

Unit-5:-

Spectroscopic techniques & Applications:-

General features of absorption of spectroscopy:-

*Spectroscopy :- *

Spectroscopy is the study of interaction of electromagnetic radiation with matter (substance).

→ In general electromagnetic radiation of different lengths absorbed are measured with the help of a spectrometre.

→ Changes in absorption are recorded against wavelength, the graph obtained contains different absorption bands this graph is called absorption spectrum, this is useful to know the structure of the compound.

→ There is so many spectroscopy are present for knowing the different structures of the compounds.

They are :-

(i) UV-visible spectroscopy :- In this spectroscopy radiation absorbed in the range of ~~200 nm~~ 200 nm - 800 nm. In this spectroscopy the spectrum is obtained by the changes in electronic energy levels. It is useful to detect the conjugation [double bonds, triple bonds].

(ii) IR Spectroscopy :- In this spectroscopy radiations absorbed in $12,500 \text{ cm}^{-1}$ - 500 cm^{-1} , this radiation can

bring about changes in vibrational and rotational energy levels of molecules.

NMR Spectroscopy :-

In this spectroscopy, the electromagnetic radiations of range 60-300 MHz frequency are used; the sample which is analysed is placed at in a varying magnetic field. It is useful to determine the structure of the molecule.

Spectrophotometer :-

A spectrophotometer is an instrument used to study the absorption of light by substances. It consists of a spectrometer and photometer. Spectrometer resolves polychromatic light into light of different wave lengths. Photometer detects the transmitted light and gives absorbance.

Electromagnetic Spectrum :-

Electromagnetic radiation extending from cosmic rays to radio waves are a part of an electromagnetic spectrum. It consists of different electromagnetic radiations according to their wave lengths; (or) their frequencies. It is known as the complete electromagnetic spectrum.

Logarithmic scale has been adopted to represent the electromagnetic spectrum gives the diagrammatic representation.

* Different types of Spectroscopic techniques :- *

1) Atomic Spectroscopy :-

Deals with interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state called ground state.

Mono atomic substances existing in gaseous state absorb electromagnetic radiation resulting in transition of electrons from ground level to excited level.

$$\Delta E = h\nu$$

ΔE = difference between two energy levels.

ν = frequency of photons.

h = planks constant = 1.65×10^{-27} erg·sec.

2) Molecular Spectroscopy :-

Deals with interactions of the electromagnetic radiation with molecules; which results transitions between the rotation and vibrational energy levels and electronic transitions.

Molecular spectra ~~external~~ extended from cosmic rays

to radio waves. Different types of spectra given by molecular species.

(i) Electronic spectra.

(ii) UV spectra.

(iii) NMR spectra.

(iv) Raman spectra.

(v) Mass bover spectra.

→ The absorption or emission process occurs through out the electromagnetic spectrum ranging from γ (gamma to radio region (NMR)).

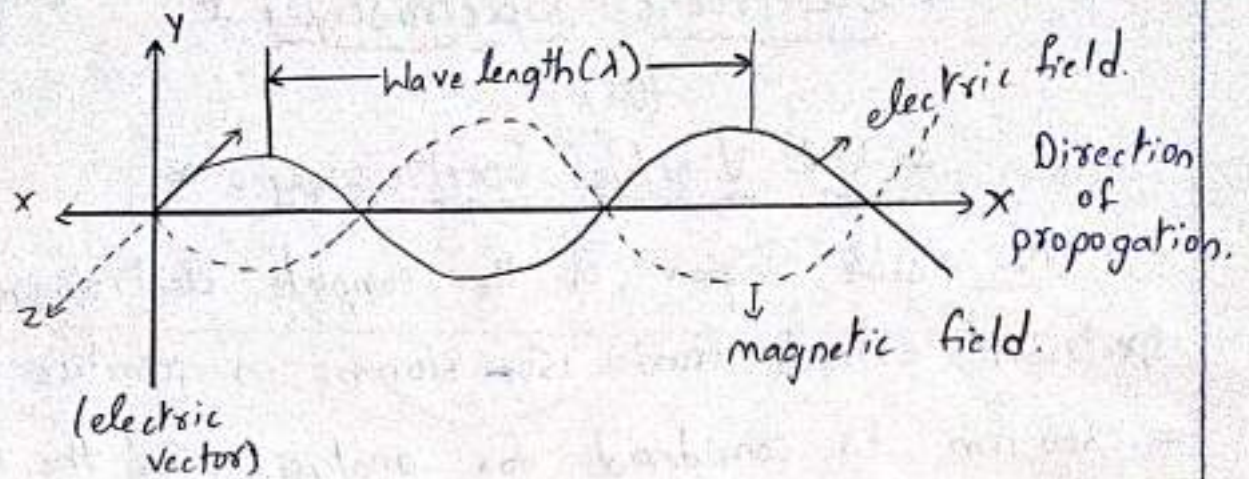
→ The way in which the measurement of radiation with matter.

The radiation of frequency emitted or absorb is carried out experimentally and the energy levels.

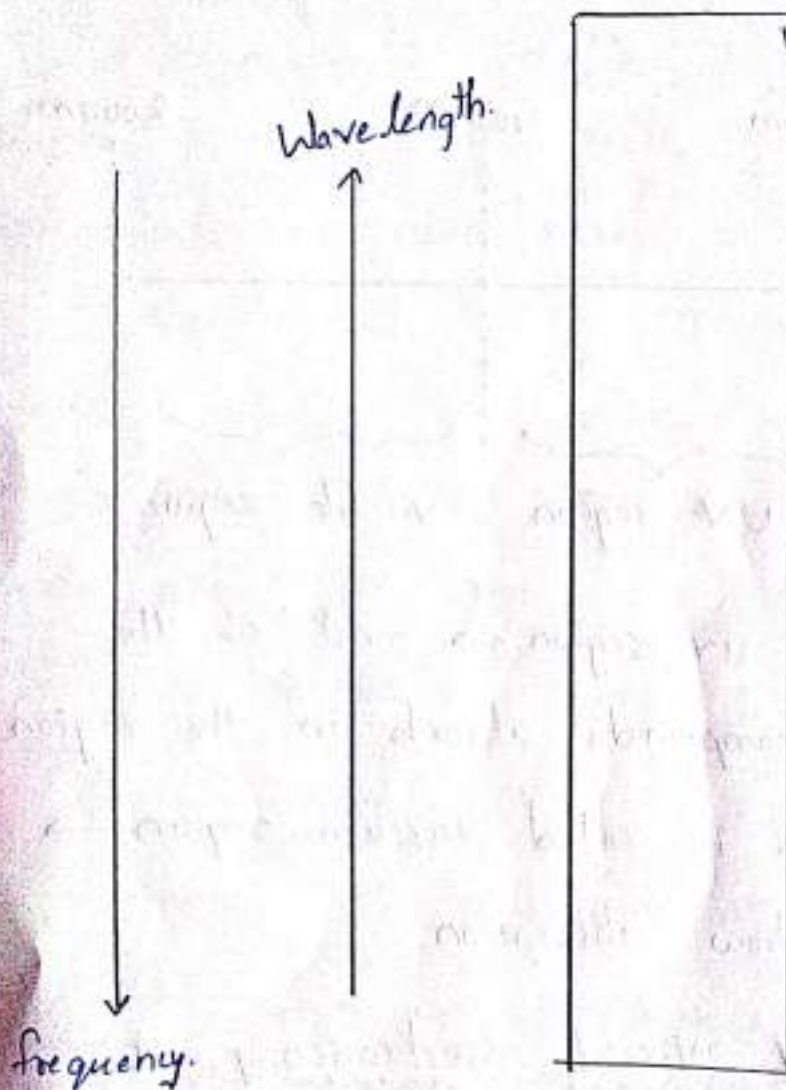
This phenomenon is known as 'Spectroscopy'.

The electromagnetic spectrum gives the diagrammatic representation

→ It represents the electromagnetic radiation moving along the x-axis, the electric field varies in the direction y-axis and the corresponding magnetic field varies in the direction of z-axis



Representation of electromagnetic wave (spectrum).



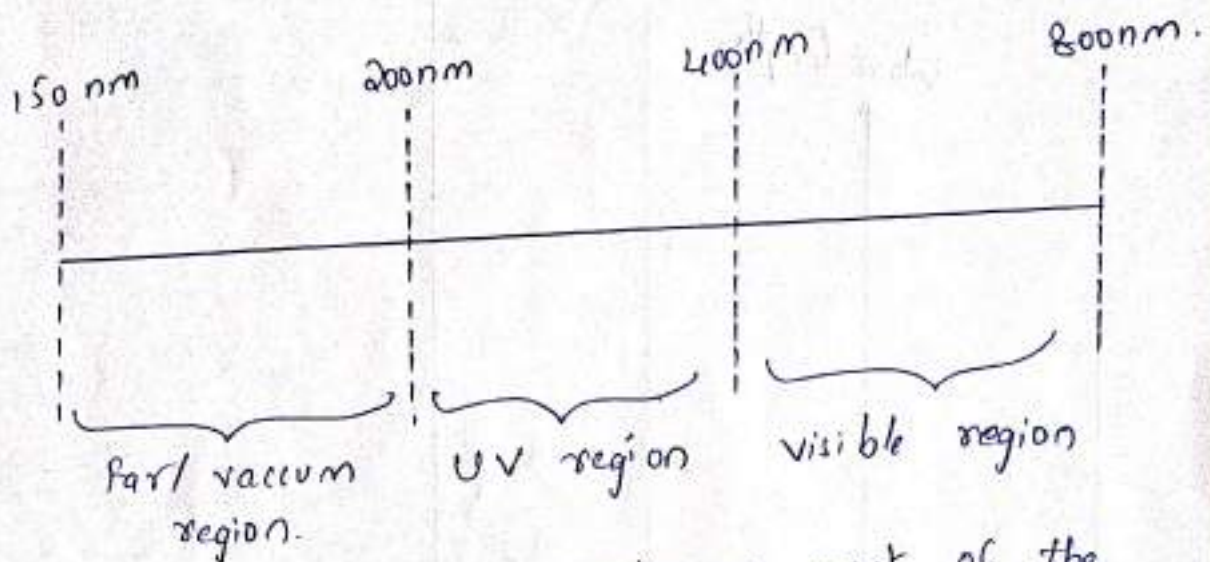
The electromagnetic spectrum.

* Electronic Spectroscopy *

(OR)

* UV-Visible Spectroscopy :- *

UV-visible region of the complete electromagnetic spectrum extends from 150-800 nm; in practice 200 to 800 nm is considered for analysis. In the region below 200 nm oxygen and nitrogen present in air absorb strongly.



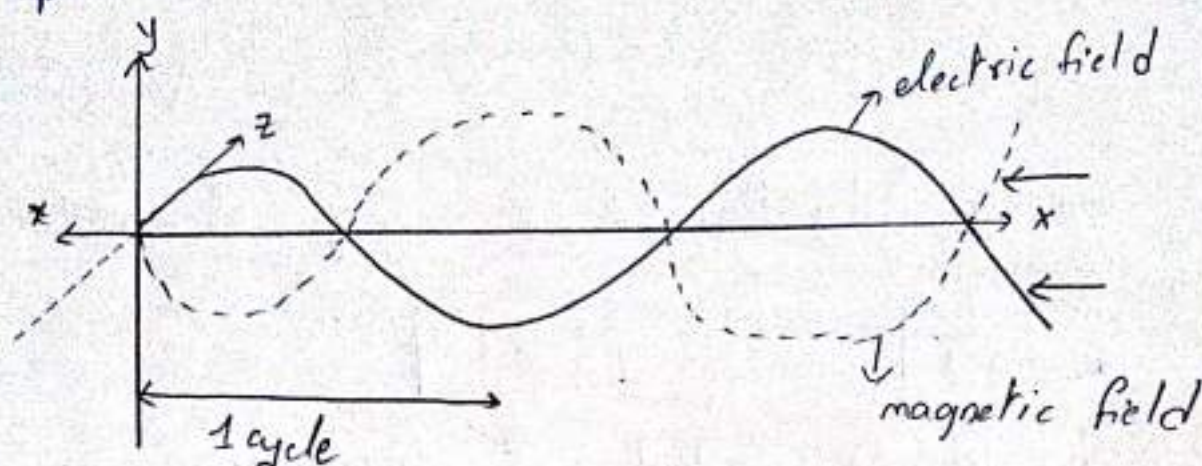
→ 200-380 near UV region → most of the unsaturated organic compounds absorb in the region.

→ Below 200 nm is called vacuum region → Saturated compounds show absorption.

* Theory of UV-Visible Spectroscopy :- *

According to quantum mechanics, electro-

magnetic radiation has dual nature, that of wave and particle.



Wave nature :-

Electromagnetic radiation of a wave with electric and magnetic fields which are mutually perpendicular to each other.

Wave length (λ) or frequency (ν)

$\rightarrow \lambda$ = the distance between two successive crests (or) troughs. It is expressed in meters (m), micrometer (μm), \AA , nm.

Wave number = $\bar{\nu}$

$$\bar{\nu} = \frac{1}{\lambda}$$

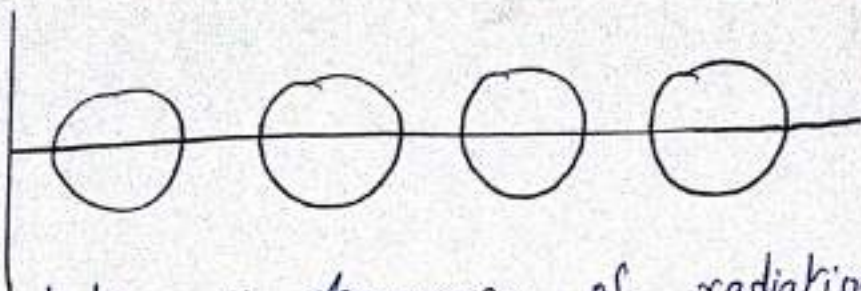
$$\bar{\nu} = \text{cm}^{-1}$$

Frequency ν = cycles/sec (or) hertz (Hz).

Particle (or) photon nature :-

Electronic radiation is treated as a spectrum of discrete particles or energy packets called

photons.



Energy radiation \propto frequency of radiation.

$$E = \frac{hc}{\lambda}$$

$$\text{or } E \propto h\nu$$

h = plank's constant; ν = frequency;

c = velocity of light.

* Principle of UV-visible spectroscopy :- *

UV-visible spectra arises due to the absorption of ultra-violet (UV) or visible radiation by the sample resulting in electronic transition within the molecule or ion; the relationship between energy absorbed in an electronic transition (E), frequency (ν), wavelength (λ) and wave number ($\bar{\nu}$) of radiation producing the transition is

$$\Delta E = h\nu = \frac{hc}{\lambda} = h\bar{\nu}c$$

h = plank's constant ; c = velocity of light.

ΔE = energy absorbed during electronic transition in a molecular or ion from lower energy state (E_1) or ground state, higher energy state (E_2) excited state.

Therefore the energy absorbed is given by

$$\Delta E = E_2 - E_1 = h\nu$$

The wave length corresponding to such transition is given by

$$\lambda = \frac{hc}{\Delta E}$$

* Electronic Spectroscopy (UV-Visible) :- *

The spectroscopy in which electronic transitions takes between electronic states by the absorption of electromagnetic radiation. In this spectroscopy UV-electromagnetic radiations are used. These radiations are suitable for electronic transitions.

Electronic spectroscopy is to find out the conjugation i.e., presence of double or triple bonds in the given molecules.

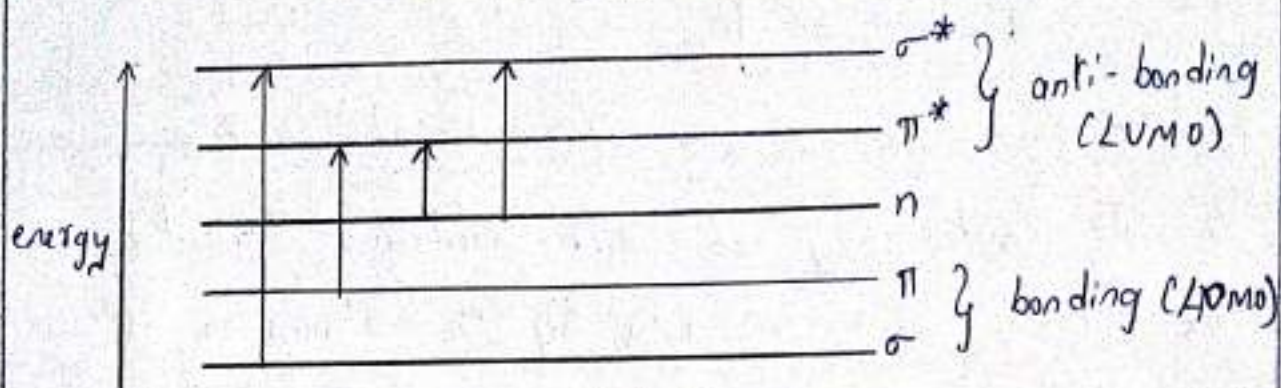
* Types Of Electronic transitions :- *

→ Transitions means transfer i.e., an electron will move or transfers from ground state molecular orbital to an excited state molecular orbitals are called electron transitions.

→ Electronic transitions between the ground state and excited states (when a compound is subjected to E.M.R in UV and visible region radiation is absorbed.)

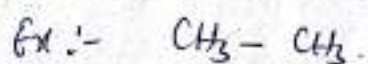
→ Important electronic spectroscopy because there are follows the selection rules of electronic spectroscopy. They are

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



Different possible transitions.

(i) $\sigma \rightarrow \sigma^*$:- These are occur's from lower energy bonding ' σ ' molecular orbitals to higher energy anti-bonding ' σ^* ' molecular orbitals. Generally, these are possible in alkanes. Because these compounds having single bonds only. These transitions required high energy.



(ii) $\pi \rightarrow \pi^*$:- These occurs from lower energy bonding ' π ' molecular orbitals to anti-bonding ' π^* ' molecular orbitals. These are ~~are~~ occurred in unsaturated compounds and the compounds containing double bonds, the absorption band corresponding to transitions in conjugated system is called 'K band'.

Ex: Alkenes, Carbonyl compounds, aromatic compounds.

(iii) $n \rightarrow \pi^*$:- the transitions between non-bonding (n) electrons and anti-bonding π^* molecular orbitals are called as $n \rightarrow \pi^*$ electronic transitions. These are occurs in the compounds containing hetero atoms having at least one lone pair of electrons; is called 'R band'.

Ex: Carbonyl compounds.

(iv) $n \rightarrow \sigma^*$:- These electronic transitions are occurs from non-bonding electrons to higher energy anti-bonding σ^* molecular orbitals. These transitions occurs in the compounds containing hetero atoms having atleast one pair of electrons. (hydro bonding sensitive)

Ex: $\text{CH}_3 - \ddot{\text{O}}\text{H}$, $(\text{CH}_3)_3\text{N}$ etc

* Selection rules for Electronic Spectroscopy :- *

All possible transitions are not allowed, there are certain selection rules the quantum theory imposes on electronic transitions to determine which are allowed and which are forbidden.

The position of absorption band and its intensity is governed by the following selection rules.

1) Energy requirement:-

The energy is required for the transition is

$$\boxed{\lambda = \frac{hc}{\Delta E}} \quad \text{or} \quad \boxed{\Delta E = \frac{hc}{\lambda}} \quad \text{or} \quad \boxed{\Delta E = h\nu}$$

The position of absorption band corresponding to the wave length radiation.

2) Probability interactions:-

The probability interactions between radiant energy and absorbing system.

probability transition $E_{\text{max}} > 10^4 \rightarrow$ allowed transition

probability transition $E_{\text{max}} < 10^3 \rightarrow$ not allowed
(or)
forbidden.

3) Spin Selection rule:-

Electronic transitions takes place between states of same spin multiplicity.

(i.e.) singlet-singlet, triplet-triplet.

4) Symmetry of ground states and excited states:-

Electronic transitions Takes place between ground and excited states. Wave functions can't be anti-symmetric, they must be symmetric. (Gerade)

(Ungerade)

gerade \rightarrow gerade is forbidden.
ungerade \rightarrow gerade is allowed.
ungerade \rightarrow ungerade is forbidden.

5) Angular momentum rule:-

Transitions moment integral must be non-zero
 \rightarrow Electronic transitions takes place by absorption of radiations.

6) One electron transition is allowed:-

The transitions of 1 electron from lower energy state to higher state by the absorption of UV (or) visible radiation gives more intensive band.

The transitions 2 or more the electrons are forbidden that gives less intensive band.

The following rules are also considered to selection rules for electronic spectroscopy.

(i) Geometry of the ground state molecular orbital.

(ii) Geometry of the excited state molecular orbital.

* Instrumentation of (UV-Visible) / Electronic Spectroscopy :- *

* Instrumentation :- The following are the important components of UV spectrometer.

(i) Light source function :- It generates a beam of polychromatic radiation. It has high intensity which covers the desired range of wave length, most common radiation hydrogen discharge lamp quartz halogen lamps etc.

(ii) Monochromator function :- Polychromatic radiation beam coming from the light source passes through a monochromator; which separates it into individual wave lengths.

monochromators \rightarrow gratings, colour filters.

(iii) Sample Cell function :- It holds the sample either in form of solution or as quartz cuvettes are used in spectroscopy.

(iv) Detector function :- Transmitted light from sample cell falls on the detector where it converted into electric current.

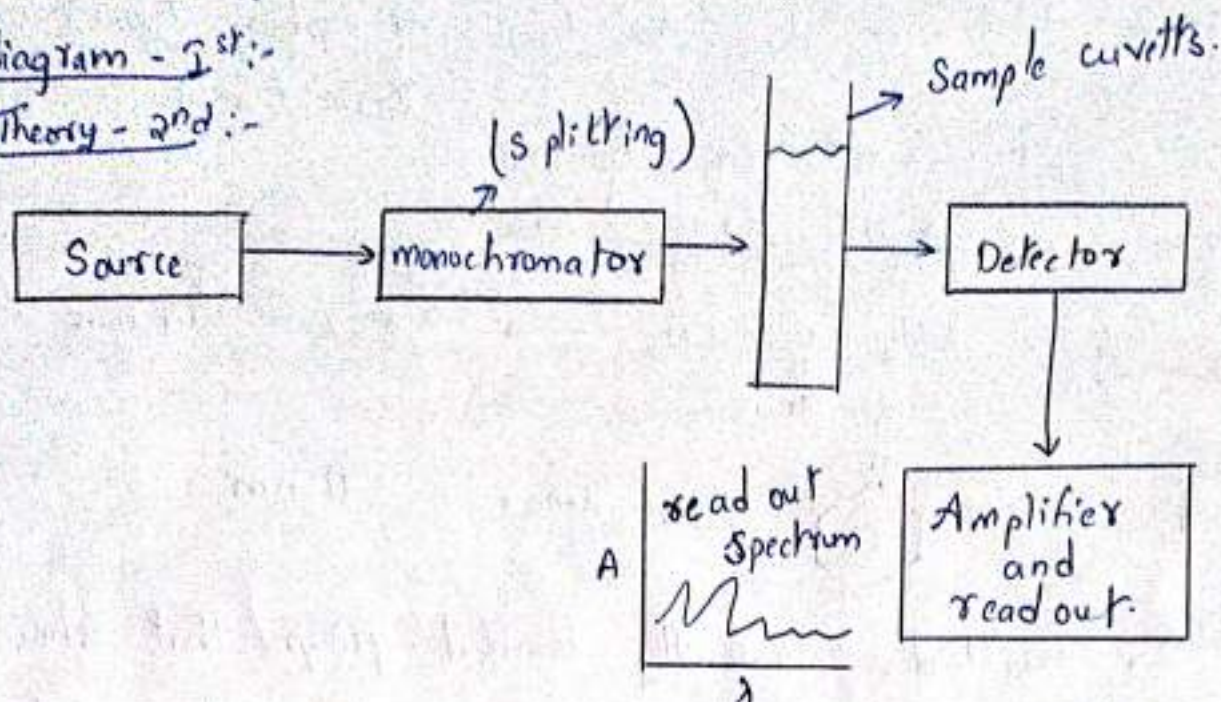
photo voltaic cell can be used as photo detector.

(v) Recorder :- It is a display device, which

automatically draws the spectrum.

Diagram - 1st:-

Theory - 2nd:-



Schematic diagram of a single beam instrument.

Terms in electronic spectroscopy :-

* Concept of chromophore and auxochrome :- *

There are two terms mainly present in electronic spectroscopy. They are 1) chromophore. 2) auxochrome.

1) Chromophore :- chromo means colour; defined as the unsaturated part of compound which is responsible for giving colour the compound is called chromophore.

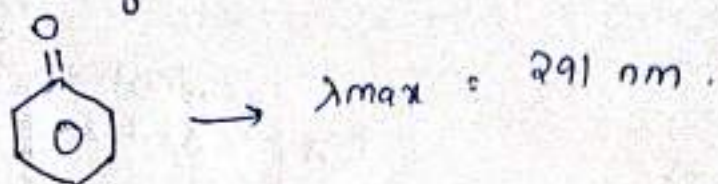
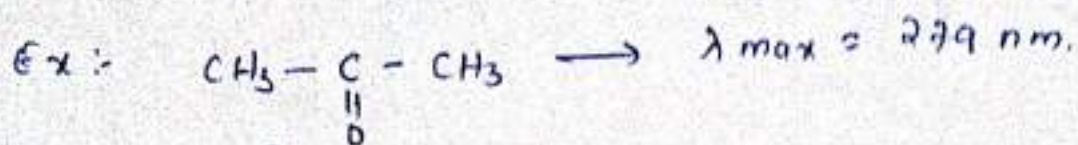
Ex :- $C=C$; $C=O$, NO_2 etc.

chromophore is a functional group containing

multiple bond capable of absorbing radiations above 200 nm; due to (2 chromophore types) (transitions)

$\pi \rightarrow \pi^*$ transitions.

$n \rightarrow \pi^*$ transitions.



\rightarrow Isolated covalently bonded group that shows a characteristic absorption in the UV-visible region is known as chromophore.

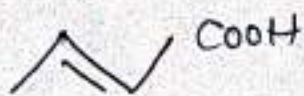
2) Auxochrome:-

Auxochrome is an auxiliary group. It self it doesn't absorb in UV-visible zone.

\rightarrow Auxochrome is a functional group with non-bonding electrons that doesn't absorb radiation in near UV region but when it attached to chromophore increases wavelength and intensity of absorption, maximum due to effect of chromophore its ability to extend conjugation of chromophore by sharing of non-bonding electrons.

Ex: $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-OR$,

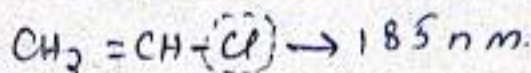
$-X$ groups



$\lambda_{max} = 204 \text{ nm}$



$\lambda_{max} = 234 \text{ nm}$



* Different Shifts in absorbance and intensity: *

(i) Bathochromic shift :- The shift of λ_{max} towards to the longer wave length. Shift of an absorption maximum to the longer wave lengths is called 'bathochromic shift'.

It occurs due to substituent and solvent effects.

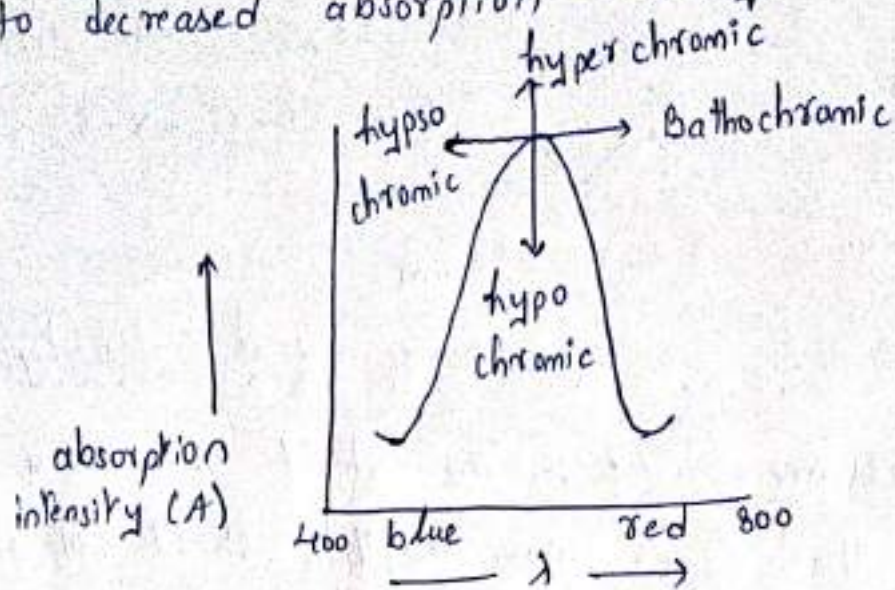
Ex:- Benzene and phenol.

(ii) Hypsochromic shift :- the shift of λ_{max} towards to the shorter wave length, shift of an absorption maximum to the shorter wave length is known as hypsochromic shift.

It occurs due to substituent and solvent effect. Ex:- Aniline \rightarrow Aniline hydrochloride.

(iii) Hyperchromic shift :- It is the effect leading to increased absorption intensity.

(iv) Hypo chromic shift :- It is the effect leading to decreased absorption intensity.



* Applications of electronic Spectroscopy :- *

* Applications of UV-Visible Spectroscopy :- *

a) Detection of functional groups :-

The technique is applied to detect the presence (or) absence of the chromophore.

b) Extent of conjugation :-

The extent of conjugation in polyenes can be estimated. Addition of unsaturation with the increase in the number of double bonds shifts the absorption to longer wave length.

Ex :- Ethylene - colourless

β - carotene - 11 Conjugated double bonds.

- orange red in color.

c) Qualitative analysis :-

UV-Visible spectroscopy is used for characterising aromatic compounds and conjugated obfins.

d) Detection of conjugated and non-conjugated compounds.

e) Identification of an unknown compound :-

An unknown compound can be identified by comparison of its spectrum with the known spectra.

f) Examination of poly nuclear hydro carbons.

g) Applications of UV spectroscopy in quantitative analysis :-

Quantitative analysis :-

(i) It can be used to find out molar concentration of the solute under study.

(ii) Detection of isomer i.e. cis (or) trans isomers.

(iii) Determination of molecular weight using Beer's law.

(iv) Determination of structure of several vitamins.

(v) To study "Kinetics" (Rate of enzymatic reactions, bio-medical studies) of chemical reaction.

(h) UV-visible spectroscopy is also used in environmental chemistry to determine the concentration of various metal ions.

(i) Examination of poly nuclear hydrocarbons :-

Identification of poly nuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compound.

* Vibrational Spectroscopy :- *

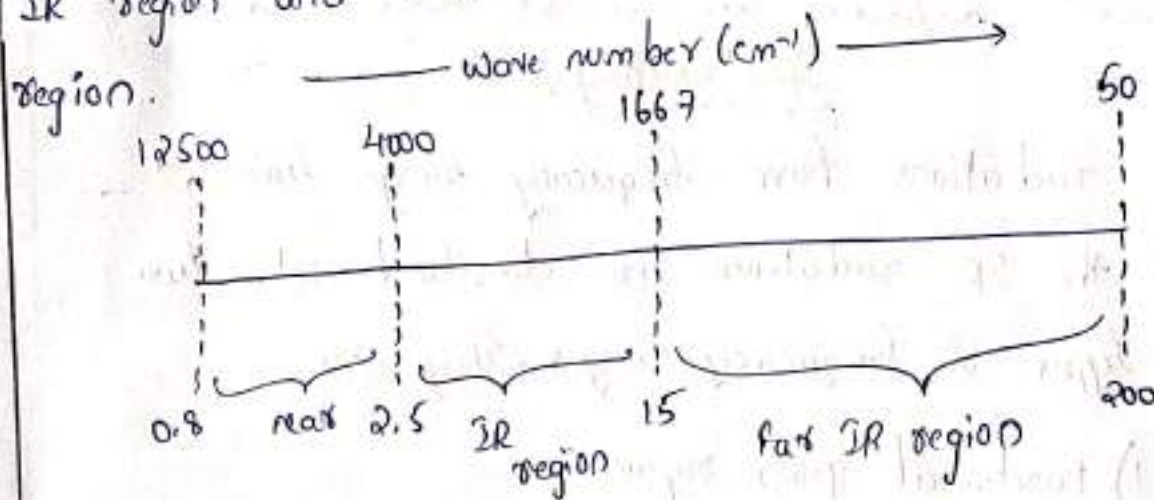
(or)

* IR Spectroscopy :- *

IR means infra-red radiations. These are one of electromagnetic radiations. IR spectroscopy is also called as "Vibrational spectroscopy".

→ IR region of the complete electromagnetic spectrum extends from 12500 cm^{-1} - 50 cm^{-1} . The most important region being $4000 - 667 \text{ cm}^{-1}$ in which molecular vibrations can be detected and measured.

→ The region from $4000 - 12500 \text{ cm}^{-1}$ is called as near IR region and from $667 - 50 \text{ cm}^{-1}$ is called far infrared



→ Near IR region extends from $12500 - 4000 \text{ cm}^{-1}$ frequency region. In this regions overtones and combination bands appear.

→ The region between $4000 - 667 \text{ cm}^{-1}$ covers fundamental

Vibrations. Almost all functional groups absorb in this region.

→ Molecules show pure rotational motions in this region.

→ Middle IR region contains functional group and finger print region.



The region between 1400cm^{-1} - 667cm^{-1} is complex as it involves stretching and bending vibrations.

* Different regions in IR or vibrational Spectroscopy :- *

IR radiations have frequency range 4000cm^{-1} - 667cm^{-1} the IR radiations are classified into two different types of frequency ranges. They are.

1) functional group region.

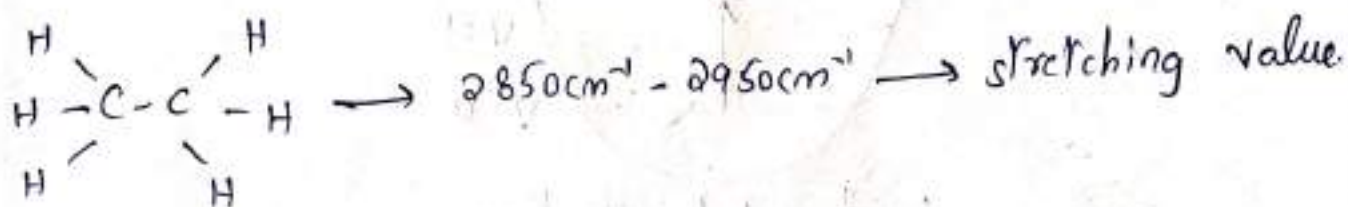
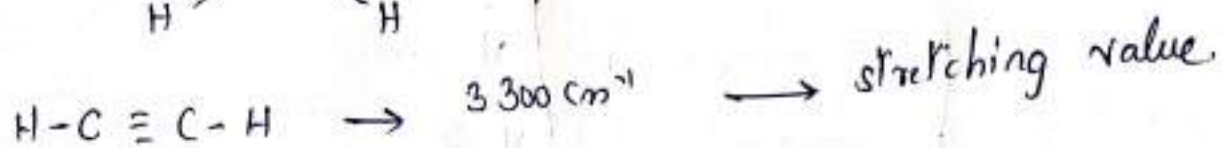
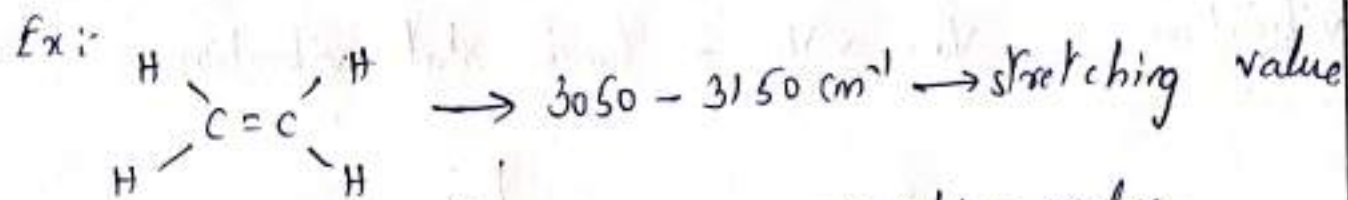
2) finger print region.

Functional group region :-

This functional group region has frequency range 4000cm^{-1} - 1400cm^{-1} . This region has frequency range

This region mainly useful for the determination of functional groups that present in the molecule. There are two types vibrations are present.

1) stretching : 2) bending.



Finger Print region:-

It is an important region in IR spectroscopy.

This region is one of useful for the determination of absorption bands of different compounds, this finger print region has a range; $1400 \text{ cm}^{-1} - 667 \text{ cm}^{-1}$

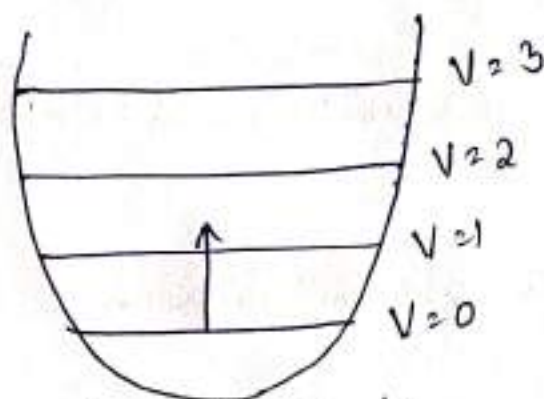
→ This region is very useful to determine the two compounds having exactly same spectra when run in the same medium under similar conditions.

→ near IR regions fundamental vibrations overtones appear.

1) Fundamental vibrations :-

the vibrations in which, the electronic transitions takes place from v_0 (Zeroth vibrational level) to v_1 (first vibrational level).

These vibrational transitions are called fundamental vibrations $v_0 \rightarrow v_1$ — fundamental vibrations



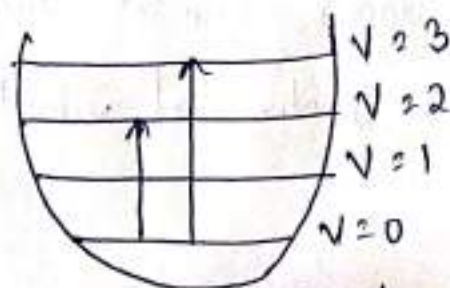
Fundamental vibrations.

2) Overtone :- These are vibrations in which the electronic transitions takes place from zeroth vibrational level to next higher vibrational level. $v=2$, $v=3$ are called overtones.

The combination of the all bands gives hot bands

$v_0 \rightarrow v_2$ is first overtone.

$v_0 \rightarrow v_3$ is second overtone.



Overtone.

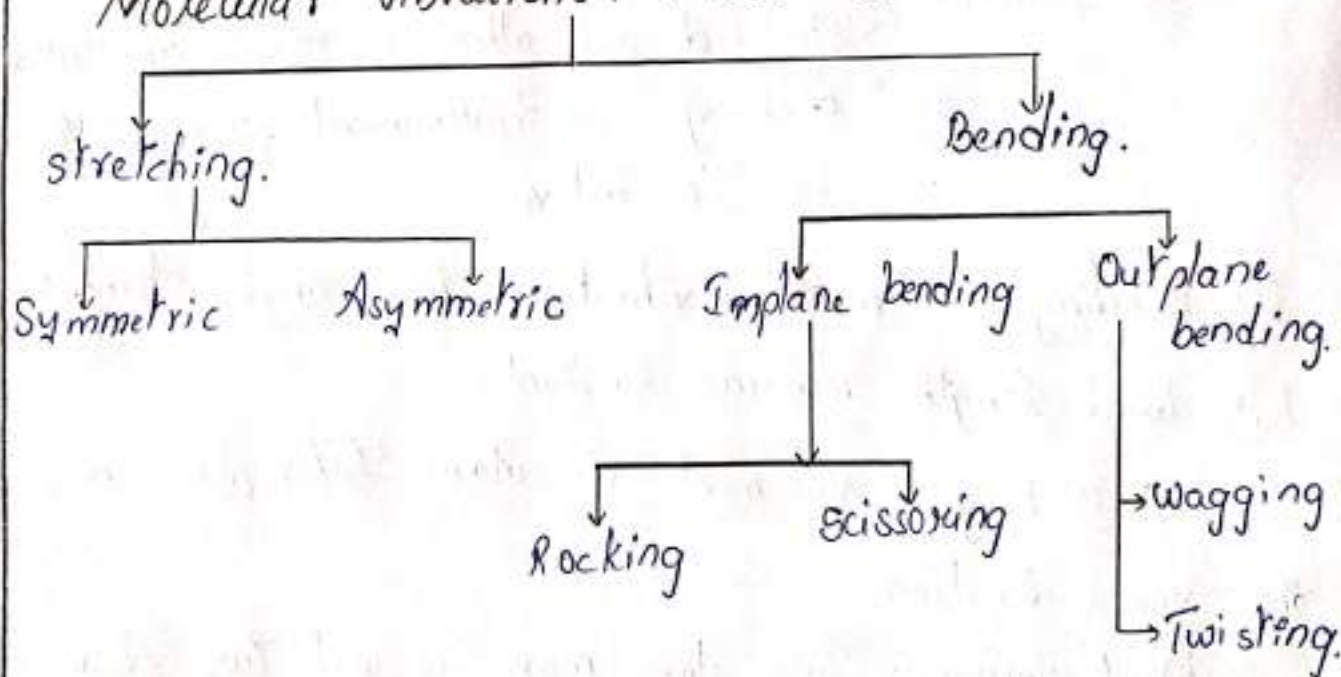
* Theory of Vibrational Spectroscopy :- *

→ In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibrations, absorption occurs.

→ A molecule to absorb IR radiation; the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule.

→ If the frequency of the radiation matches the vibrational frequency of the molecule, then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

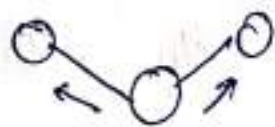
Molecular Vibrations :- Mode of Vibrations:



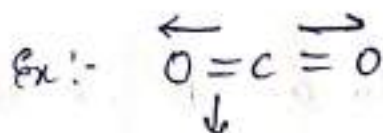
1) Stretching :- Bond angle remains constant but bond length changes.

a) Symmetric stretching :- $\overleftarrow{\text{O}} = \text{C} = \overrightarrow{\text{O}}$

The movement of atoms occurs in the same direction with respect to central atom in a molecule



Symmetric



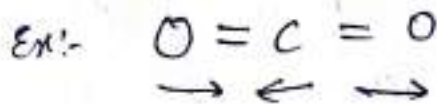
no change in the dipole moment of the molecule hence it is IR active.

b) Asymmetric stretching :-

One atom moves towards and the other moves away from the central atom.



Asymmetric



In this vibrations one bond is stretched and other is compressed causes a change in dipole moment, hence it is IR active

2) Bending :- In this vibrations bond angle changes but bond length remains constant.

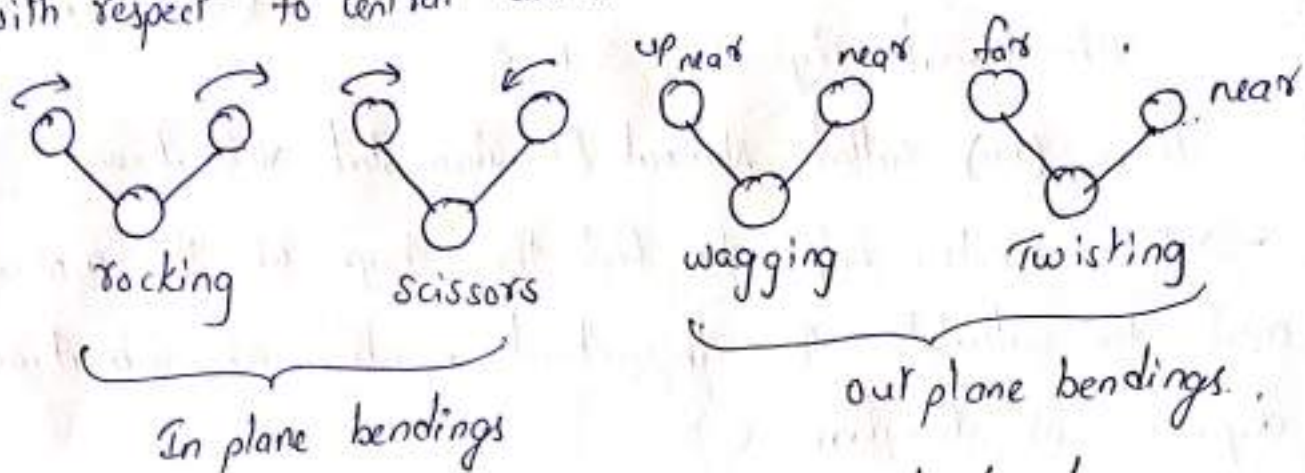
a) Rocking :- Movement of atoms takes place in the same direction.

b) Wagging :- Two atoms move up and two down

the plane with respect to the central atom.

c) Scissoring :- Two atoms approach each other.

d) Twisting :- One of the atom moves up the plane where as the other ~~moves~~ moves down the plane with respect to central atom.



* Comparison between stretching and bending

Vibrations:- *

- less energy require to bending.
- more energy require to stretching.
- stretching vibrations occurs at higher frequencies than bending.
- Symmetrical stretching easier than Asymmetric stretching.
- Bending vibrations occurs at lower wave number, lower frequency than stretching.

* 1.2 Vibrations :- Active (or) Forbidden :- *

For non-linear molecule, the vibrational degree
are = $3N - 6$

For linear molecule rotation around the molecular axes
is not possible. ($y, z \rightarrow$ not x)

$$\text{vibrational degrees} = 3N - 5$$

These (are) called Normal / Fundamental vibrations.

→ IR Spectra helps to find the shape of the molecule
and to calculate the theoretical number of vibrational
degrees of freedom.

Ex:- 1) $C_6H_6 \rightarrow$ non-linear \rightarrow vibrational degrees of
freedom = $3N - 6$ $N =$ no. of atoms.

$$3 \times 12 - 6$$

$$\Rightarrow 36 - 6 = 30$$

$$2) CO_2 \rightarrow 3N - 5 \rightarrow 3 \times 3 - 5 \Rightarrow 9 - 5$$

no. of vibrational degrees of freedom $\Rightarrow 4$.

$$3) H_2O \rightarrow 3N - 6 \rightarrow 3 \times 3 - 6 = 3 \rightarrow \text{no. of vibrational degree of freedom.}$$

$$4) SO_2 \rightarrow 3N - 6 \rightarrow 3 \text{ no. of vibrational degree of freedom.}$$

$$5) HCN \rightarrow 3N - 5 \rightarrow 9 - 5 = 4 \text{ no. of vibration degree of freedom.}$$

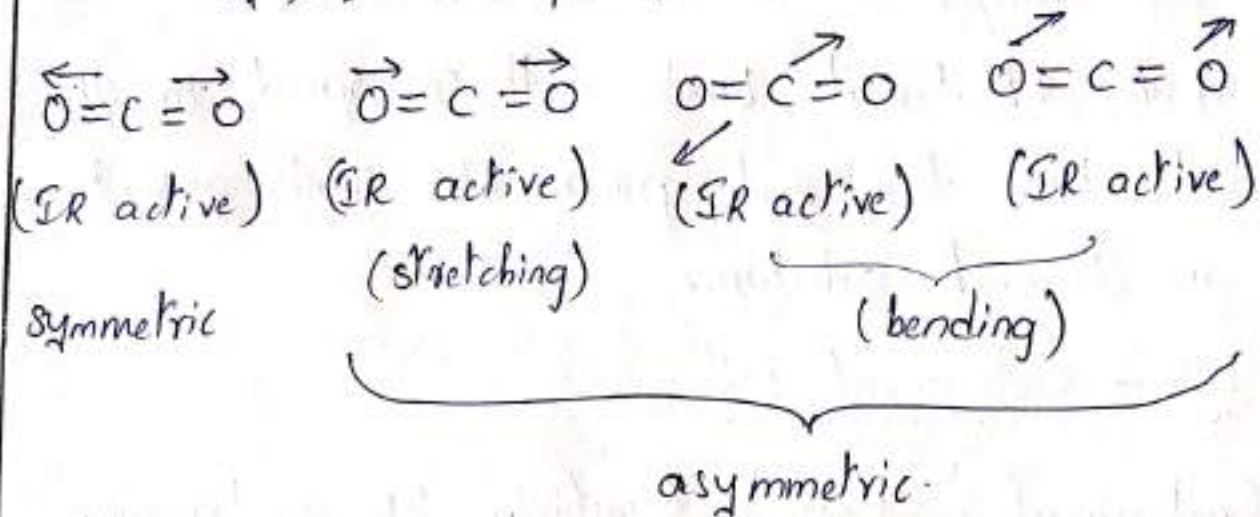
$$6) CH_4 \Rightarrow 3N - 6 \rightarrow 9 \Rightarrow \text{no. of vibrational degrees of freedom.}$$

* Selection Rules of IR / Vibrational Spectroscopy *

1) The most fundamental requirement for IR activity is that a vibration must cause change in the dipole moment of the molecule.

Ex: HCl , CO - polar (IR active)

H_2 , N_2 - non-polar (IR inactive)



2) Second rule :- (followed from the harmonic oscillator) absorption of radiation, only transition for which $\Delta v = \pm 1$ can occur where v is the change in vibrational quantum number between 2 vibrational energy levels.

$$\Delta v = v_2 - v_1$$

at room temperature $v=0$, $v=1$ (transitions)

* Applications of IR Spectroscopy :- *

1) Widely used to detect the functional groups

in a chemical substance.

2) A set of geometrical isomers (cis-trans).

3) From the band spectrum, we can get information about the chemical structure of the surface molecule.

4) In biology \rightarrow IR spectroscopy is most commonly employed to quantitate secondary structure or to determine changes in the structures.

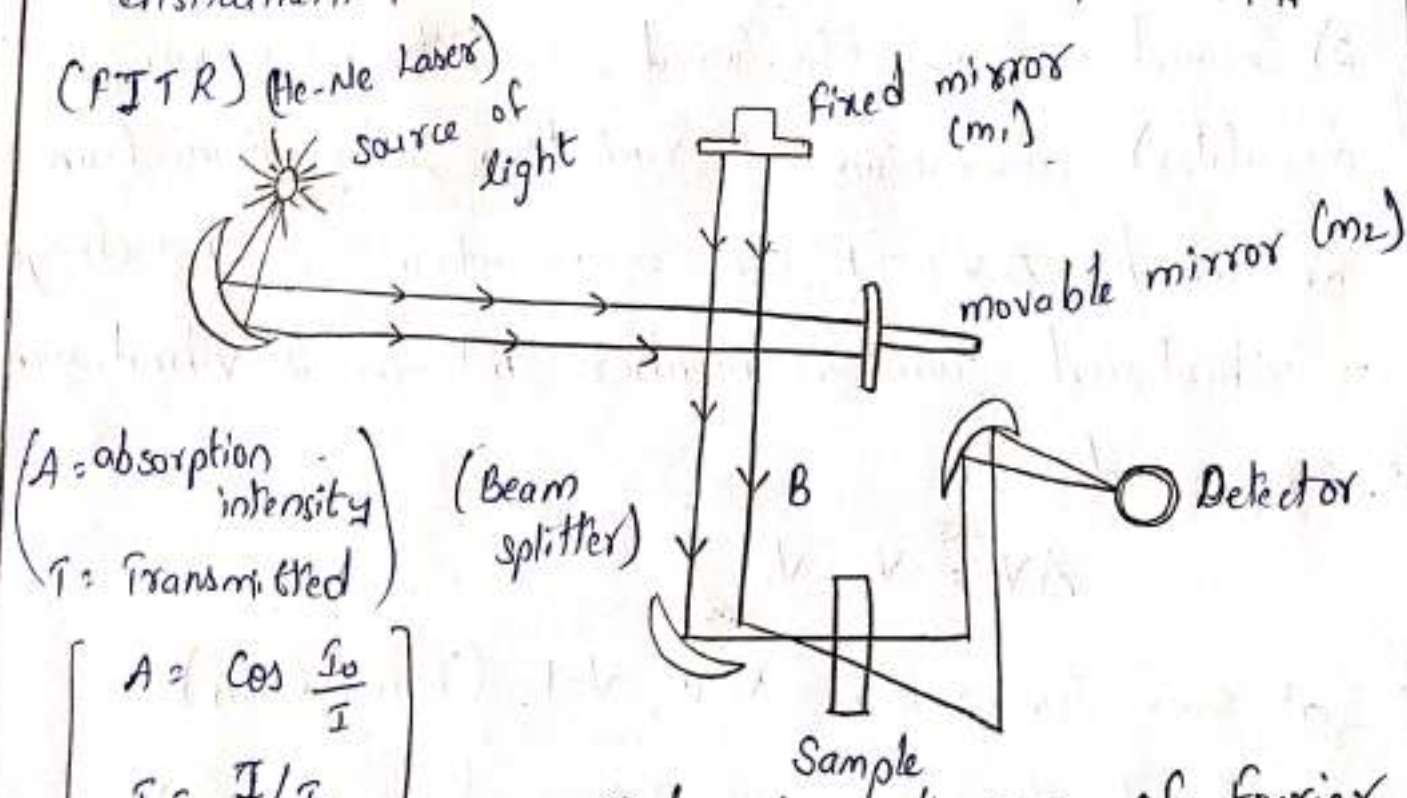
5) The Vibrational bands will correspond to the characteristics functional groups of bonds present in a chemical substance.

IR - Instrumentation:-

Instrument:- Fourier transform IR spectroscopy

(FTIR) (He-Ne Laser)

Source of light



(A = absorption intensity)
(I = Transmitted)

$$\begin{bmatrix} A = \cos \frac{I_0}{I} \\ I = I/I_0 \\ A = \cos I/I \end{bmatrix}$$

Schematic diagram of Fourier Transform IR spectrometer.

NMR Spectroscopy: (Nuclear Magnetic Resonance Spectroscopy)

①

Introduction:-

→ NMR means "Nuclear Magnetic Resonance Spectroscopy". This spectroscopy is very useful in the study of various "Organic compound structures". It plays an important role in the determination of the structures of the organic compounds.

→ The Electromagnetic radiations that are used in this NMR Spectroscopy is Radiowave. Because this radiation are useful for "Nucleus Excitations".

→ It is a branch of a spectroscopy in which radio frequency wave induce transition b/w magnetic Energy levels of nuclei of a molecule.

Principle of NMR:- (Theory) (Basics):-

NMR spectroscopy depends upon the absorption Energy where nucleus of an atom is excited from its lowest Energy nuclear spin to the next higher one. The nuclear Energy levels produced by keeping the nuclei in a magnetic field. The Energy required for transitions falls in radio-frequency region 60-500 MHz.

When spin returns to its base level Energy is emitted at the same frequency. The signal matches this transfer measured processed to yield "NMR spectrum" for concerned nucleus.

NMR spectroscopy is of the types ^1H NMR, ^{13}C NMR
↓ ↓
(Proton NMR) (Carbon NMR)

^1H NMR → used to determine the no. of H & types of H atoms in a molecule.

^{13}C NMR → used to determine the type of 'C' atoms in a molecule

→ the source of energy in NMR is radio wave

→ The nuclei act as a tiny bar magnet. These nuclear magnets are randomly placed. But in presence of external magnetic field, they oriented with applied field (or), against applied field more nuclei are oriented with applied field because lower energy.

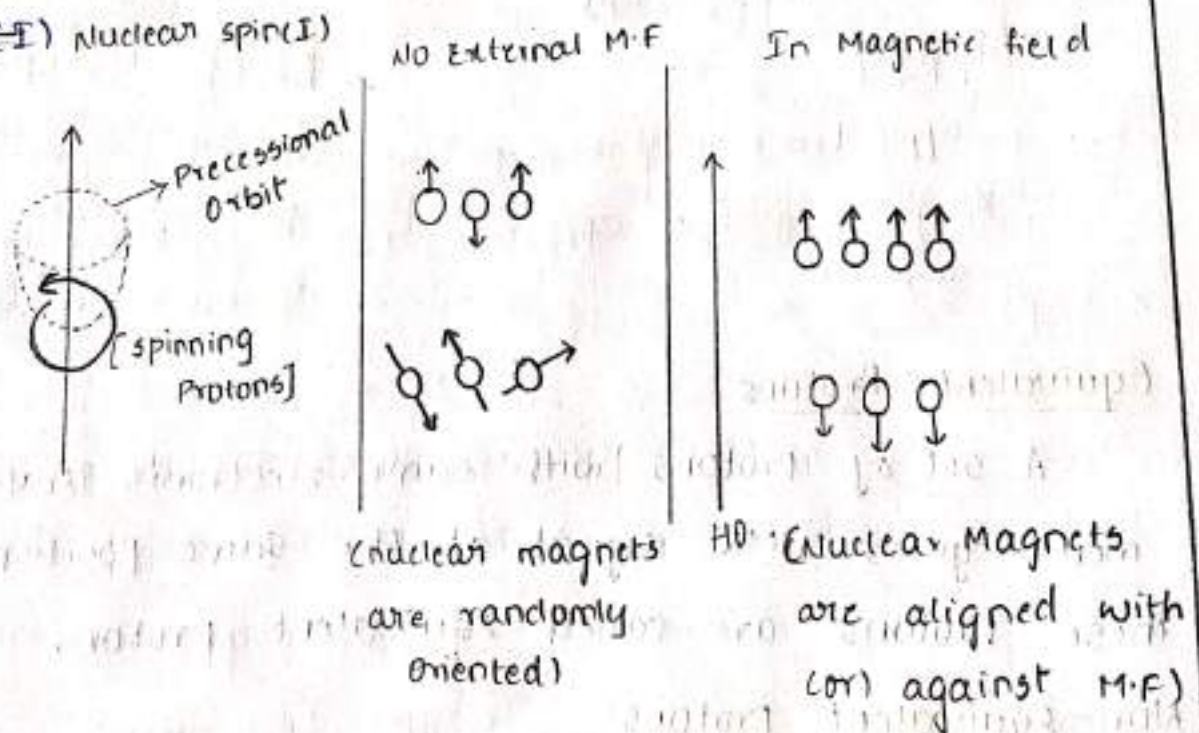
→ If a proton is placed in a magnetic field, it precesses with certain frequency region. The proton may be aligned either with external magnetic field or against the magnetic field.

The proton absorbs energy ($h\nu$) & moves from one energy state to the other & this transition is called flipping of proton. The energy required to bring about transition or flip proton depends upon the strength of the external magnetic field. The stronger the magnetic field, the greater the tendency of a nuclear magnet to get aligned with it & higher frequency is required for flipping.

Proton to higher Energy. When the quantum Energy ($h\nu$) of Electromagnetic radiation matches with differences of Energy b/w 2 Energy states at field strength H_0 , nucleus & radio frequency beam in resonance. Absorption takes place & a signal is observed.

* All protons do not absorb at the same frequency. It depends applied magnetic field strength (H_0) & Protons in immediate Electronic Environment

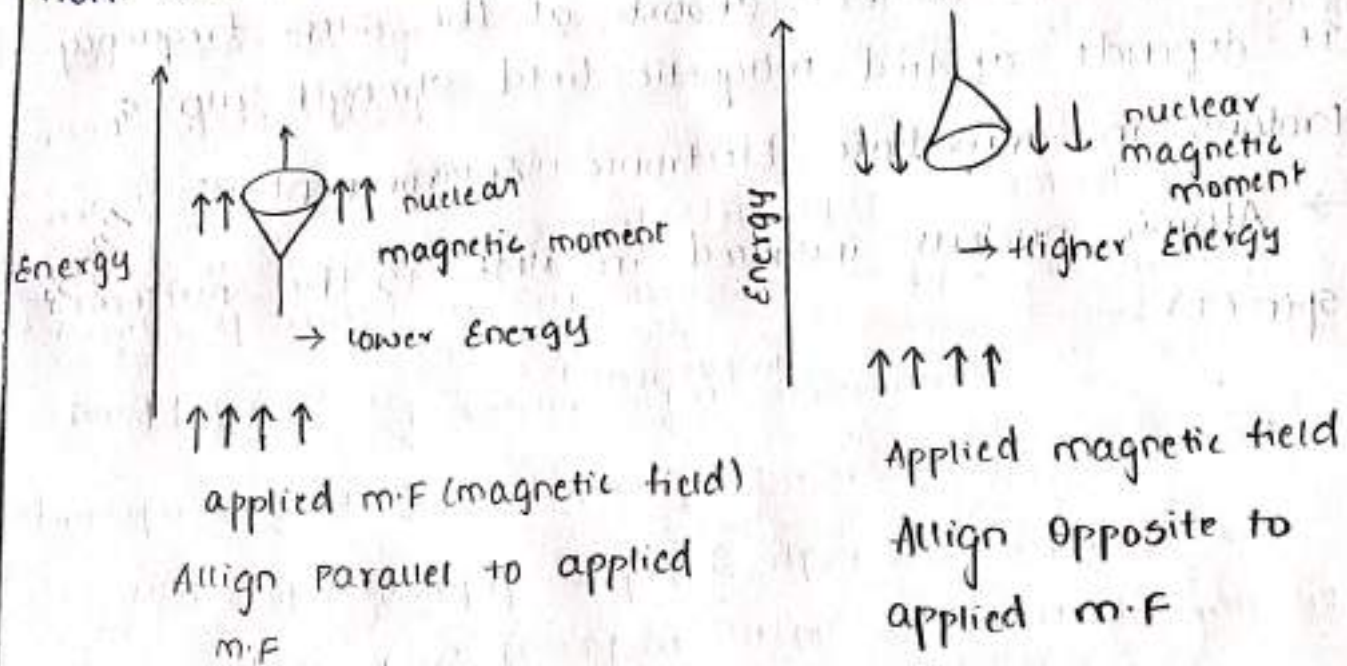
→ Atomic nucleus involved in NMR is the ~~nuclear~~ spin (I) Nuclear spin (I)



There are 2 different Energy states for a Proton in Magnetic field

(a) a lower Energy state with nucleus aligned in the same direction as H_0

(2) A higher Energy state with the nucleus aligned opposite to H_0 . When the Energy is applied externally (nu) & it matches the Energy difference (ΔE) on absorption takes place. The nucleus flips its spin from one Orientation to other.



Equivalent Protons:

A set of protons with same electronic environment gives NMR signal at the same position. These protons are called Equivalent protons.

Non-Equivalent protons:

Protons with different electronic environment (Position), the protons are called non-equivalent protons.

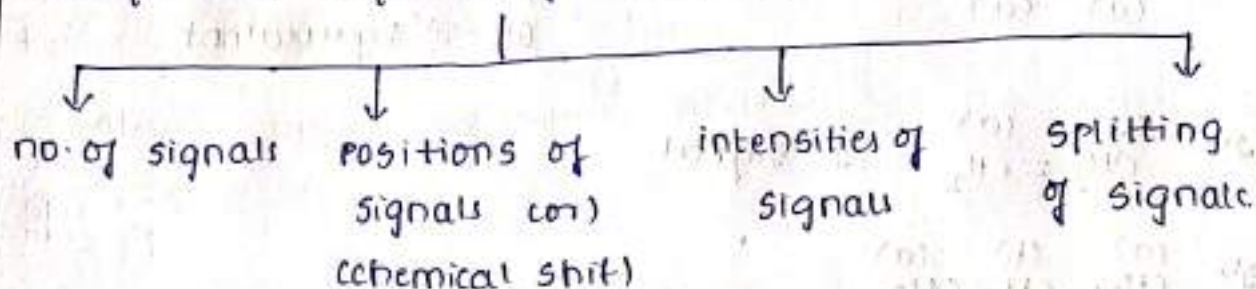
⇒ atomic nucleus involved in NMR is the nucleus spin (I). Its value depends on the mass no. & atomic no. of that nucleus.

⇒ If the nucleus having $I \neq 0$, it can be spin active

⇒ ^1H , ^{13}C , ^{19}F → $I = \text{angular momentum} = 1/2$

⇒ ^{12}C , ^{16}O , ^{32}S → $I = \text{Angular momentum} = 0$

Important aspects of NMR spectrum



① The no. of signals: Tells us how many different kinds of protons are there in a molecule.

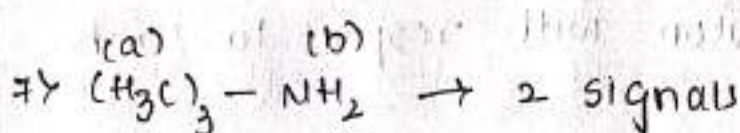
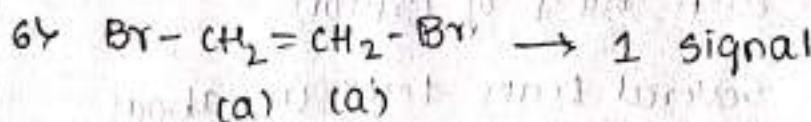
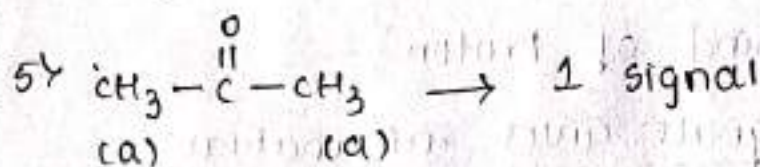
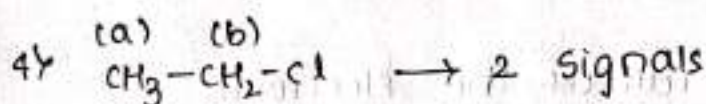
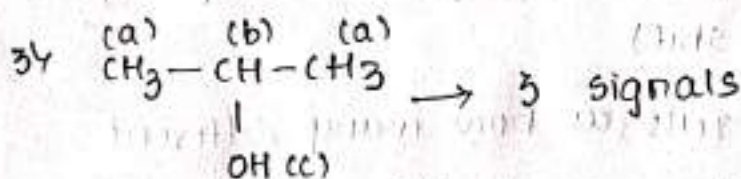
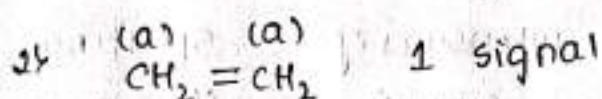
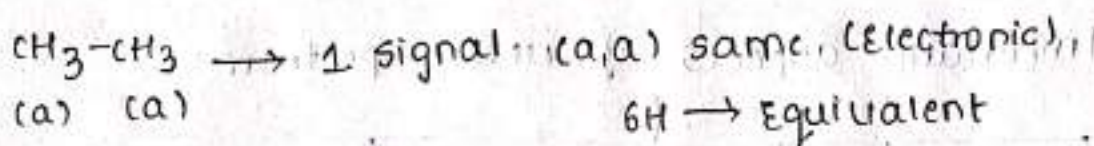
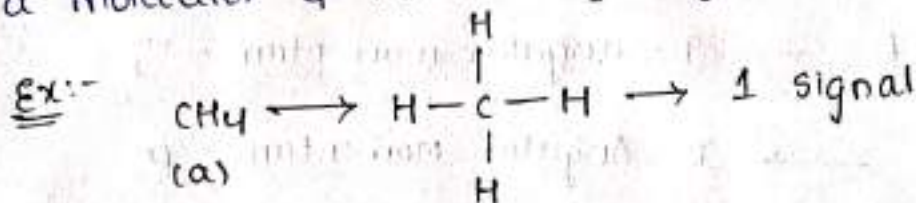
② The position of signals: Tells us the electronic environment of each kind of proton.

③ The intensities of signals: Gives information regarding the no. of each kind of proton.

④ splitting of signals: Several peaks tell us about the environment of proton with respect to each other.

① No. of signals:-

The no. of 'signals' in a NMR spectrum tells us how many sets of Equivalent Protons are there in a molecule & how many signals produced.



Position of Signals / chemical shifts:-

The position of signals helps us to know the molecule. Whether the protons are aromatic, aliphatic, primary, secondary, tertiary, phenylic, allylic, vinylic etc.

→ When the molecule is placed in (external) applied field, then the induced magnetic field opposite the applied field then the proton get low field and are in "shielded zone".

→ Induced magnetic field is parallel to applied field then the proton get high field are called "deshielding zone".

Due to the presence of shielding & deshielding of protons, the positions of NMR signals will be changed.

→ The protons which are in shielding appears at lower values & the proton which are deshielding appears at higher values.

→ And the position of these NMR signals can be indicated by the chemical shifts values.

→ shielded protons are having low chemical shift values.

→ deshielded protons are having high chemical shift values.

→ shifts in the position of NMR absorption which arise due to the shielding & de-shielding of protons.

by the electrons are called chemical shifts.
→ For measuring chemical shifts of various protons, signal for TMS is taken as a reference & chemical [TMS → Tetra Methyl silane] shifts for various sets of equivalent protons are measured with respect to TMS.

Characteristics of TMS

- 1) It is miscible with almost all organic solvents.
- 2) It has lower electronegativity of Si shielding of equivalent protons in TMS is greater than almost all organic compounds.
- 3) It is highly volatile & can be easily removed from the system.
- 4) It does not undergo intermolecular association with the sample.
- 5) It is chemically inert, the difference in the absorption position of the proton with respect to TMS signal is called chemical shift. It is represented by δ value for TMS $\delta = 0$.

$$\delta \text{ of sample} = \nu_s - \nu_{\text{TMS}}$$

ν_s : resonance frequency of sample

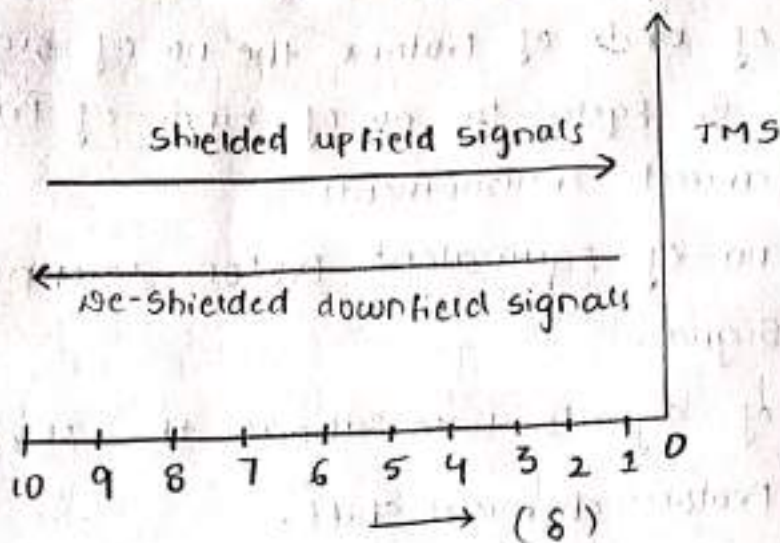
ν_{TMS} : resonance frequency of TMS

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{operating frequency in mega cycles}} \times 10^6 \text{ ppm}$$

operating frequency in mega cycles

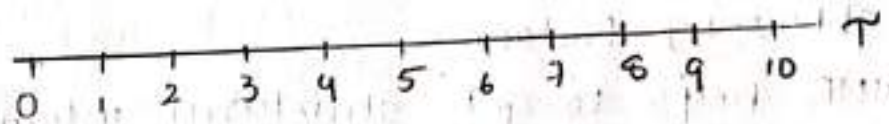
$$\delta = \frac{\Delta \nu}{\text{Operating frequency}}$$

Operating frequency



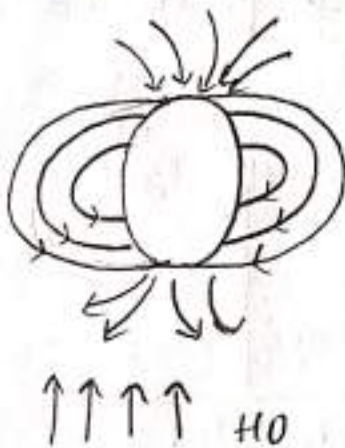
In τ scale

$$\tau = 10 - \delta$$

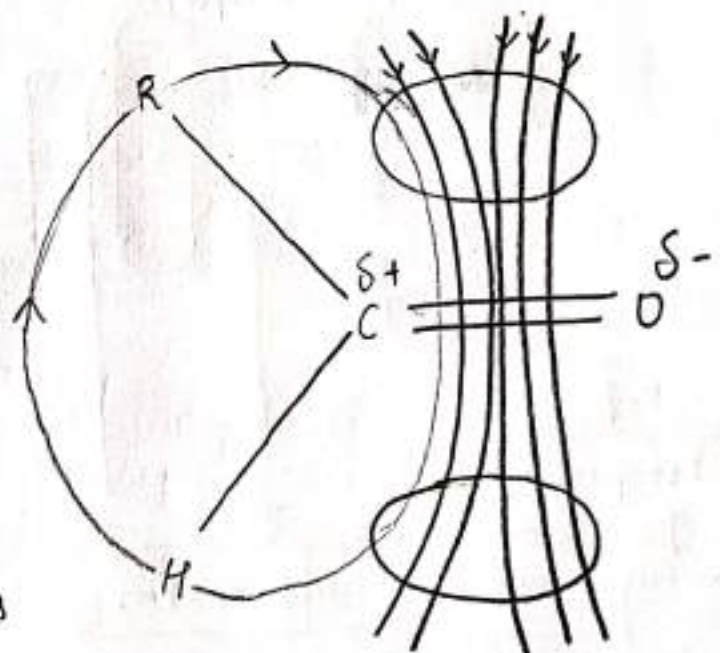


Factors affecting the chemical shifts:

- ① Inductive effect
- ② vanderwalls deshielding
- ③ Anisotropic effect
- ④ Hydrogen bonding



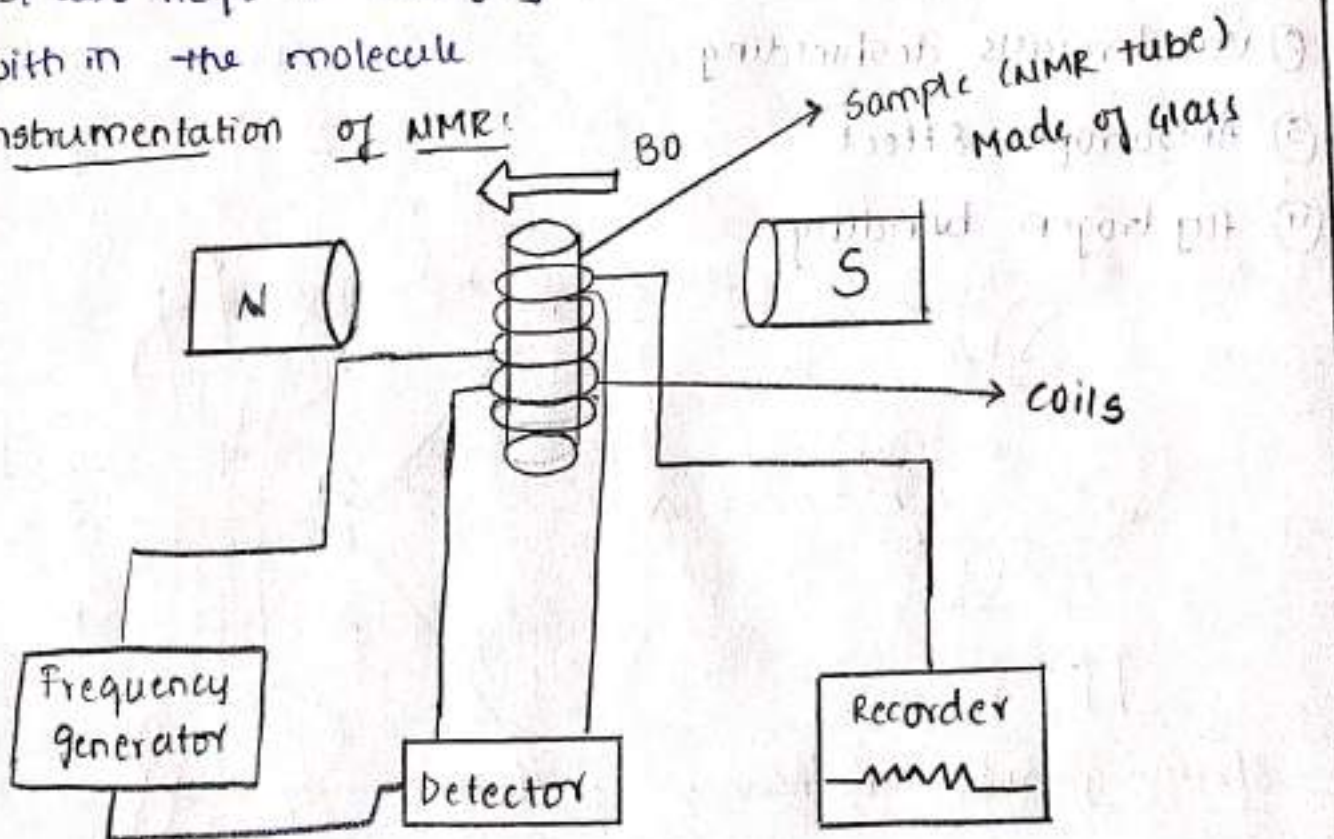
Shielding about the nucleus



Applications of NMR spectroscopy:

- ① NMR spectrum of a compound gives information about the no. of kinds of Protons. the no. of signals in the spectrum is equal to no. of kinds of Protons in different chemical environments.
- 2) Tells us the no. of Equivalent Protons causing the splitting of a signal.
- 3) The position of signals tells about the Electronic Environment of Proton chemical shift.
- 4) The multiplicity of signals tells information about neighbouring Protons.
- 5) NMR helps to get structural information from the spectrum of an unknown compound.
- 6) It also helps in studying the stereo-chemical details within the molecule.

Instrumentation of NMR:



Instrumentation:

- A sample to be investigated is taken in NMR tube (made of glass) & kept b/w the pole faces of magnet.
- A coil is coil round the NMR tube. Energy is fed into the coil.
- A radio frequency source on the sample. A signal is detected, if there is resonance b/w nucleus of sample & source.
- The Energy transfer from the source to detector via nuclei.
- The detector gives an output to recorder (Oscillography) ^{Process}
Recorder gives the signals of protons of the molecule.
- Radio frequency source happens increase the field strength increase the frequency of every set of protons till the resonance happens.
- When a proton (or) set of equivalent protons arrives for resonance, detector generates a signal which further produces a signal on the charge paper.

Rotational Spectroscopy:

Rotational Spectrum Principle:

Microwave spectroscopy deals with the pure rotation motion of molecules and is known as rotational spectroscopy.

The conditions for observing resonance in that region is the molecule must possess 'permanent dipole moment'. When a molecule having dipole moment rotates, it generates an electric field which interacts with the electric component of the microwave radiation. During this interaction energy can be absorbed or emitted and thus rotation of molecule gives rise to a spectrum.

If molecules are not having dipole-moment, interaction is not possible and these molecules are 'microwave inactive'. Eg: H_2 , Cl_2 otherwise the molecules like HCl , CH_3Cl etc having dipole moment and this interaction gives rise to a spectrum, such molecules are 'microwave active'.

Selection Rule: In order for a molecule to give rotational spectrum, the molecule must have a dipole moment; but all transitions are not permitted there is a selection rule.

$$\text{i.e. } \boxed{\Delta J = \pm 1}$$

From the above rule, it shows that only those transitions are permitted in which there is an increase or decrease

by unity in the rotational quantum number. It means that $J=0 \rightarrow J=2 \rightarrow J=4$ transitions are not possible, such transitions are forbidden.

In general the molecule from the state J to $J+1$ would have

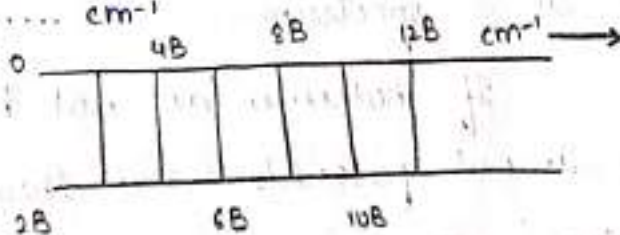
$$E_{J+1} - E_J = B(J+1)(J+2) - BJ(J+1)$$

$$= B(J+1) [J+2-J]$$

$$= B(J+1) \cdot 2$$

$$= 2B(J+1) \text{ cm}^{-1}$$

Thus, a stepwise raising of the rotational energy gives rise to an absorption spectrum which consists of lines at $2B, 4B, 6B, \dots \text{ cm}^{-1}$



Classification:

From microwave studies, molecular symmetry and molecular parameters can be determined.

1) Linear molecules: Molecules in which all atoms are arranged in straight line, such as HCl and carbon oxy sulphide (CS_2).

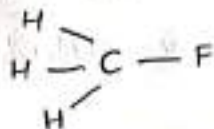
H-Cl, O-C-S. For linear molecule, the moment of inertia I_B and I_C are same i.e. $I_B = I_C$ and I_A is negligible because it is very small, approximately we take zero i.e. $I_A = 0$.

Thus for linear molecules, we have

$$I_B = I_C, I_A = 0$$

(ii) Symmetric Tops:

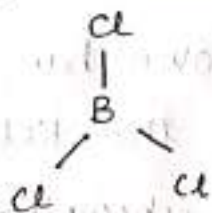
Consider a molecule such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon.



For symmetric top molecule $I_B = I_C \neq I_A$, $I_A \neq 0$, symmetric top molecules are divided into 2 classes basing on their moment of inertia.

(a) If $I_B = I_C > I_A$, the molecule is called prolate symmetric top. eg: CH_3F

(b) If $I_B = I_C < I_A$, the molecule is called oblate symmetric top. eg: BCl_3

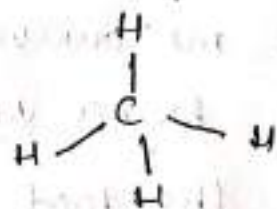


(iii) Spherical tops:

When a molecule has all three moments of inertia are identical, such molecule is called spherical top.

eg: CH_4

For spherical tops $I_A = I_B = I_C$

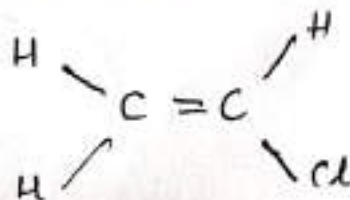
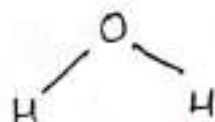


(iv) Asymmetrical tops:

When a molecule has all three moments of inertia are different, such molecule is called asymmetric top.

eg: H_2O , $\text{CH}_2=\text{CHCl}$

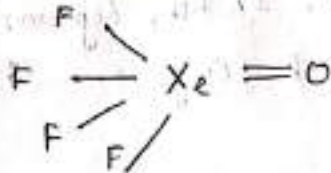
For asymmetric tops, $I_A \neq I_B \neq I_C$



Applications :

(i) Structure of Xenon oxyfluoride molecule

The microwave spectrum of this molecule is a characteristic of a symmetric top and is consistent with C_{4v} symmetry of the molecule.



(ii) Determination of bond distances in polyatomic molecules :

It measures the bond length of polyatomic molecules.

(iii) The Microwave oven :

In recent years, the microwave oven has become a very familiar and use cooking device for in the kitchen. Its mode of operation depends upon the absorption by the food of microwave radiation in which it is placed.

The water molecules in the food absorb the microwave radiation and thereby raised to the higher rotational state. The biological molecules in the food, are far too big to be able to rotate.

As with many other excited states, the excess rotational energy of the water molecules is re-emitted as heat and the food becomes cooked.