv*) The formation of a septet and a doublet must be due to $(CH_3)_2CH$—group which forms a part of the molecule and so on. From the intensities of the signals (peak areas) the ratio between different kinds of protons can be found.

NMR spectroscopy is an important tool in the hands of an organic chemist for getting structural information from the spectrum of an unknown compound. It also helps in studying the stereochemical details within the molecule. Although important, it cannot replace other techniques such as ultraviolet, infra-red, Mass etc. Leaving aside the functional groups, a large part of an organic molecule consists of carbon-hydrogen skeleton and this tool is most useful in the investigation of this structural feature of the molecule —rather than the complete structure. These days, *nmr* spectroscopy is gaining importance in the quantitative analysis of the compounds. For example, the ratio of alcohol and water in the given sample can be determined from the values of δ. It becomes possible due to the property of chemical exchange.

5.19 Some Important NMR Spectra

Following are given nuclear magnetic resonance spectra of some important compounds. Each spectrum is explained by describing the total number of signals observed alongwith their multiplicities and positions of absorption.

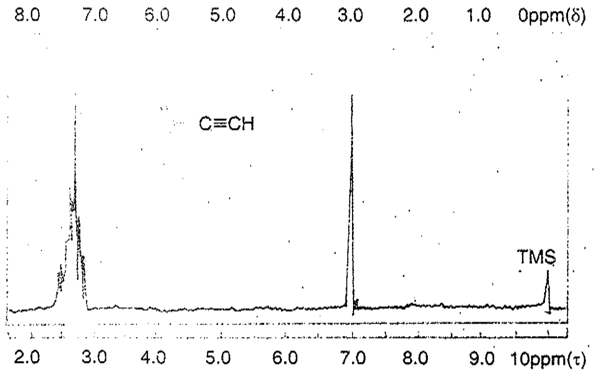


Fig. 5.33. NMR spectrum of phenyl acetylene. Varian catalogue spectrum No. 186

Signals and their absorption positions

(*i*) One proton singlet 6.95τ

(*ii*) Five proton unsymmetrical multiplet 2.4–2.8τ

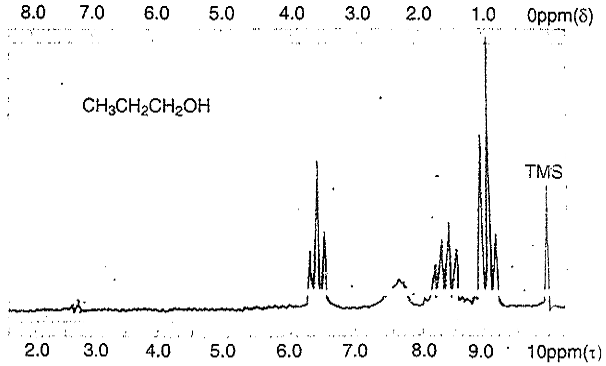


Fig. 5.34. NMR spectrum of n-Propanol. Varian catalogue spectrum No. 43.

Signals and their absorption positions

(*i*) Three proton triplet = 9.1τ

(*ii*) Two proton sextet (—CH_2—) = 8.45τ

(*iii*) Two proton triplet (CH_2—O) = 6.4τ

(iv) One proton singlet (hump) due to O—H = 7.7τ

In the *nmr* spectrum of n-propanol (CH_3—CH_2—CH_2—OH), we observe that a two proton triplet for CH_2—O appears downfield (6.4τ) as compared to a one proton singlet due to O—H group at 7.7τ. It looks rather surprising. It may be due to the rapid intermolecular chemical exchange of the hydroxyl proton which shifts the position of its absorption.

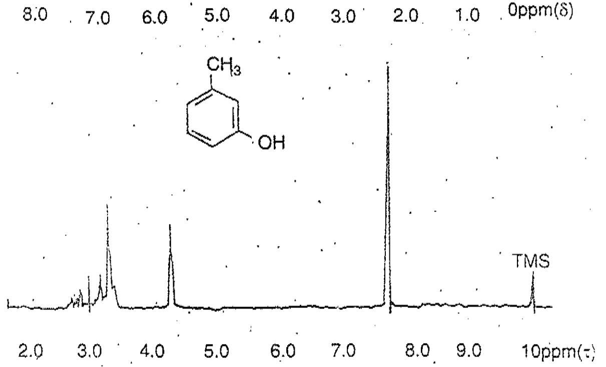


Fig. 5.35. NMR spectrum of meta-Cresol. Varian catalogue spectrum No. 160.

Signals and their absorption positions

(*i*) three proton singlet (CH_3) = 7.75τ

(*ii*) one proton singlet (OH) = 4.32τ.

(*iii*) four proton unsymmetrical pattern = 2.75 – 3.5τ

Signals and their absorption positions

(*i*) three proton doublet = 8.25τ

(*ii*) one proton quartet = 5.5τ

(*iii*) one proton singlet for —COOH (off the scale) = –0.98τ

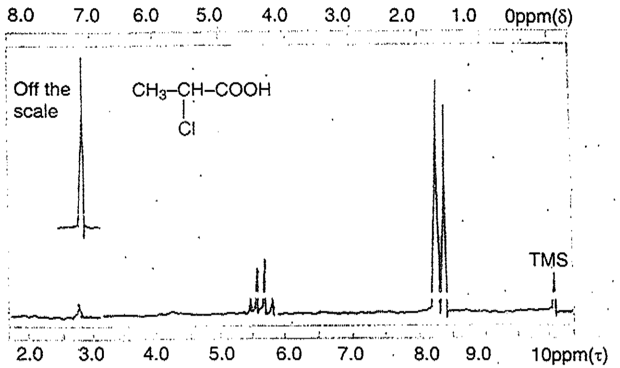


Fig. 5.36. NMR spectrum of α-chloropropanoic acid. Varian catalogue spectrum No. 25.

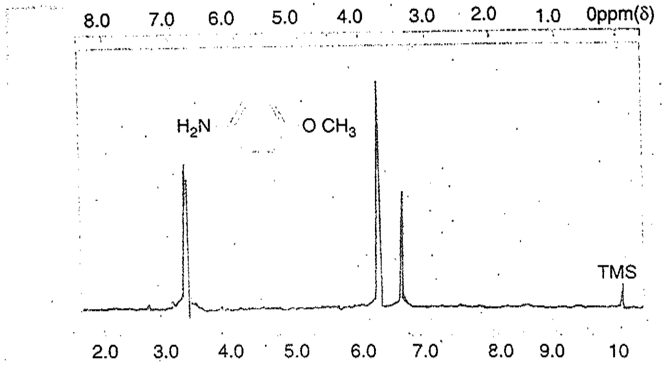


Fig. 5.37. NMR spectrum of p-anisidine. Varian catalogue spectrum No. 171.

Signals and their absorption positions

(*i*) two proton singlet (NH_2) = 6.6τ

(*ii*) three proton singlet (OCH_3) = 6.25τ

(*iii*) four proton unsymmetrical pattern = 3.45 – 3.20τ

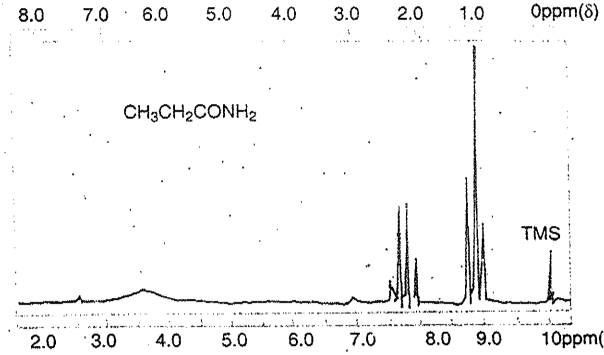


Fig. 5.38. NMR spectrum of Propionamide. Varian catalogue spectrum No. 40.

Signals and their absorption peaks

(*i*) three proton triplet = 8.85τ
(*ii*) two proton quartet = 7.7τ
(*iii*) two proton hump = $2.9 - 4.0\tau$

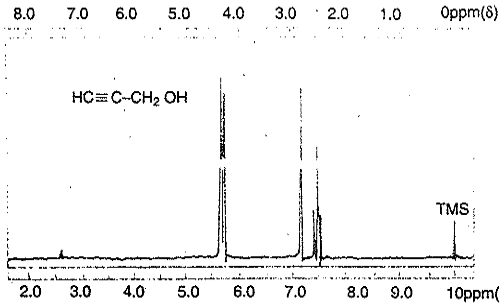


Fig. 5.39. NMR spectrum of 2- Propyne-1ol. Varian catalogue spectrum No. 21.

Signals and their absorption positions

(*i*) one proton singlet (H—C ≡) = 7.5τ
(*ii*) one proton singlet (—OH) = 7.15τ
(*iii*) two proton singlet (nearly doublet) = 5.65τ

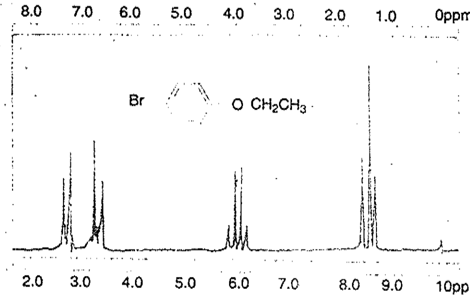


Fig. 5.40. NMR spectrum of para-bromophenetole. Varian catalogue spectrum No. 198.

Signals and their absorption positions

(*i*) three proton triplet = 8.6τ
(*ii*) two proton quartet = 6.8τ
(*iii*) four proton symmetrical pattern (double doublet) = $2.6 - 3.4\tau$

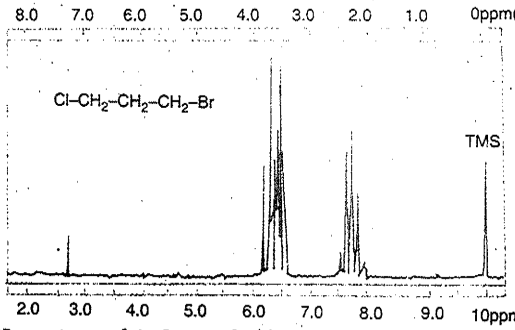


Fig. 5.41. NMR spectrum of 1– Bromo–3 chloropropane. Varian catalogue spectrum No. 29.

Signals and their absorption positions

(*i*) two proton pentet = 7.65τ
(*ii*) two proton triplet (—CH_2Br) = 6.48τ
(*iii*) two proton triplet (—CH_2Cl) = 6.2τ

Two triplets appear with a small difference in chemical shift.

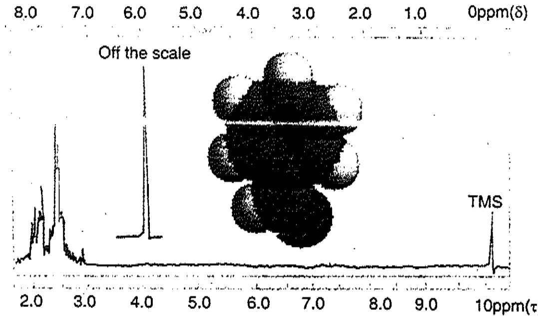


Fig. 5.42. NMR spectrum of Benzaldehyde. Varian catalogue spectrum No. 151.

Signals and their absorption positions

(*i*) five proton unsymmetrical pattern = $1.75 - 2.70\tau$
(*ii*) one proton singlet (CHO) = 0.15τ (off the scale)

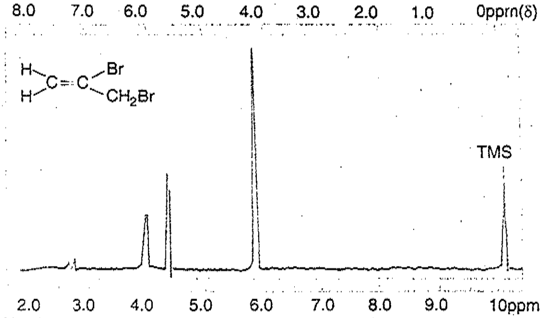


Fig. 5.43. NMR spectrum of 2, 3– dibromo propene. Varian catalogue spectrum No. 17.

Signals and their absorption positions

(*i*) two proton singlet = 5.8τ
(*ii*) one proton doublet = 4.38τ
(*iii*) one proton doublet = 3.98τ

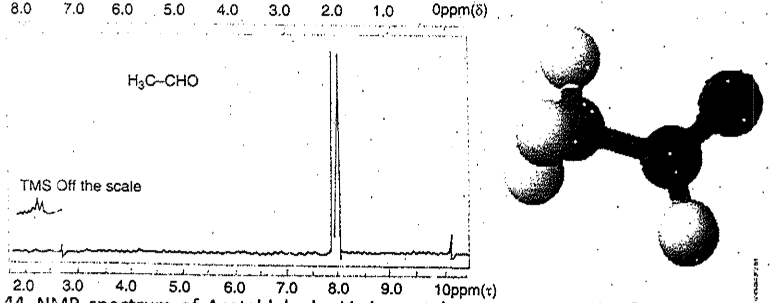


Fig. 5.44. NMR spectrum of Acetaldehyde. Varian catalogue spectrum No. 6.

Signals and their absorption positions

(*i*) three proton doublet = 7.8τ

(*ii*) one proton quartet = 0.15τ (off the scale)

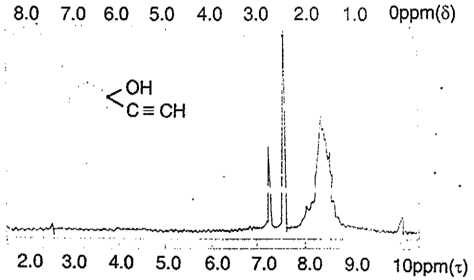


Fig. 5.45. NMR spectrum of 1-ethynyl 1-cyclohexanol. *Courtesy*. Varian Associates, California.

Signals and their absorption positions

(*i*) unsymmetrical pattern (Ring) = 7.9 – 9.0τ

(*ii*) one proton singlet (≡ C—H) = 7.5τ

(*iii*) one proton singlet (—OH) = 7.2τ

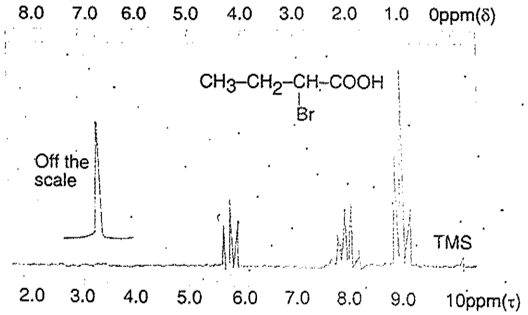


Fig. 5.46. NMR spectrum of α-bromo butanoic acid. Varian catalogue spectrum No. 66.

Signals and their absorption positions

(*i*) one proton triplet (—CHBr—) = 5.8τ

(*ii*) three proton triplet (CH_3) = 8.9τ

(*iii*) two proton pentet = 7.9τ

(*iv*) one proton singlet (—COOH) = – 0.95τ (off the scale)

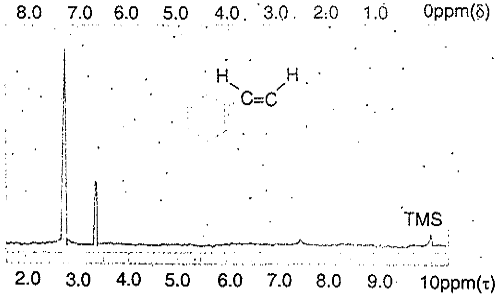


Fig. 5.47. NMR spectrum of cis-stilbene. Varian catalogue spectrum No. 305.

Signals and their absorption positions

(*i*) two proton singlet = 3.45τ

(*ii*) ten proton singlet due to two phenyls = 2.80τ

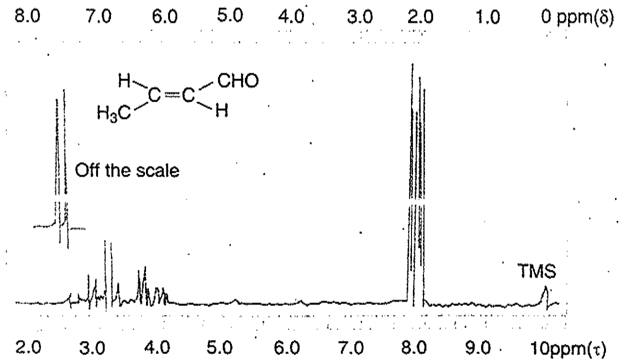


Fig. 5.48. NMR spectrum of Crotonaldehyde Varian catalogue spectrum No. 60.

Signals and their absorption positions

(*i*) one proton doublet (CHO) = 0.2τ (off the scale)

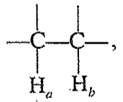
(*ii*) one proton double doublet (H^a) = 3.8τ

(*iii*) one proton multiplet (double quartet, 8 lines) = 3.1τ

(*iv*) three proton double doublet = 7.95τ

5.20 Double Resonance* (Spin Decoupling)

This technique involves the irradiation of a proton or a group of equivalent protons with sufficiently intense radio-frequency energy to eliminate completely the observed coupling to the neighbouring protons. A signal for a particular proton or a set of equivalent protons is split up into a multiplet under the influence of the neighbouring proton/protons under different environments.

Consider the case of a compound  $-\underset{H_a}{\overset{|}{\underset{|}{C}}}-\underset{H_b}{\overset{|}{\underset{|}{C}}}-$, in which H_a and H_b are in different environments.

Clearly, in its *nmr* spectrum, two doublets corresponding to each proton should be observed at different field strengths.

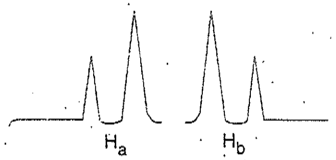


Fig. 5.49. Two doublets.

It has been observed that if we irradiate H^a with correct frequency energy (intense) so that the rate of its transitions between the two energy states (spin states) becomes much larger, then the life time of this nucleus in any one spin state will be too short to resolve coupling with H_b. In such

---

* Double Irradiation.

a case, H_b proton will have one time average view of H_a and hence H_a will come to resonance only once and H_b will appear as a singlet (not doublet).

In the same way, if we irradiate H_b with sufficiently intense radio frequency energy, then due to its rapid transitions between the two spin states, H_a will have one time average view of H_b and hence H_b will come to resonance only once and H_a will also appear as a singlet.

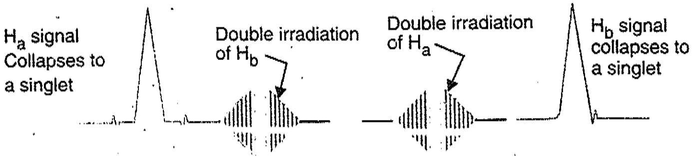
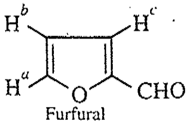


Fig. 5.50. Spin decoupling.

It may be noted that the time (*dt*) needed to resolve the two lines of a doublet is related to the separation between the lines, *i.e.* coupling constant J. Thus, the formation of doublet in the above example is possible if each spin state of H^a has a life time greater than *dt*. With double irradiation, the said life time becomes still less and thus, due to the increase in the rate of transition, coupling is not possible and thus, singlets result.

In this technique, we make simultaneous use of two radio frequency sources. In addition to the normal *nmr* instrument, a second tunable radio frequency source is needed to irradiate H_a at the necessary frequency and the recording of the spectrum is done in the same way. It is called double resonance or double irradiation. Since the multiplet collapses to a singlet in the process, it is also called spin decoupling[*].

Double resonance technique is a powerful tool for simplifying a spectrum and is of great value to organic chemists working with complex molecules. It helps in the identification of coupled protons in spectra that are too complex for detailed analysis. We know that the *nmr* spectrum of Furfural (furan 2-aldehyde) is quite complex.



Furfural

Proton H_a couples with H_b which splits H_a into a doublet but H_a also couples with H_c so that each line of H_a is further split into two giving four lines in all for H_a proton. Similarly, four lines result for each of H_b and H_c. Thus. a spectrum consisting of 12 lines (three multiplets) results for three protons. Each multiplet is found to show two different value of J (see Fig. 5.51).

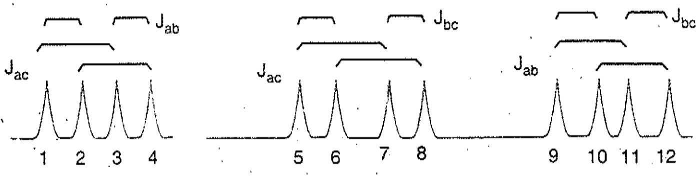


Fig. 5.51.

The effect of strong decoupling[**] eliminates the coupling of H_a with H_b and H_c. This results in the collapse of each of the four line multiplet (for H_b and H_c) into the doublet. In the 12 line spectrum, we find that J_{bc} value is very small as compared to J_{ac} and J_{ab}.

---

[*] Due to the greater strength of the irradiation used for decoupling, this technique is not suitable when the chemical shift between the two protons is small. For such a case, another technique called 'Tickling' is applicable.

[**] Protons can be decoupled provided these are about 20 cps apart.

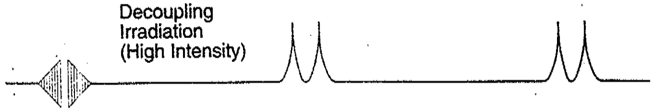


Fig. 5.52. Double Irradiation.

Now if spin tickling (low intensity irradiation) is carried out by weakly irradiating one line of spectrum due to the proton H_a, we observe that the line 7, 8 of H_c signal and the lines 11, 12 of H_b are further split[*] (see Fig. 5.53).

Here the lines 5 and 6 are associated with one particular spin orientation of H_a while the lines 7 and 8 are associated with the opposite spin orientation of H_a. Also we say that the lines 5 and 7 are associated with one spin orientation of H_b while the line 6 and 8 are associated with opposite spin orientation of H_b. In the H_b part of the spectrum, lines 9 and 10 originate due to one spin orientation of H_a while the lines 11 and 12 from its opposite spin orientation. Also the lines 9 and 11 are the result of one spin orientation of H_c while the lines 10 and 12 due to its opposite spin orientation.

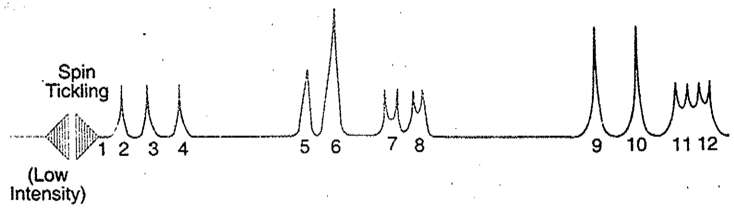
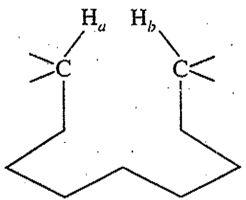


Fig. 5.53. Spin Tickling

Since spin tickling on line 1 in the spectrum of H_a has been shown to disturb the lines 7, 8 and 11, 12; hence we say that all these lines arise from the same spin orientation of H_a. Thus, it is clear that the signs of J_{ac} and J_{ab} must be of the same type and is opposite to that of J_{bc}. Hence this technique is of great value in determining the absolute sign for the J value.

5.21 Nuclear Overhauser Effect (N.O.E.)



The nuclear overhauser effect is of great value in studying the molecular geometry of the compounds. It tells whether the two protons are in close proximity within the molecule or not. An important consequence of this effect is that the line intensities observed in the normal spectrum may not be the same as in the decoupled spectrum. Consider a molecule in which two protons are close enough to allow through-space interactions of the fluctuating magnetic vector. For this effect, the number of intervening bonds between the two concerned protons have no significance. Consider a hypothetical molecule in which two protons are in close proximity.

In such a compound, if we double irradiate H_b, then this proton gets stimulated and the stimulation is transferred through space to the relaxation mechanism of H_a. Thus, due to the increase in the spin lattice relaxation of H_a, its signal will appear more intense by 15—50%. Thus, we say that if the intensity of absorption of H_a signal is increased by double irradiating H_b, then the protons H_a and H_b must be in close proximity in a molecule.

---

[*] Not decoupled.

5.22 NMR Spectrum at more than one Radio-Frequency

It may be noted that the chemical shift positions for the various sets of protons are field dependant. If we work the spectra of a particular compound at different radio-frequencies, then it has been found that the value of coupling constant (measured in cps) remains the same whatever the applied field. Scanning at different radio-frequencies tells clearly whether a particular signal is a multiplet or a few singlets. Let us consider a case in which a doublet is observed and is being suspected as two singlets. For this, the spectrum of the same compound is re-run at a higher radio-frequency. Now the signal will appear at a different field strength but if the distance between the two peaks (coupling constant J) remains the same, then it is necessarily a doublet. If the distance between the two peaks increase by working at a higher radio-frequency, the formation of two singlets can be safely declared. Sometime, it happens that at a certain radio-frequency, the two signals in the *nmr* spectrum overlap and thus, the analysis becomes difficult. This technique helps in simplifying such a complex spectrum. The multiplets can be pulled apart by scanning the spectrum of the same compound at a higher radio-frequency. Thus, the complex spectrum is improved[*]. For example, in the *nmr* spectrum of 4-chlorobutyric acid ($ClC^4H_2C^3H_2C^2H_2C^1OOH$) at 60 mega cycles sec^{-1}, the quintet for the central methylene and the triplet for C_2-methylene overlap and thus complexity arises. But the signals get apart by working the spectrum at 200 mega cycles sec^{-1}. At 200 mega cycles sec^{-1}, two distinct signals (quintet and triplet) are observed with different chemical shifts.

5.23 Deuterium Exchange Reactions

It has been found that if a few drops of deuterium oxide are added in the sample, the D_2O exchanges with the labile protons such as —OH, —NH, —SH and also with the reactive methylene protons flanked by the carbonyl groups. The mechanism involves the same course as is seen in **proton exchange reactions.**

When a little D_2O is added to ROH, then due to rapid exchange, ROH becomes ROD.

$$ROH + D_2O \rightleftharpoons R—OD + H—OD$$

Thus, the signal for —OH proton normally observed in ROH will be missing in the PMR spectrum and instead, a signal for proton in H—OD will appear. Similarly, if a little D_2O is added to RCOOH, then due to rapid exchange, it becomes RCOOD.

$$RCOOH + D_2O \rightleftharpoons RCOOD + H—OD$$

Clearly, the signal for the proton in RCOOH (in the PMR spectrum) which normally appears (in the absence of D_2O) at a negative tau value will be missing or diminished and a signal for proton corresponding to H—OD appears instead. This technique which is employed for detecting the presence of OH, NH groups etc. is called **deuteration.** For the deuterium exchange technique, two spectra are run.

(*i*) One with the sample dissolved in a solvent other than D_2O.

(*ii*) Second spectrum with the sample dissolved in the same solvent and containing a few drops of D_2O.

On comparing the two spectra, if the peak areas are seen to diminish then the sample may contain —OH, —NH, —SH group in which deuterium exchange is possible.

5.24 C^{13}–nmr Spectroscopy

C^{13}-nuclear magnetic resonance is a relatively new technique. There are considerable differences between the H^1 *nmr* and C^{13} *nmr* spectra both in the mode of recording as well as appearance.

---

[*] The degree of improvement of the spectrum depends upon the differences in chemical shift and also upon the coupling constants involved.

The spin quantum number, I for C^{12} is equal to zero. It is, therefore, non-magnetic and does not give any *nmr* signal. C^{13} has a spin quantum number equal to ½ and its nuclear magnetic resonance can be observed in a magnetic field of 23,500 gauss at 25.2 mega cycles per second. It may be noted that with the same magnetic field, H^1 *nmr* is observed at 100 mega cycles per second. The natural abundance of C–13 isotope is only 1.11%. The low abundance further reduces the sensitivity of absorption. Although the low abundance had been a major obstacle for the advent of C^{13} *nmr*, we now know that the nature's choice had been a very fortunate one. Since with higher abundance, probably, neither proton nor C^{13} *nmr* would ever have even become a meaningful technique for the organic chemist because of the great complexity of spectra that would result from heteronuclear and homonuclear spin-spin coupling. H^1 *nmr* spectrum is normally obtained by sweeping either the excitation frequency or the field through the region of nuclear precession frequencies. The inefficiency of this method is clear from the fact that only one line can be observed at a given point in time. The problem arises when C^{13} with intrinsically narrow lines covering a wide absorption range are studied. It is, therefore, advantageous to excite the whole band of frequencies simultaneously. It is done by using a strong pulse of radio-frequency covering a large band of frequencies which is capable of exciting all resonances of interest at once. At the end of the pulse period, the nuclei will precess freely with their characteristic frequencies reflecting with the chemical environment.

Each C^{13} resonance in organic molecule is spin coupled not only to the directly attached proton but also to the proton(s) which is (are) two to four bonds away. The value of the coupling constant also differs accordingly. The value of the coupling constant is over 125 cps for the C^{13} absorption when it couples with the proton directly attached to it ($J_{C—H} > 125$ cps). The value of coupling constant is nearly 20 cps when the coupling proton is two to four bonds away. C^{13} *nmr* spectra, therefore, appear as multiplets with unresolved long range couplings. Each signal appears as a broad peak. The complexity in the spectrum further increases by the overlap of multiplets due to the large number of one bond C—H couplings.

Development of a proton decoupling technique was most significant in simplifying C^{13} *nmr* spectra. In this technique, a single H^1 decoupling frequency as the centre of a finite excitation band is utilised. It is called **proton noise decoupling.** This single frequency is modulated by a pseudo random noise generator yielding effective excitations throughout a preset band width. The band width can be set broad enough to cover all protons in a sample.

Chemical Shift in C^{13} *nmr*. For almost all organic molecules, complete C^{13} spectra appear between low field carbonyl carbons and high field methyl carbons in the range 0 to 200 ppm (δ value). TMS is the common internal reference which is used for C^{13} *nmr*. One of the advantages of using CMR[*] in organic chemistry is that many of the functional groups containing carbons are directly observable. The CMR spectrum detects:

(*i*) the total number of protons

(*ii*) the total number of carbon atoms and also

(*iii*) the presence of carbonyl group in the organic compound.

Medium induced and concentration dependant chemical shifts are negligible in C^{13} *nmr* because the nuclei studied are buried in the molecular framework. Unlike protons which are in the periphery of a molecule, C^{13} chemical shifts are, however, extremely sensitive to substitution and molecular geometry. It may be noted that highly substituted carbon atoms resonate at lower field. Carbon atoms separated by several bonds strongly influence each other if these are spatially close (NOE).

The state of hybridisation is the dominating factor determining the chemical shift of a carbon atom. sp^3 hybrid carbon atoms absorb upfield while sp^2 carbon atoms absorb at lower field strength.

$$sp^3 > sp > sp^2$$

---

[*] CMR means C^{13} *nmr*

The carbonyl carbon has been the most investigated of all carbon atoms by CMR. The resonance of carbonyl carbons of all aliphatic ketones absorb farthest downfield with δ value equal to 200 ppm. The esters and lactones appear between 160–180 δ.

In an unsaturated framework, delocalisation of charge across the π electron system produces large effect on the value of the chemical shift. In aromatic compounds, the electron donating substituents *viz.* —NH$_2$, —OH delocalise their lone electron pairs into the π system, thus, increasing the charge density at the ortho and the para carbons. Substituents with lone pairs, thus, shield ortho and para carbons while the electron attracting groups have a deshielding influence. Carbonyl carbons are particularly important in describing the position of chemical shift. The carbonyl carbon bears a partial positive charge and hence resonate at the lower field (higher δ value). In the case of conjugated carbonyls, the positive charge can be delocalised and as a result of it, the carbonyl carbon resonates upfield.

5.25 F^{19}– nmr

Fluorine with mass number 19 is the naturally occurring isotope. Like ^{1}H, we know that it has $I = \frac{1}{2}$. Except for the appropriate radio-frequency source, no major modification in the instrument required for F^{19}– spectrum of an organic compound is needed. Chemical shifts are commonly measured with CFCl$_3$ as the standard. The range of chemical shift covered by fluorine containing compound is 0–200 ppm compared to 0–10 ppm in case of proton magnetic resonance. Moreover, signals corresponding to fluorine resonances are well separated on the spectrum. Clearly, the values of coupling constants (J) in such compounds have higher values.

(*i*) Geminal F – F coupling ranges from 43 – 370 cps

(*ii*) Vicinal F – F coupling ranges from 0 – 39 cps

(*iii*) In case of cis fluorines, coupling constant varies from 0–58 cps while its values range from 106 –148 cps in case of trans fluorines.

Coupling between (H^1) and F^{19} is also very strong. Geminal H–F coupling ranges from 42 – 80 cps (J value) while Vicinal H × F has coupling constant between 1.3 – 29 cps. For cis H × F, J = 0–22 cps while trans isomer has the value of coupling constant equal to 11–52 cps. It is important to note that fluorine atoms attached to benzene also couples with protons on the ring. For ortho H × F, coupling constant ranges from 7.4 – 11.8 cps. For meta and para H × F couplings, the value of J ranges from 4.3–8.0 cps and 0.2–2.7 cps respectively.

EXAMPLE. *Let us consider the nmr spectrum of 1-bromo-1-fluoroethane (CH$_3$CHFBr). Let the spectrum be recorded in an external field of 14092 gauss (i) at 60 MHz frequency for proton ^{1}H and (ii) at 56.42 MHz for F^{19}.*

Case I. In the *pmr* (proton magnetic resonance, coupling between CH$_3$—CH— should give rise to (*i*) one proton quartet at low field and (*ii*) a three proton doublet at upfield.

Case II. The presence of fluorine atom (F^{19} nucleus) complicates the above spectrum. The doublet for CH$_3$ is further split by F^{19} and hence each line of the doublet is further split into two by a large vicinal H × F coupling. The value of J in the new multiplet is 22 cps. Thus, the signal for CH$_3$ group will be **a double doublet.**

The quartet due to CH proton is also under the influence of fluorine atom. Thus, each line of this quartet is split into two by geminal H × F coupling. In this multiplet, the value of J is 50 cps. Thus, the signal due to CH is **doublet of quartets.**

5.26 Nuclear Magnetic Resonance Spectra of Carbocations

There are certain carbocations which are sufficiently stable under definite conditions and their proton magnetic spectra can be easily studied. For example, alkyl fluorides in liquid sulphur dioxide react with Lewis acid (like antimony pentafluoride) to give a solution of carbocation. Consider the formation of carbocation from tert-butyl fluoride (in liquid SO$_2$) with antimony pentafluoride.

$$\underset{\substack{\tau\ 8.65 \\ \text{(doublet)}}}{(CH_3)_3C{-}F} + SbF_5 \xrightarrow{\text{Liq.}SO_2} \underset{\substack{\tau\ 5.65 \\ \text{(singlet)}}}{(CH_3)_3\overset{+}{C}.\ SbF_6^-}$$

In carbocation, central carbon is sp^2 hybridised and thus deshielding causes absorption at lower field. Similarly, consider when isopropyl fluoride reacts with antimony pentafluoride in liquid sulphur dioxide. The positions of absorption are shown :

$$\underset{\substack{\tau\ 8.77\quad \tau\ 5.34 \\ \text{(quartet) (multiplet)}}}{(CH_3)_2CHF} + SbF_5 \longrightarrow \underset{\substack{\tau\ 4.97\quad \tau\ 3.50 \\ \text{(doublet) (septet)}}}{(CH_3)_2\overset{+}{C}H\ .\ SbF_6^-}$$

We see that the signal due to positively charged carbon atom in the carbocation suffers remarkable downward shift.

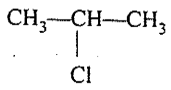
5.27 Applications of NMR Spectroscopy

The *nmr* spectroscopy is very widely used for the detailed investigation of an unknown compound.

1. Identification of structural isomers. The distinction between the following isomers can be easily made from their *nmr* spectra:

(*i*) CH$_3$CH$_2$CH$_2$Cl

(*a*)



$CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3$

(*b*)

In the isomer '*a*' three signals are observed whereas we see only two signals in the spectrum for '*b*' which is a clear distinction between the above isomers. The three signals for isomer '*a*' in order of decreasing tau values are:

(*i*) A three proton triplet (CH$_3$—)

(*ii*) A two proton sextet (—CH$_2$—) and

(*iii*) A two proton triplet (—CH$_2$Cl)

For isomer (*b*), two signals have their multiplicities as:

(*i*) doublet (6H)—upfield and

(*ii*) septet (1H)—downfield

Similarly, distinction between the position isomers like propanol—1 and propanol—2 can be made:

$\overset{d}{C}H_3\overset{c}{C}H_2\overset{b}{C}H_2\overset{a}{O}H$

Propanol–1

Four signals

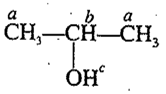
(*i*) *a*–Singlet (1H)

(*ii*) *b*–Triplet 2H

(*iii*) *c*–Sextet (2H)

(*iv*) *d*–Triplet (3H)

Tau value increases



$\overset{a}{C}H_3{-}\underset{\displaystyle OH^c}{\underset{|}{\overset{b}{C}H}}{-}\overset{a}{C}H_3$

Propanol–2

Three signals

(*i*) *a*–doublet (6H)

(*ii*) *b*–Septet (1H)

(*iii*) *c*–Singlet (1H)

Tau value decreases

2. **Detection of hydrogen bonding.** Intermolecular hydrogen bonding shifts the absorption for a concerned proton downfield. The extent of hydrogen bonding varies with the solvent, concentration of the solution and the temperature. Intramolecular hydrogen bonding also shifts the absorption downfield. The two types of hydrogen bonding can be distinguished as the intramolecular hydrogen bonding is not concentration dependant.

3. **Detection of aromaticity.** Protons attached to the benzoyl, polynuclear and heterocyclic compounds whose π electrons follow Huckel's rule [*i.e.* $(4n + 2)$ π electrons where $n = 1, 2, 3$...(whole number)] are extremely deshielded due to the circulating sextet (ring current) of π electrons. As a result of this, the signal for the aromatic protons appear at a very low field than that observed even for benzene. From this, the aromatic character of the compound under investigation can be predicted.

4. **Distinction between Cis-Trans Isomers and Conformers.** The cis and trans isomers of a compound can be easily distinguished as the concerned protons have different values of the chemical shifts as well as the coupling constants.

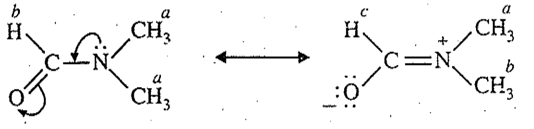
(Cis) $J_{cis} = 7 - 12$ cps

(Trans) $J_{trans} = 13 - 18$ cps

Similarly, the various conformations of a compound, the axial and equitorial positions of the proton or group carrying a proton can be distinguished from their different values of the coupling constants.

5. **Detection of electronegative atom or group.** It is known that the presence of an electronegative atom or group in the neighbourhood of the proton cause deshielding and the signal is shifted downfield. Greater the electronegativity of the adjacent atom, smaller is the tau value of absorption for the concerned proton. Fluorine causes more downward shift as compared to oxygen and oxygen in turn causes more downward shift as compared to nitrogen and so on.

6. **Detection of some double bond character due to resonance.** In some compounds, the molecule acquires a little double bond character due to resonance. Due to this, two signals can be expected for apparently equivalent protons. It is due to the hindered rotation which changes the geometry of the molecules. Consider N, N dimethyl formamide. It can be written in the following resonating structures:



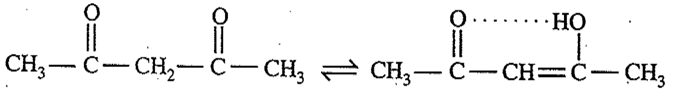
(*a*) (*b*)

For structure (*a*), two signals (singlets) should be expected with peak areas 6 : 1 as the two methyls are exactly equivalent.

In structure (*b*), the presence of double bond restricts rotation and now the two methyl groups remain no longer equivalent (Geometrical isomers). For this structure, two signals appear for two methyl groups.

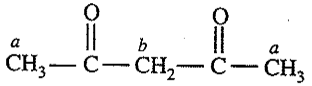
7. **Importance in quantitative analysis.** NMR spectroscopy is gaining importance for the quantitative analysis of the compounds. Equilibrium mixtures can be analysed when the proton signals of the components are well separated. In the *nmr* spectrum of pure ethanol (CH_3CH_2OH), a triplet is formed for the OH proton but when water is added in alcohol, then due to proton exchange, the triplet collapses to a singlet. The position of this singlet depends upon the water content in alcohol. From the values of the chemical shift, the ratio of water and alcohol can be estimated by comparing with the known results.

Keto-enol tautomerism has also been studied in the same manner. Consider acetyl acetone in equilibrium with the enolic form.



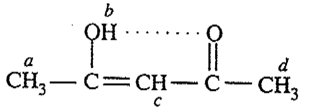
(Keto) (Enol)

The *nmr* spectrum of pure acetyl acetone shows signals for the following kinds of equivalent protons:



$a = 7.86\tau$
$b = 6.35\tau$ [ketonic]

Ketonic



$a = 8.03\tau$
$b = -4.3\tau$
$c = 4.4\tau$
$d = 7.87\tau$ [enolic]

A distinct two proton singlet at 6.35τ appears due to the ketonic form whereas all the eight protons in the enolic form are observed as four signals. Quantitatively, the number of enol protons relative to the keto protons yields the ratio as under:

enol protons : keto protons = 8 : 2 or 4 : 1

Thus, we say that 80% of enolic form and 20% of the ketonic form are present in the equilibrium mixture of acetyl-acetone.

5.28 Important Features in Nuclear Magnetic Resonance Spectroscopy

1. **The fundamental property** of an atomic nucleus in NMR is the nuclear spin (I), the value of which depends upon the mass number and the atomic number of the nucleus. The nuclei with I > 0 can be spin active: ^1H, ^{13}C, ^{31}P, ^{19}F have nuclear spin equal to 1/2 and are spin active but ^{12}C, ^{16}O etc with I = 0 are not spin active. Spin active nuclei behave as spinning nuclear magnets.

2. **The precessional frequency** is equal to the number of revolutions per second made by the magnetic moment vector of the nucleus around the external field, H_O.

3. **Chemical shift** is defined as the difference in the resonance frequency of a given proton compared to that of methyl protons of tetramethyl silane (TMS) under the experimental condition. The chemical shift is independent of the operating frequency of the instrument but is dependent upon the solvent.

4. **Anisotropic effect :** The magnetic fields associated with the electron circulations induced by H_O, in molecules containing π-bonds are anisotropic. They do not sum to zero in overall possible orientations of the molecule with respect to H_O. Thus, the phenomenon is called anisotropic effect.

5. **Shielding of nucleus :** When the effective magnetic field experienced by the nucleus is less than that of the applied field, the nucleus is said to be shielded. The signal for shielded proton appears upfield (*i.e.* lower value of δ).

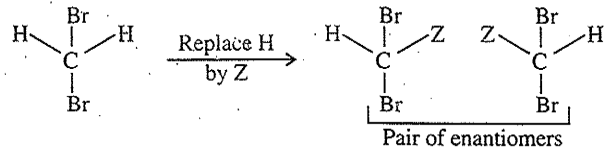
6. **Deshielding of nucleus :** When the effective magnetic field experienced by the nucleus is more than the applied field, then the nucleus is said to be deshielded. The deshielding of proton

is caused when it is surrounded by electronegative atoms or groups. Ethylenic, aromatic and aldehydic protons are highly deshielded : For such protons, the signal appears downfield (*i.e.* at higher value of δ).

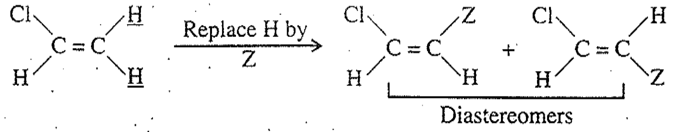
7. **Effect of change of solvent :** Sometimes a signal of interest is obscured by other signals in the spectrum. In such a case, the change of solvent may induce shift changes in the signal to observe it. Clearly, Benzene possesses high magnetic anisotropy and also tend to form sandwich-like collision complexes with carbonyl compounds. Due to this property, it is particularly used to identify various signals in the complex spectrum.

8. **Hydrogen bonding :** Hydrogen bonding causes deshielding of protons. Greater the degree of hydrogen bonding, greater the downfield shift. The position of the resonance signal for proton in compounds containing OH, NH depend upon the concentration of the liquid compound and also on the state of the subtance. For the spectrum of neat ethanol (polymeric aggregates of molecules), the signal for OH appears as a broad peak at δ5.28 ppm. But on dilution with non-polar solvent (like CCl_4), the proton resonates upfield and give, a sharp signal. Clearly, extent of hydrogen bonding decreases on dilution and so is the deshielding.

9. **Equivalence of Protons :** A set of chemically equivalent protons are also magnetically equivalent and they possess the same frequency and only one characteristic spin-spin interaction with the nuclei of the neighbouring group. All the three protons of methyl group are magnetically equivalent because as a result of the rotation about C—C bond, all the three protons have the same time averaged chemical environment and hence the same resonance frequencies. The chemically equivalent protons should also be stereochemically equivalent. The stereochemical equivalence of protons may be looked at by labelling the hydrogen atoms in a compound as enantiotropic or diastereotopic. For example, in the structure of ethyl bromide, one of the methylene proton is replaced by Z. If we get a pair of enantiomers then the pair of protons are enantiotopic (*i.e* equivalent) and only one *pmr* signal is obtained for them.



Consider vinyl chloride (CH_2=CHCl) molecule. The replacement of either of the protons by Z give compounds which are nothing but diastereomers.



Such a pair of protons are non-equivalents and produce two signals in NMR spectrum. Such a pair of protons are diastereotopic.

10. **Spin-Spin Splitting :** Splitting occurs only between nuclei with different chemical shifts, *i.e* between magnetically non-equivalent protons. The coupling interaction takes place between the neighbouring protons, most often through bonds and results in the splitting of spectral lines. Coupling also takes place between protons on the same carbon atom provided these are in stereo chemically different environment.

11. **Coupling constant :** The coupling constant is a measure of the coupling interaction between the nuclei. The spacing between the lines within a coupled multiplet is constant. This constant distance, called coupling constant is denoted by 'J' and is expressed in Hertz (Hz).

12. **Spin-Spin Relaxation :** It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice.

13. Greater resolution is obtained in CMR spectra than that in proton magnetic resonance spectra.

14. In PMR spectra, we get information regarding chemical shift, coupling constant and the number of the sets of equivalent protons, the information obtained from CMR spectroscopy is the number of carbon atoms, carbonyl group etc in a molecule.

15. The strength of the earth's magnetic field is about 0.57 gauss.

16. Nuclear magnetic resonance is unusual in that the different energetic states required for obtaining the spectrum are created by external magnetic field. In ultra-violet and infra-red, these states are already present in the molecule.

17. Integration is the measurement of the area under the peak which is proportional to the number of protons giving rise to that peak.

18. The induced magnetic field of circulating aromatic electrons is larger than in alkenes. It is due to a large effective ring of electrons. As a result, the benzenoid or aromatic protons have greater value of δ than the alkene protons. Thus PMR is a valuable tool to detect aromaticity.

19. The methylene protons of freely rotating methylene group, when adjacent to a chiral centre, are non-equivalent. Such protons are diastereotopic. Such protons have different chemical shifts and split each other's signals and have different coupling constants.

20. The spin-spin coupling patterns are described by the use of alphabetical notation. The protons with a large chemical shift difference are assigned letters which are widely separated in the alphabet (e.g; AX) system. The protons with close chemical shifts are given letters which are also close in the alphabet like AB system. When the protons are chemically equivalent but magnetically non-equivalent, a prime is used. Thus AB system will become AA′BB′.

21. The spin active nuclei other than hydrogen present in an organic compound introduce additional complications in the spectrum since these nuclei will take up spin orientations with respect to the applied field and may cause spin-spin splitting of the proton signals. The heteroatoms like ^{13}C, ^{19}F and ^{31}P are spin active as they possess nuclear spin equal to half.

22. The relative abundance of C-13 isotope is only 1.1%. In an organic compound, ^{13}C isotope may couple into hydrogen resulting in the heteronuclear coupling between ^{1}H and ^{13}C. For example, the spectrum of chloroform (CH Cl_3) exhibits an intense singlet due to the absorption of uncoupled hydrogen. In addition, it shows two weak outer bands for the absorption of coupling hydrogen in $^{13}CHCl_3$. The relative intensity of the coupled ^{13}CH peaks is directly proportional to the ratio $^{13}C/^{12}C$.

23. Coupling between the nuclei of ^{1}H and ^{19}F is also interesting, ^{19}F occurs in 100% abundance and its nuclear spin is equal to 1/2. It can take up two spin orientations in exactly the same way as hydrogen. Thus, hydrogen couples with fluorine for H—C—F group. It is vicinal coupling and coupling constant is 60 Hz. For H—C—C—F, the value of coupling constant is 20 Hz.

Consider the NMR spectrum of 2, 2, 2-trifluoroethanol

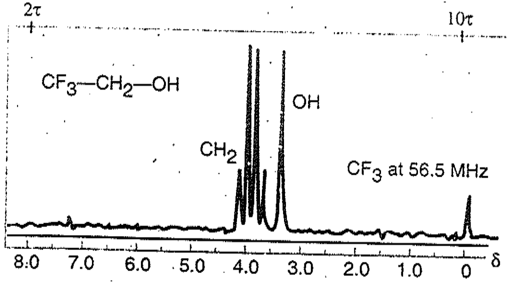


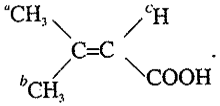
Fig. 5.54. The CH_2– group is split into a quartet by three fluorine atoms.

The signal for —CH_2— does not appear as a singlet but appears as a quartet by coupling with three vicinal ^{19}F atoms. It is quite similar to the splitting of —CH_2— by CH_3— group in ethyl alcohol. The coupling constant is 8 Hz.

24. ^{31}P-isotope has 100% natural abundance and possess nuclear spin equal to 1/2. Hydrogen couples with ^{31}P and as a result, P-H absorption appear as doubtes with coupling constant equal to 200-700 Hz.

25. Molecules which have symmetry elements do not show any cis or trans splitting. In cis and trans stilbenes, the ethylenic protons are magnetically equivalent, no splitting is caused.

26. The technique of Nuclear Overhauser Effect is very useful to determine the stereochemical relationships in molecules like $(CH_3)_2C{=}CHCOOH$



. The irradiation of *cis*-methyl group ($^aCH_3$) shows a 17% increase in the integral intensity of ^cH. Irradiation of the far methyl group ($^bCH_3$) causes no change in the integral intensity of H^c.

27. The quarternary carbons exhibit small nuclear overhauser enhancements. The reason is that the magnitude of the observed NOE depends upon its distance from nearest hydrogen. The quarternary carbons being deeply buried inside the complex structures exhibit less NOE than those on the outside of the molecule.

28. *cis* and *trans*-2-Butenes can be distinguished on the basis of C-13 NMR spectroscopy. The stereochemical influence of γ-effects in alkenes is assigning configuration to geometrical isomers. γ-effect for *cis* is stronger by 5.4 ppm. Thus, *cis* and *trans*-2-Butenes can be easily distinguished from the chemical shift of methyl carbons. These are 11.4 ppm for *cis* isomer and 16.8 ppm for the *trans* isomer.

5.29 Simple Problems on Nuclear Magnetic Resonance

1. **Calculate the chemical shift in ppm (δ) for a proton that has resonance at 126 Hz downfield from TMS on spectrophotometer that operates at 60 MHz.**

Ans. The chemical shift (δ) can be calculated by applying the relation :

$$\delta = \frac{\Delta\nu(\text{in cps}) \times 10^6}{\text{Frequency of spectrophotometer in cps (or Hz)}}$$

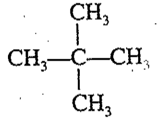
Substituting the values, $\delta = \dfrac{126 \times 10^6}{60 \times 10^6} = 2.1$

Thus, chemical shift, δ = **2.1 ppm.**

2. (*a*) **How will you differentiate (*i*) Chlorobenzene from 1, 2-dichloroethane and (*ii*) Benzene from acetone by NMR spectra ?**

(*b*) **Indicate what NMR spectra you expect from the following compounds.**

(*i*) $CH_3—CH_2—CH_2—CH_3$

(*ii*)


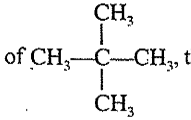
$$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—CH_3$$

Ans. (*a*) Chlorobenzene shows a singlet due to 5H at about δ7.3 while in 1, 2-dichloroethane, a singlet due to a set of four equivalent protons is formed at higher field value *i.e* at δ 2.5. Protons are highly deshielded in chlorobenzene.

(*b*) Benzene can be easily distinguished from acetone by NMR spectra. Protons are highly deshielded in benzene and a signal is observed at δ 7.27 whereas a singlet in case of acetone appears upfield at about δ 2.5.

(*c*) In $^aCH_3—^bCH_2—^bCH_2—^aCH_3$, there are two kinds of equivalent protons and thus two signals are expected for it. The two signals are :

(*i*) A 6H triplet and (*ii*) a 4H quartet.

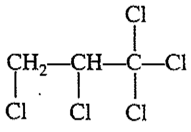


In case of $CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—CH_3$, there are 12 protons which are chemically as well as magnetically equivalent. For this compound, one signal is formed upfield at about δ 1.0.

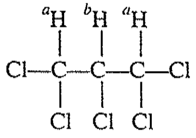
3. **An organic compound with molecular formula, $C_3H_3Cl_5$ gave the following pmr data.**

(*a*) A triplet 5.48 τ (4.52 δ) (*b*) A doublet 3.93 τ (6.07 δ) 2H. Assign a structural formula to the compound consistent with its pmr data given above.

Ans. The formation of a triplet and a doublet suggest that there are two kinds of protons. A doublet due to 2H appearing at low field is clearly more deshielded by greater number of chlorine atoms. The possible structures of the compound may be written as :



(*i*)



(*ii*)

structure (*ii*) looks more probable. Deshielding due to four chlorine atoms bring the two proton absorption at 3.93 τ. Thus, the given data is consistent with structure (*ii*).

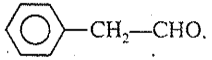
4. **A compound with molecular formula C_8H_8O gives the following PMR spectrum.**

(*i*) **Multiplet τ 2.72 (δ 7.28) 5H** (*ii*) **Doublet τ 7.2 (δ 2.8), 2H**

(*iii*) **Triplet τ 0.22 (δ 9.78) 1H.**

Give the structural formula.

Ans. From the data, it is clear that there are three sets of equivalent protons in the compound. A multiplet at 2.72 τ for five protons is due to benzene ring or C_6H_5. A two proton doublet and one proton triplet in the spectrum shows the presence of —CH_2—CH— as a part of the structure. A signal at 0.22 τ, for proton at very low field shows the presence of —CHO group.

Thus, the structure of the compound is : 

5. **An organic compound with molecular formula C_5H_{12} show two signals in its NMR spectrum.**

(*i*) **A triplet at 0.90 δ, 6H** (*ii*) **Multiplet at 1.28 δ due to six protons.**

Ans. Organic compound (C_5H_{12}) is a saturated hydrocarbon with two sets of equivalent protons. The chemical shift values tells that the protons are highly shielded. The most probable structure appears to be $\overset{a}{CH_3}—\overset{b}{CH_2}—\overset{b}{CH_2}—\overset{b}{CH_2}—\overset{a}{CH_3}$.

The '*a*' set of protons (6H) exhibit the presence of terminal methyl groups and for this, the signal appears slightly upfield at 0.90 δ. Another set of 6H gives a signal for three —CH_2— groups. The PMR structure of *n*-pentane is shown below.

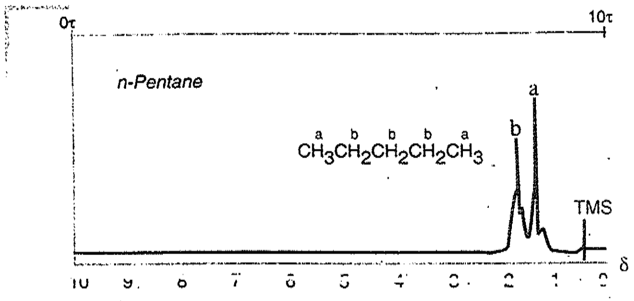


Fig. 5.55. PMR spectrum of *n*-Pentane.

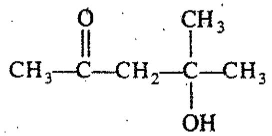
6. **A compound with molecular formula, $C_6H_{12}O_2$ shows four signals :**

   (*i*) Singlet 1.1 δ (6H). (*ii*) Singlet 2.1 δ (3H) (*iii*) singlet 2.6 δ (2H) and (*iv*) singlet 3.9 δ (1H). Propose a structure consistent with the given data.

Ans. From the given data, it appears that there are four types or sets of protons and their signals appear as singlets *i.e* no splitting is caused.

A six proton singlet upfield (1.1 δ) is highly shielded and this unit is most likely to be $-\underset{|}{\overset{|}{C}}(CH_3)_2$

A three proton singlet at 2.1 δ shows a methyl group which may be linked to carbonyl group. Thus, another unit is CH_3CO- in it. A two proton singlet is due to the presence of $-CH_2-$ group. Since no splitting of signal is caused, therefore, $-CH_2-$ group should be in between the above two units. From the given molecular formula, the remaining part is OH group which forms a singlet at 3.9 δ. From this information, the most probable structure of the compound is :



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

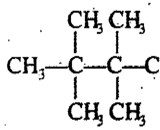
(4-Methyl-4 hydroxy pentan-2-one)

7. **Predict the structural formula for the compounds with the following molecular formulae showing only one PMR signal each.**

   (*i*) C_8H_{18} (*ii*) C_2H_6O (*iii*) C_5H_{12}.

Ans. Since only one PMR signal appears, the structural formula corresponding to the molecular formula is

(*i*) C_8H_{18} is :

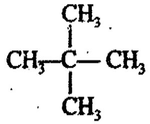


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

(All the hydrogen atoms in this structure are equivalent)

(*ii*) C_2H_6O is : CH_3-O-CH_3 (Dimethyl ether)

(*iii*) C_5H_{12} is :



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

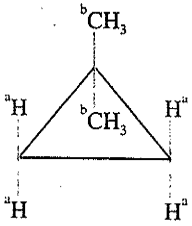
(2, 2-Dimethyl propane)

8. **Predict the number of signals in PMR spectroscopy of each of the following :**

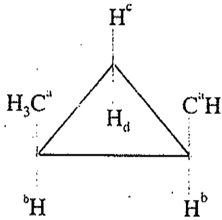
   (*i*) 1, 1-Dimethyl cyclopropane (*ii*) cis-1, 2-Dimethyl cyclopropane

   (*iii*) trans-1, 2-Dimethyl cyclopropane(*iv*) 1, 2-Dichloropropane.

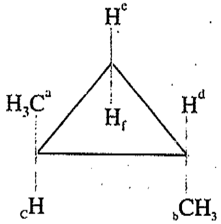
Ans. The structures of all the four given compounds are :



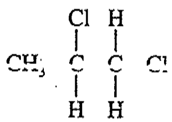
(i)



(ii)



(iii)



(iv)

(*i*) In this molecule, there are two sets of protons and thus two signals will appear in its NMR spectrum.

(*ii*) For this structure, there are four sets of equivalent protons and thus, its spectrum will show four signals.

(*iii*) For this structure, six signals will appear because there are six sets of equivalent protons in it. In other words, there are six types of protons which are in different chemical environments and six signals will be formed in its PMR spectrum.

(*iv*) There are four sets of equivalent protons in 1, 2-dichloro propane.

Hence, four signals appear in its NMR spectrum.

9. **Predict the number of signals, their multiplicities and chemical shifts with respect to TMS as reference for the PMR spectrum of cinnamaldehyde. Draw the spectrum of this compound.**

Ans. The structure of cinnamaldehyde is $C_6\overset{c}{H_5}\overset{b}{C}H=\overset{a}{C}H\overset{d}{C}HO$. Four sets of equivalent protons are present in the molecule of cinnamaldehyde. Thus, four signals will be formed in the NMR spectrum. The multiplicities of signals and the probable chemical shift is described as under.

(*i*) A doublet for the proton H^b appears at 7.5 δ. It is due to its coupling with proton H^a. Since there two protons are in trans position, the value of coupling constant, J is 16.3 Hz.

(*ii*) A multiplet for 5H aromatic ring appears downfield at 7.4 δ.

(*iii*) A highly deshielded doublet at 9.64 δ appears for the aldehydic proton with coupling constant equal to 7.41 Hz.

(*iv*) A doublet of doublet at 6.60 δ for H^a proton is due to the vicinal and trans coupling with H_b and H_d.

The PMR spectrum of cinnamaldehyde is shown below.

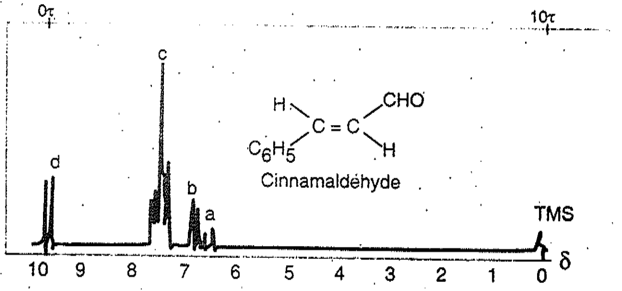
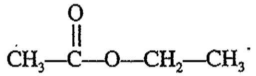


Fig. 5.56. PMR spectrum of cinnamaldehyde.

10. **Predict the structure of an organic compound with molecular mass 88 whose PMR data is given below :**

(*i*) A triplet (1.23 δ) 3H (*ii*) A singlet (1.97 δ) 3H (*iii*) A quartet (4.06 δ) 2H.

Ans. The formation of a triplet and a quartet at 1.23 δ and 4.06 δ respectively shows that $CH_3—CH_2—$ is a part of the structure. A singlet for three equivalent protons upfield shows CH_3 group. The probable structure consistent with the given data can be written as:



$$CH_3—\overset{\overset{\displaystyle O}{||}}{C}—O—CH_2—CH_3$$

The two proton quartet being close to oxygen atom is relatively deshielded and hence appears downfield.

11. **A compound having molecular formula $C_9H_{11}Br$ showed the following signals in PMR data.**

(*i*) Multiplet (δ 2.25), 2H **(*ii*) Triplet (δ 2.75) 2H**

(*iii*) Triplet (δ 3.38) 2H **(*iv*) Singlet (δ 7.22), 5H**

Assign the structure of the compound giving reasons.

Ans. Molecular formula $C_9H_{11}Br$

(*i*) A five proton singlet at 2.78 τ shows the presence of an aromatic ring.

(*ii*) A two proton quintet at 7.75 τ, two proton triplet at 7.25 τ and two proton triplet at 6.62 τ (downfield) shows the following combination:

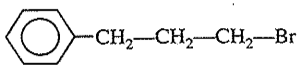
$$—{}^aCH_2—{}^bCH_2—{}^cCH_2—Br$$

$—{}^aCH_2$ forms a two proton triplet downfield as it is directly attached to the aromatic ring. These two protons are under the influence of two protons *i.e* $—{}^bCH_2$.

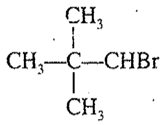
$—{}^bCH_2$ protons are under the influence of four protons (two on either side) and thus, forms a quintet.

$—{}^cCH_2Br$ protons also forms a triplet.

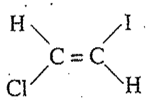
Thus, the structure consistent with the given data is :



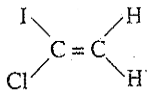
12. **What will be the multiplicity of each kind of proton in the following molecules.**



(*i*)

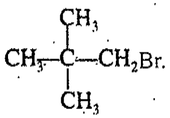


(*ii*)



(*iii*)

Ans. (*i*)



$$CH_3—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—CH_2Br.$$

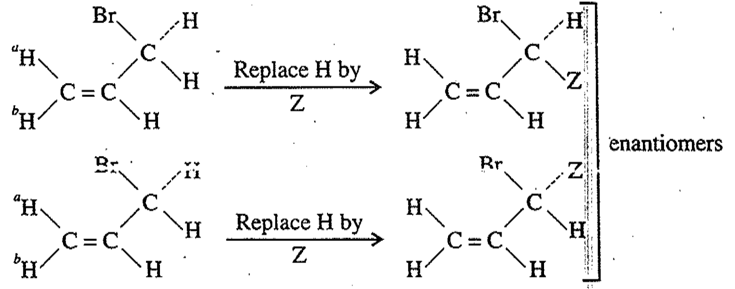
This compound has two sets of equivalent protons, *i.e*, a set of nine protons and a set of two protons. Both two signals are observed as singlets in the PMR spectrum.

(*ii*) It has two types of protons and thus, two signals are formed. Due to spin-spin coupling, both the signals are observed as doublets.

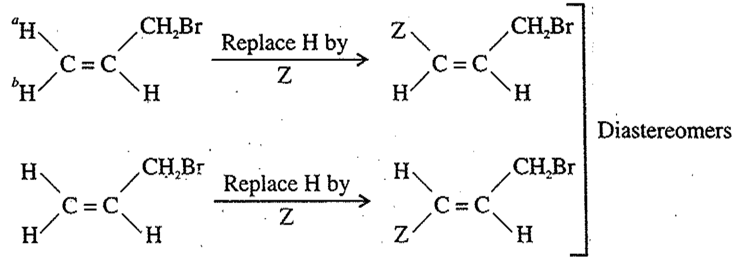
(*iii*) In this compound, both the protons are in different environments. Thus, two signals will appear and both are observed as doublets.

13. **How many different types of protons are present in allyl bromide ?**

Ans. There are four sets of equivalent protons in allyl bromide ($CH_2=CH—CH_2Br$). The two allylic protons in allyl bromide are enantiomeric and hence identical. It is proved by replacing either of this hydrogen by an atom or group Z.



The protons which are labelled '*a*' and '*b*' are diastereotopic. The replacement of either of these hydrogen result in the formation of compounds which are diastereomers.



Hence four signals will appear in its PMR spectrum.

14. **An aromatic compound (Molecular mass = 135) gives the following signals in its PMR spectrum.**

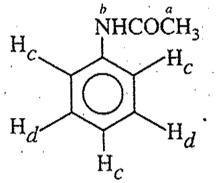
(*i*) Singlet (2.09 δ), 3H **(*ii*) A distorted singlet (3.09 δ) 1H**

(*iii*) A multiplet (7.27 δ), 3H **(*iv*) A multiplet (7.75 δ), 2H.**

Predict the structure of the compound.

Ans. The appearance of singlet at 2.09 δ for three protons shows the presence of methyl group. A distorted singlet at 3.09 δ for one proton is due to amide proton.

Two multiplets must be due to the aromatic ring. Thus, the probable structure of the compound is



15. **A nitrogen containing compound (mol. mass = 73) shows the following signals in its PMR spectrum.**

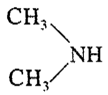
(*i*) Singlet (0.60 δ) 1H (exchangeable with D_2O)

(*ii*) Triplet (1.05 δ) 6H

(*iii*) Quartet (2.61 δ) 4H.

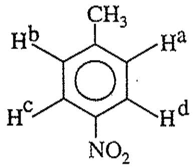
Ans. The presence of triplet and a quartet at 1.05 δ and 2.61 δ shows that CH_3—CH_2— is a part of the structure. It amounts to 29 mass units.

A one proton singlet which appears upfield and is exchangeable with D_2O may be linked with nitrogen. Thus, NH is also a part of the structure. The probable structure of the compound is :



16. **Predict the number of signals and their multiplicities for the PMR spectrum of p-Nitrotoluene.**

Ans. The PMR spectrum of *p*-Nitrotoluene will consist of five signals. The multiplicities of signals and the approximate values of chemical shifts can be described below.



(*i*) The signal for CH_3— group appears as a singlet upfield at about 2.4 δ.

(*ii*) All the four protons of the benzene ring will appear as doublets. The protons '*c*' and '*d*' will show signals slightly downfield than the protons 'a' and '*b*'. The reason is that they experience additional deshielding being ortho to the nitro group. The probable position of absorption for '*c*' and '*d*' is δ 8.0. While those ortho to methyl show signal at 7.2 δ.

5.30 Short Questions with Answers

1. **Which type of nuclei show magnetic properties for the purpose of NMR spectroscopy ?**

Ans. A nucleus with an odd atomic number or an odd mass number has a nuclear spin which can be observed by the NMR spectrometer. A wide variety of nuclei including ^1H, ^{13}C, ^{15}N, ^{19}F and ^{31}P have suitable magnetic properties and can be studied by NMR spectroscopy.

2. **Which property of certain atomic nuclei is involved in NMR spectroscopy ?**

Ans. A large number of spin active nuclei such as ^1H, ^{13}C, ^{19}F etc have permanent magnetic moments $\left(\text{nuclear spin} = \frac{1}{2}\right)$ and can be studied by NMR spectroscopy.

3. **How many types of orientations take place when a proton is placed in a magnetic field ?**

Ans. When a proton is placed in a magnetic field, it starts precessing in the radio wave region and is capable of taking up one of the two orientations w.r.t the axis of external field.

(*i*) the proton has spin quantum number I of $+\frac{1}{2}$ (alignment with the external field or α-spin state).

(*ii*) the proton has quantum number I of $-\frac{1}{2}$ (alignment against the external field or β-spin state)

4. **Which spin state has higher energy ?**

Ans. Alignment against the external field or *β*-spin state possesses higher energy.

5. **^{13}C is NMR active while ^{12}C is not Explain.**

Ans. The reason is that the isotope ^{13}C (whose abundance is only 1.1%) has a nuclear spin equal to $\frac{1}{2}$. While ^{12}C isotope does not have a nuclear spin and does not absorb in NMR.

6. **How many spin states are possible for ^1H nucleus ?**

Ans. We know that the number of spin states for a given nucleus is written by the expression (2I + 1) where I is the angular momentum of that nucleus.

For proton, $I = \frac{1}{2}$

Therefore, the number of nuclear states for ^1H nucleus $= 2\times\frac{1}{2}+1 = 2$.

7. **When the irradiation with radio frequency, the nucleus or proton comes in resonance and absorption takes place ?**

Ans. A nucleus is in resonance when it is irradiated with radio frequency photons having energy equal to the energy difference between the spin states. Thus, for a nucleus to be in resonance, a right combination of magnetic field and electromagnetic radiation to flip its spin is needed.

8. **What is the strength of the earth's magnetic field ?**

Ans. The strength of earth's magnetic field is about 0.57 gauss.

9. **What happens when just the right amount of electromagnetic energy strikes the proton ?**

Ans. When a photon with just the right amount of electromagnetic energy strikes the proton, the proton's spin can flip from *α* to *β*-spin state.

10. **Do you need any solvent for determining the NMR of an organic compound ?**

Ans. Yes. The usual procedure for determining PMR (Proton magnetic resonance) spectra involves dissolving the sample in a suitable solvent containing no protons. Carbon tetrachloride and deuterochloroform are used most frequently.

11. **Why TMS is used as a reference standard in NMR spectroscopy ?**

Ans. Tetramethylsilane (TMS) has an advantage that its absorption position is far away from the absorptions due to protons in most of the organic compounds. All the equivalent protons in TMS are highly shielded and assigned an arbitrary value equal to zero (0 δ or 10 τ). Thus, it becomes possible to device a scale in which most of the proton resonances will be of the same sign.

12. **Halogen nuclei have large dipole moments but still these are practically non-magnetic whereas ^{14}N and ^2H are magnetic for the purpose of high resolution NMR spectroscopy. Explain.**

Ans. The halogen nuclei (Cl, Br, I) have large magnetic moments but the mechanism of dipole relaxation is so effective that these nuclei become practically non-magnetic for the purpose of high resolution NMR spectroscopy. But in case of ^{14}N and ^2H, quadrupole relaxation is less effective so that their resonance lines can be observed more easily.

13. **What is meant by induced magnetic field ?**

Ans. The magnetic field that is set up by the motion of electrons in a molecule in response to the application of an external field is termed induced magnetic field.

14. **Define the term 'chemical shift'.**

Ans. The chemical shift *i.e* δ-value in ppm is the position of an absorption peak relative to that of a reference compound which is usually TMS (Tetramethyl silane).

15. **What decides the value of chemical shift w.r.t TMS ?**

Ans. The chemical shift is largely dependent on the presence or absence of electron density. When bonded to a group which withdraws part of the electron density around the proton, then the proton is said to be deshielded. More the deshielding of proton, more downward is the absorption position (τ-value decreases). A proton is said to be shielded when it is surrounded by electrons whose induced magnetic field opposes the external magnetic field and shields the proton from the nucleus. In order to bring such a proton to resonance, the applied field has to be increased. In such a case, absorption occurs upfield.

16. Give the relative decreasing order of δ-values for 3°–, 2°–, 1°– protons of alkanes as compared to CH_4 hydrogens.

Ans. Shielding increases with the number of hydrogens on carbon. Thus, δ-value decreases in the order : $R_3CH > RCH_2 > RCH_3 > CH_4$.

17. In a given organic compound, two kinds of protons exhibit signals at 50 Hz and 200 Hz using a 60 MHz NMR instrument. What would be their equivalent positions using 90 MHz spectrometer. Also convert the signals at 50 and 200 Hz into δ and τ values.

Ans. We know that the resonance frequencies are directly proportional to field strength.

Thus, at 90 MHz spectrometer, the positions of the signals are

(*i*) $\frac{50 \times 90}{60} = 75$ Hz and (*ii*) $\frac{200 \times 90}{60} = 300$ Hz

Chemical shift of signals at 50 and 200 Hz are

$$\frac{50}{60} = \mathbf{0.83\ \delta} \text{ or } \mathbf{9.17\ \tau} \text{ and } \frac{200}{60} = \mathbf{3.33\ \delta} \text{ or } \mathbf{6.67\ \tau}.$$

18. What do you say about the induced magnetic fields in the multiple bonded systems ?

Ans. In the multiple bonded systems, induced magnetic fields are produced. These induced field lines divide the immediate environment into two regions. In one region, the proton is shielded and in the other, it is deshielded from the applied field. In other words, in one region, the induced field acts to oppose the external field while in the other, it reinforces the external field.

19. Can you predict whether the given compound is aromatic or not by PMR spectroscopy ?

Ans. Yes. The induced magnetic field of circulating aromatic electrons is larger than in the alkanes due to large effective ring of electrons. Due to this, the aromatic protons absorb downfield *i.e.* with higher δ-value (6.0 – 8.5 ppm).

20. What is spin-spin splitting ?

Ans. It is the interaction of the magnetic fields of two or more nuclei, both through their connecting bonds and space. Spin-spin splitting causes the PMR signals to split and thus, appear as multiplets, *i.e* doublets, triplets etc.

21. Define coupling constant (J).

Ans. The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant.

22. What is meant by (n + 1) rule in spin-spin coupling ?

Ans. The protons on adjacent carbon atoms with different electronic environments cause spin-spin coupling. The signal that is being split by n equivalent protons appears as a multiplet with (n + 1) peaks. It is called (n + 1) rule. For example in CH_3—CH_2—Cl, the signal for CH_3 protons under the influence of —CH_2— equivalent protons appears as a triplet.

23. Do spin-spin coupling giving multiplets has any relation with coupling constants ?

Ans. Non-equivalent protons on adjacent carbon atoms usually show splitting and appears as multiplets. The presence of one split absorption necessitates the presence of another split signal in the spectrum. The coupling constants in these multiplets must be the same.

24. What do you mean by shielding and deshielding of a nucleus ?

Ans. Shielding is caused when the effective magnetic field experienced by the nucleus is less than that of the applied field ($H_{eff} < H_o$). But the electron withdrawal from a proton by the neighbouring electronegative atom or group deshields the proton.

25. Explain why methyl, methylene, methyne and quarternary carbons (and their attached hydrogens) come to resonance to successively lower field.

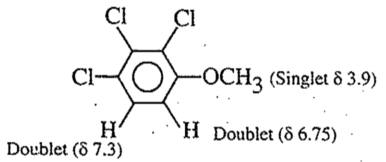
Ans. We know that hydrogen is more electropositive than carbon. Every replacement of hydrogen by an alkyl group cause downward shift in the resonance of that carbon and the remaining hydrogens on it. Thus, we write :

	CH_4	$MeCH_3$	Me_2CH_2	Me_3CH	Me_4C
δ_C	–2.3	8.4	15.9	25.0	27.7
δ_H	0.23	0.86	1.33	1.68	—

26. A compound with molecular formula, $C_7H_5OCl_3$ shows a three proton singlet at δ 3.9 and two one proton doublets (J = 8 Hz) at δ 6.76 and 7.3. Identify the compound.

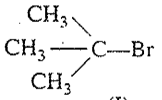
Ans. The three proton singlet at δ 3.9 must be due to OCH_3 group. The two are proton doublets at δ 6.76 and δ 7.3 must be single protons in different environments.

The probable formula of the compound is



27. The pmr spectrum of a mixture of methyl iodide and tert-butyl bromide shows two singlets at δ 2.20 and δ 1.8 with relative integrals of 5 : 1. What is the mole percent of each compound in the mixture ?

Ans.



(I)

CH_3—I

(II)

In compound (I), Br is attached to carbon which is next to three methyl groups but I is directly attached to carbon in CH_3I.

Thus, it appears that protons in CH_3I are more deshielded and hence absorb at δ 2.2. Being more shielded, the protons in tertiary butyl bromide absorbs at δ 1.8. Keeping the relative integrals in view, we write :

$$\frac{5 \text{ protons of } CH_3I \times \frac{1}{3} \text{ molecule per proton}}{1 \text{ proton of } (CH_3)_3\,C—Br \times \frac{1}{9} \text{ molecule per proton}} = \frac{15 \text{ molecules of } CH_3I}{1 \text{ molecule of } (CH_3)_3\,C—Br}$$

$$\therefore \quad \text{Mole fraction of } CH_3I = \frac{15}{15+1} = \frac{15}{16} = 0.938.$$

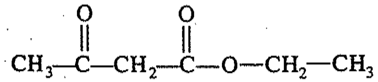
Hence, the sample contains 93.8 percent methyl iodide.

28. The molecular formula of the organic compound is $C_6H_{10}O_3$. Its pmr spectrum shows the following signals.

Chemical shift (δ)	*Multiplicity*	*Integral ratio*
1.2	Triplet	5.9
2.2	Singlet	5.4
3.5	Singlet	3.5
4.1	Quartet	4.0.

Ans. From the integral ratio between protons; triplet, singlet, singlet and quartet are in the ratio 3 : 3 : 2 : 2.

A three proton triplet and two proton quartet show that $CH_3—CH_2—$ is a part of the molecule. Two singlets are $—CH_2—$ and $CH_3—$. Now two carbons and three oxygen atoms are left. The probable formula of the compound is :

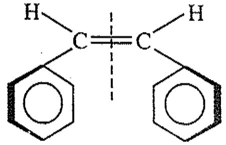


$$CH_3—\overset{O}{\overset{\|}{C}}—CH_2—\overset{O}{\overset{\|}{C}}—O—CH_2—CH_3$$

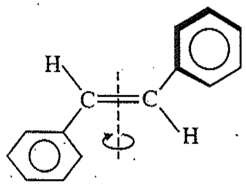
It is in agreement with the given data.

29. How will you distinguish *cis* and *trans*-stilbene by means of NMR spectroscopy ?

Ans. *cis* and *trans*-isomers can be written as :



cis-stilbene



trans-stilbene

cis-stilbene has a plane of symmetry and thus two ethylenic protons in it are magnetically equivalent and do not couple.

But *trans*-stilbene has two fold axis of symmetry. Two olefinic proton in it lies in the plane of two phenyl rings and is thus, deshielded. Two olefinic protons in *trans*-stilbene absorb at relatively lower field as compared to olefinic protons in *cis*-stilbene.

30. What do you know about magnetically non-equivalent protons ?

Ans. The protons may be chemically equivalent but magnetically non-equivalent. Magnetically equivalent protons have the same coupling constant to every other nucleus in the system.

31. What is the effect of hydrogen bonding and rapid exchange ?

Ans. Due to hydrogen bonding and rapid exchange, the coupling of hydroxyl protons with protons on neighbouring carbons is not generally observed. It is also true for NH protons except that one does not see the NH proton itself as a clear multiplet due to electrical and magnetic properties of nitrogen.

32. Mention some important characteristics of solvents used in NMR.

Ans. (*i*) It should be chemically inert and magnetically isotropic.

(*ii*) It should be devoid of hydrogen atom and

(*iii*) It should dissolve the substance to a reasonable extent.

33. NMR has quantitative significance as well. Explain.

Ans. When alcohol contains same quantity of water, then rapid proton exchange occurs.

$$ROH^* + HOH \rightleftharpoons ROH + HOH^*$$

Due to this, a singlet is observed for the hydroxyl proton. The position of the singlet peak for the OH proton is slightly shifted depending upon the water content in alcohol and hence, it helps in the quantitative analysis of ethanol–water and acetic acid–water mixtures.

34. The observed chemical shift of proton is 300 Hz from TMS and the operative frequency of the spectrometer is 100 MHz. Calculate the chemical shift in terms of δ (ppm).

Ans. The chemical shift in terms of $\delta = \frac{300}{100} = 3$ ppm.

35. A proton H_b is coupled to four equivalent neighbouring protons H_a. What will be multiplicity and the relative intensity of the lines in the signal H_b ?

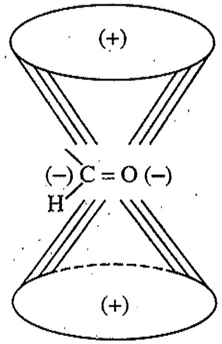
Ans. H_b will appear as a quintet with relative intensities of lines in the ratio 1 : 4 : 6 : 4 : 1.

36. What do you understand by the terms shielding and deshielding of a nucleus ?

Ans. When the effective field felt by the nucleus is less than that of the applied field ($H_{eff} < H_o$), the nucleus is said to be shielded. But the electron withdrawal from proton by the neighbouring electronegative atom or group causes deshielding of proton.

37. Aldehyde proton appears much downfield in the PMR spectrum. Explain.

Ans. The reason is that the aldehydic proton is strongly deshielded (range 9-10 δ, ppm) as it lies in the deshielding zone of the carbonyl group.



(An aldehyde)

38. Acetylene protons are more shielded than ethylenic protons. Explain.

Ans. In the external applied field, the ethylene molecule is so oriented that the plane of its double bond lies at right angles to the applied field and as a result, the induced magnetic field caused by the circulation of π-electrons is diamagnetic around the carbon atoms and paramagnetic in the region of protons.

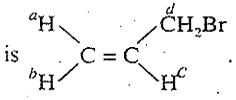
On the other hand, when acetylene molecule is placed in an external field, it is so oriented that the place of its triple bond lies parallel to the direction of the applied field. Thus, the molecule assumes a vertical orientation rather than horizontal orientation. Hence, the induced magnetic field caused by the circulation of π-electrons of the triple bond opposes the applied field in the region of protons. Thus, the acetylenic protons feel smaller field strength and resonance occurs at higher applied field.

39. In case of OH and NH resonances, broad signals are observed. Explain.

Ans. The reason is that the relaxation times of these types of protons are often shortened by chemical exchange processes and other nuclear phenomena.

40. How many different types of protons are present in allyl bromide molecule ?

Ans. The formula of allyl bromide is



. Four types of protons are present in allyl bromide molecule.

41. Aromatic protons are more deshielded than ethylenic protons, although both the types of protons are attached to sp^2 hybridised carbon atom. Explain.

Ans. Loops of π-electrons are delocalised cylindrically over the benzene ring. The loops of these electrons are caused to circulate in the presence of applied field producing ring currents. The induced current is diamagnetic at the centre of the ring and paramagnetic outside the ring. Thus, the aromatic protons (around the periphery of the ring) feel much greater field than the applied field. As a result, resonance occurs at lower values of the applied field. These protons are said to be much deshielded.

42. How will you distinguish between equitorial and axial protons in cyclohexane ?

Ans. It is observed that equitorial protons in cyclohexane rings come to resonance at about 0.5 δ higher value than the axial protons. The reason for this is anisotropic deshielding by σ-electrons in the βγ bonds.

43. How will you distinguish between inter and intra-molecular hydrogen bonding on the basis of PMR spectroscopy.

Ans. It is known that intermolecular hydrogen bonding is concentration and temperature dependent. The extent of hydrogen in the concentration solution will be more and as a result, deshielding to proton will be more and thus, resonance occurs at higher value of δ. As the solution is diluted, the degree of hydrogen bonding decreases and protons resonate at lower values of δ.

On the other hand, Intra-molecular-hydrogen bonding does not effect the value of chemical shift on dilution.

FURTHER READING

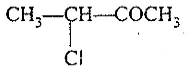
1. A. Ault and G.O. Dudey, An introduction to nuclear magnetic resonance spectroscopy–Holden-day (San Francisco), 1978.
2. L.M.Jackman and S. Sternhell, Applications of nuclear magnetic resonance spectroscopy in organic chemistry, Pergamon, New York, 1972.
3. J.W. Akitt, NMR and Chemistry: An introduction to Nuclear magnetic resonance spectroscopy, Chapman and Hall, 1973.
4. L.F. Johnson and W.C. Jankowski, Carbon-13 NMR spectra, Wiley, New York (1972), (contains 500 assigned C^{13} spectra).
5. Interpretation of Carbon–13 NMR spectra. F.W. Wehrli and T. Wirthlin, Heyden, 1976.
6. NMR spectra catalogue, volumes 1 and 2, Varian Associates, Palo Alto, California (U.S.A.).
7. J.H. Noggle and R.E. Schirmer. The nuclear overhauser effect; chemical applications. Academic Press, London (1971).
8. J.W. Emsley, J. Feeney and L.H. Sutcliffe, High resolution nuclear magnetic resonance spectroscopy, Volume I, Pergamon, New York, Vol. I 1965, Volume II 1966.
9. W.R. Anderson jr and R.M. Silverstein, Anal, Chem, 37, 1417 (1965).
10. K. Nakanishi, V. Woods and L.H. Durham, A guide book to the interpretation of NMR spectra, Holden-day, San Francisco, 1967.
11. "J.W. Cooper." Advanced techniques in Fourier Transform Nmr in Transform Techniques in Chemistry. P. Griffitles, Ed. Plenum Press, New York, 1978.

REVIEW QUESTIONS

1. Describe briefly the theory of *nmr* spectrometry. What information can be obtained from the *nmr* absorption peaks ?
2. What do you understand by the positions of the signals in an *nmr* spectrum? How many signals are expected in each of the following compounds? (*a*) Propane (*b*) Isobutane (*c*) Ethanol (*d*) Cyclobutane (*e*) Ethylmethyl ether (*f*) Ethyl acetate (*g*) Butanal (*h*) Glycol (*i*) α-alanine (*j*) Caprolactum.
3. (*a*) What is meant by the term chemical shift?
   (*b*) Write with examples, the shielding and the deshielding effects involved in *nmr* spectroscopy.
   (*c*) Describe with examples the various factors which affect the magnitude of the chemical shift.

4. (*a*) Define the term chemical shift and describe the factors which influence it.
   (*b*) Briefly describe how *nmr* spectrum of a compound is scanned?
5. (*a*) What do you understand by the term "Splitting of the signals"? Explain with examples.
   (*b*) Describe briefly the difference in the positions of absorption as noted in the case of acetylene and benzene.
6. (*a*) Explain clearly the term 'spin-spin coupling'. Why does a peak for a particular set of protons split into a multiplet? Give examples.
   (*b*) Write a short note on the use of solvents in the *nmr* spectrometry.
7. (*a*) An unknown compound gave on elemental analysis : 62.1% carbon and 10.35% hydrogen. Its *nmr* spectrum consisted of a quintet centred at 7.25τ and a triplet appeared at 5.25τ. Suggest a suitable structure for the unknown compound.
   (*b*) Write a short note on chemical exchange as observed in *nmr* spectroscopy.
8. (*a*) What do you understand by *nmr* absorptions by nuclei other than protons?
   (*b*) A compound has a molecular formula $C_{10}H_{13}Cl$. Assign its structure with the help of the following data:

Singlet	1.57δ	6H
Singlet	3.07δ	2H
Singlet	7.27δ	5H

9. (*a*) Write brief notes on the following:
   (*i*) Chemical shift
   (*ii*) Spin-spin coupling
   (*iii*) Coupling constant
   (*b*) Explain why *nmr* spectrum of benzene is observed at a lower field whereas that of acetylene is observed at a higher field strength.
10. (*a*) Describe briefly what information can be obtained from an *nmr* spectrum.
    (*b*) Write a detailed note on coupling constant.
11. (*a*) An optically active compound on elemental analysis was found to contain C = 40%, H = 6.6% and O = 53.3%. Its *nmr* spectrum consists of four singlets at δ values of 10.95, 5.93, 4.6 and 2.8 in the ratio of 1 : 1 : 1 : 3. Assign a suitable structure to the unknown compound.
    (*b*) Describe briefly the various applications of the *nmr* spectroscopy.
12. (*a*) Write the possible isomers corresponding to the following molecular formulae and draw their *nmr* structures.
    (*i*) C_4H_{10} (*ii*) C_2H_6O (*iii*) C_4H_8O (*iv*) $C_4H_6O_2$ (*v*) $C_4H_8O_2$
    (*b*) "NMR spectroscopy is the most important tool compared to ultra-violet and infrared for the structure determination of an unknown organic compound." Justify this statement.
13. (*a*) Which of the following atoms do not exhibit nuclear magnetic resonance?
    C^{12}, O^{16}, N^{14}, N^{15}, H^2, F^{19}, C^{13}, P^{31}
    (*b*) How many kinds of H^1's are therein :
    (*i*) $CH_3—CH_2—CH_3$?
    (*ii*) $CH_2 = CH_2$?
    (*iii*) $CH_3—CH = CH_2$?
    (*iv*) $C_6H_5—CH_3$?
14. Sketch the expected PMR spectra of the following compounds taking TMS as the standard reference:
    (*i*) CH_3CH_2Cl
    (*ii*) $CH_2Br—CH_2Br$
    (*iii*) $(CH_3)_2CH—CH_3$
    (*iv*) 
    $CH_3—\underset{Cl}{CH}—COCH_3$
    (v) $CH_3—CH_2CHO$

15. A pale yellow organic compound with molecular formula $C_6H_5NO_3$ is found to show two signals in the NMR spectrum.
    (*i*) Unsymmetrical pattern-multiplet = 1.8 – 2.9τ (4H)
    (*ii*) Singlet = 0.1τ (1H)
    Describe the spectrum of the compound and explain the position of each band.

16. (*a*) What is meant by the term chemical shift? Name the various factors on which the value of chemical shift depend and discuss one in detail.
    (*b*) Give the probable δ values to the various kinds of protons in the compound, $CH_2=CH—C\equiv CH$ with respect to TMS as the standard.

17. A hydrocarbon containing 90.9% carbon shows the following four signals:
    (*i*) Unsymmetrical multiple = 2.82τ (5H)
    (*ii*) Triplet 9.1τ (2H)
    (*iii*) Triplet 8.85τ (2H)
    (*iv*) Singlet 8.6t (3H)
    What is the structure of the compound?

18. (*a*) Write a short note on deshielding due to hydrogen bonding in NMR spectrum taking at least four examples.
    (*b*) Name some important solvents, used in *nmr* spectroscopy. What are the important characteristics of the solvents used in this technique?
    (*c*) Why is TMS used as a standard reference?

19. Write a detailed note on spin-spin coupling.

20. What do you mean by Proton exchange reactions? How does spin decoupling occurs in certain groups?

21. Describe the probable values of the chemical shifts and the relative intensities for the following molecules taking TMS as the reference:(*i*) Mesitylene (*ii*) 3 methoxy–4 pentyne–2 one (*iii*) Methyl tert butyl ether (*iv*) N, N-dimethyl acetamide (*v*) Diethyl Succinate (*vi*) Vanillin (*vii*) Dibromo ethyl acetate (*viii*) 2-phenyl ethanol.

22. (*a*) Describe clearly what do you know about coupling constant?
    (*b*) How will you distinguish between Cis and Trans isomers with the help of *nmr* spectroscopy?

23. Describe some important applications of nuclear magnetic resonance.

24. (*a*) A compound with molecular formula $C_{12}H_{14}O_4$ gives the following signals in the *nmr* spectrum:
    (*i*) Unsymmetrical multiplet = 2.6τ (7.1 squares)
    (*ii*) Quartet = 5.6τ (7.2 squares)
    (*iii*) Triplet = 8.5τ (10.8 squares)
    (*b*) Describe how does inductive effect shift the normal position of a proton.

25. (*a*) What do you mean by diamagnetic and paramagnetic effects in *nmr* spectroscopy? Explain with suitable examples.
    (*b*) Write short notes on:
    (*i*) Spin-spin coupling
    (*ii*) Areas of the various signals
    (*iii*) Deshielding due to hydrogen bonding

26. What do you understand by terms, 'double resonance' and 'spin tickling'? How are these helpful in simplifying the spectra?

27. Write notes on:
    (*i*) Nuclear overhauser effect.
    (*ii*) Deuterium exchange reactions

28. Briefly describe C^{13} *nmr* spectroscopy. What are the extra advantages of it over proton magnetic resonance spectroscopy?

MULTIPLE CHOICE QUESTIONS

Choose the Correct answer:

1. How many NMR signals are formed for 2-chloro propene.
   (*a*) 2 (*b*) 3 (*c*) 1 (*d*) none
2. Tell the number of NMR signals in case of 1, 2 dichloropropane.
   (*a*) 2 (*b*) 3 (*c*) 4 (*d*) 5
3. Write the multiplicity of the signals in $CH_3CH_2OCH_2CH_3$ in NMR spectrum
   (*a*) Two triplets (*b*) a triplet and a quartet
   (*c*) two singlets (*d*) Two singlets and two triplets.
4. Write the multiplicity of signals in CH_3CH_2OH in NMR spectroscopy.
   (*a*) singlet, triplet and quartet (*b*) Two triplets and a quinlet.
   (*c*) Three singlets (*d*) None of these.
5. In an organic compound, the proton linked to sp^2 hybridised carbonation is more deshielded than that linked to
   (*a*) sp hybridised carbon (*b*) sp^3 hybridised carbon
   (*c*) Both of these (*d*) None of these.
6. In ethyl benzene ( $\overset{a}{CH_2}-\overset{b}{CH_3}$), the tau value for CH_2 proton will be ______ than those of CH_3 protons.
   (*a*) lower (*b*) higher (*c*) much higher (*d*) not sure
7. Out of the olefinic, aldehydic and aromatic protons, the decreasing deshielding has the order:
   (*a*) olefinic > aldehydic > aromatic (*b*) aldelydic > olefinic > aromatic
   (*c*) aromatic > olefinic > aldehydic (*d*) olefinic > aromatic > aldehydic
8. Which of the following solvents cannot be used in NMR spectroscopy?
   (*a*) CCl_4 (*b*) CS_2 (*c*) $CHCl_3$ (*d*) $(CCl_3)_2C=0$
9. The spin is an integer 1, 2, 3... for a nucleus having
   (*a*) even number of protons and neutrons
   (*b*) odd mass number
   (*c*) even mass number and odd number of protons
10. NMR spectra are observed in ... region
    (*a*) radio frequency (*b*) microwave (*c*) uv/vis (*d*) X-ray
11. Write the number of signals and their multiplicities for the NMR spectrum of the compound, $Cl\,F_2C\text{-}CH_2Cl$.
    (*a*) one, triplet (*b*) two, singlet (*c*) two, triplets (*d*) None of these
12. For two sets of protons for $CH_3\text{-}CH_2\text{-}CO–$, part of an organic compound, the value of J for these two sets will be
    (*a*) different (*b*) same (*c*) may be same or different
13. The signal (s) for a compound like $A–CH_2–CH_2–B$ will be:
    (*a*) two triplets (*b*) two singlets (*c*) one singlet (*d*) one triplet

14. Nuclear overhauser effect helps in predicting the

    (*a*) geometry of the molecule
    (*b*) two different protons in close proximity
    (*c*) protons on adjacent carbon atoms
    (*d*) olefinic protons

15. The pair of compounds which can be distinguished by NMR spectroscopy are:

    (*a*) CH_3CH_2OH and $CH_3O–CH_3$
    (*b*) $CH_3CH_2CH_2OH$ and $CH_3CH(OH)CH_3$
    (*c*) CH_3CH_2CHO and CH_3COCH_3
    (*d*) All of these

16. The NMR spectroscopy is useful for the detection of

    (*a*) hydrogen bonding
    (*b*) aromaticity
    (*c*) geometrical isomers
    (*d*) all of these

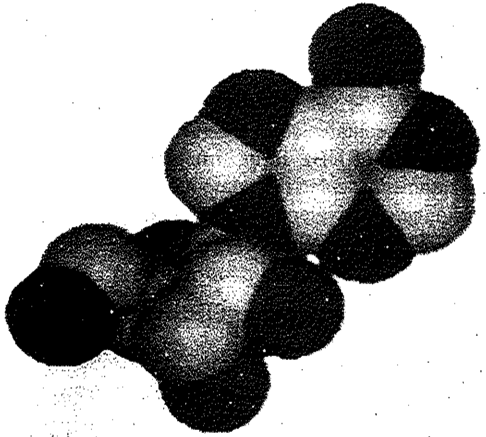
ANSWERS **1.** (*b*) **2.** (*c*) **3.** (*b*) **4.** (*a*) **5.** (*c*) **6.** (*a*) **7.** (*b*) **8.** (*c*) **9.** (*c*) **10.** (*a*) **11.** (*a*) **12.** (*b*) **13.** (*a*) **14.** (*a*, *b*) **15.** (*d*) **16.** (*d*)

CHAPTER

6

Numerical Problems on UV; IR and NMR

6.1 Double Bond and/or Ring Equivalents
6.2 Problem Set with-Solutions



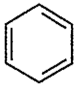
6.1 Double Bond and/or Ring Equivalents

If the molecular formula of the compound is given, then the number of double bonds and/or ring equivalents (DBE) can be easily calculated. The structure of the organic compound determined from the given spectroscopic data can be, thus, confirmed. The number of DBE from various types of compounds with the given molecular formula can be determined as follows:

Type A. If the compound is a hydrocarbon with general formula C_xH_y, then

$$\text{DBE} = x + 1 - \frac{y}{2}$$

Consider a compound with molecular formula, C_6H_6. The number of DBE in it $= 6 + 1 - \frac{6}{2} = 4$. Some possible structures consistent with the given molecular formula are

(*i*)  Three double bonds and one ring.

(*ii*) $CH_2 = CH—C \equiv C—CH = CH_2$. Two double bonds and one triple bond.

Note. A triple bond may be regarded as equivalent to two double bonds. The presence of a triple bond ($C \equiv C$, $C \equiv N$ etc.) can be easily recognised from the infra-red spectroscopic data.

Type B. If the compound contains one or more divalent atoms (sulphur, oxygen etc.) in addition to the elements carbon and hydrogen, then the presence of divalent atom/atoms can be ignored while calculating DBE. Consider an oxygen containing compound, $C_xH_yO_z$. For such a compound.

$$\text{DBE} = x + 1 - \frac{y}{2}$$

EXAMPLE 1. *Find the double bond and/or ring equivalents for the compounds with molecular formulae (i) $C_3H_8O_3$ (ii) $C_6H_6O_2$.*

SOLUTION. (*i*) For the molecular formula $C_3H_8O_3$, the number of DBE

$$= 3 + 1 - \frac{8}{2} = 0$$

(*ii*) The number of DBE for the molecular formula $C_6H_6O_2$

$$= 6 + 1 - \frac{6}{2} = 7 - 3 = 4$$

Type C. If the molecular formula of the compound contains some monovalent elements like halogen (Cl, Br, I etc.), then for calculating the number of DBE in its structural formula, each halogen atom may be considered as a hydrogen atom. Consider the compound with molecular formula $C_xH_yX_z$.[*] The number of double bond and/or ring equivalents (DBE) for such a compound

$$= x + 1 - \frac{y + z}{2}$$

Consider a compound with molecular formula $C_{10}H_7Br$. The number of DBE in the compound is equal to

$$10 + 1 - \frac{7 + 1}{2} = 11 - 4 = 7$$

Type D. If the compound contains nitrogen atom or some trivalent phosphorus atoms, then the number of trivalent atoms are subtracted from the number of hydrogen atoms present in the molecular formula. Consider a compound with general formula, $C_xH_yN_z$. The number of DBE in its structural formula can be calculated as

$$x + 1 - \frac{y - z}{2}$$

EXAMPLE 2. *Calculate the number of double bond and/or ring equivalents in the compounds with molecular formulae (i) $C_{12}H_{12}N_2$ and (ii) $C_6H_8O_3N_2$.*

---

[*] represents halogen atom.

(*i*) For the compound with molecular formula $C_{12}H_{12}N_2$,

$$\text{DBE} = 12 + 1 - \frac{12 - 2}{2} = 13 - 5 = \mathbf{8}$$

(*ii*) The number of DBE present in the structure with molecular formula, $C_6H_8O_3N_2$

$$= 6 + 1 - \frac{8 - 2}{2} = 7 - 3 = 4$$

In case, the phosphorus atom is pentavalent, then corresponding to each phosphorus atom, three hydrogen atoms are subtracted from the number of hydrogen atoms given in the molecular formula for calculating DBE.

Note. The number of nitrogen atoms, if present in an organic compound must be odd,[**] if the molecular weight of that compound is odd.

6.2 PROBLEM SET WITH SOLUTIONS

An organic compound contains 66.6% carbon, 11.1% hydrogen. In UV, it gave a characteristic band at 275 mμ ε_{max}17. In infra-red, bands are formed at 2941–2857 (m), 1715 (s) and 1460 cm^{-1} (m). In NMR, three signals appear at (i) 7.52 τ quartet, (2H), 7.88 singlet, (3H) and 8.93 τ Triplet, (3H). Determine the structural formula of the compound.

The compound contains

$$C = 66.6\%$$
$$H = 11.1\%$$
$$O = 100 - (66.6 + 11.1) = 22.3\%$$

From this data, the empirical formula of the compound is found to be C_4H_8O. This must be the molecular formula since eight hydrogen atoms are shown by NMR spectrum.

(*i*) The absorption at 275 mμ ε_{max} 17 is characteristic of a carbonyl group due to $n \rightarrow \pi^*$ transition (forbidden band).

(*ii*) The absorption at 2941 – 2857 cm^{-1} (*m*) in the IR spectrum is due to C—H stretching, at 1715 cm^{-1} (*s*) is characteristic of saturated ketonic group and that at 1460 cm^{-1} (*m*) may be due to C—H bending.

(*iii*) The NMR spectrum reveals three kinds of protons.

The presence of a triplet at 8.93 τ and a quartet at 7.52 τ is characteristic of $CH_3—CH_2—$ group in the compound. The singlet at 7.88 τ is due to methyl group adjacent to a carbonyl group. Hence, the probable structure of the compound is $\mathbf{CH_3CH_2—CO—CH_3}$. The structure contains one double bond. Also the number of DBE from the molecular formula $C_4H_8O = 4 + 1 - \frac{8}{2} = \mathbf{1}$.

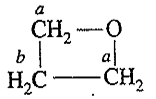
PROBLEM 2. *An organic compound with molecular mass 58 is transparent above 200 nm in its ultra violet spectrum. In infra-red, the absorption bands formed are (i) 2941–2857 cm^{-1} (m) (ii), 1458 cm^{-1} (m) and in NMR spectrum, two signals are formed (i) Triplet 5.25τ (J = 7.1 cps, 29.4 squares) and (ii) quintet 7.25 τ (τ = 7.1 cps, 14.6 squares).*

SOLUTION. The formation of a triplet at 5.25 τ and a quintet at 7.25 τ in the ratio 2 : 1 can be explained if two $—CH_2$ groups form one set and another-CH_2 group form another set of protons. It means that four protons (of $—CH_2—$ groups) are exactly in the same environment while two protons of $—CH_2$ group are in different environment.

Thus, $—CH_2—CH_2—$ and $—CH_2—$ are the parts of the structure. It amounts to 42 mass units. The remaining 16 mass units correspond to an atom of oxygen.

[**] An exception to this rule is the presence of the element with fractional atomic weight in the compound.

Considering the multiplicity of the signals, the structure of the compound is written as

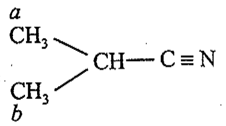


The triplet for '*a*' protons at a low field confirms that oxygen is directly linked to two —CH_2 groups. Oxygen atom causes deshielding of their protons. The same value of coupling constant for the two signals tell that carbon atoms to which protons with different chemical shifts are linked are the adjacent carbon atoms.

In Infra-red spectrum, the signal at 2941-2857 cm^{-1} shows C—H str while that at 1458 cm^{-1} shows C—C str.

PROBLEM 3. *An organic compound with molecular mass 69 is transparent above 200 nm. The absorption bands in Infra-red spectrum are (i) 2941 cm^{-1} (m), (ii) 2273 cm^{-1} (m) and 1460 cm^{-1} (m). In NMR, two signals are formed. One is septet at 7.28 τ (J = 6.7 cps, 4.2 squares) and another is doublet at 8.67τ (J = 6.7 cps and 25.8 square).*

SOLUTION. Two absorption bands-a septet and a doublet with the same values of coupling constant suggest the presence of $(CH_3)_2CH$— as a part of the structure. This amounts to 43 mass units. The remaining 26 mass units corresponds to C≡N group. The presence of —CN group is confirmed by an Infra-red band at 2273 cm^{-1} due to C≡N str. Thus, the structure of the compound under examination should be


$$\overset{a}{CH_3}\diagdown CH—C \equiv N \; / \underset{b}{CH_3}$$

The ratio in the two sets of protons is 1 : 6 which is in accordance with the given data. Also a one proton septet slightly downfield is due to the presence of C≡N group directly linked to it.

The signals at 2941 cm^{-1} (*m*) and at 1460 cm^{-1} (*m*) corresponds to C—H str and C—C str respectively.

PROBLEM 4. *A hydrocarbon containing 85.7% carbon and 14.3% hydrogen is transparent above 210 mμ in ultraviolet spectrum. In its Infra-red, bands are formed at (i) 3022 (m), 1676 (m) and at 965 cm^{-1} (s).*

Two signals appear in its NMR spectrum (i) 8.40 τ doublet and (ii) 4.45 τ quartet in the integral area ratio as 3 : 1 respectively. Determine the structural formula of the compound.

SOLUTION. The compound contains

C = 85.7%

H = 14.3%

From this, the empirical formula of the compound is found to be C_4H_8.

(*i*) Since the ultraviolet spectrum is transparent above 210 mμ, it shows the absence of conjugation and carbonyl group.

(*ii*) In IR, absorption at 3022 cm^{-1} (*m*) show C—H str in aromatic compound or in =C—H type of compound. Since carbonyl group is absent, the band at 1676 cm^{-1} (*m*) may be due to C=C stretching. Thus, the hydrocarbon must be unsaturated.

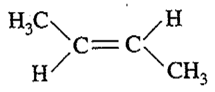
(*iii*) In NMR, two signals are formed. The doublet 8.40 τ must be a methyl group attached with —CH=.

The second signal due to one proton quartet appears downfield at 4.45 τ. It must be due to deshielding by the presence of the double bond. This amounts to

CH_3—CH=

The molecular formula is exactly the double of it. Hence, the probable structure of the compound is CH_3—CH = CH—CH_3.

In infra-red spectrum, a band at 965 cm^{-1} is characteristic of an alkene in which hydrogen atoms are trans. Thus, the exact structure of the compound is:



Trans-Butene-2

PROBLEM 5. *A compound with molecular mass 71 is transparent in the ultraviolet spectrum. In Infra-red, medium bands are formed at (i) 2941–2857 cm^{-1}, 2247 cm^{-1} and at 1460 cm^{-1}. Two singlets are formed at (i) 5.78 τ (16.8 squares) and (ii) 6.51τ (23.9 squares).*

SOLUTION. Two sets of protons are in the ratio 2 : 3. Thus, CH_3 — and —CH_2— may be the parts of the structure. The carbon atom carrying these two sets of protons cannot be directly linked otherwise the splitting of signals into multiplets would result.

An absorption band at 2247 cm^{-1} should be due to C ≡ N str which is also in accordance with the odd molecular mass of the compound. Thus, the units; CH_2, CH_3 and C ≡ N amount to 55 mass units. The remaining 16 mass units correspond to an atom of oxygen.

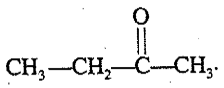
Thus, the probable structure of the compound under examination is CH_3O—CH_2—C ≡ N.

This structure is in accordance with the given data as the two proton singlet appears slightly downfield being surrounded by oxygen and cyanide group on either side. The absorption band at 2941, 2857 and at 1460 cm^{-1} corresponds to C—H str and C—C str respectively.

PROBLEM 6. *An organic compound with molecular mass 72 absorbs at 274 nm ε_{max} 17. In infra-red, a strong absorption band is formed at 1715 cm^{-1} and medium absorption bands are formed at 2941–2857 cm^{-1} (m) and at 1460 cm^{-1} (m). The signals in the nuclear magnetic resonance spectrum are (i) 7.52 τ quartet (J =7.3 cps, 12 squares) 7.88 τ singlet (17.6 squares) and 8.93 τ (Triplet) (J= 7.3 cps, 18.2 squares).*

SOLUTION. In the NMR spectrum, a quartet and a triplet with the same value of coupling constant and having proton ratio 2 : 3 suggests CH_3—CH_2— as a part of the structure. The three sets of protons are in the ratio 2 : 3 : 3. A three proton singlet may be due to CH_3—group. This amounts to 44 mass units. The remaining 28 mass units correspond to carbonyl group $\left(>C=O\right)$.

The presence of carbonyl group is confirmed by the formation of a strong absorption band at 1715 cm^{-1} due to C = O str. It is further confirmed from ultraviolet spectrum which shows a band at 274 nm with low extinction coefficient. It is the result of $n \rightarrow \pi^*$ transition. The absorption bands at 2941 – 2857 cm^{-1} and 1460 cm^{-1} are due to C—H str and C—C str. Thus, the structure consistent with the given data can be written as


$$CH_3—CH_2—\overset{\overset{\large O}{\|}}{C}—CH_3.$$

PROBLEM 7. *A compound with molecular weight 116 gave the following spectral information:*

(*i*) *UV : 283 mμ ε_{max} 22.*

(*ii*) *IR : 3000 — 2500 (b), 1715 (s), 1342 cm^{-1} (w).*

(*iii*) *NMR : 7.88 τ Singlet (3H), 7.40 τ Triplet (2H), 7.75 τ Triplet (2H) and — 1.1 τ singlet (1 H).*

Find the structural formula of the compound.

SOLUTION. In the ultraviolet spectrum, the absorption at 283 mμ of low intensity indicates the presence of carbonyl group.

The presence of carbonyl group is further confirmed by a strong band at 1715 cm^{-1}. A very broad band at 3000–2500 cm^{-1} is most characteristic of acids (O—H stretching) and it appears as a result of strong hydrogen bonding.

The presence of an acid group (—COOH) is also shown by NMR which gives a signal (singlet) at the negative tau value. Thus, the compound under investigation contains

(*i*) —CO— group and

(*ii*) —COOH group

Further two triplets result at 7.4τ and 7.75τ having the same integral area. It must be due to —CH$_2$—CH$_2$—, clearly, two methylene groups must be under different environments and thus, couple to give rise to two triplets. The appearance of a three proton singlet at 7.88τ must be a methyl group attached with the carbonyl group. Hence, the compound under investigation is

$$\underset{\substack{\text{Singlet}\\(7.88\ \tau)}}{CH_3}—CO—\underset{\substack{\text{Triplet}\\(7.75\ \tau)}}{CH_2}—\underset{\substack{\text{Triplet}\\(7.40\ \tau)}}{CH_2}—\underset{\substack{\text{Singlet}\\(—1.1\ \tau)}}{COOH}$$

PROBLEM 8. *An organic compound with molecular mass 88 absorbs at 206* nm ε_{max} *50. In infra-red medium absorption bands formed are (i) 3049-2924 and (ii) 1445 cm^{-1}. Also strong absorption band is formed at 1736 cm^{-1} (s). Following signals are formed in its NMR spectrum.*

(i) 1.93τ singlet (5.9 squares), (ii) 5.88τ triplet (J = 7.0 cps, 12.2 squares), (iii) 8.33τ sextet (J = 7.0 cps, 11.6 squares) and 9.05τ triplet (J = 7.0 cps, 18.6 squares).

SOLUTION. The sets of protons with different chemical shift are in the ratio 1 : 2 : 2 : 3. The formation of a triplet, a sextet and a triplet with the same value of coupling constant (J = 7.0 cps) show that CH$_3$—CH$_2$—CH$_2$ as a part of the structure. A one proton singlet at very low field suggests as CH—also as a part of the structure. This amounts to 56 mass units. The remaining 32 mass units shows the presence of two oxygen atoms. The formation of a strong absorption band at 1736 cm^{-1} shows the presence of an ester. The medium bands at 3049–2924 cm^{-1} and 1445 cm^{-1} are due to C—H str and C—C str or C—O str respectively. Thus, the most probable structure of the compound is $H—\underset{\underset{O}{\|}}{C}—O—CH_2—CH_2—CH_3$ (*n*-Propyl formate). It cannot be $CH_3—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—O—H$, because in such a case C═O str for acid would appear at 1720 cm^{-1} or below.

An absorption band at 206 nm ε_{max} 50 does not give any definite information.

PROBLEM 9. *A compound with molecular mass 104 is transparent below 210 nm. In the infra-red spectrum, the medium bands formed are (i) 3125-2857and 1449 cm^{-1} (s). A strong band is formed at 1718 cm^{-1} and also weak bands result at 2695 cm^{-1} and 2625 cm^{-1}. In the NMR spectrum following signals are observed.*

(i) – 0.95τ singlet (5.4 squares), 5.87τ singlet (11.2 squares), 6.34τ quartet (J = 7.1 cps, 10.6 square) and 8.73τ triplet (J = 7.1 cps, 16.2 squares).

SOLUTION. In the compound under examination, the sets of protons with different chemical shifts are in the ratio 1 : 2 : 2 : 3. A quartet and a triplet with the same value of coupling constant (J = 7.1 cps) shows CH$_3$—CH$_2$ as a part of the structure. A two proton singlet means a —CH$_2$— group. A singlet with the negative τ value (at — 0.95τ) may be due to —COOH group. It amounts to 88 mass units. The remaining 16 mass units correspond to an oxygen atom. Thus, most likely structure consistent with the given data is a $\overset{a}{CH_3}—\overset{b}{CH_2}—O—\overset{c}{CH_2}—COO\overset{d}{H}$.

In the structure, '*c*' set of protons appears downfield being surrounded by oxygen atom and carboxyl group compared to '*b*' set of protons.

The bands at 2695 cm^{-1} and 2625 cm^{-1} do not give any definite information.

PROBLEM 10. *A pale yellow compound is slightly acidic in nature and gave the following data:*

(*i*) *UV : 280 mμ ε_{max} 6600*

(*ii*) *IR : 3460 (v, sh), 3035 (m), 1608 (m), 1585 (m), 1510 (s) 1360 (s), 1320 (s) 740 cm^{-1} (v, s). The band at 3460 cm^{-1} does not shift even on diluting the sample.*

(*iii*) *NMR : – 2.1 τ (singlet) 1 H and unsymmetrical pattern 2.61—2.75 τ (4 H).*

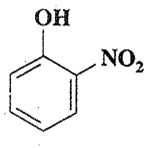
SOLUTION. The band at 280 mμ ε_{max} 6600 indicates the presence of conjugation or some benzenoid compound. The benzene ring may carry some groups which cause bathochromic and hyperchromic shifts.

In infra-red, the band at 3035 cm^{-1} (*m*) is due to C—H stretching of aromatics or ═C—H group. The band at 3460 cm^{-1} (*v*, *sh*) may be due to N—H stretching of amines or O—H stretching which exhibit hydrogen bonding. Since the position of the band is not concentration dependent, the type of hydrogen bonding must be intramolecular.

A one proton singlet at – 2.1τ which is the result of intramolecular hydrogen bonding, probably speaks of the presence of O—H group. An unsymmetrical pattern at 2.61–2.75τ indicates clearly an aromatic ring.

At the moment – OH group and the aromatic ring are detected. Now we are to search for the group which causes intramolecular hydrogen bonding. Benzene is disubstituted as the aromatic signal is a four proton unsymmetrical pattern.

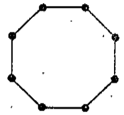
In the IR data, we see two sharp peaks at 1510 cm^{-1} and 1360 cm^{-1} which are most characteristic of the nitro group. The nitro group must be in the ortho position (to cause intramolecular hydrogen bonding) which is supported by a band at 740 cm^{-1} (characteristic of ortho disubstituted benzene). The presence of nitro group also lends pale yellow colour to the compound. Thus, the structure of the compound is:



ortho nitrophenol

PROBLEM 11. *A compound with molecular mass 112 is transparent in the ultraviolet spectrum. In the infra-red spectrum, it shows two bands 2941 cm^{-1} (m) and 1464 cm^{-1} (m). In the NMR, it forms a singlet at 8.48τ.*

SOLUTION. The formation of a singlet at a high field in the NMR spectrum shows that the compound is a cycloalkane. The cycloalkane with molecular mass 112 appears to be cyclo-octane. The absorption band at 2941 cm^{-1} is due to C—H str and that at 1464 cm^{-1} is due to C—C str.



PROBLEM 12. *Molecular formula : C$_3$H$_7$NO*

(*a*) *UV : 238 mμ ε_{max} 10500*

(*b*) *IR : 3428 (m), 2941 – 2857 (w), 1681 (s) and 1452 cm^{-1} (w).*

(*c*) *NMR : (i) 1.87τ singlet (1 H), (ii) 7.30τ singlet (3 H) and 8.1τ singlet (3 H).*

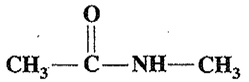
SOLUTION. In UV spectrum, the absorption at 238 mμ ε_{max} 10,500 is characteristic of conjugation.

The infra-red absorption band at 2941 – 2857 cm^{-1} (*w*) is due to C—H stretching. The band at 3428 cm^{-1} (*m*) shows N—H stretching and that at 1681 cm^{-1} (*s*) is a result of C═O stretching which is in conjugation with the lone pair of electrons on nitrogen atom.

NMR spectrum shows three signals. The three proton singlet at 8.1τ shows CH_3 group adjacent to the nitrogen atom. Another three proton singlet at 7.30τ shows a methyl group.

The third signal which is a one proton singlet must be $-\ddot{N}H-$.

From this the structure of the compound can be written as:



$$CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_3$$

The absorption of proton attached with the nitrogen atom is a singlet and appears at 1.87τ. The downfield shift can be explained by the fact that the above structure exists in the following resonating structures:

I II

In structure II, the nitrogen atom acquires a little positive character which causes much deshielding and shifts the N—H absorption downfield.

PROBLEM 13. *Molecular weight = 100*

UV : λ_{max} 274 mμ ε_{max} 2050

IR : 3031 (v), 2941 (w), 1725 (s), 1608, 1504 (w), 1060 (s) and 830 cm^{-1} (s).

NMR : (i) Singlet 7.65τ (3H), (ii) Singlet 6.18τ (3H),

Unsymmetrical pattern 2.15 – 2.8τ (4H)

SOLUTION. In the ultraviolet spectrum, the absorption at 274 mμ ε_{max} 2050 may be due to conjugation, acid, ester or aromatic ring substituted with group which cause bathochromic shift.

In infra-red, the band at 3031 cm^{-1} is due to =C—H stretching or the C—H stretching from an aromatic ring while that at 2941 cm^{-1} (*w*) is the result of C—H stretching from an alkyl group. The band at 1725 cm^{-1} (*s*) is probably due to C=O stretching. The presence of ester is indicated by C—O stretching at 1060 cm^{-1} (*s*). Bands at 1608 cm^{-1} are characteristic of an aromatic ring and are the result of C==C stretching.

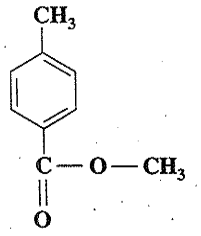
The presence of aromatic ring is also supported by unsymmetrical pattern at 2.15–2.8τ in the *nmr* spectrum. The two signals each as three proton singlet at 7.65τ and an 6.18τ mean two methyl groups. Thus, the compound under investigation consists of:

(*i*) methyl group ($-CH_3$),

(*ii*) Ester group ($-\overset{\overset{O}{\|}}{C}-O-CH_3$) and

(*iii*) the benzene ring.

The four proton unsymmetrical pattern further reveals that the ring is disubstituted. A strong band at 830 cm^{-1} is characteristic of a para-disubstituted benzene ring. Thus, the structure of the compound is:



PROBLEM 14. *An organic compound with molecular weight 108 is not acidic in nature but can be easily oxidised to a crystalline compound (mpt. 122°C). It gives the following spectral data:*

UV : λ_{max} 255 mμ ε_{max} 202

IR : 3402 (s, b) 3065 (w), 2288 (m), 1499 (w, sh) and 1455 cm^{-1} (m).

NMR : 2.74τ (singlet 24.5 squares), 5.4τ (singlet, 9.5 squares) and 6.10τ (singlet, 4.8 squares).

SOLUTION. The ultraviolet absorption at λ_{max} 255 and ε_{max} 202 tells the presence of aromatic ring in the compound.

The formation of a strong and broad band at 3402 cm^{-1} indicates N—H or O—H stretching. Since, the band is broad, it is more likely to be hydrogen bonded O—H group. The medium peak at 3065 cm^{-1} is due to C—H stretching from an aromatic ring while that at 2888 cm^{-1} (*m*) indicates C—H stretching from methyl or methylene group. The two more peaks at 1499 (*w, sh*) and 1455 cm^{-1} are characteristic of an aromatic ring.

From the NMR data, we see three types of protons. All these protons are singlets and are in the ratio 1 : 2 : 5. If hydroxyl group is present, then one oxygen atom and eight hydrogen atoms (1 + 2 + 5) amounts to 24 mass units. The remainder (108 – 24 = 84) mass units corresponds to seven carbon atoms. Thus, the molecular formula of the compound is C_7H_8O.

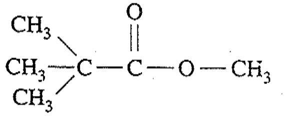
The five proton singlet suggests monosubstituted benzene ($-C_6H_5$). Incorporating OH group, we are left with $-CH_2-$ to get the above molecular formula.

Thus, the structure of the compound is $C_6H_5CH_2OH$.

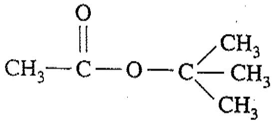
The structure is strictly in accordance with the given data. This compound can be easily oxidised to benzoic acid which melts at 122°C.

PROBLEM 15. *An organic compound with molecular mass 116 is transparent below 210 nm. In the infra-red spectrum, absorption bands are formed at 2924 cm^{-1} (m), 1745 cm^{-1} (s) and 1456 cm^{-1} (m). In the NMR spectrum, two singlets are formed at 8.03τ and 8.55τ having ratio 1 : 3.*

SOLUTION. The two signals in the NMR spectrum are two singlets in the proton ratio 1 : 3. It is possible only if CH_3- and $-C(CH_3)_3$ are the parts of the structure. A strong band at 1745 cm^{-1} (*s*) in the infra-red spectrum is due to C=O str in an ester. Thus, the probable structure of the compound may be:



I



II

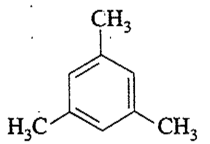
The structure I appears more consistent with the given data as the signal due to CH_3- is slightly downfield, being directly linked with electronegative oxygen atom. The infra-red bands at 2924 cm^{-1} (*m*) and 1456 cm^{-1} (*m*) are due to C—H str and C—C str. Esters are transparent down 210 nm which is consistent with the given data.

PROBLEM 16. *An organic compound with molecular mass 120 absorbs in ultraviolet spectrum at 268 nm ε_{max} 480. In infra-red spectrum, medium absorption bands are formed at (i) 3067–2907 cm^{-1} (ii) 1608 cm^{-1} (m) and 1473 cm^{-1} (m). The NMR spectrum shows absorptions as below:*

(*i*) 3.21τ singlet (10.4 squares) and (*ii*) 7.74τ singlet (31.0 squares).

SOLUTION. Two singlets in the NMR spectrum are formed in the proton ratio 1 : 3.

A singlet at 3.21τ appears to be due to an aromatic ring. Clearly, the aromatic ring should be trisubstituted with three nuclear protons. Thus, the proton ratio should be 3 : 9. The nine proton singlet corresponds to three CH_3— groups. Thus, the most probable structure of the compound under examination should be


1, 3, 5-trimethyl benzene

The set of nine equivalent protons (three methyl groups) forms a singlet which appears upfield. The infra-red band at 1608 cm^{-1} corresponds to C=C str due to aromatic ring. A band at 3067–2907 cm^{-1} is due to C—H str due to ring. An ultraviolet band at 268 nm ε_{max} 480 is also due to π–π* transition due to aromatic ring.

PROBLEM 17. *A volatile compound with molecular mass 130 contains 73.85% carbon and 13.85% hydrogen. The compound is transparent above 210 mμ in ultraviolet region. In its infra-red region, bands are formed at 2960–2851 (m), 1342 (w) and 1075 cm^{-1} (s) Only one singlet at 8.95τ is formed in its nmr spectrum. Find the structural formula of the compound.*

SOLUTION. The compound contains

$$C = 73.84\%$$
$$H = 13.85\%$$
$$O = 100 - (73.85 + 13.85) = 12.31$$

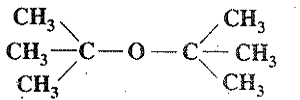
From this data, the empirical formula of the compound is $C_8H_{18}O$.

Since the compound is transparent above 210 mμ in the ultraviolet region, it shows the absence of carbonyl group, conjugation etc.

In the infra-red spectrum, there is a most characteristic band at 1075 cm^{-1} (s) for an ether (C—O stretching) in C—O—C group.

The other bands at 2960—2851 (*m*) and at 1342 cm^{-1} (*w*) are for C—H stretching and C—H bending vibrations respectively.

The appearance of only one singlet at the high field (8.95τ) reveals that all the alkyl groups in the compound are in exactly similar environments. It is only possible if the structure of the compound is



This structure is strictly in accordance with the given data.

PROBLEM 18. *A compound with molecular formula $C_9H_5NO_4$ forms the following bands in its infra-red spectrum.*

3000–2500 (b), 2225 (m), 1715 (s), 1605, 1518 (s), 1344 (s) and 900–700 cm^{-1} (s).

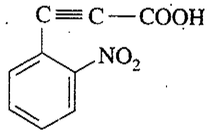
In NMR spectrum, two bands are formed as (i) –1.1τ (singlet, 5.3 squares) and (ii) Unsymmetrical pattern 2.6–2.75τ (21.1 squares). Determine the structural formula of the compound.

SOLUTION. In the infra-red spectrum, the strong band at 1715 cm^{-1} indicates a saturated ketone but the negative tau value in the NMR spectrum reveals the presence of a carboxylic group. Thus, the strong band at 1715 cm^{-1} may be due to the presence of —COOH in conjugation with the double bond, triple bond or the aromatic ring. The presence of —COOH is further confirmed by a broad band at 3000—2500 cm^{-1} which is characteristic of —COOH group.

The symmetrical pattern at 2.6–2.75τ clearly indicates an aromatic ring. Thus, the presence of an aromatic ring and COOH group in the compound is confirmed.

Further a band at 2225 cm^{-1} may be due to C≡N or C≡C group. The bands at 1605, 1575 cm^{-1} may be as a result of C=C stretching from an aromatic ring. The appearance of two strong bands at 1518 and 1344 cm^{-1} indicates clearly the presence of a conjugated nitro group in the compound. Since the compound contains only one nitrogen atom and also nitro group is indicated, the possibility of C≡N group in the compound is ruled out. Thus, the band at 2225 cm^{-1} must be due to C≡C stretching. C≡C must also be in conjugation with —COOH group as a strong band for —COOH group appears at a low wave number [—C ≡ C—COOH].

Another strong band between 900—700 cm^{-1} indicates orthodisubstitution in benzene ring. Hence the most probable formula of the compound with the given molecular formula is:



The total number of DBE in this structure is equal to 8.

Also DBE calculated from the molecular formula

$$= 9 + 1 - \frac{5-1}{2}$$
$$= 10 - 2 = \mathbf{8}$$

PROBLEM 19. *An organic compound with molecular weight 130 shows the following bands in the infra-red spectrum:*

(i) 3082 – 2860 (m), (ii) 1825 (s), (iii) 1755 (m) and 1455 cm^{-1} (m).

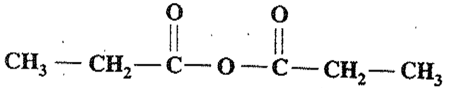
In its NMR spectrum, two signals result (i) Triplet 8.7 τ (7.3 squares, J = 7.1 cps) (ii) quartet 7.8 τ (4.9 squares, J = 7.1 cps).

SOLUTION. In the infra-red spectrum, we see two bands at 1825 cm^{-1} (s) and 1755 cm^{-1}(m). Out of these one is strong and the other is less intense. These two bands are characteristic of acyclic anhydride *i.e.*,

(—CO.O—CO)

The band at 3082 – 2860cm^{-1}(m) indicates C—H stretching.

In the NMR spectrum, a triplet and a quartet are in the ratio 7.3 : 4.9, *i.e.*, 1.5 : 1, or 3 : 2. The three proton triplet at 8.7 τ and a two proton quartet at 7.8τ indicates CH_3—CH_2— as a part of the structure. Clearly, the structure of the compound can be written as:



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

This structure is in accordance with the given data and its molecular weight is 130.

PROBLEM 20. *An organic compound with molecular mass 153 shows ultraviolet absorption at 223 nm ε_{max} 100. In infra-red spectrum, the bands are formed at (i) 3125–2899 cm^{-1} (m), 2688 cm^{-1} (w), 2604 cm^{-1} (w), 1715 cm^{-1} (s) and 1439 cm^{-1} (cm). The following signals are formed in the NMR spectrum.*

(i) – 1.93 τ singlet (7.8 squares), 5.48 τ quartet (J = 7.2 cps 7.4 squares) and 8.17 τ doublet (J = 7.2 cps, 22.4 squares).

SOLUTION. In the NMR spectrum, it is observed that the three signals are formed in the proton ratio 1 : 1 : 3. A quartet and a doublet with the same value of coupling constant shows CH_3—CH— as a part of the structure. A singlet at —1.93 t shows —COOH group in addition. This amounts to 73 mass units. The remaining 80 mass units correspond to Br atom. With this information, the most probable structure of the compound is CH_3—CH(Br) COOH. An infra-red band at 1715

cm^{-1} (s) is due to C = O str of —COOH group. A band at 3125–2899 cm^{-1} is due to C–H str and that at 1439 cm^{-1} is due to C—C str. The ultraviolet absorption band at 223 nm ε_{max} does not give any authentic information.

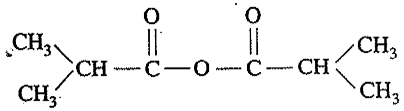
PROBLEM 21. *A compound with molecular mass 158 absorbs in the ultraviolet region at 225 nm ε_{max} 50 (hexane). In infra-red spectrum, absorption bands are formed at 3077-2857 cm^{-1} (m), 1828 cm^{-1} (s), 1757 cm^{-1} (m) and 1457 cm^{-1} (m).*

In NMR, two signals are observed (i) 7.30 τ septet (J = 6.7 cps, 6.4 squares) and (ii) 8.80τ doublet (J = 6.7 cps, 37.2 squares).

SOLUTION. In the NMR spectrum, a septet and a doublet with the same value of coupling constant shows $(CH_3)_2CH$— as a part of the structure.

In the infra-red spectrum, a strong band at 1828 cm^{-1} and a medium band at 1757 cm^{-1} shows the presence of anhydride $—\overset{\overset{O}{\|}}{C}—O—\overset{\overset{O}{\|}}{C}—$.

Thus, $(CH_3)_2CH$— and —CO—O—CO— amounts to 115 mass units. The remaining 43 mass units may also be the isopropyl group. Hence, the most probable structure of the compound is:



$$(CH_3)_2CH—\overset{\overset{O}{\|}}{C}—O—\overset{\overset{O}{\|}}{C}—CH(CH_3)_2$$

A band at 3077— 2857 cm^{-1} is due to C—H str and that at 1456 cm^{-1} is due to C—C str. An absorption band at 225 nm ε_{max} 50 does not give any authentic information.

PROBLEM 22. *A compound with molecular weight 130 gave a negative iodoform test. It absorbs at 292 mμ ε_{max} 16 in the ultraviolet spectrum. In its infra-red spectrum, the various bands are (i) 3042 (m), 2941 (w), 2862 (w), 1722 (s), 1605, 1575 (m) and 1462 cm^{-1} (m).*

In the NMR spectrum, three signals are present (i) multiplet, 2.73τ (26.5 squares), (ii) doublet 7.2τ (10.3 squares) and (iii) triplet, 0.22τ (5.2 squares).

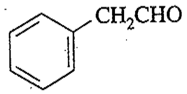
SOLUTION. The ultraviolet absorption at 292 mμ ε_{max} 16 is characteristic of a carbonyl group (an aldehyde or a ketone).

The presence of a carbonyl group is further supported by a strong band at 1722 cm^{-1}. It can only be due to an aldehydic group as there are characteristic C—H stretching absorptions at 2862 cm^{-1} (w) and 2740 cm^{-1} (w) from —CHO group.

The absorption at 3042 cm^{-1} is due to =C—H stretching or C—H stretching from an aromatic ring and that 2941 cm^{-1} is due to C—H stretching from a methyl or methylene group. The absorption bands at 1605 cm^{-1} and 1575 cm^{-1} indicates an aromatic ring C—C str which is further confirmed by a five proton multiplet at 2.73τ in the NMR spectrum.

A triplet due to one proton at a low field (0.22τ) is clearly an —CHO group which is also indicated by infra-red spectrum.

Another two proton doublet at 7.2τ is —CH_2— group attached to the aromatic ring. Hence, the structure of the compound is:



Phenyl acetaldehyde

This compound does not show iodoform test.

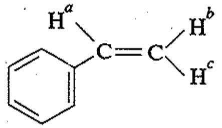
PROBLEM 23. *An organic compound with molecular formula C_7H_8Br yields a primary alcohol on hydroboration. The spectral data of the compound is given below:*

(i) *UV : λ_{max} 282 mμ ε_{max} 450.*
(ii) *IR : 3033 (m), 1646 (m), 1602 (m), 1582 (v), 820 (s) and 710 cm^{-1} (m).*
(iii) *NMR : 2.62—2.74τ (asymmetrical pattern, 18.9 squares), 4.30τ (double doublet, 4.7 squares), 3.30 τ (double doublet, 4.9 squares) and 4.86τ (double doublet, 5.0 squares).*

Determine the structure of the compound.

SOLUTION. The ultraviolet spectrum does not give much information as the band at 282 mμ ε_{max} 450 may be due to conjugation or aromatic ring substituted by the groups causing bathochromic shift.

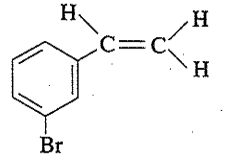
The infra-red band at 3033 cm^{-1} indicates =C—H stretching or C—H stretching from an aromatic ring. The absorption bands at 1602 and 1582 cm^{-1} (v) are characteristic of C = C stretching of an aromatic ring. It is further confirmed by a four proton asymmetrical pattern observed at 2.62—2.74τ in the NMR spectrum. The band at 1646 cm^{-1} (m) is also due to C=C stretching. There are three double doublets formed in the NMR spectrum. It is only possible if there are three protons and each one is in a different environment, Thus, the part of the possible structure is:



Each proton is split by two other protons in different environments. Thus, three double doublets result. Each proton is deshielded by the presence of the double bond and thus, signals appear downfield.

The proton '*a*' is highly deshielded by the ring and is also split by other two protons. For this, the signal appear at 3.30 τ. The proton '*c*' is deshielded more as compared to proton '*b*' due to its relative proximity to the ring. Thus, from the given data, we say that proton '*c*' absorbs as double doublet at 4.30 τ as compared to proton '*b*' which absorbs at 4.86 τ.

The bromine atom must be present in the meta position which is indicated by two bands at 710 cm^{-1} and 820 cm^{-1}. Hence, the structure of the compound constituent with given data is:



PROBLEM 24. *A compound molecular mass 164 absorbs at 220 nm ε_{max} 1800. In infra-red spectrum, absorption bands are formed at 3077 cm^{-1} (w), 2976 cm^{-1}(w), 1745 cm^{-1} (s) 1608 cm^{-1} (m), 1497 cm^{-1} (m) and 1456 cm^{-1} (m).*

In NMR, the signals formed are (i) 2.7 τ singlet (16.5 squares), (ii) 5.70 τ triplet (J = 7.3 cps, 6.2 squares), (iii) 7.07 triplet (J = 7.3 cps, 6.7 squares) and (iv) 7.98 τ singlet (10.2 squares).

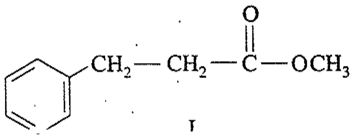
SOLUTION. In NMR, the signals are formed in the proton ratio 2.5 : 1 : 1 : 1.5 or 5 : 2 : 2 : 3.

The formation of two triplets with the same value of coupling constant shows that —CH_2—CH_2— is a part of the structure.

A five proton singlet at 2.71 τ shows the presence of an aromatic ring C_6H_5—.

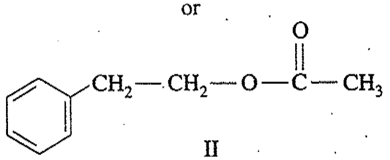
A three proton upfield singlet shows —CH_3 group in the compound. Thus, the units

C_6H_5, —CH_2 — CH_2 — and CH_3— amount to 120 mass units. A strong band at 1745 cm^{-1} in the infra-red spectrum suggests that the compound is an ester. Thus, —COO (of ester) amounts to the remaining 44 mass units of the compound of molecular mass 164. The bands at 1608 cm^{-1} (*m*) and 1497 cm^{-1} (*m*) support the presence of benzene ring. The band at 1456 cm^{-1} (*m*) is due to C—C str. Thus, the probable structure of the compound may be



I

or



II

The structure II looks more probable because three proton singlet is relatively less deshielded.

PROBLEM 25. *An organic compound with molecular mass 160 absorbs at 212 nm* ε_{max} *60 in the ultraviolet spectrum.*

In infra-red, the bands are formed at (i) 2941–2857 (m), (ii) 1742 (s), (iii) 1460 (m), (iv) 1056 (s) and (v) 1260 cm^{-1} *(s). In the NMR spectrum, three signals are observed.*

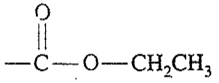
(i) Singlet 7.5 τ (5.3 squares), (ii) triplet 8.71 τ (16.5 squares, J = 7.2 cps) and (iii) quartet 5.84 τ (10.8 squares, J = 7.2 cps).

SOLUTION. The absorption at 212 mμ ε_{max} 60 in the ultraviolet region indicates an acid or ester.

The presence of aromatic ring is ruled out since there is no such characteristic band in the infra-red as well as in the NMR spectrum.

A strong band at 1742 cm^{-1} is characteristic of C=O stretching in an ester. The presence of ester is supported by two strong bands due to C—O stretching at 1056 cm^{-1} and at 1260 cm^{-1}. The band at 2941–2857 cm^{-1} (*m*) is due to C-H stretching in methyl or methylene group.

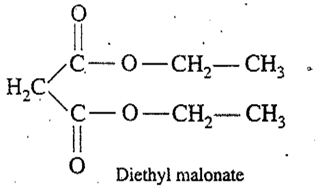
The three proton triplet and a two proton quartet at 8.71 τ and 5.84τ respectively with exactly the same value of J (coupling constant) indicates CH_3CH_2— group in the compound. A part of the structure can, thus, be written as:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3$$

This amounts to 73 mass units. If we double it, then subtracting 146 mass units from the molecular weight 160, the remainder 14 mass units corresponds to —CH_2—. For —CH_2— group, the signal appears as a singlet at 7.5 τ.

Hence, the probable structure of the compound is



Diethyl malonate

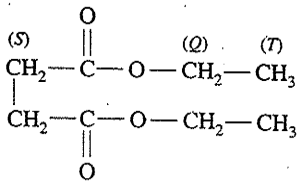
The structure is strictly in accordance with the given data and the molecular weight.

PROBLEM 26. *An organic compound with molecular mass 174 shows absorption in ultraviolet region at 213 nm* ε_{max} *60. In infra-red, absorption bands are formed at 2941 – 2857* cm^{-1} *(m), 1745* cm^{-1} *(s) and 1458* cm^{-1} *(m).*

In NMR, the signals observed are (i) 5.86 τ quartet (J = 7.2 cps 10.4 squares), (ii) 7.40 τ singlet (10.8 squares) and (iii) 8.73 τ triplet (J = 7.2 cps, 16.0 squares).

SOLUTION. In the NMR, the signals are formed in the proton ratio 2:2:3. The formation of a quartet and a triplet with the same value of coupling constant suggests that CH_3—CH_2— is a part of the structure. Also a two proton singlet is formed. It may be due to —CH_2— group in the structure.

In infra-red spectrum, the formation of a strong band at 1745 cm^{-1} shows the presence of an ester. Thus, —COO is a part of the structure. Thus, CH_3CH_2—, —CH_2— and —COO units amount to 87 mass units. The molecular mass 174 is just double of it. Thus, the probable structure of the compound is:



A low field triplet indicates that its carbon is directly linked with oxygen atom.

An absorption band at 2941–2857 cm^{-1} indicates C—H str in infra-red and that at 1458 cm^{-1} indicates C—C str.

PROBLEM 27. *An organic base with molecular formula* $C_{14}H_{19}N$ *shows the following spectral data:*

UV : (i) 222 nm ε_{max} *20,400*
(ii) 210 nm ε_{max} *20,000*
IR : 3022 (m), 1600 (m), 1510 (m), 1680 (w), 750 and 695 cm^{-1} *(m).*
NMR : (i) Singlet 7.15τ (3H), (ii) singlet 8.5 τ (3H), (iii) complicated 8.0 τ (4H), (iv) complicated 8.35τ (4H); multiplet; 3.45τ (3H) and multiplet 2.95 τ (2H).

Determine the structural formula of the compound.

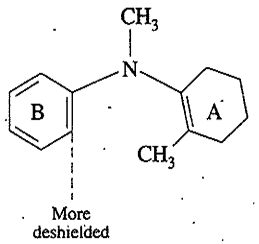
SOLUTION. From the absorptions in the ultraviolet spectrum, nothing can be said with certainty.

The infra-red absorption at 3022 cm^{-1} indicates =C—H stretching or C—H stretching from an aromatic ring. The appearance of bands at 1600 (m), 1510 cm^{-1} (*m*) indicates the presence of an aromatic ring. Further the bands at 750 and 695 cm^{-1} (*m*) shows that the aromatic ring must be substituted. The weak band at 1680 cm^{-1} is characteristic of C=C stretching. The presence of the aromatic ring is further confirmed by multiplets in the region 2.95 – 3.45 τ. The two proton multiplet at 2.95 τ must be due to two ortho positions with respect to the N-substituted group on the ring. The remaining three protons show another slightly less deshielded multiplet at 3.45 τ.

The two signals each of three proton singlet at 7.15 τ and at 8.5τ indicate two methyl groups. The singlet at 7.15 τ is slightly deshielded being attached with nitrogen which in turn is attached with the aromatic ring.

The remaining two signals (complicated) corresponding to eight protons in almost similar environments indicate four methylene groups in ring A. The four proton signal at 8.0τ corresponds to two methylene groups which are attached with the carbon atoms carrying a double bond.

From this entire discussion, the structural formula of the compound under investigation is probably.



This structure corresponds to the molecular formula $C_{14}H_{19}N$. The double bond equivalents corresponding to this structure can be calculated as:

$$14 + 1 - \frac{19-1}{2} = 15 - 9 = 6$$

From this structure also, the number of ring and double bond equivalents can be noted as equal to six. Hence the above structure is correct.

PROBLEM 28. *An organic compound with molecular formula C_4H_9NO gives the following spectral data:*

UV : λ_{max} *220 mμ* ε_{max} *63.*

IR : *3500 (m), 3402 (m), 2960 (w), 1682 (s), 1610 (s).*

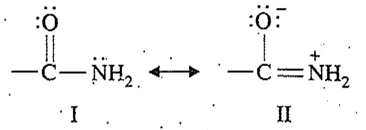
NMR : *9.0 τ doublet (23.2 squares) ; 7.9 τ Septet (3.8 squares);*

1.92τ Singlet (7.5 squares). Determine the structural formula of the compound.

SOLUTION. From the absorption at 220 mμ ε_{max} 60 in the ultraviolet region, nothing can be said with certainty. The presence of a primary amide is indicated by two bands at 3500 and 3402 cm^{-1}. These two bands are the result of N—H stretching. A strong band at 1682 cm^{-1} also indicates the presence of an amide group. The band at 2960 cm^{-1} is due to C—H stretching and that at 1610 cm^{-1} (*s*) is due to N—H bending. From this much data, we say that — $CONH_2$ is a part of the structure.

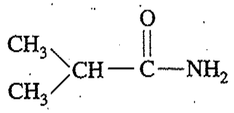
The NMR spectrum is most informative. The doublet at 9.0 τ and a septet at 7.9 τ in the ratio 6 : 1 indicates clearly an isopropyl group *i.e.*, $(CH_3)_2$ CH— group.

Another two proton singlet appears at a very low field due to much deshielding. This signal is due to two protons of the primary amide group. The appearance of this signal at a very low field may be explained by writing the resonating structure of amide as:



The double bond character between C and N and also the positive charge developed on nitrogen atom in structure II cause greater deshielding of protons attached with nitrogen atom and hence, signal appears at 1.92 τ.

Thus, the structure of the compound is



$$(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-NH_2$$

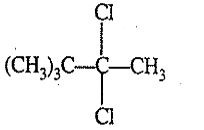
From the given molecular formula (C_4H_9NO), the number of ring and double bond equivalents are calculated as:

$$4 + 1 - \frac{9-1}{2} = 5 - 4 = 1$$

This is in accordance with the structure which is determined.

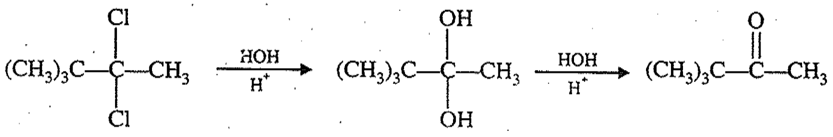
PROBLEM 29. *A compound 'A' shows two signals around τ 8.8 and τ 6.0 (relative intensity 3 : 1) in the NMR spectrum. On treatment with acid, it gives a new compound 'B' which also shows two singlets around τ 9.0 and τ 8.0 (relative intensity 3 : 1). In IR spectra of A and B, strong absorption in 1700 cm^{-1} region is observed in case of 'B'. Assign structures for 'A' and 'B' giving your reasons in detail.*

SOLUTION. Compound A. The presence of two singlets (upfield) in the ratio 3 : 1 shows methyl groups. These may be probably tert-butyl [$(CH_3)_3C$– group] and methyl (—CH_3) groups. The compound is not aromatic as the protons in it are fairly shielded. Compound A on hydrolysis gives a compound 'B' in which the intensity ratio of the protons remain the same. But compound B shows an absorption at 1700 cm^{-1} which is clearly due to carbonyl (ketonic group). Thus, the probable structure of the compound 'A' appears to be :



$$(CH_3)_3C-\underset{Cl}{\overset{Cl}{C}}-CH_3$$

The compound 'A' an hydrolysis (treatment with acid) forms ketone as below :



(A)
(Intensity ratio 3 : 1)

(Intensity ratio 3 : 1)

PROBLEM 30. *An organic compound A (molecular formula : $C_9H_{10}O_2$) exhibits the following spectral data :*

IR : *1745 cm^{-1} (s), 1225 cm^{-1} (br, s), 749 cm^{-1} (s); 697 cm^{-1}(s)*

UV : λ_{max} *at 268 nm, 264 nm, 262 nm, 257 nm*

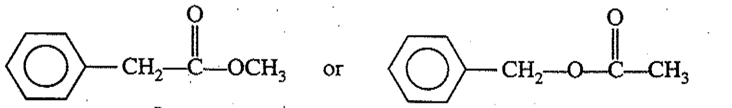
$^1H_{NMR}$: *δ 1.96 (3H, singlet); 5.00 (2H, singlet) ; 7.22(5H, singlet)*

Deduce the structure of the compound A.

SOLUTION. In PMR, three signals are formed with three equivalent sets of protons, *viz.*, 3H, 2H and 5H.

A three proton singlet upfield is due to CH_3 group which may be linked to oxygen atom. Also a two proton singlet relative downfield is due to CH_2 directly attached to benzene.

A little deshielding is due to the fact that it is directly linked to the benzene ring. For the aromatic ring, a highly deshielded 5H singlet appears at 7.22 δ. Subtracting C_6H_5, CH_2 and CH_3 units from the molecular formula, COO is left. The compound appears to be an ester and its probable structural formulae can be written as :



I

II

---

* In IR, a strong band at 1745 cm^{-1} is most characteristic of an ester.

Structure (*ii*) appears more likely, as a two proton singlet (CH_2) is more deshielded being linked with electronegative oxygen and also directly attached to the benzene ring.

Also a broad band at 1225 cm^{-1} is due to C—O bending in esters. λ_{max} in UV 268 nm confirms substituted benzene ring. The benzene ring is monosubstituted as is clear from a band at 749 cm^{-1} in Infra-red.

PROBLEM SET I (UNSOLVED)

1. An organic compound with molecular weight 54 is transparent to ultraviolet spectrum above 200 nm. In the infra-red, it forms bands at 3290 (*w*), 2128 (*w*) and 620 cm^{-1} (*s*). In its NMR spectrum, three signals are observed (*i*) Singlet 7.6 (5.2 squares), quartet 8.5 (J = 7.1 cps, 9.9 squares), (*iii*) triplet 8.8 τ (J = 7.1 cps, 16.1 squares). Determine the structure of the compound.

2. An organic compound with molecular formula C_3H_6O absorbs at 176 nm ε_{max} 15000. In the infra-red, bands are obtained at 2.84 (*s*) 7.81 (*s*) and at 6.06 µ* (*m*).

   In NMR spectrum, four signals are observed (*i*) 4.8 (double doublet, 8.2 squares); (*ii*) 4.3 (multiplet-complicated, 4.1 squares), (*iii*) 6.2 (singlet, 4.2 squares) and (*iv*) 7.9 τ (Doublet, 7.9 squares). Name the compound.

3. A compound with molecular weight 58 gives the following spectral data:

   UV — No λ_{max} above 200 nm.

   IR — 3005 cm^{-1} (*w*), 2950–2840 cm^{-1} (*w*) and 1405 cm^{-1} (*m*).

   NMR — 5.35 (doublet, 9.3 squares), 5.62 multiplet, 4.7 squares) 7.82 τ (doublet, 13.7 squares). Determine the structure.

4. An organic compound with molecular weight 60 on heating with sodium hypobromite gives out nitrogen with effervescence. In NMR, it shows a broad band at 2.5 τ.

   In UV, it absorbs at 222 nm ε_{max} 62. The bands observed in the infra-red spectrum are (*i*) 3490 cm^{-1} (*m*), 3385 cm^{-1} (*m*), 1675 cm^{-1} (*s*). Determine the structure.

5. Molecular weight—59

   UV — λ_{max} 220 mµ ε_{max} 60.

   IR — 3495 (*m*), 3354 (*m*), 2950 – 2840 (*w*) and at 1670 cm^{-1} (*s*).

   NMR — 3.5 τ (Broad singlet, 5.8 squares) 7.90 τ (singlet, 8.5 squares). Determine the structure of the compound.

6. Molecular formula—C_3H_8O.

   UV — Transparent above 200 nm.

   IR — 3410 (*b*, *s*), 2950—2840 (*w*), 1275 (*s*), 1045 cm^{-1} (*s*).

   NMR; 5.42 (singlet, 5.4 squares); 6.4 (triplet, 11.0 squares); 8.1 (sextet, 10.9 squares) ; 9.0 τ (triplet, 16.5 squares). Determine the structure of the compound.

7. An organic compound containing 38.7% carbon and 9.67% hydrogen is transparent to UV above 200 nm. In NMR spectrum, it gives only two signals (*i*) 5.3 τ (singlet, 7.2 squares), 5.62 τ (singlet, 15.1 squares). In the infra-red spectrum, it absorbs at 3540 (*s*), 3025(*w*) and at 1285 cm^{-1}(*s*). Find the structure of the compound.

8. An organic compound with molecular weight 70 gives the following spectral data:

   UV — 285 mµ ε_{max} 23.

   IR — 3060 cm^{-1} (*w*), 1785 cm^{-1} (*s*).

   NMR — 8.4 (Triplet, 8.9 squares), 8.8 τ (quintet, 4.5 squares). What is the structure of the compound?

9. Molecular formula : C_3H_5NO.

   UV — Transparent above 200 nm.

   IR — 3040 (*w*), 2245 (*m*), 1460 cm^{-1} (*s*).

   NMR — 5.72 τ (singlet, 5.7 squares), 6.48 τ (singlet, 8.8 squares). Determine the structural formula of the compound.

10. Determine the structure of the compound with molecular weight 74. In infra-red spectrum, it absorbs at 3560 (*s*), 2960 — 2850 (*w*), 1320 (*w*), 1145 cm^{-1} (*s*). In the NMR spectrum, two signals are observed (*i*) 6.5 (singlet, 3.4 squares), (*ii*) 8.95 τ (singlet, 31.0 squares).

11. A volatile organic compound with molecular weight 74 gives the following spectral data :

    UV — Transparent above 200 nm.

    IR — 3.28 (*w*), 3.39 – 3.50 (*w*) and 8.92 µ* (*s*).

    NMR — 6.1 (singlet, 13.0 squares), 6.45 (septet, 4.1 squares) and 8.9 τ (doublet, 25.4 squares). Find out the structure of the compound.

12. Molecular weight : 75

    UV — 275 mµ ε_{max} 20.

    IR — 2950 – 2841 (*w*), 1565 (*s*), 1375 cm^{-1} (*s*).

    NMR : 5.8 τ quartet (J = 6.9 cps, 5.9 squares), 8.15 τ triplet J = 6.9 cps, 8.9 squares). Find the structure of the compound.

13. Molecular Formula : $C_3H_8O_2$

    IR — 3525 (*s*), 3025 (*w*), 1290 (*w*), 1140 cm^{-1} (*s*).

    NMR — 5.7 (singlet, 7.8 squares); (*ii*) 5.85 (singlet, 23.1 squares); (*iii*) 6.4 (triplet, 15.2 squares); (*iv*) 6.52 τ (triplet, 15.3 squares). Determine the structure of the compound.

14. A compound containing 47.4% carbon and 10.5% hydrogen gives five signals in the NMR spectrum. (*i*) 5.60 (singlet, 3.8 squares); 5.75 (singlet, 3.9 squares); 6.2 (doublet, 7.4 squares); 6.4 (sextet, 4.1 squares); 8.7 τ (doublet, 11.2 squares). It is transparent above 210 nm in UV. In its infrared spectrum, the various absorption bands are formed at (*i*) 3510 (*s*, *b*); (*ii*) 2950–2841 (*w*) and (*iii*) 1240 cm^{-1} (*s*). Determine the structure.

15. Molecular weight : 83

    UV — Transparent.

    IR — 3.39 – 3.50 (*w*); 4.44 (*m*), 7.81 µ (*w*).

    NMR — 9.05 τ (singlet). Find out the structure of the organic compound.

16. An organic compound with molecular formula $C_5H_4O_2$ gives the following spectral data:

    UV — *i*) 274 nm ε_{max} 13000

    ii) 228 nm ε_{max} 2200

    IR — 3070 (*w*), 2755 (*w*), 2840 (*w*), 1704 (*s*); 1670 (*m*), 1170 cm^{-1} (*s*).

    NMR — 0.55 (singlet, 5.7 squares); 2.5 (double doublet, 5.8 squares) 2.8 (double doublet, 5.6 squares); 3.5 τ (double doublet, 6.0 squares). Determine the structure of the compound.

17. Write the name and the structural formula of the compound with the following spectral data :

    UV — Transparent above 210 nm.

    IR — 3.23 (*w*), 8.47 µ (*s*).

    NMR — 5.8 τ (singlet). Molecular weight of the compound is 88.

---

* Use wavelength-wave number conversion table for getting corresponding values in cm^{-1}.

18. Molecular formula : $C_4H_{10}O_2$

UV — Transparent above 200 nm.

IR — 3015 (*w*), 1165 cm^{-1} (*s*).

NMR — 6.25 (singlet, 9.5 squares); 6.10 τ (singlet, 14.4 squares). Determine the structure.

19. An organic compound containing 58.8% carbon, 9.8% hydrogen absorbs at 240 mμ ε_{max} 60 in the ultraviolet spectrum. The other spectral detaiis are:IR : 2950 – 2840 (*m*), 1720 (*s*), 2660 cm^{-1} (*b*, *w*).

NMR — – 0.92 τ (singlet, 3.2 squares); 9.15 τ (singlet, 29.1 squares). What is its structure?

20. Molecular weight 100.

UV — 292 mμ ε_{max} 22.

IR — 3.37 – 3.50 (*w*), 5.84 (*s*), 7.93 μ (*w*).

NMR — 8.4 (singlet, 22 squares) ; 8.55 (doublet 15.1 squares); 8.85 (multiplet, 7.2 squares); 9.1 τ (doublet, 43.00 squares). Determine the structural formula of the compound.

21. An organic compound with molecular formula $C_6H_{12}O$ gives a positive iodoform test.

UV — 282 nm ε_{max} 22.

IR — 2950–2840 (*w*), 1710 cm^{-1} (*s*).

NMR — (*i*) 7.9 (singlet, 8.5 squares); (*ii*) 8.9 τ (singlet, 25.8 squares). Find the structural formula consistent with the given data.

22. Determine the structural formula of the compound with molecular weight 100. Its spectral details are :

UV — Transparent.

IR — 3402 (*s*, *b*), 3095 (*w*), 1040 cm^{-1} (*s*).

NMR — 6.05 (quartet, 17.2 squares); 5.4 τ (singlet, 8.9 squares).

23. Molecular weight : 100

UV — 204 nm ε_{max} 60.

IR — 3040 (*w*), 2860 (*m*), 1735 (*s*), 1670 (*m*), 1210 cm^{-1} (*s*).

NMR — 4.5 (complicated, 4.4 squares); 4.65 τ (double doublet, 8.6 squares), 6.05 (quartet, J = 7.1 cps, 8.7 squares); 8.60 τ (triplet, J = 7.1 cps, 13.0 squares). Determine the structure of the compound.

24. Molecular formula : $C_6H_{15}N$.

UV — Transparent above 200 nm.

IR — 2950 – 2840 (*w*), 1280 cm^{-1} (*w*).

NMR — 7.4 τ (quartet, J = 6.9 cps, 6.7 squares); 8.85 τ (triplet, J = 6.9 cps, 10.5 squares). What is the structural formula of the compound?

25. Molecular weight : 106.

UV — 260 nm ε_{max} 300.

IR — 3025 (*w*), 2870 (*w*), 1602 (*m*), 1578 (*m*) and 810 cm^{-1} (*s*).

NMR — 2.95 (Symmetrical pattern, 7.1 squares); 7.85 τ (singlet, 10.7 squares). Determine the structure of the compound.

26. An organic compound with molecular weight 107 shows a characteristic absorption in the ultraviolet spectrum at 258 mμ ε_{max} 210. The other details being :

IR — 3.28 (*w*), 6.23 (*m*), 6.32 (*m*), 2.93 (*s*) and 3.02 μ (*s*).

NMR — 2.75 (Unsymmetrical pattern, 16.2 squares); 7.7 (Singlet, 6.5 squares); 4.16 τ (singlet, 6.4 squares). Determine the structure of the compound.

PROBLEM SET II (UNSOLVED)

Determine the structures of the organic compounds consistent with the details in each of the following problems:

27. Molecular weight 108

UV — 260 mμ ε_{max} 280

IR — 3498 (*s*), 3305 (*s*), 3030 (*w*), 1608 (*m*), 1450 (*m*), 695 (*m*), 780 cm^{-1} (*m*).

NMR — 2.55 (Unsymmetrical multiplet, 36.2 squares); 4.8 (Singlet, 7.1 squares); 5.2 τ (singlet, 15.0 squares).

28. Molecular weight = 108.

UV — λ_{max} 258 nm ε_{max} 220.

IR — 3525 (*s*), 3015 (*w*), 2940 (*m*), 1602 (*m*) 1502 (*m*), 790 (*m*), and 680 cm^{-1} (*m*).

NMR — 2.7 (Unsymmetrical pattern, 23.1 squares) : 4.65 singlet, 5.5 squares) and 7.8 τ (singlet 16.0 squares).

29. Molecular weight : 113.

UV — No lmax above 210 nm.

IR — λ_{max} 3.40 (*m*), 7.90 (*w*), 14.49 μ [2940 (*m*), 1265 (*w*) and 690 cm^{-1} (*s*)].

NMR — 6.5 (double doublet, 8.9 squares); 6.7 (multiplet, 4.6 squares), 8.75 τ (doublet, 14.0 squares).

30. M^+ = 118

UV — 206 nm ε_{max} 70.

IR — λ_{max} 3.32 (*w*), 3.38–4.0 (*b*, *w*), 5.81 μ (*s*) [3010 (*w*), 2950–2500 (*b*, *w*), 1720 cm^{-1} (*s*)].

NMR — –0.95 (singlet, 8.9 squares); 7.5 τ (singlet, 18.2 squares).

31. M^+ = 120

UV — λ_{max} 254 nm ε_{max} 203.

IR — 3.30 (*w*), 3.65 (*w*), 5.74 (*s*), 6.24 μ (*m*) [3020 (*w*), 2740 (*w*), 1742 (*s*) and 1602 cm^{-1} (*m*)].

NMR — 0.55 (triplet, 5.3 squares); 2.75 (singlet, 27.0 squares); 7.2 τ (doublet, 11.0 squares).

32. Molecular weight = 121.

UV — Transparent above 210 nm.

IR — λ_{max} 3.31 (*w*), 3.24 (*m*), 6.0 (*m*), 16.34 μ (*s*) [3045 (*w*), 2920 (*m*), 1665 (*m*), 590 cm^{-1} (*s*)].

NMR — 8.5 (Singlet, 14.0 squares); 4.2 (Singlet, 4.5 squares); 4.35 τ (Singlet, 4.6 squares).

33. Molecular weight = 120

UV — λ_{max} 265 nm ε_{max} 290.

IR — λ_{max} 3.31 (*w*), 3.39–3.5 (*w*), 6.33 (*m*), 7.93 μ (*w*) [3015 (*w*), 2950–2840 (*w*), 1578 (*m*), 1260 cm^{-1} (*w*)].

NMR — 2.95 (Unsymmetrical pattern, 17.2 squares), 7.4 (Quartet, J = 7.1 cps, 8.5 squares) ; 7.55 (Singlet, 13.0 squares); 8.5 τ (Triplet, J = 7.1 cps 12.9 squares).

34. M^+ = 123

UV — 264 nm ε_{max} 283.

IR — λ_{max} 2.93 (*b*, *s*), 3.02 (*b*, *s*), 3.31 (*w*), 6.24 (*m*), 8.54 (*s*), [3402 (*b*, *s*), 3310 (*b*, *s*), 3015 (*w*), 1601 (*m*), 1170 cm^{-1} (*s*)].

NMR — 2.8 (Unsymmetrical pattern, 18.0 squares), 5.1 (Singlet, 13.2 squares) 4.82 τ (Singlet, 8.7 squares).

35. M$^+$ = 126

UV = 274 nm ε_{max} 502.

IR —— 2.84 (*s*), 3.31 (*w*), 6.32 (*m*), 6.83 μ (*m*) [3510 (*s*), 3015 (*w*), 1582 (*m*), 1462 cm^{-1} (*m*)].

NMR —— 2,60 (Singlet, 8.9 squares) : 5.05 τ (Singlet, 9.1 squares).

36. Molecular weight = 130.

UV —— λ_{max} 205 nm ε_{max} 60.

IR —— 3.39–3.50 (*w*), 5.76 (*s*), 7.87 (*w*), 8.51 μ (*s*) [2950 2840 (*m*), 1736 (*s*), 1270 (*w*), 1175 (*s*)].

NMR —— 6.2 (doublet, 9.2 squares); 8.1 (singlet, 13.4 squares); 8.25 (multiplet, 4.5 squares); 8.7 (doublet, 13.0 squares); 8.9 (multiplet, 9.1 squares) and 9.1 τ (triplet, 13.2 squares).

37. M$^+$—135.

UV —— λ_{max} 237 nm ε_{max} 10,500.

IR —— λ_{max} 2.92 (*m*), 3.31 (*m*), 5.98 (*s*), 6.24 (*m*) [3420 (*m*), 3015 (*m*), 1670 (*s*), 1602 cm^{-1} (*m*)].

NMR —— 2.1 (Singlet, 4.5 squares) 2.7 (Unsymmetrical pattern, 23.0 squares) and 8.5 τ (Singlet, 13.0 squares).

38. Molecular weight = 137.

UV —— λ_{max} 211 nm ε_{max} 6200.

IR —— λ_{max} 2.87 (*s*), 2.94 (*b, s*), 3.02 (*s*), 6.0 (*s*), 6.32 (*m*), 3.29 (*w*) [3480 (*s*), 3401 (*b, s*), 3309 (*s*), 1665 (*s*), 1582 (*m*), 3035 cm^{-1} (*m*)].

NMR —— 2.6–2.7 (Unsymmetrical pattern, 21.2 squares); 3.15 (broad singlet, 9.8 squares), 5.3 τ (singlet, 5.1 squares).

39. Molecular weight = 138.

UV —— λ_{max} 255 nm ε_{max} 202.

IR —— λ_{max} 3.31 (*m*), 6.24 (*m*), 8.47 μ (*s*) [3020 (*w*), 1602 (*m*) and 1180 cm^{-1} (*s*)].

NMR —— 2.65 (Symmetrical pattern, 6.4 squares); 5.8 τ (singlet, 9.8 squares).

40. M$^+$ = 138.

UV —— λ_{max} 205 nm ε_{max} 65.

IR —— 2.89 (*s*), 3.27 (*w*), 5.86 (*s*), 6.65 (*m*), 6.87 μ (*m*) [3460 (*s*), 3055 (*w*), 2662 (*w*), 1705 (*s*), 1502 (*m*) and 1455 cm^{-1} (*m*)].

NMR —— –1.2 (Singlet, 7.2 squares), 2.5 (Unsymmetrical pattern, 29.1 squares), 4.85 τ (singlet, 7.4 squares).

41. Molecular weight – 146.

UV —— λ_{max} 203 nm ε_{max} 60.

IR —— λ_{max} 3.32 (*m*), 3.39 (*m*), 5.79 (*s*), 3.74 μ (*b, m*), [3010 (*w*), 2942 (*m*) 1725 (*s*), 2670 cm^{-1} (*b, m*).

NMR – 0.95 (Singlet, 10.4 squares); 8.2 (Triplet, 21.2 squares : 8.8 τ (Triplet, 21.0 squares).

42. M$^+$ = 136.

UV —— λ_{max} 254 mμ ε_{max} 203.

IR —— λ_{max} 2.92 (*b, s*), 3.31 (*w*), 3.40 (*m*), 6.17 (*m*), 6.24 μ (*m*), [3420 (*b, s*), 2940 (*m*), 1620 (*m*), 1602 cm^{-1} (*m*)].

NMR —— 1.92 (Singlet, 4.7 squares); 2.75 (Unsymmetrical multiplet, 24.1 squares); 8.45 τ (Singlet, 28.0 squares).

43. Molecular weight = 148.

UV — λ_{max} 254 mμ ε_{max} 200.

IR — 3.31 (*w*), 5.47 (*s*), 5.60 (*s*), 6.24 μ (*m*) [3015 (*w*), 1825 (*s*), 1785 (*s*), 1602 cm^{-1} (*m*)].

NMR — 2.75 τ (multiplet).

44. Molecular weight = 148

UV — λ_{max} (*i*) 206 nm ε_{max} 13000 (*ii*) 204 nm ε_{max} 250

IR — 3.32 (*w*), 3.77 (*b, w*), 5.86 (*s*), 6.16 (*m*), 6.32 μ (*w*) [3010 (*w*), 2648 (*b, w*), 1705 (*s*), 1625 (*m*), 1582 cm^{-1} (*m*)].

NMR — – 0.95 {Singlet, 7.2 squares); 2.3 (doublet, 6.9 squares); 2.45 (Unsymmetrical multiplet 35.8 squares); 3.5 τ (doublet, 6.8 squares).

45. M$^+$ = 150

UV — λ_{max} 205 mμ ε_{max} 75.

IR — λ_{max} 2.89 (*s*), 3.29 (*w*), 3.75 (*b, w*), 5.81 (*s*), 7.90 μ (*w*), [3460 (*s*), 3035 (*w*), 2650 (*b, w*), 1720 (*s*), 1265 cm^{-1} (*w*)].

NMR — – 0.97 (Singlet, 6.5 squares); 5.5 (Singlet, 7.0 squares); 6.4 τ (Singlet, 6.8 squares).

46. Molecular weight = 152.

UV — λ_{max} 281 mμ ε_{max} 10,600.

IR — λ_{max} 3.39 – 3.49 (*w*), 3.62 (*w*), 5.92 (*s*), 6.24 (*m*), 6.64 μ (*m*) [2940–2860 (*w*), 2756 (*w*), 1688 (*s*), 1602 (*m*), 1504 cm^{-1} (*m*)].

NMR — 0.22 (singlet, 8.2 squares); 2.52 – 3.04 (complex symmetrical pattern, 25.0 squares); 3.52 (singlet, 8.3 squares); 6.12 τ (singlet, 24.8 squares).

47. M$^+$ = 153.

UV — λ_{max} 282 nm ε_{max} 22.

IR — 3.31 (*w*), 6.45 (*s*), 7.54 (*s*), 8.51 μ (*s*) [3051 (*w*), 1550 (*s*), 1325 (*s*), 1175 cm^1 (*s*)].

NMR — 1.75 (Unsymmetrical pattern, 18.3 squares); 5.4 τ (Singlet, 13.7 squares).

48. Molecular weight = 156.

UV — λ_{max} 205 nm ε_{max} 70.

IR — λ_{max} 2.92 (*s*), 3.26 (*m*), 4.45 (*m*), 5.74 (*s*), 5.97 (*s*), 8.46 μ (*s*) [3415 (*s*), 3060 (*w*), 2246 (*m*), 1742 (*s*), 1674 (*s*) and 1182 cm^{-1} (*s*)].

NMR — 3.24 (singlet, 7.5 squares); 4.49 (singlet, 7.6 squares) ; 5.62 (singlet 23.0 squares) and 7.90 τ (singlet, 22.0 squares).

49. Molecular weight = 162.

UV — λ_{max} 285 nm ε_{max} 1430.

IR — λ_{max} 2.93 (*s*), 3.01 (*s*), 3.30 (*w*), 6.24 (*m*), 6.33 μ (*m*) [3402 (*s*), 3318 (*s*), 3025 (*w*), 1602 (*m*), 1578 (*m*), 690 cm^{-1} (*s*)].

NMR — 2.82 (complex unsymmetrical pattern, 14.4 squares); 6.15 τ (singlet, 9.5 squares).

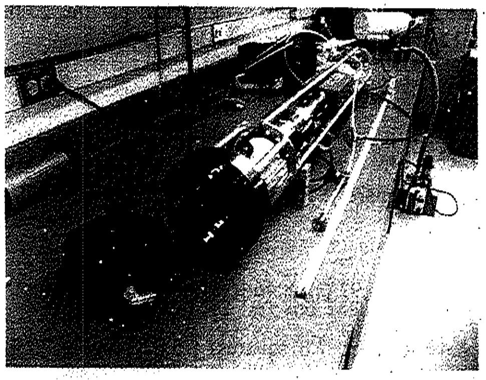
50. Derive the possible structure of organic compound constent with the following spectroscopic data:

(i) M$^+$ = 71.
(ii) UV — No absorption maximum above 210 nm.
(iii) IR — Absorptions at 3.4 – 3.50, 4.45 and 6.85 μ.
(iv) *pmr* signals at 5.78 (singlet) and 6.51 τ (singlet) in the ratio of 16.8 : 23.9.

CHAPTER

7

Mass Spectrometry

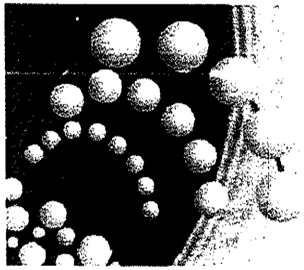


7.1 Basic principles
7.2 Theory
7.3 Instrumentation
7.4 Mass Spectrum
7.5 Determination of Molecular Formula
7.6 Mclafferty Rearrangement
7.7 Metastable Ions or Peaks
7.8 The Nitrogen Rule
7.9 General Fragmentation Modes
7.10 Important Features of the Mass Spectra of Hydrocarbons
7.11a Alkenes (Olefines)
7.11b Acetylenes (Alkynes)
7.11c Cycloalkanes
7.11d Cycloalkenes and Cycloalkynes
7.12 Aromatic Compounds
7.13 Alcohols
7.14 Phenols
7.15 Thiols and Thiophenols
7.16 Ethers, Acetals and Ketals
7.17 Aliphatic Aldehydes and Ketones
7.18 Cyclic Ketones
7.19 Aliphatic and Aromatic Acids
7.20 Esters
7.21 Amides
7.22 Halogen Compounds
7.23 Amines
7.24 Nitro Compounds
7.25 Aliphatic Nitriles
7.26 Important Features in Mass Spectroscopy
7.27 Simple Problems on Mass Spectroscopy
7.27 Short Questions with Answer

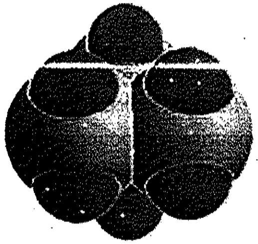
7.1 Basic Principles

Mass spectrometry is the most accurate method for determining the molecular mass of the compound and its elemental composition. In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionised and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge, *i.e.* m/e ratio (value). For most ions, the charge is one and thus, m/e ratio is simply the molecular mass of the ion.

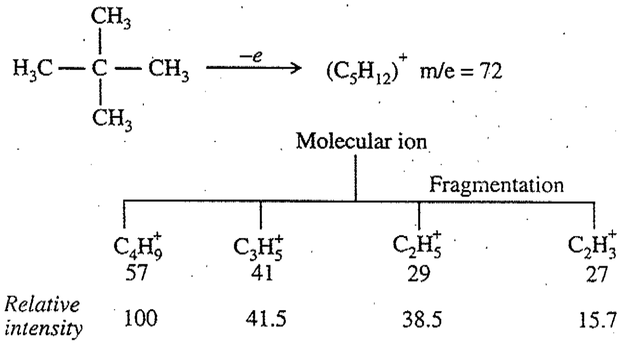
Thus, for Neopentane



Mass Spectrometry



Neopentane



$$H_3C-C(CH_3)_2-CH_3 \xrightarrow{-e} (C_5H_{12})^+ \quad m/e = 72$$

	$C_4H_9^+$ 57	$C_3H_5^+$ 41	$C_2H_5^+$ 29	$C_2H_3^+$ 27
Relative intensity	100	41.5	38.5	15.7

The molecular ion (here $C_5H_{12}^+$) is called parent ion and is usually designated as M^+. It is positively charged molecule with an unpaired electron.

The set of ions (fragment ions or daughter ions) are analysed in such a way that a signal is obtained for each value of m/e that is represented. The intensity of each signal represents the relative abundance of the ion producing the signal. The largest peak in the structure is called the base peak and its intensity is taken as 100. The intensities of other peaks are represented relative to the base peak.

Note. The molecular ion (parent ion) peak may not be confused with the base peak. The base peak has 100% abundance. Mass spectrum of a compound is a plot which represents the intensities of the signals at various m/e values. It is highly characteristic of a compound. No two compounds can have exactly similar mass spectra. A single mass spectrum is equivalent to dozens of physical properties of that compound for revealing the structure. Mass spectra is used in two general ways:

(*a*) To prove the identity of two compounds.

(*b*) To establish the structure of a new compound.

The mass spectrum of a compound helps to establish the structure of a new compound in several different ways:

(*a*) It can give the exact molecular mass.

(*b*) It can give a molecular formula or it can reveal the presence of certain structural units in a molecule.

7.2 Theory

A parent ion results when one electron is removed from the parent molecule of the substance

$$M(g) + e \longrightarrow M^{+}(g) + 2e$$

The m/e value of the parent ion is equal to the molecular mass of the compound. In a few cases, the parent ion peak may be the base peak and can be easily recognised. In most of the cases, parent ion peak is not the base peak and is often of very small abundance. Many elements occur naturally as isotopes, out of these the lightest one greatly predominates. The mass spectrometer is designed to perform three basic functions. These are:

(*i*) To vapourise compounds of varying volatility.

(*ii*) To produce ions from the neutral compounds in the vapour phase.

(*iii*) To separate ions according to their mass over charge ratio and to record them. The plot of m/e values taken along abscissa and their relative intensities along the ordinate is called the mass spectrum.

$$M^{+}(g) \longrightarrow m_1^{+} + m_2$$

or

$$m_1 + m_2^{+}$$

Neutral particles, produced in the process of fragmentation (whether neutral molecules or radicals) cannot be detected in the mass spectrometer.

The mass spectrum of Neopentane is shown as follows:

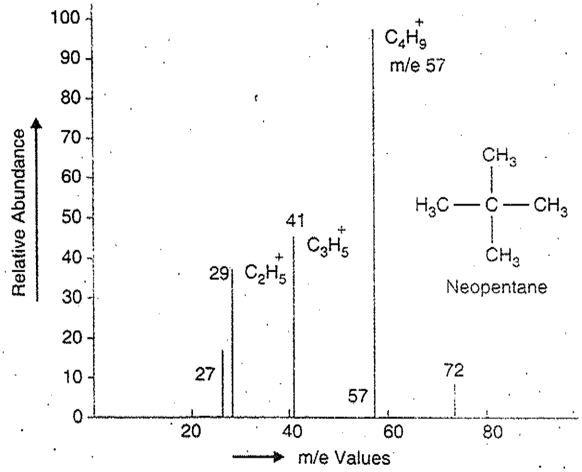
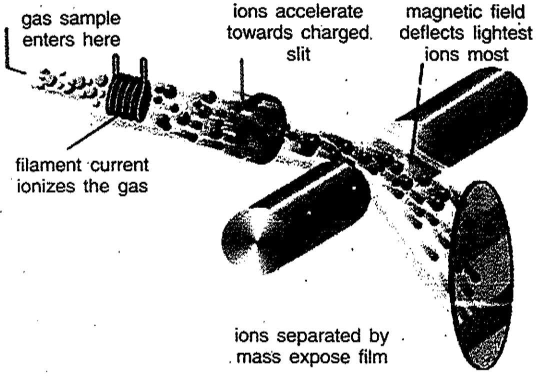


Fig. 7.1. Mass spectrum of Neopentane.

7.3 Instrumentation

The instrument needed to produce the mass spectrum of a compound consists of the following parts:

(*a*) Ion source. The first and an important step in obtaining the mass spectrum is to ionise the sample under examination. The minimum energy required to ionise an atom or a molecule is called **ionisation potential**. The common technique used for the production of ion in mass spectrometer is by the bombardment of electrons. The bombarding electrons are produced from an electrically heated tungsten filament. A few mgm of the substance is produced as a vapour in the source at an operating pressure of 10^{-6} mm. The vapour is allowed to pass through a slit A into the ion chamber. Here, it is bombarded by a stream of electrons produced from a tungsten filament. The bombarding electrons have energy of about 70 eV. Due to bombardment, the molecules generally lose one electron to form a parent ion radical*.



Instrumentation

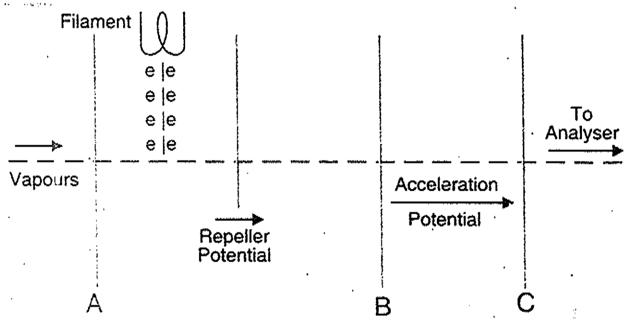


Fig. 7.2. Ionisation of sample and acceleration of ions.

The bombardment of electron may result in the following types of ions:

(*i*) $AB(g) + e \longrightarrow AB^{*} + e$

$\longrightarrow AB^{+} + 2e$ (most probable)

$\longrightarrow AB^{+n} + (n + 1).e$ (least probable)

$\longrightarrow A^{+} + B^{-} + e$

$\longrightarrow A^{+} + B + 2e$

$\longrightarrow AB^{-}$ (electron capture—less probable)

The energy required for removing one electron from the neutral parent molecule is usually 10 eV. With this much energy, no ions are formed, *i.e.*, no fragmentation of the parent ion takes place. But if the energy of the bombarding electron is around 70 eV, then additional energy is consumed in fragmenting the parent ion. This results in the formation of fragment ions or the daughter ions. The positive ion (fragment) whether even electron or odd electron species is detected in the mass spectrometer whereas the neutral molecules or the radicals are left undetected.

(*b*) Mass analyser. The positively charged ion (parent or fragment ions) produced in the ion chamber are accelerated by applying an acceleration potential. These ions then enter the mass analyser. Here the fragment ions are differentiated on the basis of their m/e ratio. The positive ions are directed through a slit B. Repeller potential is applied between A and B. The ions are accelerated

---

* Ion radical is formed by the removal of one electron since all organic molecules are even electron species without exception.

by applying an acceleration potential, of the order of 8 kV through the slit C. Acceleration potential is applied between the plates B and C, (see Fig. 7.2). The positive ions travel through whole of the analyser portion of the mass spectrometer with high velocity and are separated according to their m/e ratio.

Dempster's mass spectrometer is used for the purpose. The positive ions travel in a circular path through 180° under a magnetic field H. Suppose an ion having a charge e is accelerated through a voltage V. Then the kinetic energy of the ions is expressed as:

$$\frac{1}{2}mv^2 = eV \qquad ...(1)$$

where v = velocity of the ions after acceleration

V = potential applied

It may be noted that a massive ion will travel, slowly in a circular path compared to the lighter fragment.

In a magnetic field H, any ion will experience force Hev. It produces an acceleration of v^2/r in a circular path of radius r.

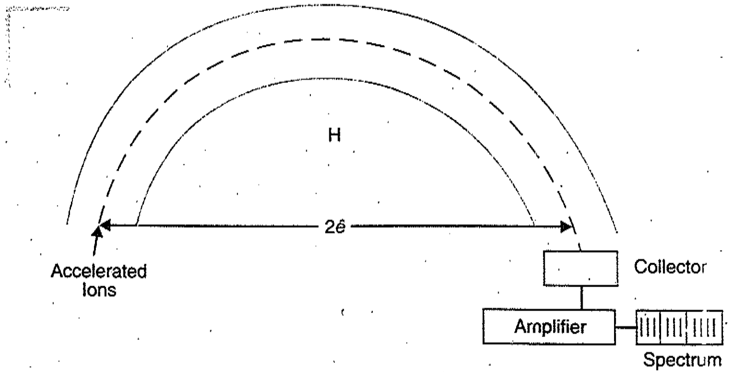


Fig. 7.3. Dempster's mass spectrometer.

Hence, from Newton's second law of motion

$$Hev = \frac{mv^2}{r} \qquad ...(2)$$

Squaring both sides

$$H_2 e^2v^2 = \frac{m^2v^4}{r^2}$$

$$H^2e^2 = \frac{m^2v^2}{r^2} \qquad ...(3)$$

But $\frac{1}{2}mv^2 = eV$ (from 1)

∴ $mv^2 = 2\ eV$

Putting the value of mv^2 in (3)

$$H^2e^2 = \frac{m\ .\ 2\ eV}{r^2} \quad \text{or} \quad H^2e = \frac{2\ mV}{r^2}$$

or

$$\frac{m}{e} = \frac{H^2r^2}{2V}$$

From this equation, it is clear that at a given magnetic field strength and accelerating voltage, the ions of m/e value will follow a circular path of radius r. The ions of various m/e values reach the collector, amplified and recorded. The mass spectrum can be obtained either by

(*i*) Changing H at constant V or

(*ii*) Changing V at constant H

when magnetic field is varied, the method is called magnetic scanning. It is called electric voltage scanning when potential is varied at constant field strength H.

Limitation and Modification

The limitation in the above instrument is that the resolving power is limited by initial spread of translational energy of ion leaving the source. The problem is overcome by passing the ions through electric field prior to the magnetic field. The electric field effects will cause focussing of the ions by placing a slit between the electrostatic and magnetic analysers. The ions of closely defined kinetic energies can be thus, selected prior to mass analysis. Instruments incorporating such a system are called **Double focussing mass spectrometers.** These instruments are capable of attaining much higher resolving power than single focussing instruments. It is possible to distinguish between the ions which have the same integral mass but differ in exact masses. This may be possible for isotopes of elements which do not have integral masses.

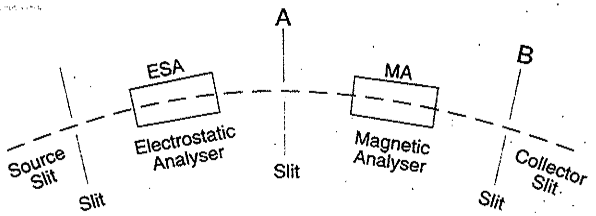


Fig. 7.4. Passage through Electrostatic and Magnetic analysers.

Ion detector

The ions which are separated by the analyser, are detected and measured electrically or photographically. The ions pass through the collecting slit one after the other and fall on the detector. The spectrum is scanned by going up the scale. The ion currents are amplified using a direct current amplifier. The spectrum is recorded by using a fast scanning oscillograph. In this type of recording, three to five records of the same peak are made with galvanometers having different sensitivities.

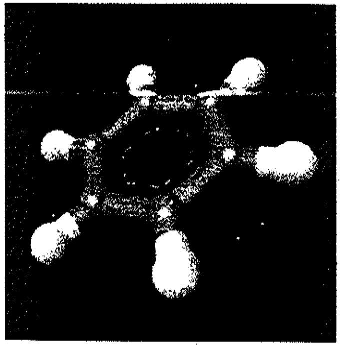
7.4 Mass Spectrum

It is a record of the masses and the relative abundances of the molecular ion and the positively charged fragments formed from it by the electron bombardment. The m/e ratios are taken along the abscissa while the relative abundances are taken along the ordinate. Base peak is the highest peak or the most intense peak in the spectrum. Relative abundance of an ion means the percentage of the total ion current.

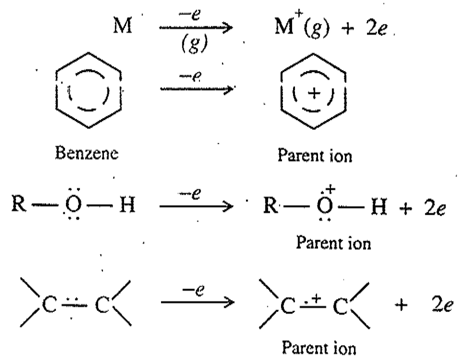
The molecular ion or parent ion

The electron bombardment with energy 10-15 eV usually removes one electron from the molecule of the organic compound in the vapour phase. It results in the formation of molecular ion. The highest occupied orbital of aromatic system and non-bonding electron orbitals on oxygen and nitrogen atoms readily lose one electron. An electron from double bond (two π-electrons) or triple bond (four π-electrons) is usually lost. In alkanes, the ionisaion of C—C sigma bonds is easier than that of C—H bonds.

The mass of the parent ion gives the molecular mass of the sample. In the mass spectrum, it is important to locate the molecular ion at the high mass region of the spectrum. The stability of the parent (molecular) ion decides its relative abundance. The peak intensity of the molecular ion differ from one compound to another. In some cases, parent ion peak is not formed which means that the rate of decomposition of parent ion is too high for its detection. It is important to note that the rate of decomposition of the molecular ion increases with the molecular size in the homologous series. Larger molecular ion provides more possible reaction path ways for detection.



Benzene



$$M \xrightarrow[(g)]{-e} \overset{+}{M}(g) + 2e$$

$$R-\ddot{O}-H \xrightarrow{-e} R-\overset{+}{\dot{O}}-H + 2e$$

Exercise. Predict the relative abundance of the parent ion in case of (*i*) propane and (*ii*) *n*-pentane.

Ans. The relative abundance of the propane molecular ion is more.

The abundance of the molecular ion peak can be increased with respect to the abundance of fragment ions by running the spectrum at low ionisation potential, *i.e.*, by bombarding low energy electrons.

Some important features of the parent ion peak are as follows:

(*a*) The molecular ion peak in aromatic compounds is relatively much intense due to the presence of π-electron system.

(*b*) Conjugated olefines show more intense molecular ion peak as compared to the corresponding non-conjugated olefines with the same number of unsaturation. Conjugated olefines are more stable than the corresponding non-conjugated olefines.

(*c*) Unsaturated compounds give more intense peak as compared to the saturated or the cyclic molecule.

(*d*) The relative abundance of the saturated hydrocarbon is more than the corresponding branched chain compound with the same number of carbon atoms. For example, the molecular ion peak for *n*-pentane is more intense than that of neopentane.

(*e*) The substituent groups like — OH, — OR, — NH_2 etc. which lower the ionisation potential increase the relative abundance in case of aromatic compounds. Also the groups like — NO_2, — CN etc. which increase the ionisation potential, decrease the relative abundance of the aromatic compounds.

(*f*) Absence of molecular ion peak in the mass spectrum means that the compound under examination is highly branched or tertiary alcohols. Primary and secondary alcohols give very small molecular ion peaks.

(*g*) In case of chloro or bromo compounds, isotope peaks are also formed alongwith the molecular ion peak. In case of bromo compounds, M^+ and $(M^+ + 2)$ peaks are formed in the intensity ratio 1 : 1. In case of chloro compounds, M^+ and $(M^+ + 2)$ peaks are formed in the intensity ratio 1 : 3.

Important. Nitrogen containing compounds with an odd number of nitrogen atoms in the molecule must have an odd molecular mass. An even number of nitrogen atoms or absence of nitrogen atoms in the compound show that the molecular mass of the compound must be even.

7.5 Determination of Molecular Formula

The mass spectrum is a plot representing the m/e values of the various ions (parent as well as fragment ions) against their corresponding relative abundances. The peak on the extreme right (*i.e.*, particle of highest mass) corresponds to the molecular mass of the original molecule. In case of straight chain hydrocarbons, the abundance of the parent ion peak is fair and it also gives $(M^+ + 1)$ peak which is of 9.9% abundance compared to the parent peak. Consider that a compound forms peaks at m/e values of 100, 85, 71, 57, 43 (100%) etc. Clearly, it is a straight chain alkane because fragment peaks are formed 14 units apart. In case of straight chain hydrocarbon, a peak due to $C_3H_7^+$ is most abundant *i.e.*, a **base peak**. Thus, a molecular formula of the compound can be obtained. In case an organic compound gives fragment as well as parent peaks in pairs which are two units apart, then

(*a*) if the pair of peaks are in the intensity ratio of 1 : 3, then it must be a chloro compound.

(*b*) If the pair of peaks appear in the intensity ratio of 1 : 1, then it must be a bromo compound.

Let us determine the molecular formula of the compound from the following mass spectrum.

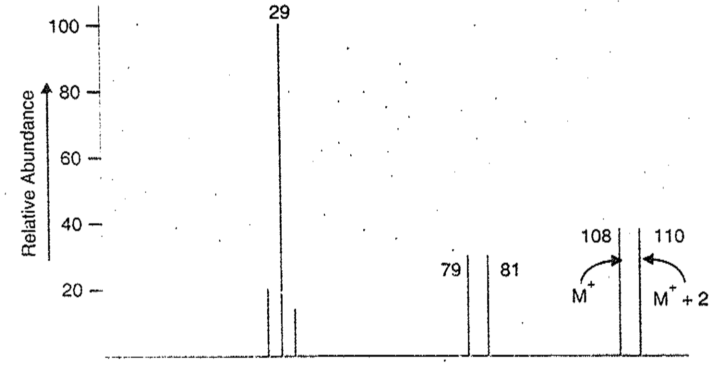


Fig. 7.5. Mass spectrum of Ethyl bromide.

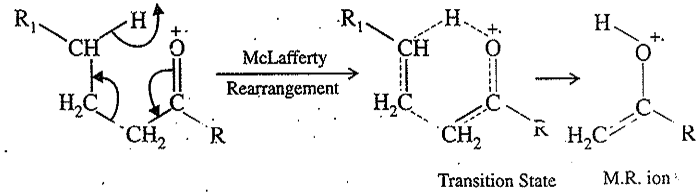
As the pair of peaks are of equal intensity, it is a bromo compound. The isotopes of bromine are $_{79}Br$ and $_{81}Br$. The pair on the extreme right corresponds to M^+ and $(M^+ + 2)$ peaks. The spectrum corresponds to the molecular formula C_2H_5Br.

In some cases, a McLafferty rearrangement ion peak gives an important clue in the determination of molecular formula of the compound. For example, all straight chain aldehydes containing a γ-hydrogen atom form a base peak at m/e 44 (McLafferty rearrangement ion peak). Also in aldehydes a fairly abundant M peak (parent peak) follows a less abundant $(M^+ - 1)$ peak. Let us consider a simple mass spectrum having m/e values at 72, 71, 44 (100%), 43, 29 etc.

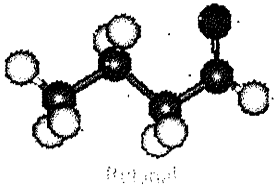
Here a signal at m/e 44 (100%) is due to McLafferty rearrangement ion. This shows that it is a straight chains aldehyde as M^+ peak at 72 also accompanies M^+–1 peak at 71 and hence the formula of the compound is $CH_3CH_2CH_2CHO$.

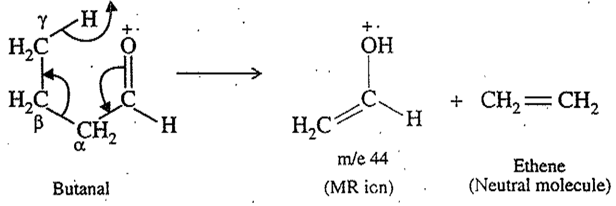
7.6 McLafferty Rearrangement

It involves the migration of γ-hydrogen atom followed by the cleavage of a β-bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds through a sterically hindered six membered transation state. Consider a general compound (ketone).



Butanal contains a γ-hydrogen atom. The McLafferty rearrangement ion formed in this case is shown below:

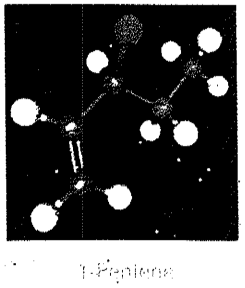


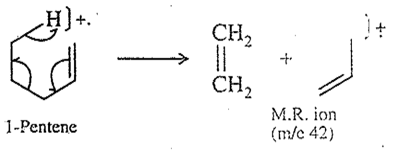


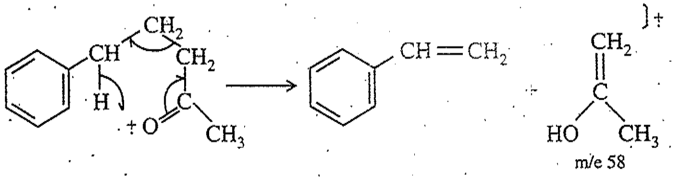
Similarly, a large number of organic compounds, viz. ketones, amines, alcohols, esters, acids which contain a γ-hydrogen atom forms a McLafferty rearrangement ion.

Thus, the molecular formula of the unknown compound can be determined from the various fragment ions and also the parent ion of the mass spectrum.

More examples of McLafferty rearrangement are:

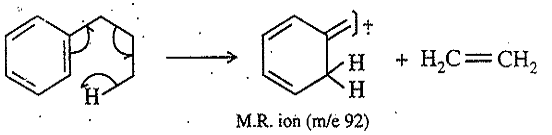






Note. The structural requirement for this rearrangement is a side chain containing at least three carbon atoms, the last bearing a hydrogen atom and a double bond which may be a carbonyl group, an olefinic double bond or an aromatic system.

n-propyl benzene shows a McLafferty rearrangement ion peak in large abundance at m/e 92.



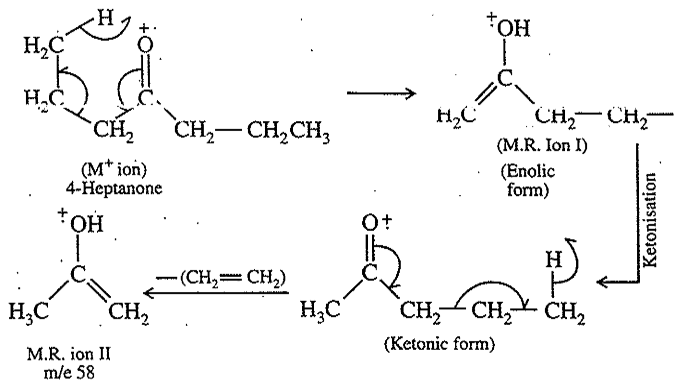
---

* McLayferty rearrangement-ion

A double McLafferty rearrangement is also reported in certain ketones. The second hydrogen atom originates exclusively from the γ-position. A secondary hydrogen is preferred to a primary hydrogen atom in this process. The mechanism involves.

(*i*) Ketonisation of the intermediate enol ion by the hydrogen transfer.

(*ii*) Hydrogen transfer to enolic oxygen. Consider the McLafferty rearrangement in 4-Heptanone.



7.7 Metastable Ions or Peaks

Metastable peaks can be easily determined in a mass spectrum. Some important characteristics of these peaks are:

(*i*) They do not necessarily occur at the integral m/e values

(*ii*) These are much broader than the normal peaks and

(*iii*) These are of relatively low abundance.

Formation of metastable ions. Consider that M_1^+ is the parent ion and m_1^+ is the daughter ion. If the reaction $M_1^+ \rightarrow m_1^+$ takes place in the source, then the daughter ion, m_1^+ may travel the whole analyser region and is recorded as m_1^+ ion. On the other hand, if the transition M_1^+ to m_1^- occurs after the source exist and before arrival at the collector, then m_1^+ is called a metastable ion. We know that in double focussing mass spectrophotometer, there are two field free regions. These are called drift regions. The ions pass through these regions after acceleration. The first field free region refers to the portion of the ion path immediately before the electrostatic analyser. The second field free region lies between electrostatic analyser and magnetic analyser.

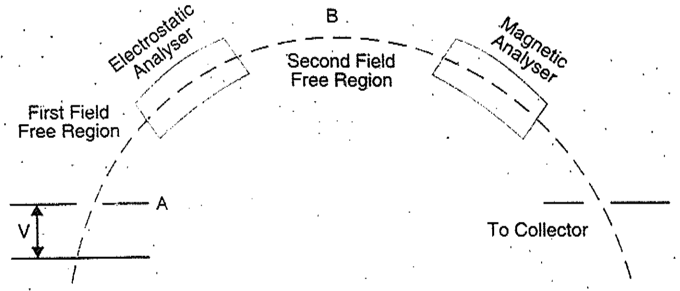


Fig. 7.6. Showing first and second field free regions.

An ion with charge *e* after being accelerated through a potential, V volts will possess kinetic energy equal to eV. Thus, all ions arriving at A will have translational energy equal to eV and thus, energy of the ion will be independent of its mass.

Now suppose the reaction, $M_1^+ \rightarrow m_1^+$ occurs in the second field free region, then the daughter ion (m_1^+) will have kinetic energy equal to $\frac{m_2}{m_1}$ eV. Also the neutral particle $(M_1 - m_1)$ will have kinetic energy equal to $\frac{M_1 - m_1}{M_1}$ eV. It may be noted that the neutral particle is not detected by the mass spectrometer.

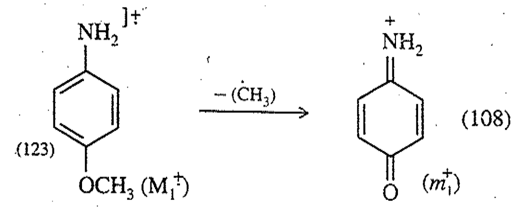
Thus, m_1^+ ion formed in the second field free region will have less kinetic energy than it would have possessed if it were formed in the source. Clearly, the peak for the daughter ion (m_1^+) will not appear at the normal position for m_1^+ on the mass scale. Instead, the signal (peak) appears at m_1^2/M_1. Hence, we conclude that the position of the metastable peak (m^*) due to the reaction $M_1^+ \rightarrow m_1^+$ occurring in the second field free region is such that

$$m^* = m_1^2/M_1$$

Important notes. 1. It is important to remember that for a reaction $M_1^+ \rightarrow m_1^+$, m^* (metastable peak) has a distance below m_1 on the mass scale. The distance is approximately similar to the distance that m_1 lies below M_1.

2. The relative abundance of the metastable peak (m^*) is often of the order of 10^{-2} or less compared to the abundance of parent or the daughter ions in 70 eV spectrum.

Consider the formation of metastable peaks in the spectrum of p-aminoanisole. The parent (molecular) ion appears at m/e 123. Suppose the fragmentation of parent ion into daughter ion, (due to the loss of methyl radical, *i.e.*, loss of 15 mass units) takes place in between the electrostatic and the magnetic analysers, *i.e.*, in second field free region. The position of the metastable peak can be calculated as follows:

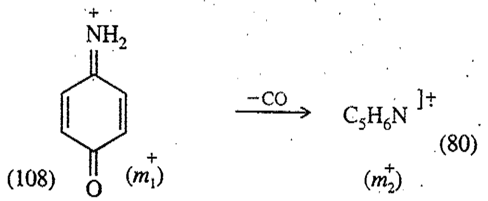


The position of the metastable peak

$$m^* = \frac{m_1}{M_1} = \frac{108 \times 108}{123} = \mathbf{94.8}$$

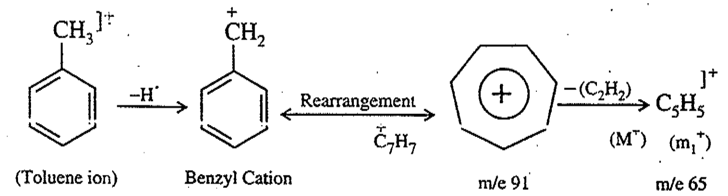
We see that the position of metastable peak (94.8) below m_1^+ ion (108) is approximately the same as m_1 ion is below M_1^+ (123) on the mass scale which is linear.

The position of the metastable peak due to the following fragmentation in the second field free region can also be determined.



The position of metastable peak $m^* = \frac{80 \times 80}{108} = \mathbf{59.2.}$

EXAMPLE 2. *Consider the mass spectrum of toluene. Two strong peaks at m/e 91 and at m/e 65 are formed. The peak at m/e 91 is due to the formation of tropylium cation (stable) which loses a molecule of acetylene (26 mass units) to give $C_5H_5^+$ (m/e 65).*



Suppose the transition $C_7H_7^+$ (91) to $C_5H_5^+$ (65) occurs in the second field free region, then a metastable peak is formed. The position of the broad metastable peak is determined as:

$$m^* = \frac{m_1^2}{M_1} = \frac{65 \times 65}{91} = \mathbf{46.4.}$$

A metastable peak in case of toluene appears at 46.4 in the mass spectrum.

Importance of metastable peaks. The metastable peaks in the mass spectrum greatly contribute in structure elucidation. From the positions of the parent ion and the daughter ion, the position of the metastable ion is calculated as above and confirmed in the spectrum under examination. In the spectrum of toluene, the formation of less intense metastable peak at 46.4 lends weight to the structure of toluene. It is due to the fragmentation of $C_7H_7^+$ ion to $C_5H_5^+$ ion in the second field free region. Similarly, the presence of metastable peaks at the expected positions of the suspected compounds lends weight to its structure.

Why metastable peaks are broadened. The most likely reason for the broadening of the metastable peak is the possibility that some of the excitation energy leading to bond capture may be converted into additional kinetic energy.

7.8 The Nitrogen Rule

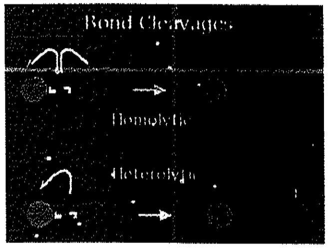
Many signals (peaks) can be ruled out as possible molecular ions simply on the grounds of reasonable structural requirements. The nitrogen rule is often helpful in this regard. It states that **a molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms. An odd numbered molecular mass requires an odd number of nitrogen atoms.** This rule holds for all compounds containing carbon, hydrogen, oxygen, nitrogen, sulphur and halogens.

An important corollary of this rule states that the fragmentation at a single bond gives an odd numbered ion fragment from an even numbered molecular ion. Similarly, an even numbered ion fragment results from an odd numbered molecular ion. For this corollary to hold, the fragment ion must contain all the nitrogen atoms of the molecular ion. To explain the nitrogen rule, let us consider nitro-benzene ($C_6H_5NO_2$). The signal for molecular ion appears at m/e 123; *i.e.*, at odd numbered molecular mass since the compound contains only one (odd number) nitrogen atom. Two important ion fragments which are formed in the mass spectrum of this compound are (*i*) NO_2^+ at m/e 46 and (*ii*) NO^+ at m/e 30. Both these fragment ions appear at even mass number.

Consider a compound containing two (even number) nitrogen atoms, say 2, 4-dinitrophenol. Its molecular ion (M^+) signal appears at m/e 184. The fragment ions appear at (*i*) $M^+ - H)$ *i.e.*, at m/e 183 and (ii) $(M^+ - H—CO)$ *i.e.*, at m/e 155. Thus, we see that the fragment ions containing both the nitrogen atoms appear at odd mass number. This proves the validity of the nitrogen rule.

7.9 General Fragmentation Modes

The relative abundance of the fragment ion formed depends upon (i) the stability of the ion and (*ii*) also the stability of the radical lost. The stability of the ion can be judged by stabilisation of the charge which depends upon (*a*) Resonance (*b*) Inductive effect, (c) Polarisability and so on. The radical site is reactive and can form a new bond. The formation of a new bond is a powerful driving force for ion decompositions. The energy released during bond formation is available for the cleavage of some other bonds in the ion. Some important fragmentation modes are described below:

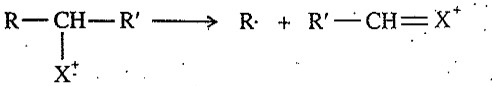


Homolytic and Heterolytic

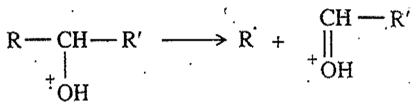
1. **Simple cleavage.** This process involves homolytic or heterolytic cleavage of a single covalent bond. The homolytic cleavage is initiated by a radical site.

(i) **Homolytic cleavage.** Odd electron ions have an unpaired electron which is capable of new bond formation. When a bond is formed, energy is released. The energy released by bond formation can help offset the energy required for the cleavage of some other bond in the ion. Homolytic cleavage reactions are very common and can be classed in the following types:

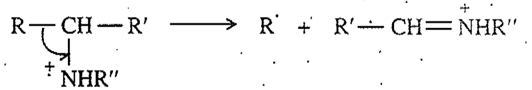
(*a*) **Mode I.** This fragmentation mode operates in compounds in which a hetero atom is singly bonded to a carbon atom. Parent ion is formed by the removal of one electron from the hetero-atom. A new bond is formed with the adjacent atom through the donation of the unpaired electron and the transfer of an electron from the adjacent bond.


$$\underset{\overset{|}{X^{\dot{+}}}}{R-CH-R'} \longrightarrow R\cdot + R'-CH{=}X^{+}$$

More abundant peaks are formed by the cleavage of carbon-carbon bond which is in the α-position to the hetero atom in the mass spectra of alcohols, amines, ethers etc.

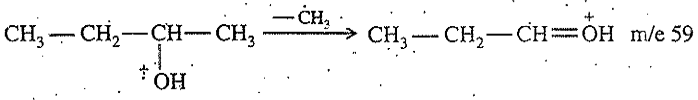

$$\underset{\overset{|}{\dot{+}OH}}{R-CH-R'} \longrightarrow \dot{R} + \underset{\overset{||}{+OH}}{CH-R'}$$

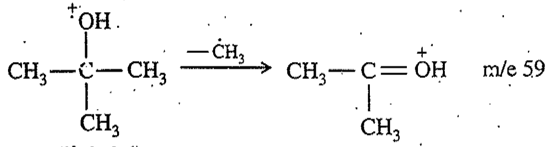

$$R-CH_2-\overset{\dot{+}}{O}-CH_2-R' \longrightarrow RCH_2-\overset{+}{O}{=}CH_2 + \dot{R'}$$


$$\underset{\overset{|}{\dot{+}NHR''}}{R-CH-R'} \longrightarrow \dot{R} + R'-CH{=}\overset{+}{N}HR''$$

The mass spectra of three isomeric butyl alcohols are different. Secondary and tertiary butanols undergo this type of simple cleavage. *n*-Butanol undergoes elimination to give a peak at m/e 56.

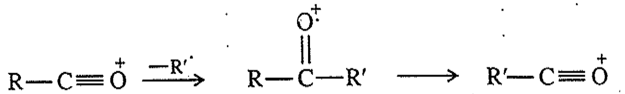
Consider the cleavage in 2-Butanol (2°) and 2-Methyl-2-butanol.


$$CH_3-CH_2-\underset{\overset{|}{\dot{+}OH}}{CH}-CH_3 \xrightarrow{-\dot{C}H_3} CH_3-CH_2-CH{=}\overset{+}{O}H \quad m/e\ 59$$


$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{\dot{+}OH}{|}}{C}}-CH_3 \xrightarrow{-\dot{C}H_3} CH_3-\underset{\underset{CH_3}{|}}{C}{=}\overset{+}{O}H \quad m/e\ 59$$

(3°-alcohol)

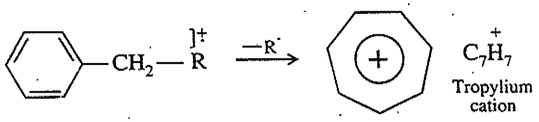
(*b*) **Mode II.** When a hetero atom is attached to a carbon atom by a double bond, α-cleavage is the preferred fragmentation mode.


$$R-C{\equiv}\overset{+}{O} \xrightarrow{-\dot{R'}} R-\overset{\overset{O^{\dot{+}}}{||}}{C}-R' \longrightarrow R'-C{\equiv}\overset{+}{O}$$

This type of fragmentation is shown by many compounds such as ketones, esters, amides etc. Compounds containing C ≡ N or C=S groups do not show this type of fragmentation. In ketones, significant peaks are observed due to the cleavage of carbon-carbon bond which is alpha (α) to the carbonyl group. Unsymmetrical ketones show two types of peaks since either alkyl group can be lost. The elimination of a bigger alkyl radical is preferred. In the same way, the fragmentation mode in aldehydes, esters and amides leads to the cleavage of C—H, C—O and C—N bond respectively.

The presence of amino and hydroxyl groups which are electron donating in nature reduce the relative abundance of acylium $(R{-}C{\equiv}\overset{+}{O})$ ion. The presence of electron withdrawing substituents such as nitro and cyano increase the relative abundance of the ion.

(*c*) **Mode III.** Benzylic cleavage is an energetically preferred fragmentation mode. It involves the cleavage of a carbon-carbon bond which is beta (β) to the aromatic ring.



m/e 91

Considerable stabilisation of the tropylium cation is provided by the aromatic-system. Thus, the mass spectrum of ethyl benzene has a very intense ($M^{\dot{+}}$—CH_3) ion at m/e 91.

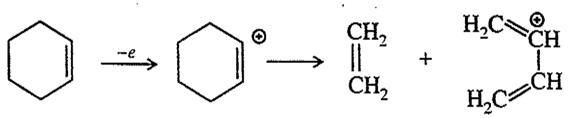
(ii) Heterolytic cleavage. It may be noted the cleavage of C—X (X = O, N, S, Cl) bond is more difficult than that of a C—C bond. In such a cleavage, the positive charge is carried by the carbon atom and not by the hetero atom. It can be shown in the fragmentation of alkyl halide. In the spectra of monohalogenated compounds, hydrocarbon ions are formed in more abundance. As the size of the halogen atom increases, the C—X bond becomes weak. Accordingly C—X bond in alkyl bromides and iodides are easily broken while alkyl chlorides are less susceptible to fragmentation. In *n*-butyl bromide and *n*-butyl iodide, simple cleavage leads to the loss of halogen atom. It forms a more abundant even electron ion at m/e 57. In *n*-butyl chloride, cleavage of C—Cl is difficult. Thus, elimination of HCl by a rearrangement process gives rise to a peak at m/e 56.

In ethers, the cleavage of C—O bond leads to the formation of an alkyl ion rather than an alkoxy ion. In di-*n*-propyl ether, propyl ion appears as a base peak at m/e 43. If the stability of the positive charge at carbon atom is increased by alkyl substitution, then this fragmentation mode is preferred. Consider the following compounds and their fragmentation modes.

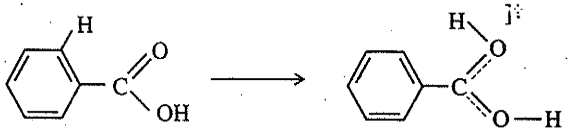
$$R-CH_2-\overset{+}{\dot{C}l} \longrightarrow \dot{C}l + R\overset{+}{C}H_2$$

$$R-\overset{\dot{+}}{O}-CH_2R' \longrightarrow \overset{+}{R} + R'-CH_2\dot{O}$$

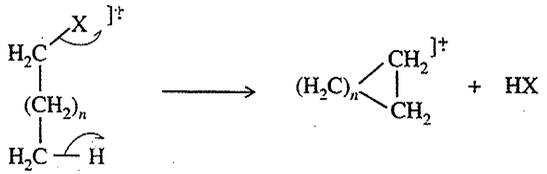
2. **Retro-Diel's-Alder reaction.** This reaction is an example of multicentred fragmentation which is characteristic of cyclic olefines. It involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed. This process is not accompanied by any hydrogen transfer rearrangement. The charge can be carried by any one of the fragments. The more highly substituted or more conjugated fragment which has a lower ionisation potential carries a charge. In simple system, the charge is carried by a diene.



3. **Hydrogen transfer rearrangements.** The simplest rearrangement involves the transfer of a hydrogen atom from one part of the molecule to another. These processes are very common in mass spectrometry. These involve intramolecular hydrogen transfer rearrangements in aliphatic hydrocarbons and aromatic compounds. Rearrangements involving the migration of groups heavier than hydrogen are called skeletal rearrangement processes. Consider hydrogen transfer from the ortho position in benzoic acid prior to fragmentation.

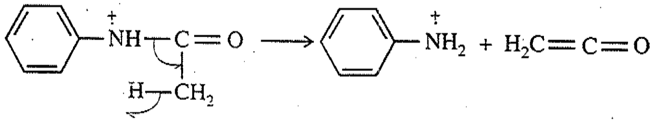


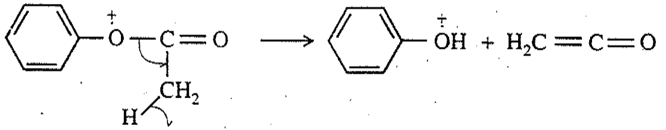
In hydrogen transfer rearrangements, generally a six membered transition state is formed but other transition states are also common.



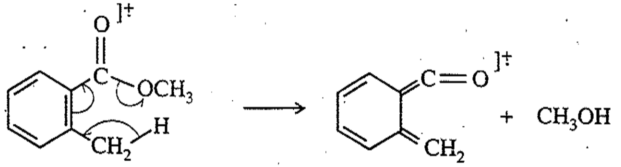
Elimination reactions operate not only from the molecular ion but also from the fragment ion. The positive charge generally remains on the carbon containing fragment. Alcohols usually eliminate a molecule of water from the molecular ion. *n*-Butyl and *n*-Pentyl chlorides undergo hydrogen chloride elimination by the abstraction of α-hydrogen atom by 1, 3 mechanism.

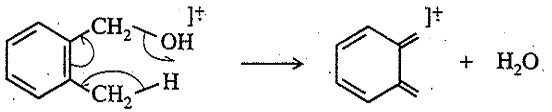
The elimination of ketene ($CH_2 = C = O$) is a characteristic fragmentation mode of *n*-alkyl amides and O-acetates of phenols.

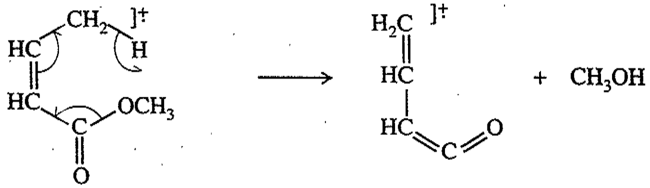




In ortho, substituted aromatic compounds or in cis olefines, the substituent and a hydrogen atom can come in close proximity so as to eliminate a neutral molecule.







Such an elimination distinguishes (*i*) between cis and trans isomers and (*ii*) ortho substituted compound from meta and para substituted isomers.

4. **McLafferty rearrangement ion.** This rearrangement involves the cleavage of a β-bond followed by a γ-hydrogen transfer. The mechanism involves a six membered transition state (For details, see page 277).

7.10 Important Features of the Mass Spectra of Hydrocarbons

(*a*) **Alkanes (saturated hydrocarbons).** Some important features of the mass spectra of alkanes are as follows:

(*i*) The relative height of the parent peak decreases as the molecular mass increases in the homologous series.

(*ii*) Groups of peaks in the mass spectrum are observed 14 mass units apart. The most abundant peaks correspond to $C_nH^+_{2n+1}$ ion.

(*iii*) The most intense peaks are due to C_3 and C_4 ions at m/e 43 and m/e 57 respectively.

(*iv*) There is no preferred charge stabilisation site to favour any specific cleavage.

(*v*) The peaks corresponding to $C_nH^+_{2n+1}$ ions are also accompanied by $C_n\ H^+_{2n}$ and $C_n\ H^+_{2n-1}$ ions in much less abundance.

The mass spectrum of dodecane ($C_{12}H_{26}$) is shown below:

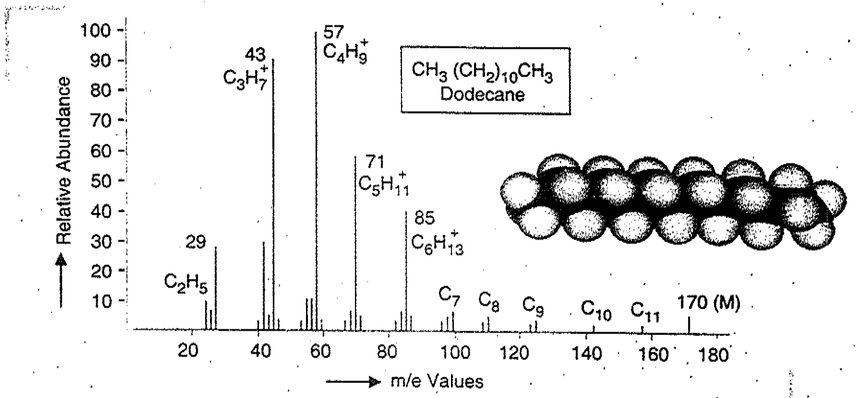


Fig. 7.7

It is very important to note that relative abundance of the ion (fragment ion) formed depends upon the (*i*) stability of the ion formed and also (*ii*) the stability of the radical which is lost.

Note. The stability of the carbocation has the order

allylic > tertiary > secondary > primary > methyl. The stability of the free radical lost depends upon:

(*i*) The length of the straight chain since it allows greater dispersal of the odd electron. Greater the dispersal of odd electron, greater is the stability of the free radical. *n*-butyl free radical is more stable than *n*-propyl free radical. Greater the stability, easier the formation.

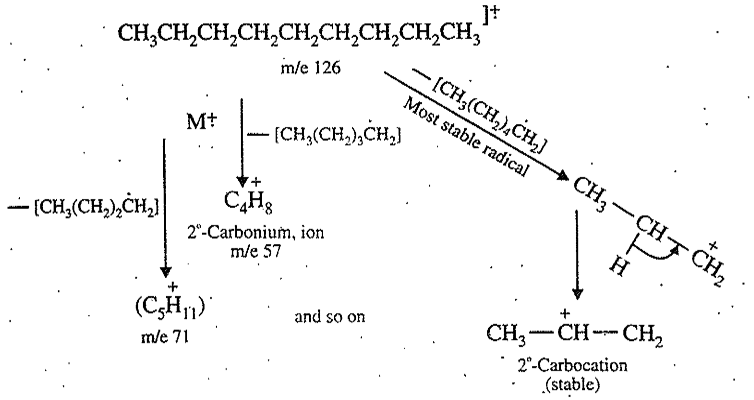
(*ii*) The nature of the free radical, whether primary, secondary or tertiary.

Explanation of the mass spectrum of dodecane. The $C_4H_9^+$ ion (m/e 57) is the base peak (100% abundance). It is due to the formation of the most stable secondary carbonium ion and the elimination of the most stable secondary free radical. As expected, the peaks are formed at 14 mass units apart with decreasing abundance. $C_3H_7^+$ ion peak is much abundant for the same reasons. The relative abundance goes on decreasing from m/e 57 to 71 to 85 and so on. As expected, the molecular ion peak is much less intense.

Also, we notice small peaks for $C_n\ H_{2n-1}^+$ and $C_n\ H_{2n}^+$ ions.

Exercise. Draw the mass spectrum of *n*-nonane (C_9H_{20}).

Hints. The M^+ and $M^+ + 1$ peaks are formed at m/e 128 and 129. The other signals which appear in the spectrum are m/e 43, 57, 71, 85, 99 alongwith other less intense peaks.



In the mass spectrum, also mention the approximate relative abundance of each fragment ion.

(*b*) **Branched chain alkanes.** Some important features of the mass spectra of branched chain alkanes are:

(*i*) Bond cleavage takes place preferably at the site of branching. Due to such cleavage, a more stable secondary or tertiary carbonium ion results.

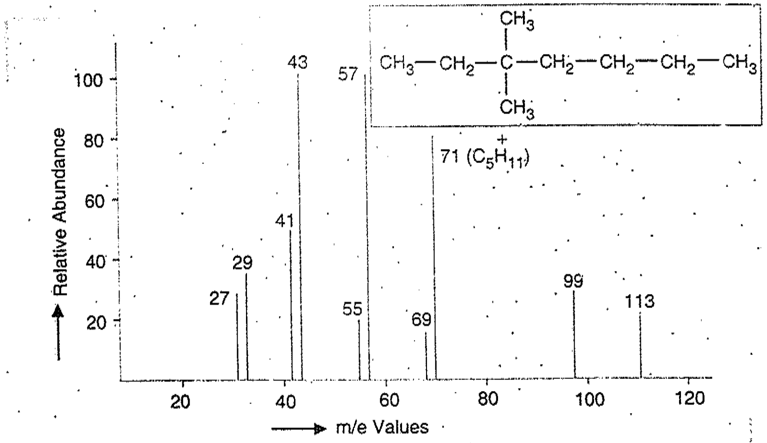


Fig. 7.8. Mass spectrum of 3, 3-Dimethyl heptane.

(*ii*) Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by the delocalisation of lone electron.

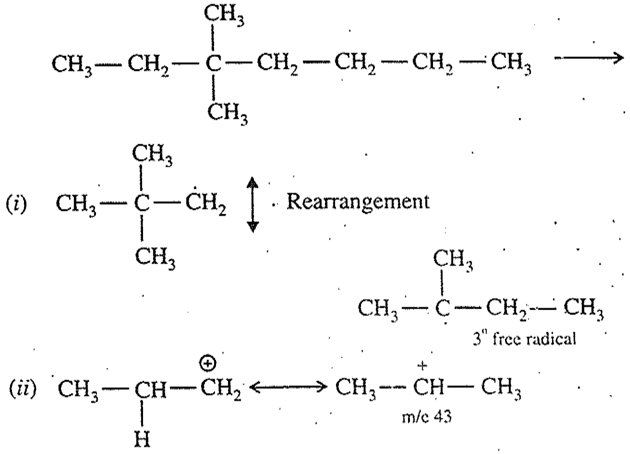
(*iii*) The relative abundance of the parent ion is least and is mostly not observed.

(*iv*) Great number of fragments result from a branched chain compound compared to the straight chain compound. It is due to greater pathways available for cleavage.

(*v*) The signals corresponding to $C_n\ H_{2n+1}^+$ ions follow weak signals which appear 2 units below them. Consider the mass spectrum of 3, 3-dimethyl heptane (Fig. 7.8).

Explanation. As expected, the loss of tertiary free radical forms a peak due to $C_4H_9^+$ ion at m/e 57. Also the loss of *n*-butyl free radical results in the formation of tertiary carbonium ion at m/e 71 in much abundance. The peak at m/e 71 is formed due to the loss of methyl radical in less abundance. **As expected, the branched chain compound does not form any molecular ion.**

The much abundant peak at m/e 43 ($C_3H_7^+$) is formed due to the loss of most stable free radical.



Also small peaks are formed due to the formation of alkenyl cation.

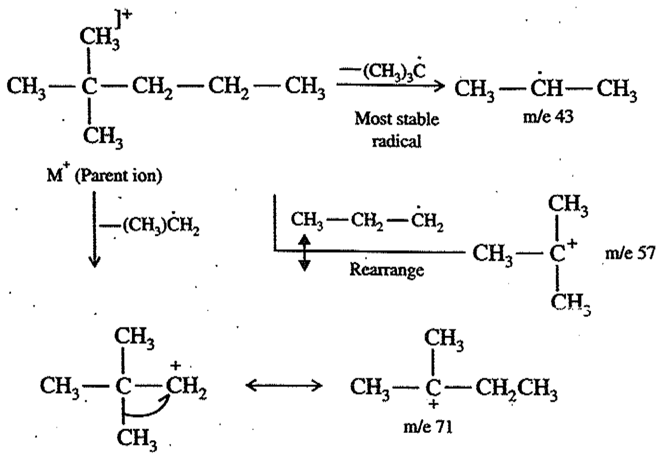
Note. The compounds in which parent ion peak (M^+) is formed, we also notice ($M^+ + 1$) peak whose relative abundance will be N × 1.1% of the abundance of C^{12} containing ion. Here N is the number of carbon atoms. In *n*-nonane, the M^+ (parent ion peak) ion is formed at m/e 128. The $M^+ + 1$ ion is formed in 9 × 1.1 = 9.9% of the abundance of m/e 128. The peak at m/e 44 is 3.3% of the abundance of m/e 43. Clearly, the signal at m/e 44 is not due to $C_3H_8^+$ ion.

Let us consider the mass spectrum of 2, 2 dimethyl pentane. Some important peaks of this spectrum can be predicted as follows:

(*i*) No parent ion (M^+) peak is expected in this compound.

(*ii*) Peaks due to $C_3H_7^+$ ion, $C_4H_9^+$ ion at m/e 43 and 57 are formed in substantial abundance due to the removal of most stable radical.

A much abundant peak at m/e 71 is also expected due to the formation of tertiary carbonium ion. The peak at m/e 57 due to tertiary carbonium ion ($C_4H_9^+$) follows a less abundant peak at m/e 41 ($C_3H_5^+$) due to the loss of methane molecule. Some less abundant peaks (peaks with less percentage of relative abundance) are also expected due to $C_nH_{2n-1}^+$ ions (alkenyl ions).



Exercise. Draw the mass spectrum of 2,2-dimethyl pentane.

Exercise. Draw the mass spectra of (*i*) *n*-Heptane and (*ii*) 2,2-dimethyl hexane. Also predict the approximate relative abundance of each peak.

7.11A Alkenes (Olefins)

Some important features of the mass spectra of olefins are:

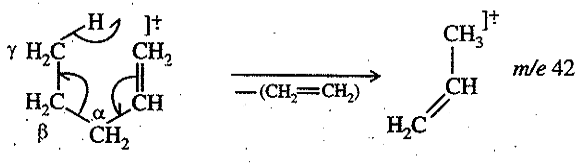
(*a*) The molecular ion peak in the spectra of unsaturated compounds is more intense than the corresponding saturated analogues. The reason is the better resonance stabilisation of the charge on the cation formed by the removal of one of the π-electrons. Mono-olefines contain $C_n H^+_{2n-1}$ ions in their mass spectra.

(*b*) The relative abundance of the molecular ion peak decreases with increasing molecular mass.

(*c*) A cyclic olefine also shows group of peaks which are 14 mass units apart.

(*d*) The general mode of fragmentation induced by a double bond is the allylic cleavage.

(*e*) The C_nH_{2n} ions (fragments) formed by McLafferty rearrangement are more intense. For example, Mc Lafferty rearrangement ion is formed at m/e 42 from 1-pentene due to the loss of ethylene molecule.



1-Pentene (M)

(M.R. ion)

7.11B Acetylenes (Alkynes)

For 1-Butyne and 2-Butyne, the molecular peak is the base peak. The relative abundance of the molecular ion peak decreases as the molecular mass of the alkyne increases. In alkynes, the fragment ions are generally formed by the loss of alkyl radicals. Thus, M^+-15, M^+-29 etc. peaks are generally noticed in the mass spectra of alkynes.

7.11C Cycloalkanes

Some important characteristics of the mass spectrum of cycloalkanes are:

(*i*) The relative abundance of the molecular ion of cycloalkane is more as compared to the corresponding alkane.

(*ii*) It favours cleavage at the bond connecting the ring to the rest of the molecule.

(*iii*) Fragmentation of the ring is usually characterised by the loss of two carbon atoms as C_2H_4 (28 mass units) and $C_2H_5^+$ (29 mass units).

(*iv*) The stability of the fragment ion depends upon the size of the ring.

(*v*) Fragment ions are commonly observed by the loss of alkenes or alkenyl ions. The side chain on the ring breaks and the lone or odd electron remains on the ring.

Consider the mass spectrum of *n*-propylcyclohexane.

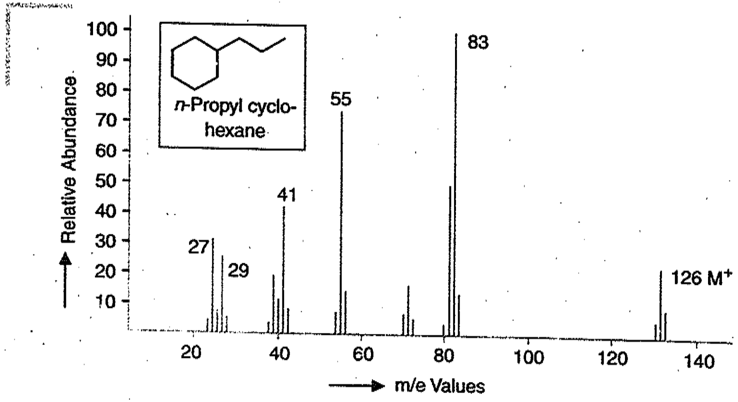


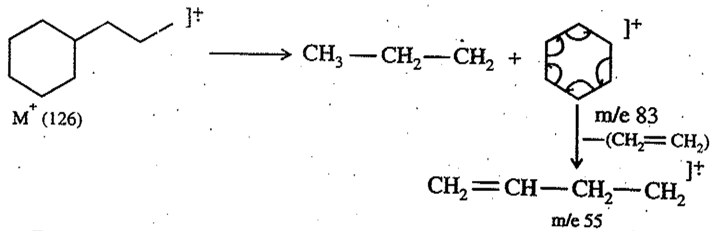
Fig. 7.9. Mass spectrum of *n*-propylcyclohexane.

(*a*) The peak m/e 128 is the molecular ion peak and is quite abundant.

(*b*) The largest peak (base peak) at m/e 83 is formed by the loss of the side chain. The lone electron remains on the ring. This positively charged ion radical appears at m/e 83.

(*c*) The ion radical shows retro-Diel's-Alder reaction and a fragment ion is formed at m/e 55. The abundance of this ion is very large.

The various fragmentation modes are described as under:



Exercise. Draw the mass spectrum of *n*-propylcyclobutane and also write the related abundance of ions formed in its mass spectrum.

7.11D Cycloalkenes and Cycloalkynes

(*a*) Cycloalkenes. A double bond in the alicyclic ring introduces a possible pathway involving retro Diels-Alder reaction. Consider the mass spectrum of cyclohexene.

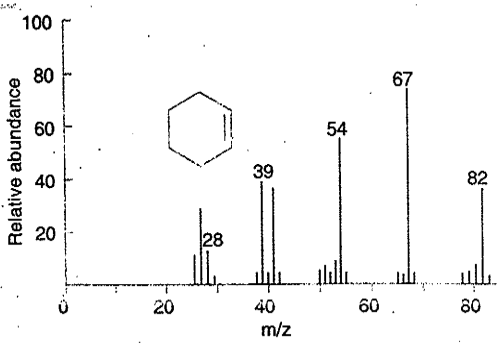


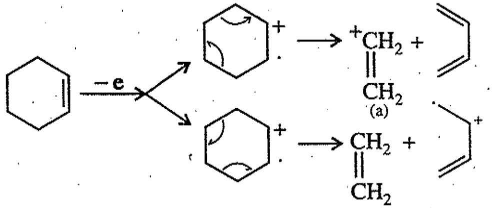
Fig. 7.10. Mass Spectrum of Cyclohexene.

Cyclic olefines usually show a distinct molecular ion peak. A unique mode of cleavage is a type of retro-Diels-Alder reaction.

The retro-Diels-Alder reaction is an example of a multicentered fragmentation mode which is characteristic of cyclic olefines.

The fragmentation mode involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed.

This does not involve any hydrogen transfer rearrangement. Consider the retro-Diels-Alder reaction in case of cyclohexene.



In the mass spectrum of cyclohexene, the peak at m/e 54 is formed in fairly high abundance.

The path forming (*a*) seems more viable because the ion (*a*) is resonance stabilised *i.e.*, the radical and the positive charge are stabilised by Resonance forming a peak at m/e 54 which is intense.

(*b*) Cycloalkynes : Consider the mass spectrum of Phenylacetylene.

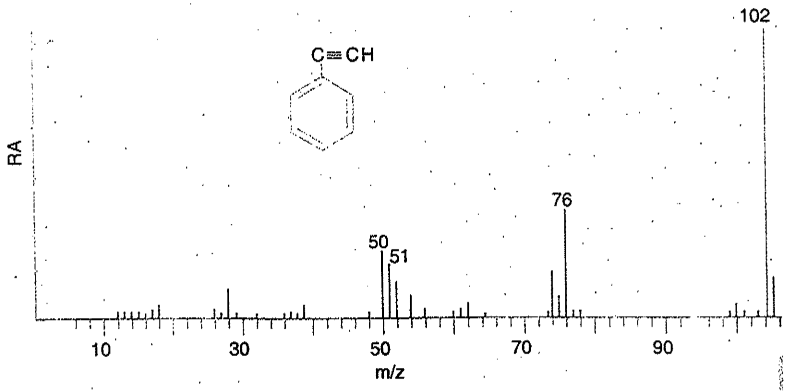
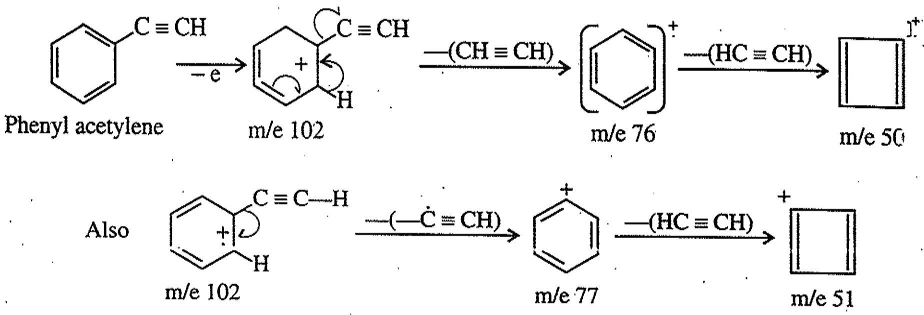


Fig. 7.11. Mass spectrum of Phenylacetylene.

Its various fragmentation modes are described as under :



In the mass spectrum of phenylacetylene, the base peak appears at m/e 102. The abundance ratio (about 9%) of the masses of m/e 102 and 103 reveals a maximum of eight carbon atoms. The relatively intense peaks at m/e 76 and 50 shows the presence of benezene ring.

7.12 Aromatic Compounds

Some important features of the mass spectra of aromatic compounds are:

(*i*) The molecular ion peak in aromatic compounds is fairly abundant as compared to the corresponding alkanes and alkenes containing the same number of carbon atoms.

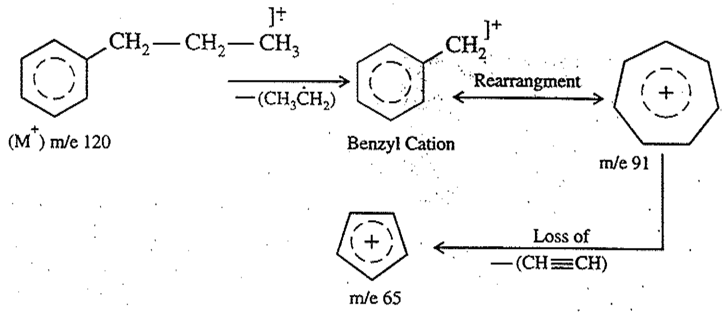
(*ii*) In aromatic compounds, $M^{+} + 1$ and $M^{+} + 2$ are also noticed. The reason is fairly large abundance of the molecular ion peak.

(*iii*) In case of polynuclear hydrocarbons, doubly or triply charged ions (M^{2+}, M^{3+} ions) are possibly formed. Doubly charged molecular ions (m/2e) appear at integral m/e values.

(*iv*) If the aromatic ring is substituted by an alkyl group, a prominent peak is formed at m/e 91.

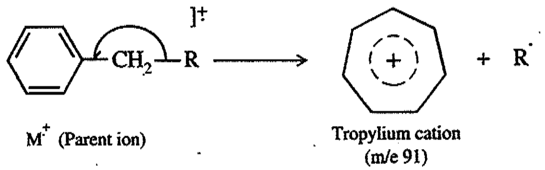
Here benzyl ($C_6H_5\overset{+}{C}H_2$) cation formed rearranges to tropylium cation ($C_7H_7^{+}$).

The fragmentation pattern of *n*-propyl benzene is shown below:



The benzyl cation formed rearranges to more stable tropylium cation which appears at m/e 91. Tropylium cation in turn loses a molecule of acetylene to form $C_5H_5^{+}$ at m/e 65.

Cleavage of a carbon-carbon bond which is in the β-position to the aromatic ring is an energetically favoured fragmentation mode.



The mass spectrum of ethyl benzene has a (M^+—CH_3) peak in large abundance. The fragment ion appears at m/e 91 and it is a base peak. Tropylium cation, then loses a molecule of acetylene, *i.e.*, 26 mass units to form a peak at m/e 65.

The mass spectrum of ethyl benzene is shown below:

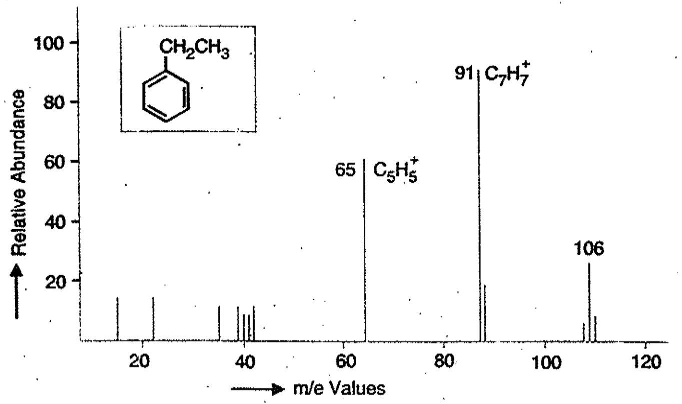


Fig. 7.12. Mass spectrum of Ethyl benzene.

Note. In the absence of an easily cleaved side chain, aromatic molecules give abundant molecular ions. For example in the mass spectrum of naphthalene (10 π electron system), $C_{10}H_8$, the molecular ion is highly abundant. The mass spectrum of Naphthalene is shown below:

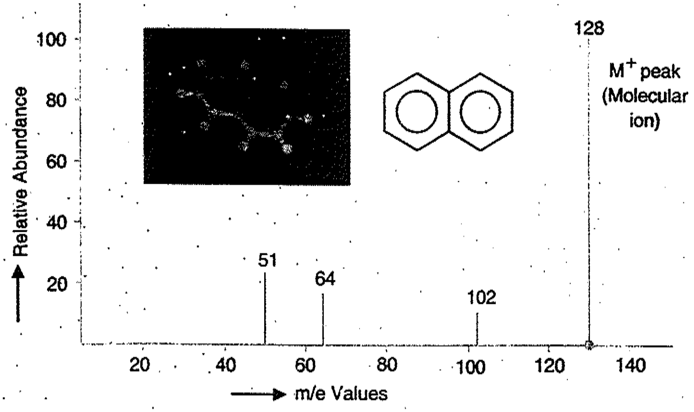


Fig. 7.13. Mass spectrum of Naphthalene.

The mass spectrum of *m*-xylene is shown below (Fig. 7.13): In this case also, the base peak appears at m/e 91 due to the formation of Tropylium cation. Thus, like alkyl benzenes, Xylenes also involve easy loss of alkyl group $(M—CH_3)^+$ ion.

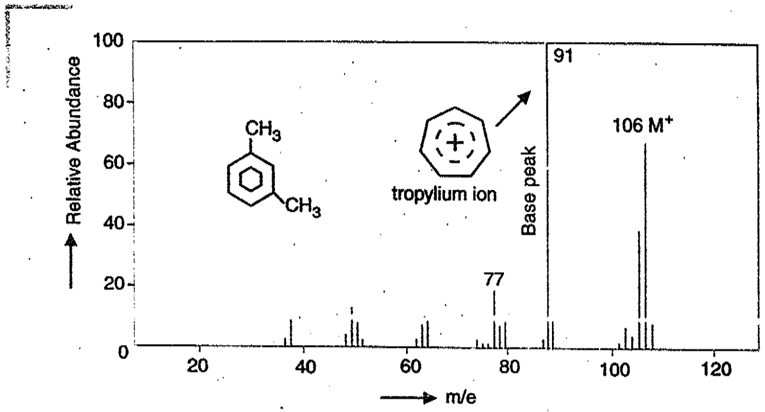


Fig. 7.14. Mass spectrum of m-Xylene.

In the spectrum of *n*-butyl benzene, characteristic peaks at m/e 91 and 65 are obtained which are typical of alkyl benzenes due to tropylium ion and cyclopentadienyl cation. Also a peak at m/e 92 in fair abundance is due to McLafferty rearrangement ion.

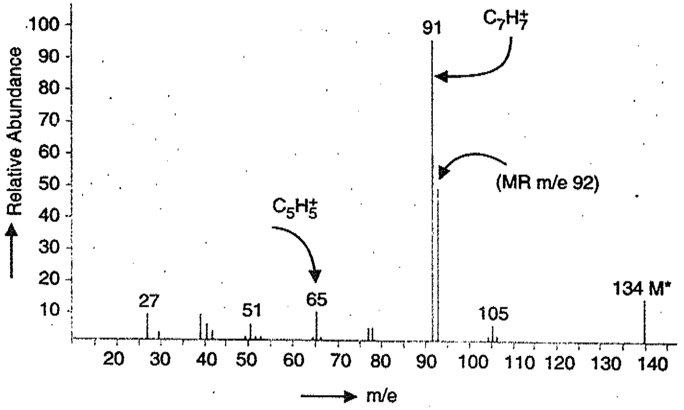
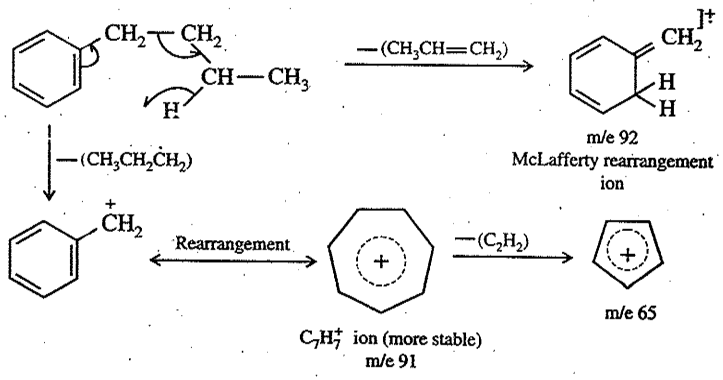


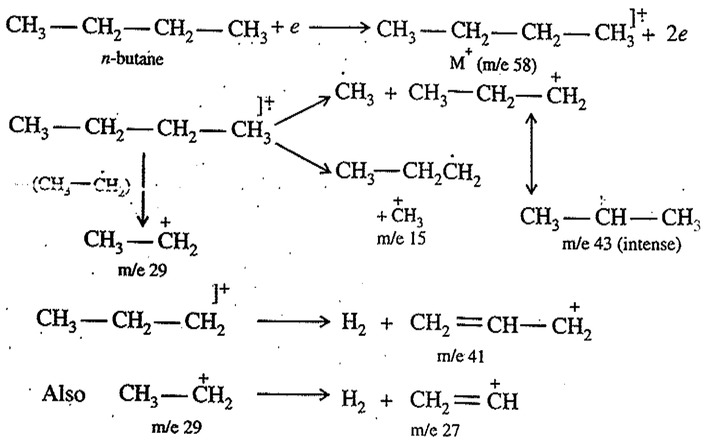
Fig. 7.15. Mass spectrum of n-butyl benzene.

The various fragmentation modes of n-butyl benezene.

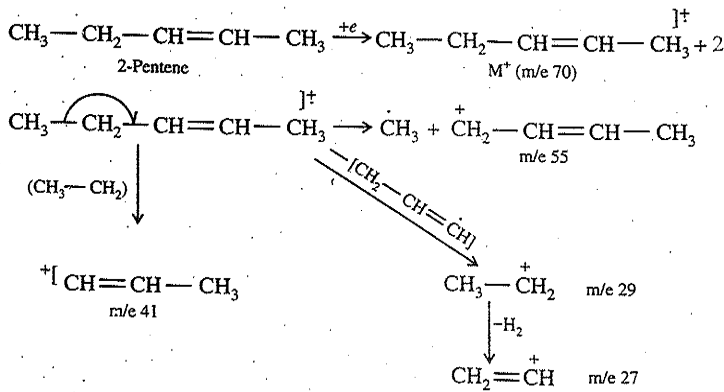


Examples for Practice

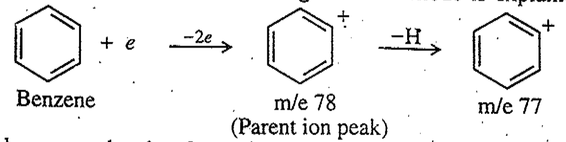
1. **Fragmentation of *n*-Butane.** The various fragmentation modes of *n*-butane giving parent ion and daughter ion peaks are:



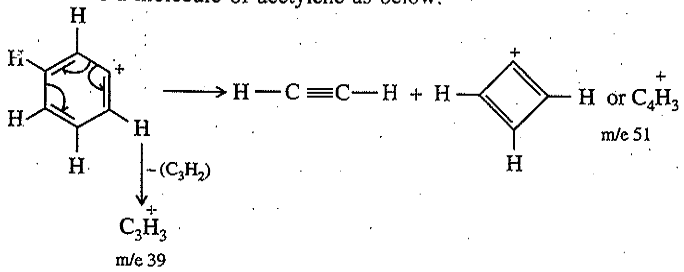
2. **Fragmentation of 2-Pentene.** The mass spectrum of 2-Pentene shows m/e peaks at 70, 55, 41, 39, 29, 27. The formation of these signals is explained below:



Fragmentation of Benzene. The parent peak in case of benzene is formed at m/e 78. other important peaks appear at 77, 51 and 37. The fragmentation mode is explained below:



Phenyl cation loses a molecule of acetylene as below:



7.13 Alcohols

Some important features of the mass spectra of alcohols are:

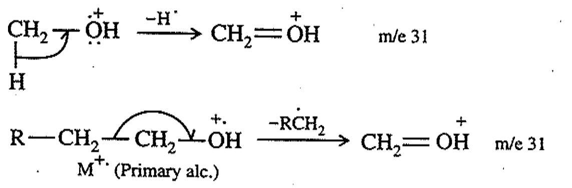
(*a*) The molecular ion peak of primary and secondary alcohol is usually of low abundance. It is not detected in tertiary alcohols.

(*b*) The parent ion peak is formed by the removal of one electron from the lone pairs on the oxygen atom of primary and secondary alcohols.

(*c*) The number of fragmentation modes in alcohols depend upon the fact whether it is primary, secondary or tertiary alcohol.

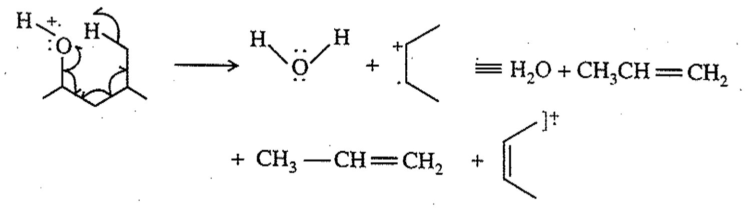
(*d*) The fragmentation of carbon-carbon bond adjacent to oxygen atom (α-cleavage) is the preferred fragmentation mode.

(*e*) The signal at m/e 31 appears in large abundance in the mass spectrum of methanol and other aliphatic primary alcohols. This signal corresponds to the formation of oxonium ion ($CH_2{=}\overset{+}{O}H$) and is formed by the cleavage of carbon-hydrogen bond in methanol.

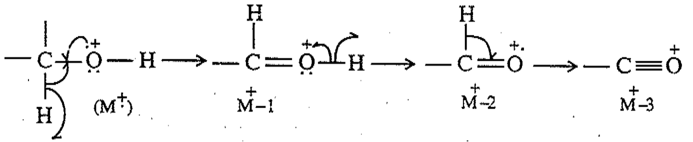


(*f*) Primary alcohols show $M^+ - 18$ peaks, corresponding to the loss of water.

(*g*) A primary alcohol having a chain of four or more carbon atoms shows a peak which corresponds to $M^+ - (18 - C_nH_{2n})$. It can be shown mechanistically as follows:



(*h*) Long chain members may show peaks corresponding to successive loss of H-radicals at M—1, M—2, and M—3. It can be represented as shown.



(*i*) The $CH_2{=}\overset{+}{O}H$ is the most significant peak in the spectra of primary alcohols.

(*j*) Secondary alcohols cleave to give prominent peaks due to $R{-}CH{=}\overset{+}{O}H$ at m/e 45, 59, 73 ... Tertiary alcohols fragment to give prominent peaks due to $RR'C{=}\overset{+}{O}H$ at m/e 59, 73, 87 ..

(*k*) In addition to the α-cleavage, primary alcohols also undergo β-, γ-, δ- cleavage to form peaks at m/e 45, 59, 73 ...

EXAMPLES. Consider the mass spectrum of 1-Butanol. It is shown below.

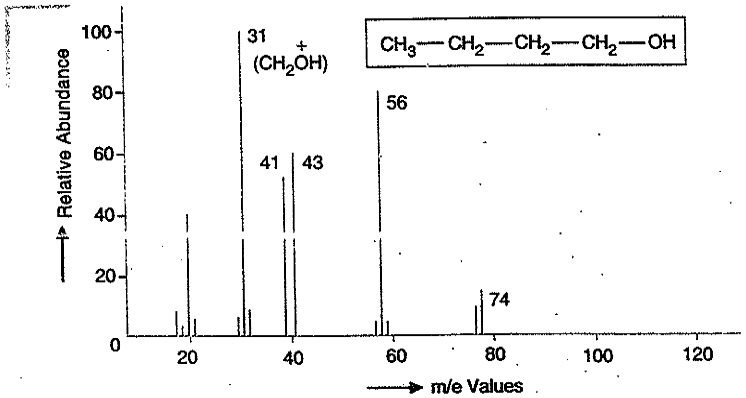
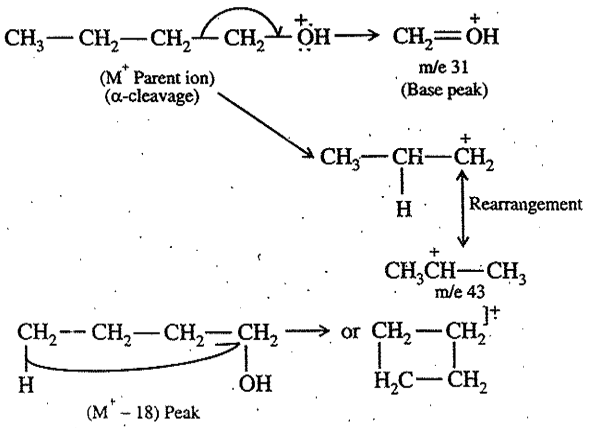


Fig. 7.16. Mass spectrum of 1-Butanol.

The various fragmentation modes of 1-butanol (shown above) are explained below:



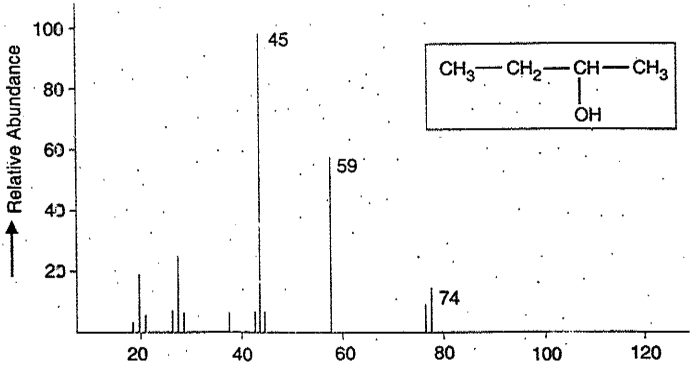
$CH_3—CH_2—CH_2—CH_2—\overset{+\cdot}{\ddot{O}}H \longrightarrow CH_2{=}\overset{+}{O}H$

$CH_3—CH—\overset{+}{CH_2}$ (H) $\longleftrightarrow CH_3\overset{+}{C}H—CH_3$

$CH_2—CH_2—CH_2—CH_2$ (H, OH) $\longrightarrow$ or $CH_2—CH_2 / H_2C—CH_2]^{+\cdot}$

EXERCISE. Draw the mass spectrum of 1-Hexanol and mention the relative abundance of each signal.

EXAMPLE. Consider the mass spectrum of 2-Butanol (secondary alcohol). It is shown below.



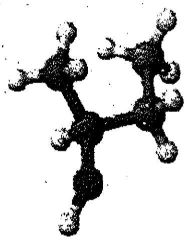
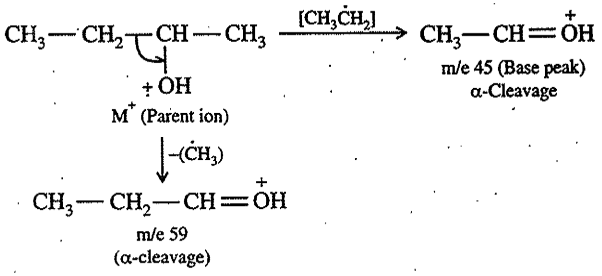


Fig. 7.17. Mass spectrum of 2-Butanol.

The various fragmentations shown in the figure can be explained as follows:



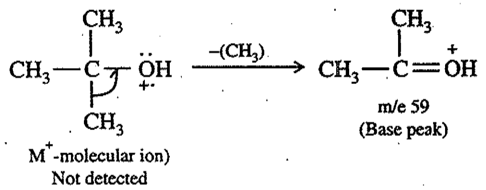
$CH_3—CH_2—CH(\overset{+\cdot}{O}H)—CH_3 \xrightarrow{[CH_3\dot{C}H_2]} CH_3—CH{=}\overset{+}{O}H$

$\big\downarrow -(\dot{C}H_3)$

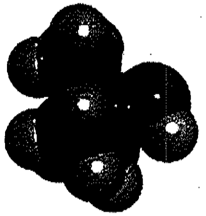
$CH_3—CH_2—CH{=}\overset{+}{O}H$

Exercise. Draw the mass spectrum of 2-methyl butanol-1 and also mention the relative abundance of the various fragment ions.

In case of tertiary alcohol, the molecular ion peak is not formed. The signal due to α-cleavage is the most significant and is the base peak. Consider the mass spectrum of tertiary butyl alcohol (2-methyl, 2-propanol).

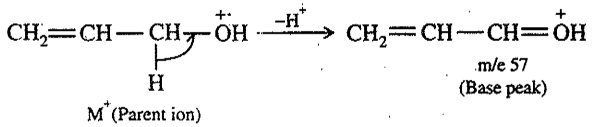


$(CH_3)_3C—\overset{+\cdot}{\ddot{O}}H \xrightarrow{-(CH_3)} (CH_3)_2C{=}\overset{+}{O}H$



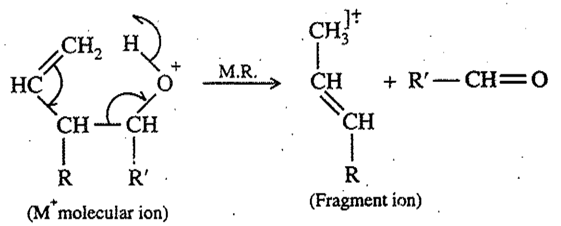
In case of cyclic alcohols, the fragmentation patterns are quite complicated. In case of cyclohexanol, molecular ion peak appears at m/e 100. It loses a hydrogen radical to form $M^+ - 1$ peak at m/e 99. This, in turn loses a molecule of water to form a signal at M^+ —H — H_2O at m/e 81.

In allyl alcohol, ($\overset{+}{M}$ — H) ion is formed due to its high stability.



$CH_2{=}CH—CH_2—\overset{+\cdot}{O}H \xrightarrow{-H^+} CH_2{=}CH—CH{=}\overset{+}{O}H$

The McLafferty rearrangement ion peak has also been reported in these compounds.



Aromatic alcohols

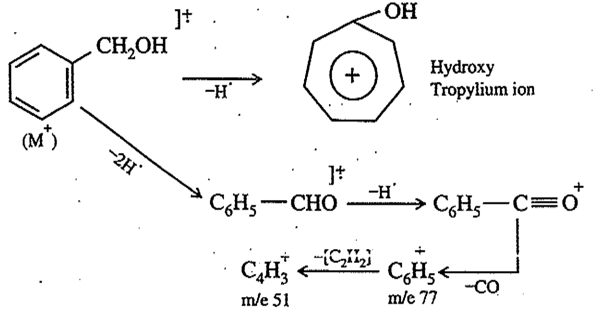
Some important features of the mass spectra of aromatic alcohols are:

(*a*) The relative abundance of the parent ion ($\overset{+}{M}$) of aromatic alcohols is fairly large.

(*b*) Some of the fragment modes of benzyl alcohol are loss of one, two or three hydrogen atoms.

(*c*) The fragment ion, (M^+ —H) further eliminates CHO radical.

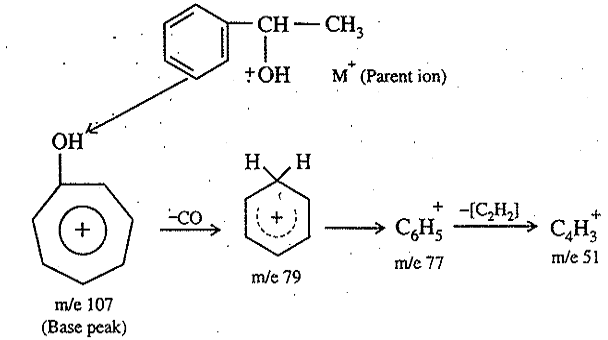
(*d*) (M^+—H) fragment of benzyl alcohol also rearranges to form hydroxy tropylium ion.



(*e*) The —OH group in the benzylic positions fragments in a way which favour charge retention on the aryl group.

EXAMPLE. Consider the mass spectrum of 1-Phenyl ethanol. The base peak corresponds to the elimination of methyl radical. The peak at m/e 107 is the base peak and is represented by hydroxy tropylium ion. Hydroxy tropylium ion further loses a molecule of carbon monoxide to give fragment ion at m/e 79. Its relative abundance is fairly large.

Further it loses hydrogen to form phenyl cation (m/e 77) which in turn eliminates a molecule of acetylene as usual. The various fragment ions are shown below :



EXAMPLE. Deduce the structure of the compound with molecular formula, $C_5H_{12}O$. There is a metastable peak at (m^*) 43.3. The spectrum of the compound is shown below:

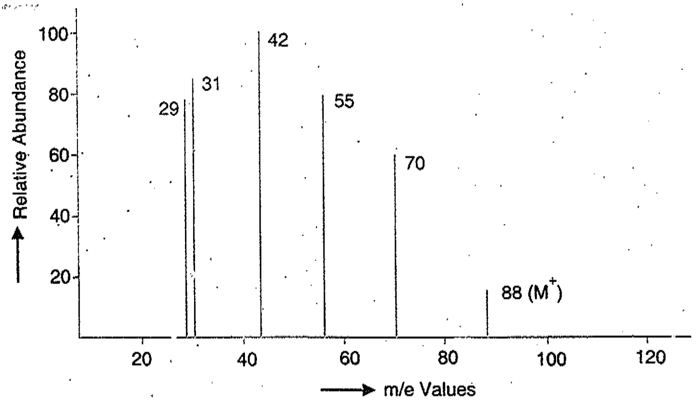
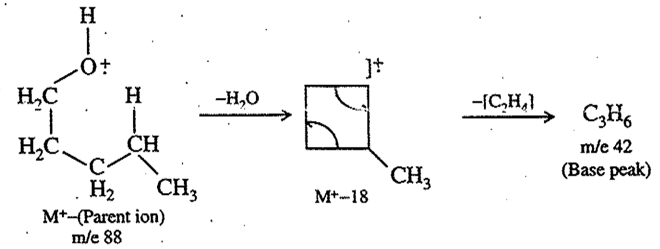


Fig. 7.18. Mass spectrum of 1-Pentanol.

SOLUTION. The appearance of a significant peak at m/e 31 reveals that the compound may be primary alcohol. It is due to $CH_2{=}\overset{+}{O}H$ ion.

Another peak at m/e 70 is M^+— 18 signal. Clearly, it is formed by the loss of water molecule from the parent ion. This also supports that the component is primary alcohol. The base peak at m/e 42 is of even mass number. It is formed by the rearrangement process.

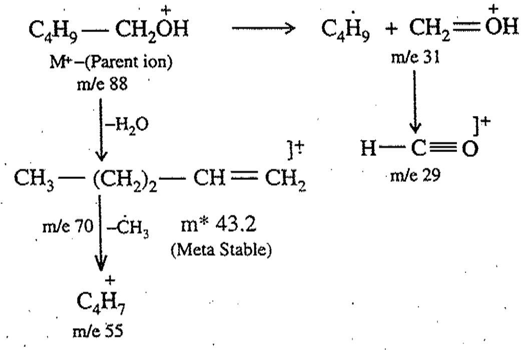


We know that a primary alcohol also loses a molecule of ethylene after the elimination of water molecule. (M^+—18—C_2H_4).

The signal at m/e 55 is due to the elimination of methyl radical from the fragment ion formed at m/e 70. The metastable peak (m^*) at 43.2 is explained due to the fragmentation reaction $m_1^+ \rightarrow m_2^+$ (*i.e.*, 70 to 55) in the second field free region.

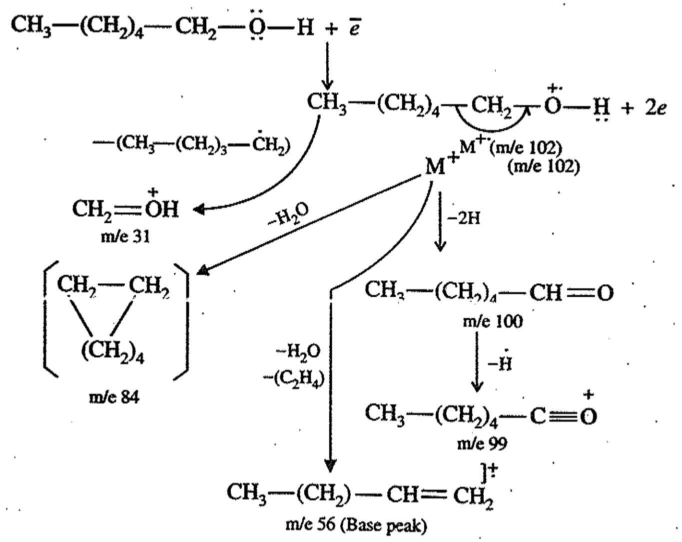
$$m^* = \frac{m_2^2}{m_1} = \frac{55 \times 55}{70} = \mathbf{43.2}$$

The structure of the compound is thus, 1-Pentanol. The various fragmentation patterns are shown below:

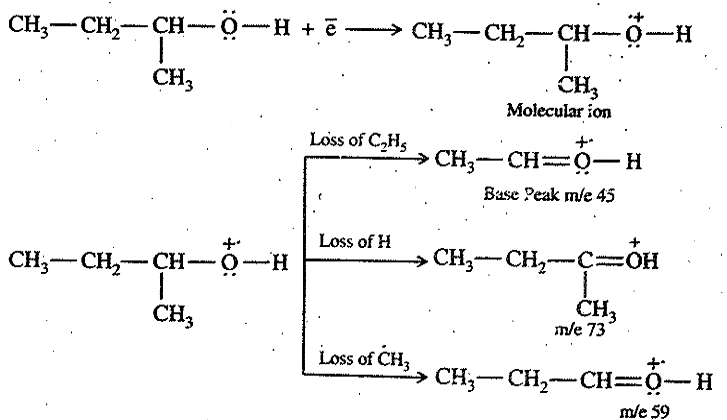


Fragmentation of 1-Hexanol. The various fragmentation modes of 1-Hexanol are shown below:

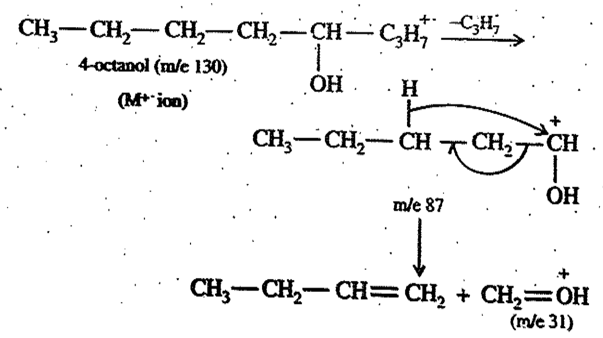
1-Hexanol



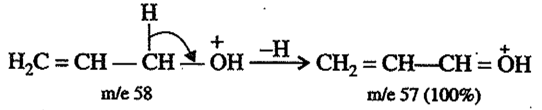
. The various fragmentation patterns of sec-butyl alcohol are shown below:



The various fragmentation ions formed in the case of 4-octanol ($M^{+\cdot}$. m/e 130) are shown below:



Unsaturated Alcohols. In unsaturated alcohols, the loss of hydrogen radical from the hydroxyl group is most likely and the resulting ion-possesses high stability. Thus, in allyl alcohol, a peak at m/e 57 is formed in 100% abundance.



Alicyclic alcohols. Consider the mass spectrum of cyclohexanol. The base peak in this case is formed at m/e 57. The molecular ion peak is of low abundance. Loss of water molecule produces an ion radical at m/e 82 is fair abundance. The mass spectrum of cyclohexanol is shown in figure.

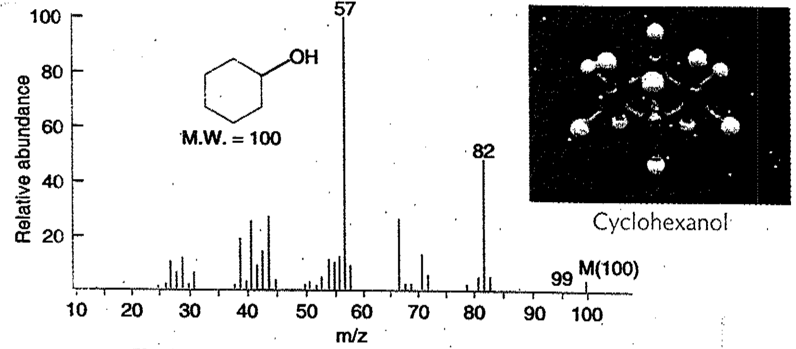
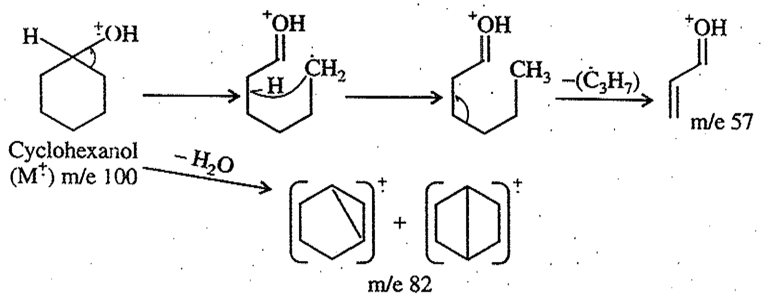


Fig. 7.19. Mass spectrum of Cyclohexanol.

The various fragmentation modes are shown below :



7.14 Phenols

Some important features of the mass spectrum of phenols are:

(*a*) The molecular ion peak (M+.) is intense.

(*b*) The peak due to the loss of hydrogen radical, $M^{+\cdot}$—H is small.

(*c*) The fragment ion due to the loss of carbon monoxide is most significant. M–29 is less intense than M–28.

(*d*) Cresols form very intense (M–H) peak due to the formation of hydroxy tropylium ion.

(*e*) In catechol ($\overset{+}{M}$ – 18) peak is intense while $\overset{+}{M}$—28 and $\overset{+}{M}$—29 ions are formed in abundance in resorcinol and quinol.

The mass spectrum of phenol is shown in figure 7.20.

(*i*) Consider the fragmentation modes in phenol.

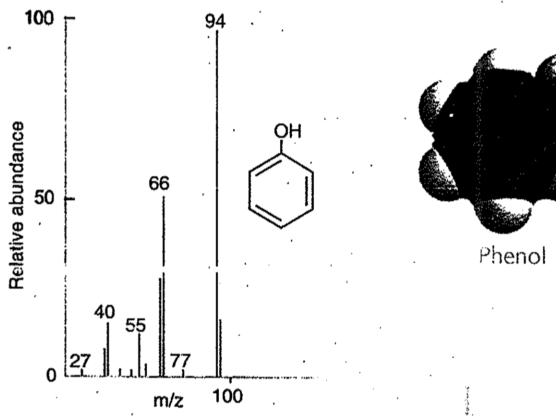
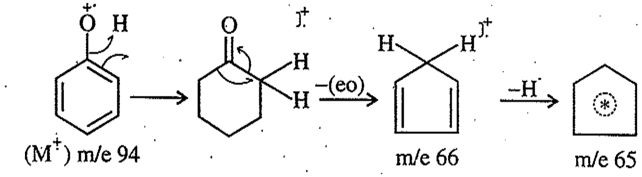
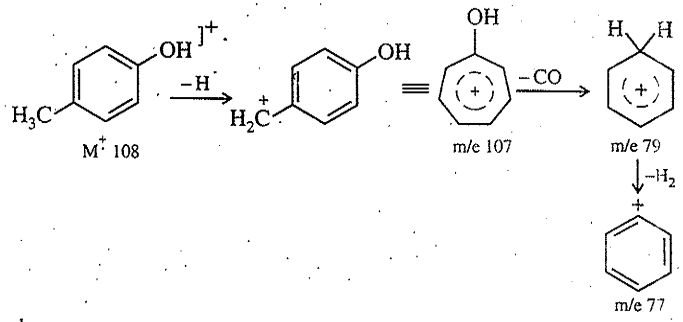


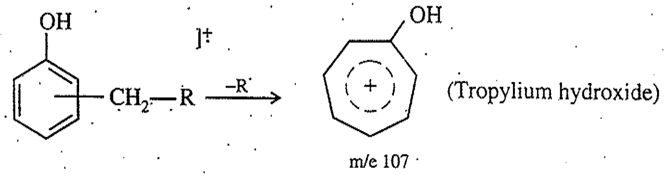
Fig. 7.20. Mass Spectrum of Phenol.



(*ii*) Consider the fragmentation modes in *p*-cresol.



In general,



7.15 Thiols and Thiophenols

A. Thiols : Some important features of the mass spectra of thiols are :

(*a*) The molecular ion peak in thiol is more intense than that in alcohols.

(*b*) Like alcohols, they undergo α-cleavage leading to the formation of ions in the series m/e 47, 61, 75... etc.

(*c*) Unlike alcohol, the elimination of H_2S in thiols is less important.

They involve the transfer of hydrogen atom from the third or fourth carbon atom down the chain to S–H group. The transfer from the fourth carbon is more likely as it involves a six membered ring intermediate.

(*d*) Thiols with five or more carbon atoms lose ethylene and H_2S in concerted the step to form [M — {$H_2C = CH_2 + H_2S$}] ion consider the mass spectrum of pentane-1-thiol.

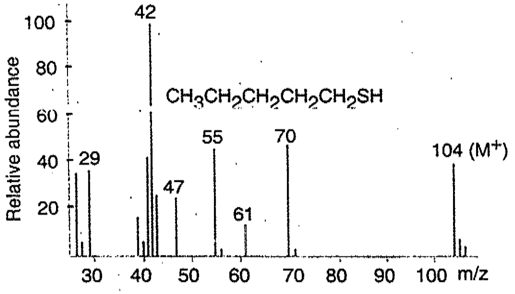
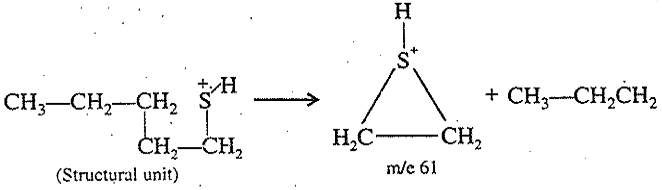


Fig. 7.21. Mass spectrum of I-pentanethiol..

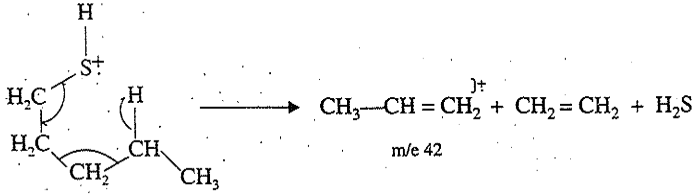
In this case, (*i*) the molecular ion peak is formed at m/e 104. (*ii*) The ion at m/e 47 is the result of α-cleavage. It also indicates that thiol is primary.

(*i*) $\underset{\text{Pentane-1-thiol }(M^{+}) \text{ m/e } 104}{CH_3—CH_2—CH_2—CH_2—CH_2—SH]^{+}} \longrightarrow \underset{\text{m/e } 47}{CH_2=\overset{+}{S}H}$

(*ii*) The peak at m/e 61 is due to an ion containing sulphur indicating the presence of following structural unit.



(*iii*) A base peak results due to the loss of ethene and H_2S



(B) Thiophenol. Some important features of the mass spectrum of thiophenols are :

(*a*) Thiophenol shows an intense peak at 110.

(*b*) The various ions formed during formentation include (*i*) M—H (m/e 109) (*ii*) [M—(HC≡CH)] (m/e 84), (M—SH) m/e 77 and [M—CS] m/e 66.

(*c*) The loss of hydrogen from the molecular-ion gives thiotropylium ion which then loses CS to form an ion at m/e 65.

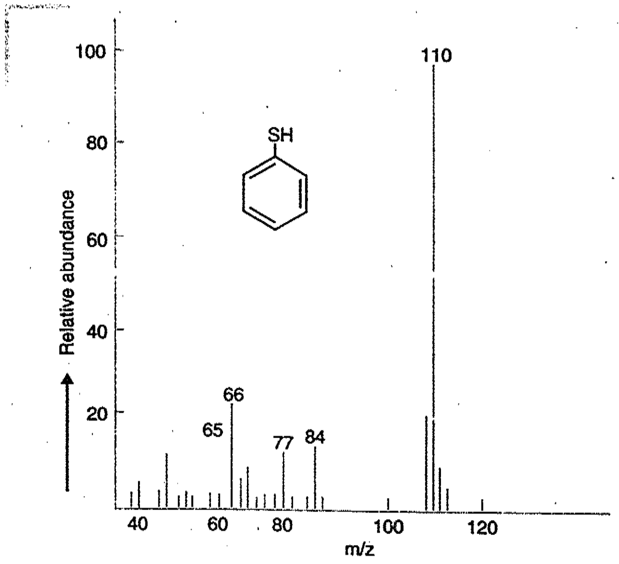
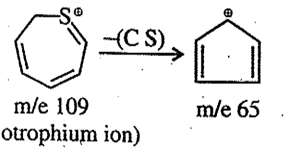
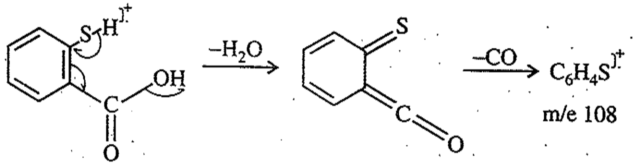


Fig. 7.22. Mass spectrum of Thiophenol.

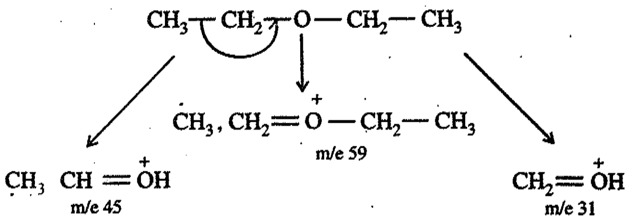


Note. In case of ortho substitution, say in thiosalicyclic acid, the ions are formed due to the elimination of water and carbon monoxide.



7.16 Ethers, Acetals and Ketals

(*i*) Aliphatic ethers show molecular ion peak almost of negligible abundance. The presence of oxygen atom in ethers can be known from strong peaks at m/e 31, 45, 59 etc. and these peaks represent $R\overset{+}{O}$ and $RO\overset{+}{C}H_2$ fragments. The most characteristic fragmentation mode is the loss of one of the alkyl groups to form an oxonium ion $(R\overset{+}{O})$ or the alkyl cation. The ions so formed is the result of α-cleavage. The ion may further fragment to lose an alkene and this step becomes important when α-carbon atom is substituted. Out of the two alkyl groups around the oxygen atom in ethers (ROR′), the longest or the bulkier group is preferentially lost. Consider the various fragmentation modes in diethyl ether.



The mass spectrum of isopropyl, *n*-pentyl ether is shown in figure (7.17).

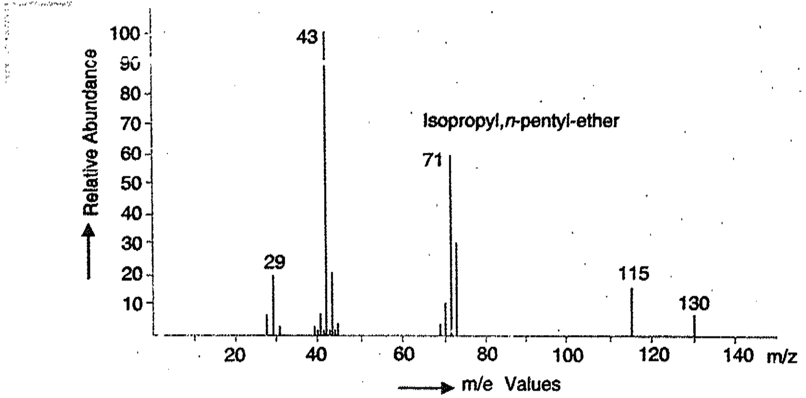
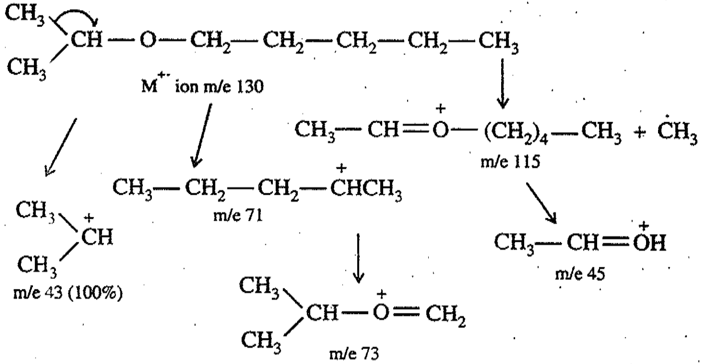
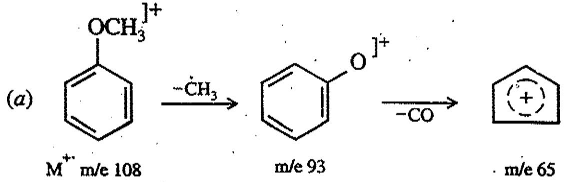


Fig. 7.23. Mass spectrum of Isopropyl, n-pentyl ether.

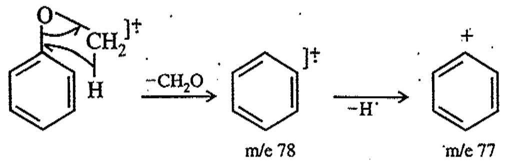
Its various fragmentation modes are :



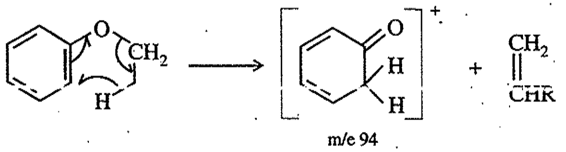
(*ii*) **Aryl Ethers.** In case of aromatic ethers, the molecular ion peak is fairly abundant. Methyl phenyl ethers show two main fragmentations. Primary fission occurs at the bond β- to the ring. Loss of methyl gives an ion M.–15. It further splits to lose carbon monoxide. The fragmentation pattern is shown below:



(b)



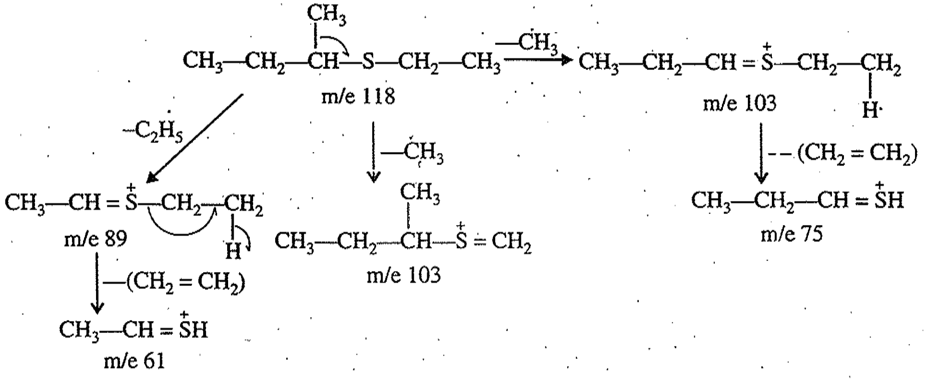
Also in general.



(*iii*) **Thioethers :** Some important features of the mass spectra of thioethers are :

- (*a*) The molecular ion peaks of thio-ethers are more intense than aliphatic ethers.
- (*b*) α-cleavage of C–S bond with positive charge on sulphur is the favoured mode of fermentation. The smallest alkyl chain is lost compared to the usual behaviour in which bigger chain is lost.
- (*c*) β-cleavage of the bond form $RCH{=}\overset{+}{S}H$ ions giving rise to peaks at m/e 46, 61, 75, 89.

Consider the fragmentation pattern in the mass spectrum of sec-butyl ethyl ether.



7.17 Aliphatic Aldehydes and Ketones

(*a*) **Aliphatic Carbonyl Compounds**

Some important features of the mass spectra of aliphatic aldehydes and ketones are:

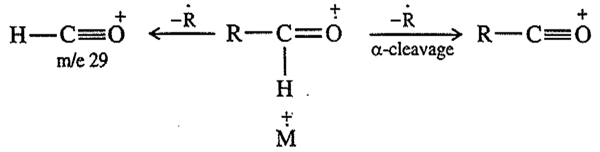
(*a*) The intensity of the molecular ion peak decreases as the alkyl chain length increases.

(*b*) The major fragmentation processes are α- and β-cleavage. In α-cleavage, the bigger group on either side of the carbonyl group (ketone) is preferably lost.

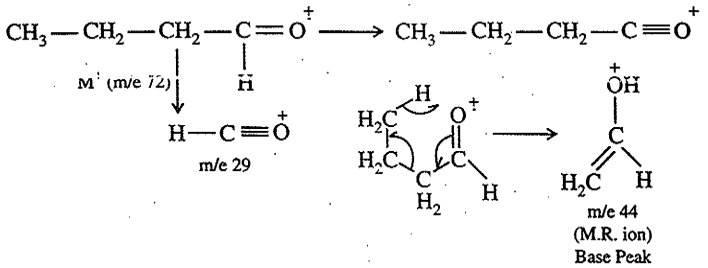
(*c*) In aldehydes and ketones containing γ-hydrogen atom, McLafferty rearrangement ion is most significant. In an aldehyde, which is not α-substituted, a peak due to this is formed at m/e 44. It may be base peak.

(*d*) The McLafferty rearrangement ion in methyl ketones which are not α-substituted appears at m/e 58 and is quite abundant.

(*e*) In lower aldehydes, α-cleavage is prominent with retention of charge on oxygen.



(*f*) In aldehydes, methyl or alkyl radical is preferably lost compared to hydrogen radical. Consider the various fragmentation modes of butanal.



Consider the mass spectrum of Pentanal.

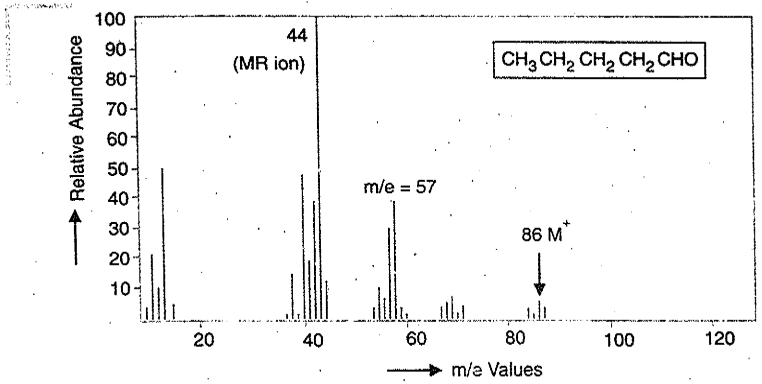
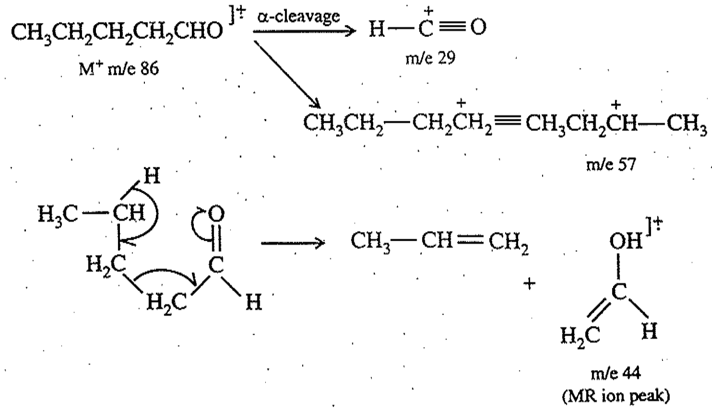


Fig. 7.24. Mass spectrum of Pentanal.

The various fragmentation modes of pentanal are :



Consider the mass spectrum of 3-pentanone.

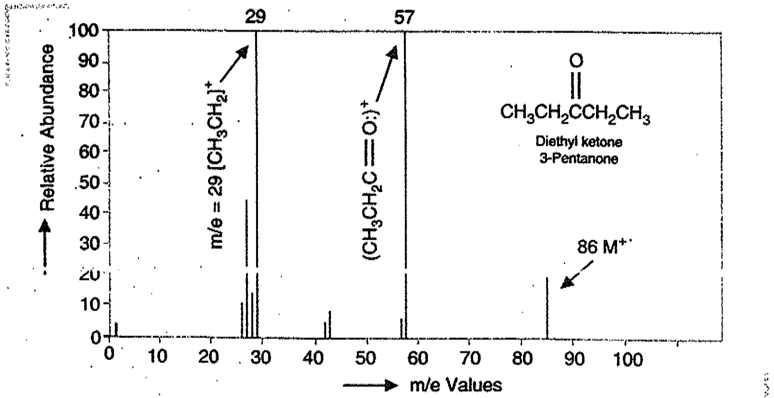
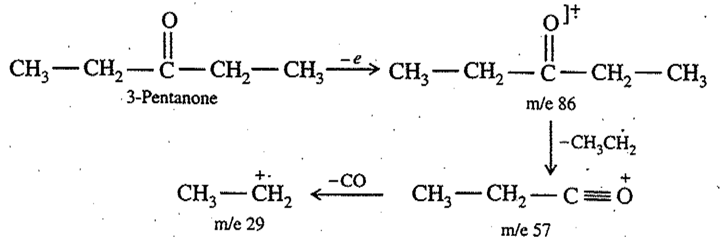


Fig. 7.25. Mass spectrum of 3-pentanone.

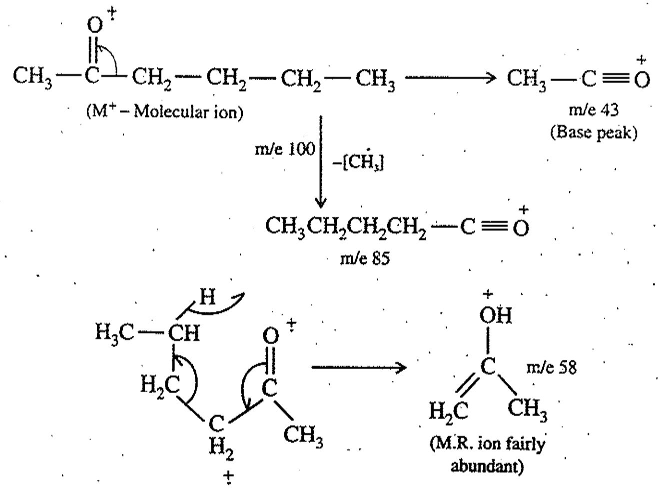
The various fragmentation modes in the spectrum of 3-pentanone are shown below :



$$\underset{\text{3-Pentanone}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3} \xrightarrow{-e} \underset{m/e\ 86}{CH_3-CH_2-\overset{\overset{O]^{+\cdot}}{\|}}{C}-CH_2-CH_3} \xrightarrow{-CH_3\dot{C}H_2} \underset{m/e\ 57}{CH_3-CH_2-C\equiv\overset{+}{O}} \xrightarrow{-CO} \underset{m/e\ 29}{CH_3-\overset{+\cdot}{C}H_2}$$

In 3-Pentanone there is no γ-hydrogen atom and thus, no McLafferty rearrangement ion peak is formed.

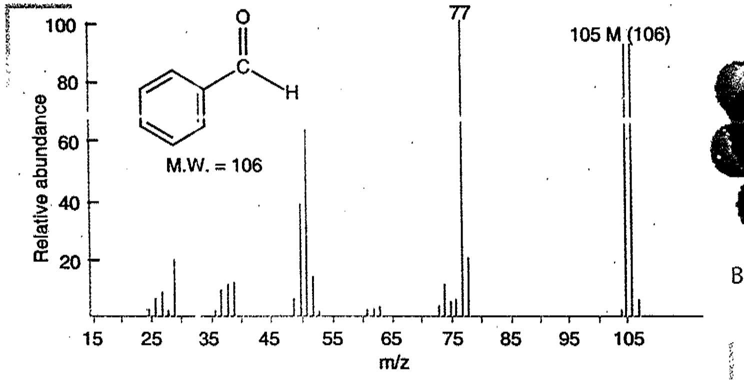
Consider the various fragmentation modes of 2-hexanone.

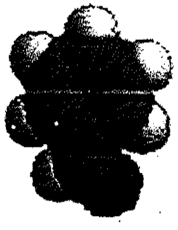


From the fragment ions draw the mass spectrum of 3-hexanone.

(*b*) **Aromatic aldehydes and ketones**

In these compounds, parent ion peak is intense. $\overset{+\cdot}{M}$—1, $\overset{+\cdot}{M}$—28 due to the elimination of CO in benzaldehyde are formed. Peak at m/e 77 due to $C_6H_5^+$ followed by the one at m/e 51 due to $C_4H_3^+$ also result. Consider benzaldehyde.



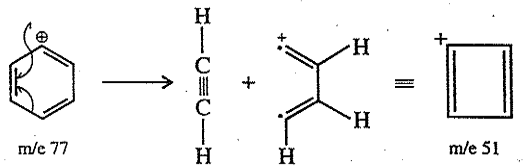


Benzaldehyde

Fig. 7.26 Mass spectrum of Benzaldehyde.

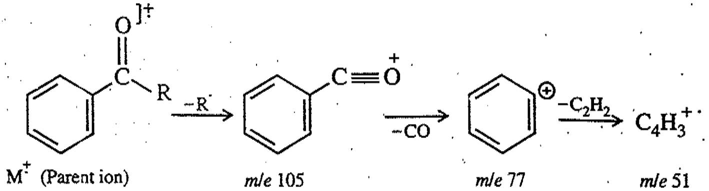
$$\underset{(M^{+\cdot}-1)}{C_6H_5-C\equiv\overset{+}{O}} \xleftarrow{-(\dot{H})} \underset{(M^{+\cdot})}{C_6H_5\overset{+}{C}HO} \xrightarrow{-(CO)} \underset{m/e\ 78}{C_6H_6^{+}} \xrightarrow{-(\dot{H})}$$

$$\underset{m/e\ 77}{C_6H_5^+} \xrightarrow{-(C_2H_2)} \underset{m/e\ 51}{C_4H_3^+}$$



In ketones, the loss of larger group is preferred by an α-cleavage.

Consider the fragmentation of alkyl phenyl ketone:



7.18 Cyclic ketones

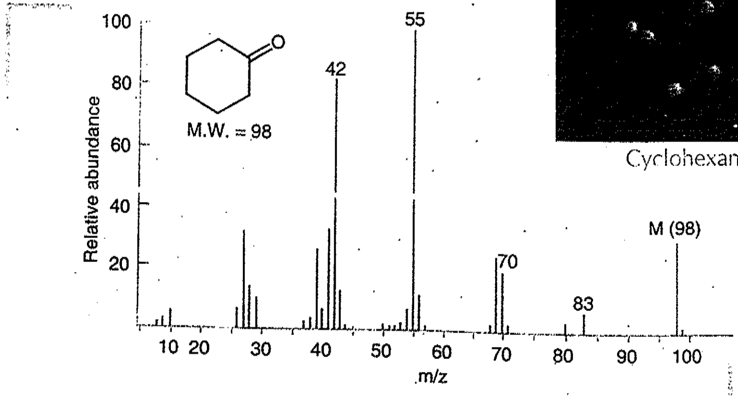
Some important features of the cyclic ketones are :

(*a*) The molecular ion peak of cyclic ketones is quite intense.

(*b*) A base peak in cyclopentanone or Cyclohexanone is formed by α-cleavage followed by hydrogen transfer rearrangement. A peak due to $CH_2{=}CH{-}C{\equiv}\overset{+}{O}$ is formed at m/e 55.

(*c*) Peaks are formed by the loss of ethylene, carbon monoxide molecules in fair abundance in case of cyclohexanone.

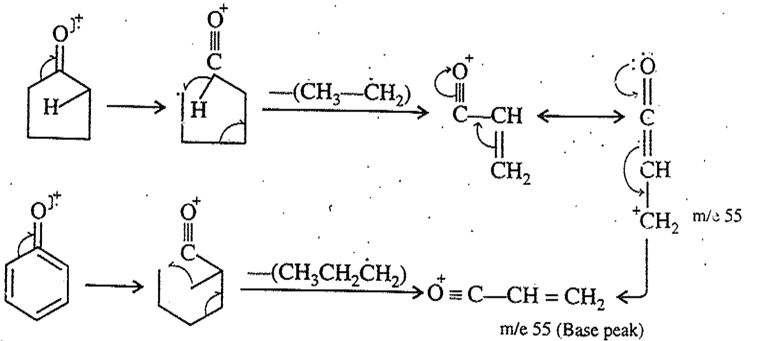
The mass spectrum of cyclohexanone is shown below :



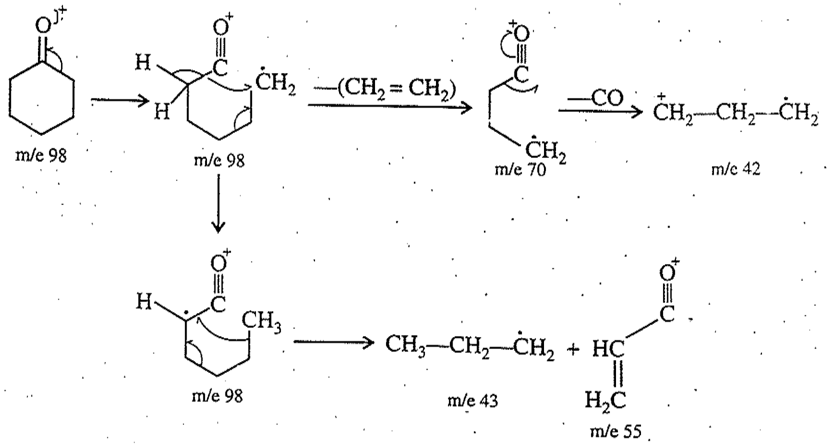
Cyclohexanone

Fig. 7.27. Mass spectrum of Cyclohexanone.

The fragmentation pattern in Cyclopentanone and Cyclohexanone are shown.



Significant peaks in Cyclohexanone are due to the following framentation modes :



7.19 Aliphatic and Aromatic Acids

(A) Aliphatic Acids : Some important features of the mass spectra of acids are:

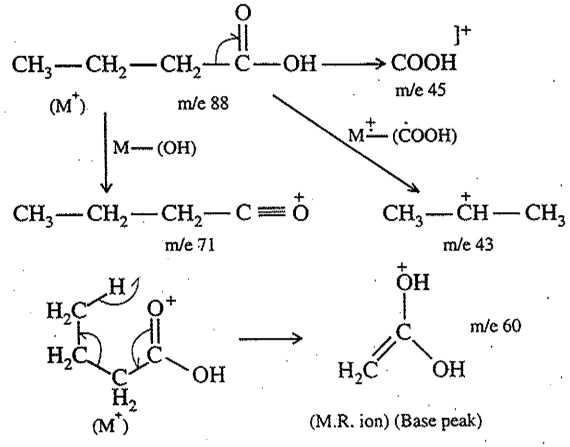
(*a*) The molecular ion peak in aliphatic acids is less intense as compared to that of aromatic acids.

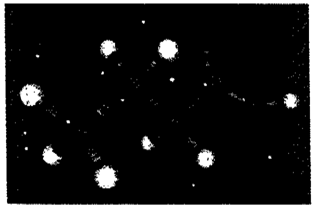
(*b*) Carboxyl group is directly eliminated by α-cleavage and a signal is formed at m/e 45.

(*c*) If α-carbon atom is not substituted in aliphatic acids containing a γ-hydrogen atom, a McLafferty rearrangement ion is formed at m/e 60. It is often the base peak.

(*d*) In short chain acids, $\overset{+}{M}$—OH and $\overset{+}{M}$—COOH peaks are prominent.

The various fragmentation modes in butanoic acid are :





Butanoic acid

Consider the mass spectrum of Pentanoic acid.

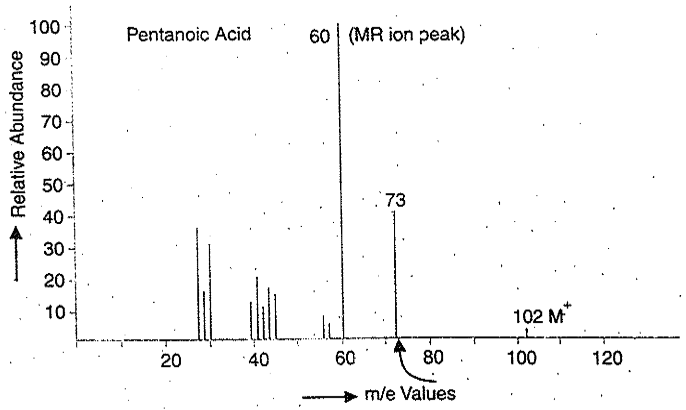
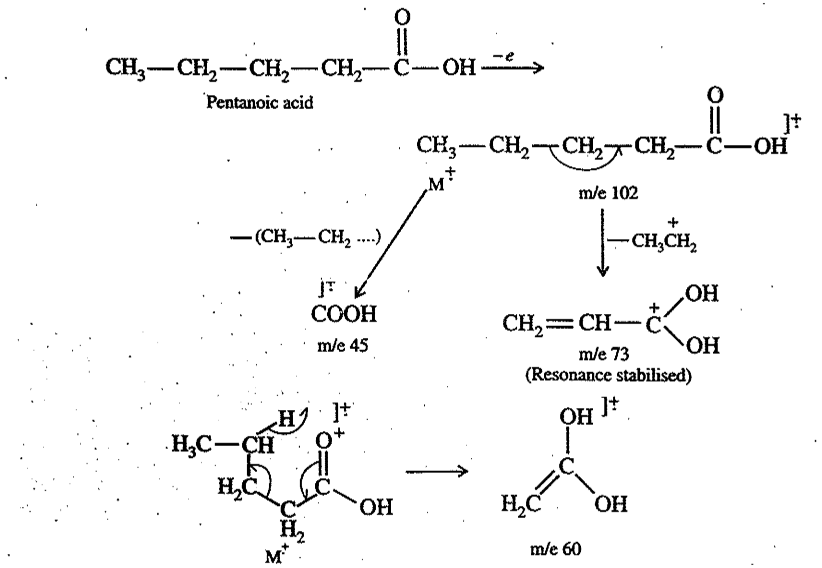
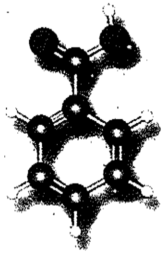


Fig. 7.28. Mass spectrum of Pentanoic acid.

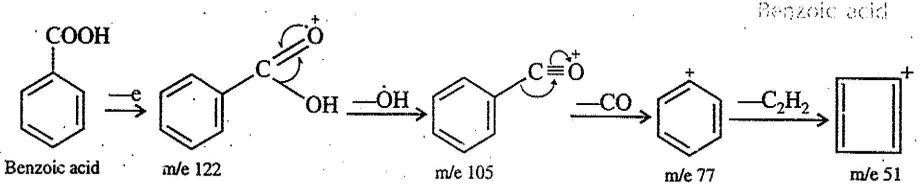
The various fragmentation modes of pentanoic acid are:



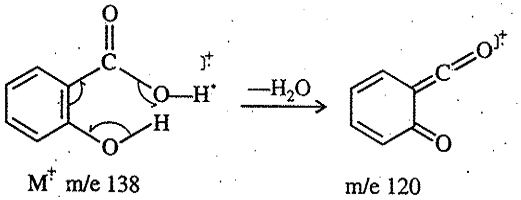
(B) **Aromatic acids.** In aromatic acids, the parent ion peak is intense. Some other prominent peaks are M — 17 and M —45. If an alkyl group is present or any other hydrogen bearing group is present ortho to —COOH group, then a signal due to M–18 (loss of water molecule) is also observed. It is called **ortho effect.**


Benzoic acid

Consider the various fragmentation modes in benzoic acid. In benzoic acid, (M⁺ – OH) peak is quite prominent. It is followed by another peak due to the loss of CO molecule. It appears at m/e 77. This in turn loses a molecule of acetylene.



When an aromatic acid is orthosubstituted, a water molecule gets eliminated from the molecular ion provided hydrogen atom is suitably located in the ortho group. Consider saticyclic acid.



7.20 Esters

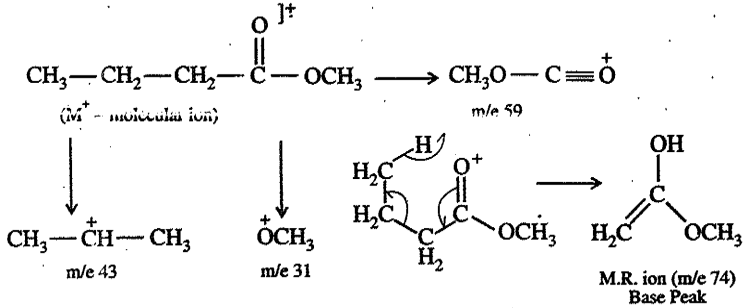
Some important features of the mass spectrum of esters are:

(*a*) The molecular ion peak is weak.

(*b*) The fragment ion due to α-cleavage is usually observed.

(*c*) In methyl esters, peaks due to R—CO⁺, R⁺, CH₂O⁺ and CH₃OCO⁺ (m/e 59) are observed.

(*d*) The methyl esters not substituted at the α-carbon atom show McLafferty rearrangement ion at m/e 74. Methyl substitution at a carbon atom shifts the position of McLafferty rearrangement peak at m/e 88. The various fragmentation modes of methyl butanoate are shown below:



(*e*) The molecular ion peak is comparatively more intense. Benzyl acetate and alkyl acetate eliminate neutral ketene molecule to form a base peak.

The mass spectrum of 1-propyl ethanoate is shown.

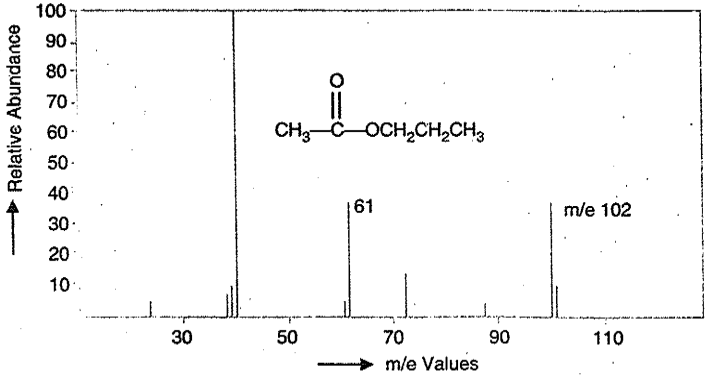
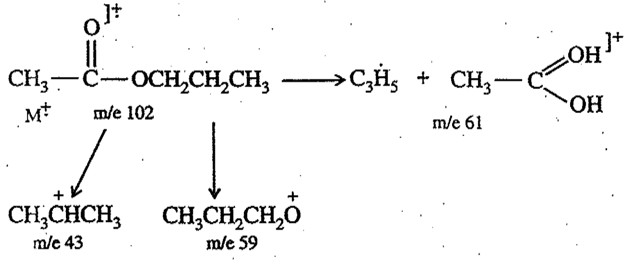
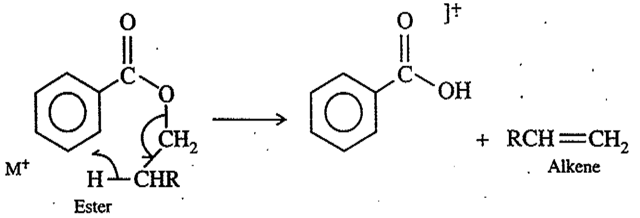


Fig. 7.29. Mass spectrum of n-Propyl ethanoate.

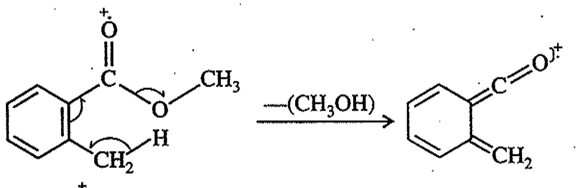
It can be distinguished from methyl butanoate by a peak at 61. It is due to McLafferty rearrangement ion.



In case of esters where alkyl group is ethyl or higher, alkene is usually lost.



In aromatic esters in which ortho position is occupied by an alkyl group, the hydrogen atom of alkyl group interacts with the ester function resulting in the elimination of an alcohol molecule. It is called ortho effect. This fragmentation mode is shown below :



M⁺ ion

7.21 Amides

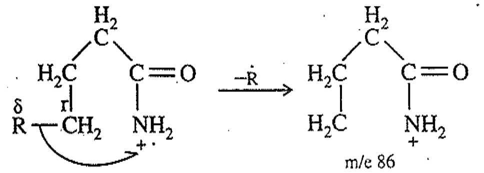
Some important features of the mass spectra of aliphalic amides are:

(i) The molecular ion peak of straight chain monoamides is usually discernible.

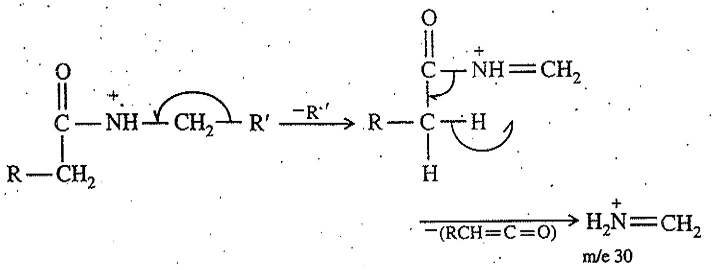
(ii) The McLafferty rearrangement peak in amides is usually the base peak.

(iii) The M.R. ion appears at m/e 59. Primary amides give a strong peak at m/e 44 due to $H_2N{-}C{\equiv}\overset{+}{O}$.

(iv) A moderate peak at m/e 86 results from γ δ-carbon-carbon cleavage, possibly accompanied by cyclisation.



(v) When the N-alkyl groups on C_2 are longer and the acyl moiety is shorter than C_3, another mode of cleavage predominates. This is the cleavage of the N-alkyl group beta to the nitrogen atom, and cleavage of the C—N bond with migration of an α-H atom of the acyl moiety.



(b) **Aromatic amides** : In aromatic amides, the parent or molecular ion peak is relatively intense. The primary fragmentation mode forms an aroyl cation which in turn loses a molecule of carbon monoxide.

Consider the mass spectrum of benzamide.

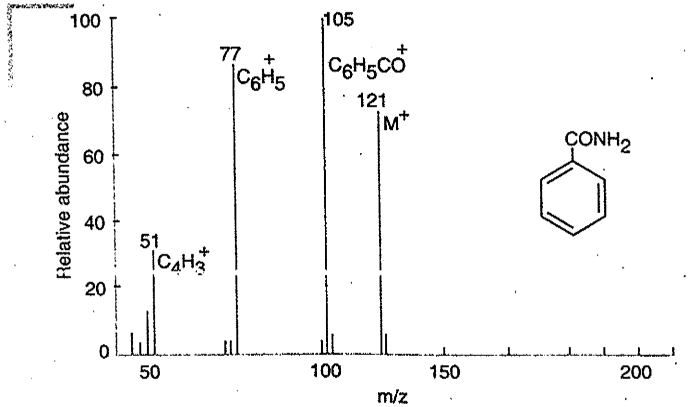


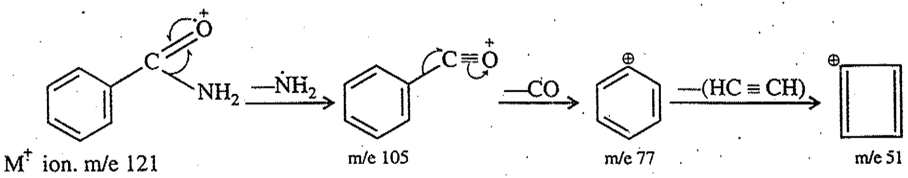
Fig. 7.30. Mass spectrum of Benzamide.

The various fragmentation modes as observed in the spectrum of benzamide are :

(i) Molecular ion peak is observed at m/e 121.

(ii) Benzoyl cation peak is observed at m/e 105 as the base peak.

(iii) Further loss of CO forms another peak at m/e 77 due to $C_6H_5^+$ ion which in turn loses a molecule of acetylene.



7.22 Halogen Compounds

Some important features of the mass spectra of halogen compounds are:

(a) The molecular ion abundance of a particular alkyl halide increases as the electronegativity of the halogen substituent decreases.

(b) The relative abundance of the molecular ion decreases with increase in chain length and increase in branching.

(c) Compounds containing chlorine and bromine show characteristic isotope peaks. A compound containing one chlorine atom shows M + 2 peak which is one third in intensity of parent peak.

(d) A monobromo compound shows (M + 2) peak which is of the same intensity compared to the parent peak.

(e) In the parent ion, charge resides on the halogen atom.

(f) Important fragmentation mode is α-cleavage with charge retention by the halogen containing fragment. Another mode leads to the loss of halide radical.

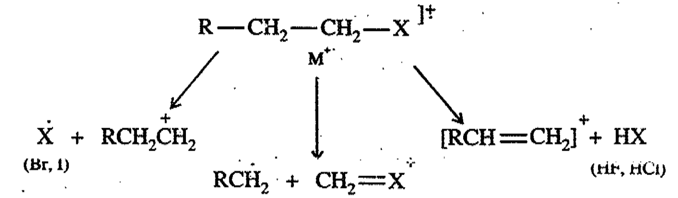
$$R{-}CH_2{-}\overset{+}{\dot{X}} \longrightarrow CH_2{=}\overset{+}{X} + R$$

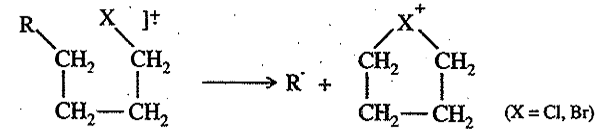
$$\underset{(M^+)}{R{-}CH_2{-}\overset{+}{\dot{X}}} \longrightarrow R\overset{+}{C}H_2 + X \text{ (Preferable mode)}$$

EXAMPLE. *In the mass spectrum of ethyl chloride, we observe (i) 64 (M^+), 66(M^+ + 2) [Intensity ratio 1 : 3] (ii) 29 (Base peak) (The loss of Cl radical is the preferable mode)*

EXAMPLE. *In the mass spectrum of ethyl bromide, CH_3CH_2Br, the peaks at m/e 108, 110 and m/e 79 and 81 are formed in equal intensity. The peak at m/e 29 due to the loss of Br radical is the base peak (100% abundance).*

Consider the fragmentation modes of *n*-alkyl halide.





The mass spectrum of 1-Bromohexane is shown below:

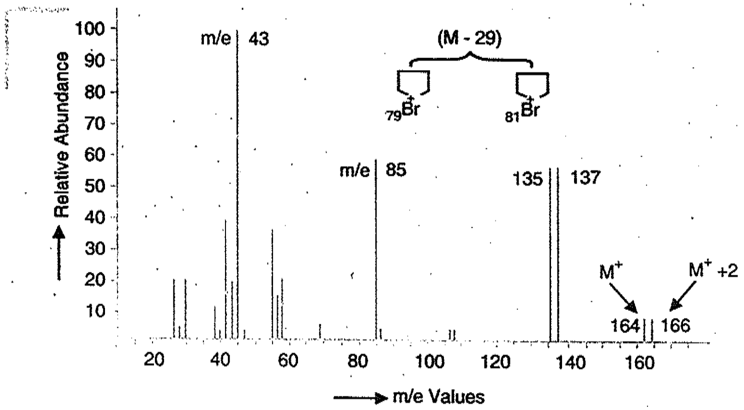
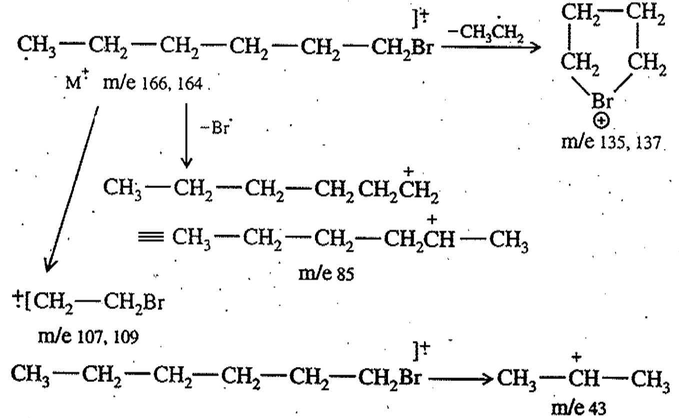


Fig. 7.31. Mass spectrum of 1-Bromohexane.

The various fragmentation modes of 1-Bromohexane are shown below:



Exercise : Draw the mass spectrum of Ethyl chloride and Ethyl bromide.

6.23 Amines

(*a*) Aliphatic Amines

Some important features of the mass spectra of aliphatic amines are described below:

(*a*) If the molecular ion is formed at the odd mass number, then the molecule carries an odd number of nitrogen atoms.

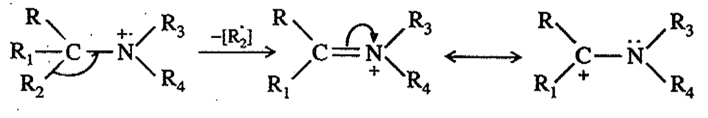
(*b*) The molecular ion peak in monoamines is formed in very small abundance and is undetectable in long chain or branched chain amines.

(*c*) For primary amines, the base peak is formed at m/e 30 due to $CH_2{=}\overset{+}{N}H_2$. It results from the molecular ion by α-cleavage.

(*d*) Higher homologues of amines may appear at m/e 44, 58, etc. but their relative abundance is much less.

(*e*) The parent ion may lose an alkene to form a fragment ion at $M^+{-}C_nH_{2n}$.

(*f*) Loss of largest branch from the α-carbon atom is preferred.



Here $R_2 > R_1$, or R

When R or R_1=H, then M^+—1 signal is formed. The same type of cleavage is also noted in case of alcohols. This effect is more pronounced due to the better resonance stabilisation of fragment ion as the electronegativity of nitrogen is less compared to oxygen.

(*g*) In higher aliphatic alkyl amines, β-cleavage is not very significant. γ-cleavage is sometimes preferred.

Consider the mass spectrum of Ethyl amine. The various signals alongwith their relative abundance are shown below:

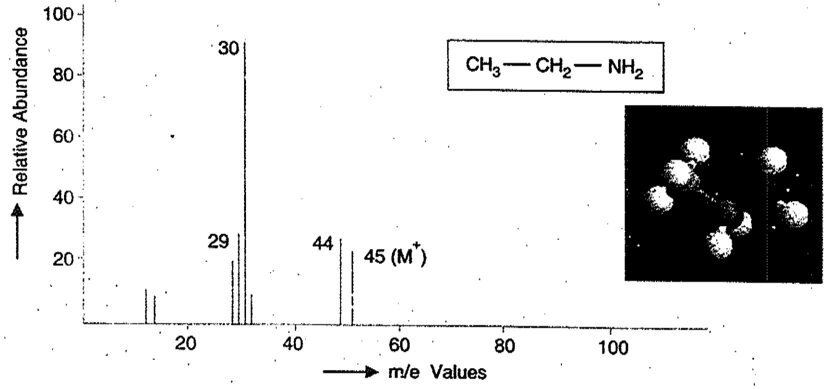
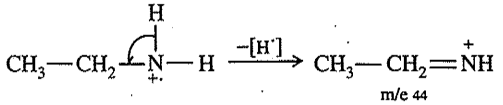


Fig. 7.32. Mass spectrum of Ethyl amine.

Here the molecular ion peak appears at m/e 45. The α-cleavage results in the formation of a base peak at m/e 30. The parent ion loses a hydrogen radical. The various fragmentation modes are shown below:

$$\underset{\substack{M^{+}\ (\text{Molecular ion})\\ m/e\ 45}}{CH_3-CH_2-\overset{+\cdot}{N}H_2} \longrightarrow \underset{m/e\ 30}{CH_2=\overset{+}{N}H_2}$$



$$CH_3-CH_2-\overset{H}{\underset{+\cdot}{N}}-H \xrightarrow{-[H^{\cdot}]} \underset{m/e\ 44}{CH_3-CH_2=\overset{+}{N}H}$$

In amines, a hydrogen radical is lost from the parent ion to give M^+ —1 peak (see rules above). In higher aliphatic amines, β-cleavage is not very significant. γ-cleavage is sometimes preferred.

Note. A peak at m/e 30 is a good but not the conclusive evidence for a straight chain primary amine. The fragmentation of the parent ion formed from secondary and tertiary amine leads to a peak at m/e 30, 44, 58, 72 ....

(*b*) **Aromatic amines.** In aromatic primary amines, a parent ion is formed by the loss of one electron from the lone pair present on the nitrogen atom.

The elimination of hydrogen radical and HCN molecule are very common from the parent ion. Thus, in primary aromatic amines, M^+ –1, M^+ –27 signals are often observed. The elimination of 27 mass units give a signal due to cyclopentadienyl cation. For N-alkyl amines, α-cleavage of the alkyl group is common.

Consider the mass spectrum of aniline.

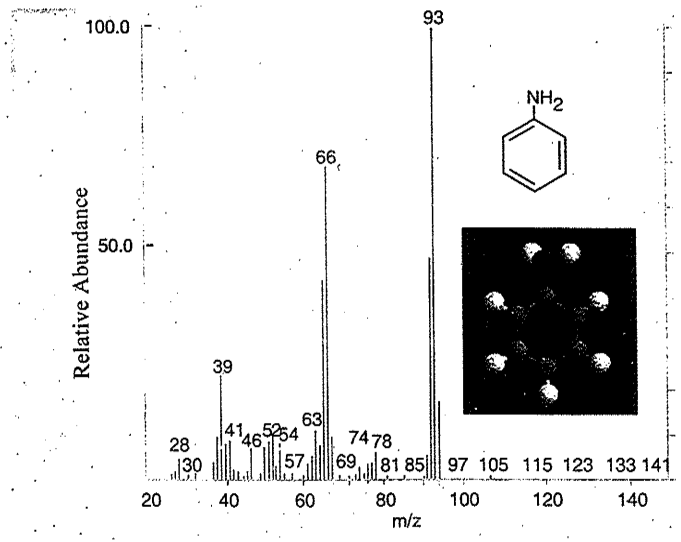
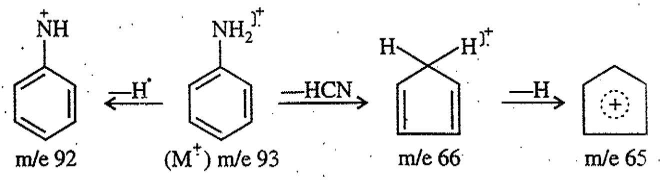
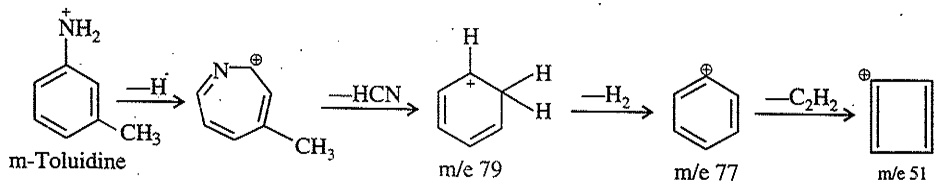


Fig. 7.33. Mass spectrum of Aniline..

The various fragmentation modes in aniline are :



Note. In case of toluidines (*o*, *m* or p-toluidine), the molecular ion loses hydrogen to form a base peak at m/e 106 which further lose a molecule of HCN. In fact, toluidine loses, hydrogen atom to form azatropylium ion at m/e 106.



6.24 Nitro Compounds

Some important features of the mass spectra of nitro compounds are as follows:

(*a*) The molecular ion peak in aliphatic nitro compounds is usually absent but it is prominent in aromatic compounds.

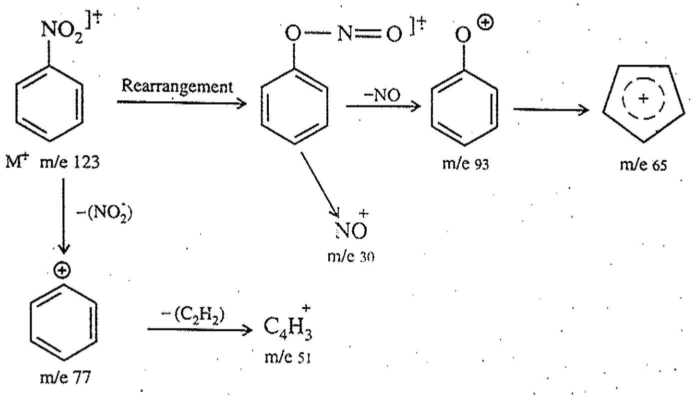
(*b*) In aliphatic compounds, the signals due to $\overset{+}{N}O$ and $\overset{+}{N}O_2$ are usually observed.

(*c*) In aromatic nitro compounds, the signals for $\overset{+}{N}O$, $\overset{+}{N}O_2$, $[M—NO]^+$, $[M—NO_2]^+$ are commonly observed.

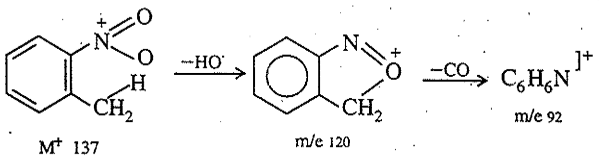
(*d*) If a hydrogen containing group is also present ortho to the nitro group, then M—OH peak is also observed.

For Aromatic nitro compounds, the molecular ion peak appears at odd mass number for one nitrogen atom and is fairly strong. Also strong characteristic peaks are observed by the elimination of nitro radical ($NO_2^{\cdot}$) and also nitrosonium radical ($NO^{\cdot}$) is lost forming phenoxy cation.

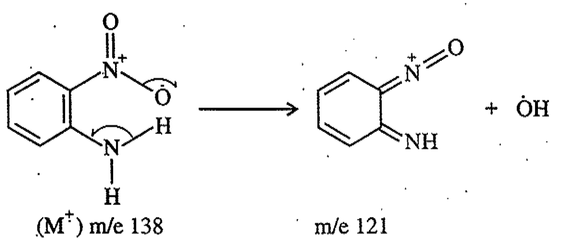
Consider the fragmentation modes in nitrobenzene.



When a substituent is present in the meta or para position, the fragmentation modes are similar to those as observed in nitro benzene. But when the substituent is present in the ortho position, then it interacts with the nitro group as follows:



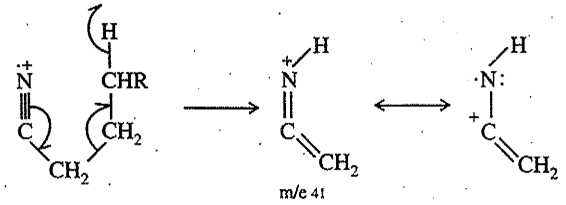
Similarly, consider the fragmentation in ortho nitroaniline.



7.25 Aliphatic Nitriles

Some important features of the mass spectra of aliphatic nitriles are:

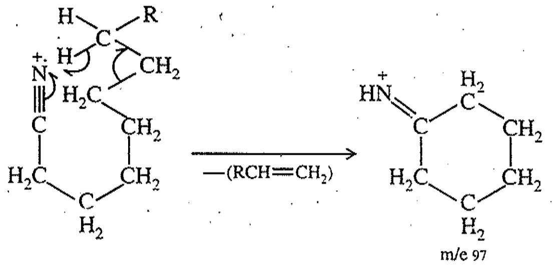
(*i*) The molecular ion peak of aliphatic nitriles is weak or may be absent.



(*ii*) A weak but diagonistically useful (M–1) peak is formed by the loss a α-hydrogen atom to form a stable ion.

(*iii*) The base peak of straight chain nitriles between C_4 and C_9 is m/e 41. This peak is due to the ion resulting from hydrogen rearrangement in a six membered transition state.

(*iv*) A peak at m/e 97 is characteristic and intense in straight chain nitriles C_8 and higher. The following mechanism has been suggested.



7.26 Important Features in Mass Spectroscopy

1. Mass spectrophotometer gives a record of the relative abundance of ions according to the m/e ratio.
2. Molecular ion peak is not generally visible in case of alcohols.
3. A peak corresponding to the ion of maximum abundance is called the base peak.
4. The molecular ion or the parent ion peak may or may not be the base peak. Usually, it is not. The molecular ion has usually the highest m/e value in the spectrum and its m/e value is equal to the molecular mass of the compound. M + 1 and M + 2 peaks also appear in very low abundance and are called isotope peaks.
5. The molecular ion is usually not much stable and tends to fragment. The fragmentation of molecular ion produce daughter ions of definite m/e value which help in structure determination.

6. In McLafferty rearrangement, an alkane molecule is lost in a cyclic rearrangement with γ-hydrogen.
7. The intensity of M + 1 peak is valuable to know the number of carbon as well as nitrogen atoms. In case nitrogen is absent, the number of carbon atoms can be calculated by dividing the relative intensity of M + 1 peak by 1.1.
8. In a typical case, if M + 2 peak of the parent ion looks larger than the M + 1 peak, the compound may contain Sulphur, Chlorine or bromine atom.
9. If a compound contains chlorine atom, then pair of peaks are obtained at two mass units apart in the intensity ratio 1 : 3. But in case, bromine atom is present, then pair of peaks at two mass unit apart are of equal intensity.
10. The most intense peak in the mass spectrum is called the **base peak.** Its relative intensity or abundance is taken as 100 and the intensities of other peaks, including the parent peak are expressed as percentage of parent peak.
11. Mass to charge ratio (m/z) is a dimensionless ratio of the mass number of the given particle to the number (z) of the charge carried by the particle. Usually the particle is singly charged and the ratio is often expressed as m/e. Doubly charged particle are insignificant in the mass spectra of organic compounds. But the peak corresponding to stable doubly charged ions may be sometimes useful.
12. The relative abundance (RA) of the given ion tells its intensity relative to the base peak which is the most intense peak in the spectrum.
13. Fragmentation of the molecular ion occur by the cleavage of bonds in two ways *i.e.*, heterolytic or homolytic.

    Heterolytic cleavage is designated by the arrow (↷) to denote the transfer of a pair of electrons in the direction of the charged site as shown below:

    $$R{-}CH_2{-}\overset{+\cdot}{\ddot{Cl}}: \longrightarrow R\overset{\oplus}{C}H_2 + :\ddot{Cl}:$$

    Hemolytic cleavage is designeted by the fishhook arrow (↼) to denote the transfer of the single electron as shown below.

    $$R{-}CH_2{-}\overset{+}{\dot{C}H}{-}\dot{C}H_2 \longrightarrow R' + CH_2{=}\overset{+}{C}H{=}CH_2$$
14. Metastable ions are generally broader than the normal peaks and also these are of low abundance. Moreover, these ions do not necessarily occur at the integral m/e values.
15. According to **Even electron rule,** an even electron species will not normally break into two odd electron species because the total energy of this product mixture would be too high. In such a case, an ion degrades to another ion and a neutral molecule. For example.

    $A^+ \longrightarrow B^+ + N$ (Most likely)

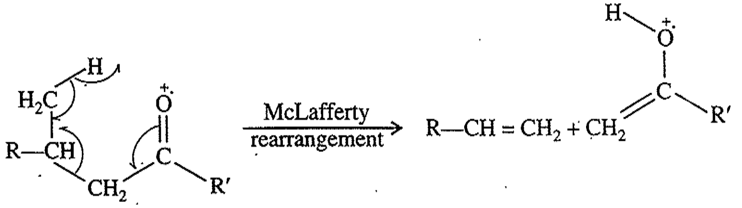
    (Even electron species)

    $A^+ \longrightarrow B^{+\cdot} + \dot{N}$ (Less probable)

    But the radical ions (odd electron species) fragment by the loss of radicals or even electron molecules. Thus,

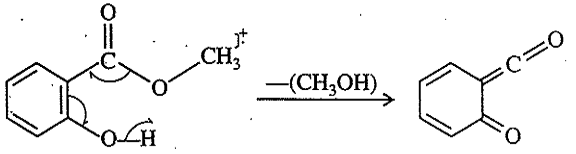
    $A^{+\cdot} \longrightarrow B^+ + \dot{C}$

    $B^{+\cdot} \longrightarrow C^{+\cdot} + N$ (Where N stands for any neutral molecule)
16. McLafferty rearrangement involves β-cleavage of a bond with γ-hydrogen rearrangement to form a cation radical and a neutral molecule. This rearrangement is meant for compounds, containing γ-hydrogen with respect to a multiple bond.



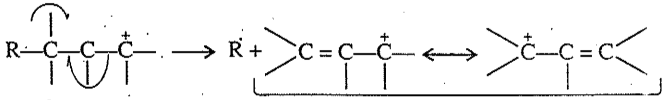
(Molecular ion) (Neutral fragment) (Fragment ion)

In case. ester. acid etc are orthosubstituted. then a loss of alcohol or water takes place through a six membered transition state. It is an ortho effect. Consider the following fragmentation mode.



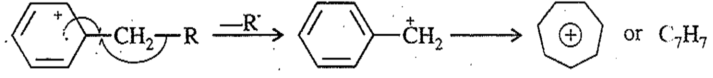
m/e 152 m/e 120

17. Allylic cleavage involves a cleavage of carbon- carbon bond, beta to double bond. This type of cleavage is more likely because of the resonance stabilisation of allyl cation. This type of fragmentation mode can be explained as the basic of homolytic fission induced by a radical site.



Resonance stabilisation

18. Benzylic cleavage involves the cleavage of carbon-carbon bond beta to aromatic ring. It is an energetically favourable fragmentation mode and is shown below:



m/e 91 Tropylium ion

19. An important factor which governs the mass spectral pathway is the stability of ions, radicals or neutral molecules formed as a result of fragmentation of molecular ion. The most prominent peaks in the mass spectrum should correspond to the most stable fragment ions. The relative abundance of an ion depends upon its (*i*) stability (*ii*) rate of formation and (*iii*) rate of further decomposition.

20. McLafferty rearrangement peak in case of unsubstituted aidehydes appears at m/e 44, that for ketone at m/e 58, for acids at m/e 60 and for methylesters at m/e 74.

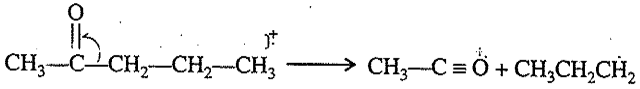
21. According to nitrogen rule when a molecule or ion contains an odd number of nitrogen atoms, it will have an odd mass number. When the molecule is devoid of nitrogen or contains an even number of nitrogen atoms, then the mass number of the molecule will be even. In other words, a species with zero or even number of nitrogen atoms, odd electron ions will have an even mass number and vice-versa.

22. In case of primary alcohols, a prominent peak with high relative abundance is also due to (M–H_2O) ion.

7.27 Simple Problems on Mass spectroscopy

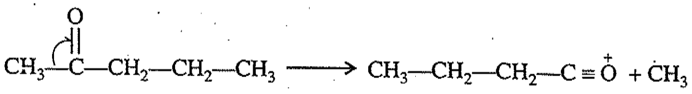
1. Predict the structure of the compound whose peaks in the mass spectrum have m/e values 86, 71, 58, 43 (100%)

SOLUTION. The peak at m/e 86 appears to be the molecular ion peak. Thus, the molecular mass of the compound is 86. The peak at m/e 58 is the McLafferty rearrangement peak for ketones which contain a γ-Hydrogen atom. Thus, the probable structure is Pentan-2- one. The various fragmentation mode, are shown below:



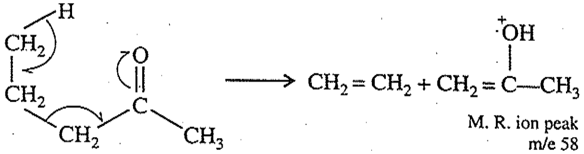
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3^{+\cdot} \longrightarrow CH_3-C\equiv\overset{+}{O} + CH_3CH_2\dot{C}H_2$$

m/e 43 (Intense)



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH_2-CH_2-C\equiv\overset{+}{O} + \dot{C}H_3$$

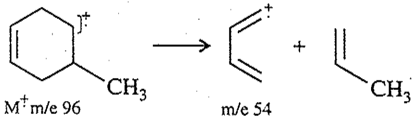
m/e 71 (less abundant)



M. R. ion peak m/e 58

2. A hydrocarbon with molecular mass C_7H_{12} (M^+ at m/e 96) shows large peaks at m/e 54 and due to M–15. What structure can be assigned to the compound ?

SOLUTION. Compared to saturated hydrocarbon (C_7H_{16}), the given compound (C_7H_{12}) is deficient of four hydrogen atoms. A large (M–15) peak points to the presence of branched methyl group. As the compound is hydrocarbon, the peak at m/e 54 is due to C_4H_6 which is nothing but butadiene. The parent hydrocarbon appears to be cyclic alkene with a branched methyl group. The most likely structure of the compound is 4-methyl cyclohexene. The fragmentation mode is shown below:



M^+ m/e 96 m/e 54

The elimination of butadiene is the result of retro-Diels Alder reaction.

3. What is the most characteristic feature of the mass spectra of compounds containing one bromine atom.

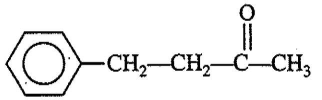
SOLUTION. A compound which contains one bromine atom exhibits a pair of peaks of almost equal intensity and the peaks are 2 mass units apart. It is due to equal abundance of ^{79}Br and ^{81}Br isotopes.

4. Predict the structure of the organic compound which exhibit m/e peaks at 15, 43, 57, 91, 105 and 148 in its mass spectrum.

SOLUTION. The peak at m/e 148 appears to be the molecular ion peak. Thus, the molecular mass of the compound is 148.

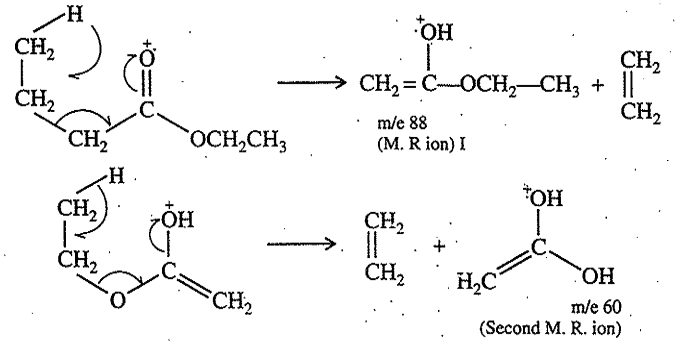
The peak at m/e 15 is due to methyl group and that at m/e 43 may be due to CH_3CO-group.

A prominent peak at m/e 91 is clearly due to benzyl group ($C_6H_5CH_2^+$) which rearranges to most stable tropylium cation. Adding CH_2 to benzyl unit, a peak at m/e 105 should be due to $C_6H_5CH_2\overset{+}{C}H_2$. Combining all these units, the most likely structure of the organic compound is :



5. Ethyl butanoate shows two characteristic peaks in its mass spectrum due to odd electron ions at m/e 88 and 60 and an abundant ion at m/e 71. Explain the fragmentation.

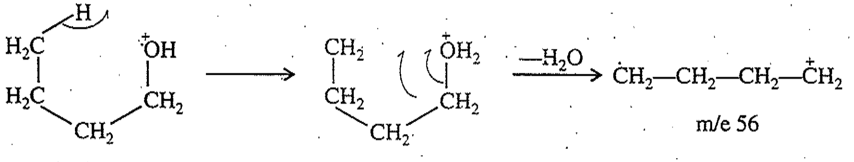
SOLUTION. It is known that methyl ester which is not α-substituted exhibits Mclafferty's rearrangement peak at m/e 74. Since a peak is formed at m/e 88, the ester can be ethyl butanoate or methylbutanoate with methyl group at α-position. Thus, m/e 88 is the result of McLafferty rearrangement.



6. How will you distinguish between the isomeric alcohols with molecular formula $C_4H_{10}O$ by mass spectroscopy?

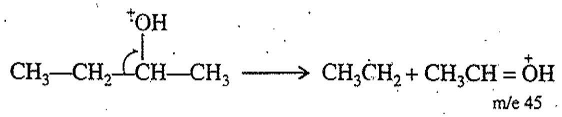
SOLUTION. The Isomeric alcohol, of molecular formula $C_4H_{10}O$ are primary, secondary and tertiary alcohols.

(*a*) In primary alcohol, $CH_3–CH_2CH_2CH_2OH$, the base peak results by the loss of water molecule and it appears at m/e 56 as below:



(M^+ ion)

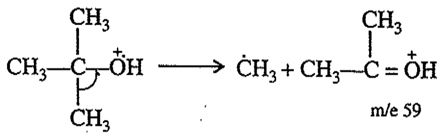
(*b*) In secondary alcohol, $CH_3CH(OH)\ CH_2CH_3$, a base peak is formed at m/e 45 by the loss of ethyl radical.



$$CH_3—CH_2—\underset{}{\overset{\overset{+}{O}H}{CH}}—CH_3 \longrightarrow CH_3\dot{C}H_2 + CH_3CH=\overset{+}{O}H$$

m/e 45

(*c*) In tertiary alcohol, $(CH_3)_3$ C–OH, the base peak is formed at m/e 59 by the loss of methyl radical.

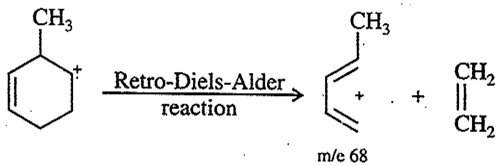


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\overset{+}{O}H \longrightarrow \dot{C}H_3 + CH_3—\overset{CH_3}{C}=\overset{+}{O}H$$

m/e 59

7. How can you distinguish between 3-methyl and 4-methyl cyclohexene on the basis of mass spectroscopy?

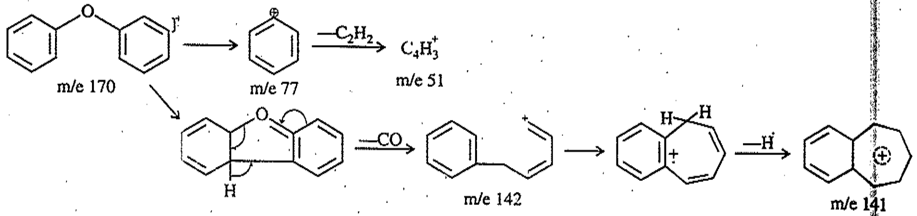
SOLUTION. It is known that in cyclic alkenes, a retro-Diels-Alder reaction gives, a charged diene fragment and neutral ethylene molecules. Clearly, the m/e value of diene gives a useful information about the position of the double bond. 3-Methyl cyclohexene gives a diene fragment as shown below:



4-Methyl cyclohexene does not form a diene fragment.

8. Describe the various fragmentation mode, of diphenyl ether.

SOLUTION. In diphenyl ether, the peak due to the ion formed by the loss of carbon monoxide is quite prominent. The various fragmentation modes are shown:



7.27 Short Questions with Answer

1. **Define mass spectroscopy.**

Ans. In mass spectroscopy, the vapours of the substance are bombarded with energetic electrons. The molecular ion and fragment ions are formed which are separated according to their m/e ratio. Mass spectrum of a substance is a plot between m/e values of the ions versus relative abundance.

2. **What do you mean by the base peak ?**

Ans. The most intense or the abundent peak in the mass spectrum of the compound is called the base peak.

3. **Name some compounds in which the molecular ion peak is not often visible.**

Ans. In case of alcohols, especially, tertiary alcohols and also in case of highly branched compounds, the molecular ion peak or the parent peak is not often visible.

4. **What do you know about M^+ and $M^{+\cdot}$ ion ?**

Ans. $M^{+\cdot}$ is called the parent ion radical when the neutral gaseous molecule of the substance loses an electron.

$$M(g) + e \longrightarrow M^{+\cdot} + 2e.$$

All the organic compounds are even electron species. M^+ ion is a cation which is trivalent carbon less one electron pair bond.

5. **How a molecular ion is a powerful tool for structure determination ?**

Ans. The molecular ion of an organic compound is no longer stable and thus tends to fragment. The various fragment ions formed are studied in the form of their m/e values against their relative abundances which provide an excellent tool for structural determination of the compound.

6. **Do all the bonds in a molecular ion undergo fission ?**

Ans. No. All the bonds in a molecular ion do not undergo fission. Some bonds break rapidly while others do not. The reason is that 70 ev energy may not be sufficient to break all the bonds.

7. **At what pressure, the vapours of the given sample are introduced in the mass spectrometer? Explain.**

Ans. The vapours of the substance under examination are introduced at low pressure ($10^{-5} - 10^{-6}$ mm) in the spectrometer. The reason is that it is necessary to minimise the collisions between ions and the un-ionised molecules. Such collisions produce new ions which are difficult to interpret in the spectrum.

8. **What is the most characteristic feature of compounds containing one bromine atom? Do fluorine and iodine containing compounds show the same feature in their mass spectra ? Give reasons.**

Ans. The compound containing one bromine atom gives a pair of peaks of equal intensity separated by two mass units. The reason is that the isotopes ^{79}Br and ^{81}Br occur in equal abundance (ratio 1:1). Fluorine and iodine do not have isotopes and thus M + 2 peak is not observed when fluorine or iodine atom is present in the compound.

9. **What do you understand by Nitrogen rule ?**

Ans. According to this rule, a molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms. An odd numbered molecular mass requires an odd number of nitrogen atoms.

10. **Describe the importance of metastable peaks.**

Ans. The metastable peaks in the mass spectrum greatly contribute in structure elucidation. From the position of the parent ion and the daughter ion, the position of the metastable ion is calculated and confirmed in the spectrum under examination. Metastable peaks are broadened and less intense. The most likely reason for this is that some of the excitation energy leading to bond capture may be converted into additional kinetic energy.

11. **Predict the relative abundance of the parent ion in case of (*i*) Propane and (*ii*) *n*-Pentane.**

Ans. The relative abundance of propane is more than that of *n*-Pentanes. The abundance of the molecular ion peak can be increased with respect to the abundance of fragment ions by running the spectrum at low ionisation potential, *i.e.*, by bombarding low energy electrons.

12. **What is McLafferty rearrangement ?**

Ans. The loss of an alkene fragment by a cyclic rearrangement of a carbonyl compound with γ-hydrogen is termed as McLafferty rearrangement.

13. **What is typical in the mass spectrum of a compound containing (*i*) one bromine atom (*ii*) one chlorine atom?**

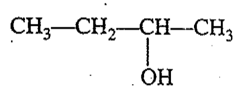
Ans. In the mass spectrum of such a compound, pairs of peaks are formed for the molecular ion and the fragment ions at two units apart with a relative abundance equal to 1:1. Similarly, peaks are seen for a compound containing one Cl– atom but with a relative abundance of 3:1.

14. **How will you distinguish three isomeric butanols on the basis of mass spectrometry ?**

Ans. The isomeric butanols are :

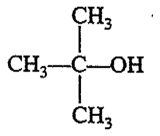
$CH_3CH_2CH_2CH_2OH$

Butan-1-ol
(1°-)
(*i*)



$CH_3—CH_2—CH(OH)—CH_3$

Butan-2-ol
(2°-)
(*ii*)

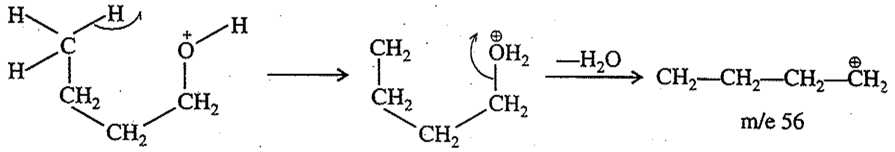


$CH_3—C(CH_3)_2—OH$

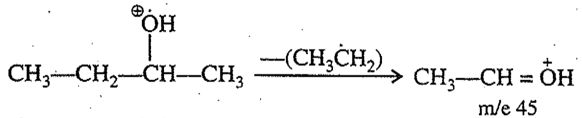
2-Methyl propan-2-ol
(3°-)
(*iii*)

In such alcohols, the m/e value for the base peak easily distinguishes the Isomeric butanols.

(*i*) In Butan-1-ol, the base peak is formed at m/e 56 by the loss of water molecule.

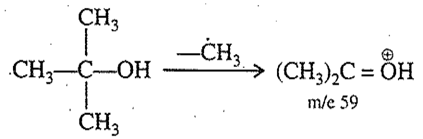


(*ii*) In butan-2-ol, the base peak is formed at m/e 45 which is formed by the loss of ethyl radical.



$$CH_3—CH_2—\overset{\oplus\cdot}{\underset{|}{OH}}\!\!\!\!\!CH—CH_3 \xrightarrow{—(CH_3\dot{C}H_2)} \underset{m/e\ 45}{CH_3—CH=\overset{+}{O}H}$$

(*iii*) In 2-methyl propan-2-ol the base peak is formed at m/e 59 by the loss of $\dot{C}H_3$ radical.



$$CH_3—C(CH_3)_2—OH \xrightarrow{—\dot{C}H_3} \underset{m/e\ 59}{(CH_3)_2C=\overset{\oplus}{O}H}$$

15. **Describe some special features of amines which help to identify them.**

Ans. Some of the special features are :

(*i*) An odd molecular mass of the compound indicates the presence of nitrogen atom.

(*ii*) Since amines have the tendency to capture protons. Thus, a (M + 1) peak shows increase in intensity if the pressure of the ion source is increased.

(*iii*) If the amine is present in the form of a salt, it does not volatilise in the mass spectrometer but docompose to give a free amine and acid. In case the acid component is HCl or HBr, then strong peaks at m/e 36 and 38 for HCl and m/e (80 and 82) for HBr are obtained. It may be noted that in case Cl or Br is present in the organic compound, then the pair of peaks are not formed in such intensity.

16. **Predict the postions of McLafferty rearrangement peaks for unbranched aldehydes and acids containing γ-hydrogen atom.**

Ans. The McLafferty rearrangement peak for an unbranched aldehyde appears at m/e 44 and that of unbranched acid at m/e 60.

17. **Which is the most abundant or the base peak in the mass spectrum of toluene ?**

Ans. The base peak in the mass spectrum of toluene appears at m/e 91. It is due to the formation of benzyl cation which at once gets rearranged to most stable tropylium cation ($C_7H_7^+$ ion).

18. Predict about the most intense peaks which appear in case of straight chain and branched chain alkanes.

Ans. The most intense peaks for the straight chain and branched chain \alkanes appear at m/e 43 and m/e 57due to $C_3H_7^+$ and $C_4H_9^+$ ions. The relative abundance of parent ion peak decreases with the increase in the chain length. In case of branched chain, the parent ion peak is not observed.

19. What do you say about the molecular ion peak in the mass spectrum of alcohols ? Which peak is of largest abundance in primary alcohols ?

Ans. The molecular ion peak of primary and secondary alcohol is usually of low abundance and it is undetectable in tertiary alcohols. In primary alcohols, the signal at m/e 31 appears in large abundance. This signal corresponds to the formation of oxonium ion ($CH_2{=}\overset{+}{O}H$).

20. How will you characterise a primary amine by means of a mass spectrum ?

Ans. The molecular ion peak is formed at the odd number and also for the primary amine, the base peak apears at m/e 30 due to $CH_2{=}\overset{+}{N}H_2$. It results from the molecular ion by α-cleavage.

21. How would you distinguish between Ethylamine, diethylamine and triethylamine on the basis of mass spectoscopy ?

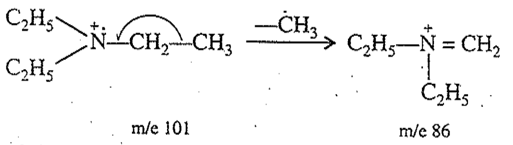
Ans. (*i*) In the case of ethylamine, the base peak is formed at m/e 30.

$$\underset{m/e\ 45}{CH_3\text{—}CH_2\text{—}\overset{+\cdot}{N}H_2} \xrightarrow{-\dot{C}H_3} \underset{m/e\ 30}{H_2C=\overset{+}{N}H_2}$$

(*ii*) In the mass spectrum of diethylamine, the intense peak at m/e 58 is formed. It is due to the loss of methyl radical.

$$\underset{m/e\ 73}{CH_3\text{—}CH_2\text{—}\overset{+\cdot}{N}H\text{—}CH_2\text{—}CH_3} \xrightarrow{-\dot{C}H_3} \underset{m/e\ 58}{CH_3\text{—}CH_2\text{—}\overset{+}{N}H=CH_2}$$

(*iii*) In case of triethylamine, the most intense peak is formed at m/e 86 by the loss of methylradical.

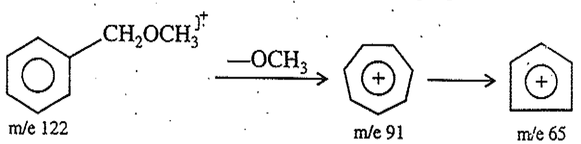


$$\underset{m/e\ 101}{(C_2H_5)_2\overset{+\cdot}{N}\text{—}CH_2\text{—}CH_3} \xrightarrow{-\dot{C}H_3} \underset{m/e\ 86}{C_2H_5\text{—}\overset{+}{N}(C_2H_5)=CH_2}$$

It may be noted that in each case, further fragmentation of this initially formed fragment ion produces a peak at m/e 30.

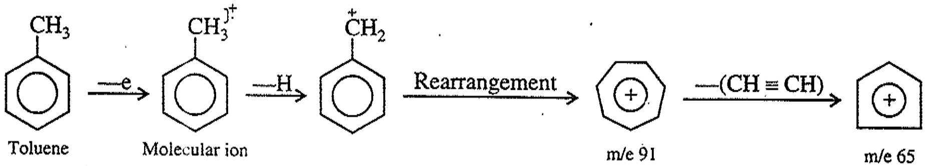
22. Give the typical fragmentation pattern in benzyl methyl ether.

Ans. Benzyl methyl ether fragments by the loss of methoxy radical to give benzyl cation which rearranges to more stable tropylium cation. Thus the peak due to this is the base peak. It further fragments to give a peak at m/e 65 due to $C_5H_5^+$.



23. In the mass spectrum of toluene, strong peaks are formed at m/e 91 and m/e 65. Also a broad peak appears at 46.4. Justify the origin of these signals.

Ans. The signal at m/e 91 is due to the formation of benzyl cation which atonce rearranges to give tropylium cation ($C_7H_7^+$). The signal at m/e 65 is due to $C_5H_5^+$ cation. The signal at m/e 46.4 is the result of metastable peak which is broad.



In case, the decomposition or fragmentation of $C_7H_7^+$ (m/e 91) to $C_5H_5^+$ occurs after acceleration before reaching the magnetic analyser, a metastable peak at m/e 46.4 is formed.

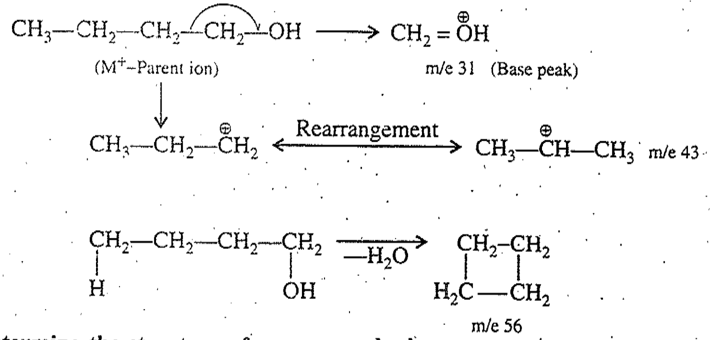
$$\text{Metastable peak,}\quad m^+ = \frac{(m_2)^2}{m_1} = \frac{65\times 65}{91} = 46.4.$$

24. Determine the structure of the compound whose m/e values in the mass spectrum are 100, 85, 71, 57, 43 (base), 41, 29 and 27.

Ans. As the signals at m/e 14 mass units apart, the compound under investigation is *n*-heptane. For this, the molecular ion peak appears at m/e 100 ($C_7H_{16}^+$). The loss of methyl radical (15 mass units) gives a signal at m/e 85 due to $C_6H_{13}^+$. Then, signals apear at 14 mass units apart and the base peak at m/e 43 is due to $C_3H_7^+$ ion. A signal at m/e 41 is due to the loss of hydrogen ($C_3H_5^+$ cation).The signals for $C_2H_5^+$ and $C_2H_3^+$ appear at m/e 29 and m/e 27 respectively. The compound under examination is *n*-Heptane.

25. Determine the structure of the compound whose m/e values are m/e 74 (Molecular ion), 56, 43 and 31 (base peak).

Ans. The formation of a base peak at m/e 31 shows that the compound under investigation is primary alcohol. It is due to the formation of $CH_2{=}\overset{+}{O}H$ ion. Primary alcohols do form parent ion peak whereas such signal for tertiary alcohol is not detected. The parent ion peak at m/e 74 corresponds to 1-Butanol ($CH_3CH_2CH_2CH_2OH$). The peak at m/e 56 is due to the loss of water and that at m/e 43 is due to $C_3H_7^+$ cation.

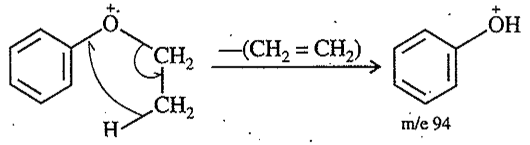


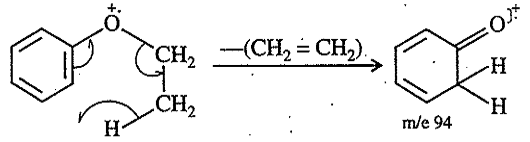
26. Determine the structure of a compound whose mass spectrum gives signals at m/e values at 45 (Molecular ion), 44, 30 (base peak) and 29.

Ans. The signal at m/e 30 is due to $CH_2{=}\overset{+}{N}H_2$ ion in primary amines. The compound under investigation appears to be $CH_3\text{—}CH_2\text{—}NH_2$ since the molecular ion peak appears at m/e 45. The α-cleavage results in the formation of base peak at m/e 30. The parent ion loses a hydrogen radical to give the signal at m/e 44.

27. How do you explain that m/e 94 ion is formed in the mass spectrum of phenetol ?

Ans. The peak of m/e 94 is formed as a result of McLafferty rearrangement which can be shown below.





FURTHER READING

1. D.H. Williams and I. Howe, Principles of Mass Spectrometry. McGraw-Hill, London (1972).
2. Millard, B.J. (ed.), Quantitative Mass Spectrometry, London; Heydon and Son, 1978.
3. McLafferty, F.W., Interpretation of Mass Spectra 2nd ed. New York; W.A. Benjamin, 1973.
4. Hamming, M. and Foster, N., Interpretation of Mass Spectra of Organic Compounds, New York; Academic Press 1972.
5. Johnstone, R.A.W., Mass Spectrometry for Organic Chemists. Cambridge, Cambridge University Press 1972.
6. Frigerio, A., Essential Aspects of Mass Spectrometry, New York; Spectrum Publishers, 1974.
7. Shrader, S.R., Introduction to Mass Spectrometry, Boston, Allyn and Bacon, 1971.
8. J.H. Beynon and A.E. Williams, Mass and Abundance Tables for use in Mass Spectrometry. Elsevier, Amsterdam.
9. K. Biemann, Mass Spectrometry, Organic Chemical Application, McGraw Hill, New York, 1962.
10. Middeditch, B.S. (ed.). Practical Mass Spectrometry, New York; Plenum, 1979.

REVIEW QUESTIONS

1. Describe some basic principles of mass spectrometry.
2. Describe in detail how will you scan the mass spectrum of an organic compound?
3. (*a*) Write a brief note on the molecular ion or the parent ion.
   (*b*) Write a note on McLafferty rearrangement.
4. What do you understand by metastable ions or peaks? How these are recognised in the mass spectrum and what is their importance?
5. Describe some important features of the mass spectra of the hydrocarbons (only alkanes and alkenes).
6. How can the mass spectrum be used to find the molecular formula of the organic compound?

7. Determine the structure of the compound which shows m/e peaks at 88, 70, 55, 42, 31 (much intense) and 29.

From the m/e values, it appears that the molecular mass of the compound is 88. The presence of much intense signal at m/e 31 shows the α-cleavage in primary alcohol. For straight chain primary alcohols, we know that following signals are expected in the mass spectrum.

(*i*) (M^+—18) due to the loss of water. This signal appears at m/e 70. This supports the structure as primary alcohol.

(*ii*) (M^+—18—C_2H_4) signal. The peak corresponding to this ion appears at m/e 44 (88—18—26).

(*iii*) Further, a signal at m/e 55 is due to (M^+—18—CH_3), *i.e.* 88—18—15 = 55. This signal lends weight to the structure of the compound as primary alcohol. Keeping in view the given data, the structure of the alcohol (1°) with molecular mass 88 is 1-Pentanol (CH_3—CH_2—CH_2CH_2—CH_2OH).

8. Wirte some important features of the mass spectra of aromatic hydrocarbons with examples.
9. Give some important features of the mass spectrum of primary, secondary and tertiary alcohols.
10. The various m/e values for a hydrocarbon are given as below:100, 43 (100%), 57, 85, 71, 41 and 29. Tell the structure of the compound and also show its various fragmentation modes. (Ans. *n*-heptane)
11. Describe some important features of the mass spectra of amines. Give examples.
12. Describe some important features of the mass spectra of (*i*) Aldehydes (*ii*) Ketones and (*iii*) Acids.
13. Find the structure of the organic compound whose mass spectrum shows m/e values as 114, 85, 72 (M.R. ion), 57, 41 and 29. (Ans. 3-Pentanone)
14. Write notes on: (*a*) Metastable peaks (*b*) Molecular ion peak (*c*) Relative abundance of the parent and the fragment ions.
15. Describe in detail the instrumentation for scanning the mass spectrum of an organic compound.
16. What is mass spectrum? Write what you know about the formation and the stability of the molecular ion?
17. How will you proceed to determine the molecular formula of an organic compound by making use of mass spectrometer?
18. Write detailed description of (*i*) McLafferty rearrangement and (*ii*)Metastable ions. What is the importance of metastable ions?
19. Write in detail the general fragmentation modes in mass spectrometry.
20. Draw the mass spectra of the isomeric compounds having the molecular formula $C_4H_{10}O$.

NUMERICAL PROBLEMS ON MASS SPECTROMETRY

21. Predict the structure of the compound whose peaks in the mass spectrum have m/e values 57 (100% abundance), 41, 29 and 27.
22. Determine the structure of the compound whose m/e values in the mass spectrum are 100, 85, 71, 57, 43 (base), 41, 29 and 27.
23. What is the structure of the compound whose peaks in the mass spectrum appear at m/e values 99, 71, 57, 43, 41 and 29.
24. The peaks in the mass spectrum appear at m/e values 124, 122, 81, 79 43 (base peak), 41, 29 and 27. What is the structure of the organic compound?
25. Predict the structure of the organic compound whose peaks in the mass spectrum appear at m/e values 102, 87, 73, 59, 45 (base peak) and 29. Confirm the structure by describing the various fragmentation modes.
26. The mass spectrum of an organic compound shows peaks at m/e values 86, 85, 44 (M.R. ion), 57 and 41. Tell the structure and confirm it by showing the various fragmentation modes.
27. Determine the structure of the organic compound which forms peaks in the mass spectrum at m/e values 162, 134 (M.R. ion), 119, 91 and 65. Confirm the structure by describing the various fragmentation modes.

28. What is the structure of an organic compound which shows various m/e values at 102, 85, 60 (M. R. ion), 57, 41 and 29. The compound on heating with an alcohol in presence of concentrated sulphuric acid gives fruity smell.

29. Describe the various fragmentation modes for the organic compound whose peaks in the mass spectrum appear at m/e 136, 105, 77 and 51.

30. Determine the structure of an organic compound whose mass spectrum is detailed below: m/e 152 M^+, 121, 120, 92, 65 and 64.

31. Predict the structure of an organic compound whose m/e values in the mass spectrum appear at 172 (M^+), 143, 141, 129, 87, 74 (M.R ion), 59, 56, 43 and 41. Justify each signal by writing the fragmentation mode.

32. An organic compound reduces Tollen's reagent. When its mass spectrum is scanned, the various signals appear at m/e values 100, 71, 58, 43, 41 and 29. Describe the fragmentation mode justifying the position of each signal.

33. The various ions formed in the mass spectrum of an organic compound appear at m/e values 102, 87, 74 (M.R. ion), 71, 59, 43, 41 and 29. Describe the various fragmentation modes justifying the position of each signal.

34. Justify the position of each signal formed in the mass spectrum of an organic compound at m/e 88, 70, 55, 43, 42 (base peak) 41 and 31. Write the structure of the organic compound and also name it.

35. An organic compound forms various fragment ions at m/e values 87, 86, 72, 71, 59 (M.R. ion), 44 and 43. Name the compound and confirm it by describing the various fragmentation modes.

36. The molecular ion peak in the mass spectrum of a compound appears at m/e 108. Some other important peaks appear at 93, 65, 78, 77 and 51. Determine the structure of the compound.

37. In the mass spectrum of an organic compound, the molecular ion peak appears at m/e 102. Some other important peaks appear at 87, 59, 45 (100%) and 43. Name the compound and confirm the structure by showing various fragmentation modes.

38. An organic compound shows only two signals (singlets) in its NMR spectrum. The various signals in its mass spectrum appear at m/e values 57, 43, 41 and 29. Name the compound and show its various fragmentation modes.

39. An organic compound forms a molecular ion peak in its mass spectrum at m/e 114. The other prominent peaks appear at m/e 85, 72 (M.R. ion), 57, 41 and 29. Name the compound and confirm it by writing the various fragmentation modes.

MULTIPLE CHOICE QUESTIONS

Choose the Correct answer:

1. The molecular ion peak is usually intense for
   (*a*) aromatic compounds (*b*) conjugated olefins
   (*c*) alcohols (*d*) Neoalkanes
2. McLafferty rearrangement ion peak in mass spectrum is usually the basic peak for
   (*a*) aldehydes (*b*) ketones
   (*c*) acids (straight chain) (*d*) all of these
3. In the mass spectrum of straight chain hydrocarbon
   (*a*) peaks are observed at 14 mass unit a part.
   (*b*) peaks at 43 and 57 are most intense
   (*c*) abundance of parent peak decreases with increase in molecular mass.
   (*d*) all of these.
4. In alkyl substituted hydrocarbons, the most abundant peak is observed at
   (*a*) m/e equal to molecular mass (*b*) 91 due to tropylium ion
   (*c*) at 65 due to $C_5H_5^+$ (*d*) None of these

5. In case of polynuclear hydrocarbons, the base peak appears
   (*a*) as parent ion peak (*b*) at 91 due to tropylium ion
   (*c*) at 77 due to phenylcation (*d*) None of these
6. In case of long chain primary alcohols, the mass spectrum consists of
   (*a*) base peak of m/e 31
   (*b*) molecular ion peak of much lower abundance
   (*c*) peak at m/e 43 of about 60% abundance
   (*d*) all of these
7. For an organic compound, the mass spectrum has the following m/e values: 124, 122 (low abundance), 43 (base peak), 107, 109, The organic compound is:
   (*a*) *n*-Propyl chloride (*b*) *n*-propylalcohol (*c*) n-Propyl bromide (*d*) None
8. The m/e values for the mass spectrum of an organic compound appears at 106. $M^+ - 1$ appears 105. The other prominent peaks are at 77,51. The organic compound can be:
   (*a*) C_6H_5CHO (*b*) $CH_3(CH_2)_4CHO$ (*c*) $C_6H_5CH_2CH_3$ (*d*) None of these
9. Following peaks are obtained in the mass spectrum of an organic compound
   m/e values 88 73 60(MR ion), 45.
   The organic compound should be:
   (*a*) $CH_3CH_2COOCH_3$ (*b*) $CH_3COOCH_2CH_3$
   (*c*) $CH_3CH_2CH_2COOH$ (*d*) None
10. Following peaks are obtained in the mass spectrum of an organic compound.
   m/e values 102 (M^+ ion), 74 (MR ion), 59, 43.
   The organic compound should be:
   (*a*) $CH_3CH_2CH_2CH_2COOH$ (*b*) $CH_3CH_2COOCH_2CH_3$
   (*c*) $CH_3CH_2CH_2COOCH_3$ (*d*) None.

ANSWERS: **1.** (*a, b*) **2.** (*d*) **3.** (*d*) **4.** (*b*) **5.** (*a*) **6.** (*d*) **7.** (*c*) **8.** (*a*) **9.** (*c*) **10.** (*c*)

Answer to Problems

CHAPTER I

2. (*b*) (i) 800 cm^{-1} (*ii*) 35087.7 cm^{-1}
4. (*a*) 4.83 × 1014 sec^{-1} (*b*) 100.49 kcals mode^{-1}.

CHAPTER II

P2 – 1 7.16 kcal mode^{-1}

1. (*b*) 59.6 × 10–13 ergs
7. (*b*) (*i*) 232 nm (*ii*) 235 mm (*iii*) 535 nm
   (*iv*) 273 nm (*v*) 232 nm (*vi*) 354 nm
13. (*a*) 254 nm (*b*) 237 nm (*c*) 317
   (*d*) 285 nm
18. (*i*) 242 nm (*ii*) 246 nm (*iii*) 351 nm
   (*iv*) 239 nm (*v*) 239 nm (*vi*) 254 nm
20. (*a*) (*i*) $n \to \pi^*$ transition (R-band)
   $n \to \pi^*$ transition (K-band)
   (*ii*) Second with high value of ε_{max}.

27.		
	(*i*) $n \to \pi^*$	R-band
	(*ii*) $n \to \pi^*$	R-band
	(*iii*) $n \to \pi^*$	K-band
	(*iv*) $n \to \pi^*$	K-band
	(*v*) $n \to \pi^*$	B-band

CHAPTER III

P_3 — 1 $CH_3 — C \equiv CH$
P_2 — 2 $CH_3 — CH{=}CH_2$ (Trans).
P_3 — 3 $C_6H_5CH_2OH$.

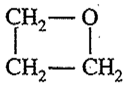
9. (*c*) $CH_3CH_2CONH_2$
12. (*a*) (*i*) 3300 cm^{-1} (O—H bonded)
   (*ii*) 1700 cm^{-1} (C=O stretching)
   (*iii*) 3050 cm^{-1} (C—H stretching aromatic)
   (*iv*) 1540 and 1590 cm^{-1} (C=C stretching armatic)
   (*v*) 2990 cm–1 (C—H stretching of methyl group).

CHAPTER IV

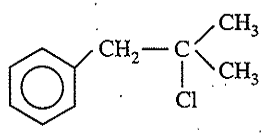
13. (*i*) Stoke's (4227 A°) (*ii*) antistokes (3882A°)
14. 3295 A° 18. 1973 cm^{-1}
21. 893 cm^{-1}

CHAPTER IV

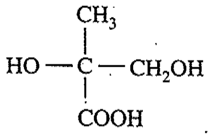
7. (*a*)



8. (*b*)



11.



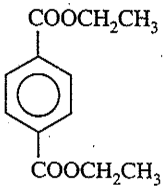
$$HO-\underset{COOH}{\overset{CH_3}{C}}-CH_2OH$$

13. (*b*) (*i*) Two (*ii*) One (*iii*) Four and (*v*) Two

15. *p*-nitro phenol.

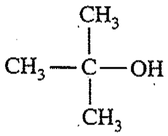
17. 1 methyl,
1 phenyl,
cyclopropane

24. (*a*)



CHAPTER VI

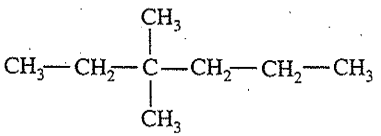
21.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

22. *n*-Heptane

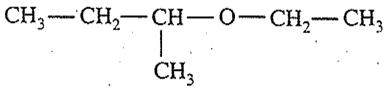
23.



$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-CH_3$$

24. $CH_3—CH_2—CH_2Br$

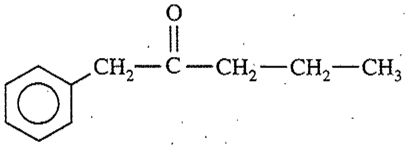
25.



$$CH_3-CH_2-\underset{CH_3}{CH}-O-CH_2-CH_3$$

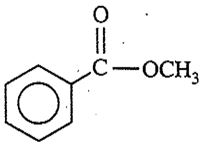
26. Pentanal

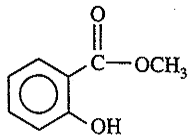
27.



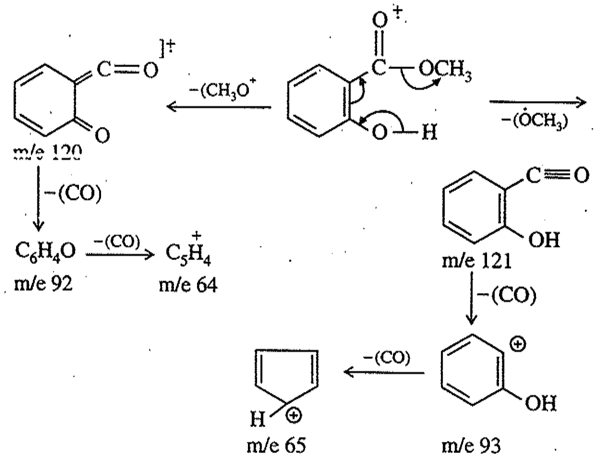
28. Pentanoic acid.

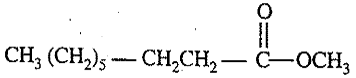
29.

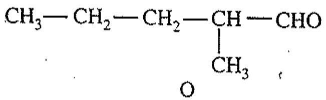


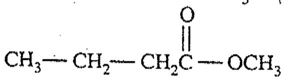
30. 

Some of its important fragment ions can be shown as below:

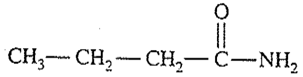


31. 
$CH_3(CH_2)_5-CH_2CH_2-C(=O)-OCH_3$

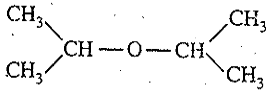
32. 
$CH_3-CH_2-CH_2-CH(CH_3)-CHO$

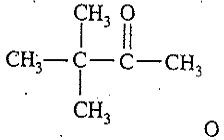
33. 
$CH_3-CH_2-CH_2C(=O)-OCH_3$

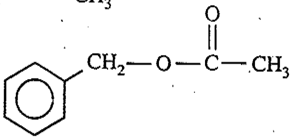
34. 1-Pentanol

35. 
$CH_3-CH_2-CH_2-C(=O)-NH_2$ (Butanamide)

36. Anisol

37. 
$(CH_3)_2CH-O-CH(CH_3)_2$

38. 
$CH_3-C(CH_3)_2-C(=O)-CH_3$ (3, 3-dimethyl-2-Butanone)

39. 

Subject Index

A

Absorbance, 13, 90
Absorptivity, 16
Absorption bands
  — formation, 18
  — types, 26
  — intensity shifts, 25
Absorption laws, 12
Absorption spectra of condensed ring systems, 49
Alicyclic dienes, 33
Allowed transitions, 22
Anisotropic effects, 204
Antibonding orbitals, 31
Antistokes lines, 164-165
Applications of
  — IR, 144
  — NMR, 245
  — UV, 56
Auxochrome, 24
Auxochromic groups, 24

B

B-band, 26, 29
Base peak, 297
Bathochromic effect, 25
Beer's law, 13
Bending vibrations, 76
Bent catacondensed compound, 49
Bicyclic system 37
Bioluminescence, 53
Biphenyl hindered rotation in UV, 51, 52
Blue shift, 25
Bonding orbitals, 31, 32
Born-oppenheimer approximation, 59

C

^{13}C-NMR, 242
Catacondensed systems, 49
Centrosymmetric vibrations, 83, 178
Chemical equivalence, 197
Chemical exchange, 220
  — effect of temperature, 221
Chemically equivalent protons, 195
Chemical shift (NMR), 198
  — definition, 199
  — measurement, 200
  — shielding, 201
  — factors affecting, 203
Chopper, 90
Chromophore concept, 23
Chromophores
  unconjugated, 24
Circulating bond electrons, 202-203
Combination bands, 82
Conjugated compounds
  — Carbonyl, 42
  — diene, 30
  — polyene, 38
  — poly-yne, 38
  — triene, 30
Conjugation
  — IR, 85-86
  — UV, 30
Coupled vibrations, 84
Coupling constant (NMR), 222
  — geminal, 224
  — long range, 226
  — vicinal, 225
Correlating charts in
  — IR, 95, 96, 120, 121
  — NMR, 227-299

Crossed conjugated systems, 45
Cumulative double bonds, 102
Coplanarity, 51

D

Delta (δ), definition, 199, 200
Definitions of
  — frequency, 3
  — wave-length, 3
  — wave number, 3
Deformations
  — rocking, 77
  — scissoring, 77
  — twisting, 77
  — wagging, 77
Degenerate vibrations, 84
Degrees of freedom, 81
Deshielding effect, 202-203
Detector thermopile, 90
Deuterium exchange reactions, 242
Diamagnetic shielding, 202
Diene conjugated
  — rules for estimating UV absorption, 33
Dihedral angle, 205
Difference bands, 82
Dipole moment, 76
Dispersion, 2
Dispersion grating, 90
Distortion of the chromophore, 37
Double beam spectrophotometer
  IR, 90
  UV, 17
Double bond equivalents (DBE), 267
Double Irradiation, 240
Double Resonance, 239

E

$E^{1\%}_{1cm}$ -bands, 18
E-bands, 27
Effective field strength, 202
Electromagnetic radiations, 1
Electric quadrupole moment, 220
Electronic effects, 85
Electronic excitations 20-22
Electronic excitation energy, 17
Electronic spectroscopy
  Important features, 58
  theory of, 19
Electronic transitions
  for charge transfer complexes, 53
  symmetry restrictions, 22
  type (UV), 19
Electromagnetic spectrum, 5
Electronegativity
  NMR,relationships, 203
Emission spectrum, 2
Enantiomers, 76
Endocyclic conjugated double bonds, 34
Energy curve for diatomic molecule, 18
Energy
  — vibrational-rotational, 76
Equivalent protons, 195
Exocyclic conjugated double bonds, 34
Extinction coefficient, 13

F

^{19}F-NMR, 244
Far Infra-red region, 6, 75
Far UV region, 15
Fermi resonance, 84, 85
Field effect, 80, 142
Fineness of absorption band
  —effect of temperature, 29
  —effect of solvent, 27
Finger print region, 96
Flipping of proton, 192
Fluorescence, 52
Forbidden bands, 22
Forbidden transitions, 83
Force constant, 78
Fragmentation (in mass) of
  — Benzene, 314
  — Benzaldehyde, 329
  — 2,2-Dimethylpentane, 308
  — 3,3-Dimethylheptane, 307
  — n-Butane, 314
  — Butanoic acid, 331
  — 1-Butanol, 319
  — 2-Butanol, 320
  — 1-Hexanol, 320
  — 2-Hexanone, 328
  — methyl butanoate, 333
  — neopentane, 291, 292
  — nitrobenzene, 339
  — n-nonane, 306
  — 1-Pentanol, 319
  — 2-Pentene, 314
  — 1-Phenylethanol, 318
  — n-Propylbenzene, 311
  — n-Propylcyclohexane, 309
Frank-condon Principle, 60
Free electron model, 62
Frequency, 3
Fundamental bands, 80
  — factors influencing number of, 80
Further reading
  — IR, 158
  — Mass, 350
  — NMR, 262
  — Raman, 187
  — UV, 68

G

Geminal coupling constant, 224
Geminal protons, 224
General fragmentation modes (mass), 302
  — Heterolytic cleavage, 303
  — Homolytic clevage, 302
  — Retro-Diel Alder, 303
Globar, 90
Grating, 17
Gyromagnetic ratio, 191
Gyroscopic motion, 191

H

Harmonic oscillator, 80
Heteroannular dienes, 33
Heterocyclic compounds, 49
Hindered rotation, 58
Homoannular dienes, 33
Hooke's law, 78
Hydrogen bonding
  —IR, 87
  —NMR, 206
  —UV, 28, 29
Hydrogen-deuterium discharge lamp, 15
  Hyperchromic effect, 25
  Hypochromic effect, 26
  Hypsochromic effect, 25

I

Important features of the mass spectra of
  — Acids, 331-332
  — Alcohols, 315-321
  — Aldehydes and ketones, 326-330
  — Alkanes, 305
  — Alkenes, 308
  — Alkynes, 308
  — Amides, 334
  — Amines, 337
  — Aromatic compounds, 311
  — Ethers, acetals, ketals, 324
  — Esters, 332
  — Halogen compounds, 335
  — Nitriles, 340
  — Nitro compounds, 339
  — Phenols, 321
  — Thiols and thiophenols, 322
Important terms and definitions, in
  — IR, 157
  — NMR, 247
  — Raman, 184
  — UV, 63
Important tips for interpreting
  — IR, 155

— NMR, 232
Inaccessible region, 17
Induced magnetic field, 193
Inductive effect, 206
Indigotin, 68
Infra-red spectra
  — acetates, 123
  — acetylene (alkynes) 101
  — acid anhydrides, 127
  — acid halides, 126
  — amides, 129
  — amines, 132
  — amino acids, 132
  — anilides, 135
  — alcohols, 108
  — aldehyde, 114
  — alkanes, 98
  — alkenes, 100
  — aromatic hydrocarbons, 103
  — carbonyl compounds, 114
  — carboxylic acids, 124
  — C-H stretching, 98
  — cycloalkanes, 102
  — dimers, 89
  — electronic effects, 85
  — esters, 123
  — ethers, 112
  — finger print region, 96
  — halogen compounds, 106
  — heterocyclic compounds, 140
  — hydrogen bonding, 87
  — Imides, 130
  — Ketones, 114
  — lactams, 130
  — lactones, 123
  — mesomeric effect, 87
  — N-H bending, 123-125
  — N-H stretching, 123-125
  — nitriles, 137
  — nitrites, 136
  — nitro compounds, 136
  — nujole, 91-92
  — O-H stretching 108-110
  — Phenols, 108
  — ring strains, 141
  — sulphonic acids, 139
  — sample techniques, 91
  — scanning, 90
  — solvents, 93
Infra-red spectroscopy
  — principles of, 76
  — molecular vibrations, 76
Instrumentation
  — IR, 90
  — Mass, 292
  — NMR, 198
  — Raman, 167
  — UV, 16
Intensity shifts, 25
Interacting nuclei
  — vicinal-gauche, 226
  — vicinal-anti 226
Introduction
  — IR, 75
  — Mass, 291
  — NMR, 191
  — Raman, 164
  — UV, 11

J

J. Coupling Constant, 222

K

K-Bands, 26
  — ketones, 42
  — α, β-unsaturated, 33
  — rules for estimating absorption, 33, 44
keto-enol tautomerism
  study of, 55

L

Lambert's law, 12
Linear catacondensed system, 49
Longitudinal relaxation, 194
Long range coupling 226

M

Magnetic equivalence, 195
Magnetic moment, 192
Magnetic properties of the nuclei, 218
Mass spectrometry
  — Basic principles, 291
  — double focussing, 295
  — instrumentation, 292
  — theory, 292
Mass spectra of
  — Aniline, 338
  — Benzaldehyde 329
  — Benzamide, 335
  — 1-Bromohexane, 336
  — Butanol, 316
  — 2-Butanol, 316
  — n-Butylbenzene, 313
  — Cyclohexanol, 321
  — Cyclohexanone, 330
  — Cyclohexene, 310
  — 3,3-Dimethylheptane, 306
  — Do-decane, 305
  — Ethylamine, 337
  — Ethylbenzene, 312
  — Isopropyl-n-pentylether, 325
  — Naphthalene, 312
  — Phenylacetylene, 310
  — n-Propylcyclohexane, 309
  — 1-Pentanethiol, 323
  — Pentanal 327
  — 1-Pentanol, 318
  — 3-Pentanone, 328
  — Pentanoic acid, 331
  — Phenol, 322
  — n-Propylethanoate, 333
  — Thiophenol, 324
  — m-Xylene, 313
  — McLafferty rearrangement, 298
  — Mesomeric effect 85
Mass spectrum (Fragmentation of)
  — Alcohols, 305
  — Aliphatic acids, 331
  — Aliphatic aldehydes and ketones, 326
  — Aliphatic amines, 337
  — Aliphatic nitriles, 331
  — Aromatic aldehydes, 329
  — Aromatic acids, 332
  — Aromatic amines, 338
  — Aromatic compounds, 311
  — Alkanes, 305
  — Alkenes (olefins), 308
  — Alkenyl ion (Alkynes), 308
  — Amides, 334
  — Benzene, 314
  — Cycloalkanes, 309
  — 2,2-dimethylpentane, 308
  — 3, 3-dimethylheptane, 306
  — Dodecane, 305
  — Esters, 332
  — Ethylbromide, 297
  — Ethers, acetals, ketals, 324
  — Halogen compounds, 335
  — naphthalene, 312
  — n-nonane, 306
  — nitrocompounds, 339
  — phenols, 321
  — Thiols and thiophenols, 322
Mass spectroscopy
  — Basic principles, 291
  — Base peak, 292
  — Dempster's mass spectrometer, 294
  — Determination of molecular formula, 297
  — Double focussing, mass spectrometer, 295
  — Field free region (drift region), 297
  — Fragmentation modes, 302
  — Heterolytic cleavage, 303
  — Homolytic cleavage, 302
  — Hydrogen transfer rearrangement, 304
  — Ion detector, 295
  — Ion source, 292
  — Mass analyser, 293

— McLafferty rearrangement, 298
— Metastable ions, 299
— molecular ion, 295
— nitrogen rule, 301
— parent ion, 295
— Retro-diel Alder reaction, 303
— Tropylium cation, 301
Metastable ions, 299
formation, 299
— in o-aminoanisole, 300
— importance of, 301
Metastable peaks, 301
broadened, 301
Micron, 3
Millimicron, 3
Molar absorptivity, 22
Molar extinction coefficient, 12
Molecular vibration, 76
Moment of inertia, 175
Monochromatic light, 17
Monochromator, 17
Mulling reagents, 91
— Chlorofluoro carbon oil, 91
— hexachlorobutadiene, 91
— nujole, 92
— Multiple peaks (NMR), 210
Mutual exclusion Principle, 175

N

Nanometer, 3
Near Infra-red region 6, 75
Nernst glower, 90
Nitrogen rule, 301
Nuclear magnetic resonance
— absorption by other nuclei, 217
— anisotropy, 204
— ^{13}C- 242
of carbocations, 244
carbonyl compounds, 243
chemical exchange, 220
chemical shift, 198
coupling constant, 222
deshielding effect, 204
— deuterium exchange, 242
— diamagnetic shielding, 201
— dihedral angle, 225
— double bond, anisotropy of 201-202
— double irradiation, 240
— double resonance, 239
— hydrogen bonding, 206
in qualitative analysis, 240
— inductive effect, 203
— nernst glower, 90
— nuclear overhauser effect, 241
— nuclear constant, 193
— number of signals, 195
— paramagnetic shielding, 202
— quadrupole relaxation, 194
— solvents, 207
— spectrometer, 5
— spin-spin coupling, 211
— spin tickling, 241
— TMS, 200
— van der Waal's deshielding, 204
Nuclear overhauser effect, 241
Nujole, 91-92

O

Optical density, 13
Optical path length, 13
Orbitals, 30
— bonding, 30-32
— antibonding, 30-32
— pi(π), 31
— sigma (σ), 31
Overtones, 82

P

Paramagnetic shielding, 202
Parameters of Raman lines, 168
— degree of polarisation, 169
— frequency shifts, 169
— intensity of, 169
Parent ion, 295

Peak area, 209
Peak intensities, 212-213
Pericondensed, 49
Phosphorescence, 52
Photon, 2
Poly-enes, 38
Poly-ynes, 38
Position of signals
— ppm, 200, 201
Precessional motion, 191
Precessional frequency, 191
Precessional angular velocity, 191
Proton counting, 209
Proton noise decoupling, 243

Q

Quadrupole moment, 194
Quartz region, 15
Quinones, 45

R

R-bands, 26
Radiation
— fluorescent , 52
— phosphorescent, 53
Radiation source
IR, 90
UV, 15
Radiofrequency source, 198
Radiowaves, 6
Raman frequency, 164
Raman shift, 164
Raman spectra of diatomic molecules, 170
Raman spectroscopy
— applications of, 182
— conditions for, 167
— importance of, 181
— Releigh line, 172
— Raleigh scattering, 165, 166
— Red shift, 25
— Reduced mass, 78
— Reference compound (NMR), 198
Relaxation Processes, 194
— Quadrupole, 194
— spin-spin, 194
— spin-lattice, 194
Resonance (Fermi), 85
Resonance splitting, 142
Restricted Rotation
— NMR, 231
UV, 51
Ring currents, 202-204
Raman spectra of diatomic molecules
— pure rotational, 170
— rotational-vibrational, 173
— pure vibrational, 171
Rules for calculating absorption max.
— conjugated dienes and trienes, 33
— α, β-Unsaturated carbonyl, 42
— acyl benzenes, 48
Rule of mutual exclusion Principle, 175

S

Sampling techniques (IR), 91
— Solids, 91
— liquids, 93
— gases, 93
— solutions, 93
Secondary magnetic fields, 202-204
Selection rules, 83
Silica cells, 17
Singlet state, 19
Solvent effects, 27
Solvents for
— IR, 95
— NMR, 207
— UV, 27
Spectra
— Absorption, 3
— emission, 3
Spectrophotometer, 12-13
Spectroscopy
— definition of, 2

Shielding
- — dependence on electron density, 202, 204
- — diamagnetic anisotropic effect by
- — double and triple bonds, 204

Spin decoupling
- — by chemical exchange, 220
- — through double irradiation, 240

Spin-lattice relaxation, 194
Spin number (I), 217
Spin-spin coupling, 211
- — of other nuclei than hydrogen, 217

Spin-spin Coupling Constant
- — ^{13}C-Hydrogen, 242
- — Correlation with hybridisation, 243
- — electro-negativity effects on, 243-244
- — ^{19}F-Hydrogen, 244
- — ^{14}N-Hydrogen, 244

Spin-spin relaxation, 194
Spin tickling, 241
Splitting of signals, 210
Stereochemically equivalent protons, 196
Steric effects
- — NMR, 246
- — UV, 51

Stokes lines, 164-165
Stretching vibrations, 77
Steric hindrance and Coplanarity, 51
Symmetry restrictions
- in electronic transitions, 22

T

Tau (τ), 198
Tetramethyl silane (TMS), 198
Theory of
- — Raman effect, 164
- — Raman spectra, 164

Thermopile principle, 90
Transannular interactions, 241
Transitions
- — allowed, 22
- — forbidden, 22
- — $n \rightarrow \sigma^*$ 21
- — $n \rightarrow \pi^*$ 21, 27
- — $\pi \rightarrow \pi^*$ 21, 27
- — $\sigma \rightarrow \sigma^*$ 20
- — Transition probability, 22
- — Transmittance, 90
- — Triplet State, 19
- — Tungsten filament lamp, 17

U

Ultra-violet spectra
- — aldehydes, 41
- — benzene, 47
- — benzene substituted chromophores, 47
- — bicyclic compounds, 37
- — compounds with N and O bonds, 47
- — condensed ring systems, 49
- — equitorial and axial, 58
- — Heterocyclic compounds, 49-50
- — non-conjugated dienes, 32, 33
- — ketones, 41
- — $n \rightarrow \pi^*$ transition, 21, 27
- — $\pi \rightarrow \pi^*$ 21, 27
- — $n \rightarrow \sigma^*$ 21
- — $\sigma \rightarrow \sigma^*$ 20
- — geometrical Isomers, 57
- — hydrogen bonding (UV), 58
- — pericondensed system, 49
- — quinones, 45
- — solvent effects, 27
- — solvent corrections, 45
- — steric effects, 51, 58

α,β-Unsaturated
- — acids, 42
- — aldehydes, 42
- — carbonyl compounds, 40
- — condensed ring systems, 49
- — esters, 42
- — ketones, 42
- — vitamins A and K, 56-57

Units
- — IR, 6
- — NMR, 6
- — UV, 9

Woodward Fieser Rules
- — dienes, 33
- — for carbonyl compounds, 42

V

Vacuum ultra-violet region, 17
vander Waal's deshielding, 204
Vibrational bands, 80-82
Vibrational degrees of freedom, 82
Vibrational frequency, 78
- — factors influencing, 84

Vibrational modes
- — fundamental, 80

Vibrational Raman Spectra
- — of polyatomic molecules, 174

Vibrational rotational bands, 173
Vibrations
- — bending, 77
- — deformations, 77
- — molecular, 76
- — stretching, 77
- — symmetric, 77
- — unsymmetric, 77

Vicinal coupling, 225
Visible range, 5
Visible range, 5
Visible spectrum, 5

W

Wavelength
- — micron, 3
- — millimicron, 3
- — wave number (cm^{-1}), 3

Woodward Fieser Rules for
- — conjugated dienes and trienes, 33
- — α, β-Unsaturated Carbonyl Compounds, 42
- — Acyl benzeues, 48

Compound Index

A

Acetaldehyde, **IR**, 86 **NMR**, 237 **UV**, 26
Acetanilide, **IR** 135
Acetone, **IR**, 86, **NMR**, 195, **UV**, 26
Acetonitrile, **IR** 138 **UV** 29
Acetophenone, **IR** 86 **UV** 26
Acetylacetone, **NMR**, 207
1-Acetyl-4-methylcyclohex-3-enone **IR** 118
— Acrolein **IR** 95 **UV** 26
— Acrylonitrile **IR** 138
— Allyl alcohol **IR** 141 Mass-321
— p-Aminoacetophenone **IR** 87
— Aniline **IR** 133 **UV** 25 **Mass** 338
— p-Anisidine **IR** 135 **NMR** 235
— Anisole **UV** 54 **Mass** 325
— Anthracene **UV** 27

B

Benzaldehyde **IR** 115 **Mass** 329 **NMR** 237 **UV** 27
Benzamide **IR** 86, 131, **Mass** 335
Benzene **IR** 104 **Mass** 296, 314 **UV** 27 **NMR** 195
Benzil **UV** 46
Benzoic acid **IR** 126 **UV** 27 **Mass** 332
Benzoic anhydride **IR** 128
Benzonitrile **IR** 139
Benzoyl chloride **IR** 126
Benzyl alcohol **IR** 112 **Mass** 318 **NMR** 230
Benzylamine **IR** 141
Biphenyl **UV** 70
p-Bromobenzoic acid **UV** 49
α-Bromobutanoic acid **NMR** 238
1-Bromo-2-chlorobutane **NMR** 237
1-Bromo hexane **Mass** 336
p-Bromopheretol **NMR** 236
1-Bromo-3-chloropropane **NMR** 236
2-Bromopropane **IR** 108
α-Bromopropanoic acid **NMR** 230
2-Bromothiophene **UV** 50
2-Bromo-4-tert.butylcyclohexanone **IR** 117
1,3-Butadiene **IR** 100 **UV** 30
2,3-Dimethylbutadiene **UV** 30
Butanal **IR** 122 **Mass** 298
1-Butanol **Mass** 316
2-Butanol **Mass** 316, 317
Butanamide **IR** 131
Butane **Mass** 314
t-Butylamine **NMR** 197
n-Butyl benzene **Mass** 313
sec-butyl ethylether **Mass** 326
n-Butyl ether **IR** 113
n-Butyl vinylether **IR** 85
n-Butyric anhydride **IR** 128

C

Camphoquinone **UV** 46
Carbon dioxide **IR** 85
Carbon disulphide **IR** 94 **NMR** 209
Carbon tetrachloride **IR** 94 **UV** 28 **NMR** 209
Coronene **UV** 49
β-carotene **UV** 40
Chloral hydrate **UV** 57
Chloroacetone **IR** 117
p-chloroacetophenone **UV** 48
p-chloroanisol **NMR** 231
2-Chloropropane **NMR** 245
Chlorobenzene **IR** 107 **UV** 48
Chloroform **IR** 94 **UV** 28
α-chloropropanoic acid **NMR** 235
2-chloropropene **NMR** 196
2-chloropyridine **UV** 50
Chrysanthenone **IR** 145
Cinnamaldehyde **IR** 150 **NMR** 253
m-cresol **IR** 104 **NMR** 234
p-Cresol **IR** 112 **Mass** 322
Cinnamic acid **IR** 125
Crotonaldehyde **NMR** 239 **UV** 26
Cyclobutane **NMR** 195
Cyclobutanone **IR** 102, 115

Cyclohexadiene **UV** 38
1,2-Cyclohexanediol **IR** 111
Cyclohexane **IR** 103 **NMR** 203
Cyclohexanone **IR** 115 Mass 330
Cyclohexanol **Mass** 321
Cyclohexene **IR** 101 **Mass** 310
Cyclopentane **IR** 102
Cyclopentadiene **UV** 49
Cyclopentanone **IR** 115 **Mass** 330
Cyclopropane **IR** 102
2-chloropropanone **NMR** 196
Chloropropanone **IR** 86
Chloropyridine **UV** 50

D

1-Decene **IR** 100
Deuterium oxide **NMR** 208
Deuteromethane **NMR** 208
Di-n-butylether **IR** 113
Dichloroacetone **IR** 117
1,2-dichloroethane **IR** 147
1,2-Dichloropropane **NMR** 196
1, 1-Dibromo-3, 3-dichloropropane **NMR** 220
1,1-Dibromethane **NMR** 197, 213
2,3-Dibromopropane **NMR** 237
Dichloroethylacetate **NMR** 230
Diethylether **IR** 188 **NMR** 197 **UV** 28
1,1-Difluoro-1, 2-dichloroethane **NMR** 218
2,3-dimethylene bicyclo (2, 2,1) heptane **UV** 37
N, N-Dimethylacetamide **IR** 141
Dimethylamine **IR** 134
2,3-Dimethyl butadiene **UV** 26
Dimethylformamide **NMR** 246
2,5-Dimethyl p-nitroaniline **UV** 51
3,3-Dimethylheptane **Mass** 306
2,4-dimethylpentane **IR** 99
2,2-Dimethylpentane **Mass** 308
Dimethylsulphoxide **NMR** 208
Dioxane **IR** 93 **NMR** 209 **UV** 29
Diphenyl **UV** 26
Dodecane **IR** 98 **Mass** 305

E

Ethanol **IR** 108, 109, **NMR** 230 **UV** 28
Ether **IR** 195
Ethylacetate **IR** 123
Ethylamine **Mass** 337
Ethyl benzene **Mass** 312 **NMR** 197
Ethylbromide **Mass** 297 **NMR** 211
Ethylcyanide **IR** 138
Ethyl-3, 7-dimethylocta-3, 6-dienoate **IR** 145
Ethylene **UV** 31
Ethyledene dibromide **NMR** 147
Ethylene glycol **IR** 88
Ethylgeranate **IR** 145
Ethylmethyl ketone **IR** 116
1-Ethynyl-1-cyclohexanol **NMR** 238

F

Formaldehyde **IR** 86
Fluorescein **UV** 53
Fumeric acid **IR** 127
Furan **NMR** 230 **UV** 50
Furan-2-aldehyde **NMR** 240 **UV** 50

G

Glycine **IR** 132
Glycol **IR** 88 **NMR** 282

H

Hexachlorobutadiene **IR** 93
4-Heptanone **Mass** 299
Hexadiene **UV** 38
Hexane **UV** 28
1,3,5-Hexatriene **UV** 30
2-Hexene **IR** 106
2-Hydroxypyridine **UV** 51
1-Hexanol **Mass** 319
2-Hexanone **IR** 122 **Mass** 328
1-Hexyne **IR** 102, 106

I

Isoduril **UV** 46
Isopropyl ether **IR** 228 **NMR** 230
Isopropyl-n-pentylether **Mass** 335
Isopropyl alcohol **NMR** 195

K

7-keto-bicyclo [2,2,1] heptane **IR** 142

L

Lycopene **UV** 40

M

Maleic acid **IR** 127
Malic acid **NMR** 226
Mesitylene **NMR** 197
Methanol **IR** 109 **NMR** 186 **UV** 28
p-Methylacetophenone **IR** 118
p-Methoxyacetophenone **IR** 87
p-Methoxychlorobenzene **NMR** 283
Methyl benzoate **IR** 86
Methyl butanoate **Mass** 333
2-Methyl biphenyl **UV** 26
Methyl chloride **UV** 21
Methyl cyanide **IR** 138
Methyl cyclohexadiene **NMR** 220
2-Methyl cyclohexanol **IR** 110
Methyl cyclopropane **NMR** 196
Methyl iodide **UV** 21
Methyl cyanide **IR** 138
3-Methyl pentane **IR** 99
2-Methyl pentane **IR** 126
2-Methyl propanamide **IR** 129
2-Methyl propanal **IR** 115
2-Methyl propene **NMR** 215
2-Methyl pyridine **UV** 50
Methylvinylketone **IR** 86 **UV** 26

N

Naphthalene **UV** 27 **Mass** 312
p-Nitroacetophenone **IR** 87
p-Nitroaniline **UV** 49
p-Nitrobenzaldelyde **IR** 148
Neopentane **Mass** 291, 292
Nitrobenzene **IR** 131 **Mass** 339 **UV** 27
p-Nitrobenzoic acid **IR** 148
Nitroethane **IR** 136 **NMR** 283
Nitromethane **IR** 137 **NMR** 283 **UV** 47
2-Nitrofuran **UV** 50
o-Nitrophenol **IR** 269 **NMR** 271
o-Nitrotoluene **UV** 51 **Mass** 339
p-Nitrotoluene **NMR** 256
Nitrosomethane **UV** 47
Nujole **IR** 92

P

Pencillin **IR** 130
Pentacene **UV** 48
Pentanal **Mass** 327
Pentane **NMR** 252
1-Pentane thiol **Mass** 323
2-Pentanone **Mass** 333
3-Pentanone **Mass** 328
Pentadiene1, 3 **IR** 100 **UV** 26
1-Pentanol **NMR** 234 **Mass** 313
1-Pentene **Mass** 298, 308
2-Pentene **Mass** 314
Pentyne **UV** 39
Phenol **IR** 111 **Mass** 322 **UV** 27
Pentanoic acid **Mass** 331
1-Phenylethanol **Mass** 318
Phenetole **IR** 114
Phenylacetate **IR** 87
Phenylacetaldehyde **IR** 276 **NMR** 253
Phenylacetylene **NMR** 235 **Mass** 310, 311
Propanal **IR** 119 **NMR** 197
Propanoic acid **IR** 125
Propanol-2 **IR** 110 **NMR** 245
Propanone **IR** 86
Propen-1-ol **IR** 147 **NMR** 282
Propanamide **NMR** 235
Propylacetate **Mass** 333
n-Propylamine **IR** 134
n-Propylbenzene **Mass** 311
n-Propylchloride **NMR** 195
n-Propylcyclohexane **Mass** 309
Propyne **IR** 106
Propyl formate **NMR** 197, 230
2-Propynyl-1-ol **NMR** 236
Propyl iodide **NMR** 230
Pyridine **IR** 140 **NMR** 230
Pyridone-2 **UV** 51, 57
Pyrrole **NMR** 220 **UV** 27, 50
Pyrrole-2-aldehyde **UV** 50

Q

Quinoline **UV** 27
p-quinone **IR** 120

S

Stilbene (cis) **NMR** 238, 260 **UV** 52, 57

T

Trichloroacetone **IR** 117

Tetrahydrofuran **UV** 28
Tetramethylsilane **NMR** 195
Thiophene **UV** 27, 50 **Mass** 324
Thiophenol mass 324
p-Toluidine **IR** 135
Toluene **IR** 106 **UV** 27 **Mass** 301
Trichloroacetonitrile **NMR** 209
1,1,2-Trichloroethane **NMR** 211, 212
2,3,4-Trichloroanisol **NMR** 259
Trichloroacetic acid **NMR** 208
Trifluoroethanol **IR** 284 **NMR** 249, 284
2,4,6-Trimethylacetophenone **UV** 51

U

Urea **IR** 280 **NMR** 282

V

Verbenone **IR** 145
Vitamins
  A_1, A_2 **UV** 57
  K_1, K_2 **UV** 57

W

Water **IR** 24

X

m-Xylene **IR** 104 **Mass** 313
o-Xylene **IR** 104
p-xylene **IR** 105 **NMR** 195