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AUTHOR'S INTRODUCTION

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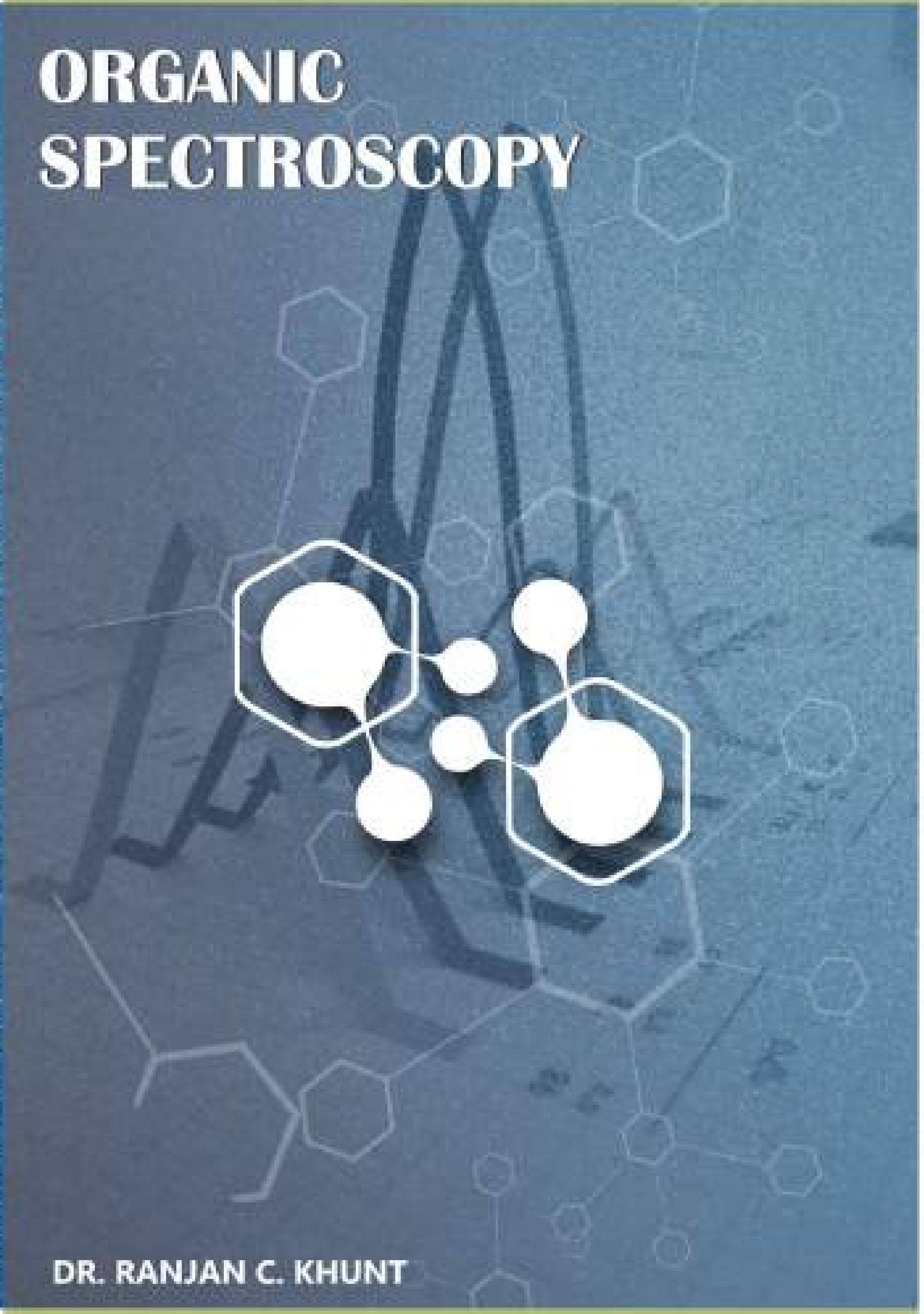
ORGANIC SPECTROSCOPY

DR. RANJAN KHUNT



ORGANIC SPECTROSCOPY

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Preface

Today spectroscopy is the most important tools for the structure elucidation of unknown compounds. This book ”Organic spectroscopy” is primarily written for those students who like to have a basic and effective knowledge of spectroscopy as an important subject at the undergraduate as well as postgraduate level. It will help them venture into the weird but fascinating, field of advanced spectroscopy in future.

The content of this book is such that students can gradually understood comprehensive knowledge of techniques. The book has a large number of illustrative diagram including spectrum as well as instrument diagram related to the techniques. Each chapter contains individually solved problems. The last chapter of this book contains combine application of all the spectroscopic techniques related solved problems.

The author had to seek permission from the relevant source for reproducing data and spectra of compounds.

I express my heartfelt thanks to Saurashtra university for giving me the opportunity to publish this book for providing financial Grant. I am particularly thankful to Prof. Pratapsinh Chauhan, Hon. Vice Chancellor of Saurashtra University, Prof. Girishbhai Bhimani, Director, IQAC of Saurashtra University, Prof. Alok Chakrwal, Co-coordinator, IQAC, Saurashtra University and other committee members of

50th year celebration of Saurashtra university in the successful publication of this book.

I also appreciate the support of my research students Mr Kaushikkumar Lunagariya and Ms. Jyoti Gohel for their indigenous support for typing, content and formatting the book. I am also thankful to Mr. Yashwantsinh Jadeja, Project coordinator at CoE of Chemistry department and Bhagywanti for NMR data and Kaushik Pambhar and Ashish Dhamsaniya for providing sample contents.

I express my sincere thanks to the faculty members and students of chemistry departments for their kind support to write this book.

-Author

Contents

Chapter 1

Electromagnetic Spectrum

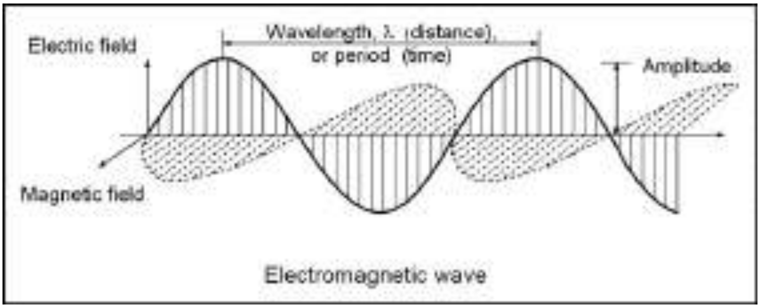
Introduction

Spectroscopy is a branch of physical science which deals with the study of the interaction between the molecule and electromagnetic radiation. For determination of energy difference between the molecular energy level as well as energy emitted or absorbed by atoms or molecule are studied under the title of “spectroscopy”. The instrumental device used for this type of specific study is known as “spectrophotometer”.

The result of the above process obtain from the “spectrophotometer” is represented as a “continuous graph of electrical transmittance (or absorption) of the function of wavelength or wave number” which is known as “spectrum”.

Electro-Magnetic Radiation

Electromagnetic radiation is a form of energy that is transmitted through space. Electromagnetic radiation is a mixture of the electrical and magnetic component which are perpendicular To each other and also perpendicular to propagation line as a shown in the figure.



During irradiation of “EMR” on the molecule, which component of “EMR” interacts with it, is an important study in spectroscopy.

Unit of EMR

1) **Wavelength:** The paint ‘xy’ on wave represent the wavelength.

   “The distance between two crests or valley is known as wavelength”. It symbolised by ‘λ’. It is measured in μ, Å, mm, cm, m etc.

   $1\mu = 10^{-4}\text{cm} = 10^{-6}\text{ m}$

   $1\text{Å} = 10^{-8}\text{ cm} = 10^{-10}\text{m}$

2) **Wave number:** The total no. of complete waves present in the unique box is known as wave number. It can be symbolised by $\bar{\upsilon}$ & It is measured in cm^{-1}.

   $\bar{\vartheta} = \frac{1}{\lambda}\text{ cm}^{-1}$. or “K” (Kaysers) (1)

   (i.e. reciprocal of wavelength is called wave number)

3) **Frequency:** the number of waves passing through at a given point a unique time is known as frequency.

   Frequency is symbolised by “ν” & their units are μ, Å, nm, cm, m etc.

   $\upsilon \propto \frac{1}{\lambda}$ (2)

   $\upsilon = \frac{c}{\lambda}$ c = velocity of light (3)

   $\upsilon = c\bar{\vartheta}$ (4)

Theory of EMR

According to the quantum theory, light has a dual nature i.e. wave and particle. The consist of a stream of energy bunch is also important.

This concept was confirmed by physicist Max-plank means the concept of ‘Light quanta packet’.

Particles are considered as an energy bundle called ‘photons’ According to Einstein- Plank relation.

E= hν where h=6.63 × 10^{-27} erg.sec & h= plank constant (5)

∴ energy depends on frequency but not on the intensity of radiation.

$$\therefore E = \frac{hc}{\lambda} \qquad \text{but } \nu = \frac{c}{\lambda} \text{ and } \bar{\nu} = \frac{1}{\lambda} \qquad (6)$$

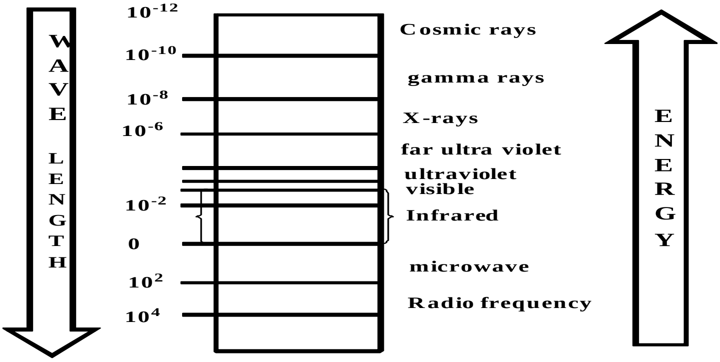
$$\therefore E = hc\bar{\nu} \qquad (7)$$

Equation 5, 6, 7 told us about the relation of energy with frequency, wavelength and wave numbers.

Energy has a direct relation with frequency and wave number but the reciprocal relation with ‘wavelength’.

Different component of EMR & spectroscopy:

Molecule absorbs the radiation, it is energy is increase as per the photon relation with energy(eq. 5,6,7)



Energy absorb by molecule is not continuous absorption throughout the whole range but absorb only those frequency which is enough for a particular physical change thus, when molecule interact with EMR, it may change their energy from E_1 to E_2 by absorption of radiation frequency ν

$$\therefore E_2 - E_1 = nh\nu \qquad \text{n is integer} \qquad (8)$$

After absorption of radiation energy is utilised for the internal energy of a molecule is raising, the study of above reaction is known as "absorption spectroscopy" or after absorption, the excited species come back to the ground state by emitting this energy as a radiation with a different frequency is known as "emission spectroscopy".

❖ Type of molecular Energy [Energy distribution in molecule]:

Apart from translation energy, the internal energy of molecule may be regarded as the sum of rotational, vibrational and electronic energies.

$$E_{Internal} = E_{vib.} + E_{elec.} + E_{rot.} \qquad (9)$$

(i) Translational energy:

As per the Brownian of the atom, the kinetic component of energy is called translation energy which passes three degrees of freedom.

$$E_{translation} = \frac{3}{2}KT \text{ or } \frac{3}{2}RT \qquad (10)$$

R= NK = 1.987 cal/mole

N= avagadro number

T= room temperature

K= Boltzmann constant=1.38×10^{-16} erg/deg.

(ii) Rotational energy:

The energy which is associated with the rotational motion of the whole molecule is known as rotational energy.

$E = \frac{1}{2}Iw^2$ I= moment of Inertia,

w= Angular velocity (11)

(iii) Vibrational energy:

It is associated with vibration of the constituent atom of the molecule. It is expressed as a sum of each vibrational level

$$E_{vib} = h\nu_0\left(\nu + \frac{1}{2}\right) \quad \text{for } \nu=0, 1, 2, 3.... \qquad (12)$$

(iv) Electronic Energy:

This type of energy has a relation with the motion of the electron. By increasing the electronic energy the kinetic and potential energy of electronic are increased. During the position of the nucleus is an unaltered.

Chapter 2

Ultraviolet Spectroscopy

❖ Introduction:

Ultraviolet and visible spectroscopy is also known as electronic spectroscopy. Generally, it can be used to determine the degree of unsaturation within the molecules.

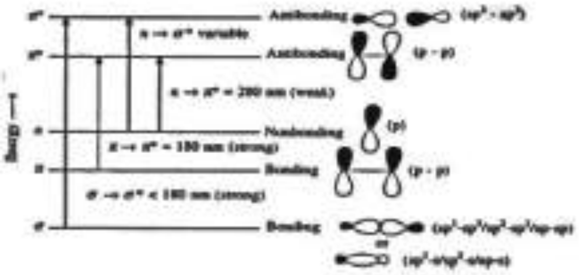
❖ Theory of Ultra-Violet absorption:

Ultra-violet absorption associated with the measurement of energy by electrons is promoted to the excited level. When a continuous radiation passes through a transparent material some of the portion of the radiation absorbed by a molecule and the residual passes through the prism, yields a spectrum with gaps of absorption region, which is known as an absorption spectrum.

The intensity of absorption depends on the nature of molecule as well as the wavelength of light. In the case of ultraviolet and visible spectroscopy, the transition that the result of absorption of EMR transition between electronic energy level.

The most favourable transition of an electron from higher occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

Most of the molecule; highest occupied with the formation of 6- band. The π-orbitals lie at somewhat higher as compare to 6- orbitals. The possible electronic transition is illustrated in fig.(2)



Electronic energy levels and electronic transitions

❖ The ultraviolet spectrum:

Generally, an electronic transition occurs due to the absorption of EMR in the range of 10 nm to 780 nm. So this region is known as a ultra-violet visible region which is further divided into the following region.

(1) **Far (vacuum) ultraviolet region(10-200 nm)**

The absorption below 200 nm (atomic absorption) appeared in this region. To study the specific system in this region, a vacuum is necessary, so this region is known as ‘vacuum- UV’ region.

(2) **Near UV region (200-380):**

The atmosphere is transparent in this region. The absorption due to p & d electronic transition appears in the range of the ultraviolet spectrum.

(3) **Visible region (380-780):**

If enough no. of π bond in conjugation, absorption takes place in this region.

❖ Type of transition:

The important transition occur in ultraviolet absorption spectrum are classified below

(A) Transition between bonding and anti-bonding orbitals.

The transition between bonding to antibonding orbitals are illustrated in fig.(2) they are of two types:

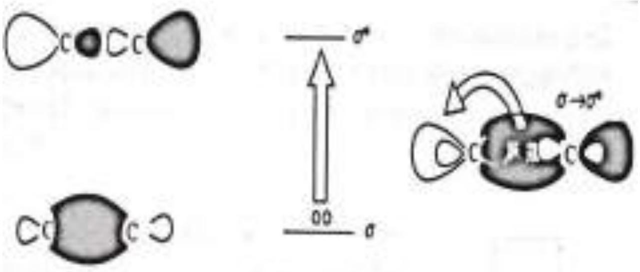
(i) $\sigma \rightarrow \sigma^*$ (bonding σ to anti-bonding σ^*)

(ii) $\pi \rightarrow \pi^*$ (bonding π to anti-bonding π^*)

(i) $\sigma \rightarrow \sigma^*$ transition (120-200 nm)

- → The transition of bonding σ orbital to anti-bonding σ^* requires large energies corresponding to absorption in the far ultraviolet region (120-200 nm).
- → This transition is possible in a saturated hydrocarbon containing just σ bonds remain transparent in near ultraviolet region.

  Example: CH_4, $CH_3CH_2CH_3$, C_6H_{12} etc.



(a) σ→σ* Transition

(ii) $\pi \rightarrow \pi^*$ transition (180-250 nm)

- → This type of transition occurs in compound contain the double bond.
- → Transition from bonding to anti-bonding p_i to anti-bonding p_1 is called $\pi \rightarrow \pi^*$ transition.
- → This type of transition occurs with a compound containing double or triple bond, aromatic ring, a carbonyl group and diazo group etc.
- → The molar absorptivity of $\pi \rightarrow \pi^*$ is very high because the π & π^* orbitals are situated in the same plane, so probability of the jump of the electron is high.

- → This band designated as “1/k band” with ε value > 10,000.
- → The benzenoid band also appears due to $\pi\to\pi^*$ transition at 180 nm with $\varepsilon_{max} > 2000$.
- → Ethylenic band also appears due to $\pi\to\pi^*$ transition at 200 nm.

(B) Transition between non-bonding atomic orbitals and anti-bonding orbitals.

This type of transition also illustrated in fig.(2) which is further classified in two groups

(1) $n\to\pi^*$ (non-bonding atomic orbital to anti bonding π^*)
(2) $n\to\sigma^*$ (non-bonding atomic orbitals to anti bonding σ^*)

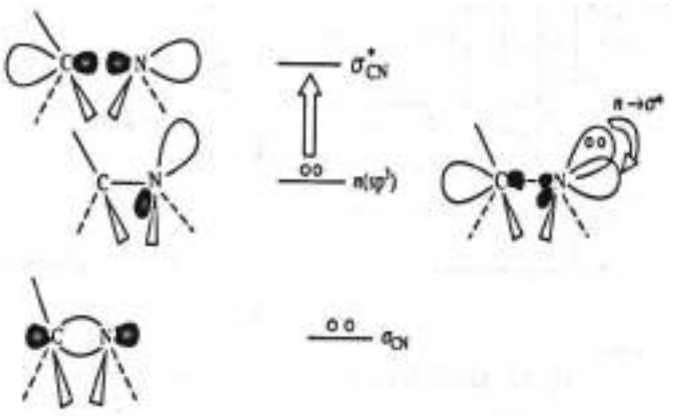
(1) $n\to\pi^*$

- → This type of transition occurs on those compound which possesses double bond with a hetero atom.
- → Non-bonding electrons are held more loosely than σ bonding electrons and consequently undergo transition at higher wavelength
- → This type of transition is An important characteristic of aldehyde and ketone and also sensitive toward chromophoric substitution.
- → This transition designated as “R-Band”.

(2) $n\to\sigma^*$

- → The excitation of a unsaired electron on oxygen, Nitrogen or any hetero Atom to an anti-bonding σ orbital is called $n\to\pi^*$ transition.

→ This transition requires less energy as compared to σ→σ*, so absorption takes place at higher wavelength & shows less value of molar absorptivity.



(b) n→σ* Transition

❖ **The absorption laws and measurement of absorption intensity.**

The absorption of light by matter (molecule) is explained by the following laws:

(a) Beer's law: This law state that absorption of light is proportional to the number of absorbing molecules in the light path and will increase with respect to concentration.

$K \propto c$ (13)

$K = \epsilon c$

ϵ= molar absorptivity constant, c= concentration

(b) Lambert's law: It states the absorption of incident light by the homogeneous medium is independent of the intensity of incident light but decreasing rate depends on the thickness of absorbing medium.

$-\frac{dI}{dt} = KI$ I= Intensity of incident light (14)

t = thickness of medium

from the eq.(13)

$$\int_{t_0}^{t} -\frac{dI}{I} = K.dt$$

$$In\frac{I}{I_0} = -Kt$$

$$\log\frac{I}{I_0} = e^{-Kt} \qquad (15)$$

From the eq. K=∈c

$$\log_{10}\left(\frac{I}{I_0}\right) = -\in ct$$

$$\log_{10}\left(\frac{I_0}{I}\right) = \in ct \qquad (16)$$

This eq. (16) is known as Lambert-Beer's law.

From this equation state that "The absorbance of a molecule depends on concentration and thickness of the medium".

Limitation:

→ This is only applicable for a dilute solution.

→ It fails to explain the effect at temperature, nature of solvent and wavelength.

Importance terminology and concept in ultraviolet spectroscopy:

Chromophore and Auxochrome:

(i) **Chromophores:** It is defined as an isolated functional group present in the molecule which is capable of absorbing the radiation in the range of 200-800 nm.

The typical examples are C=C, C≡C, C=N, C≡N, C=O, N=N etc. chromophore compound is self-colour compound.

For example, Carotine which possesses large no. of conjugated double bonds as a result $\pi \rightarrow \pi^*$ transition is possible at a higher wavelength (440 nm).

(ii) **Auxochrome:** It is defined as an auxiliary functional group which interacts with chromophore leading to the absorption at a higher wavelength. Such as presence of –OH, $-NO_2$, $-NH_2$, etc. interaction with chromophore causing the shift at a higher wavelength.

Types of shift:

In the presence of other substance or polar and no polar solvent; deviation occurs from the standard absorption position is known as chemical shift. There are two different types of shift appeared in ultraviolet spectra.

(A) Shift related to wavelength
(B) Shift related to molar absorptivity

(A) Shift related to wavelength:

According to the increasing or decreasing the value of wavelength, it can be further divided into two groups:

(1) Bathochromic shift:

The shift occurs towards the longer wavelength is called bathochromic shift. Ultraviolet absorption shift towards visible range, so It is also known as 'red shift'.

In presence of polar solvent the absorption band of C=O group. The shift toward longer wavelength which is known as bathochromic shift.

(2) **Hypsochromic shift:**

The shift occurs towards the shorter wavelength is called Hypsochromic shift. Ultraviolet absorption shift towards far UV region, so it is also known as blue-shift.

$n \rightarrow \pi^*$ absorption band of C=O group shift towards shorter wavelength in presence of non-polar solvent is an example of the Hypsochromic shift.

(B) Shift related to molar absorptivity

If the intensity of absorption band increases or decrease; the molar absorptivity of the molecule is an increase or decrease is further divided into two groups:

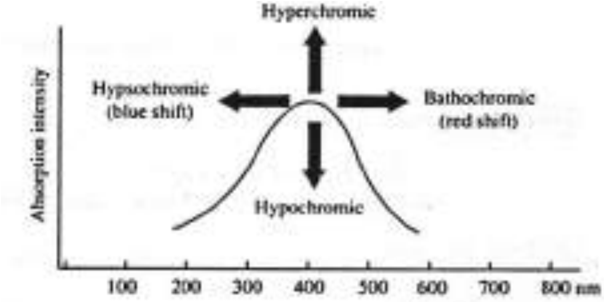
1. **Hyperchromic effect**
2. **Hypochromic effect**

(1)Hyperchromic effect: It is the effect leading to increased absorption intensity.

<u>Example:</u> In the ionic solution of phenol, primary And secondary bands shows this effect.

(2)Hypochromic effect: The shift which leading to decrease absorption intensity is known as a Hypochromic effect.

The ionic solution of Benzilic acid; the intensity of primary and secondary band shows this effect.

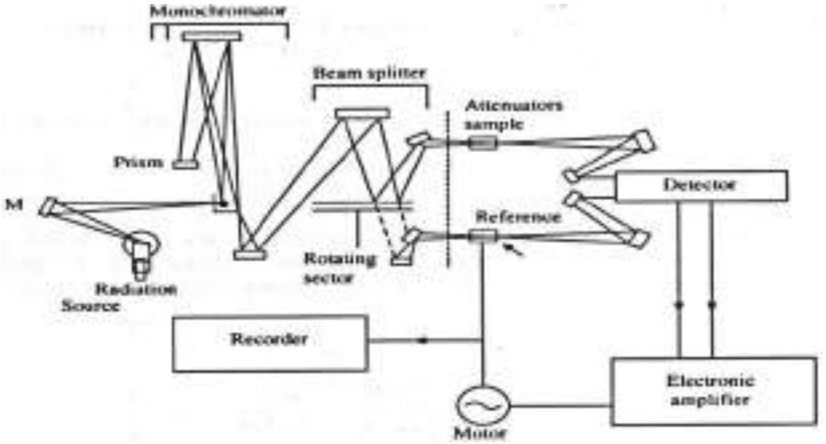


Effects of substituents on the position and intensity of an absorption band.

❖ Ultraviolet- visible spectrometer:

The essential components of an automatic recording ultraviolet- visible spectrometer are as under:

1) Source of radiation
2) Sample and reference cell
3) Monochromator
4) Detector(photocell or photomultiplier tube)
5) Amplifier and Recorder



1) **Source of Radiation:** To emit ultraviolet radiation in the range of 200-400 nm.

→ It must generate a beam of radiation with sufficient power.

→ Its output should be stable.

Generally following three types of source radiation are available for the ultraviolet spectrophotometer.

a) **Tungsten filament lamp(Xenon discharge lamp)**

In this lamp, Xenon gas is filled under pressure in the range of 10-30 atm. The Xenon lamp possesses two tungsten electrode separated by 8mm distance.

The intensity of the UV radiation produced by Xenon discharge lamp is much greater than hydrogen lamp.

b) **Hydrogen Discharge lamp**

In this lamp; Hydrogen gas is filled under relatively high pressure. When electric current possesses through the lamp. An excited molecule of hydrogen will be produced which emits the UV radiation.

c) **Deuterium lamp:**

Deuterium lamp is used in place of hydrogen. The intensity of radiation is 3 to 5 times more effective than hydrogen lamp.

2) Sample and Reference cell:

For recording the absorption spectra, Identical cells made up of Quartz or silica.

The monochromatic beam is split into two equal intensity beam is split into two equal intensity beam by means of mirror reference cell which contain only pure solvent other through the solution.

3) Monochromator

To disperse the polychromatic light into monochromatic light according to wavelength.

Monochromator device divide in three different components.

(i) Entrance slit: It sharply defined the incoming beam of radiation.

(ii) Dispersing device: To resolve the incoming radiation dispersing device used. Following are used dispersing device. (a) Filter (b) Prism (c) Different gravity

(a) Filter: It will be absorbed the unwanted radiation. Generally, glass which is coloured by pigment used as a filter.

(b) Prism: It is made up of quartz or fused silica. Fused silica prisms are little transparent in short wavelength region than quartz prism.

(c) Different grating: It consists of a large number of parallel lines ruled at the close interval on the polished surface of Aluminium or glass. Each part scattering light radiation approximately 5000-6000 line per are drawn.

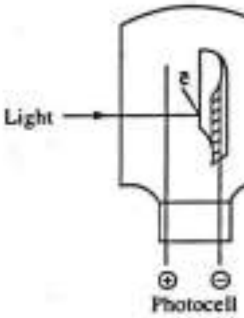
(iii) Exit slit: It allowed passing the radiation of required wavelength.

4) Detector:

It is must respond to all the light radiation. The response should be rapid.

Generally, photocell or photomultiplier tube are used as a detector in the ultraviolet spectrometer.

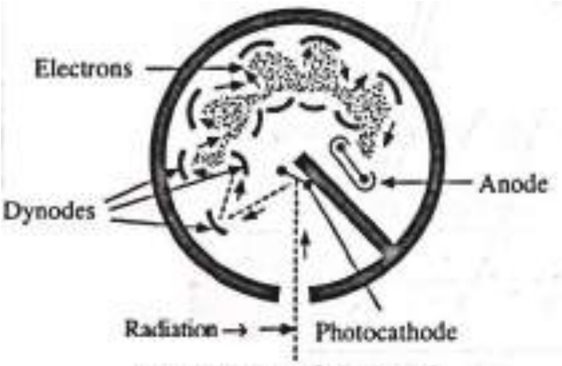
(a) Photocell: The device consists of a light sensitive cathode in the form of half of metal which contained in an evacuated tube. The anode is also a presence in the tube which is fixed more or less along the axis of the tube.



Photocell

The current is created between cathode and anode is regarded as a measure of radiation falling on a detector.

(b) **Photomultiplier tube:** photomultiplier tube is a combination of photodiode and electron multiplying amplifier. A photomultiplier tube consists of an evacuated tube which contains one photocathode and 9-15 electrode known as dynods.



Multiplication of electrons in a photomultiplier tube

5) Amplifier and Recorder.

Amplifier, amplify the signal and recorder is record the plot of wavelength versus absorption.

❖ Factor affecting the position of absorption bands

1. Conjugation:

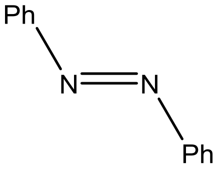
A conjugation system contains alternate double bond require lower energy for the $\pi \rightarrow \pi^*$ transition than an unconjugated system.

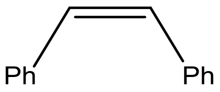
If π electron distributes is delocalised over a whole system, hence decreasing $\pi \rightarrow \pi^*$ transition energy resulting wavelength is increased with absorption.

2. Steric hindrance

The ultraviolet spectroscopy is very sensitive to distortion of chromophore intensity toward steric repulsion which opposes the coplanarity of conjugated π bonds.

For example : Azo Benzene





$\pi \rightarrow \pi^*$	λ_{max}	320	(21300)	281	(5260)
$n \rightarrow \pi^*$	λ_{max}	443	(510)	433	(1520)

3. Solvent effect:

→ The intensity and position of absorption band greatly affected by the polarity of the solvent.

→ It happens due to the solvate capability of the solvent.

→ Conjugated dienes and aromatic hydrocarbons exhibit very little solvent shift.

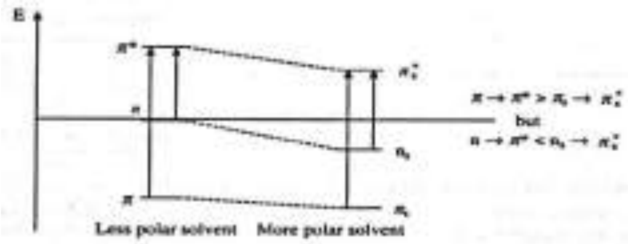
→ α, β unsaturated carbonyl compounds display two different types of shift.

(1) $\pi \rightarrow \pi^*$ band shows Bathochromic shift in presence of polar solvent.

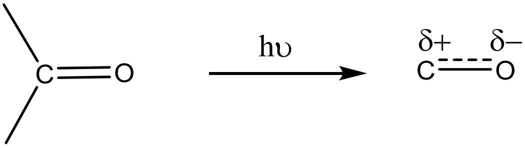
(2) $n \rightarrow \pi^*$ band shows Hypsochromic shift in presence of polar solvent.

This effect may be due to the effect of solvation on the relative energies of n, π & π^* orbitals.

π^* & n orbitals are more stabilise as compare to π orbital in presence of polar solvents.



Factor affecting to the C=O group absorption

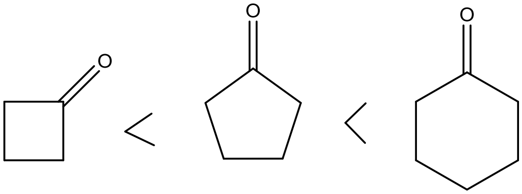


The absolute result of solvation is that energy of $\pi \rightarrow \pi^*$ transition becomes less while $n \rightarrow \pi^*$ transition become increase.

The following factor is affecting to the absorption of C=O compounds.

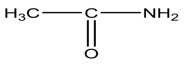
(1) **Size of ring**

The size of the ring is inversely proportional to the ring strains. By increasing the size of the ring, ring stain is decreased resulting in the energy difference between $n \rightarrow \pi^*$ value increase. So λ_{max} gradually decrease.

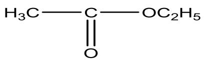


(2) **Neighbouring group effect (Inductive effect)**

If the neighbouring group shows positive inductive effect(+I); donate the electron to carbonyl carbon; $n \rightarrow \pi^*$ transition decrease and for withdrawing the electron. $n \rightarrow \pi^*$ transition energy decrease so hypsochromic and bathochromic shift appeared respectively.



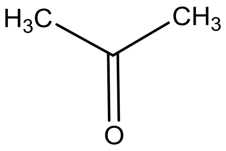
$H_3C-C(=O)-NH_2$ 220 nm



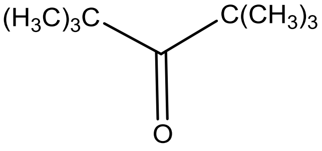
$H_3C-C(=O)-OC_2H_5$ 207 nm

(3) Steric hindrance

If the size of the surrounding group is an increase, decrease the energy of $n \rightarrow \pi^*$ transition resulting in the bathochromic shift.



λ_{max}= 279nm



λ_{max}=295 nm

Frank Condon principle

The relative intensity of electronic spectra may be interpreted in terms of 'Frank-Condon principle'. It is stated that 'monovalent of nuclei is negligible during the time of electronic transition.'

The time requires for electronic transition is so small that the atom in a molecule does not get a chance, their internuclear distance.

During absorption, a molecule is being transformed into different energy level represented by a different potential curve.

There is no section rule to restrict vibration transition accompanying the electronic transition. The transition occurs between those levels where vibration wave functions are maximum.

Selection rule for electronic transition:

The selection rule is useful for the interrelation of the relative intensity of absorption band.

If there is a change in the number of unpaired electron in the ground state and excited state which is known as forbidden transition.

During the electronic transition; if redistribution of electron takes place within their original orbital (i.e. d→d or p→p) is known as forbidden transition i.e. molecule must have a centre of symmetry.

If during the electric transition; there is no change in their azimuthal number but may change their dipole moment is known as allowed transition.

Requirement of Frank-Condon Principle:

- → An electronic in which nuclei do not move can be presented by a verticle line.
- → The most move favourable transition will occur from the most probable orbital i.e. HOMO
- → At room temperature, all molecule are likely to present in vibrational ground level i.e. ν=0
- → The final state of vibrational transition depends on relative position.

General application of UV-Visible spectra:

(1) Determination of structure

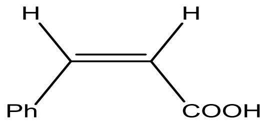
Identification of degree of unsaturation

- o 220-250 nm (λ_{max})(ϵ =1000) only two double bonds in conjugation.
- o 260-300 nm (λ_{max})(ϵ =200-100) benzene
- o 270-300 nm (λ_{max})(ϵ <1000) carbonyl compound

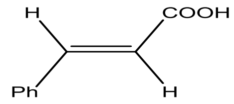
(2) Geometrical isomerism:

Ultraviolet spectroscopy can be easily distinguished geometrical isomer.

Trans isomer appeared at higher λ_{max} with greater $\in$ value as compared to cis-isomer.



Cis-Cinnamic acid



Trans-Cinnamic acid

$\lambda_{max}=261nm$

$\in_{max}=10700$

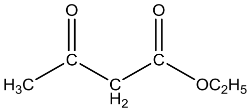
$\lambda_{max}=272\ nm$

$\in_{max}=15900$

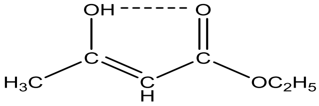
(3) Tautomerism:

Ultraviolet spectroscopy has been extended for the study of tautomers in solution phase.

Example: ethyl acetoacetate



Ketone



Enol

$n \rightarrow \pi^*$

$\lambda_{max}=275\ nm$

$\pi \rightarrow \pi^*$

$\lambda_{max}=244\ nm$

(4) Hydrogen bond:

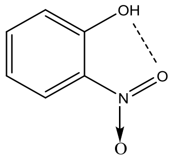
Hydrogen bonding involves electron-cloud transfer from the hydrogen atom to the neighbouring electronegative atom and it is positive between proton donor and acceptor group.

The hydrogen bond formation takes place between the molecule as well as within the molecule.

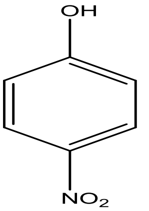
Due to the formation of H-bond; $n \rightarrow \pi^*$ transition energy increases while $\pi \rightarrow \pi^*$ energy decreases, as a result, blue shift and a red shift occurs respectively.

(5) **Steric Hindrance**

Intramolecular H-bond



o-nitrophenol



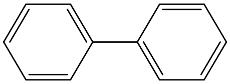
p-nitrophenol

$\lambda_{max}=271$ nm

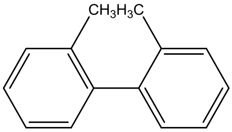
$\lambda_{max}=262$ nm

The steric effect can be realised by the study of ultraviolet spectroscopy (example: Biphenyl and o,o - Dimethyldiphenyl)

Simple Biphenyl has a free rotation around C-C single bond is coplanar and coaxial but the introduction of Methyl group at o-position disturb coplanarity as a result absorption band shift towards shorter wavelength.



1,1'-biphenyl



2,2'-dimethyl-1,1'-biphenyl

$\lambda_{max}=248$ nm

$\lambda_{max}=280$ nm

$\epsilon_{max}=19000$

$\epsilon_{max}=740$

(6) Ultraviolet spectroscopy is useful for the study Quantitative analysis as well as for the detection of impurities.

(7) Ultraviolet spectroscopy has great extend for quantitative analysis on the basis of Lambert beer law.

(8) It is also useful for the study of charge-transfer complexes.

(9) It is also applicable for the study of chemical reaction

(10) Ultraviolet spectroscopy is useful for the study of stereo isomerism (configuration).

❖ Ultraviolet absorption of some organic compounds.

(I) Extension of conjugation:

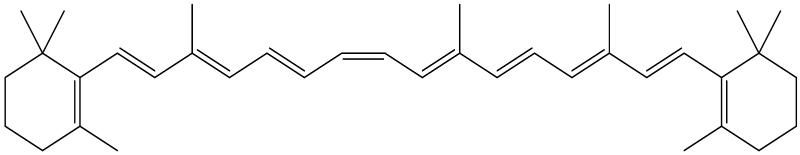
Ultraviolet spectra of alkenes are determined by the π electron which is excited at lower energy than the σ electrons.

Ethylene exhibit two peaks of unequal intensity, both are due to $\pi \rightarrow \pi^*$ transition: 165 nm & 210 nm.

Alkyl substitution of the parent compound shifts the absorption at longer wavelength i.e. bathochromic shift which is increase with increasing the number of the ethylinic units.

Conjugation system attack the ultraviolet absorption. If this π electron distributes is delocalised over a whole system. Hence it decreasing the $\pi \rightarrow \pi^*$ transition energy resulting in the absorption at a longer wavelength.

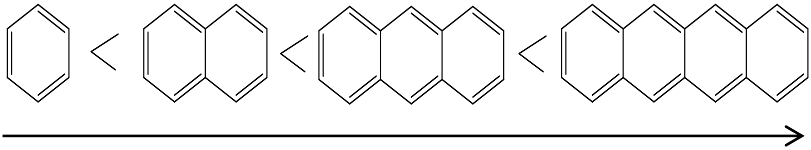
Example: β- carotene.



β- Carotene possess eleven ethylinic double bond with conjugation due to localization of π=electrons over a whole molecule system require very low energy for $\pi\rightarrow\pi^*$ resulting in the shift in visible range i.e. λ_{max}= 451 nm.

(II) Polynuclear compound:

In polynuclear aromatic compounds, by increasing the number of rings, π bond conjugated system becomes extended. As a result of this resulting the energy difference between $\pi\rightarrow\pi^*$ is decrease which shifts the absorption band towards longer λ_{max}.



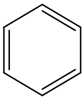
λ_{max} increase

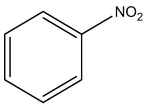
(III) Comparative studies of the two compounds:

(a) Benzene and Nitrobenzene

Benzene is simple containing three double bonds with conjugation in the ring. It absorbs the ultraviolet radiation due to the ethylinic double bond with extra double bond, so it is colourless.

The increase of Nitrobenzene $-NO_2$ group present as a chromophore which extends the conjugation as well as $n\rightarrow\pi^*$ transition resulting the absorbance appeared in the visible range. Thus it is coloured.

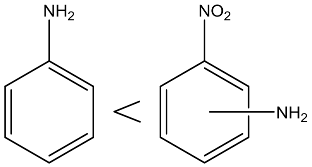




(b) Aniline and o/m/p Nitro Aniline

In the case of aniline; there is no any chromophore group present on a benzene ring but only –NH_2 group present as an auxochrome but it does not show an effect in colourless.

While in the case of NO_2 aniline, NO_2 group act as a chromophore which extent the λ_{max} as well as $\in_{max}$ also due to the presence of –NH_2 group as an auxochrome so not only colour but the intensity of the colour is also increased.

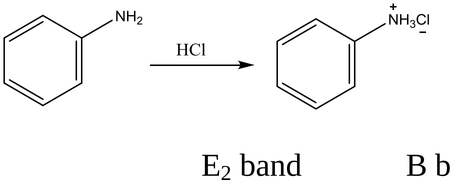


λ_{max} and $\in_{max}$

- **Ultraviolet absorption of Aniline and Aniline cation**

Aniline, which possesses –NH_2 group (auxochrome) present on the benzene ring. Nitrogen of –NH_2 contains loan pair of electron. So two types of transition are possible (i) $n \to \pi^*$ (ii) $\pi \to \pi^*$

But in the case of anilinium cation loan pair of electrons utilises for the salt formation. i.e. These electrons are not available for the interaction with π electron of the ring. So obtained spectrum is almost identical with that of the benzene ring.

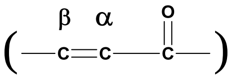


		E_2 band	B band
Aniline	λ_{max}	230(1800)	280(1430)
Anilinium	λ_{max}	203(7500)	254(160)
Benzene	λ_{max}	204(7900)	254(200)

Example: Woodward & Fisher Rules for Diene system

	$\pi \to \pi^*$ transition
→Acyclic and heteoannular diene	214 nm
→Homoannular diene	253 nm
→Addition for each substituent	
R=alkyl	5 nm
-OR	6 nm
-Cl, -Br	5 nm
-OCOR	0 nm
-Extra double bond	30 nm
-Exocyclic double bond	5 nm
-Ring residue	5 nm
-Cis bond	39 nm

(1) Rules for Enone

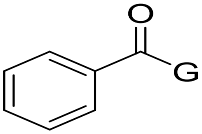


$(\overset{\beta}{-C}=\overset{\alpha}{C}-\overset{O}{\overset{\|}{C}}-)$

Acyclic six membered ring	215 nm
Acyclic five membered ring	202 nm
-C=C-CHO	210 nm
-C=C-C(O)-OR/H	197 nm
Homodiene	39 nm
Increment for	

	α(nm)	β(nm)	γ(nm)	δ(nm)
R=alkyl group	10	12	18	18
OR	35	30	17	31
OH	35	30	30	50
-SR	-	80	-	-
-Cl	15	12	12	12
-Br	25	30	25	25
-COR	6	6	6	6
$-NH_2$, -NHR, $-NR_2$	-	95	-	-
Exocyclic double bond		10	nm	

(2) Rules for Arone system

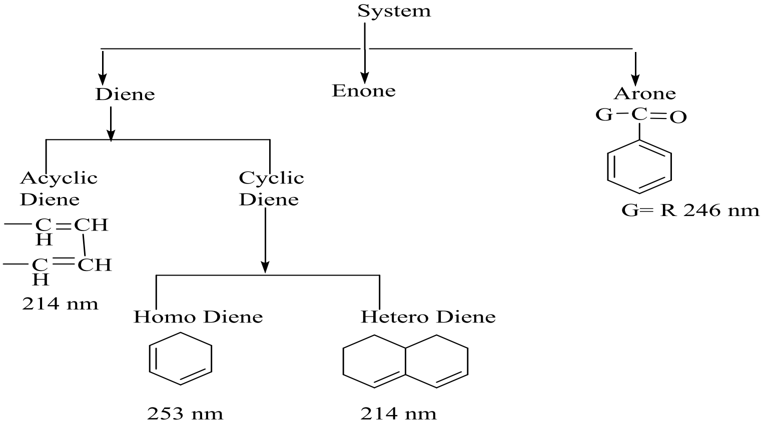


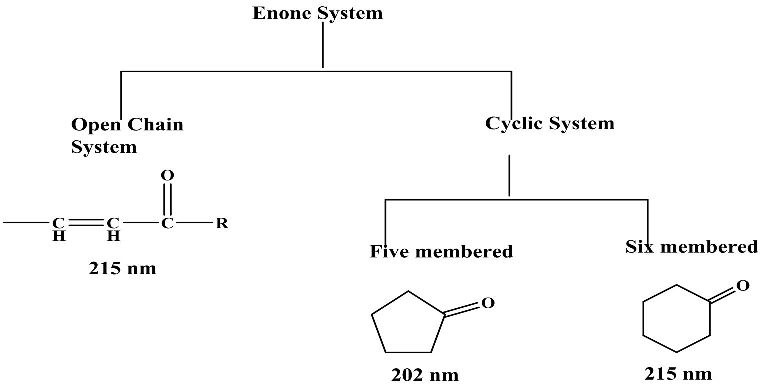
G= alkyl group	246 nm		
= H	250 nm		
=OH/OR	230 nm		
	Ortho(nm)	Meta(nm)	Para(nm)
Alkyl	3	3	10
-OH, -OMe, -OR	7	7	25
O^-	11	20	78
Cl^-	0	0	10
Br	2	2	15
NH_2	13	13	58
NHAc	20	20	45
NHMe	-	-	73
NMe_2	20	20	85

Calculation of λ_{max} :

(1) To decide the parent system.

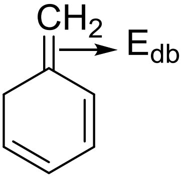
Parent system identification by following:

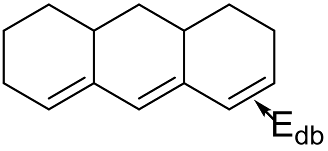


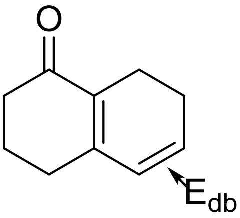


(2) Add the value of extra double bond.

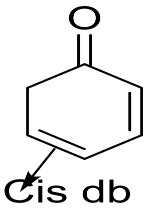
Ex.

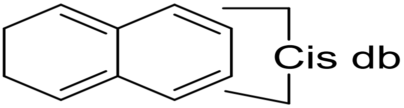




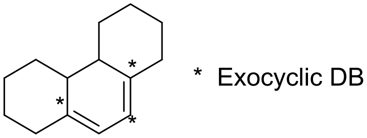


(3) Add the value of Cis Double bond:

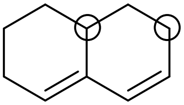




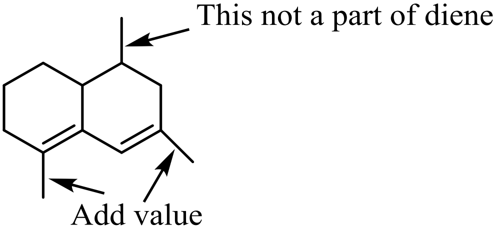
(4) Add the value of exocyclic double bond:



(5) Add the value of ring residue:

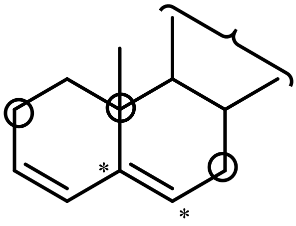


(6) Substitution value:



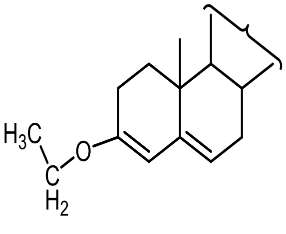
❖ **Calculate the λ_{max} for folloeing compounds.**

1)



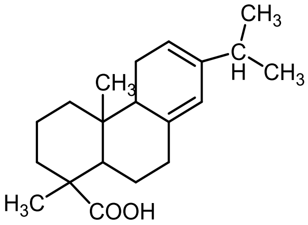
Base value (hetero)	214 nm
Extra double bond	00 nm
Cis bond	00 nm
Ring residue 3×5	15 nm
Exocyclic DB	05 nm
Total	234 nm

2)



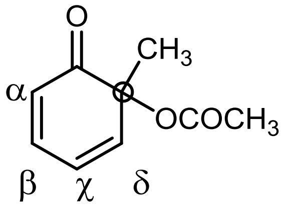
Base value (hetero)	214 nm
Extra double bond	00 nm
Cis bond	00 nm
Ring residue 3×5	15 nm
Exocyclic db	05 nm
-OR	06 nm
Total	240 nm

3)



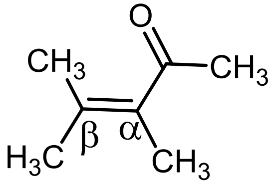
Base value (homo diene)	253 nm
Extra double bond	00 nm
Cis bond	00 nm
Ring residue 3×5	15 nm
Exocyclic db	05 nm
substitution alkyl	05 nm
Total	278 nm

4)



Base value (six member Enone)	215 nm
Extra double bond	30 nm
Cis bond	39 nm
Ring residue 3×5	18 nm
Total	302 nm

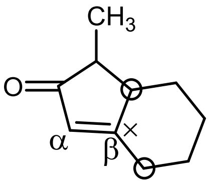
5)



Acyclic Enone

Base value	215 nm
Substitution α	10 nm
β(2 CH_3 ×12)	24 nm
Total	249 nm

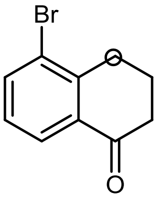
6)



Five member Enone

Base value	202 nm
Ring residue β position: 2×12	24 nm
Exocyclic db	05 nm
Total	231 nm

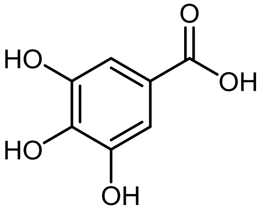
7)



Arone z= Alkyl group

Base value	246 nm
Ring residue(ortho)	03 nm
(meta-Br)	02 nm
Total	251 nm

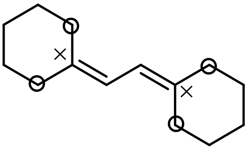
8)



Arone G= -OH

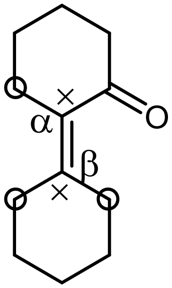
Base value	230 nm
Substitution m= 2×-OH	14 nm
p= -OH	25 nm
Total	269 nm

9)



Acyclic diene	214 nm
Extra db	00 nm
Cis bond	00 nm
Ring Residue 4×5	20 nm
Exocyclic db 2×5	10 nm
Total	244 nm

10)

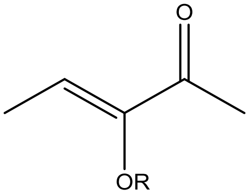


6-memebered Enone

Base value	215 nm
Ring Residue α	10 nm
β 2×12	24 nm
Exocyclic db 2×5	10 nm
Total	259 nm

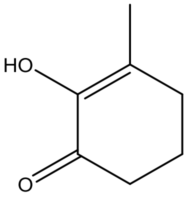
Example for Practice:

(1)



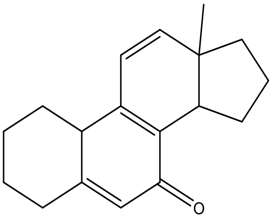
λ_{max}=239 nm

(2)



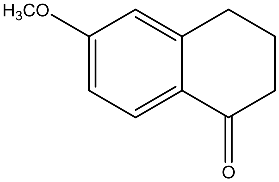
λ_{max}=274 nm

(3)



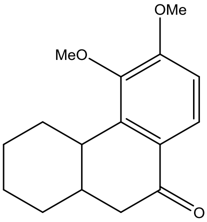
λ_{max}=329 nm

(4)



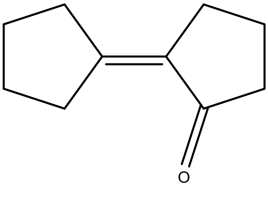
λ_{max}=274 nm

(5)



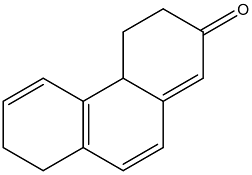
λ_{max}=281 nm

(6)



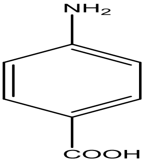
λ_{max}=259 nm

(7)



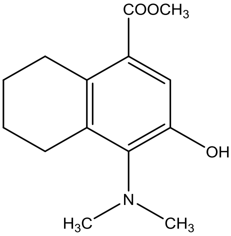
λ_{max}=410 nm

(8)



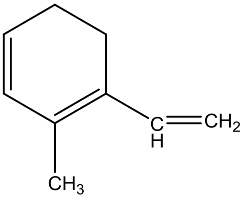
λ_{max}=288 nm

(9)



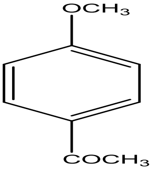
λ_{max}=344 nm

(10)



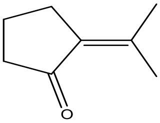
λ_{max}=298 nm

(11)



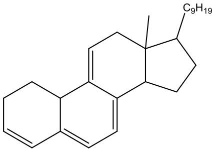
λ_{max}=271 nm

(12)



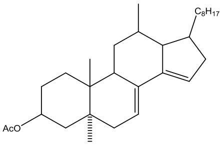
λ_{max}=302 nm

(13)



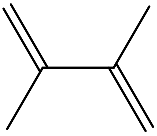
λ_{max}=353 nm

(14)



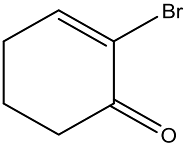
λ_{max}=244 nm

(15)



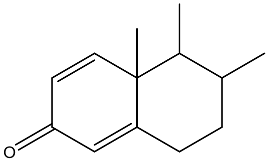
λ_{max}=227 nm

(16)



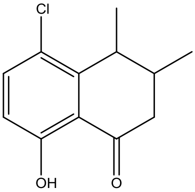
λ_{max}=252 nm

(17)



λ_{max}=244 & 227 nm

(18)



λ_{max}=256 nm

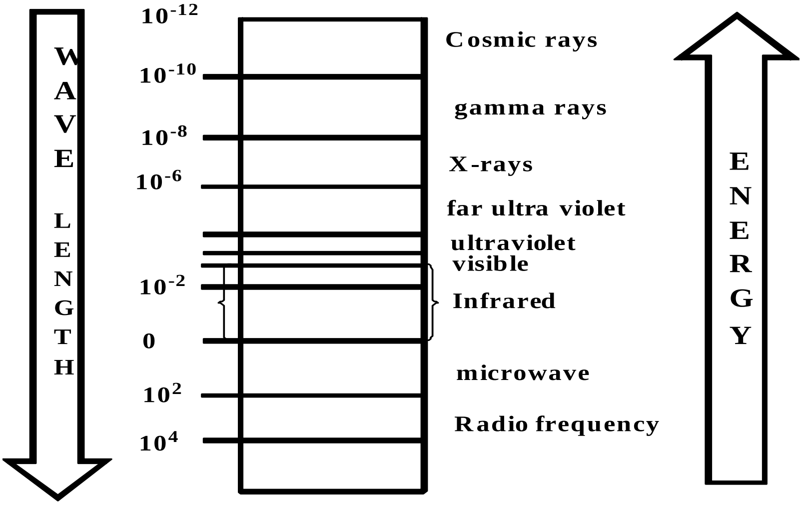
Chapter 3

Infrared Spectroscopy

Introduction:

Infrared spectroscopy is an important tool for the organic chemist. It is one of the most widely used tools the detection of functional group in the pure compound as well as in mixture for the comparison purpose.

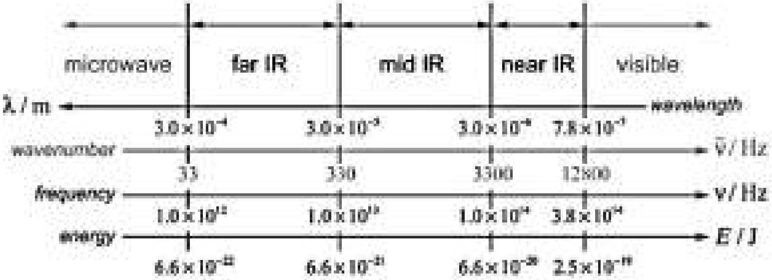
Infrared refers to that part of the electromagnetic spectrum between the visible and microwave region. In a molecule; atoms join by covalent bonds are not fixed at one position but continual vibration with each other. The energy associated with these motion correspond to frequencies in the region of infrared waves, which stretches from 4000-400 cm^{-1}.



Range of infrared:

Infrared rays lie between ultra-violet visible and microwave radiation in electromagnetic radiation.

Infrared radiation further divided into three different parts



The near IR radiation passes 10-37 K.Cal energy per mole while middle IR and far IR radiation passes 1-10 K.Cal and 0.1-1 K.Cal energy per mole.

Middle Infrared region i.e. from 4000-400 cm-1 region is more useful for the organic chemist.

Theory of IR:

The molecule absorbs the radiation in the range of infrared and organic molecule converted it into the vibrational and rotational spectrum is obtained.

For the study of vibrational spectroscopy being with a diatomic molecule as the model vibrator as a harmonic oscillator. The diatomic molecule (two atoms join with each other by a covalent bond) obey Hooke’s law. Vibration is to and ‘fro’ motion of atoms connected by a bond in the molecule as well as its gravity centre. The elongation and compression of bond alternately resulting in the displacement of the atom from their equilibrium position. Let the displacement be “a”, an external force “F” is required for the displacement. A restoring force “f” arises in the bond in opposite direction of the displacement, for the equilibrium position: i.e. $F=-f$ …………… (i)

According to classical harmonic motion; the displacement of an atom is directly proportional to the applied force.

$F \propto a$ ………………… (ii)

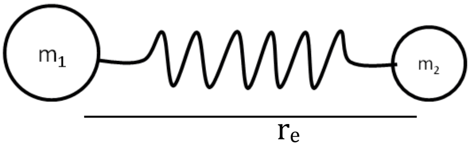
$F \propto -a$ ………………… (iii)

$F = -ka$ …………………(iv)

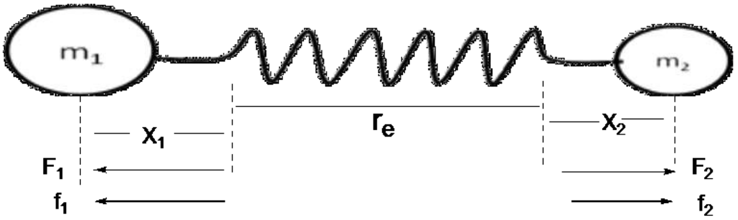
k is proportionality constant which measures the 'stiffness' at the bond, hence also known as " force constant" for the relevant bond.

Frequency of vibration of diatomic molecules:

Consider a diatomic molecule "AB" of masses m1 and m2 separated by an equilibrium bond length re.



Consider either the bond is elongated and compressed on "X" axis.



According to simple harmonic motion;

Restorment force

$f_1 = k(X_2 - X_1)$ and ………….(v)

$f_2 = -k(X_2 - X_1)$ …………..(vi)

According to Newton's second law

$f = ma$ …………………(vii)

Here, m= mass and a = acceleration due to motion,

This can be defined as $\frac{d^2x}{dt}$.

From the equation (vii) & (v) and (vii) & (vi)

$f_1=m_1a_1 = k\ (X_2 - X_1)$ or
$= m_1\frac{d^2x_1}{dt^2} = k(X_2 - X_1)$ …… (viii)
$f_2=m_2a_2 = -k(X_2 - X_1)$ or
$= m_2\frac{d^2x_2}{dt^2} = -k(X_2 - X_1)$ ………(ix)
Eq. (viii) & (ix) can be solved by
$X_1 = A_1\cos(2\pi\vartheta_t + \emptyset)$ ………(x)
$X_2 = A_2\cos(2\pi\vartheta_t + \emptyset)$ ………. (xi)
Where ν= linear frequency
∅= phase of the vibration
From the second order different of x1 and x2 eq. (x) & (xi)
$\left(\frac{d^2x_1}{dt^2}\right) = -4\pi^2V^2A_1\cos(2\pi\vartheta_t + \emptyset)$ ………….(xii)
$\left(\frac{d^2x_2}{dt^2}\right) = -4\pi^2V^2A_2\cos(2\pi\vartheta_t + \emptyset)$ …………. (xiii)
Solving one of the eq. (viii) by putting the value of $\frac{d^2x_1}{dt^2}$
$-4\pi^2V^2A_1\cos(2\pi\vartheta_t + \emptyset) = k(A_2 - A_1)\cos(2\pi\vartheta_t + \emptyset)$
………… (xiv)
$\therefore(k - 4\pi^2V^2m_1)A_1 = kA_2$ …………. (xv)
$\therefore kA_1 = (k - 4\pi^2V^2m_2)A_2$ …………. (xvi)
By cross multiplication of (xv) & (xvi)
$(k - 4\pi^2V^2m_2)(k - 4\pi^2V^2m_2) = k^2$ …………. (xvii)
$k^2 + 16\pi^2V^4m_1m_2 - 4\pi^2V^2k(m_1 + m_2) = k^2$ … … (xviii)
$\therefore 4\pi^2V^2m_1m_2 = (m_1 + m_2)k$ …………..(xix)
$\therefore v = \frac{1}{2\pi}\sqrt{\left(\frac{m_1+m_2}{m_1m_2}\right)k}$ ……. (xx)
$\therefore v = \frac{1}{2\pi}\sqrt{\frac{k}{r}}$ Where $r = \frac{m_1m_2}{m_1m_2}$ which is known as reducing mass

Since $c = v\lambda$ or $\frac{v}{c} = \frac{1}{\lambda}$ ..... (xxi)

Where λ is measured in cm and wavenumber in cm^{-1},

∴ modify eq. (xxi)

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{r}}$$

This equation is used for the calculation of “k” force constant.

Modes of fundamental vibration:

A molecule has as many degrees of freedom as the total degree of freedom of its individual atoms. Each atom has 3 degrees of freedom corresponding to the Cartesian coordinates(x, y, z) necessary to explain their relative position. A molecule possesses n atoms, therefore, has a 3n degree of freedom. For nonlinear molecules, three degrees of freedom for rotation and three degrees of freedom for translation (vibration) to avoid duplication for non-linear molecule, while linear molecule, only two degrees of freedom are two;

∴ linear molecule

Degree of freedom= 3n-5 & non-linear molecule;

Degree of freedom= 3n-6.

In this type of vibration, there is no change in the centre of gravity of the molecule.

There are two types of molecular vibrations: (i) stretching and (ii) bending.

Stretching Vibration:

A stretching vibration is movement of atoms along the bond axis such that inter-atomic distance is increasing or decreasing

According to the direction of stretching, it can be further divided into two parts.

(a) Symmetrical stretching

In diatomic molecules both atoms of the bond are coming near to central paint (gravity centre) at the same time and go far from the centre paint at the same time is known as " symmetrical stretching" vibration.

These vibrations are generally IR inactive because it does not bring change in dipole moment.

(b) Asymmetrical stretching

In diatomic molecules out of the two atoms, when one atom comes near to central paint while other goes away from the central point is known as "asymmetrical stretching" vibration.

These vibrations required higher energy as compare to stretching vibration, and absorption occurs at a higher frequency.

Bending vibration:

A bending vibration is correlated to change in bond angles between bonds with a common atom or the movement of a group of atoms with respect to one another.According to presence of atom in plane; bending vibration divided into two groups

(i) In-plane bending
(ii) Out of plane bending

(i) In-plane bending:

During vibration, the position of atom changes in the same plane, then it is known as In-plane bending vibration.

On the basis of the motion of atoms, it can be further classified into two groups:

a) Scissoring
b) Rocking

a) Scissoring: If atoms of the molecule come near to each other or far from each other without a change in bond length as well as plane, then it is known as scissoring vibration.

b) Rocking: Whole molecules can vibrate just like rock i.e. structural units swing back and forth within the plane.

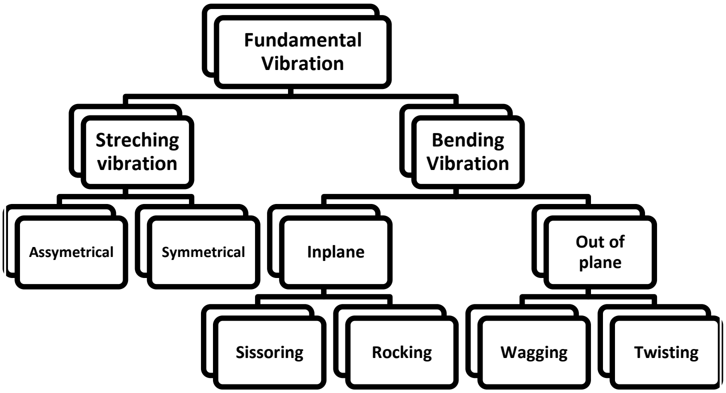
(ii) Out of plane bending:

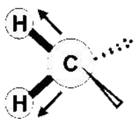
During the vibration, the atom changes their plane is known as out of plane bending vibration. i. e. the atoms swing up & down of the plane of the paper.

According to the motion of the atom, further, it can be divided into two classes.

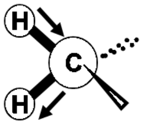
a) Wagging: The atoms associated with bond come forth and back in the plane is known as wagging deformation.

b) Twisting: The atom associated with bond play like twisting of rope i.e. atom come forth and back alternate in opposite direction is known as twisting deformation.



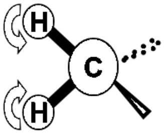


Symmetrical Vibration

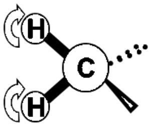


Asymmetrical Vibration

Inplane

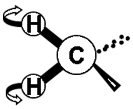


Scissoring

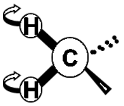


Rocking

Out of Plane



Twisting



Wagging

Infrared Activity:

There is a variety of ways in which number of molecular vibration takes place and corresponds to a total of 3N-6 or 3N-5 vibration with respect to the non-linear and linear molecules.

According to the classical theory, the condition for infrared activity is that at least one dipole moment of the component must change with respect to the normal coordinate and it is only possible when incident frequency match with the fundamental frequency. i.e. $\left(\frac{d\mu_i}{dQ}\right)_0 \neq 0$ where μ= dipole moment , Q= normal coordinate

Force constant:

In diatomic molecule, force constant can be represented as

$$K = 4\pi^2 c^2 (\vartheta)^2 r$$

K is primary function of the bond type and it will be the order of (1-25)× 10^5 dyne/cm.

Force constant for the stretching and bending must have the same units. Force necessary for deformation of angle is less than stretching of the bond.

∴ Force constant in some simple molecule.

Table: 1

Molecule	$\nu(cm^{-1})$	K.dyne/cm
HF	2907	9.7×10^5
HCl	2886	4.8×10^5
HBr	2559	4.1×10^5
HI	2230	3.2×10^5
CO	2143	18.4×10^5
NO	1904	16.0×10^5

The force constant value of double bonds lies between those of single and triple bonds(Exception: HF molecule). It can be concluded that

Single bond $<7\times10^5$

Double bond 7-15 $\times10^5$ &

Triple bond 15×10^5 dyne/cm.

Coupling of rotational and vibrations.

When substantial interaction takes place between rotations and vibration; the Born. Oppenheimer approximation is said to break-down. For the evaluation of nature and magnitude of interaction; few main interactions can be identified which may effect on absorption.

(a) Average bond length increase with increasing vibrational energy which effects on inertia as a result rotational energy depends on vibrational energy level.

(b) As the molecule goes to higher energy level, which is distracted by centrifugal force thereby perturbing the energy.

(c) In the case of the bath at higher and lower vibrational or rotational level. Molecule behaves an intermediate of the good oscillator and rigid rotor.

A consequence of all this it may be effective on the coupling of rotation & vibration; as a result on the non-constancy of rotational band spacing. Therefore it is necessary of a cross-term in the energy expression which can be represented as

$$\bar{E}_{v_j} = \left(v+\frac{1}{2}\right)\bar{\upsilon} + \overline{B_{v_J}}(J+1)$$

Where $\overline{B_{v_J}}$ = implies that of rotation constant is a functional of vibrational quantum number and

$$\overline{B_v} = \overline{B_e} - \alpha_e\left(v+\frac{1}{2}\right)$$

$\overline{B_e}$= rotational equilibrium band length

A= $+$ small constant

$$\overline{E_{0.J}} = \frac{1}{2}\bar{\upsilon} + \overline{B_o}j(J+1)$$

$$\overline{E_{1J}} = \frac{1}{2}\bar{\upsilon} + \overline{B_1}j(J+1)$$

$$\therefore \bar{w} = \bar{v} + \ [\bar{B}_1(J^1)(J^1+1) - \bar{B}_0 J(J+1)]$$

(i) ΔJ= +1. i.e. J→J+1 (R branch)

∴we can express as J'=J+1

$$\therefore \bar{w} = \bar{v} + \left(\bar{B}_1(J+1)(J+2) - \bar{B}_0 J(J+1)\right)$$

$$= \bar{v} + 2\bar{B}_1 + (3\bar{B}_1 - \bar{B}_0)J + (\bar{B}_1 - \bar{B}_0)J^2$$

Where J= 0,1,2,3,……..

(ii) ΔJ= -1 i.e. J→J-1 or J'= J-1 (P- Branch)

$$\bar{w}_p = \bar{v} + \left(\bar{B}_1(J-1)J - \bar{B}_0 J(J+1)\right)$$

$$= \bar{v} + (\bar{B}_1 + \bar{B}_0)J + (\bar{B}_1 - \bar{B}_0)J^2$$

Where J= 1,2,3,….

Since the higher energy vibrational state has a greater vibrational amplitude. thus the co-efficient of J^2 terms in the expression for P and R branches are negative

∴ for the rotational-vibrational spectra

E= $E_{\text{rotational}}$+ $E_{\text{vibrational}}$

$E_{vb} = \ hc\overline{v_0}$ And $E_{rot} = \frac{h^2}{8\pi^2 I}\left(J^1(J^1+1) - J(J+1)\right)$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}\left(J^1(J^1+1) - J(J+1)\right)$$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}\left(J^1 J - J(J+1)\right)$$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}J(J^1 - J - 1)$$

$\therefore J^1$-J= 1

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}J(-1-1)$$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}(-2J)$$

$$E_{IR} = hc\overline{v_0} - \frac{h^2}{4\pi^2 I}J \qquad \text{But } E = \frac{hc}{\lambda}$$

$$\frac{hc}{\lambda} = hc\overline{v_0} - \frac{h^2}{4\pi^2 I}J$$

$$\frac{c}{\lambda} = c\overline{v_0} - \frac{h}{4\pi^2 I}J$$

$$\bar{\vartheta} = \overline{v_0} - \frac{h}{4\pi^2 I\, c}J$$ ………… P branch

For R- branch ΔJ= +1 ∴J^1-J=+1

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}\left(J^1(J^1+1) - J(J^1)\right)$$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}\left(J^1(J^1+1-J)\right)$$

Here J^1=J+1

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}(J^1 * 2)$$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{4\pi^2 I}J^1$$

$$hc\bar{v} = hc\overline{v_0} + \frac{h^2}{4\pi^2 I}J^1$$

$$\bar{v} = \overline{v_0} + \frac{h}{4\pi^2 I\, c}J^1$$

For Q- Branch

ΔJ= 0 ∴J^1-J=0 ∴J^1=J

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}\left(J^1(J^1+1) - J(J^1)\right)$$

$$E_{IR} = hc\overline{v_0} + \frac{h^2}{8\pi^2 I}(0)$$

$$E_{IR} = hc\overline{v_0}$$

$$hc\bar{v} = hc\overline{v_0}$$

$$\bar{v} = \overline{v_0}$$

Selection rule for Infrared

a) When subject irradiated with infrared rays, it is necessary to know that whether the interaction is allowed or not. An extended use of Schrodinger wave equation give rise to quantum selection rule as

$$\Delta v = \pm 1 \qquad \text{…………} \text{(i)}$$

The eq. (i); selection rule-1 obey to restrict transition; if $\Delta\vartheta = \pm 1$ it represents absorption while $\Delta\vartheta = -1$ emission of radiation by the molecule.

From the selection rule -1; ie is clear that each allowed transition given rise to the same spectral frequency. i.e. vibrational level are equally different from each other

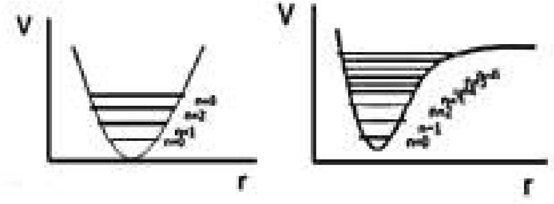
$$E_{0\rightarrow 1} = E_{1\rightarrow 2} = E_{2\rightarrow 3} \ldots\ldots = h\nu$$

b) The second selection rule is based on the physical nature of the molecules. During vibration, if dipole moment of the molecule is changed i.e. electrical vector of EMR interact with dipole moment vector of molecule resulting in resonance, molecule absorb the IR-radiation.

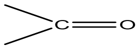
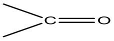
Type of IR-band.

i. **Overtone**

The harmonic oscillator only allowed vibration up to ±1 level. But harmonic oscillation possible to one or two level. But real molecules do not obey the law of simple harmonic motion. At higher amplitudes of vibration; gradually increase the distance between two level, the band loses their elasticity gradually and decrease of force constantly.



If Vibration of the molecule is completely harmonic then only fundamental band occurs. But in the real molecule; it is not possible so due to anharmonic vibration overtone occur.

Example: fundamental frequency of  is appeared at 1700 cm^{-1} then the first overtone of  the group appeared at 3400 cm^{-1}.

At lower quantum number the vibrational energy are evenly spread and transition only allowed ±1. But at the higher quantum number, it is gradually decreasing. So overtone frequency is not exactly twice and transition is also partially allowed, as a resulting intensity of overtone is 1/10 of fundamental band.

Combination band:

The combination band arise from the unharmonicities of vibration which lead to an interaction of two fundamental bands in polyatomic molecule.

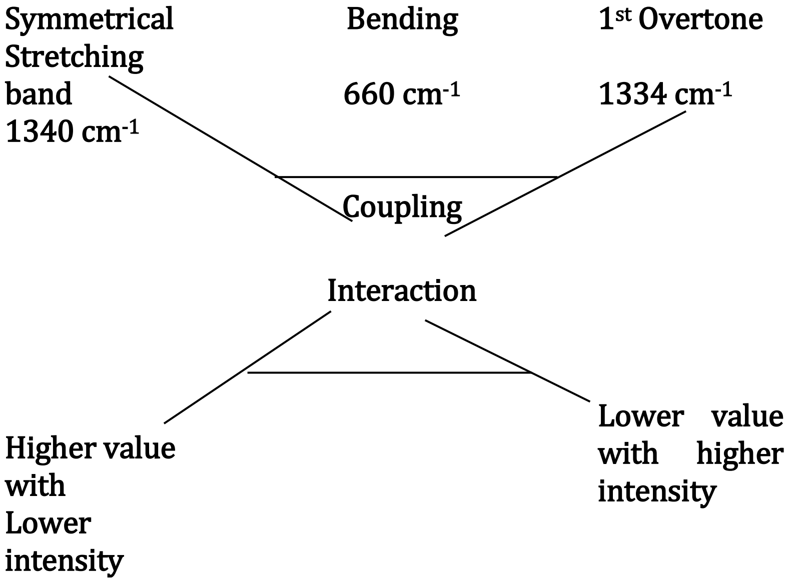
It is weak compared to fundamental and overtone

Fermi Resonance:

As we have observed in our discussion of interaction coupling can also occur between fundamental vibration and overtone or combination tone vibration. During these type of coupling, energy sharing take place between overtone and fundamental or c combinational tone and fundamental is known as “Fermi-resonance”. As a result of this interaction, the intensity of ‘overtone’ is increasing while the intensity of fundamental band is decreasing.

The most common example of Fermi resonance is absorption pattern of CO_2 molecule.

In the case of CO_2 molecule, stretching band appear at 1340 cm^{-1} in Raman spectra. While bending deformation appears at 660 cm^{-1}. Due to the coupling of these two fundamental of the C=O bending result in giving two new absorption band 1286 & 1388.5cm^{-1} having an intensity ratio of 1:09.



Fermi resonance is also appeared in aldehyde molecule C-H bending vibration is appeared at 1390 cm^{-1} and its first overtone occur at 2750 cm^{-1}, while C-H stretching seen absorption at 2872 cm^{-1}. So coupling takes place between fundamental band and overtone, asymmetrical double is observed at 2830 & 2695 cm^{-1}. i.e. overtone extent their intensity while fundamental loses their intensity.

Finger Print region:

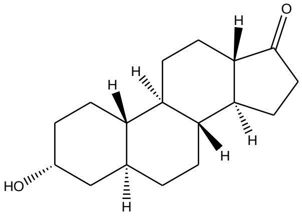
The region from the right 4000-1600 cm^{-1} to the left has a great impact on the study of the fundamental group. The absorption occurs in that region is due to stretching vibrations.

The region to the right of 1600 cm^{-1} to 600 cm^{-1} to the left is usually complex due to the both stretching and bending modes give rise to absorption here. However, each organic compound has its own identical absorption in this region. This region of infrared therefore known as 'finger-print' region. Although the region of higher frequency may appear the same for similar molecule but the pattern display in fingerprint region seen a complete super impossibility of infrared spectra.

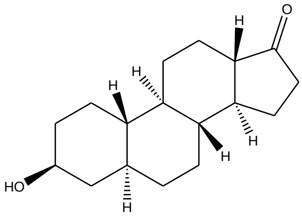
It is necessary to mention here that aromatic compound often displays numerous bands in fingerprint region as compared to their aliphatic parts.

The patterns of fingerprint region are identical and sensitive even minor chemical difference or stereochemical changes. The fingerprint region is a unique for comparison purpose.

Example: epimeric stereochemistry study at androsterone and epiandrosterone. Both are C_3 epimers. The –OH stretching frequency in a higher region, while C-O absorption band in 1260-1000 cm^{-1} make differentiate to each other in fingerprint region.



Androsterone



Epiandrosterone

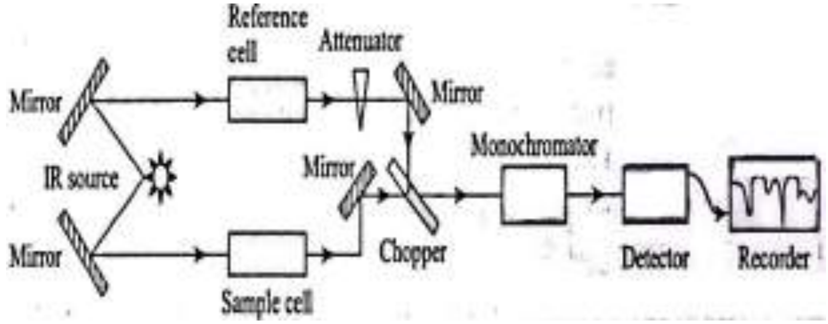
Instrumentation:

1) The conventional IR spectrophotometer

The important components of conventional IR spectrophotometer are as under

I. Source of radiation
II. Monochromator
III. Sample handling
IV. Detector
V. Recorder

The Morden double beam infrared spectrophotometer is shown in the figure.



I. **Source of Radiation:**

IR radiation is produced by electrical heating of Nernst Filament or Globar at 1000-1800^{0}C. the Nernst filament is made up of zirconium, thorium and cerium oxide. While Globar is a small rod of silicon carbide.

II. **Monochromator:**

It will disperse or resolve polychromatic light into monochromatic light.

It consists of following parts:

(a) Entrance slit: it will sharply define the incoming beam of radiation.

(b) Disperse device: It will disperse the radiation. When a sharp beam of light is allowed to pass through the filter.

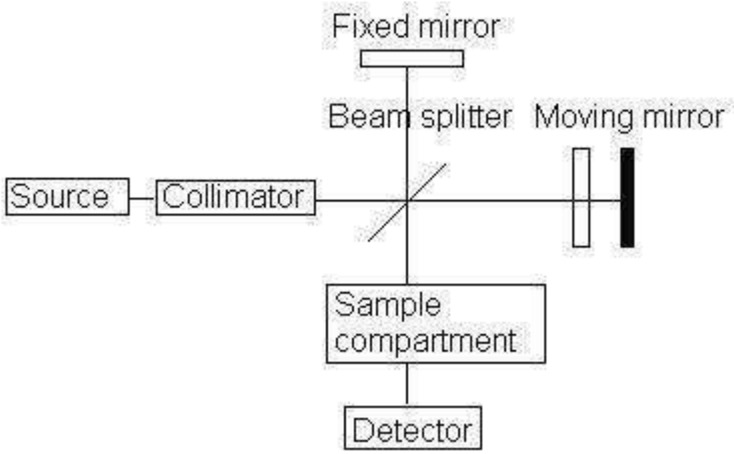
Prism or grating type disperse device are employed in infrared work. Generally, a prism made of alkyl halide is favoured because of their whole range IR inactive and simplicity. Prism made up from potassium bromide oftenly used in IR spectrophotometer.

The grating device contains series of a number of parallel equal distance lines drawn on a plane surface. Approximately 10,000 to 15,000 line/inch is drowned on the highly polished surface of the glass. Each groove acts as a scattering centre.

2) **Fourier Transform (F.T.) Infrared spectrometer**

A beam containing the entire infrared wavelength passes through a sample at once in FT-IR. The result getting after absorption also passes all wavelengths in one beam. The information contains in resulting beam is converted into frequency dominated spectra by a microprocessor.

The FTIR uses an interferometer causes two beams of IR radiation to interfere with one another, out of this two beam, one is variable. After reflection to their relative mirrors back to the beam splitter and recombine.



Advantages:

- Speed and sensitivity are better due to the scanning of all frequency at once.
- It requires less time as compared to the dispersive method.
- Resolution and accuracy are also improved.

Sample handling system:

The method used for sample preparation depends upon the nature of the sample.

1) **Gaseous Sample:** the scanning of gases or low boiling liquids by the expansion of the sample into an evacuated cell. Gas cells are available in length of few centimetres to 40 meters in coil form.
2) **Liquid sample:** Liquid may be scanned between two salt plates without a spacer. Pressing a liquid sample between flat plates produces a film of 0.01mm 0r less in thickness.
3) **Solid sample:** the solid sample is usually examined by using mull technique, thin film, pressed disc or powder method.

   Mulls are pre[pared by thoroughly grinding 2-5 mg of solid with Nujol. The mixture is examined between two salt plates.

   In a thin film, the method makes a solution of the sample in volatile solvent and press between two salt plates then after heat it to remove the solvent and make a thin film on salt plates.

In press disc method, Grind 1 mg sample with 99 mg KBr and make it fine powder then insert into "die" and press for 5 to 10 min. with 1000- 1500 psi. so powder converts into a transparent disc which can be examined.

Factor affecting IR absorption:

The variation in absorption frequency depends on the following factors:

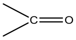
(1) **Bond strength:** Force constant is the primary function of frequency. As a result, increasing the bond strength absorption occurs at the higher region.

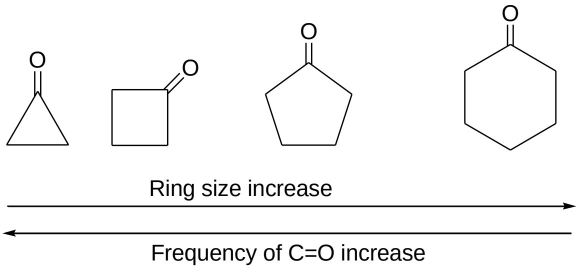
(2) **Atomic weight:** A mass of the molecule is inversely proportional to the frequency. Therefore wavenumber is decreased with increasing atomic mass.

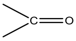
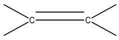
(3) **Inductive effect:** Electron donating effect of any functional group produce +ve induction which increases the electron density on "C" atom and make bond weaker as a result force constant is decreased and also decrease the frequency of absorption.

An electron withdrawing effect of any group produce –Ve induction which decreases the electron density on "C" therefore bond is more polar which increase the absorption frequency.

(4) **Hydrogen bonding:** Due to the formation of hydrogen bond; the electron density on oxygen is decreased which makes O-H band less polar as a resulting frequency is decreased.

(5) **Ring size:** By increasing the ring size, decrease the ring strain which makes the ring the  bond less polar due to the delocalization of electron, so frequency also decrease.



(6) **Resonance:** If  the group is in the conjugation of  the group; make its resonance as a resulting stability is increase and force strength decrease. Therefore IR absorption shift towards lower frequency.

(7) **S-character:** The strength of the valent bond depends on the participation of "S" alkene and alkynes.

Hybridization	S- character	Stretching frequency
sp^3	25%	2900 cm^{-1}(C-H)
sp^2	33%	3100 cm^{-1}(C-H)
sp	50%	3300 cm^{-1}(C-H)

S character increase → Frequency increase

Application:

Infrared spectroscopy is useful for the identification of functional group. Following are some application of Infrared spectroscopy:

- **Study of hydrogen bond:**

  It is possible to explain the hydrogen bond with the help of IR- spectroscopy.

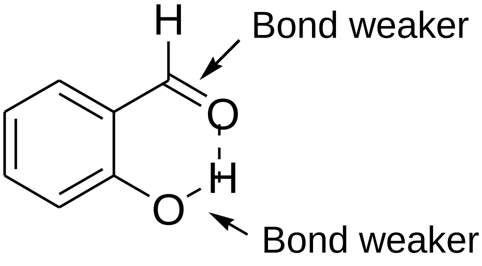
  Two types of hydrogen bond is possible

  1) Within the molecule(Intramolecular H-bond)
  2) Between the molecule(Intermolecular H-band)

Hydrogen bond formation takes place between the H of polar bond and electro-negative atom which possesses loan pair of electron.

Due to the formation of the hydrogen bond, force constant of the original bond decreases and stretching frequency of those bands also decrease.

Example:



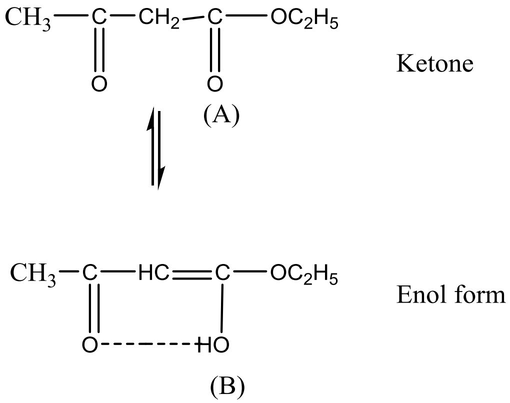
Intramolecular H–bond

Stretching frequency of O-H and C=O decrease.

- **Study of tautomerism:**

  For the study of tautomerism between two fundamental group ketone and enol;

Example:

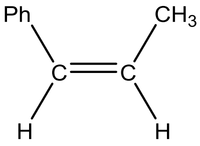


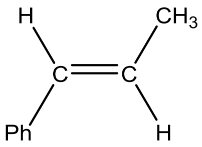
Compound A is passed two carbonyl group so -C=O stretching of ketone at 1710 cm^{-1}and C=O stretching of ester appeared at 1745.cm^{-1}.

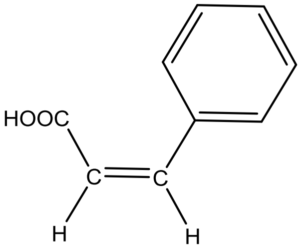
While compound (B) passes one C=O group with conjugation so -C=O stretching appeared at 1690 cm^{-1} and –OH stretching appeared at 3575 cm^{-1} as a broadband due to Intramolecular H-bond.

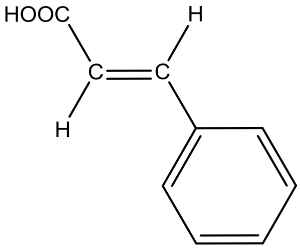
- **Geometrical isomer:**

  For the identification of geometrical isomer; IR spectroscopy is useful.









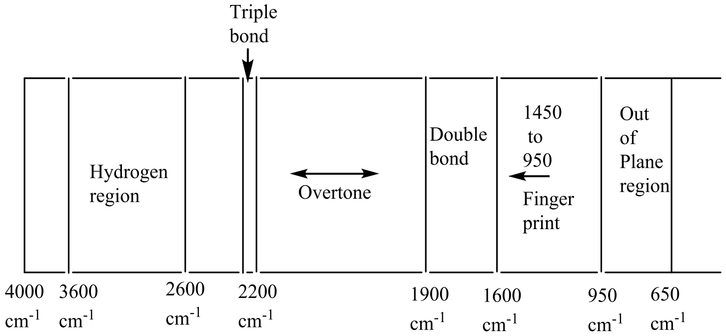
Examination of IR spectrum:

- Examine the IR spectrum from high-frequency end.
- IR –spectrum the band intensity is designated as

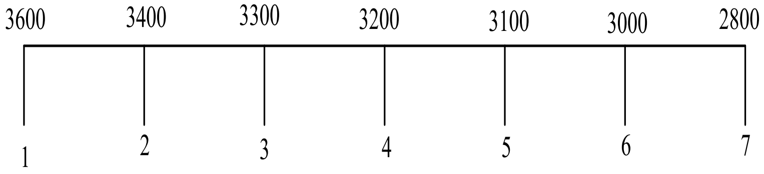
St- strong w- weak m- medium sh- sharp br- broad

Stretching	ν	Bending	δ
Scissoring	σ	Rocking	ς
Wagging	ω	Twisting	τ

❖ Assignment of band region:



(1)



	3600-3400(1→2)	-OH str.
❖	3400-3200(2→3)	-NH stretching
❖	3300(3)	-C≡C-H stretching
❖	3200(4)	=C-H stretching
❖	3100-3000(5,6)	Ar-h stretching
❖	2900-2800(7)	C-H stretching alkane.

(2)

2250	2150	1950	1850	1785	1750	1745
C≡N	C≡C	S-H	CO (anhy.)	Acid chloride	CO anhy.-1	Ester
1735	1725	1710	1680	1645	1630	1600
Acid	Aldehyde	Ketone	Amide	C=N	C=C	C=C

1450	1375	1275	1250	1150	850	750-650
-CH_2	-CH_3	C-O	C-N	C-S	NO_2	C-X
Banding	Bending	Bending	Bending			

Out of plane

Ortho	Meta	Para
780	700	830
750	730	

Hydrocarbon: **Alkane**

	Stretching	Bending
Asymmetric	2962 cm^{-1}	1450 cm^{-1}
Symmetric	2872 cm^{-1}	1375 cm-1

∴ If more than four –CH_2 group are there; then sharp band at 720 cm^{-1} twisting and wagging at 1250 cm^{-1}

.

Alkene:

	Stretching	Bending
C-H	3100	9510trans isomer (oop)
C=C	1630	
C-C	1100	730cis isomer (oop)

Alkyne:

C-H stretching	3300
C≡C stretching	2150-2200

Aromatic:

	Stretching	Bending	
C-H	3030	700-750	Mono sub.
	1600	780-750	Ortho sub.
C=C	1500	700-780	Meta sub.
	1450	820	Para sub.

>C=O frequency

- Acid -OH stretching 3600-2500 cm^{-1}
  >C=O stretching 1735 cm^{-1}
  -O-H bending 1250 cm^{-1}

- Ester ⟶ >C=O stretching 1745 cm^{-1}
  C-O-C stretching 1250 & 1075 cm^{-1}

- Anhydride: >C=O 1850 &1750 cm^{-1}
  C-O-C stretching 1250 &1075 cm^{-1}

- Acid Chloride: >C=O stretching 1765 cm^{-1}
  C-C stretching 750 cm^{-1}
- Ketone: >C=O 1715 cm^{-1}
- Aldehyde: >C=O stretching 1725 cm^{-1}
  C-H stretching 2750, 2850 cm^{-1}

- Amide: $-NH_2$ 3400-3200(br)
  3400(st)

  >C=O 1680

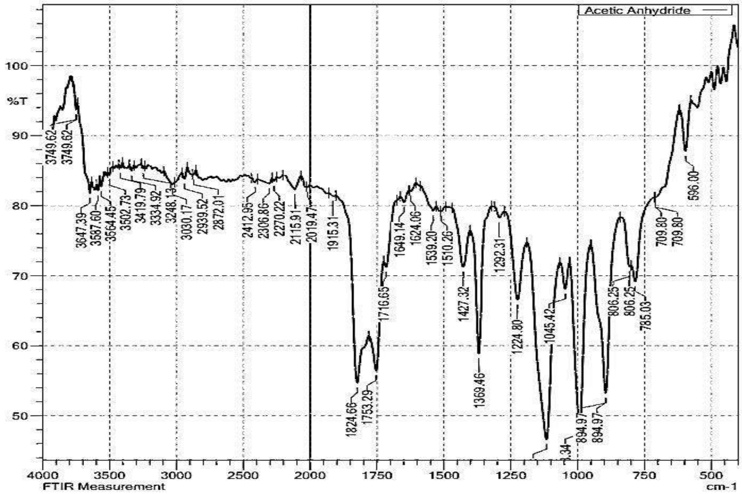
  -N-H bending 1250 cm^{-1}

- Phenol: -OH 3600(sh)→free
  3600-3400(br)
  →bonded

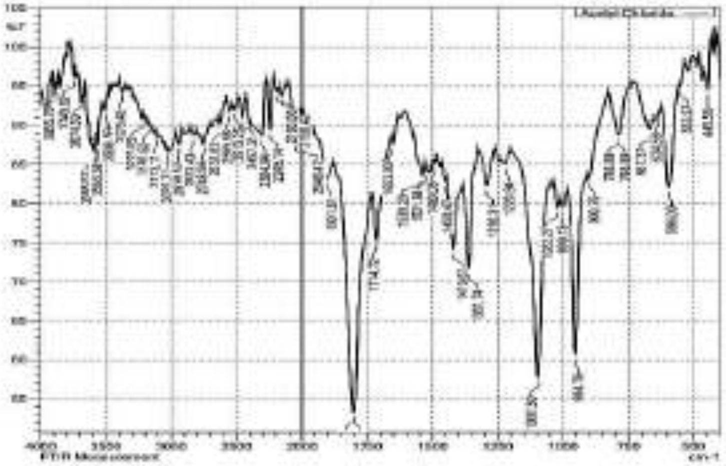
O-H	C-O	
3640	1050	Primary
3630	1100	Secondary
3620	1150	Tertiary

IR spectrum of some compound:

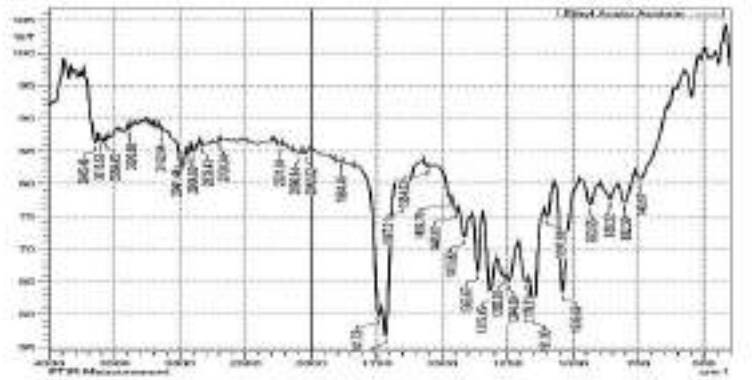
(1) Acetic Anhydride



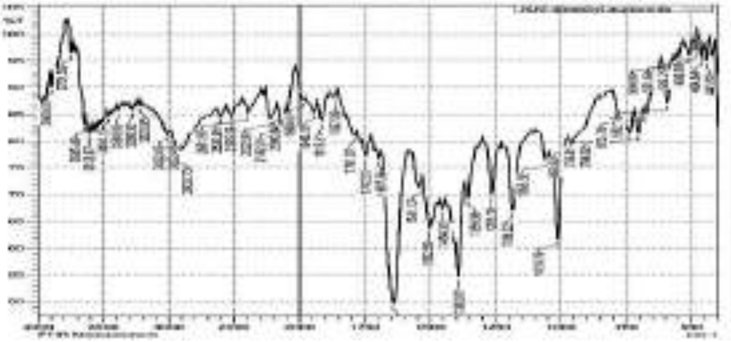
(2) Acetyl Chloride



(3) Ethyl Acetoacetate



(4) N.N' Dimethylformamide



Example:

(1) Calculate of vibration frequency; calculate the approximate frequency of the C-h stretching vibration from the given data: $K=500\ Nm^{-1}= 5.0\times10^{5}\ gs^{-2}$, M_c= mass of carbon atom= 20×10^{-24} gm, M_H = mass of Hydrogen = 1.6×10^{-24}gm.

$$\bar{\vartheta} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \quad \mu = \frac{m_c m_H}{m_c + m_H}$$

$$= \frac{1 \times 7}{2 \times 22 \times 3 \times 10^{10}} \sqrt{\frac{5 \times 10^5}{(20 \times 10^{-24})(1.6 \times 10^{-24}) \big/ (20 + 1.6)10^{-24}}}$$

$= 3.1 \times 10^5$ m^{-1}

$=3100$ cm^{-1}

(2) H-Cl str. Appeared at 2950 cm^{-1}; calculate force constant K?

$C= 3 \times 10^{10}$cm $N= 6.023 \times 10^{23}$

$$Molecular\ mass = \frac{\mu}{N}$$

$$\therefore K = 4\pi^2 c^2 \bar{\vartheta}^2 \frac{\mu}{N}$$

$$\therefore K = 4\pi^2 c^2 \bar{\vartheta}^2 \frac{m_1 m_2}{N(m_1 + m_2)}$$

$$\therefore K = \frac{4(3.14)^2 (3\times10^{10})^2 (2950)^2 \times 1 \times 35.5}{(1+35.5)\times 6.023 \times 10^{23}}$$

$\therefore K = 4.98 \times 10^5$.

(3) Calculate the Theoretical number of vibrational degree of freedom in NH_3, p- dichlorobenzene, HCN, CO_2 and Benzene.

For non-linear molecule

Vibrational degree of freedom = 3n-6

$\therefore$for NH_3 $= 3\times4-6$

$=12-6$

$=6$

∴p-dichloro benzene: $C_6H_4Cl_2$

$=3n-6$

$=3\times12-6$

$=36-6$

$=30$

For Benzene: C_6H_6

$=3n-6$

$=3\times12-6$

$=36-6$

$=30$

For linear molecule: vibrational degree of freedom$=3n-5$

For HCN $=3n-5$

$=3\times3-5$

$=9-5$

$=4$

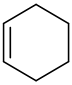
For CO_2 $=3n-5$

$=3\times3-5$

$=9-5$

$=4$

(4) **C_6H_{10}**: Cyclo hexene



3030 cm^{-1} : =C-H str.

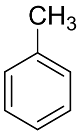
2940 cm^{-1}: C-H str. In $-CH_2$

1640 cm^{-1} : C=C str.

1435 cm^{-1}: C-H def in $-CH_2$

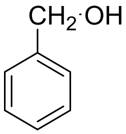
721 cm^{-1}: =CH def (Cis isomer)

Toluene: C_6H_6-CH_3



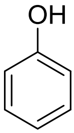
3030 cm^{-1} :Ar-H str.
2960-2850 cm^{-1} :C-H str in CH_3
1600, 1580, 1460 cm^{-1} :C=C str. In ring
730,770 cm^{-1} : C-H bending for mono substituted in ring

Benzyl alcohol: $C_7H_{10}O$



3400(be) cm^{-1}: bonded O-H str.(Intermolecular H bond)
3000 cm^{-1}:C-H of aromatic ring
2980-2840 cm^{-1}: C-H str. Of alkane
1497-1450 cm^{-1} : C=C str. In-ring
1200 cm^{-1}: O-H bending
1017 cm^{-1} :C-O str. Of primary ring.

Phenol: C_6H_5-OH



3330(br) cm^{-1} : O-H str. of bonded –OH (intermolecular)

3040 cm^{-1} : aromatic C-H stretching

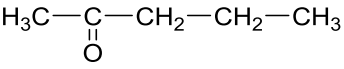
1580, 1495, 1470 cm^{-1} : C=C str. In ring

1360 cm^{-1} : O-H bending

1220 cm^{-1} : C-O stretching

800,745 cm^{-1} : C-H bending (oop)

2- Pentanone: $C_5H_{10}O$



$$H_3C-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

2970 cm^{-1}: Asymmetric C –H str in –Ch_3group

2930 cm^{-1}: symmetric C-H str in –CH_3 group

2865 cm^{-1}: symmetric C-H str in –CH_3 group

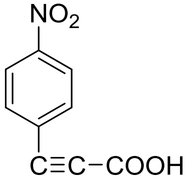
1725 cm^{-1}: C=O str in saturated ketone

1432 cm^{-1}: CH bending of –CH_2

1370 cm^{-1}: CH bending of –CH_3

1170 cm^{-1}: C-O stretching

4- Nitro-3-phenyl-prop-2-yn-1oic acid



3100 cm^{-1} : C-H str of aromatic

3200-2400 cm^{-1} : O-H str of acid

2225 cm^{-1} : C≡C str

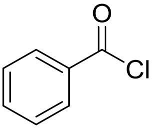
1690 cm^{-1} :

1605 cm^{-1} : } C=C str in ring

1520, 1350 cm^{-1} : NO_2 str.

950-650 cm^{-1} : p-di substituted

Benzoyl Chloride



3080 cm^{-1}: C-H str of aromatic

1790 cm^{-1}: C=O str (raised due to +I effect)

1600 cm^{-1}:

1580 cm^{-1} : C=C str in ring

1450 cm^{-1}:

750 cm^{-1}: C-H bending in OOP

690 cm^{-1}: C-Cl str

n-Butyric anhydride
$(CH_3CH_2CH_2)O$

2980 cm^{-1}: C-H str of alkane

2890 cm^{-1}: C-H str of alkane

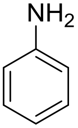
1820 cm^{-1} :

1748 cm^{-1} : C=O str of anhydride

1460,1406 cm^{-1}:C-H def in methyl group

1035 cm^{-1}: C-O str in acyclic anhydride

Aniline



3450 cm^{-1}: N-H str in primary amine

3390 cm^{-1}: N-H str in primary amine

3030 cm^{-1}: C-H str of Aromatic ring

1620, 1602: C=C str in ring
, 1499 cm^{-1}
3450 cm^{-1}: C-N str in primary amine
,1275
754,696cm^{-1}: Mono-Substituted Benzene

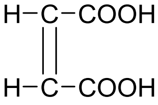
Methyl cyanide [CH_3-C≡ N]
3002 cm^{-1}: C-H str in –CH_3
2940 cm^{-1}: C-H str in –CH_3
2256 cm^{-1}: C≡ N in Alkyl cyanide
1440 cm^{-1}: C-H def in –CH_3
1370 cm^{-1}: C-H deformation

Ethyl Acetate CH_3-C(=O)-O-CH_2-CH_3
3002 cm^{-1}: C-H str of alkane
1742 cm^{-1}: C=O str of alkane
1450, 1370 cm^{-1} :C-H deformation
1240 cm^{-1}: C-O str in ester
3100 cm^{-1} :C-H str
2960-2900 cm^{-1}:C-H str.(saturated)

Distinguish the following compound By IR spectra.

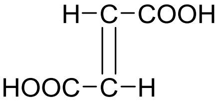
(1)

Maleic Acid



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array}$$

Fumaric acid



$$\begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

Similar peak
3030 cm^{-1}: C-H str. Of vinyl group

Distinguish peak

1650 cm^{-1}	: C=C str.	1600 cm^{-1}	:C=C str
1702 cm^{-1}	: C=O str	1680 cm^{-1}	: C=O str
750 cm^{-1}	: cis isomer	950 cm^{-1}	:trans isomer

(2)

$C_6H_5CH_2NH_2$	CH_3-CO-N$(CH_3)_2$
3100-3040 cm^{-1}:C-H str	3300 cm^{-1} :C-H str
1600-1500,1460cm^{-1}:C=C str	1675 cm^{-1} :C=O str
3500-3250 cm^{-1} :N-H str	

(3)

Propanal	**3-propane 1- alcohol**
CH_3CH_2CHO	H_3C=CH-CH_2
2720,2850 cm^{-1}:C-H str of Aldehyde	3300 cm^{-1}:C-H str of vinyl
1740-1720 cm^{-1}:C=O str	3600-3300 cm^{-1}:O-H str
1400-1000 cm^{-1}:C-C str	1650 cm^{-1}:C=C str

(4)

o- Hydroxybenzoic acid	**m-Hydroxybenzoic acid**
3400-3200 cm^{-1}: O-H str (lowering)	3600-3400 cm^{-1}: O-H str. (lowering)
Intramolecular H-bond	Intermolecular H bond
735-770 cm^{-1}: ortho sub.	710-690 and 770-730 cm^{-1}: meta sub.

Assign the structure to a compound from following IR results.

(1) M. F.: C_9H_8

IR:3310(m),3020(m),2960,2140,1605,1580,1510,1450, 4030,755 and 710 cm^{-1}

First find out double bond equivalent from following equation.

$DBE = \frac{(2a+2)-(b-d)}{2}$ a= No. of carbon

b= no. of monovalent ion

c= no of trivalent atom

$$DBE = \frac{(2 \times 9 + 2) - (8 - 0)}{2}$$
$$DBE = \frac{20 - 8}{2} = \frac{12}{2}$$
$$DBE = 6$$

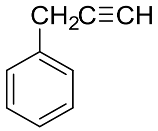
3310 cm^{-1}: C-H str of -C≡CH vibration
3020 cm^{-1}: C-H str of aromatic vibration
2960 cm^{-1}: C-H str of alkane vibration
2140 cm^{-1}: C≡C str of alkyne vibration
1605 cm^{-1}:
1580 cm^{-1}: } C=C str of aromatic vibration
1510 cm^{-1}:
1450 cm^{-1}: C-H bending of alkane
1030 cm^{-1}: C-H bending of aromatic
0755 cm^{-1}:
0710 cm^{-1}: } C-H bending of aromatic (monosubstituted)

From the above information

- → 6 double bond present
- → -C≡C group present
- → Aromatic ring present
- → CH_2/CH_2 group present

∴ From formula: C_9H_8
Phenyl ring: $-\;C_6H_5$
C_3H_4
C≡C-H $-\;C_2H$
CH_2

∴ Structure of molecule is:



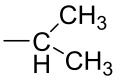
(2) The compound having molecular formula $C_{11}H_{12}$ & IR absorption at 3310, 3045, 2925,2130, 1605, 1500,1430,1380,1360,1230,1080,840 cm^{-1}; derive the structure of unknown compound.

$$DBE = \frac{(2a+2)-(b-d)}{2}$$

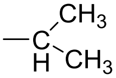
$$DBE = \frac{(2 \times 11 + 2) - (12 - 0)}{2}$$

$$DBE = \frac{24 - 12}{2}$$

$$DBE = \frac{12}{2} = 6$$

3310 cm^{-1}: C-H str of -C≡C-H
3045 cm^{-1}:C-H str of aromatic ring
2925 cm^{-1}:C-H str of alkane
2130 cm^{-1}:C≡C str of -C≡C-H
1605 cm^{-1}
1500 cm^{-1} C=C str of aromatic ring
1430 cm^{-1}
1380 cm^{-1}
1360 cm^{-1} C-H bending of  group
1230 cm^{-1}: C-H in plane bending
1080 cm^{-1}: C-H in plane bending
840 cm^{-1}: p- di substituted
From the above information

→ 6 double bond present
→ p-di-substituted phenyl ring
→ C≡C-H group present

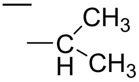
→ 

$-CH(CH_3)_2$ group present

∴ $C_{11}H_{12}$

$-\ C_6H_4$

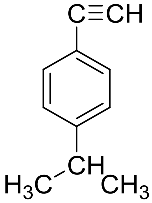
C_5H_8

$-$ 

$-CH(CH_3)_2$

C_2H

∴ Structure of unknown compound is



(3) Assign the structure of the following compound with M.F.$C_4H_8O_2$ to absorb the IR radiation at2989-2880(m), 1740(s), 1240(s) & 1045 (s) cm^{-1}.

$$DBE = \frac{(2a+2)-(b-d)}{2}$$

$$DBE = \frac{(2 \times 4 + 2) - (8 - 0)}{2}$$

$$DBE = \frac{10 - 8}{2}$$

$$DBE = \frac{2}{2} = 1$$

2989-2880 cm^{-1}: C-H str of alkane

1740 cm^{-1}: C=O str

$$\left.\begin{array}{l}1240\ cm^{-1}\\ 1045\ cm^{-1}:\end{array}\right]\text{C-O-C linkage}$$

From the above information

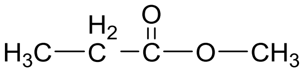
- → One double bond present
- → C=O group present
- → Ester group present

∴ $C_4H_8O_2$

$\underline{-\ CO_2}$

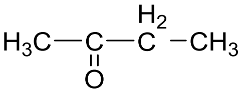
$= C_3H_8$

So.



$H_3C-\overset{H_2}{C}-\overset{\overset{O}{\|}}{C}-O-CH_3$

OR



$H_3C-\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-CH_3$

(4) Find out structure of the compound contain M.F. $C_{14}H_{12}$ & shows IR absorption at 3100-3000(m),1620-1590(s),1500-1400(s), 990, 770, 690 cm^{-1}

$$DBE = \frac{(2a+2)-(b-d)}{2}$$

$$DBE = \frac{(2 \times 14 + 2) - (12 - 0)}{2}$$

$$DBE = \frac{(28 + 2) - 12}{2}$$

$$DBE = \frac{30 - 12}{2} = \frac{18}{2}$$

$$DBE = 9$$

3100-3000 cm^{-1} : C-H str of aromatic

1620-1590 cm^{-1} : C=C str of aromatic

990 cm^{-1} : C-H bending (trans isomer)

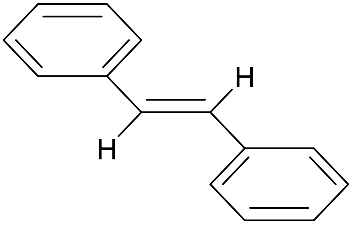
$$\left.\begin{array}{l} 770\ cm^{-1} \\ 690\ cm^{-1} \end{array}\right]\ \text{C-H bending out of plane}$$

From the above information

- → Nine double bond present
- → Phenyl ring present
- → Trans isomer present
- → Monosubstituted phenyl ring

∴ $C_{14}H_{12}$
$-C_6H_5$
$= C_8H_7$
$-C_2H_2$
$= C_6H_5$

∴ Final structure of compound:



Chapter 4

NMR Spectroscopy

NMR SPECTROSCOPY

Introduction:

NMR spectroscopy has become must important tool without any question for the organic chemist. It is a different type of absorption spectroscopy as compare to IR and UV-spectroscopy. Some of the nuclei absorb the electromagnetic radiation in the range of radio-frequency in presence of external magnetic field and governed by the characteristic of the compound.

The Jelix-Bloch and Edward Purcell have first discovered the phenomenon of nuclear magnetic resonance in 1964.

The elements which possess gyromagnetic ratio i.e. their nuclei behave like tiny bar magnets are responsible for nuclear magnetic resonance.

The nuclear magnetic resonance can be compelled to:

1. Reveal their presence
2. Self-identification
3. Environment

The principle of NMR spectroscopy:

We will try to explain the principle of NMR spectroscopy with the help of magnetic and electrical properties of some nuclei.

All nuclei carry a charge due to the presence of proton. In some nuclei, this charge deposited on their axis which resulted in spinning the nuclei and this circulation of charge (spinning of nuclei) will generate on their magnetic field (behaviour of nuclei as a bar magnet).

Considering spinning nuclei as a top, it performs a slower motion like a top on X-axis which is known as precessional motion.

The precessional arises downward to the earth due to the effect of gravitational force, which is known as “gyroscopic-motion”.

When these spinning nuclei are under applied (external) magnetic field, it feels

$\omega = \gamma H_0$ ……………. (1)

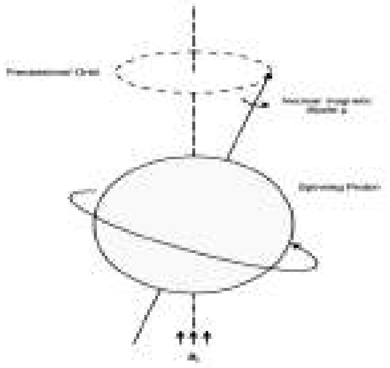
ω: Angular precession velocity

H_0: strength of applied magnetic field.

γ: Gyromagnetic ratio

r: magnetic moment of spinning nuclei

h: Plank’s constant



The relation between electromagnetic frequencies with magnetic field strength is duplicated as under

$\mathrm{v} = \frac{\gamma \mathrm{H}_0}{2\pi}$ or $\gamma \mathrm{H}_0 = \mathrm{v} * 2\pi$………………(2)

But from eq. (1) $\gamma = \frac{w}{H_0}$ put in eq.(2)

$$\frac{w}{H_0} . H_0 = 2\pi v$$

$$w = 2\pi v$$

∴ Processional frequency is nothing but "the number of resolution per second made by the magnetic vector of the spinning nuclei in presence of external magnetic field [H_0]".

Magnetic and non-magnetic nuclei:

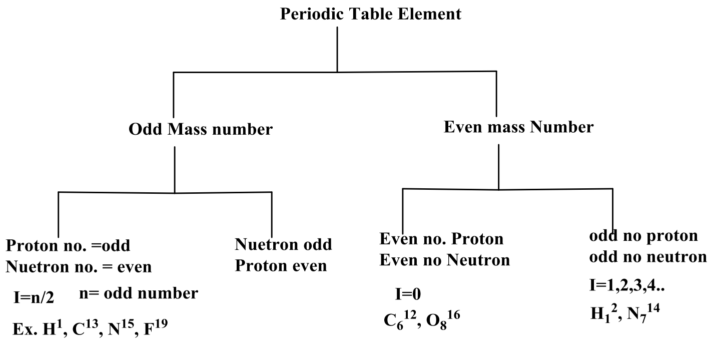
Nucleolus namely proton(+Ve), neutron (0-charge) which are present in a nucleus of an atom. Due to this positively charged particles, nucleus possesses spin just like an electron. The circulation of this positive charge, generate a dipole moment along with the spinning axis, Which can be explained by "spin quantum number". Individual proton has spin quantum number +1/2 and -1/2 only.

Three broad principles of spin quantum number:

The total of spin quantum number (±) is the characteristic of a number of nuclei present in nucleus i.e. Mass number.

The element of the periodic table can be classified into two different classes on the basis of their Mass number.

Periodic table Elements:



Chemical shift:

The chemical shift can be defined as a position of the signal with reference to the signal position of standard (reference material) in NMR spectrum.

According to the principle of NMR, all the protons give a signal at the same position but practically it is not true because Larmor frequency of a nuclear spin relates to its chemical environment.

The chemical environment surrounding the nuclei is differing due to the electron present in a molecule. This type of valence electron generates on their magnetic field in presence of external magnetic field, which is resulting in “shielding and deshielding” effect.

If the generating magnetic field favours the external magnetic field, protons are deshielding and if it opposes the applied magnetic field: protons are “shielded”.

In a molecule, the chemical environment is varied proton to proton. i.e. Electronic atmosphere differs from one proton to other hence the induced magnetic field generating by the electron is also differ which is also known as “local magnetic current”.

This local magnetic current is responsible for making a different signal for the protons which have a different chemical environment.

On the basis of the fundamental equation of NMR, the position of the signal depends on the strength of applied magnetic field is changed; the absorption frequency is also changed. i.e. position of the signal is also change, which creates a problem to identify the characteristic of nuclei.

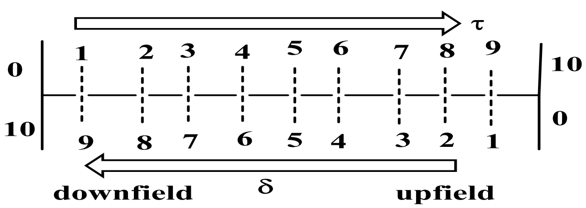
To avoid this problem, the scientist derived one standard scale for NMR spectrum.

$$Chemical\ Shift(\delta) = \frac{Frequency\ absorb\ by\ sample\ in\ Hz - Frequency\ absorb\ by\ standard\ in\ Hz}{Frequency\ of\ spectrophotometer\ Hz}$$

$$\delta = \frac{v_s - v_{std}}{v\ of\ spectrophotomater} \quad \text{ppm}$$

The unit of chemical shift is ppm i.e. parts per million of applied magnetic frequency.

The relation between τ and δ is

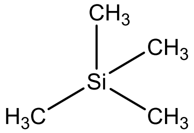


Organic chemistry is the chemistry of carbon and their covalent compound in which highest hybridization of “carbon” atom is sp^3 (four vacancies).

According to this we compare “Carbon” with “Silicon”, silicon also has SP^3 hybridization and it is more electropositive than carbon. i.e. it makes co-ordinate bond with “Carbon”.

TMS (Tetramethylsilane), when put under the external magnetic field, it absorbs the frequency in upfield as compare to another covalent compound of “Carbon”. i.e. universally it is accepted the position of TMS is 0 ppm in δ-scale.

The advantage of TMS as an internal reference standard.



- → It possesses maximum (12) number of equivalent protons.
- → It is chemically inert and magnetically isotropic.
- → It is low volatile compounds.
- → Being four methyl group, miscible with most of the organic solvents.
- → Silicon is more electron positive as compared to “C” make all the proton shielded and absorb the frequency in up field.

Shielding and deshielding of protons:

The circulation of the electron; surround the nuclei can be compared to current in the wire as a physics mechanism. The strength of this current directly proposals to the density of the electron which are responsible for generating induced a magnetic field. Without the effect of any induced magnetic field, all the protons are shielded in presence of external magnetic fields. Induced magnetic field oppose the applied magnetics fields but their strength depends on the density of electrons. i.e., which make the proton deshielded (pressice the lower frequency)

Following factors are responsible for shielding and deshielding of protons:

(1) Effect of electronegative atom:

If any electron negative atom directly attaches with carbon to which interested protons are attached; these protons are deshielded.

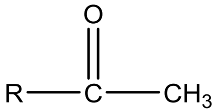
Multiple substituents strengthen the effect as compare to the single substituent

For eg.

$R-CH_3$: 0.7 to 1.3 and

$R-CH_2-R$: 1.2 to 1.4 δ ppm

If any electron withdrawing group; attach to the carbon to which interested proton is attached make the proton deshielded; due to the decreasing the electron density on carbon:



$R-\overset{\overset{O}{\|}}{C}-CH_3$

2.1 to 2.7 δ ppm

CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4
4.26	3.40	3.05	2.68	2.16	0.23

Substitution effect

$CHCl_3$	CH_2Cl_2	CH_3Cl
7.27	5.30	3.05

(2) S-character:

S-character is second important fact at which H- atom is attached.

All the hydrogen attached to the tetrahedral carbon atoms have absorbed the frequency in the range of 0-2 ppm if it is not nearby any electronegative atom or π resonance.

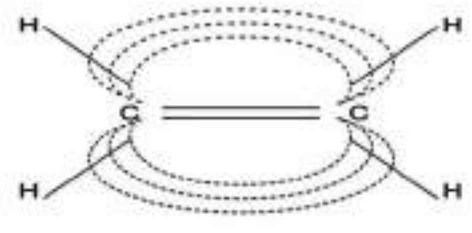
For Example,

0 ——— 1 ——— 2 δ ppm

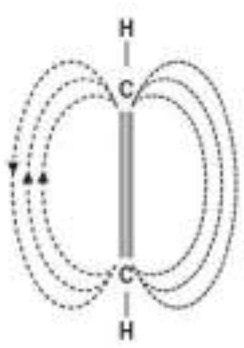
CH_4 CH_2 -CH

When ‘S’ characters are an increase, S orbital bulls their electron toward nuclei which increase the deshielding.

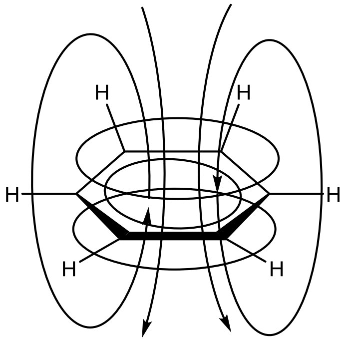
In a vinyl proton; There is a p-bond which circulate the electrons and generate a p-current as a result generate the induced magnetic field. E = which is known as Magnetic anisotropy. These resulting the proton deshielding and absorb in the down field.



In an acetylene S character is an increase but S=due to 2 π-bond it also generates π current which has a greater shielding effect. i.e. Greater Magnetic anatiotropy.



In an aromatic proton attached which sp2 carbon atom but in aromaticity ring when placed under the influenced of external magnetic field, due to the circulation of π- electron generates the ring current which is responsible for the generation of induced magnetic field.

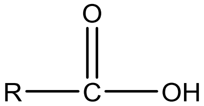
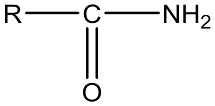


Due to this type of magnetic anisotropy; Benzene protons are deshielded and show the absorption in down field.

(3) Effect of H-bond donor:

Generally, the proton which is attached with heteroatom has a characteristic of hydrogen bond donor which exhibit variable absorption all over the range. However, the absorption depends on the concentrations, temperature and solvent used for the scanning.

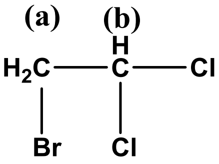
For Example;

Acid	 $R-\overset{\overset{O}{\|\|}}{C}-OH$	10.5-12.00
Phenols	$Ar-OH$	4-7
Alcohols	$R-OH$	0.5-5.0
Amines	$R-NH_2$	0.5-5.0
Amide	 $R-\underset{\underset{O}{\|\|}}{C}-NH_2$	5.0-8.0
Enols	 $-HC=\underset{H}{C}-OH$	5-15

Spin- Spin interaction:

During the absorption proton will interact with adjacent atom proton; the relating of spin between these protons is known as spin-spin will split into more than one line, this phenomenon is known as spin-spin splitting. It will happen only between non-equivalent protons.

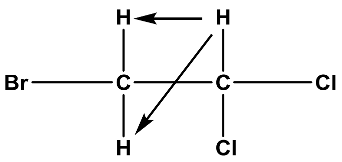
Generally, the splitting depends on the number of proton present on adjacent nuclei. i.e., it follows (n+1) rule. For example 1-Bromo 2,2 – Dichloro ethane

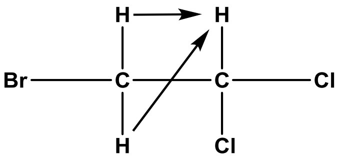


$\underset{Br}{\underset{|}{H_2C}}-\overset{H}{\underset{\underset{Cl}{|}}{C}}-Cl$

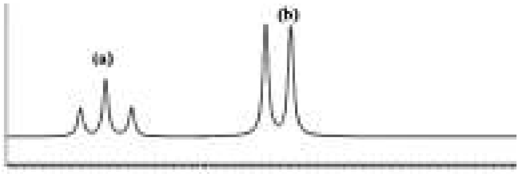
For proton (a) $-CH_2$ n=1 (n+1) = 2 doublet

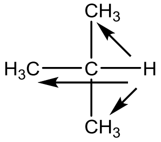
For Proton (b) $-CH$ n=2 (n+1) = 3 triplet



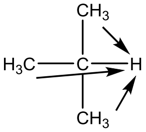


(n+1) = 3 Triplet **(n+1) = 2 Doublet**





(n+1)=10 Multiplate



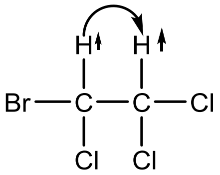
(n+1)=2 Doublet

Splitting of a pattern of Multiplate:

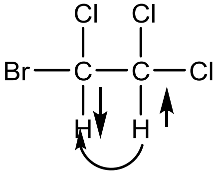
Due to the interaction of spin- spin between the hydrogen present on adjacent atom; resulting in the splitting of the signals.

The multiplicity of the signal depends on the number of hydrogen present on the adjacent atom but the pattern depends on the spin- spin matching between the interactions of spin (direction of spin).

If interaction takes between two hydrogens than the possibility of the direction are (1) parallel and (2) anti-parallel, so the possibility is 50-50 %, as a result, the signal obtained as a doublet with equal intensity.

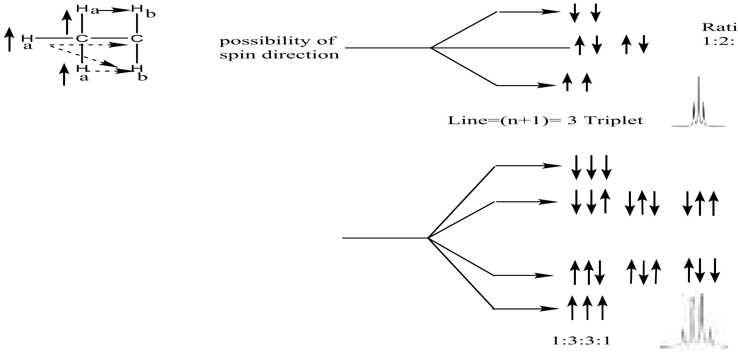


or



The interaction ratio are same i.e, $H_A \rightarrow H_B$, $H_A \leftarrow H_B$

Splitting Pattern of Ethyl Group:



→ Splitting of the signal follows the (n+1) rule.

→ Splitting patterns will be observed according to Pascal’s triangle.

1

1 1

1 2 1

1 3 3 1

1 4 6 4 1

1 5 10 10 5 1

Coupling constant (J):

Coupling constant is nothing but the measurement of relation between two interacted group or proton, which can be defined as under;

“Coupling constant is the distance between two lines of Multiplate.”

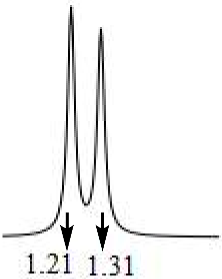
The relation (value) depends on the dihedral angle between two coupling protons. It can be theoretically calculated using Karplus equation.

$$3JHH' = A + B \cos \phi + C \cos 2\phi \text{………………..(1)}$$

Practically it can be calculated using following equation.

$$J\_HAB = Chemical\ shift\ of\ first\ line\ of\ doublet - chemical\ shift\ of\ second\ line\ of\ doublet \times operating\ frequency''$$

For example



= 1.31 – 1.21 * 60Hz
= 0.10 * 60 Hz
= 6 H

Spectrum of ethyl group

Table of coupling constant for standard group

Type	**J_{ab} (Hz)**	**J_{ab} Typical**
Ethyl	0-30	12-15
Vinyl		
(1) Geminal	0-3	0-2
(2) Vicinal	6-12	10
Ortho	6-10	9
Meta	1-3	3
Para	0-1	~0
Cis	6-12	10
Trans	12-18	17

Nomenclature of spin system: AMX, A_2B

The spin system can be designed on the basis of types of proton on which interaction is possible and also the distance between signals of these interacted protons as well as a number of protons.

For example:

- → If the signal obtained near to each other i.e. $\Delta V/J < 8$, and it possesses three types of protons that it can be designed as ABC system.
- → If system possess three types of the proton but two signals are near to each other i.e. $\Delta V/J < 8$ and one of them far from remaining two i.e. $\Delta V/J > 8$; then the system can be designed as an ABX system.
- → The system contains only two types of protons and has large chemical shift difference i.e. $\Delta V/J > 8$; it can be designed as AX system while the small difference of chemical shift i.e. $\Delta V/J < 8$ then it can be depicted as AB system.
- → If system contains three types of proton out of them one show of the absorption in upper field, second one at middle part and third one at lower field than it

can be reported as AMX system, but out of these three protons they absorbed at upper field while remaining one at down field then it can be designed as A_2X system.

On the basis of above discussion following spin system is possible.

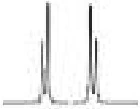
Two types of system	**Three types of system**
AB	A_2B
XY	AB_2
AX	AMX
A_2	XYZ
	X_2Y
	ABX

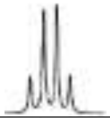
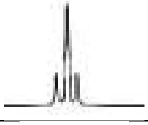
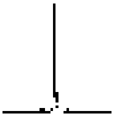
Order of the spectrum and shape of the signals:

→ The ratio of the chemical shift towards the coupling constant gives the information regarding the order of the spectrum.

→ If the $\Delta V/J > 10$, the order of the spectrum is a first-order i.e. well-resolved spectrum and the shape of the multiplate follow the Pascale triangle.

→ If the $\Delta V/J < 10$, the spectrum can be considered as a ‘Non-first order’ spectrum i.e. poor resolution and the shape of the multiplate is destroyed.

System	**Line Shape**	**$\Delta V/J$**
AX		$\Delta V/J > 15$
		$\Delta V/J > 6$
		> 3

AB		1.5
AB		0.5
A2		0

Method for the conversion of Non-first order to first – order spectrum:

In many compounds, due to the similar chemical environment, the absorption occurs in the nearby region as well as no. of protons present on the adjacent atom; shows the higher multiplicity, as a result, overlapping of signals, spectrum convert into non-first order spectrum.

To remove the complexity of the spectrum following techniques are available:

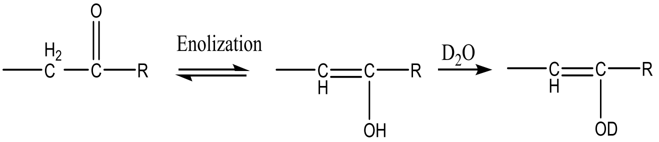
(1) Chemical techniques
(2) Instrumental techniques

(1) Chemical techniques:

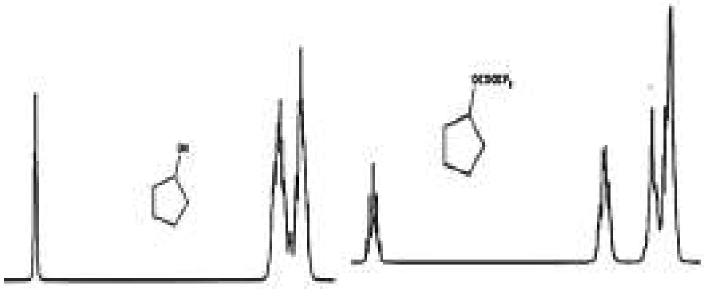
In chemical technique by using the chemicals either by labelling the protons or derivatisation of a particular group; the complex pattern of the spectrum can be removed.

For example:

i. **Deuterium labelling method:**

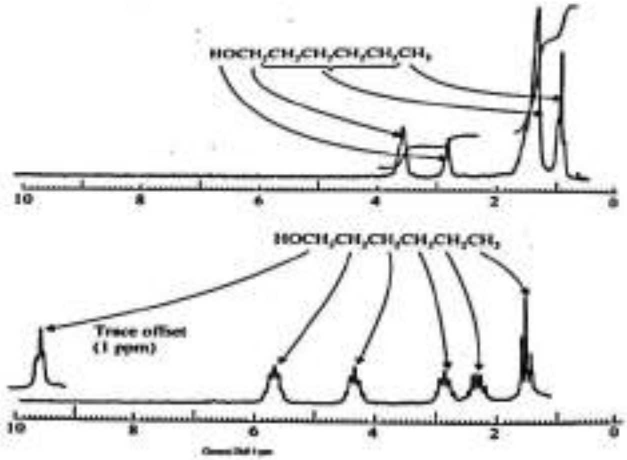


ii. **Derivatisation :**



iii. **Lanthanide shift reagent:**

` Lanthanide atom have a greater tendency to form a complex by accepting the electron into their vacant d- orbitals as a resulting density of electrons or proton of ligand is decreased and it becomes shielded (i.e. shifting of the signals), which resulted in converting non-first order spectrum to first order spectrum.

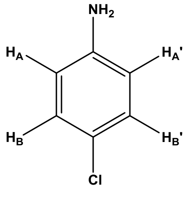


(2) Instrumental techniques:

Either increasing the strength of the magnetic field or by introducing the particular group frequency; complex spectrum can be converted into a simple spectrum.

Nomenclature for magnetic non-equivalent protons:

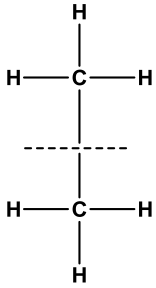
If the system possess chemically equivalent but magnetically nonequivalent protons than it absorb the frequency very close to each other but interaction takes places between them; as a result splitting of the signal is possible, which can be designated by putting the prime." For example:



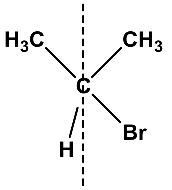
So the spinning system can be depicted as AA’BB’ system.

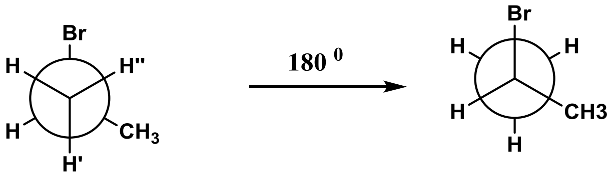
Identification of spin (protons):

The identification of spin in terms of the proton can be possible by symmetry elements. The equivalency of proton can be checked by the plane of the symmetry or by rotational axis. If it is same than a proton is chemically equivalent and vice-versa.



&



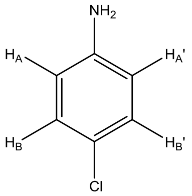


Therefore both methyl group chemically equivalent and shows only one signal as a singlet.

For magnetically equivalent.

Magnetically non-equivalent, generally observed in unsaturated compound i.e. single bond rotation is not possible.

For example,



The H_A and $H_{A'}$ are enantiomers but if we measure the distance of H_B to $H_{A'}$ and $H_{B'}$ to $H_{A'}$ are not same. i.e.(bond concentricity)

$H_B \rightarrow H_A'$: 5 [Long range coupling]

$H_B' \rightarrow H_A'$:3 [ortho coupling]

Same for H_A to H_B : 3 & H_A to H_B' : 5

So H_A and H_A' are magnetically not equivalent.

From the above discussion, it is concluded that,

→ Chemically non-equivalent → Magnetically non-equivalent

→ Magnetically non-equivalent → May be chemically equivalent.

Interpretation of ^{1}H NMR:

- → Calculate the No. of peaks (signals) observed in the spectrum. It gives types of protons present in molecules.
- → Intensity of the peaks(Signals)

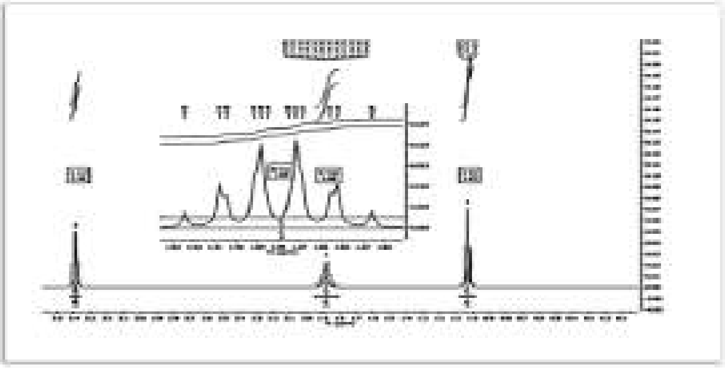
  It represents no. of protons present in individual peaks.(Area under curve).
- → Multiplicity of the signals:

  It gives the information regarding the no. of proton present on the adjacent atom.
- → Position of signals:

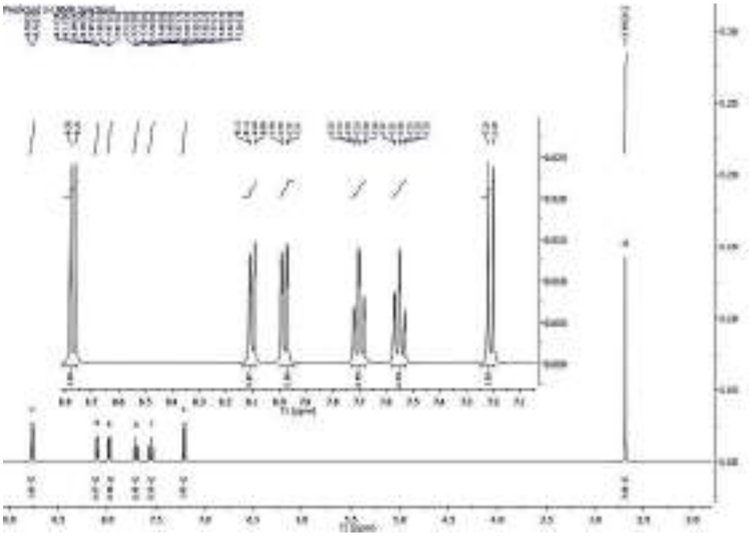
  It gives the information about the chemical atmosphere surrounding the protons.

For example

1) Propyl bromide



(4) 4- Methyl Quinoline



Instrumentation:

Two type of NMR spectrophotometer is available:

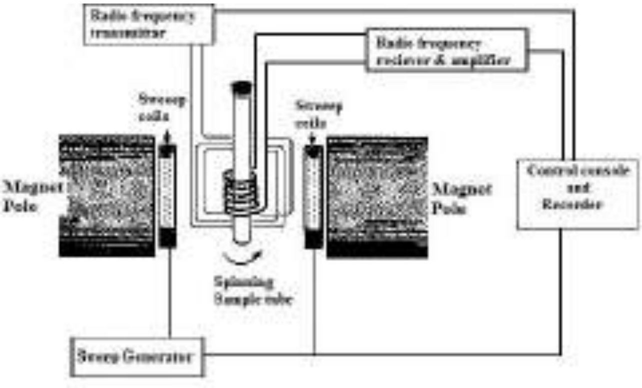
(1) Continuous wave spectrophotometer (permanent magnet)

(2) Fourier Transfer NMR Spectrophotometer

Nowadays for higher magnetic fields, strength; Fourier transform NMR is applicable while for the batch top model is available with continuous wave spectrophotometer.

→ **Continuous wave spectrophotometer**

Continuous wave spectrophotometer is working either field sweep (variant magnet) or frequency sweep. Generally, frequency is constant is more suitable than magnet.



The important component of the spectrophotometer 7 their functions are as under:

1. **Powerful Magnet:**

   Certain metal has a characteristic to produce strong magnetic fields by their superconductivity properties when it kept extremely low temperature.

   It provides homogeneous continuous magnetic field up to 2.5 tesla.

2. **Sample Probe:**

   It is typically designed devices where sample should be held between two poles of a strong magnet.

   It contains transmission coil from where RF frequency waves pass through the sample.

   It contains receiver coil at a right angle to the transmittance coil which receives output from the sample.

   It is connected with turbo air jet which spin the sample tube.

3. **Radiofrequency Oscillators:**

   It generates the RF for whole the range by electronic multiplication of natural frequency of a quartz crystal. This was held in a thermostatic block.

The directions of the RF coil is perpendicular to the magnet.

4. **Detector:**

   The detector is nothing but the receiver coil. The position of the receiver coil is perpendicular to the RF coil and magnet also.

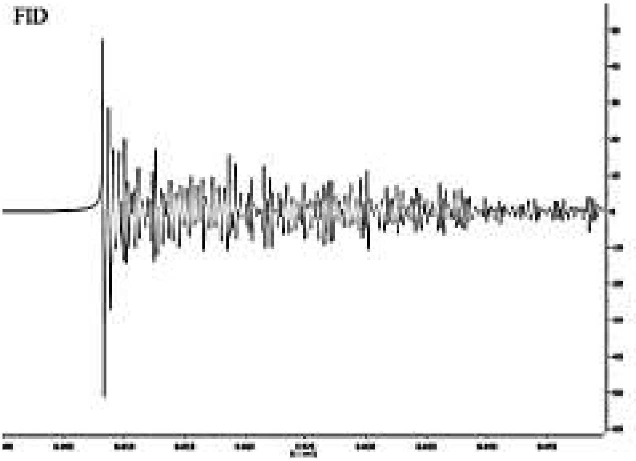
   It receives the transmit frequency from the sample & amplitude it & sends to the recorder.

5. **Recorder & Integrator:**

   It records the spectrum in the form of resonance peak on Y-axis against the strength of the magnetic field on X- axis.

Fourier Transform NMR (FT-NMR)

In Fourier transform technique, The RF frequency of interested nuclei with reference to their Larmor frequency is applied at a time. As a result, the diagram magnetisation creates in the sample. Once the excitation stops, the nucleolus will be released spontaneously by spin-spin relaxation process which is responsible for providing homogeneous field and all the nuclei showed free induction decay (FID) if it is signal spin and for multipins compound shows interferogram. This FID or interferogram converted into frequency dominant spectrum with the help of a computer.



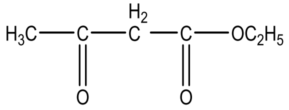
List of solvent used for the NMR Scanning:

Generally, the Deuterated solvent is used for the study of NMR in the liquid phase.

Sr. No.	Name of Solvent	Chemical Shift	
		Residual peak (δ ppm)	Peak of residual water (δ ppm)
1	CCl_4	No Peak	-
2	$CDCl_3$	7.26	1.6
3	DMDO- d_6	2.50	3.3
4	CD_3OD	4.87, 3.31	4.87
5	D_2O	4.8	4.8
6	C_6D_6	7.16	0.4
7	CD_3COOD	11.65,2.04	-
8	$(CD_3)_2CO$ (Acetone)	2.05	2.8

General application oh ^{1}H NMR:

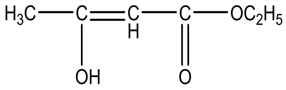
(1) Structure Determination:



$H_3C-\underset{O}{\underset{\|}{C}}-\overset{H_2}{C}-\underset{O}{\underset{\|}{C}}-OC_2H_5$

(A)

or



$H_3C-\underset{OH}{\underset{|}{C}}=\underset{H}{C}-\underset{O}{\underset{\|}{C}}-OC_2H_5$

(B)

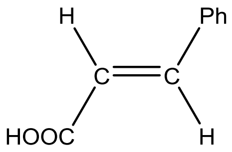
This ketone & enol form is possible in ethyl acetoacetate: After scanning for NMR:

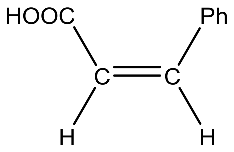
For Structure (A) CH_3 – Singlet
CH_3 – Triplet
CH_2 – Quartet
CH_2 – Signet

For different signals with peak area three & three proton as well as two-two protons.

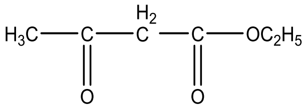
For Structure (B) CH_3 – Singlet
CH_3 – Triplet
CH_2 – Quartet
CH – Singlet
-OH – Singlet broad

(2) Identification of Geometrical Isomer:

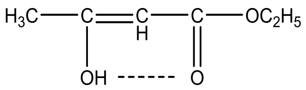




(3) In a study of H- Bond:



$H_3C-C(=O)-CH_2-C(=O)-OC_2H_5$



$H_3C-C(OH)=CH-C(=O)-OC_2H_5$

(4) Quantification of Molecular weight:

By using the reference standard and comparing integrated intensity with an unknown recognisable peak for the solution of unknown contain the known weight of each reference standard 0f unknown compound.

$$M = \frac{H_0\, M_0 n.w}{H n_0 w_0}$$

Here, M = Molecular weight of Unknown compound

M_0 = Molecular weight of Ref. Standard

H = Height (In terms of intensity of Ref. standard)

H_0= Height (In terms of intensity of unknown comp)

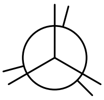
w = weight of ref. standard

w_0 = weight of unknown compound

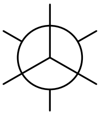
n= no. of peaks of unknown protons

n_0 = no. of peaks of Ref. std.

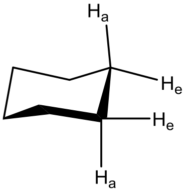
(5) For the conformational Analysis:



θ=0
j= 0

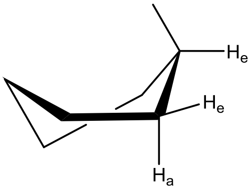


θ= 180
j=10 Hz



J_{aa}=11.4 Hz
J_{ae}= 4.2 Hz

Chair form

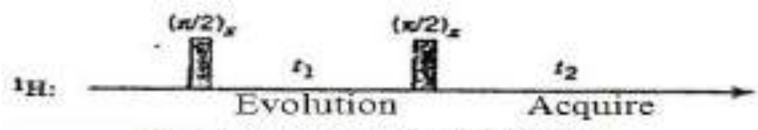


J_{ee}=2.7 Hz
J_{ae}= 4.2 Hz

Boat form

^{2}D NMR Technique:

^{2}D NMR techniques are also known as multiple plus programme. According to the mechanism of Fourier transformer NMR techniques magnetisation vector M_o staying on Z- axis which can be related to xy plane by π/2 pulses of RT. During their relaxation time, if came back to the time T_1. Now after some time interval, it can be further irradiated with different frequency pulse, So two variant with the time acquisition T_2. So it is known as ^{2}D NMR technique. [i.e. Two different frequency used with time interval T_1].



Pulse sequnces for 2D NMR

^{2}D NMR technique is also known as coherence spectroscopy. Nowadays a number of techniques are available as under:

(1) Correlation spectroscopy (COSY)

In this techniques, Two $\pi/2$ pulses are differentiated by required evaluation time T_1.If same nuclei are used for the study then it is known as Homonuclear correlation spectroscopy (HOMO-COSY). i.e. ^{1}H - ^{1}H COSY. Two different nuclei are used for the study that the technique is known as 'HETERO Nuclei Correlation Spectroscopy'. i.e. HETCOR.

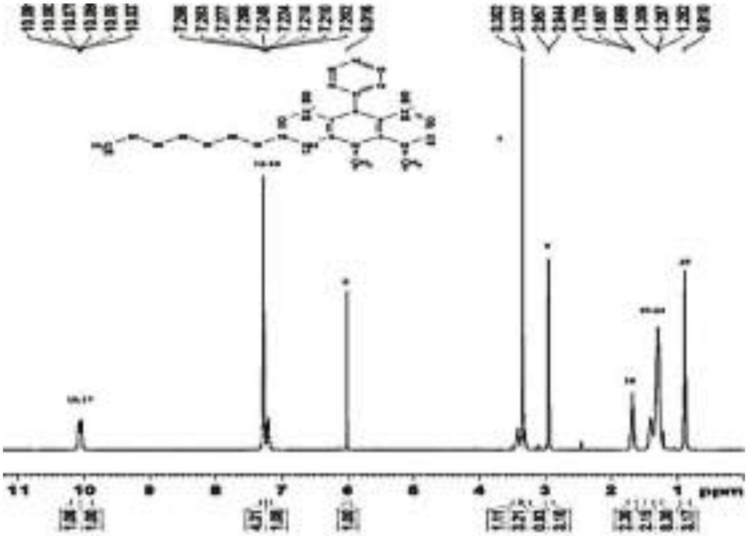
Interpretation:

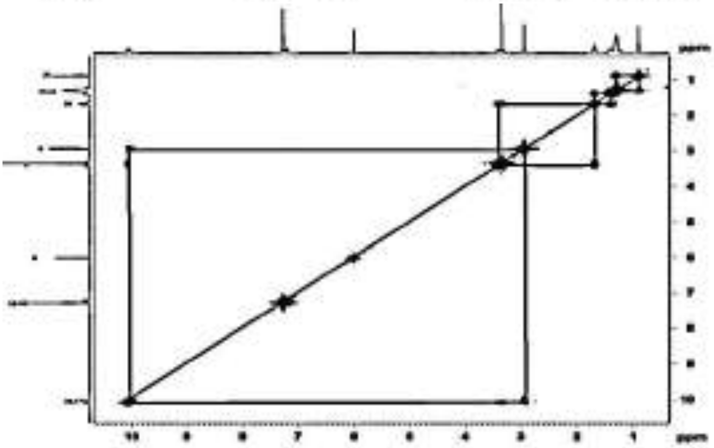
The aim of this technique is to assign all proton resonance in the spectrum.

→ The Matching of diagonal peak to the equivalent resonance in the ^{1}D spectrum.

→ Same practices do for all subsequent resonance peaks.

→ Coupled spin are then correlated with stepwise movement via starting and finishing at diagonal line peak as an intermediate cross peak.


11
10
9
8
7
6
5
4
3
2
1
ppm


ppm
10
9
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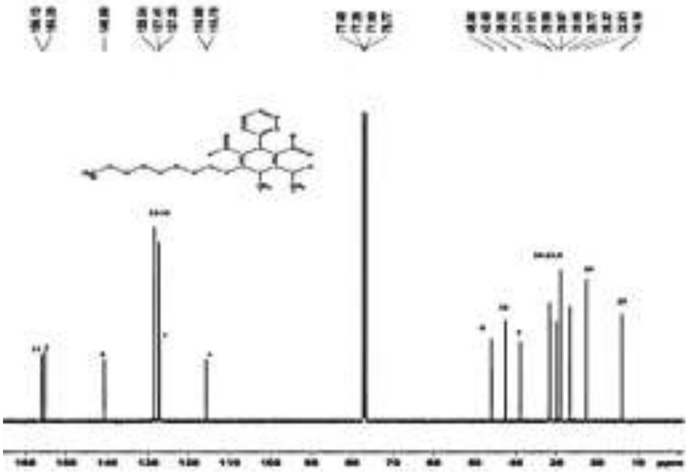
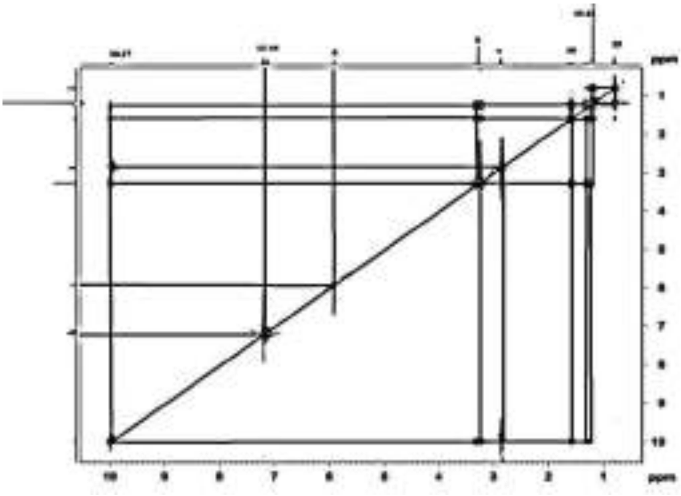

ppm

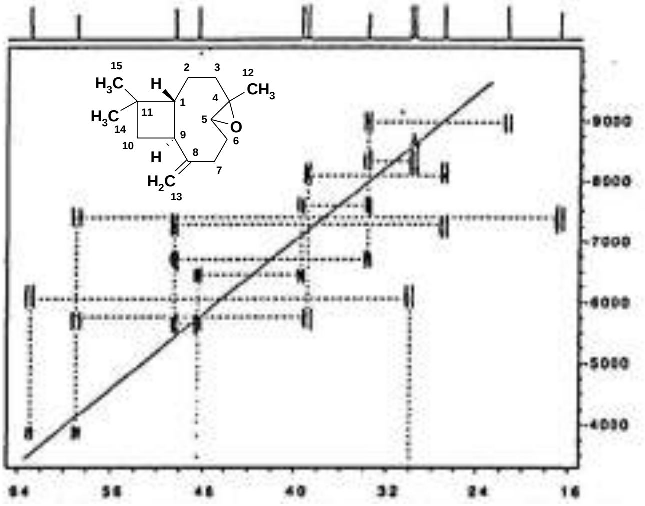
(2) Total Correlation spectroscopy (TOCSY)

In the ^{1}D spectrum of a proton; provides the information regarding coupling up to Geminal & vicinal proton within a molecule. TOCSY is able to establish a correlation between protons that present in the same spin system. i.e , provides continuous chain of spin-spin coupled protons.



(3) INADEQUATE:

Incredible Natural Abundance Double Quantum Transfer Experiment is useful for the correlating. The experiment is useful for the correlating nuclides, which possess relatively low natural abundance ratio in between 1-20 %. Generally 1D INADEQUATE use to measure carbon-carbon coupling. The complete carbon skeleton of the molecule can be traced directly in the molecule. 2D INADEQUATE is double filter INADEQUATE technique which suppresses the noise of homonuclied.



Heteronuclear Multiple Quantum Correlation (HMQC):

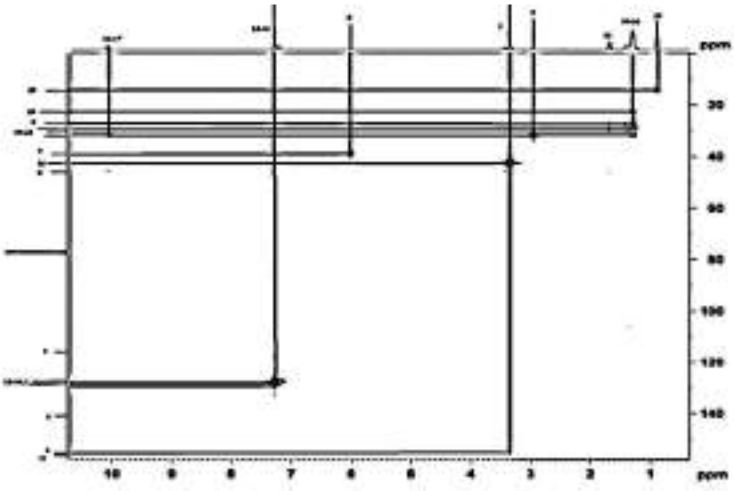
This technique is useful to detect proton signal bond relation. This ^{2}D spectrum provides a simple connectivity in which a cross peak correlates two attached nuclei.

The three most significant features illustrate are as under:

→ Known proton assignment

→ Dispersion of proton peak according to heteronuclear peak.

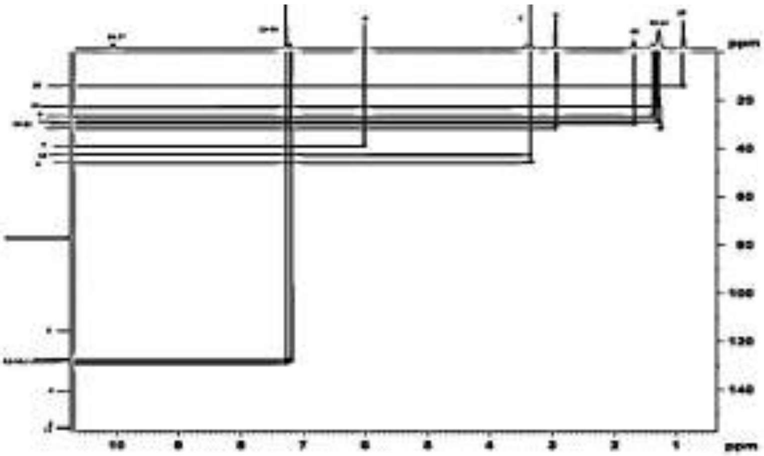
→ To identify dia-stereotropic Geminal proton.



Heteronuclear Single Quantum Correlation (HSQC)

HSQC is the same experiment as an HMBC only different is magnetisation is transferred to the heteronuclear atom by attaching proton via polarisation during t_1.

The disadvantages of HSQC over an HMBC is the greater number of pulses is utilise. As with HMBC suppression of parent resonance is required.



Resolved Spectroscopy (ROSY)

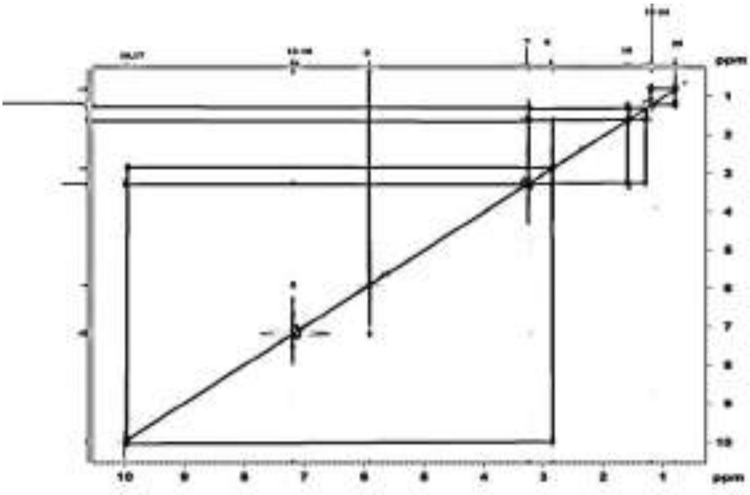
This technique is associated with simplification of crowded proton spectrum.

Following types of Resolved spectroscopy have been depicted in literature.

[1]. **Heteronuclear J- resolved:** It is a technique to separate heteronuclear coupling from the chemical shift. It is applicable for the measurement of the heteronuclear coupling constant.

[2]. **Homonuclear J-resolved:** it is a technique to separate homonuclear coupling by chemical shift. It is useful for the direct measurement of homonuclear coupling for overlapping spectrum.

[3]. **Indirect Homonuclear J- resolve:** It is a technique to separate the proton homonuclear coupling with respect to the chemical shift of attached heteroatom. It is applicable for the measurement of long-range coupling.



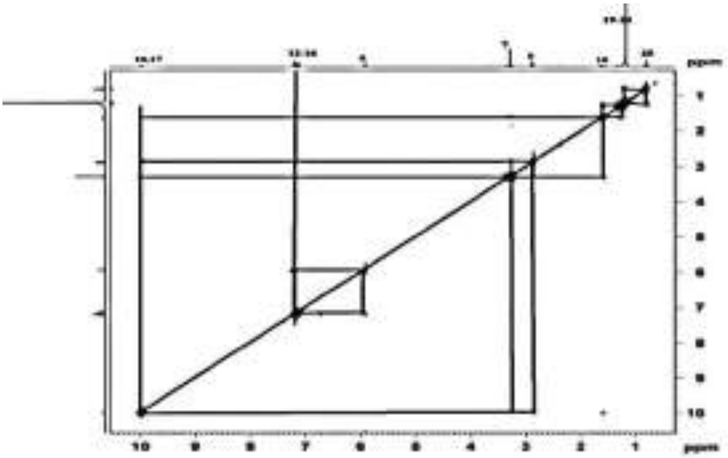
The Nuclear Overhauser Effect:

The NOE may be defined on the increasing or decreasing in the intensity of resonance when the spin transition of one of them are somehow perturbed from their equivalent population, The magnitude is represented as a relative intensity change between the equilibrium intensity. I_0 & that in the presence of NOE I such as

$$n_1\{S\} = \frac{I - I_0}{I_0} x \, 100$$

$n_1\{S\}$ = NOE observed for a spin I at the time S(spin) perturbed.

The relaxation of excited spin is possible by the transfer of energy via spin-spin relaxation or lattice relaxation. The spin-spin relaxation is directly related to the distance between these spin. The spin relaxation via space is only possible if the distance is generally less than 2-4 Å. This increases the intensity



Following techniques are reported for NOE.

[1]. **NOEs:** **I**t is established for spatial proximity between protons. It is applicable for small molecule [m.w.<<1000].

[2]. **NOESY:** It is the same technique as NOEs but it is applicable for small molecule [Mw<1000] as well as large molecules [MW>2000]. It is applicable for the measurement of intermolecular separation.

[3]. **HOESY:** It is a technique for the heteronuclear NOEs through space. ^{1}H- ^{13}C can provide useful Stereochemical information in case of homonuclear is doubtful for insufficient.

[4]. **EXSY:** It is a programme to determine qualitative exchange pathway in a dynamic system with exchange rate is slow can't be differentiated by chemical shift.

^{13}C NMR Spectroscopy:

As per the three broad principles of NMR spectroscopy; ^{12}C possess spin quantum number I=0, so it is NMR inactive but their isotope ^{13}C possess I=1/2 same as ^{1}H, so it is NMR active and shows the signal in NMR spectrum. Only the difference of ^{13}C & ^{1}H NMR is the abundance ratio of ^{13}C is 1.1% while in the case of ^{1}H is 99% so sensitivity is only 1.16% that of the ^{1}H overall sensitivity of ^{13}C compared to ^{1}H is 1/5700.

Key feature of ^{13}C NMR spectroscopy:

→ The chemical shift value for ^{13}C NMR spectroscopy is δ = 0-200 ppm with respect to the internal reference standard.

→ Due to low chance ratio ^{13}C – ^{13}C coupling is negligible; so proton decouple spectrum shows singlet for each non-equivalent carbon.

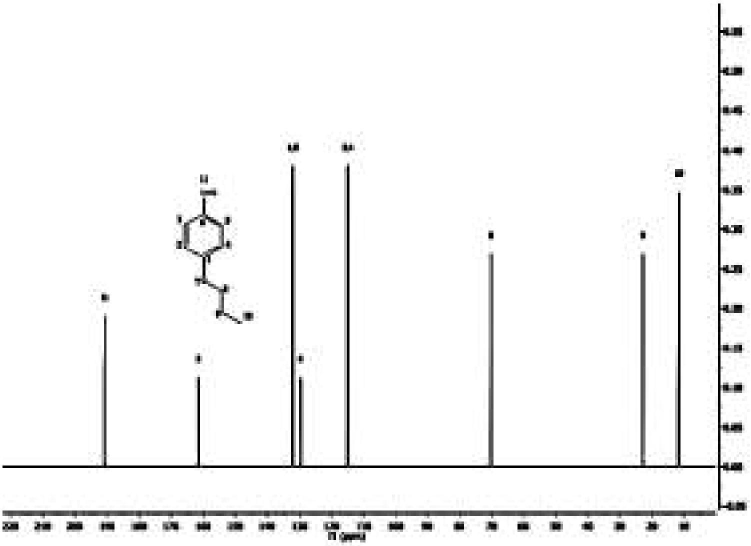
→ The peak high of the signal is related to the relaxation time to the equivalent carbon.

→ The chemical shift of carbon affected by magnetic anisotropy and electronegativity same as ^{1}H NMR.

- → The proton couple spectrum; The signal of each carbon split as a per (n+1) rule; where n= no. of protons attached to the same carbon.
- → The compares to ^{13}C gyromagnetic ratio with ^{1}H is one-fourth; so operation frequency for ^{13}C NMR is 25.2 MHz while for proton is 100MHz.

Proton Decoupled spectra:

In the technique, the coupling of the proton is completely removed with carbon atom by increasing the rate of excitation of the proton with a band of radio frequency. This resulting each proton rapidly change their spin between two spin levels in short time i.e, Proton has no sufficient time to interact with carbon nuclei. So it’s population difference between two level is zero i.e, coupling result with carbon atom is zero & each carbon peak appeared as a singlet. The no. of carbon peak appeared as a symmetry of the molecule.



OFF Resonance Decoupling:

This technique is also known as proton-coupled spectrum. In short in this technique; Proton couple with a carbon atom, where it has been directly bonded.

The splitting of the carbon signal occurs as a per (n=1) rule; where n= proton directly attached to the carbon atoms.

The disadvantage of this technique is that intensity of the signals is low due to 1.1 % abundance ratio and hetero-coupling value is high so get a broad spectrum.

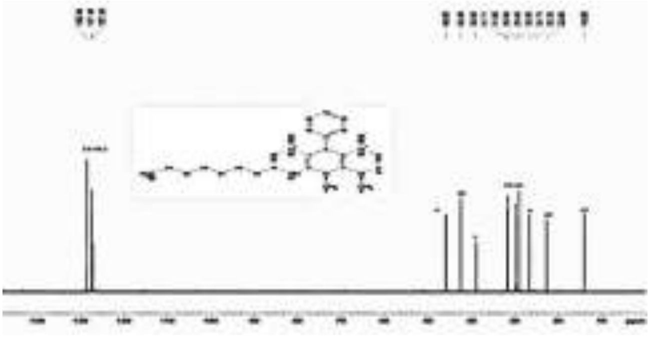
Distortionless Enhancement by Polarisation Transfer (DEPT)

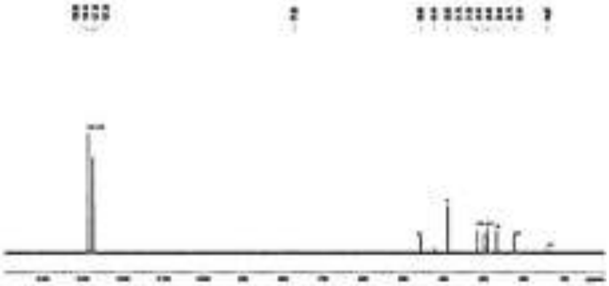
In a recent advance in proton decoupled spectrum is series of proton pulse set at 45^0, $90^0$and 135^0 as three separate experiments. The signal intensity for each practical depends on the proton attached with particular carbon atoms.

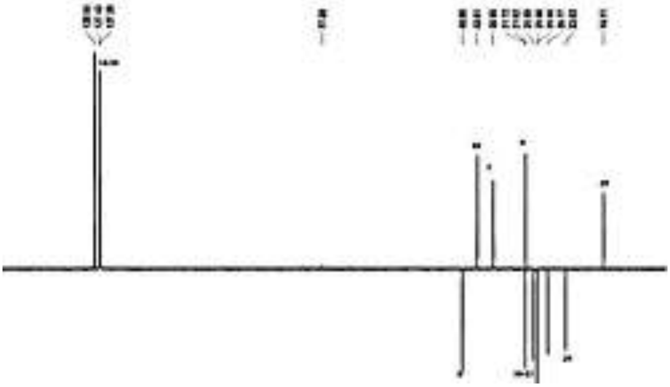
In DEPT experiment three separate spectra are obtained.

1. One is normal proton decoupled spectrum.
2. Second is run at 90^0 pulses which show only methine proton signals.
3. Third one is run at 135^0 pulse which shows methine and Methylene signal as normal while methylene signal appears as a negative peak.

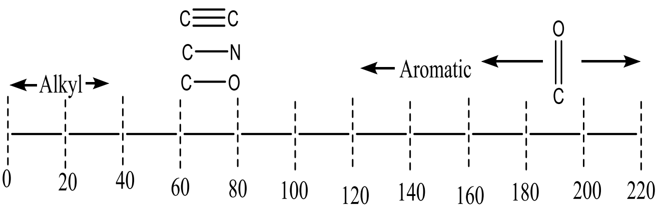
4.





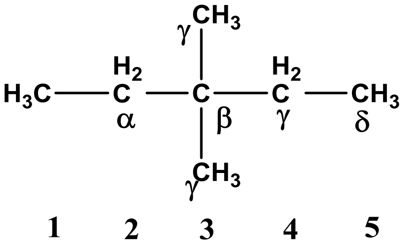


Example


C≡C
C—N
C—O
Alkyl
Aromatic
C=O
0
20
40
60
80
100
120
140
160
180
200
220

Calculation for chemical shift on ^{13}C NMR

Alkane: It can be affected up to δ effect



3,3-dimethylpentane

Calculation for C1: It has oneα, oneβ, three γ and one δ carbon.

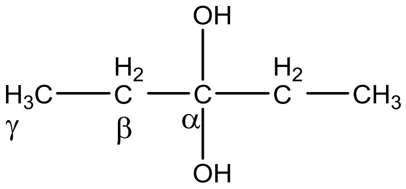
δc1 = -2.5 + (9.1 * 1)+(9.4*1)+(-2.5*3)+(.3+1)
= -2.5+9.1+9.4-7.5+0.3
=8.8

δc2 = -2.5 + (9.1 * 2) + (9.4*3) + (-2.5*1) + (.3+1)
= -2.5+18.2+28.2-2.5
=41.4

δc3 = -2.5 + (9.1 * 4)+(9.4*2)
= -2.5+36.4+18.8
= 52.7

δc6 = -2.5 + (9.1 * 1)+(9.4*3)+(-2.5*2)
=-2.5+9.1+28.2-5.0
=29.8

Branched Alkane:



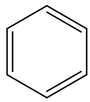
pentane-3,3-diol

$C\delta$ =-2.5 + (9.1*2) + (9.4*2) + (41*2)
= -2.5+18.2+18.4+82
=116.1

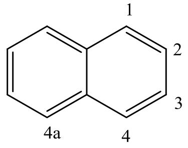
$C\beta$ = -2.5 + (9.1*2) + (9.4*2) + (-2.5*1) + 8
=-2.5+18.2+9.4 -2.5+6
= 38.6

$C\gamma$ = -2.5 + (9.1*1) + (9.4*1)+(-2.5*1)+(0.3)-10
=-2.5+9.1+9.4-2.5+0.3-10
=3.8

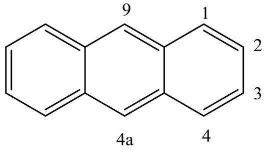
For Aromatic compound:



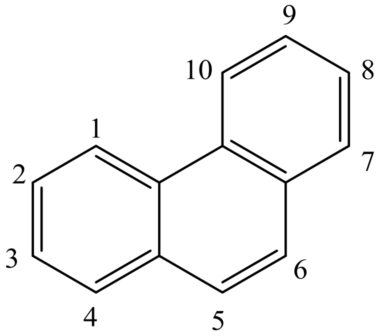
=128.5



δ_{C1}=128.1
δ_{C2}=125.9
δ_{C4a}=133.7

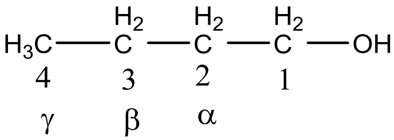


δ_{C1}=130.1
δ_{C2}=125.4
δ_{C4a}=132.2
δ_{c9}=132.6



δ_{C1}=128.3
δ_{C2}=126.3
δ_{C3}=126.3
δ_{C4}=122.2
δ_{C4a}=131.9
δ_{C9}=126.6
δ_{C10a}=130.1

For Terminal Carbon compound


$H_3C-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-OH$

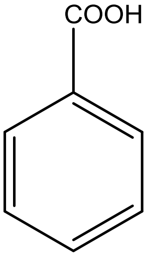
C_1 = -2.5+9.1*1+9.4*1-2.5*1+48
= 51.5

C_2 = -2.5+9.1*2+9.4*1+10
= 35.1

C_3 = -2.5+9.1*2+9.4+5.0
= 19.5

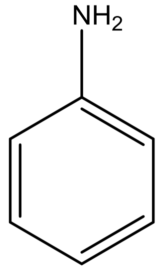
C_4 = -2.5+9.1*1+9.4*1-2.5*1
= 13.0

For Benzoic acid



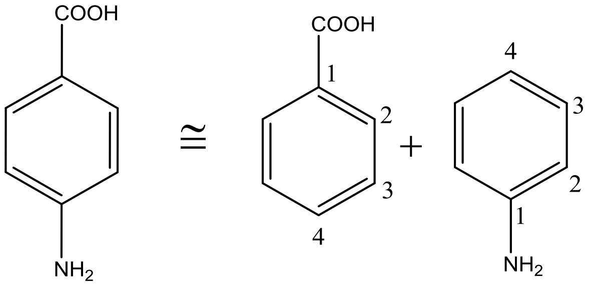
C_1 = 128.5 + 2.9 = 131.4
C_2 = 128.5 + 1.3 = 129.8
C_3 = 128.5 + 0.4 = 128.9
C_4 = 128.5 + 4.3 = 132.6

For Aniline



$C_1 = 128.5 + 19.2 = 147.7$
$C_2 = 128.5 + 12.4 = 116.1$
$C_3 = 128.5 + 1.3 = 129.8$
$C_4 = 128.5 - 9.5 = 119.0$

For 4- Amino Benzoic acid



$C_1 = 128.5 + 2.9 - 9.5 = 121.9$
$C_2 = 128.5 + 1.3 + 1.3 = 131.1$
$C_3 = 128.5 + 0.4 - 12.4 = 116.5$
$C_4 = 128.5 + 4.3 + 19.2 = 152.0$

^{1}H NMR example

(1) Assign the structure to a compound from following NMR results.

M.F. = $C_7H_5OCl_3$

Chemical shift in δ ppm	Multiplicity	No. of protons	Coupling constant
3.9	s	3H	
6.7	d	1H	9.0 Hz
7.25	d	1H	9.0 Hz

(i) First find out double bond equivalent by using following equation

$DBE = \frac{(2a+2)-(b-d)}{2}$ a= No. of carbon,

$DBE = \frac{(2*7+2)-(8-0)}{2}$ b= No. of Monovalent ion

$DBE = \frac{16-8}{2}$ d= No. of trivalent ion

$$DBE = \frac{8}{2}$$

$$DBE = 4$$

(ii) Derive the conclusion from DBE

4= Four double bond present or
= Three double bond + one Cycle
= two double bond + two cycle
= One double bond + three cycle

(iii) From the given chemical shift value it is found that

→ One alkyl group containing three equivalent proton attach with electronegative atom may be present

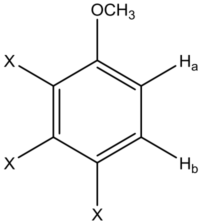
∴ -OCH_3 may be present.

→ 6.7 δppm one signal appeared as a double with coupling constant 9.0 Hz and second signal appeared at 7.25 with same coupling constant value

It means these two protons are aromatic in nature and couples with each other by ortho coupling

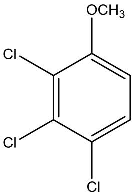
∴ From the above discussion

- One –OCH_3 group present
- Aromatic present with two proton as an ortho coupling



- H_a proton is shielded as compare to H_b means: H_a proton at ortho position of $–OCH_3$ group & H_b at ortho position of –Cl atom.

So, Structure of the compound is as below.



(2) $C_4H_7BrO_2$

Chemical shift in δppm	Multiplicity	No. of proton	Coupling constant
1.08	Triplet	3H	-
2.07	Quintet	2H	-
4.23	Triplet	1H	
10.97	Singlet	1H	

$$DBE = \frac{(2a+2)-(b-d)}{2}$$

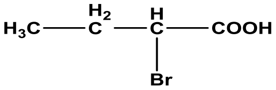
$$DBE = \frac{(2*4+2)-(8-0)}{2}$$

$$DBE = \frac{10-8}{2}$$

$$DBE = 1$$

1.08	Triplet	3H	∴-CH_3 group with neighbour 2H
2.07	Quintet	2H	- CH_2 group with 3H as a neighbour
4.23	Triplet	1H	- CH group attach with electronegative

			group & 2H as a neighbouring proton
10.97	Singlet	1H	- COOH group



$H_3C-\overset{H_2}{C}-\underset{Br}{\overset{H}{C}}-COOH$

(3) $C_{10}H_{10}O$

Chemical shift in τ ppm	Multiplicity	No. of proton	Coupling constant
7.75	Singlet	3H	-
3.40	Doublet	1H	16.5
2.60	Doublet	1H	16.5
2.8 to 2.4	Multiplate	5H	-

$$DBE = \frac{(2a+2)-(b-d)}{2}$$

$$DBE = \frac{(2*10+2)-(10-0)}{2}$$

$$DBE = \frac{22-10}{2}$$

$$DBE = 6$$

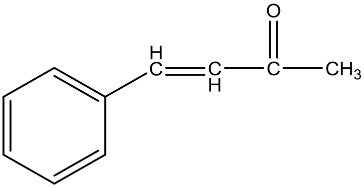
→ 7.75τ singlet 3H $-CH_3$ group attach with electron withdrawing group ∴ $-COCH_3$

→ 3.40 doublet 1H 16.5 Hz and 2.60 Doublet 1H 16.5 Hz so that both proton appeared in downfield & coupled with each other i.e, sp^2 protons ∴ -CH=CH

∴ Out of two , one appeared downfield as compare to other

∴ One attach with electron withdrawing group; in downfield while other with electron donating group at upfield.

→ 2.8 to 2.9 Multiplate 5H Aromatic ring as a mono substitution.



(4) $C_5H_9BrO_2$

Chemical shift in δ ppm	Multiplicity	No. of proton	Coupling constant
1.3	Triplet	3H	7 Hz
1.8	Doublet	3H	7 Hz
4.2	Quartet	2H	7 Hz
4.3	Quartet	1H	7 Hz

$$DBE = \frac{(2a+2)-(b-d)}{2}$$
$$DBE = \frac{(2*5+2)-(10-0)}{2}$$
$$DBE = \frac{12-10}{2} = \frac{2}{2}$$
$$DBE = 1$$

1.3	3H	Triplet	$-CH_3$ group with 2H as a neighbouring protons
1.8	3H	Doublet	$-CH_3$ group near to the carbon attached with 1 proton & electronegative atom
4.2	2H	Quartet	$-CH_2$ group with 3H as a neighbouring protons & attach with electron withdrawing group.
4.3	1H	Quartet	-CH group with 3H as a neighbouring proton attach with electronegative atom

From the above discussion

→ One CH_3-CH_2 & second CH_3-CH group present, so C_4H_9

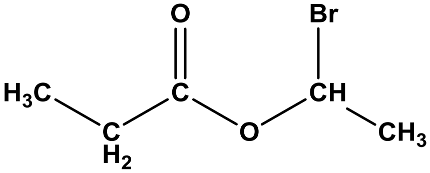
But given Molecular Formulla is

$C_5H_9BrO_2$

$\underline{-\ C_4H_9}$

$= CBrO_2$

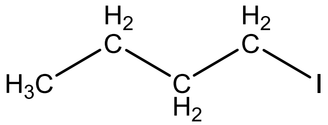
∴ COO group also present which is reflected in chemical shift of –CH_2 & -CH group



(5) Draw the different isomer corresponding to C_4H_9I show the important difference in their NMR spectra & which of the isomer has the NMR shown below data:

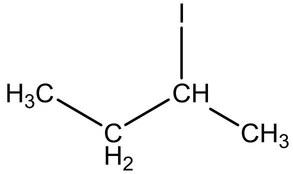
1.02	Triplet	J=7 & 12 Hz
1.72	Quintet	7 Hz
1.92	Doublet	7 Hz
4.17	Sextet	-

Structure of Isomer I



3H triplet
2H sextet
2H quintet
2H Triplet

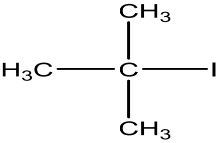
Structure of Isomer II



3H triplet
2H doublet
2H quintet
1H sextet

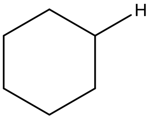
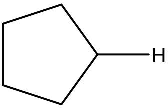
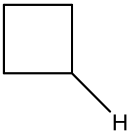
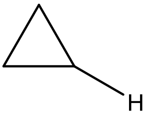
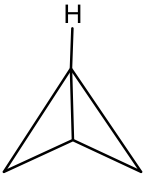
Given data match with this isomer

Structure of Isomer III


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-I$

Shown only one signal for a proton

Coupling constant value of $^1J_{CH}$

Compound	J (Hz)
sp^3	
CH_3CH_3	124.9
$CH_3\underline{C}H_2CH_3$	119.2
$(CH_3)_3CH$	114.2
CH_3NH_2	133.0
CH_3OH	141.0
CH_3Cl	150.0
CH_2Cl_2	178.0
$CHCl_3$	209.0
	123.0
	128.0
	134.0
	161.0
	205.0
sp^2	
$CH_2=CH_2$	156.2
$CH_3\underline{C}H=C(CH_3)_2$	148.4
$CH_3\underline{C}H=O$	172.4
$NH_2\underline{C}H=O$	188.3
C_6H_6	159.0
Sp	
$CH\equiv CH$	249.0
$C_6H_5C\equiv CH$	251.0
$HC\equiv N$	269.0

Some $^2J_{CH}$ Value

Compound	J (Hz)
sp^3	
$C\underline{H}_3\underline{C}H_3$	-4.5
$C\underline{H}_3\underline{C}Cl_3$	5.9
$\underline{C}H_3C\underline{H}=O$	26.7
sp^2	
$C\underline{H}_2=\underline{C}H_2$	-2.4
$(C\underline{H}_3)_3\underline{C}=O$	5.5
$CH_2=\underline{C}HC\underline{H}=O$	26.9
$^*C_6H_6$	1.0
sp	
$C\underline{H}\equiv\underline{C}H$	49.3
$C_6H_5O\underline{C}\equiv C\underline{H}$	61.0

$^{*2}J = 7.6$ (> ^2J)

The ^{13}C shift parameter in some Linear and Branched Hydrocarbons

^{13}C Atoms	Shift (ppm) (A)
α	+9.1
β	+9.4
γ	-2.5
δ	+0.3
ε	+0.1
1^0 (3^0)^a	-1.1
1^0 (4^0)^a	-3.4
2^0 (3^0)^a	-2.5
2^0 (4^0)	-7.2
3^0 (2^0)	-3.7
3^0 (3^0)	-9.5
4^0 (1^0)	-1.5
4^0 (2^0)	-8.4

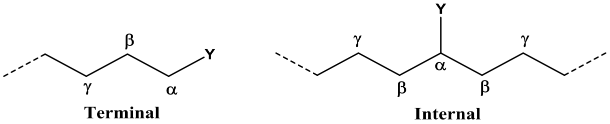
[a] The notations 1^0 (3^0) and 1^0 (4^0) denote a CH_3 group bound to a R_2CH group and to a R_3C group, respectively. The notation 2^0 (3^0) denote a RCH_2 group bound to a R_2Ch group, and so on.

The ^{13}C shift for some Linear and Branched-chain Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			

2,2-Dimethylbutane	29.1	30.6	36.9	8.9
3-Dimethylpentane	11.5	29.5	36.9	(18.8, 3-CH_3)
2,3-Dimethybutane	19.5	34.3		
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH_3)

Incremental Substituent Effect(ppm) on replacement of H by Y in alkanes. Y is Terminal or internal[a] (+ left, - right)



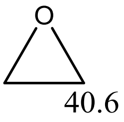
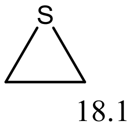
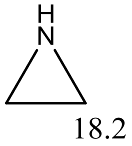
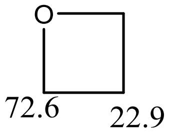
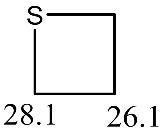
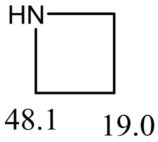
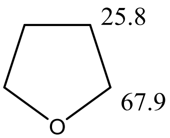
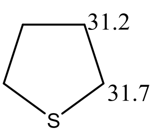
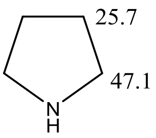
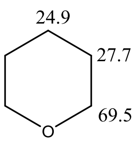
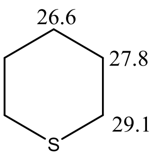
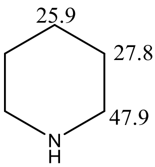
Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH_3	+9	+6	+10	+8	-2
$CH{=}CH_2$	+20		+6		-0.5
$C{\equiv}CH$	+4.5		+5.5		-3.5
COOH	+21	+16	+3	+2	-2
COO^-	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28		02	
$CONH_2$	+22		+2.5		-0.5
COR	+30	+24	+1	+1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+9	+7	-2
OH	+48	+41	+10	+8	-5
OR	+58	+51	+8	+5	-4
OCOR	+51	+45	+6	+5	-3
NH_2	+29	+24	+11	+10	-5
NH_3^+	+26	+24	+8	+6	-5

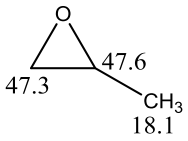
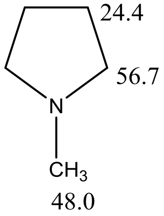
NHR	+37	+31	+8	+6	-4
NR_2	+42		+6		-3
NR_3^+	+31		+5		-7
NO_2	+63	+57	+4	+4	
CN	+4	+1	+3	+30	-3
SH	+11	+11	+12	+11	-4
SR	+20		+7		-3
F	+68	+63	+9	+6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	-6	+4	+11	+12	-1

Chemical shift of Cycloalkanes (ppm from TMS)

C_3H_6	-2.9		C_7H_{14}	28.4
C_4H_8	22.4		C_8H_{16}	26.9
C_5H_{10}	25.6		C_9H_{18}	26.1
C_6H_{12}	26.9		$C_{10}H_{20}$	25.3

Chemical Shift for saturated Heterocycles (ppm from TMS)

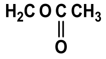
Substituted		
		
		
		
		

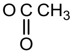
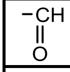
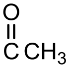
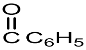
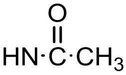
Substituted	
	

Alkene and Cycloalkene Chemical Shifts (ppm from TMS)Alkyne Chemical Shifts (ppm)

Compound	C-1	C-2	C-3	C-4	C-5	C-6
1-Butyne	67.0	84.7				
2-Butyne		73.6				
1-Hexyne	68.1	84.5	18.1	30.7	21.9	13.5
2-Hexyne	2.7	73.7	76.9	19.6	21.6	12.1
3-Hexyne	15.4	130	80.9			

Incremental Shifts of the Aromatic carbon Atoms of Mono substituent Benzenes (ppm from Benzene at 128.5 ppm, + to the left, - to the right). Carbon Atom of Substituents in parts per million from TMS[a]

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	+9.3	+0.7	-0.1	-2.9	21.3
CH_2CH_3	+15.6	-0.5	0.0	-2.6	29.2(CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH_3)
$CH{=}{=}CH_2$	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH_2)
C≡CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	-1.8	-0.1	-1.6	
CH_2OH	+13.3	-0.8	-0.6	-0.4	64.5
 $H_2C\,O\,\underset{\underset{O}{\Vert}}{C}\,CH_3$	+7.7	~0.0	~0.0	~0.0	20.7 (CH_3),66.1 (CH_2), 170.5

					(C=O)
OH	+26.6	-12.7	+1.6	-7.3	
OCH_3	+31.4	-14.4	+1.0	-7.7	54.1
OC_6H_5	+29.0	-9.4	+1.6	-5.3	
 $O\underset{\underset{O}{\|}}{C}CH_3$	+22.4	-7.1	- 0.4	-3.2	23.9 (CH_3), 169.7 (C=O)
 $-\underset{\underset{O}{\|}}{C}H$	+8.2	+1.2	+0.6	+5.8	192.0
 $\overset{\overset{O}{\|}}{C}CH_3$	+7.8	-0.4	-0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
 $\overset{\overset{O}{\|}}{C}C_6H_5$	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
 $\overset{\overset{O}{\|}}{C}CF_3$	-5.6	+1.8	+0.7	+6.7	
 $\overset{\overset{O}{\|}}{C}OH$	+2.9	+1.3	+ 0.4	+4.3	168.0
 $\overset{\overset{O}{\|}}{C}OCH_3$	+2.0	+1.2	-0.1	+4.8	51.0 (CH_3), 166.8 (C=O), 168.5
 $\overset{\overset{O}{\|}}{C}Cl$	+4.6	+2.9	+0.6	+7.0	
 $\overset{\overset{O}{\|}}{C}NH_2$	+5.0	-1.2	0.0	+3.4	
C≡N	-16.0	+3.6	+0.6	+4.3	119.5
NH_2	+19.2	-12.4	+1.3	-9.5	
$N(CH_3)_2$	+22.4	-15.7	+0.8	-11.8	40.3
 $HN\cdot\overset{\overset{O}{\|}}{C}\cdot CH_3$	+11.1	-9.9	+0.2	-5.6	
NO_2	+19.6	-5.3	+0.9	+6.0	
N=C=O	+5.7	-3.6	+1.2	-2.8	129.5
F	+35.1	-14.3	+0.9	-4.5	
Cl	+6.4	+0.2	+1.0	-2.0	
Br	-5.4	+3.4	+2.2	-1.0	
I	-32.2	+9.9	+2.6	-7.3	
CF_3	+2.6	-3.1	+0.4	+3.4	
SH	+2.3	+0.6	+0.2	-3.3	
SCH_3	+10.2	-1.8	+0.4	-3.6	15.9
SO_2NH_2	+15.3	-2.9	+0.4	+3.3	
$Si(CH_3)_3$	+13.4	+4.4	-1.1	-1.1	

Shifts for Carbon atoms of Heteroaromatics (neat, ppm from TMS)

Compound	C-2	C-3	C-4	C-5	C-6	Substituent
Furan	142.7	109.6				
2- Methyl furan	152.2	106.2	110.9	141.2		13.4
Furan-2-Carboxaldehyde	153.3	121.7	112.9	148.5		178.2
Methy 2-Furoate	144.8	117.9	111.9	146.4		159.1 (C=O), 51.8 (CH_3)
Pyrrole	118.4	108.0				
2-Methylpyrrole	127.2	105.9	108.1	116.7		12.4
Pyrrole-2-Carbozaldehyde	134.0	123.0	112.0	129.0		178.9
Thiophene	124.4	126.2				
2-Methyl thiophene	139.0	124.7	126.4	122.6		14.8
Thiophene-2-carboxaldehyde	143.3	136.4	128.1	134.6		182.8
Thiazole	152.2		142.4	118.5		
Imidazole	136.2		122.3	122.3		
Pyridine	150.2	123.9	135.9			
Pyrimidine	159.5		157.4	122.1	157.4	
Pyrazine	145.6					
2-Methylpyrazine	154.0	141.8[a]	143.8[a]	144.7[a]		21.6

[a] Assignment not certain

Shifts Position for Alkyl Halide (neat, ppm from TMS)

Compound	C-1	C-2	C-3
CH_4	-2.3		
CH_3F	75.4		
CH_3Cl	24.9		
CH_2Cl_2	54.0		

$CHCl_3$	77.5		
CCl_4	96.5		
CH_3Br	10.0		
CH_2Br_2	21.4		
$CHBr_3$	12.1		
CBr_4	-28.5		
CH_3I	-220.7		
CH_2I_2	-54.0		
CHI_3	-129.9		
CI_4	-292.5		
CH_3CH_2F	79.3	14.6	
CH_3CH_2Cl	39.9	18.7	
CH_3CH_2Br	28.3	20.3	
CH_3CH_2I	-0.2	21.6	
$CH_3CH_2CH_2Cl$	46.7	26.5	11.5
$CH_3CH_2CH_2Br$	35.7	26.8	13.2
$CH_3CH_2CH_2I$	10.0	27.6	16.2

Shift Position of Acyclic and Alicyclic Amines (neat, ppm from TMS)

Compound	C-1	C-2	C-3	C-4
CH_3NH_2	26.9			
$CH_3CH_2NH_2$	35.9	17.7		
$CH_3CH_2CH_2NH_2$	44.9	27.3	11.2	
$CH_3CH_2CH_2CH_2NH_2$	42.3	36.7	20.4	14.0
$(CH_3)_3N$	47.5			
$CH_3CH_2N(CH_3)_2$	58.2	13.8		
Cyclohexylamine	50.4	36.7	25.7	25.1
N-Methylcyclohexylamine	58.6	33.3	25.1	26.3 (N-CH_3 33.5)

Shift Positions of Thiols, Sulfides and Disulfides (ppm from TMS)

Compound	C-1	C-2	C-3
CH_3SH	6.5		
CH_3CH_2SH	19.8	17.3	
$CH_3CH_2CH_2SH$	26.4	27.6	12.6

$CH_3CH_2CH_2CH_2SH$	23.7	35.7	21.0
$(CH_3)_2S$	19.3		
$(CH3CH_2)_2S$	25.5	14.8	
$(CH3CH2CH_2)_2S$	34.3	23.2	13.7
$(CH_3CH_2CH_2CH_2)_2S$	34.1	31.4	22.0
CH_3SSCH_3	22.0		
$CH_3CH_2SSCH_2CH_3$	32.8	14.5	

Chapter 5

Mass spectrometry

INTRODUCTION

Generally in case of spectroscopy one phenomenon is common “There is an interaction between electromagnetic radiation and matter (sample).” While in case of Mass spectrometry this phenomenon is not occurring. So some people are not agree that Mass spectrometry is not a spectroscopic technique.

In case of UV, IR, and NMR sample absorb the light (electromagnetic radiation), so these are absorption spectroscopy. While Mass is differ from them.

First requirement for Mass spectroscopy is organic sample either in gaseous or vapor state.

Principle:

When organic molecule in the gaseous or vapor state at a very low pressure are subjected to 70 ev. it loses the electrons and forms a positively charged cation. This this can be accelerated and deflected by magnetic and electrical fields is depends on its mass, charge, velocity and deflecting force. In these four variable charge is negligible, velocity and deflected force are constant, so the deflection depends only on mass. If mass is high, deflection is low, and if mass is low, deflection is higher. i.e. deflection is higher for light particle and lower for heavy particle.

So when organic molecule is gaseous or vapor state, bombarded at 70 ev at reduce pressure, it loses the electron and forms a positively charged ion. This ion can be accelerated and deflecting by magnets depends on charge, velocity, mass and deflecting force but charge is negligible , velocity and deflecting force are constant so deflection only depends on mass, it is higher for light particle and lower for heavy particle.

$$\frac{m}{z} = \frac{H^2R^2}{2V}$$

Where,

H= applied magnetic field

R= radius of arc of deflection

V= applied accelerating voltage

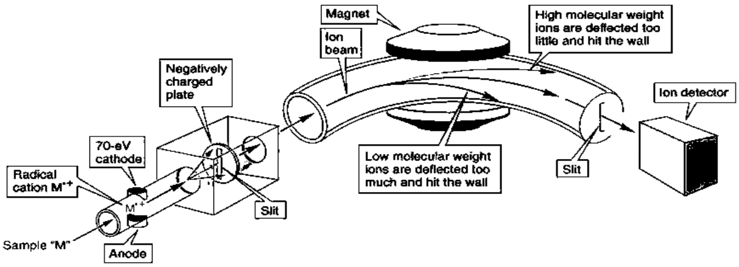
$\frac{H^2R^2}{2}$ = deflection force

$$M + e^- \ (70\ ev) \longrightarrow \underset{\text{radical cation}}{M^{\bullet +}} + 2e^-$$

The fragmentation pattern of compounds depends on the characteristic of sample and it provide detail information about molecular structure can be obtained.

Instrumentation:

Schematic diagram of a mass spectrometer.



1. The inlet system
2. The ion source (ionization chamber)
3. The electrostatic accelerating system
4. The ion separator
5. Ion collector/ read out
6. Vacuum system

Vacuum is necessary, so it can be in isolated type of situation. It will be necessary to minimize the no. of collision between ions and non-ionized molecule.

Requirement of the instrument:

1. To vaporize compounds of varying volatility
2. To produce cation
3. To separate ions
4. To detected and record them.

According to above fig. mass spectrometer possess following parts

1. Sample inlet system
2. Ionization chamber
3. Accelerating region
4. Analyzer tube
5. Detector
6. Recorder

The mass spectrometer is used for the investigation of any compound may vary in their types but generally contain following part.

1. **Sample inlet system:**
   Function: To vaporize the sample and uniformly introduce into ionization chamber.

For successful ionization, all samples must be converted in to gaseous or vaporized state, to achieve this sample must be heated at 400 ºC, so temperature of inlet system is above 400 ºC.

The rate of introducing sample in ionization chamber is remain constant, for this it consist special device of micrometer for determining the amount of sample is introduce.

Another important point is the introduction of sample vapor at low pressure (10^{-5}-10^{-6} torr) is necessary to minimize the number of collision between ions and non- ionized molecule.

Sample size is 1mg to µg.

2. **Ionization chamber/ ion source :**

Function: to produce positively charged ion and other different with m/e value.

For the production of positively charged ion, ionization of sample is necessary.

To ionize the sample different techniques are available:

a) **EI (Electron impact ionization):** In electron impact system, when sample in gaseous state bombarded at electron vault and low pressure at 10^{-5}-10^{-6} at high energy provide a molecule to emitted electron from filament and forms a positively charged ion.

Means an electron from electron beam knocks an electron from parent molecule to give parent ion.

$$M + e^{-} \longrightarrow M^{\bullet +} + 2e^{-}$$

But for this high electron vault and low pressure is require.

- Due to this pyrolysis of molecule may take place
- M^{+} ion absent
- Complex spectrum is available

So this technique is harsh technique.

b) **Field ionization:** In this technique, very high local electric field ($2x10^{8}$ v/cm) on tip of metal wire pulls off e^{-} for large molecule.

Means by creating vacuum in $2x10^{8}$ v/cm for small area and large molecule, so maximum electron attack on this molecule, it knocks the electron from parent molecule and forms parent ion.

c) **Chemical ionization:** This ionization carried out on the bases of molecular reaction.

In this technique as a reactant gas generally CH_4, isobutene and ammonia is used.

The reactant gases are stored at low pressure10^{-4} and in this tank introduce the sample.

So at low pressure reactant gas ionized and forms ion, which on interact with neutral molecule and forms chemically reactive species, which interact with sample and forms positively charged ion.

$$CH_2^{\bullet +} + CH_4 \longrightarrow C_2H_5^{+} + CH_3^{\bullet}$$

$$CH_3^{+} + CH_3 \longrightarrow C_2H_5^{+} + H_2$$

$$C_2H_5^+ + CH_4 \longrightarrow CH_5^+ + CH_4$$

$$CH_5^+ + M \longrightarrow M+1 + CH_4$$

Advantage: M+ present, simple spectrum is obtain

This technique is used for polar and high molecular weight species at 10.000g

d) **FAB (Fast atom bombardment source):** In this technique, by using highly energetic chemical species, bombarded with sample.

$$Xe + e \longrightarrow Xe^{\bullet+} + 2e^-$$

$$Xe^{\bullet+} \longrightarrow \overrightarrow{Xe} + Xe^{\bullet+}$$

$$\overrightarrow{Xe} + Xe \longrightarrow \overrightarrow{Xe} + Xe^{\bullet}$$

Fast moving atom

$$\overrightarrow{Xe} + M \longrightarrow M^{\bullet+} + Xe^{\bullet}$$

This technique is used for polar and high molecular weight species of 10,000 g.

Advantage:

- Ionization due to transition
- Minimum energy reaction , so minimize the destructive
- No deviation

3. **Ion accelerating region:**

Function: to accelerate the ion in a uniform velocity and produce ionic beam.

It contain: 1) Repleter plate 2) Ion accelerating slit 3) Ion focusing slit.

High electrostatic field about 1000 to 2000 v is applied between two accelerating slits so when ion pass through this region repleting plate replete to each other to form uniform way, after this when pass through between accelerating tube to form narrow beam due to high voltage moving ion is formed. The ion focusing plate focuses it. So, uniform beam of ion is obtained.

Suppose mass of ion is M, charge e^-, initial kinetic energy is negligible.

So, ion is accelerated velocity V.

So, kinetic energy must equal to electrostatic energy.

$$E = \frac{1}{2}mv^2$$

$$\frac{1}{2}mv^2 = ev$$

$$v^2 = \frac{2ev}{m} \quad \ldots\ldots\ldots..1)$$

Electrostatic = ev

Repellers = which direct the ion to the accelerating plate

Accelerating = accelerate the ion

Ion focusing = which directs the ion into uniform beam

4. **Analyzer tube :**

Function: to disperse the ionic beam in to different frequency according to their m/e value, an analyzer must possess following characteristic:

i) It should have a high resolution power.
ii) It should have a high rate of transmission of ions.

There are two types of analyzer:

1. Ion- trapped mass analyzer

2. Time of flight analyzer

1. **Ion- trapped mass analyzer:**

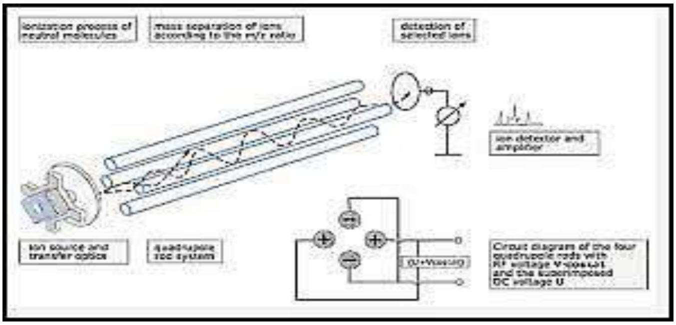
Ion- trapped mass analyzer working two way for trapping ions.

a) Three dimensional ion trap
   e.g. Quadrupole mass analyzer
b) Ion- cyclotron resonance

Both analyzer trap the ions by using combine effect of DC and RF

a) Quadrupole mass analyzer:

Principle: combination of DC and radio frequency on the four parallel opposite charge rods can be set to pass only a selected mass to charge ratio. Remaining ions do not flight through this quadrupole analyzer and will collide with these rods. As a result never complete the path up to detector.



Advantages:

- Classical mass spectrum obtained
- Relatively cheaper system
- Reproducibility of the result is possible

Limitations:

- Resolution is good for limited range
- Peak height is variable as a function of mass
- It is not suitable for pulsed ionization method

The selection of mass analyzer depends on resolution. Generally at low resolution quadrupole and lop trap working very good. Time of light and sector instruments(magnet) work better than other analyzer. Ion cyclotron resonance was performed best at ultra-high resolution.

b) Ion- cyclotron resonance:

Ion moves in a circular path under the effect of external magnetic field. The cyclotron frequency of the ions depends on their mass, by using following equation, one can measure the mass of ions.

$$\frac{mv^2}{r} = evB$$

But angular frequency $w = \frac{v}{r}$

$$w = \frac{v}{r} = \frac{eB}{m}$$

Advantages:

- The best resolution as compare to the other analyzer
- Well compatible for pulsed ionization as well as MALDI
- Non-destructive ion detection

Limitations:

- Limited dynamic range
- Strictly low pressure required
- Ion- molecule reaction is possible

2. **Time of flight (TOF):**
   Principle: a time of flight mass analyzer determine the mass dependent time; it takes ions with various masses to flight from the ion source to the detector. The necessity of this analyzer is sharp starting time.

   Ion leaving the ion source is

$$T = ev = \frac{\mathrm{mv}^2}{2} \quad \ldots\ldots\ldots\ldots\ldots.1)$$

The ion velocity(v) is the length of flight path L divided by the time

$$V = \frac{L}{T} \quad \ldots\ldots\ldots\ldots.2)$$

Put the value of V in kinetic energy equation..1)

$$\mathrm{T} = \frac{\mathrm{m}}{\mathrm{e}} = \frac{2\mathrm{vt}^2}{\mathrm{L}^2}$$

$$\therefore t = L\sqrt{\frac{m}{e}\frac{1}{2}v}$$

Advantage:

- It is compatible with pulsed ionization or fast ionization technique.
- Resolution is better than quadruple.

5. **Detector and Recorder :**

its function is to detect the ionic beam and produce a mass spectrum expressed as a bar graph in which relative abundance on ordinate is plated against m/z ratio.

Ionization technique:

Several methods are available for the ionization of sample, the most common being electron impact technique to produce ion.

1) **EI (Electron ionization):** vaporized sample is introduced under low pressure operate at pressure of 10^{-5}-10^{-6} in to a tube called ‘ion source’.

The entering molecule of sample is bombarded with electron emitted from a hot tungsten or Rh wire and then accelerated to an anode.

Limitation:

1) As the sample should be in vapor state, possibility of pyrolysis of less volatile substance or sample increase.
2) It produce molecular ion with excess internal energy, which leads to various fragmentation process. Fragmentation is drastic, complex fragmentation pattern is obtained.
3) 70 ev often destroys the molecular ion, hence the absence of very weak molecular ion peak does not allow the detection of molecular weight and empirical formula.

2) Field ionization:

Field ionization is achieved by applying a very high local electrical field of order 2×10^8 v/cm.

When the sample is subjected to a very strong electric field, it pulls off an electron forming a positive ion. It is a particular technique for the study of large molecules that do not show a parent ion.

3) Chemical ionization:

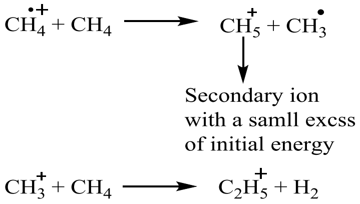
This technique based on ion-molecule reaction.

In it, reaction gas like methane, isobutane, and ammonia is introduced at high pressure (1-torr) with the sample (10^{-4} torr) to be analysed by the mass spectrometer in the ionization chamber.

When a beam of electron passes the ionization chamber. The reaction gas undergoes ionization to produce ion, which reacts with the neutral molecule to form a product.

To the product so formed are chemical reactive species and can interact with the sample and forms a positive ion.

Thus methane from $CH_4^{\bullet +}$ + CH_3^+ initially which react with a neutral molecule.



The CH_5^+ is strong proton donor and thus reacts with analyte molecule to form (M+1) ions.

$$M + CH_5^+ \longrightarrow (M+1)^+ + CH_4$$

Advantage:

1) It produces molecular ion peak.
2) As the fragmentation is reduced, it produces a spectrum which one quite simple.

4) FAB (fast atom bombardment):

Chemical ionization technique still requires molecules that are moderately volatile and thermally stable. This excludes many compounds of biological interest and importance such as peptides and carbohydrates. The most reset technique FAB overcomes. These problems polar molecules like peptide with molecular weight 10,000 can be analyzed.

In this method, Xe or Ar atoms of high translational energy are produced by the following sequence.

I) Xe atoms are ionised by bombardment of e- beam it to form Xe cation radical.

$$Xe_{atom} + e^{-} \longrightarrow Xe^{+\bullet} + 2e^{-}$$

II) They are accelerated to 6-10 K.ev. to give radical cation of high translational energy Xe^{+}

$$Xe^{+\bullet} \xrightarrow{\text{accelerate}} \overrightarrow{Xe}^{+\bullet}$$

III) Xenon radical cation is then allowed to interact with neutral xenon atoms due to which xenon radical cation passes its energy to neutral atoms hence fast moving Xe atoms are produced.

$$Xe^{+\bullet} + Xe \longrightarrow \overrightarrow{Xe} + Xe^{+\bullet}$$

IV) The resultant fast atoms are directed onto the sample held in a liquid matrix on a metal target. The liquid matrix is commonly glycerol.

Advantage:

1) Ionization is caused by the transition of energy; it minimizes destruction of molecular ion which can alert for 20-30 min.

2) This method is most effective for a relatively polar substance which is Non- volatile or thermally unstable.
3) Derivatization not required.

The positive ions produced by the interaction of the molecular ion with e^- beam are forced through the first accelerating slit by a weak electrostatic field.

So the main components of ion accelerating region are:

1) Ion repellers
2) Ion accelerating plate
3) Ion focusing plate

A potential of 1000-2000v is used to accelerate the ions through a slit system. This produces a narrow beam of the fast moving ion. Mass of ion is M, the charge is e^- initial kinetic energy is negligible. Now ions are accelerated to a velocity (v), hence their kinetic energy must be equal to their electrostatic energy, accelerated in passing through the applied volt (v).

$$\frac{1}{2}mv^2 = ev$$

$$v^2 = \frac{2ev}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Function of mass analyzer:

Its function to disperse the ionic beam according to their m/e value.

The ion produced may separately according to their mass to charge ratio(m/e) using the magnetic and electrostatic field.

The fast moving ions enter the analyzer tube. The analyzer tube is an evacuated (10^{-7} to 10^{-8} torr) curved metal tube through which ion beam passes from source.

In the analyzer tube, the ions are subjected to a uniform magnetic field(H), which is generated by an electromagnet and perpendicular to the direction of the ionic beam.

In the magnetic field, the ions are deflected along a circular path of radius (r).

i.e. $$r = mv/eh$$

$$r^2 = \frac{m^2v^2}{e^2H^2} \qquad \textbf{Or}$$

$$v^2 = \frac{r^2e^2H^2}{m^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

$$\frac{2ev}{m} = \frac{r^2e^2H^2}{m^2}$$

$$\frac{m}{e} = \frac{H^2r^2}{2v}$$

This relationship reveals that in the case of an ion with a given mass to charge ratio (m/e).

The radius of deflection can be increased by decreasing magnetic field (H) allow only ions of certain suitable m/e values to pass through the collector slit and enter into the collector.

Detection of the presence of the isotopes of the elements and the recognition of molecular ion peak:

Mass spectra often contain peak of significant intensity that is attributed to the presence of isotopes. Two of these are called the M+1 and M+2 peaks, where M is the mass of the parent ion and 1 or 2 represent mass increases due to heavier isotopes of the ½ mass unit. most elements occur naturally as several isotopes and generally, the lighter of these predominates while the heavier one occurs to a lesser extent.

The isotopic compositions of some common elements are as shown under.

Element	**M^+**	**M+1**	**M+2**
Hydrogen ^{1}H	99.98%	^{2}H 0.016	
Carbon ^{12}C	98.42%	^{13}H 1.08	
Nitrogen ^{14}N	99.62%	^{15}C 0.38	
Oxygen ^{16}O	99.76%	^{17}O 0.04	^{18}O 0-2
Sulphur ^{32}S	94.825	^{33}S 0.74	^{34}S 4-40
Chlorine ^{35}Cl	67.5%	^{36}Cl -	^{37}S 32-5
Bromine ^{79}Br	50.5%	-	^{81}Br 49-5
Iodine^{127}I	100%	-	-

Isotopic composition of element is constant:

150 (M)	100%
151 (M+1)	10.2%
152 (M+2)	0.88%
$C_7H_{10}N_4$	9.25-0.38
$C_8H_8NO_2$	9.23-0.78
$C_8H_{10}N_2O$	9.61-0.61
$C_8H_{12}N_2$	9.98-0.45
$C_9H_{10}O_2$	9.96-0.82
$C_9H_{12}NO$	10.34-0.68
$C_9H_{14}N_2$	10.71-0.5

Fragmentation value of the compound shows according to Nitrogen as well as Ring rule.

1. Nitrogen rule:

Nitrogen rule states that the compound containing an even no.of nitrogen atoms (including O) will give a molecular ion with an even mass number,
For e.g. the following ion gives their molecular ion at given mass number.

CH_4	16
CH_3OH	32
$CClF_3$	104
C_6H_5OH	94
NH_2-NH_2	32
$C_5H_5N_2$	94

An odd number of nitrogen atoms causes the molecular ion to be at odd mass number. e.g. NH_3 m/z = 17 and $C_2H_5NH_2$ = 45

It is important to note that the relationship applies to all ions and not only to the molecular ions.

2. Ring rule:

Elemental composition of any fragmentation peak can be established by using the following formula.

$$RPDB = \lambda - \frac{1}{2}Y + \frac{1}{2}Z + 1$$

Where X= No. of carbon
Y= Monovalent ion
Z= Trivalent ion

For example $C_5H_5N^+$

$$RPDB = 5 - \frac{1}{2}5 + \frac{1}{2}1 + 1$$

$$= 5 - 2.5 + 0.5 + 1$$

$$= 6 - 3$$

$$= 3$$

Value odd: $\therefore$ RPDB

For example $C_7H_5O^+$

$$RPDB = 7 - \frac{1}{2}5 + \frac{1}{2}0 + 1$$

$$= 7 - 2.5 + 0 + 1$$

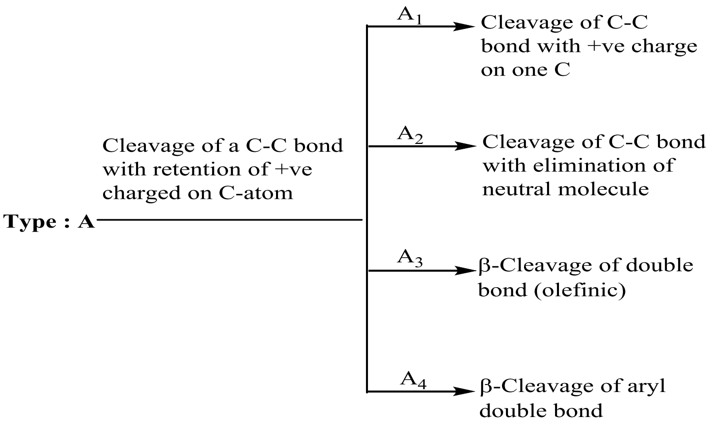
$$= 8 - 2.5$$

$$= 6.5$$

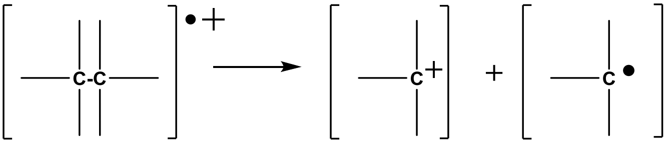
$$\therefore +\frac{1}{2} \text{ RPDB}$$

Types of Fragmentation:

The ions undergo various types of decomposition like heterolytic or homolytic cleavage of the bond, rearrangement chain branching elimination of molecule etc. leading to the formation of fragments of longer life, such formation patterns can be grouped into the following types.



Type –A$_1$: Cleavage of C-C bond



This is a saturated hydrocarbon cleavage of C-C bond.

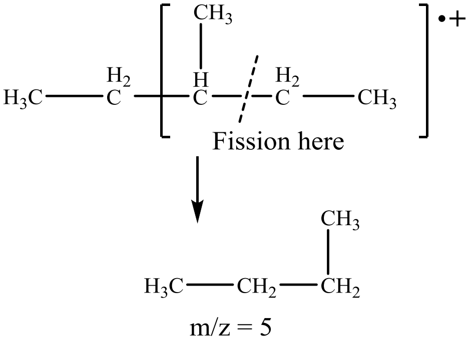
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{\text{n-Octane}}$$

e.g. $CH_3^+, CH_3\text{-}CH_2^+, CH_3\text{-}CH_2\text{-}CH_2^+, CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2^+, CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^+$

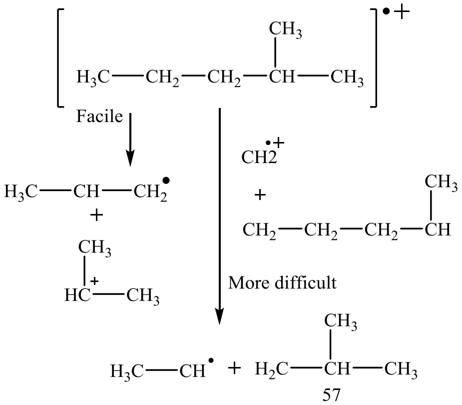
Fragmentation adjacent to branching points.

e.g.

1.



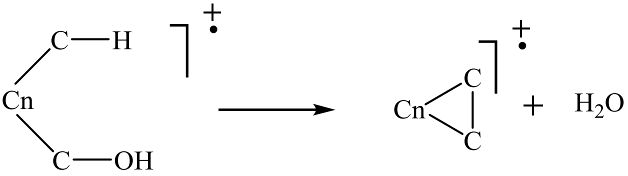
2.

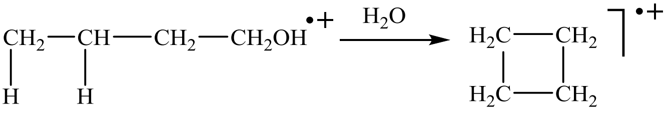


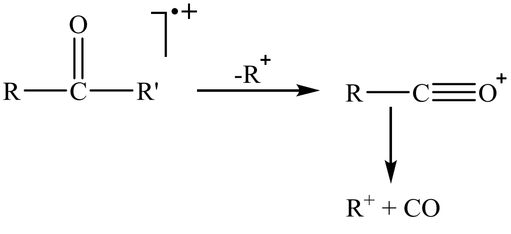
A hydrocarbon exhibits a peak at mass C_nH_{2n+1} with maximum intensity at 3, 4, and 5.

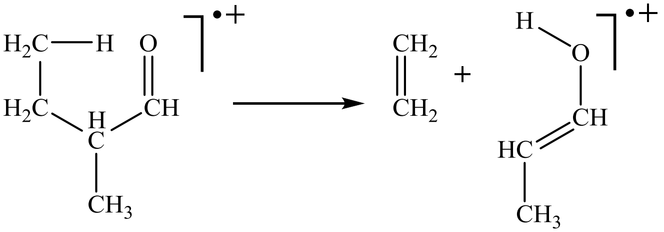
Type –A_2:

This is the cleavage of C-C single bond with the the elimination of neutral molecules. Small stable molecule like H_2O, CO_2, CO, C_2H_4 can be lost from a molecule ion e.g.

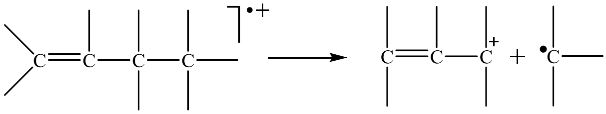






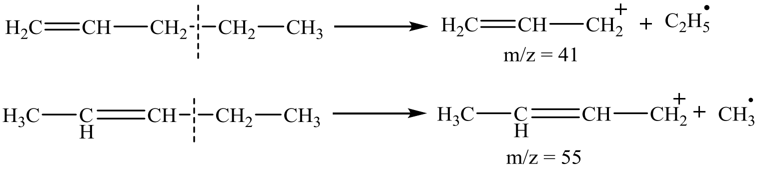


Type –A$_3$: β – Cleavage to double bond



This is the cleavage of the single bond is to C=C. it gives allylium ion. This cleavage produces intense peak with mass C_nH_{2n-1}.

e.g.



$$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_3 \longrightarrow H_2C{=}CH{-}\overset{+}{C}H_2 + C_2H_5^{\bullet}$$

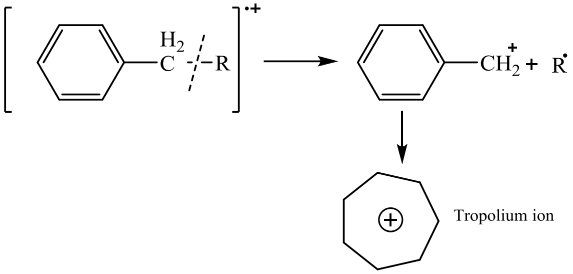
m/z = 41

$$H_3C{-}CH{=}CH{-}CH_2{-}CH_3 \longrightarrow H_3C{-}CH{=}CH{-}\overset{+}{C}H_2 + CH_3^{\bullet}$$

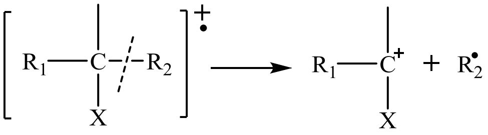
m/z = 55

Type –A$_4$: β – Cleavage to Aryl double bond

This is similar to A$_3$ type except that C=C is replaced by an aryl group.



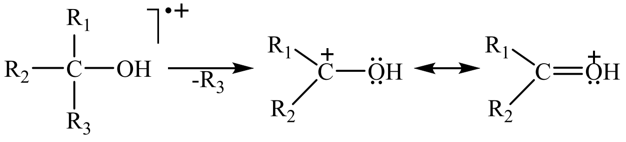
Type – B: α- Cleavage to hetero atom

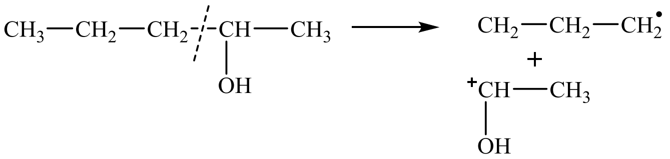


X= Cl, OH, OR, S

This is observed in alcohols, esters, sulphides and halogens.

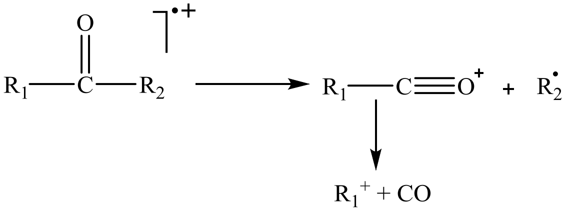
The mass spectra are characterised by intense peaks due to cleavage of C-C bond next to heteroatom.

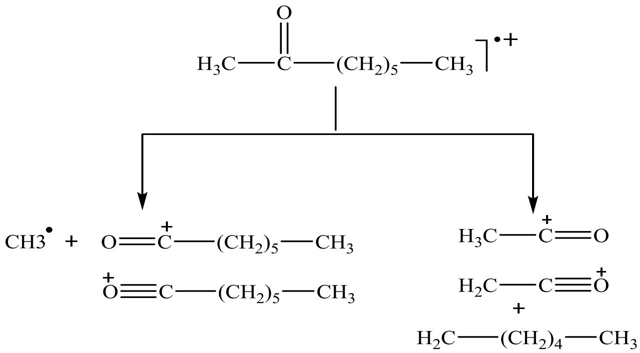




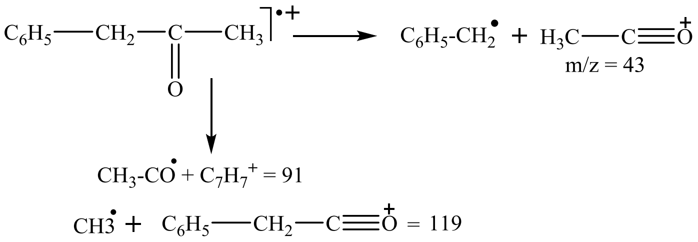
Type – C: Cleavages in carbonyl compounds

The molecular ions are prominent; the major fragmentation involves the fission of the C-C bond adjacent to the oxygen atom. The loss of larger alkyl group occurs predominantly and the base peak in ketones is often as result of this loss.

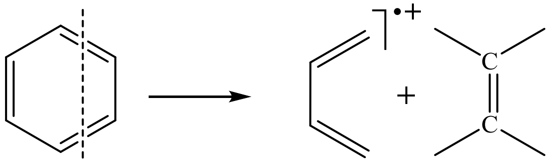




The more abundant acylion ion is generally, produced by loss of the largest alkyl group.



Type –D:



It is characterised by the cleavage of two bonds of a cyclic system with function of two unsaturated compounds.This fragmentation has the elimination of neutral molecule like olefin by cleavage of more than one sigma bonds.

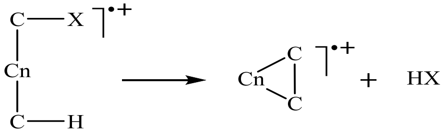
Type –E: loss of hydrogen halide

Alkyl halide may lose a molecule of HX as under.

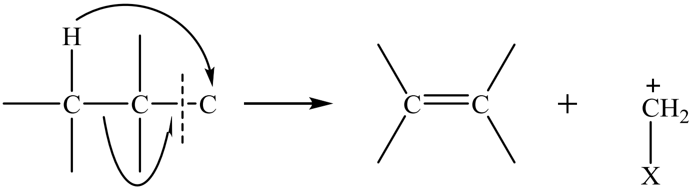
$$R—CH_2—CH_2—X^{\bullet+} \longrightarrow [R—HC{=}CH_2]^{\bullet+} + HX$$

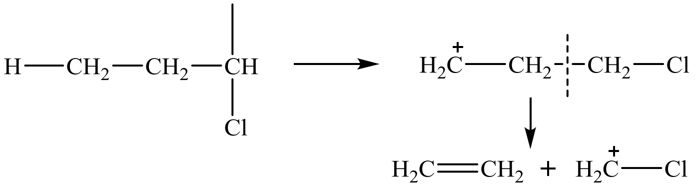
X= F,Cl

Or

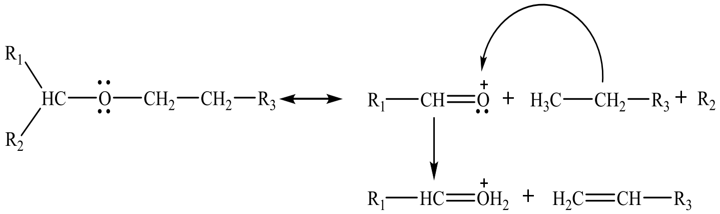


Type –F: Rearrangement followed by α – cleavage to hetero atom





Type –G: by α – cleavage followed by rearrangement



Type – H: McClafferty rearrangement

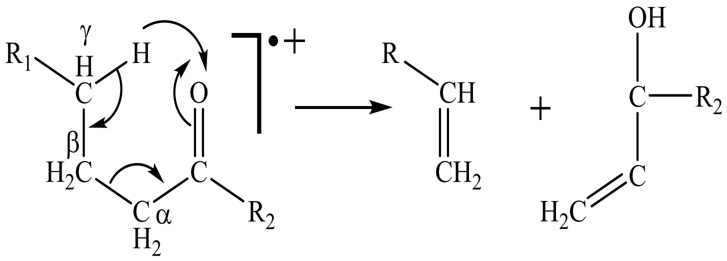
This type of rearrangement is archived by acids, aldehydes, olefins, alkyl benzenes, amides and nitriles.

This type of rearrangement is shown by the compound passes hydrogen atom at a γ- position of the carbonyl group.

This type of compounds invariably shows a relative intense peak with an even m/z value.

The rearrangement fragmentation is accompanied by a loss of a neutral molecule.

This is an intra- molecular elimination in which positive charge is retained by treatment containing oxygen.

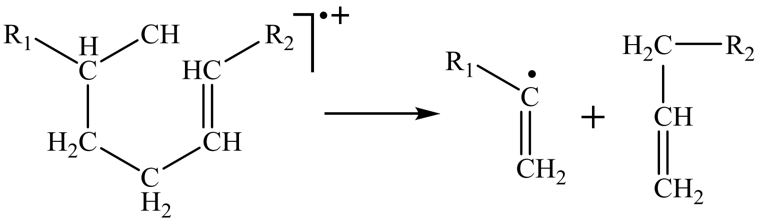


R_2 may be	m/z
H= Aldehyde	44
R= Ketone	58 - R= CH_3
OH= Acid	60
OR= Ester	74 - R= CH_3
NH_2= Amide	51

The fragmentation of a monoalkene occurs to afford two often alkene fragments, provided a membered cyclic transition state, involving x- hydrogen is positive.

The positive charge can appear either fragment.

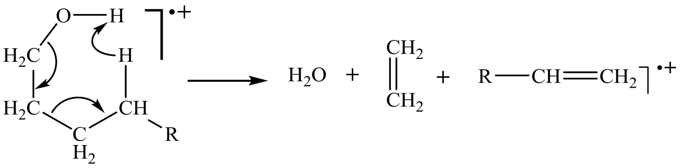
The monoalkenes can, therefore, be identified by the presence of peaks C_nH_{2n-1}(28, 41,55) and peaks at C_nH_{2n} (28, 42, 56).



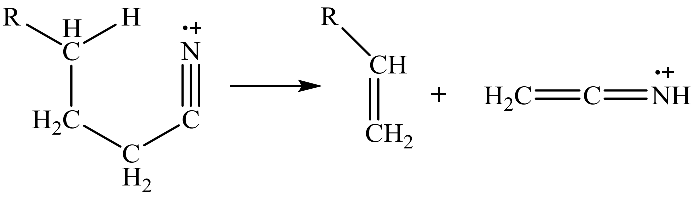
Loss of water together with the elimination of olefins from alcohols with more than four carbon atom in a chain

(McClafferty type rearrangement) accounts for the peak at M-(olefin+ H_2O).

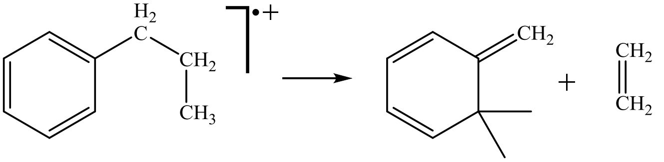
E.g. peak at M- 46, M-74, M-102

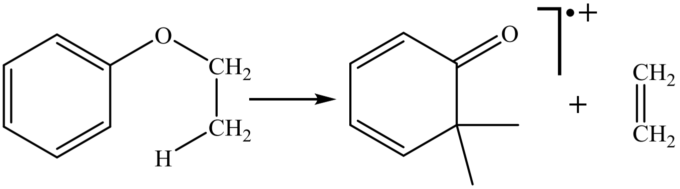


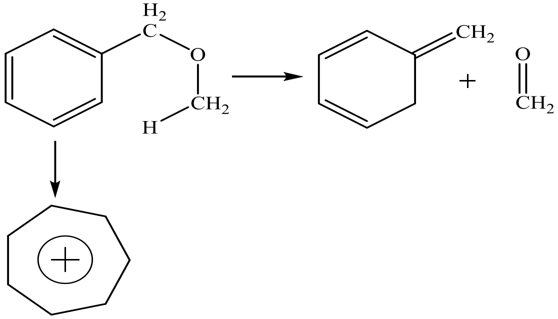
Nitriles:



Certain alkyl benzenes where the C=B bond is not carbonyl compound as above but the C_6H_6 ring, here also the same mechanism is operated.







Mass spectral characteristics:

(1) As the carbon skeleton becomes highly branched the intensity of molecular ion peak decrease.

e.g.

1.

Butane ⟶ isobutane ⟶ 2,2,4-Trimethyl pentane

2. Octane ⟶ 2,2,4-Trimethyl pentane

(2) Straight chain hydrocarbons undergo fragmentation by breaking C-C bonds resulting in a homologues series of fragmentation products.

E.g. in octane fragment peak due to hexyl ion (85), pentyl ion (71), butyl (57), propyl (43) and ethyl (29) are observed.

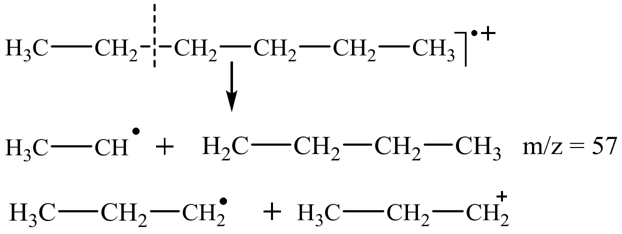
The peaks are most intense in C_2-C_5 range.

(3) They rarely eliminate $-CH_3$ group due to 17-15 are absent.

(4) The peaks at 43 and 57 are usually the base peaks due to the stability of propyl and butyl ions.

(5) In branched alkanes, there is a tendency for the bonds to capture at the branches resulting in the formation of relatively stable secondary and tertiary carbonium ion.

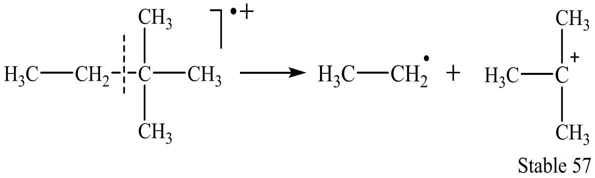
E.g. straight chain alkanes:



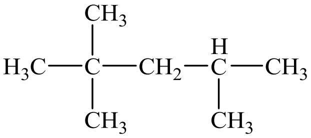
$$[H_3C-CH_2-CH_2-CH_2-CH_2-CH_3]^{\bullet+} \rightarrow H_3C-CH^{\bullet} + H_2C-CH_2-CH_2-CH_3 \quad m/z = 57$$

$$H_3C-CH_2-CH_2^{\bullet} + H_3C-CH_2-CH_2^{+}$$

Branched-chain alkanes;



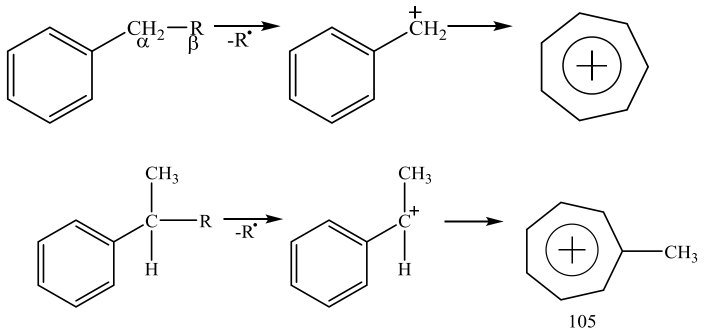
Differentiate octane and Iso-octane:

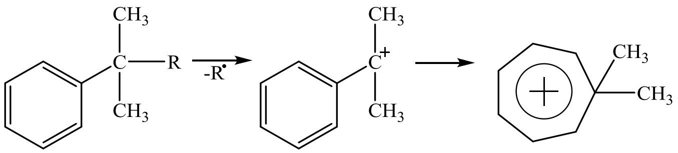
Octane	Iso-octane
$H_3C—(CH_2)_6—CH_3$	
M^+ ion peak at 114, small peaks of low intensity	M^+ ion peak is not obtained
Undergoes fragmentation by breaking C-C bonds resulting in homologues series of fragmentation products i.e. 29 Propyl 43 57 71 85 Hexyl	Cleavage of the C-C bonds of iso-octane at branched C atom is always favoured leading to the formation of secondary and tertiary C atoms as they are more stable hence fragmentation is favoured it forms + butyl carbonium ion 57.

The intensity of each peak decreases with increase in fragment at higher molecule	No effect of molecular weight on intensity
Base peak is observed at 43. i.e. propyl ion	Base peak at 57. i.e. tertbutyl ion
Several C fragments which should appear at 99 can not be observed as their ions are rather stable.	Other peaks at 29,43 are observed remaining are weak.
Other fragments within each cluster correspond to additional losses of one or two H_2 atoms.	No, any special effect.

Aromatic hydrocarbons:

1. They show much stronger molecular ion peaks than those exhibited by alkanes of comparable molecular weight.
2. $M^{\bullet+}$ ion peak is always stronger peak in benzene.
3. In alkyl benzene, the most probable cleavage is at the bond β to the ring. This gives rise to a base peak at m/e = 91 due to the formation of tropylium ion, if substituents are present on α- carbon atom, the base peak will have masses higher than 91 by an increment of 19.
   E.g. substituted tropylium ion.





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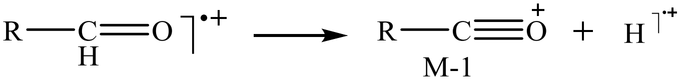
Aldehyde:

1. Aliphatic and aromatic aldehyde display molecular ion peaks. It is also prominent in aromatic aldehyde due to the resonance stabilisation of the molecular ions. In aliphatic aldehydes, its intensity decreases in compounds containing more than 4-carbon atom.

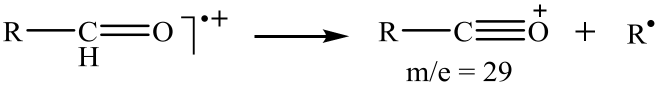
2. M-1 peak is usually as intense as the M^+ peak, it results from the loss of H_2 through cleavage.



$$\left[R-\underset{H}{C}=O\right]^{\bullet+} \longrightarrow R-C\equiv\overset{+}{O} + H^{\bullet+}$$

M-1

3. Strong absorption peak at m/e = 29 due to α-cleavage.

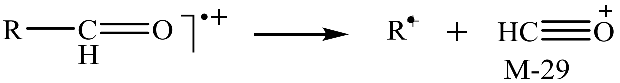


$$\left[R-\underset{H}{C}=O\right]^{\bullet+} \longrightarrow R-C\equiv\overset{+}{O} + R^{\bullet}$$

m/e = 29

Base peak

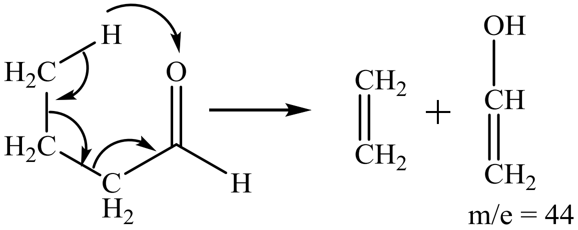
4. It will also give M-29 peak. Sometimes it can be the base peak.



$$\left[R-\underset{H}{C}=O\right]^{\bullet+} \longrightarrow R^{\bullet+} + HC\equiv\overset{+}{O}$$

M-29

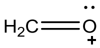
5. Rearrangement occurs if aldehyde contains a γ - H_2 atom to a carbonyl group. This gives rise to a base peak.



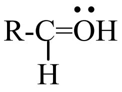
Rearrangement peaks always occur at even m/e value.

Hydroxyl compounds:

1. Molecular ion peak for primary and secondary alcohol is quite small and for tertiary alcohol is undetectable.
2. Cleavage of the C-C bond next to the oxygen atom is of general occurrence. This α-cleavage leads to the formation of stable oxonium ions.
3. Primary alcohols give prominent peak due to

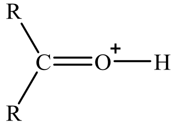

$H_2C=\underset{+}{\ddot{O}}$ (m/e=31)

Secondary alcohols cleavage to give prominent peak due to


$R-\underset{H}{\underset{|}{C}}=\ddot{O}H$

(m/e = 45, 59, 73)

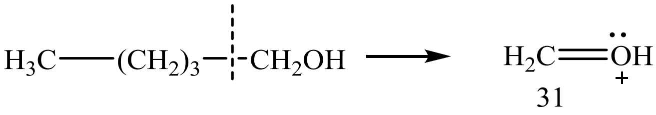
And tertiary alcohol gives



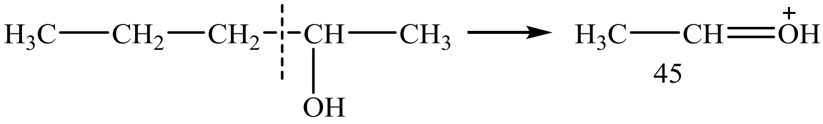
(m/e = 45, 73, 83)

Example:

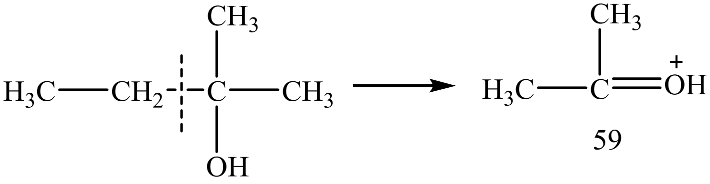
1.



2.



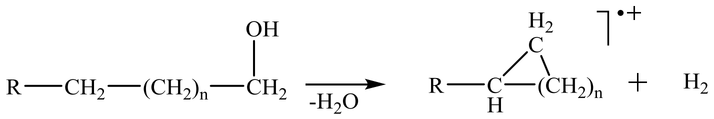
3.



This is a peak for primary alcohol. These peaks are the identification of alcohols.

A distinct and sometimes prominent peak is founded at M-18 from loss of water through a cyclic mechanism.

This peak is noticeable in primary alcohols and intensity decrease in secondary and tertiary alcohol.



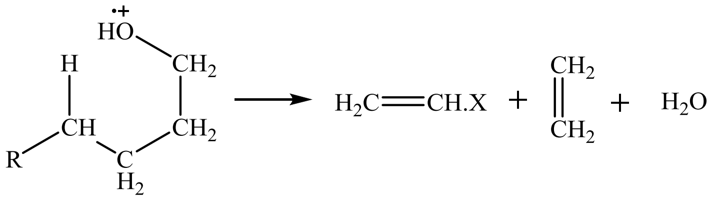
1. pentanol m/e = 70
2. 2- pentanol m/e = 70
3. 2- methyl-2-butanol = 70

Intensity decrease

Longer chain primary alcohols often suffer double elimination.

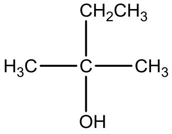
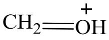
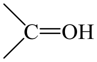
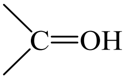
i.e. they lose one molecule of water and one of ethylene simultaneously through a six-membered cyclic mechanism, thus display (M- CH_2O and $CH_2{=}CH_2$).

Peak i.e. M-46 peak
This peak is with very small intensity in secondary and tertiary alcohol.



In isomeric pentanols M-[H_2O and $CH_2{=}CH_2$] peak is obtained at 92, is not in 1-pentanol. It is the most intense peak while in 2-pentanol and 2-butanol peak intensity is very less.

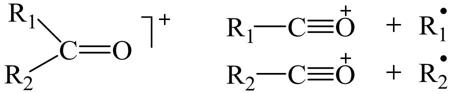
Distinguish Primary, Secondary and Tertiary alcohols:

1-Pentanol	**2-Pentanol**	**2-Methyl-2-butanol**
$CH_3(CH_2)_3$-CH_2OH	CH_3-$(CH_2)_2CHOH$-CH_3	
M^+ peak very weak	Very weak	Not detectable
Oxonium  $CH_2{=}\overset{+}{O}H$ 31	 45	 59

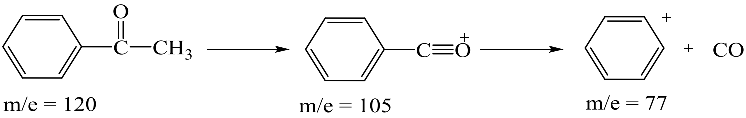
M-[H_2O and $CH_2=CH_2$]	Very weak at 42	Very weak at 42
M-[H_2O + CH_3] 55- intense peak	55- medium	55- medium
M-H_2O Medium at 70	Weak at 70	Weak at 70
M-CH_3 -	Weak at 73	Intense peak at 73

Ketones: It is very similar to aldehyde

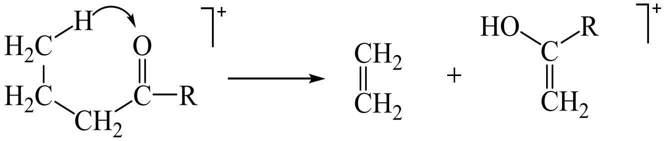
1. The M+ peak is of significant intensity.
2. α-cleavage produce $R-C\equiv\overset{+}{O}$ ion.



43, 59, 71 etc.



Meclafferty rearrangement is common



58, 72, 86 etc.

Detection of molecular formula:

1. Molecules do not occur in isotopically pure form. All atoms except F_2, P, I_2 have heavier isotopes.
2. Isotopic composition of elements is constant.

1H	^{2}H	0.016		
	^{13}C	1.08		
	^{15}N	0.38		
	^{17}O	0.04	^{18}O	0.2
	^{33}S	0.78	^{34}S	4.40
			^{37}Cl	32.5
			^{81}Br	49

Suppose that a compound contains 4 carbon atom, then for every 100ml contain ^{12}C atom about 1.08 molecule contain a ^{13}C atom they will produce 1.08% M+1 peak. ^{2}H atom will make a small contribution to M+1 peak.

Thus M+1, M+2 peaks are obtained in the mass spectrum. Thus as isotopic composition of the elements is the constant relative intensity of the peaks of the ions can be used to determine the molecular formula.

Types of ions:

1. **Molecular ion or Parent ion peak:** when a beam of electrons are bombarded on the molecules, it loses a single electron and forms M^+ ions, it is stable for 10^{-6} seconds and give a curve in the mass spectrum which is known as the parent peak.
2. **Base peak**: when a substance is bombarded with a beam of 70 ev. The molecules lose a single electron and produce M+ ions which give a strong peak in the mass spectrum known as the base peak.

3. **Negative peak**: in addition to positive ions, negative ions may be formed during the bombardment of 70 ev on the sample, but the formation of negative ion is very rare.
4. **Metastable ion**: when a fragment passing through an accelerating region it suffers from further fragmentation is called a metastable ion.
5. **Cation radical**: A part of a positive ion having an odd electron is known as a cation radical.
6. **Fragment ion**: lighter cations formed on fragmentation of molecular ions.

Molecular formula determination:

The molecular formula of an unknown compound can be determined only with the help of mass spectrometry i.e. without elemental analysis.

There are two methods for the determination of molecular formula as follow:

1. **Accurate molecular weight method:**
   - Determine the probable molecular formula on the basis of accurate mass.(Number of formula are possible)
   - Calculate the exact mass of molecular formula derived on the basis of accurate mass.
   - Put both values in the following equation and find out the error limit.
   - If the value is less than 5ppm, consider this formula correct one.

Example: Derive the molecular formula for molecular weight obtained by unit mass is 28

Possible formula related to the unit mass 28 are CO, N_2, CH_2N and C_2H_4
Exact mass of atoms which involved in probable formula are as follow;
^{12}C : 12.0000 ; ^{16}O: 15.9949 ; ^{14}N : 28.0062

So exact mass for CO:27.9949; N_2: 28.0062; CH_2N: 28.0187 and C_2H_4: 28.0312

Calculation for Error limit:

$$\text{Error limit for CO} = \frac{Mcalculated - Mobserved}{Mobserved} \times 10^6$$

$$= \frac{27.9949 - 28.0}{28} \times 10^6$$

$$= -182.142 < 5 \text{ ppm}$$

Same calculation for other derived formula are as follow

N_2 = 221.428, CH_2N = 667.857 and C_2H_4 = 1114.2827 all shows higher value

From the above calculation, The correct formula is CO.

Example: Derive the molecular formula for 100.0637 mass

The possible formula are

Types of atom	Number of atoms	Formula
Carbon & Hydrogen	-	C_8H_{14}, C_7H_{16}

Carbon Hydrogen & Oxygen	No. of Oxygen: one No. of Oxygen: Two No. of Oxygen: Three No. of Oxygen: Four	C_7O, $C_6H_{12}O$ $C_5H_8O_2$ $C_4H_4O_3$ C_3O_4
Carbon, Hydrogen and Nitrogen	No. of Nitrogen atom: Two No. of Nitrogen atom: Four No of Nitrogen atom: Six	C_6N_2, $C_5H_{12}N_2$ $C_3H_8N_4$ CH_4N_6
Carbon, Hydrogen, Oxygen and Nitrogen	No of Nitrogen atom: Two No of Nitrogen atom: Four	$C_4H_8ON_2$, $C_3H_4O_2N_2$ $C_2O_5N_2$ $C_2H_4ON_4$, CO_2N_4

By the application of Nitrogen rule to find out the correct formula from all above-derived formula.

As per the Nitrogen rule, an odd number of molecular weight contain an odd number of nitrogen and even number of molecular weight contain odd valency element or no nitrogen atom.

From the above discussion the correct formula with accurate mass are as under:

Formula	Accurate Mass	Formula	Accurate Mass
C_8H_4	11.03130	C_6N_2	100.006148
C_7H_{16}	11.12510	$C_5H_{12}N_2$	100.100048
C_3O	99.99494	$C_3H_8N_4$	100.07489
$C_6H_{12}O$	100.0887	$C_4H_8ON_2$	100.0637

$C_5H_8O_2$	100.05222	$C_3H_4O_2N_2$	100.07331
$C_4H_4O_3$	100.01612	$C_2O_3N_2$	99.99097
C_3O_4	99.97976	$C_2H_4ON_4$	100.03848
		CO_2N_4	100.002112

Calculation for finding exact formula

Calculation for Error limit:

$$\text{Error limit for CO} = \frac{Mcalculated - Mobserved}{Mobserved} \text{ x } 10^6$$

$$= \frac{100.0637 - 100.0635}{100.0637} \text{ x } 10^6$$

$$= 1.9987 < 5 \text{ ppm}$$

From the above calculation, correct formula is $C_4H_8O_2$

A simple method to determine the molecular formula:

Assume that $C_PH_QN_RO_T$

Observed molecular weight + 100.0635

$$Q = \frac{Non\ integral\ Mass + (0.0051\ X\ T) - (0.0031\ X\ R)}{0.0078}$$

Non integral mass from weight = 0.0635

Assume T and R = 1

$$Q = \frac{0.0635 + 0.0051 - 0.0031}{0.0078}$$

= 8.3974 which is not valid

Assume R= 2 and T =1

$$Q = \frac{0.0635 + 0.0051 - 0.0062}{0.0078}$$

$= 8$

Formula $C_PH_QN_RO_T$

Weight $= Weight = 12p + 8 + 28 + 16 = 100$

$$12P = 100 - 52$$

$$= 48$$

$$P = 4$$

$\therefore$ Formula is $C_4H_8N_2O$

(2) Isotope abundance method:

Generally, abundance ratio is constant for the elements which are available in nature and it is always obtained as a mixture. We can classify the elements in three group.

Group elements: H, F, P I (Abundance 99.9 %)

A + 1 group elements : C, N, Si
A + 2 group elements: O, S, Cl, Br
For group (A + 1) 13C abundance is only 1.08 %
So, $Maximum\ no. of\ Carbon = \frac{(M+1\%)}{1.1}$
For A+2 group elements Si, S, Cl, Br (Except Oxygen) are easier to identify from the intensity ratio peak.

The relative height of M, M+2, M+4 give the idea about a number of (A+2) elements. Such as Bromine atom present in the molecule so it shows the M: M+2 ratio is

51:49(≈1:1), the presence of more than one bromine atoms still change the intensity ratio of peak areas follow:

No. of Bromine atom	M: M+2: M+4: M+6
1	1:1
2	1:2:1
3	1:3:3:1
4	1:4:6:4:1

For the calculation of Oxygen atom contribution of all other (A+2) group elements and substrate this value from observed value and divided by 0.2.

The A group element such as F, P, I contribute to the M peak and hence the intensity of the M+1 and M+2 peak will be lower than M^+ peak.

Example: Derive the molecular formula from the given mass spectral data:

m/z = 142, 143

Abundance =100, 1.14

From the obtained data, It indicates that 142 is M^+ peak and 143 is M^{+1} peak.

The maximum no of carbon(c) = 1.14/1.1

= 1, i.e 12 mass unit.

$\therefore$142-12=130 which represents the hydrogen and other elements of A group.

130 = A group elements + Hydrogen
= I + Hydrogen
= 127 + Hydrogen
3 = Hydrogen so molecular formula is CH_3I

Example: Derive the molecular formula from the given mass data:

m/z	= 69	70	71
Abundance	=100	1.1	-

Therefore M+ = 69, M+1 =70 , M+2 = 71

Maximum no of Carbon(C) = 1.1/1.1 = 1 =12 mass unit

Therefore 69-12 =57 which is represents the number of Hydrogen and other elements of A group.

But in A group atomic weight of I =127 which higher than the value, so it is not possible and for phosphorus two higher value as well as for one phosphorus and other atom is a number of hydrogen is not possible.

From the above interpretation, Fluorine atom fitted very well; 3F= 57

Molecular formula is $CF3^+$

General equation to calculate % of (M+1) and (M+2) for given molecular weight:

Assume the molecular formula is $C_PH_QN_RO_TS_U$

$$\%(M+1) = 1.09P + 0.015Q + 0.037R + 0.8U + 0.037T$$

$$\%(M+2) = 0.0069P(P-1) + 0.0002PQ + 0.20T + 0.004PR + 4.9U$$

Example: Determine the molecular formula for the given mass data:

m/z	94	95	96	97
Relative abundance	100	6.1	96	1.1

Solution: M^+ peak :94 ; M+1 : 95 : M+2 : 96 so on

Relative abundance for M: M+2 = 100;96(≈1:1) which indicates the presence of Bromine,

$\therefore$94-79 =15 which is related to Carbon and hydrogen.

So the molecular formula is CH_3Br; M+1 peak intensity is high due to the contribution of fragment CH_2-Br i.e $^{13}C^1H_3Br$ = 97, means it is the M+2 peak of the CH_2-Br fragment and M+3 =97 which are only contribution of ^{13}C.

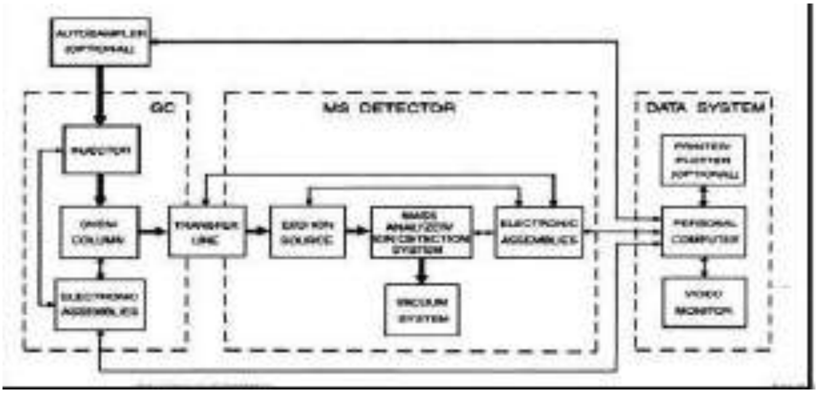
Hyphenated technique related to Mass spectrometry.

The combination of Chromatograph with Mass spectrometer i.e. GC-MS/LC-MS is a powerful analytical technique that combines the resolving power of chromatography with the detection specificity of mass spectrometry. It is a hyphenated technique in which Chromatograph attached with mass spectrometer by creating interface between this two instrument to resolve the problem arise due to the combination of these instruments which results in maximum optimisation of instruments utility.

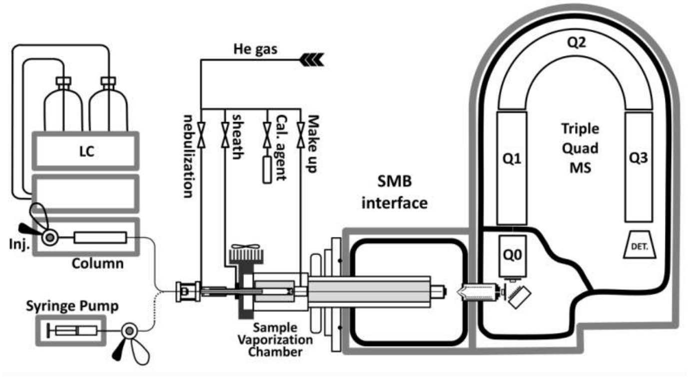
Chromatography – Mass spectrometry combination (GC-MS/LC-MS):

GC-MS/LC-MS is a powerful analytical technique that combines the resolving power of chromatography with the detection specificity of mass spectrometry. It is a hyphenated technique in which chromatography instrument attached with mass spectrometer by creating an interface between these two instruments, which results in maximum optimisation of instrument utility.

Schematic diagram of GC-MS:



Schematic diagram of LC-MS:



Chapter-6

Numerical

Spectroscopic Numerical

All spectroscopic techniques have been own their significant to determine the structure of unknown compounds.

This chapter deals with the use of different spectroscopic data; we shall determine the structure of unknown compounds. Some important point to determine the structure of unknown compounds.

1. Determination of Double bond equivalent

   From the given molecular Formulla of any organic compound; we are able to determine the degree of unsaturation.

   $DBE = \frac{(2a+2)-(b-d)}{2}$ a= No. of carbon,

   b= No. of monovalent ion

   d = No. of Trivalent ion

   For Example: C_9H_7N

$$DBE = \frac{(2a+2)-(b-d)}{2}$$

$$DBE = \frac{(2*9+2)-(7-1)}{2}$$

$$DBE = \frac{20-6}{2} = \frac{14}{2}$$

$$DBE = 7$$

No. of DBE	Remarks
0	Saturated compound
1	One double bond or one cycle
2	Two double bond or Two cycle
	One double bond & one cycle
	Two cycle
	One triple one

3	Three double bond or three cycle
	Two double bond & one cycle
	One double bond & two cycle
	One Triple bond & one cycle

One double bond is equivalent to one double bond.

2. UV spectral data: UV spectral Data always give the information regarding the degree of unsaturation.

   From the λmax and εmax indicates that the number of π bon d and types of transitions.

   - λmax > 215 : Absence of conjugated π bond.
   - εmax> 1000:π→ π*
   - εmax < 1000:n→π*
   -

3. Mass spectral data: In mass spectrometry;

   - M^+ ion give the information regarding Molecular weight
   - Fragment Pattern give the information regarding the structure.
   - Nitrogen rule: Even number of molecular weight ⇒ Even number of nitrogen or absence of Nitrogen
     - : Odd number of molecular weight ⇒ Odd no of Nitrogen.

   Pattern of the ion peak give the idea regarding abundance ratio:

   Example Br^{79} and Br^{81}: Ion peak obtained as M^+ and M^{+2} with intensity 49:51

4. IR spectral Information:

The position of the band, band intensity and type of band, pattern of overtone are important to determine the functional group and exact position of functional group in aromatic nucleus.

5. NMR spectral information:

In ^{1}HNMR position of signal, Multiplicity of signal and coupling constant value are important to assign the structure.

^{13}CNMR data are important to determine the hybridization as well as chemical environment of Carbon structure.

Solved example

(1) C_3H_6O :

UV : No maxima above 210 nm

IR: 2941, 2847,1458,1100 cm^{-1}

NMR(δppm): 4.74(Triplet,29.4 square),2.75(quintet,14.6 square)

Solution: Calculation for DBE$DBE = \frac{(2a+2)(b-d)}{2}$

$$= (2\,x\,3 + 2) - \frac{6-0}{2}$$

$$= \frac{8-6}{2}$$

$$= 1$$

DBE= 1 Means one double bond or one cycle present.

UV: No maxima above 210 nm, Hence compound is saturated.

IR: interpretation

2941: Asymmetrical stretching of alkane.

2847: Symmetrical stretching of alkane

1458: banding of alkane.

110:C-O-C Stretching

From the UV, IR and DBE it is concluded that compound may be cyclic ether.

NMR Interpretation:

In the given information, the signal intensity given in the form of square,

First to find out no of equivalent proton related to each signal:

Total no of square = Total no of proton

29.4 + 14.6 = 06 proton

44= 06 proton

So 29.4 =? So, 44/6 = 7.39 square i.e 1 proton = 7.39 square

For signal one 29.4/7.39= 3.978 = 4proton

For signal two 14.6/7.39=1.975 = 2 proton

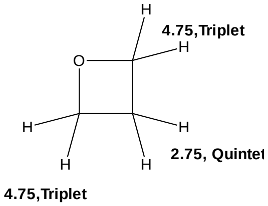
Signal one at 4.75 as a triplet indicates that two equivalent –CH_2 group with 2H as a neighboring protons attached with electronegative atom;

i.e. –**CH_2-O-CH_2**

Signal -2 at 2.75 indicates that –CH_2 group with 4H as a neighboring group

i.e. –CH_2-**CH_2**-CH_2-

From the all above discussion, the structure of the compounds is as below:



(2) C_4H_8O

IR: 2975, 1715, 1470 & 1380 cm^{-1}

NMR: 2.4 (2H, Quatret); 2.09 (3H, Singlet), 1.04 (3H Triplet)

Answer:

Calculation for $DBE = \frac{(2a+2)(b-d)}{2}$

$$= (2\ x\ 4 + 2) - \frac{8-0}{2}$$

$$= \frac{10-8}{2}$$

$$= 1$$

Hence compound may be cyclic or containing one double bond

IR 2975: C-H str of alkane

1715: $>C=O$ str

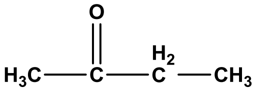
1470: $-CH_2$ banding of alkane

1380: $-CH_3$ banding of alkane

NMR: 1.04 (3H, Quatret) and 2.4 (2H,quartet) are indicates the presence of $–CH_2CH_3$ group.

2.09 (3H, Singlet) indicates that the presence of $–COCH_3$ group.

From the above solution; the structure of the given data is



$H_3C-C(=O)-CH_2-CH_3$

butan-2-one

(3) $C_{14}H_{10}O_2$

IR: 3050, 1680, 1600, 1580, 1450, 700-749 cm^{-1}

NMR: 7.5 to 7.9 5H Multiplate

Mass: 210 (M$^+$) [105] b.p: 77

Answer:

Calculation for $DBE = \frac{(2a+2)(b-d)}{2}$

$$= (2\ x\ 14 + 2) - \frac{10 - 0}{2}$$

$$= \frac{30 - 10}{2}$$

$$= 10$$

Hence Two aromatic ring may be present.

IR:

3050: C-H str. of aromatic ring

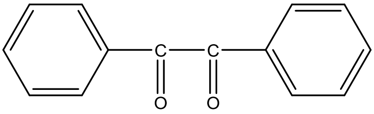
1680: Carbonyl stretching with conjugation

$\left.\begin{array}{l}1600:\\1580:\\1450:\end{array}\right\}$ C=C ring skeleton of aromatic ring

700-749: C-H str. of o.o.p. for monosubstituted phenyl ring.

NMR: 7.5 to 7.5 5H Multiplate indicates that monosubstituted phenyl ring as a dimmer group.

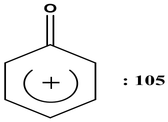
From the above interpretation; structure of the compound is



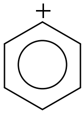
This is supported by Mass spectral data:

210(M$^+$) indicate molecular weight

105 (B.P.) due to Tropalone→



77 indicates



(4) $C_9H_{10}O$

IR: 3030, 2985, 1720, 1500, 1400, 1320, 1380, 1150, 1020

Chemical shift	Multiplicity	No. of Proton
2.10	Singlet	3H
3.6	Singlet	2H
7.0-7.4	Multiplate	5H

Answer:

Calculation for $DBE = \frac{(2a+2)(b-d)}{2}$

$$= (2 x 9 + 2) - \frac{10 - 0}{2}$$

$$= \frac{20 - 10}{2}$$

$$= 5$$

DBE = 5 indicates that compound possess aromatic ring with one extra double bond.

IR

3030: C-H str of aromatic ring

2985: C-H str of alkane

1720: Carbonyl str. of carbonyl group

$\left.\begin{array}{l}1500:\\1400:\end{array}\right\}$ C=C str. of Aromatic ring

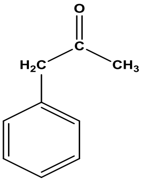
$\left.\begin{array}{l}1380:\\1320:\end{array}\right\}$ C-H of alkakne

1150:⎤
1020:⎦ C-O str. of carbonyl group

NMR:

- 2.10, Singlet of 3H indicates that methyl group attached with electron withdrawing group:
- 3.6, Singlet of 2H indicates that $-CH_2$ group shows mesomeric effect of electron donating & electron withdrawing group
- 7.0-7.4 Multiplate of 5H indicates the mono substituted aromatic ring.

From the above information the structure of the unknown compound is:



(5) C_8H_8O

UV: 251 λ_{max} $\varepsilon = 15{,}000$

258 λ_{max} $\varepsilon = 12{,}500$

IR: 3035, 2850, 2750, 2800, 1700, 145, 1390, 1310, 1215, 815 cm^{-1}

NMR:

Chemical Shift in δ ppm	Multiplicity	No. of Proton	Coupling constant
2.25	Singlet	3H	-
6.2-7.2	Doublet	2H	8.24 Hz
7.55 – 7.2	Doublet	2H	8.24 Hz
9.0	Singlet	1H	-

UV: 251 λ_{max} $\varepsilon = 15,000$
258 λ_{max} $\varepsilon = 12,500$

UV data indicates that compound is an aromatic nature with highly conjugation.

Calculation for $DBE = \frac{(2a+2)(b-d)}{2}$

$$= (2\,x\,8 + 2) - \frac{8-0}{2}$$

$$= \frac{18-8}{2}$$

$$= 5$$

It means compound contain one phenyl ring along with one extra double bond.

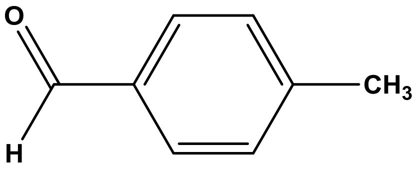
IR:

30325: C-H str. of aromatic
2850,2750: C-H str. of aldehyde
2800: C-H str. of alkane
1700: $>C=O$ str. of aldehyde
1450; C=C str. of aromatic
1390: C-H banding of alkane
1310: C-H banding of alkane
1215: C-O str. of carbonyl group
815: oop of C-H str. of aromatic (p- substitution)

NMR:

- 2.25 δppm singlet for three protons indicates that $-CH_3$ group attached with $>C=O$ group.
- 6.2 to 7.2 2H doublet with 8.24 Hz indicates that aromatic ring with ortho coupling.
- 7.55 to 7.65 2H doublet with 8.24 Hz indicates that aromatic proton with ortho coupling formyl gp as an adjacent carbon atom.

From the above interpretation the structure of the unknown compound as fellow:



Solve the example:

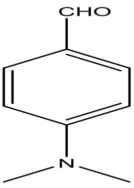
(1) $C_9H_{11}NO$

UV: 235,336 $\rightarrow \lambda_{max}$, 8650,28300 ($\varepsilon$)

IR: 3020, 2960, 2820, 2740, 1600, 1567, 1528, 1695, 820

NMR: 2.98 (6H, Singlet); 6.65 (2H doublet), 7.7 (2H,doublet) 9.72 (1H, Singlet)

Answer:

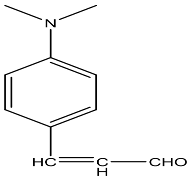


(2) $C_{11}H_{13}NO$

IR: 3010, 2960, 2820, 2740, 1600, 1567, 1528, 1695, 820

NMR: 3.1 (singlet,6H); 6.6 (doublet, 1H), 6.8(dd,1H), 7.2-7.6(4H, Multiplate),9.7 (1H,doublet)

Answer:



(3) $C_6H_{10}O_3$

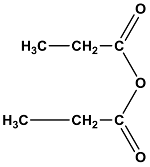
UV: 270

IR: 2985, 2950, 1460, 1380, 1820, 1750, 1050

NMR: 1.1 (3H,Triplet,7 Hz);2.4 (2H, Quatret, 7 Hz)

Mass: 29,37(B.P.) 74, 73, 150 (M^+)

Answer:



(4) $C_9H_{11}NO_2$

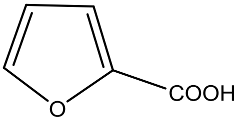
UV: 248(λ_{max}), (ε=25,800)

IR: 3500-2400, 1690, 1585, 1475, 1420, 1400

NMR: 7.3 (M, 1H); 6.6 (M, 1H), 7.8(M, 1H), 10.5 (s, 1H)

Mass: 18, 37, 38, 39, 55, 99, 112, 113, 114

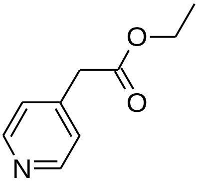
Answer:



(5) $C_9H_{11}NO_2$

IR:3010, 2965, 2872, 1620, 1500, 1600, 1375, 1050, 1740

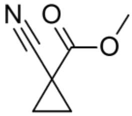
NMR(δppm):1.22(3H,Triplet,7Hz),3.25(2H,Singlet),4.1(2H, quartet,7Hz),6.92-.75(3H,multiplate),8.48(1H,Doublet,5Hz)



(6) $C_6H_7NO_2$

IR:2240, 1730

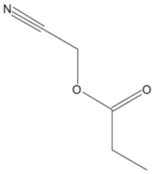
NMR(δppm):2.7(4H,Singlet),
3.8(3H,Singlet)



(7) $C_5H_7NO_2$

IR: 3000, 2280,1700

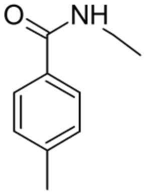
NMR(δppm):4.2(2H,Quatret),
3.55(2H,Singlet),1.2(3H, Triplet)



(8) $C_9H_{11}NO$

IR: 3010,1680,2975

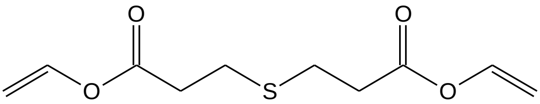
NMR(δppm):2.8(3H,Singlet),
2.9(3H,Singlet),
6.7-7.7(4H,Multiplate),
9.7(1H,Singlet)



(9) $C_{10}H_{14}O_4S$

IR: 3090,1750,1650,1150,949,878

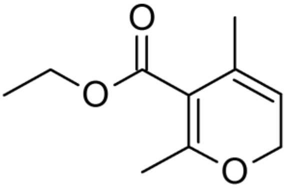
NMR(τppm):2.78(1H, Multiplate, 7Hz, 14Hz), 5.19(1H, Multiplate, 7Hz, 2Hz), 7.3(4H, Multiplate)



(10) $C_{10}H_{12}O_4$

IR: 3020, 2956, 1745, 1690, 1650,1575, 1250, 1050, 938,

NMR(τppm):4.13(1H, Singlet), 7.63(3H, Singlet), 5.70(2H, quartet),8.64(3H,Triplet)



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