

Spectroscopy

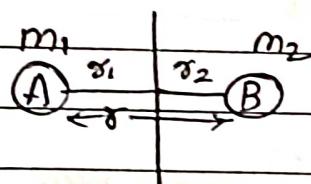
EM wave \rightarrow

(1) Microwave (Rotational spectroscopy):

$1 - 100 \text{ cm}^{-1}$

$3 \times 10^{10} - 3 \times 10^{12} \text{ Hz}$.

- It involves the transition between the rotational energy levels of a gaseous molecule having permanent dipole moment on the absorption of electromagnetic wave falling in the spectral range of $3 \times 10^{10} - 3 \times 10^{12} \text{ Hz}$ or $1 - 100 \text{ cm}^{-1}$.



Cg (Centre of gravity)

• rigid molecule

↳ no change in bond length.

\rightarrow Moments of A and B around centre of gravity (Cg)

$$m_1 r_1 = m_2 r_2$$

$$r = r_1 + r_2$$

$$\rightarrow r_2 = r - r_1$$

$$m_1 r_1 = m_2 (r - r_1)$$

$$m_1 r_1 = m_2 r - m_2 r_1$$

$$r_1 (m_1 + m_2) = m_2 r$$

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

Similarly

$$r_2 = \frac{m_1 r}{m_1 + m_2}$$

* Moments of inertia :- (I) of rotating diatomic gaseous molecule.

$$I = m_1 \omega^2 + m_2 \omega^2$$

$$I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2}$$

$$= m_1 m_2 r^2 \frac{(m_2 + m_1)}{(m_1 + m_2)^2}$$

$$I = \frac{m_1 m_2 \omega^2}{m_1 + m_2}$$

Reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$I = \mu r^2$$

(i)

* Angular Inertia = $I \omega$.

(L)

ω ^{Angular vel.}
mass

Energy of rotating molecule = $\frac{1}{2} I \omega^2$.
(Wrt angular inertia) (Eg) $= \frac{1}{2} \frac{(I \omega)^2}{I}$

$$= \frac{1}{2} \frac{L^2}{I}$$

* Angular momentum is always quantised.

$$mvr = \frac{n \hbar}{2\pi}$$

• $J =$ rotational quantum no

$$J = 0, 1, 2, 3, \dots$$

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} r$$

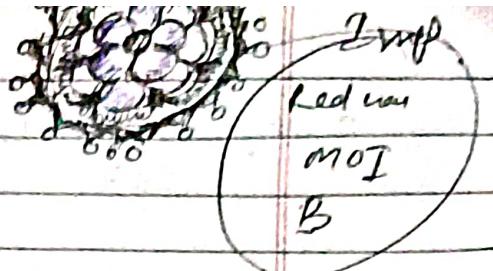
$$\omega^2 = J(J+1) \frac{\hbar^2}{4\pi^2 I}$$

$$E^2 \propto J(J+1) \frac{\hbar^2}{8\pi^2 I}$$

$$E = \frac{1}{2} I \omega^2$$

$$E_L = \frac{\hbar^2}{8\pi^2 I} J(J+1)$$

Space.



Can be converted by ν cm⁻¹

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

$$\frac{1}{\lambda} = \frac{E}{hc}$$

Always:

$$\text{freq} = \frac{\nu}{\lambda}$$

and $\nu \propto \omega_0$

Now, rotational energy can be changed into cm⁻¹.

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

$$\nu = \frac{\hbar}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}$$

$\rightarrow B = \text{rotational constant.}$

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

* Selection rule :- for rotational spectroscopy

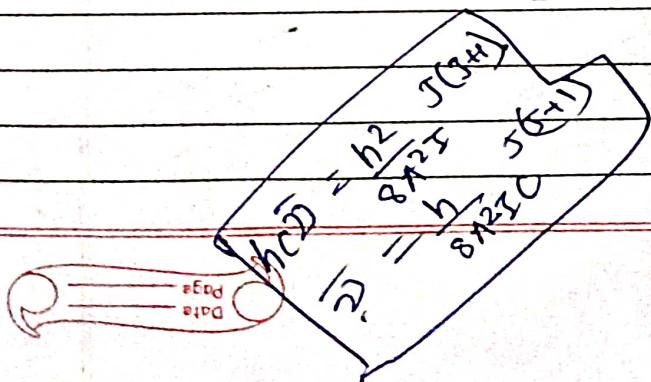
$$\Delta J = \pm 1$$

$\Delta J = +1$ Absorption ^{rotational} spectroscopy

$\Delta J = -1$ Emission ^{rotational} spectroscopy

J = rotational quantum no.

$$\nu'$$



$$* E_J = \frac{h^2}{8\pi^2 J} J(J+1) \text{ Joule.}$$

$$\nu = \frac{h}{8\pi^2 J C} J(J+1) \text{ cm}^{-1}.$$

$$\nu = BJ(J+1) \text{ cm}^{-1}.$$

$$\Delta J = \pm 1$$

ΔJ

$$\nu_J = BJ(J+1)$$

$$\nu_{J+1} = B(J+1)(J+2)$$

$$\nu_{J+1 \rightarrow J} = B(J_1)(J+2) - BJ(J+1)$$

$$\nu_{J+1 \rightarrow J} = 2B(J+1).$$

$$2\nu_{0 \rightarrow 1} = 2B$$

$$\nu_{1 \rightarrow 2} = 9B$$

$$\nu_{2 \rightarrow 3} = 6B$$

Q) The pure rotational spectrum of CN molecule in gaseous phase shows a series of equally spaced lines with interspacing 3.8 per cm^{-1} . Calculate the internuclear distance of CN molecule.

$$^{12}\text{C} = 12$$

$$^{14}\text{N} = 14 \text{ g/mole}$$

$$\Rightarrow 2B = 3.8$$

$$B = \frac{3.8}{2} = 1.9$$

$$B = 1.9$$

$$D = \frac{h}{8\pi^2 I C}$$

$$I = \frac{h}{8\pi^2 C \cdot B}$$

$$= \frac{6.64 \times 10^{-34}}{8 \times (0.14)^2 \cdot 3 \times 10^8 \times 1.9} = \frac{6.64 \times 10^{-34}}{449.59}$$

$$\frac{h}{8\pi^2} = \dots \Rightarrow 0.014 \times 10^{-42}$$

$$I = 1.4 \times 10^{-44}$$

$$M = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 14}{26} = 6.46$$

$$\text{for 1 molecule} \Rightarrow \frac{6.46}{6.023 \times 10^{23}} = 1.07 \times 10^{-23}$$

$$I = M \cdot r^2$$

$$\frac{I}{M} = r^2$$

$$\text{or } r = 3.6 \times 10^{-12} \text{ cm}$$

$$r = \sqrt{\frac{I}{M}}$$

$$r = \sqrt{\frac{1.4 \times 10^{-44}}{6.46}} = \sqrt{0.216 \times 10^{-44}} = 1.0 \times 10^{-22} \text{ m}$$

$$r = \sqrt{\frac{1.4 \times 10^{-44}}{1.07 \times 10^{-23}}} = \sqrt{0.0013 \times 10^{-44}} = 0.36 \times 10^{-11} \text{ m}$$

$$r = 0.36 \times 10^{-11} \text{ m}$$

Q) The internuclear distance of NaCl is $2.36 \times 10^{-10} \text{ m}$.

Ques. Calculate the reduced mass & mol I of NaCl

Ans. At mass of Cl = ~~35.5~~ $35 \times 10^{-3} \text{ kg/mol}$.
" " Na = $23 \times 10^{-3} \text{ kg/mol}$.

Reduced mass = $\frac{m_1 m_2}{m_1 + m_2}$

$$\Rightarrow \frac{35 \times 23 \times 10^{-6}}{(35+23) \times 10^{-2} \times 6.023 \times 10^{23}}$$

$$\frac{805}{58} \times 10^{-3} \times 10^{-23}$$

$$= 13.87 \times 10^{-26} \text{ kg/mol}$$

$$m_r = 8.30 \times 10^{-26} \text{ kg}$$

$$I = m R^2$$

$$= 13.87 \times (2.36 \times 10^{-10})^2 \text{ kg m s cm}^2$$

$$R^2 = 5.56 \times 10^{-20}$$

$$I = m R^2$$

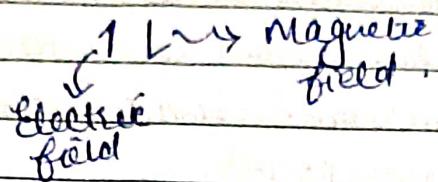
~~$$I = m R^2$$~~

$$I = 2.30 \times 10^{-26} \times 5.56 \times 10^{-20} \text{ kg m s}$$

$$I = 12.78 \times 10^{-46} \text{ kg m s}$$

9 MP

* Vibrational spectroscopy :- (IR spectroscopy).



Incident radiation frequency =
creates Resonance.

$O=C=O \rightarrow$ dipole moment creates heat
due to Resonance.

* It involves the transition between vibrational energy levels of a molecule on the absorption of radiations falling in the spectral range of $500 - 4000 \text{ cm}^{-1}$ (IR region).

* During the vibration of a molecule there should be change in dipole moment lead to the generation of an oscillating electric field. So, as the frequency of this oscillating electric field is equal to the frequency of fluctuating electric field of radiation. This phenomenon causes resonance and hence energy can be transferred from the radiation to the molecule or vice versa.

* IR Inactive molecules.

H_2, N_2, O_2 ($\mu = 0$) \rightarrow permanently.

* IR Active molecule : molecules having a permanent dipole moment and exhibit a change in dipole moment during the vibration.

$NO_2, H_2O, HCl,$



Case-II :-

- Molecules having net permanent dipole moment but due to their vibrational modes, change in dipole moment leads to the generation of IR active or spectra.

e.g. CO_2

* Types of Molecular Vibration

Molecular Vibrations (AX_2 Type)

Stretching (Bond length)

Bending.

Symmetrical



Asymmetrical



In plane

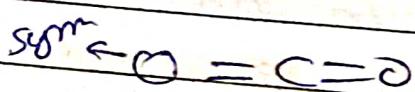
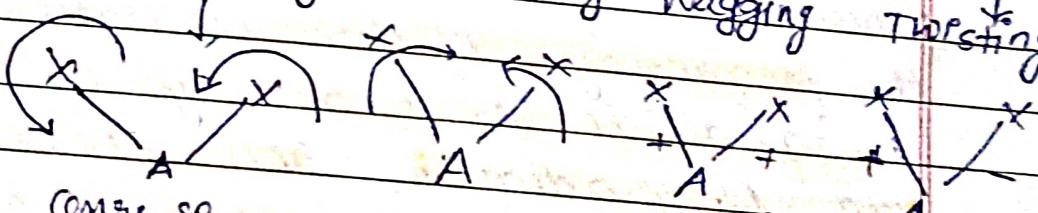
out of plane.

Rocking

Scissoring

Wagging

Twisting.

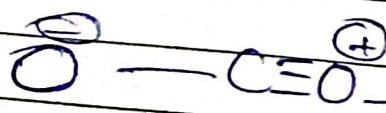


Conc se

Bonded atoms
↑ spin ↑
opp.

diff opp.

diff → same.



Asymm.

* Stretching :- In this type of vibrations the distance between atoms increases or decreases but the bond axis remains constant.
It is of two types :-



(i) Symmetric vibration : In this stretching the movement of the atoms w.r.t the central atom in a molecule is in the same dirn.

(ii) Asymmetric : In this one atom approaches towards the central atom whereas other moves away from the central element.

* Bonding Vibrations :-

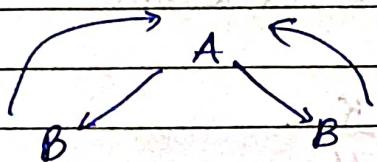
In this type of vibrations the position of the atom changes w.r.t the original bond axis but the distance between atoms remains same. It is of two types (i) -

(1) In plane^(2D) bonding vibrations : In this type atom remains in the same plane as the nodal plane of the system.
It is of two types.

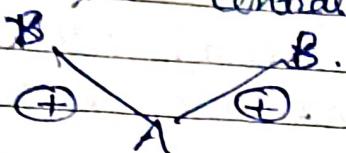
(a) Rocking : In this type of vibrations both atoms move in the same dirn.



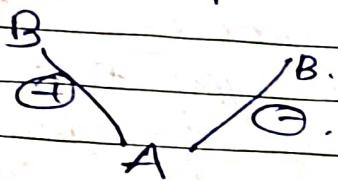
(b) Scissoring : In this both the atom swing in the opposite dirn



- (ii) Out of plane :- It is 3-D type vibration.
 It is of two type :-
 (a) wagging :- In this both the atom swing up and down the plane.
 w.r.t. the central atom.



- (b) Twisting :- In this type one atom moves up the plane and the other moves down the plane w.r.t central atom.



\rightarrow $(+)$ & $(-)$ signs indicate the motion towards and away from reader (receiver).

* **Vibrational frequency :-** (Hooke's law. = $\frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$)
 for vibrational frequency. e.g. Hooke's law

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

K = force constant.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

force constant = bond strength.

$$(\bar{\nu})^2 = \frac{1}{4\pi^2 c^2} \frac{K}{\mu}$$

$(\bar{\nu}^2 \mu) 4\pi^2 c^2 = K$

Q) Calculate the approximate frequency of the C-H stretching from the following
 $k = 500 \text{ N/m}$

$$\text{mass of C} = 20 \times 10^{-24} \text{ gm.}$$

$$\text{mass of H} = 10 \times 10^{-24} \text{ gm.}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

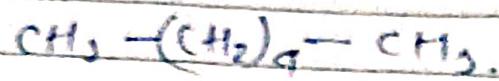
$$\mu = \frac{32 \times 10^{-48+24}}{21.6} \\ = 1.48 \times 10^{-24}$$

* Applications of IR Spectroscopy :-

- (i) Comparison bet'n two compounds (finger print Region).
The most powerful function of IR spectroscopy is establishing to identify two samples. It is based on the possibilities of two different compounds having the same IR spectra is negligible. and so this type of IR spectra is also called finger print of a molecule.
- (ii) It is categorised as : If two pure samples have different IR spectra, the compound must be different.
If they've exactly same spectra when run in the same medium under similar conditions the two samples are of the same compound.
Actually the region from 3000 to 1500 cm⁻¹ in IR spectrum is useful for ~~identifi~~ identification of functional group. This region shows the absorption due to stretching mode. The region below 1500 cm⁻¹ (1500 to 600 cm⁻¹) contains no. of vibrations caused by bending and stretching vibrations. In this content each organic compound has its own unique absorption pattern and so this part of Spectrum is called finger print region.

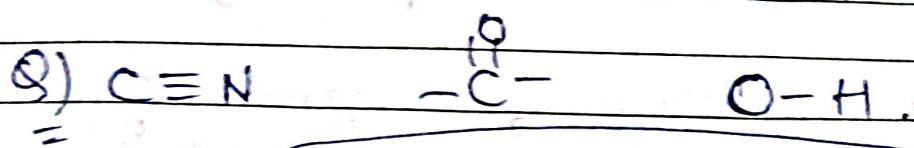


Benzene



n-hexane.

IR range for benzene will be higher than n-hexane as for $\text{C}=\text{C}$, IR range is \uparrow than $\text{C}-\text{C}$.



$1600 \text{ cm}^{-1}, 1730 \text{ cm}^{-1}, 4200 \text{ cm}^{-1}.$) \rightarrow What?

(b) The fundamental vibrational frequency of CO is 2140 cm^{-1} , calculate the force constant of the molecule. Given at mass ~~16.0~~ 18.0

$$C_{12} = 19.9 \times 10^{-27} \text{ kg.}$$

$$m = 26.6 \times 10^{-27} \text{ kg.}$$

$$\omega = \frac{19.9 \times 10^{-27} \times 26.6 \times 10^{-27}}{(19.9 + 26.6) \times 10^{-27}}$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$

$$529.34 \times 10^{-27}$$

$$46.5$$

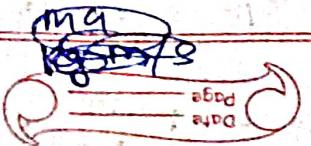
$$(2\pi\omega)^2 m = K.$$

$$4\pi^2 D^2 m = K$$

$$= 11.38 \times 10^{-27}$$

$$K = 4 \times (3.14)^2 \times (11.38 \times 10^{-27}) \times (2140)$$

$$K = 2.05 \times 10^{-18} \text{ Nm}^2/\text{kg spec}^2$$



8/1

* NMR :- Nuclear Magnetic Resonance:

→ It is a branch of spectroscopy in which radio frequency wave induced transitions between energy levels of nuclei of a molecule which are induced by nuclei keeping the nuclei in a magnetic field.

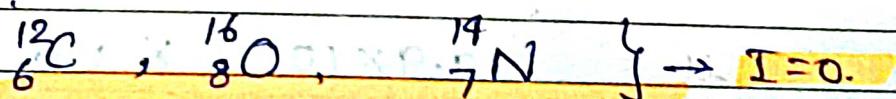
→ NMR is also the study of magnetically distinct nuclei of type in a molecule. It depends on nuclear spin quantum number (I) has -

- (i) Nuclei which have $I=0$ are spin inactive.
- (ii) Nuclei which have $I \neq 0$ are spin active.

NMR active.

* Rules for NMR active :-

• Nuclei with atomic no. even and mass no. also even will have $I=0$. and will be NMR inactive.



- Atomic no. even mass no. odd $\rightarrow I \neq 0$.
- Atomic no. odd mass no. even $\rightarrow I \neq 0$.
- Atomic no. odd mass no. odd $\rightarrow I \neq 0$.

NMR Active.



^{14}N

$$\begin{aligned} & \xrightarrow{\text{Proton}} \text{Pd operator} \\ & (3) C_6 = 6P + 7\bar{N} \\ & \quad \quad \quad = 0 + 2 = \\ & \quad \quad \quad I = \frac{1}{2} \end{aligned}$$

$$\begin{aligned} & ^{14}N \rightarrow 7P + 7\bar{N} \\ & (I=0) \\ & 7N = 1P + 1\bar{N} \\ & \quad \quad \quad I = \frac{1}{2} + \frac{1}{2} \rightarrow \frac{1}{2} \end{aligned}$$

* The possible allowed spin state is calculated by the formula. ($2I + 1$.)
 ↑
 spin quantum no.

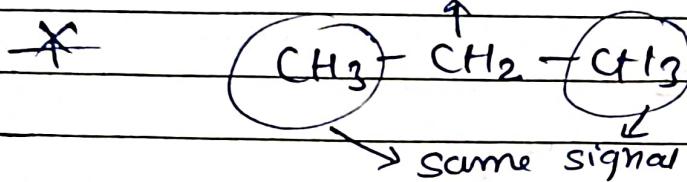


possible allowed spin state

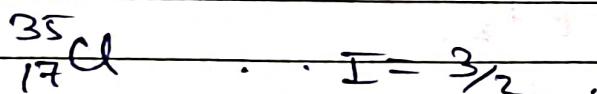
$$= 2I + 1$$

$$= 2 \times \frac{1}{2} + 1$$

$$= 2$$



no. of signal. = 2



possible allowed spin

$$\Rightarrow 2 \times 2 + 1$$

$$\Rightarrow 4$$



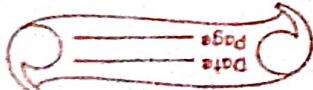
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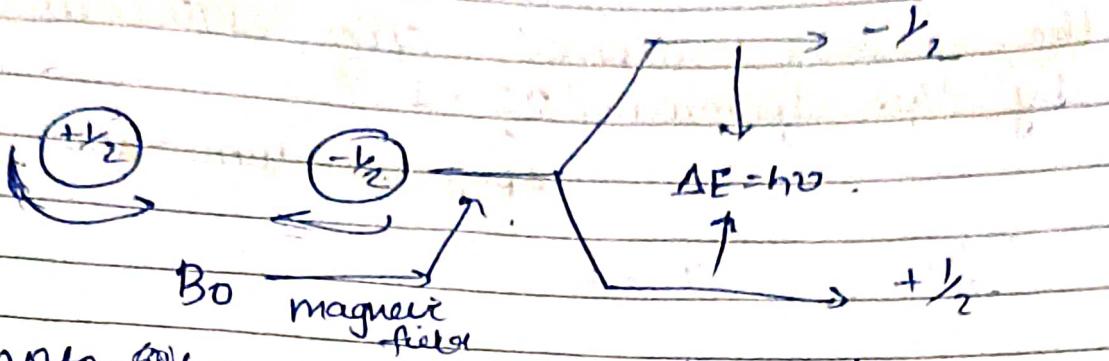
nuclei : 1H 2H ${}^{12}_6C$ ${}^{15}_7N$ ${}^{16}_8O$ ${}^{35}_{17}Cl$

I : $\frac{1}{2}$ 1 0 1 0 $\frac{3}{2}$.

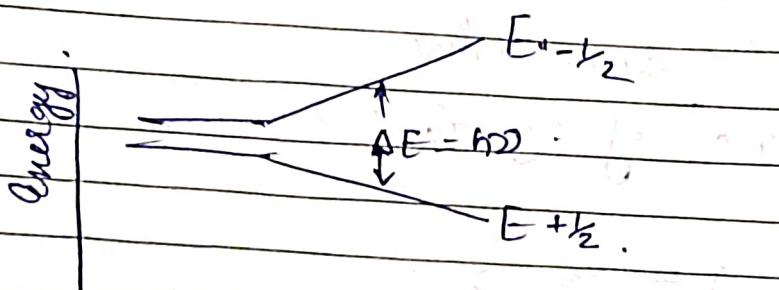
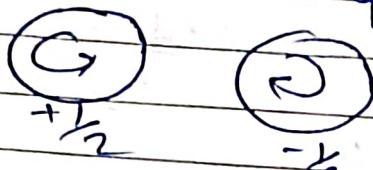
* 1H \rightarrow energy ↑↑
 \uparrow Align → magnetic field.. \rightarrow magnetic field in the opp' dirn i.e. new

Energy ↓↓





→ (ii) photon has two possible degenerate spin state in the absence of external magnetic field as



no magnetic field \hookrightarrow applied magnetic field.

$$\Delta E \propto B_0$$

$$\Delta E = K B_0 = h\nu$$

\hookrightarrow proportionality constant

$$\boxed{\Delta E = f(B_0)}.$$

* We know that,

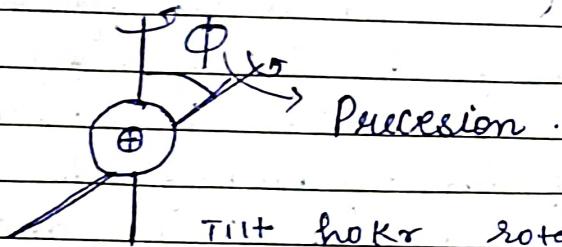
ΔE value also depends on nature of nuclei (γ).

$$\Delta E = f(\gamma B_0)$$

γ depends on the nature of nuclei.

γ = magnetic moment.

angular magnetic moment.



Tilt hokr rotate krt.

ω = angular frequency.
= precession frequency.

We also know, $\Delta E = \hbar \omega$.

$$\hbar \omega = \frac{\hbar}{2\pi}$$

$$\omega = \frac{1}{2\pi}$$

$$\text{mag. mom} = MVR$$
$$\text{ang. rot. mag.} = \frac{M}{2\pi} \hbar$$

$\gamma \rightarrow$ gyromagnetic

constant

$$\Delta E = f(\gamma B_0)$$

$$\Delta E = \frac{\hbar}{2\pi} \gamma B_0$$

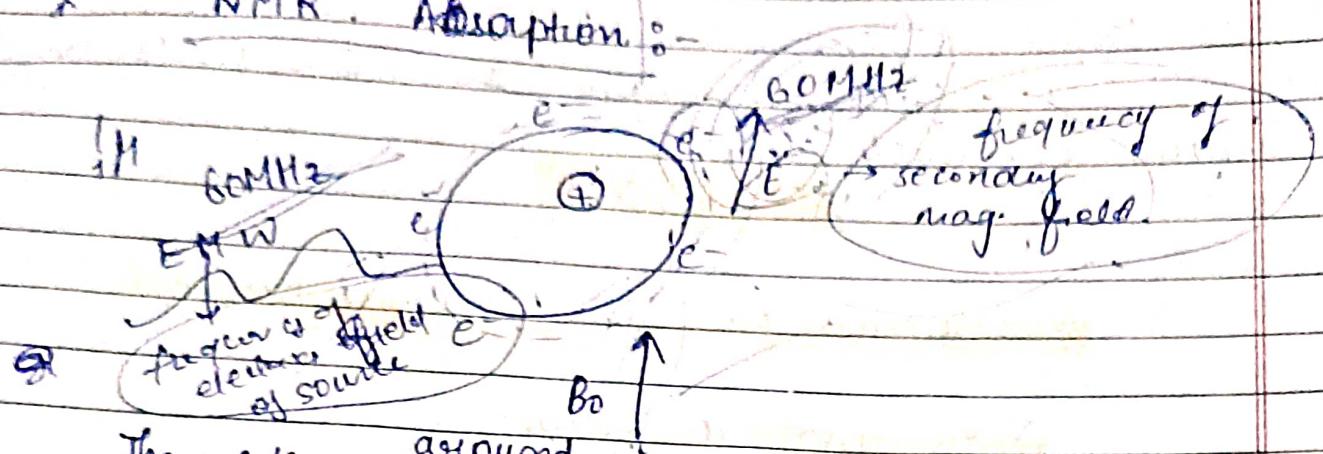
$$\Delta E = \hbar \omega$$

$$\hbar \omega = \frac{\hbar}{2\pi} \gamma B_0$$

$$\omega = \frac{1}{2\pi} \gamma B_0$$

$\gamma B_0 \rightarrow$ Larmour frequency

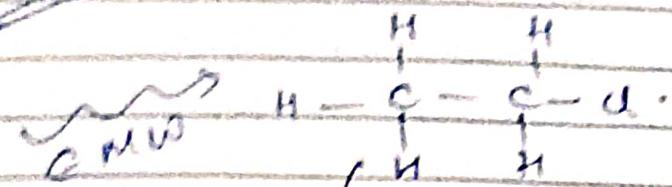
* NMR Absorption :-



The e^- s around the protons are induced to circulate in a magnetic field after electromagnetic radiation falls on the nuclei of a proton. These circulating e^- s generate a small secondary magnetic field. If the frequency of secondary magnetic field is coupled with magnetization or waves of incident radiation, then it is called nuclear magnetic resonance.

Now, when the frequency of secondary magnetic field generated by circulating e^- s becomes equal to the frequency of incident field of incident radiation, then emitted radiation is absorbed by nuclei of a given photon. and so, it is also called NMR Absorption.

10/29/24

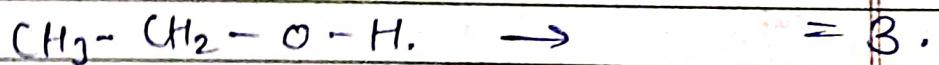
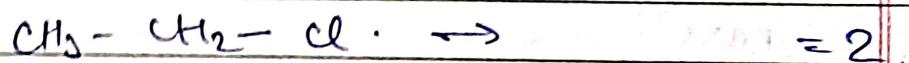
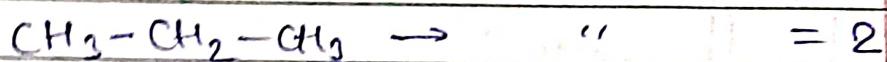
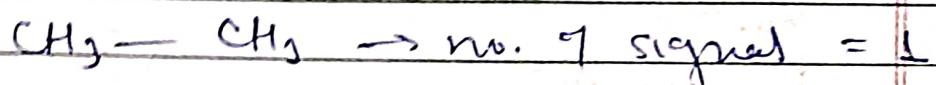


Secondary decay field
balance nuclear spin

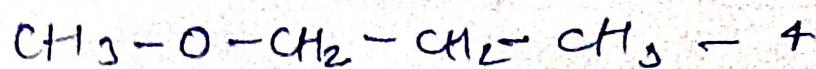
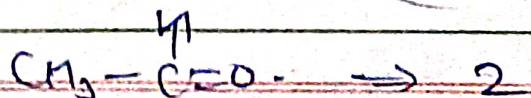
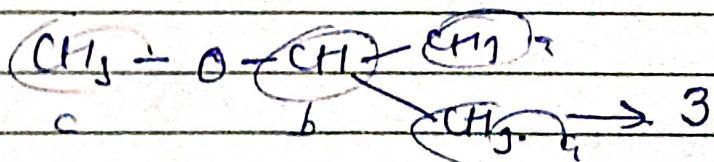
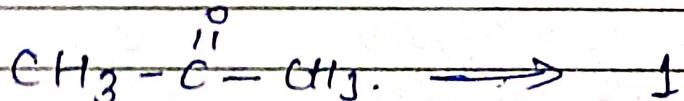
TMS

left magnetic field of EMW (source).
 → align in the dirⁿ of protons

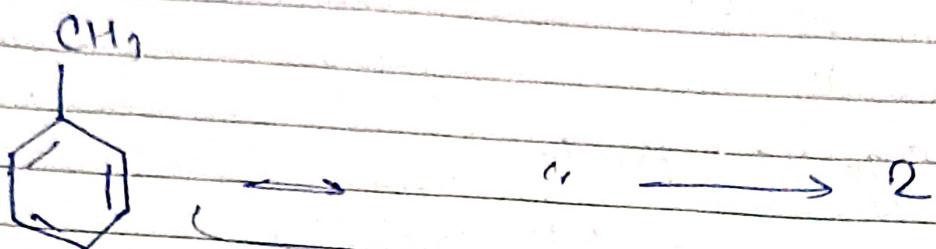
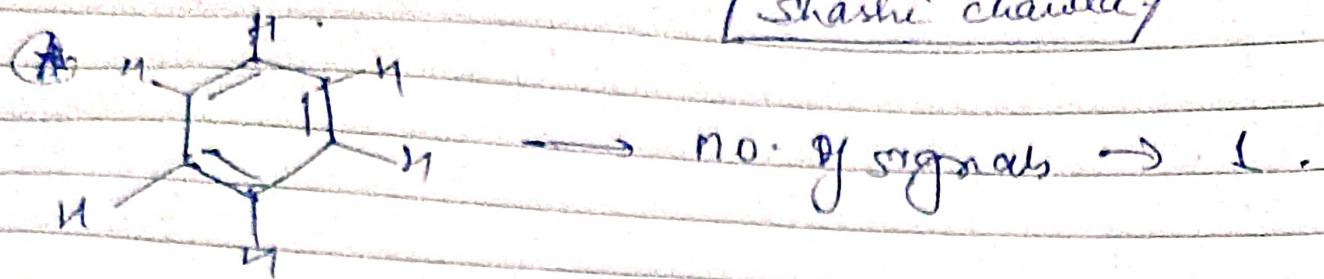
* CHEMICAL SHIFT.



Also * [Radio freq wave used.] \rightarrow MRI. \rightarrow Magnetic Resonance Image



(shashi chawla)

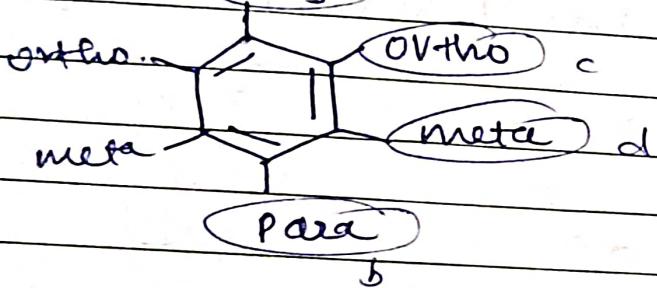


two case

I

High Resolution

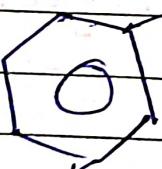
CH_3 a



Low Resolution

2

4



3

Units in NMR Spectroscopy :-

- δ (Delta) is used for expressing chemical shift position.
- These are undefined as proportional differences from TMS (Tetra Methyl Silane) as reference standard in ppm.
- Let operating frequency of the instrument = v_0 Hz
frequency of TMS = v_{TMS} Hz

frequency of unknown group of protons = v_u Hz

Chemical shift positions for resonance group of protons in a given molecule.

$$\delta = \frac{v_u - v_{TMS}}{v_0} \times 10^6$$

Q = what is the shift of the resonance from TMS of a group of nuclei with $\delta = 3.50$ at an operating frequency of 350 MHz

$$\delta = 3.50$$

~~$v_0 = 350 \times 10^6 \text{ Hz}$~~

$$\delta = \frac{v_u - v_{TMS}}{v_0} \times 10^6$$

$$\frac{v_0 \cdot \delta}{10^6} = v_u - v_{TMS}$$

$$\frac{350 \times 10^6 \times 3.5}{10^8} = v_u - v_{TMS}$$

$$= 35 \times 3.5 = v_u - v_{TMS}$$

→ Generally chemical shift have delta value ranges from 0 to 10.

→ NMR signal is plotted with magnetic field strength (B_0), decreasing to the left (down field).

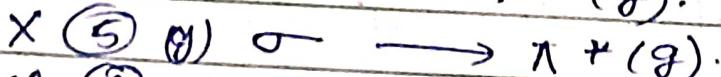
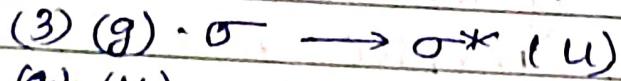
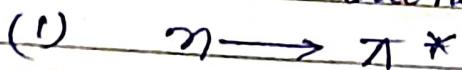
Greater the shielding of protons, smaller will be the value of delta, and the signal for TMS appears at extreme origin of the spectrum with delta $\delta = 0$.

→ At high magnetic field strength (up field), or low frequency.

* UV - Visible spectroscopy $\approx (200 - 800 \text{ nm})$

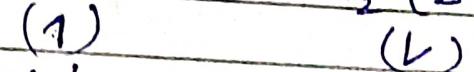
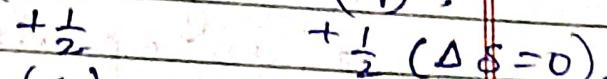
$n \rightarrow$ lone pair projector

Possible transitions

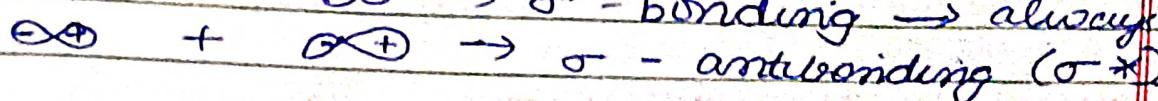
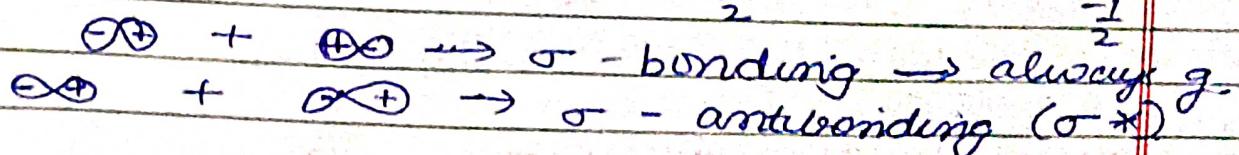
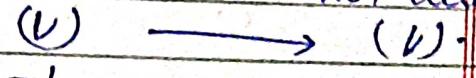


Selection rule

$$\Delta S = 0$$



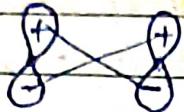
$\Delta S = -1$ not allowed



(2) Symmetry rules.

$g \rightarrow$ gerade centre of symmetry (g)

$u \rightarrow$ ungerade centre of symmetry (u).



$\sigma - g$

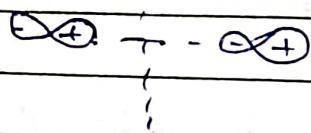
$p - u$

$d - g$

$f - u$

No symmetry in σ (Ungerade).

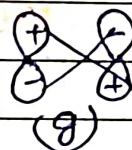
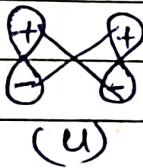
(Ungerade).



Antibonding \Rightarrow Strength of wave less

$(\sigma^*) \rightarrow$ Ungerade

tendency of e^- gain less



possible transitions:

$g \rightarrow u$ } possible

$u \rightarrow g$

$g \rightarrow g$ } not possible

$u \rightarrow u$

* Allowed electronic transitions.

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

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

(3) $\sigma \rightarrow \sigma^*$

(4) $\pi \rightarrow \pi^*$

Energy level :-

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

UV-visible Spectroscopy :- (Electronic spectroscopy).
 → It involves the transition of electrons within a molecule or ion from a lower to a higher energy level or vice versa. By the absorption or emission of radiations falling in the UV-visible range of electromagnetic spectrum.

Range :- (200 - 800 nm).

UV range :- (200 - 400 nm).

Visible range :- (400 - 800 nm).

When we are allowed to EMW in the range of 200 - 800 nm, the electronic transition occurs :-

Molecule.

(200 - 800 nm).

EMW

→ LUMO

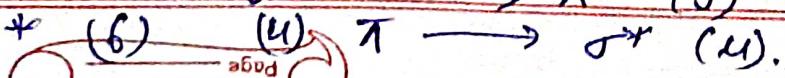
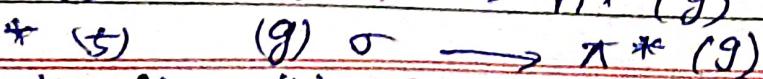
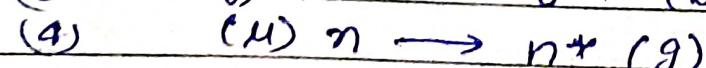
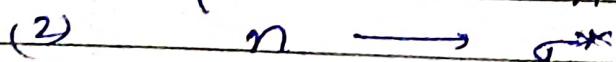
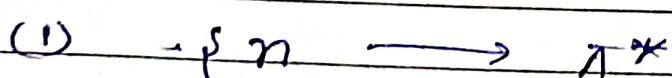
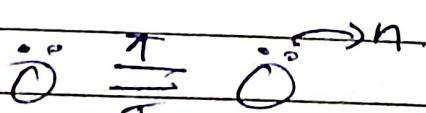
(lowest unoccupied molecular orbital) [Vacant orbitals].

→ HOMO

(highest occupied mol. orbital).

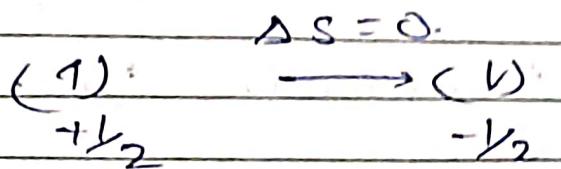
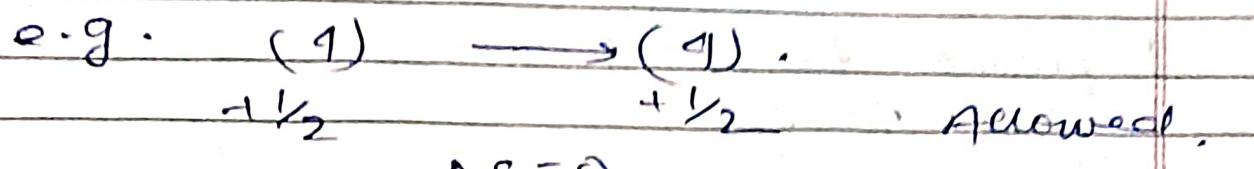
→ Electronic transition in a molecule can be classified as :-

e.g.



→ But the energy is quantised and so all possible transitions are not allowed.
It depends on :-

(1) Selection rule $\rightarrow \Delta S = 0$.



$\Delta S = -1$. not allowed.

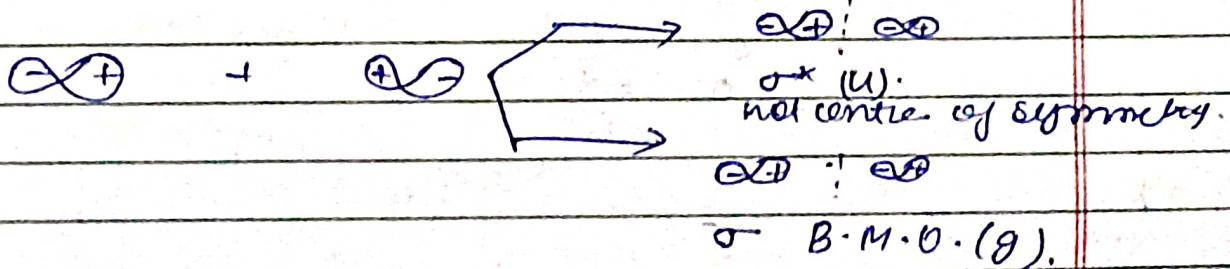
* Symmetric rule :-

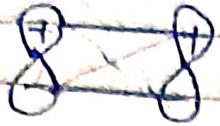
→ Structure having centre of symmetry termed as gerade (g). not having centre of symmetry termed as ungerade (u).



s-orbital = g.

→ σ bond is formed by the linear combination of atomic orbital as :-





π -bonding
no centre of symmetry.

π^* (g).
Centre of symmetry.

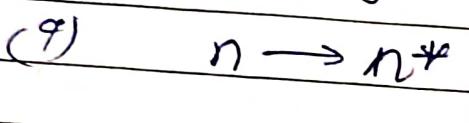
↑ possible transitions are
and therefore.



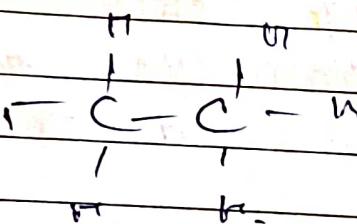
2) $n \rightarrow \sigma^*$ } forbidden (low intensity).



{ Symmetrically allowed.
(high intensity).



* Ethene



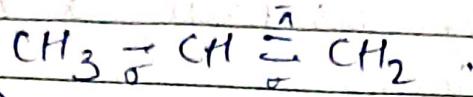
$\sigma - \sigma^*$ Excitation possible



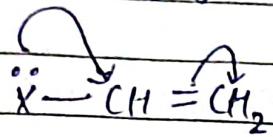
Ch

force \Rightarrow colour

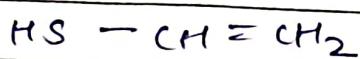
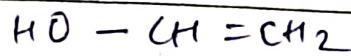
* Chromophore \rightarrow colour carrier agency.
due to conq of cov bond. (cong $\rightarrow \pi \rightarrow \pi^*$)



Aurochromic
↑
1



colour enhancing
agency.



* Chromophore.

* Chromophore :-

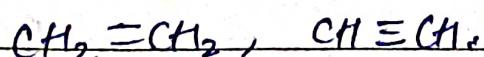
\rightarrow In greeR chromophore means colour carrier.

i.e. a chromophore is a group which is responsible for imparting colour to the compounds.

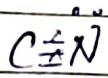
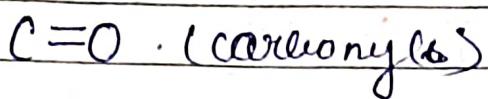
e.g. NO_2 group is a chromophore, because it ~~not~~ imparts yellow colour to the nitro compounds. But, nowadays chromophore can be defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or the visible region.

* Types of chromophore :-

(i) $\pi - \pi^*$ transition : Chromophore which contains π electrons and it undergoes $\pi - \pi^*$ transition.



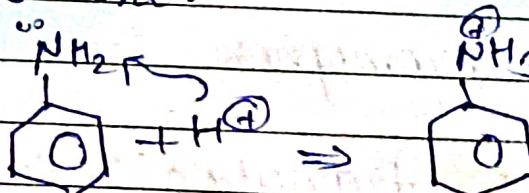
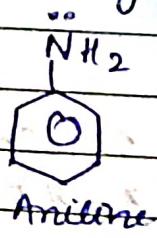
(ii) $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ is chromophore, which contain both π and n electrons. and they undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.



* Auxochromes :-

- Colour enhancing group.
- It has the ability to extend the conjugation of the chromophore by two sharing of the non-bonding O-Is. and thus shifts the C-L-P absorption band towards the longer wavelength (red or blue shift) of the spectra.
- Auxochrome by itself does not act as chromophore. e.g. -OH, -CH₃, -NH₂, -OR, etc.

* Hypso-Hypsochromic shift :- It leads to the shift of absorption maxm towards shorter wavelength. It is also called blue shift. and arises due to either the removal of conjugation or change in polarity of the solvent.



Blue shift

e.g. Absorption max^m of Aniline shift from 280 nm to 290 nm in acidic soln. results due to formation of Anilinium ion from aniline.

* **Bathochromic Shift :-** It leads to the shift of absorption max^m towards longer wavelength due to the presence of auxochrome. It is also called red shift.

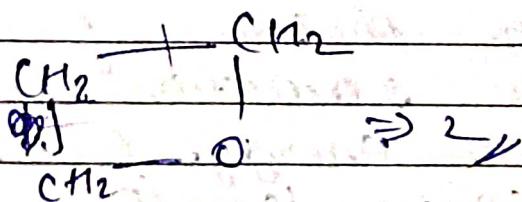
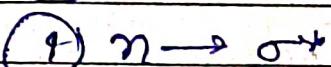
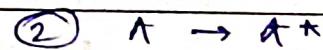
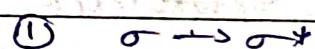
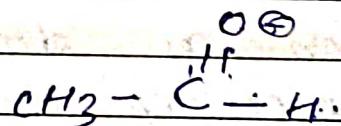
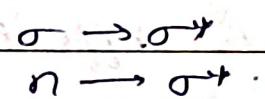
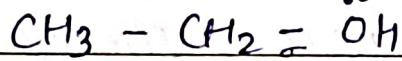
e.g.: $\pi \rightarrow \pi^*$ transitions of carbonyl compound experience bathochromic shift when the polarity of the solvent is lowered.

* **Hyperchromic effect / shift :-**

→ It leads to the increased intensity of absorption.

* **Hypochromic shift :-**

→ It leads to the decreased intensity of absorption.



UV - Visible Spectroscopy:

UV

200 - 900 nm

Visible

400 - 800 nm.

gaseous / liquid / transparent crystal.

* RAMAN Effect :-

→ When a sample is allowed to pass through a beam of monochromatic light, a very small fraction of it is scattered in all directions. If the scattered light in a direction perpendicular to the incident beam is spectrographed, it shows a strong line (Raman Rayleigh line), corresponding to the frequency of incident line and weak lines on either side of it known as anti-Stokes and Stokes line. The plot of these frequency shifts, against their intensities is RAMAN effect.

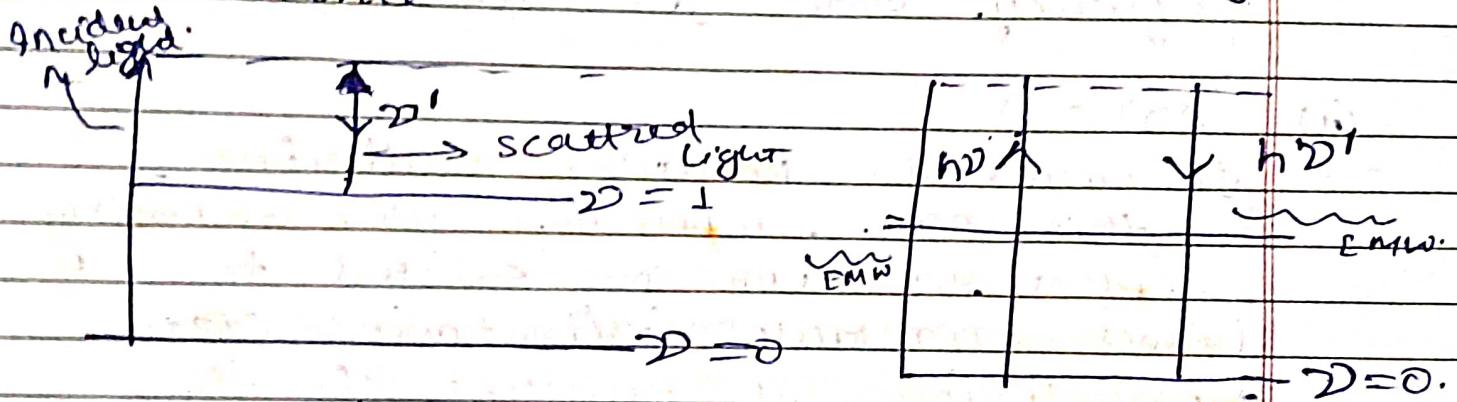
* Mechanism :-

→ It can be also understood as, when a molecule collides with photon of frequency ν . It absorbs radiation and change from ground state energy level (E) to excited state energy level (E'). acc to conservation principle.



$$E' - E = h(\nu - \nu') \\ = h\Delta\nu$$

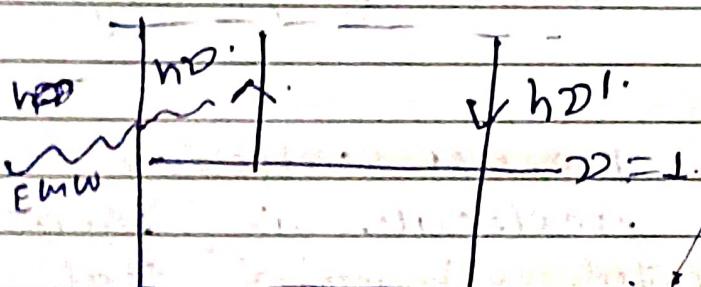
The Raman shift ($\Delta\nu$) has the same value for different frequencies of incident light for a given substance. Thus RAMAN shift is independent of the frequency of the incident light i.e. characteristics of the scattering substance.



Case (I) $\nu > \nu'$

Case (II) $\nu = \nu'$.

Raman effect
 $\Delta\nu = \nu - \nu'$



(III)

$\nu < \nu'$

{ In betw Rotational & Vibrational Phenomenon these occur



for case 1 :-

$\nu' \rightarrow$ frequency of
Scattered Radiation

(i) $\Delta\nu > 0$:-

→ It results in RAMAN scattering.
In this case, molecule returns to different vibrational state after excitation from the ground vibrational state. The molecule emits a radiation with a lower frequency than the incident light. This RAMAN scattered lines which are absorbed in the small frequency side are called STOKER lines.

(ii) $\Delta\nu = 0$.

→ It results in Rayleigh scattering.
In this case, molecule after absorbing incident radiation gets excited to higher unstable vibrational state from which it returns to the original vibrational state after emitting a radiation of similar frequency.

(iii) $\Delta\nu < 0$:-

→ It results in RAMAN scattering.
In this case, molecule is promoted from first excited vibrational state to higher unstable vibrational state by the absorption of Radiation corresponding to the frequency ν and when the excited molecule returns to the ground state, it emits radiation



which are of higher frequency than the incident light. These types of RAMAN scattering lines are called Anti Stokes.

→ The Intensity of these lines are in the order :-

Rayleigh line. > Stokes lines > Anti Stokes lines.

→ Vibrational Raman. spectra :-

The Selection rule for vibrational Raman. effect.

$$\Delta \nu = \pm 1$$

when $[\Delta \nu = +1]$.

Stokes lines corresponding to low frequency side of the incident light are observed and when

$\Delta \nu = -1$ Anti Stokes lines corresponding to high frequency side of the incident light are observed.

→ That means IR and RAMAN spectra are not ~~not~~ identical but ^{most} it is ~~approximated~~ used in the determination of molecular structures.

e.g : If a molecule has a centre of symmetry, then IR inactive but RAMAN active and vice versa.

Difference :- (IR & RAMAN)

- IR : It results due to absorption of light by vibration.
- RAMAN : Results due to scattering of light by vibrating and rotating molecules.
- IR : Change in dipole moment is essential.
- RAMAN : Change in polarisability is essential.
- IR : Water can't be used as solvent
- RAME → Water can be used as solvent
- IR : Dilute solns are preferred.
- RAMAN : Conc. solns are preferred. Otherwise weaker RAMAN lines.
- IR : Homonuclear, diatomic molecules doesn't show IR spectra.
- RAMAN : Homonuclear diatomic molecules exhibit RAMAN.