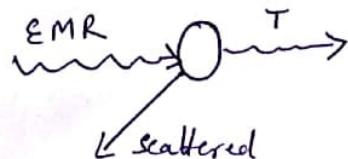


Spectroscopy Unit II

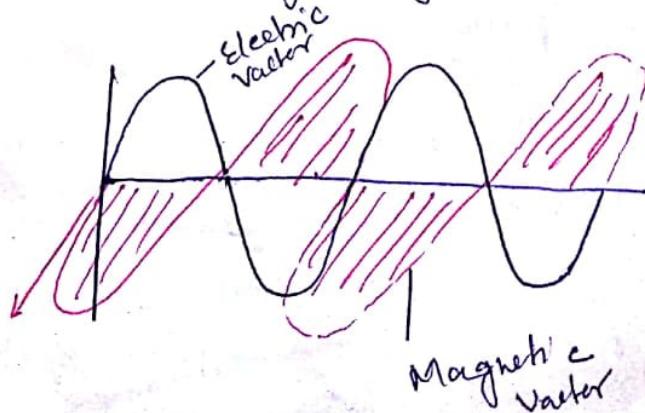
Spectroscopy is a branch of science which deals with the study of interaction of electromagnetic radiation with matter. Spectroscopy helps in determining the structure of the compound.

OR

Spectroscopy is the analysis of the electromagnetic radiation scattered, absorbed or emitted by molecules.

What is EMR?

- EMR is energy that is propagated through free space or through a material medium in the form of electromagnetic waves, such as:- radio waves, UV-visible light, Infrared Light, gamma waves etc.
- Waves or light travels in space in the form of an oscillating electric field - and this electric field generates magnetic field at right angle to itself.



Origin of spectrum

$$\boxed{\lambda \propto \frac{1}{E}} \text{ or } \boxed{\lambda \propto \frac{1}{V}}$$

A spectrum originates due to interaction of matter with EMR. Different types of radiation interact with matter or molecule in different manners by including change in different types of energy level.

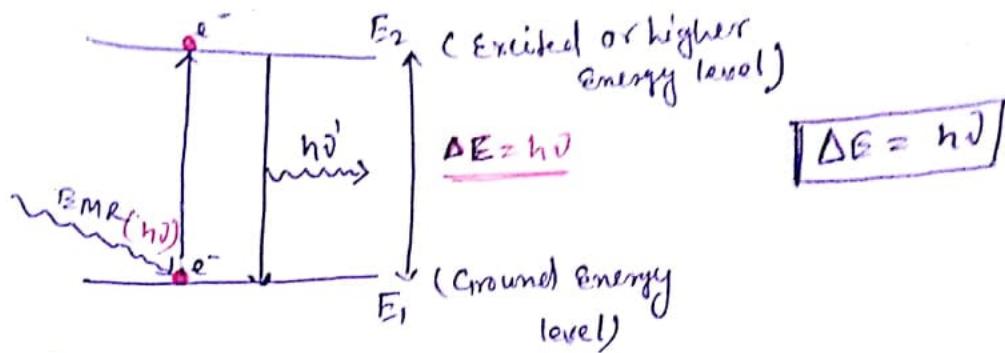
Type of Radiation	Wavelength range (λ)	Energy Change (Type of Spectroscopy)
X-rays	10 fm to 10 nm	Electronic (Core orbital)
UV (Ultra Violet)	180 - 400 nm	Electronic (Valence orbital)
Visible	400 - 800 nm	Electronic (Valence orbital)
IR	800 nm - 1 mm	Vibrational - Rotational (IR spectroscopy)
microwave	1 - 100 mm	Rotational (microwave spectroscopy)
Radio wave	100 mm - 80,000 m	Spin orientation (NMR spectroscopy)

Basic Principle of Spectroscopy -

The basic principle in spectroscopy is that the EMR provides energy equal to the energy difference (ΔE) b/w the energy levels corresponding to excited state to ground state which is equal to

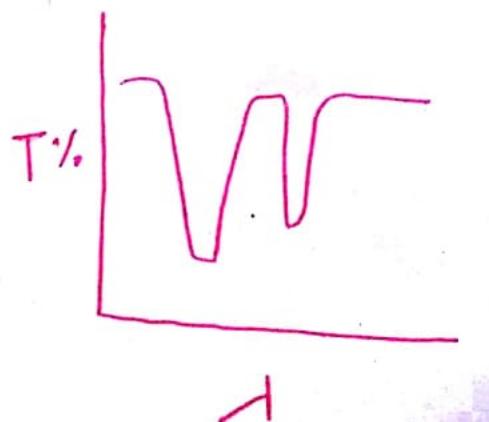
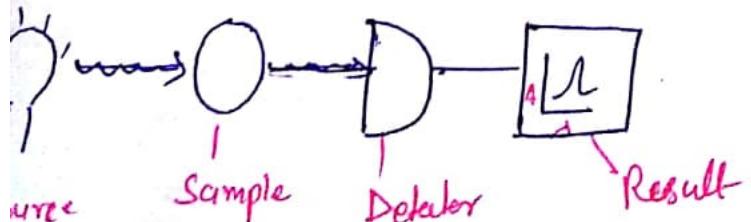
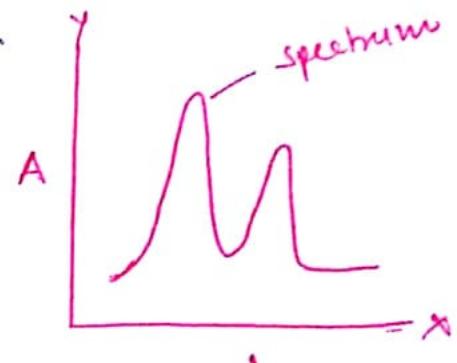
$$\boxed{\Delta E = h\nu}$$

frequency of radiation
Planck's constant



The e^- molecule/atom undergoes a transition from the lower energy to the higher energy level with the absorption of a photon ($h\nu$) of energy. ($h\nu = \Delta E = E_2 - E_1$) results absorption spectrum. When e^- in a molecule/atom returns to the ground state energy is released ($h\nu'$), ~~energy~~ results Emission spectrum. Energy released ~~or~~ emitted or absorbed is plotted against λ (wavelength), the graph is obtained is called spectrum.

Hence, A spectrum is a plot of intensity of absorption or transmittance of electromagnetic radiation as a function of wavelength (λ) over a particular range.



Types of spectroscopy -

① Atomic spectroscopy -

2) Molecular Spectroscopy

① Atomic spectroscopy :-

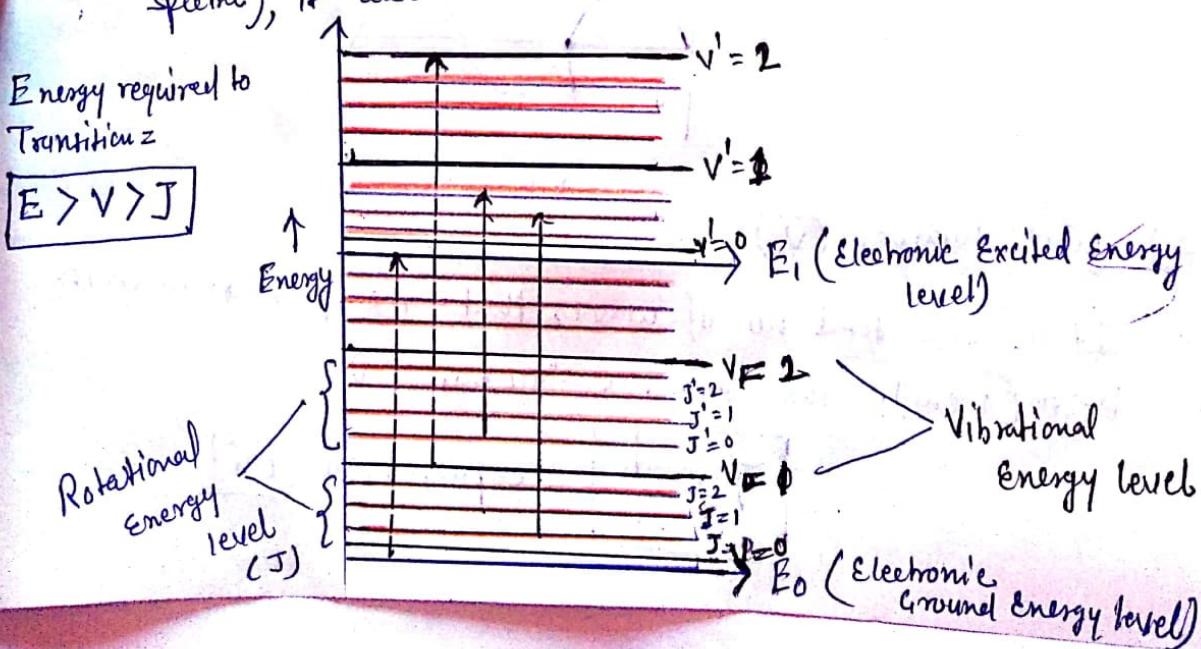
which arises from the transitions of an electron b/w the atomic energy levels.

In atomic spectroscopy, only electronic transitions are involved. That's why electronic spectra can be used to obtain detailed information about electronic structure of atoms.

2) Molecular Spectroscopy

This spectroscopy arises from the transitions of an e^- b/w the molecular energy levels.

The energy of a molecule can change not only as a result of electronic transitions but also b/cas it can make transition between its rotational and vibrational states. Thus, although molecular spectra is more complicated (than atomic spectra), it also contains more information.



Each electronic level is sub-divided into no. of vibrational energy levels. Each vibrational level in turn consists of number of closely spaced rotational energy levels. The energy required for transitions follows the order

Electronic > Vibrational > Rotational

When energy is absorbed by molecule, then it can bring about excitation of

electron from one molecular orbital to higher energy molecular orbital. It can also lead to vibration of the nuclei i.e. it can excite a nucleus from ground state to higher energy level. It can also cause the molecule to rotate as a whole exciting it from ground state rotational energy to a higher rotational energy level.

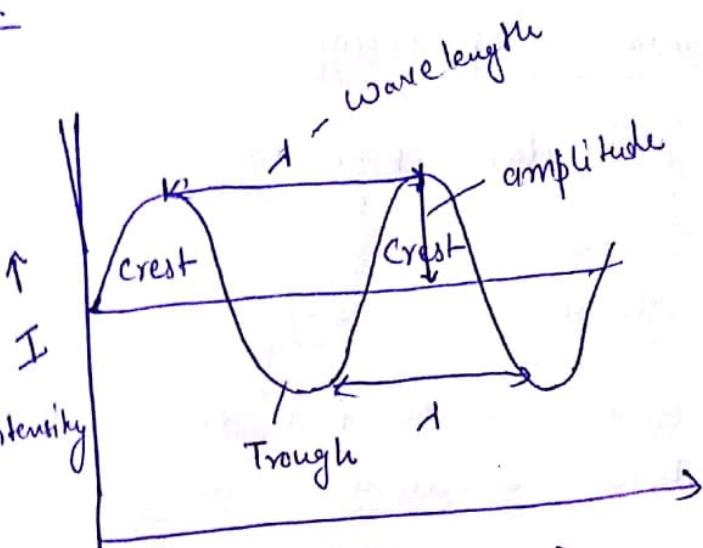
Rotational Band Spectra - The band spectra obtained as a result of transition from one rotational level of a vibrational level to a higher rotational level is called Rotational Band spectra. The energy required is very small and it take place in microwave region.

Vibrational - Rotational Band spectra - The band spectra obtained as a result of transitions from one vibrational energy level to next higher vibrational level are called Vibrational Band spectra. The band spectra obtained as a result of transition from vibrational and rotational levels to next vibrational and rotational levels are called Vibrational-Rotational Band spectra. The energy required for these transitions is available from the infra-red region.

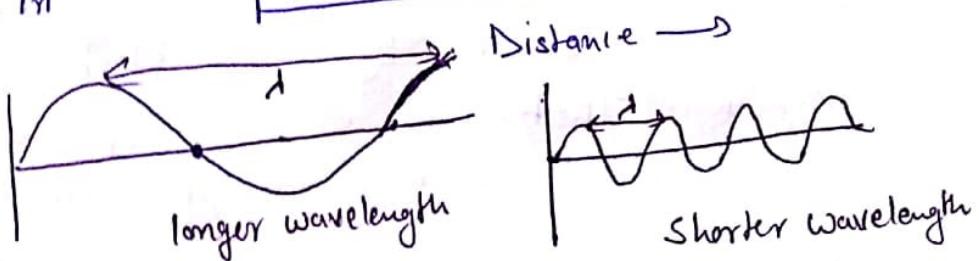
Terminology of EMR

1) Wavelength (λ)

Distance b/w two consecutive crests & troughs in a particular wave is called wavelength. Intensity



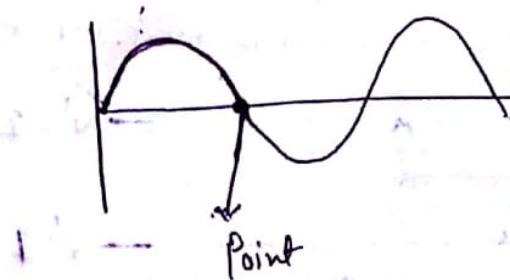
wavelength is expressed in (μm) , nm , & \AA .



2) Frequency (ν)

frequency is the no. of waves which pass through a given point in one second. The symbol for frequency is "nu" (ν)

It is expressed in cycles/sec (cps) or Hz or sec^{-1} .



3) Wave number ($\bar{\nu}$)

It is the total no. of waves that are present in unit length (1 cm). The symbol is "number" ($\bar{\nu}$)

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

expressed in cm^{-1}

4)

Velocity (c)

Velocity is the linear distance travelled by a wave in one sec. It is expressed in m/s.

$$\text{Velocity } (c) = \text{wavelength } (\lambda) \times \text{frequency } (\nu)$$

$$c = \nu \lambda$$

$$\text{or } \nu = \frac{c}{\lambda} \quad \text{or } \lambda \nu = \frac{1}{\lambda}$$

$$\text{or } \nu = c \lambda$$

5) Energy possessed by wave

Acc. to Planck's equation

$$E = h\nu$$

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

OR

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

~~h = Planck~~

h = Planck's constant

$$6.625 \times 10^{-34} \text{ Js} \quad 3 \times 10^{10} \text{ cm/s}$$

c = Velocity of wave (radiation)

λ = Wavelength of radiation

UV-Visible Spectroscopy

Ultra Violet-Visible Spectroscopy

Wavelength range — UV & Visible radiations are used

UV radiation — 200 - 400 nm

Visible radiation = 400 - 800 nm

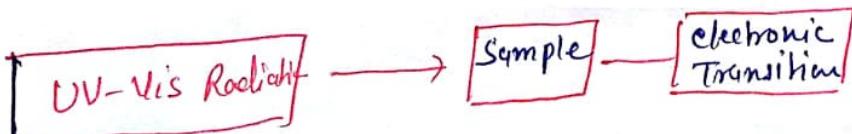
→ It is type of absorption spectroscopy

→ Electronic Transition take place so it is also called Electronic spectroscopy.

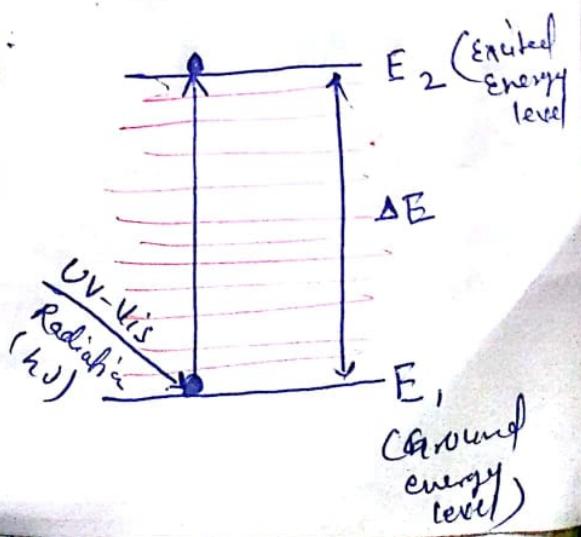
Principle of UV-Visible spectroscopy:—

On passing EMR (UV-Visible range - 200 - 800 nm) to compound a part of the radiation is absorbed by the compound. After the absorption of energy, the e⁻s in the orbital at lower energy are excited to the orbital of higher energy level.

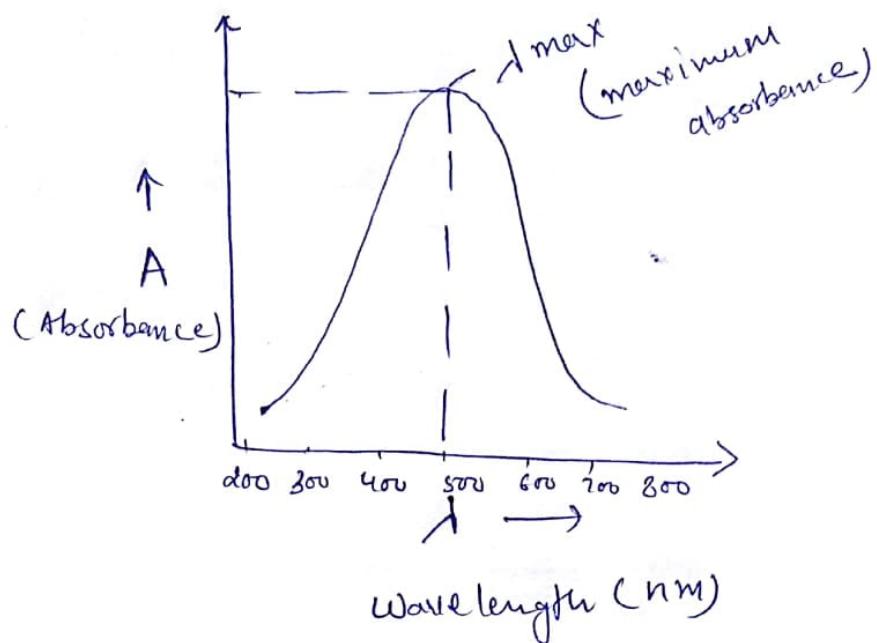
The energy absorbed by the e⁻s will equal to the difference b/w two energy levels. ($\Delta E = E_2 - E_1 = h\nu$). During this stage, spectra electronic excitation occur. Hence, it is also called "Electronic spectroscopy".



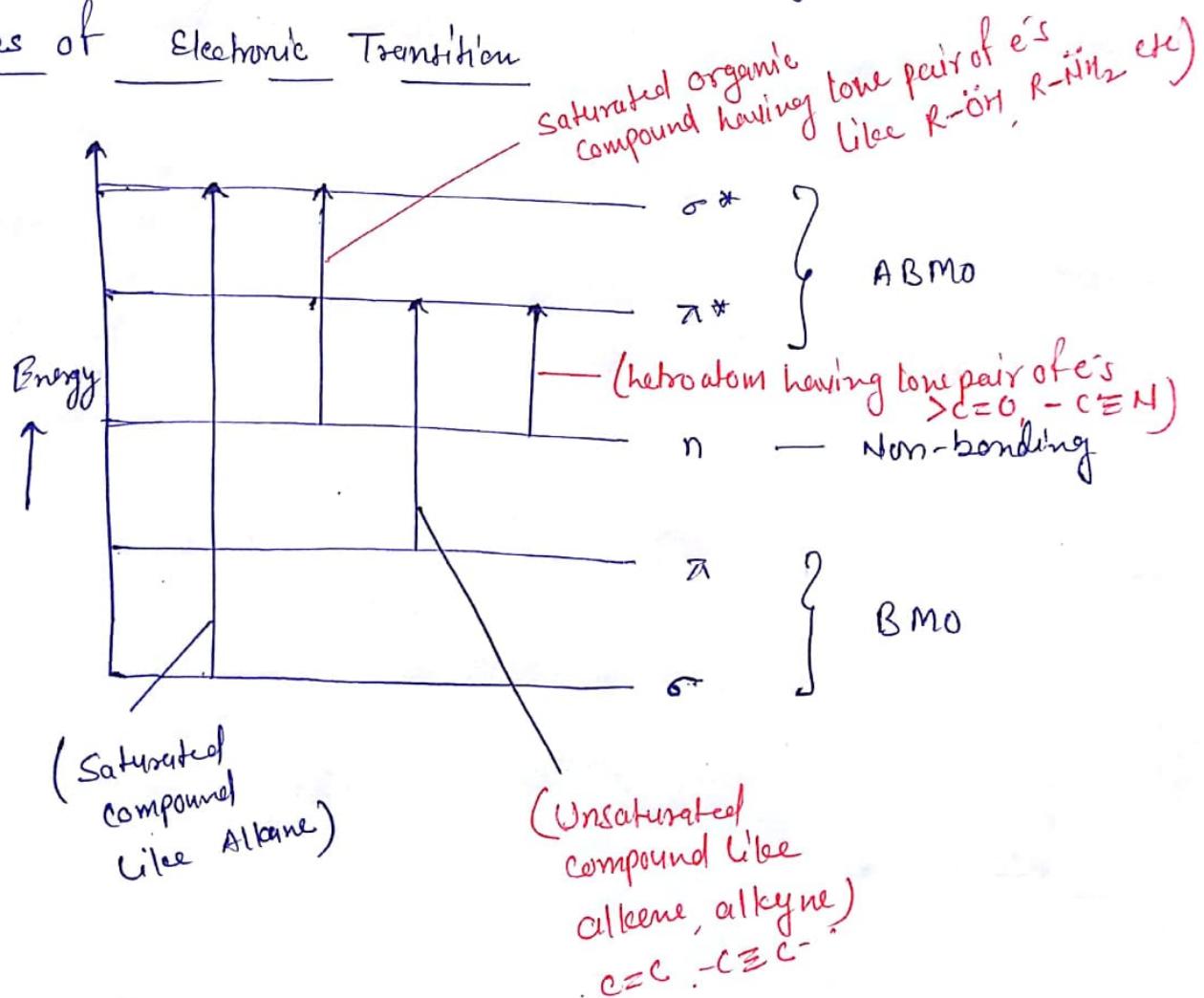
$$\boxed{\Delta E = h\nu}$$



$$A \propto \frac{1}{T}$$



Types of Electronic Transition



- 1) $\sigma - \sigma^*$ Transition \rightarrow e.g. alkane \rightarrow higher energy
- 2) $\pi - \pi^*$ Transition \rightarrow e.g. alkene, alkyne
- 3) $n - \sigma^*$ Transition \rightarrow alcohol, amine, ethers
- 4) $n - \sigma^*$ Transition \rightarrow >C=O , $\text{>C}\equiv\text{N}$ etc \rightarrow lower energy

- 1) $\sigma - \sigma^*$ transition: In these transitions, electrons get excited from σ bonding molecular orbital to σ^* antibonding molecular orbital. Energy required is very high. These transitions takes place in compounds having single bonds (alkanes).
- 2) $\pi - \pi^*$ transition: In such transitions electrons move from π , non-bonding molecular orbital to π^* anti bonding molecular orbital.

Energy required is comparatively less than that of $\pi - \sigma^*$ transition. These transitions occur in saturated organic compounds which have lone pair of electrons.

Example : Methanol, alkyl halides, amines
 3) $\pi - \pi^*$ transitions : The electrons move from π bonding molecular orbital to π^* antibonding molecular orbital. Energy required is less than that of $n - \sigma^*$ transition. Such transitions occur in compounds which have multiple bonds i.e. alkenes, alkynes.

4) $n - \pi^*$ transitions : The electrons move from non-bonding molecular orbital to an antibonding π^* molecular orbital. Such transition occurs in compounds which contain a hetero atom having lone-pair of electrons.

Example : $\text{>} \text{C=O}$, $\text{>} \text{C}\equiv\text{N}$

Ques : What is Chromophore?

Ans : The functional group that shows a characteristic absorption in U.V or visible region and gives colour to the compound is called Chromophore.

Example : Diazo group $-\text{N}=\text{N}-$

and $-\text{C}\equiv\text{N}$, $-\text{C}\equiv\text{C}-$

Ans 1
Ex 1

Ques : What is Auxochrome?

Ans : It is auxiliary group that combines with chromophore and shift the absorption towards longer wavelength and also

result in increase in intensity of the band

Example: R_2N , $-\text{OH}$, $-\text{OCH}_3$, $-\text{NH}_2$ etc.

This happens due to ability of the auxochromes to extend the conjugation of chromophore by sharing the non-bonding electrons. This causes delocalisation of electrons resulting in decrease in energy of the system, consequently E_{\max} increases.

Ques: What is Bathochromic shift?

Ans: When the absorption maxima shifts towards longer wavelength either due to presence

of an auxochrome or change of solvent, the shift is called Bathochromic Shift or Red Shift.

Ques: What is Hypsochromic Shift?

Ans: When the absorption maxima shifts towards shorter wavelength either due to removal of ~~conjugation~~ auxochrome or by change of solvent, the shift is called Hypsochromic Shift or blue shift.

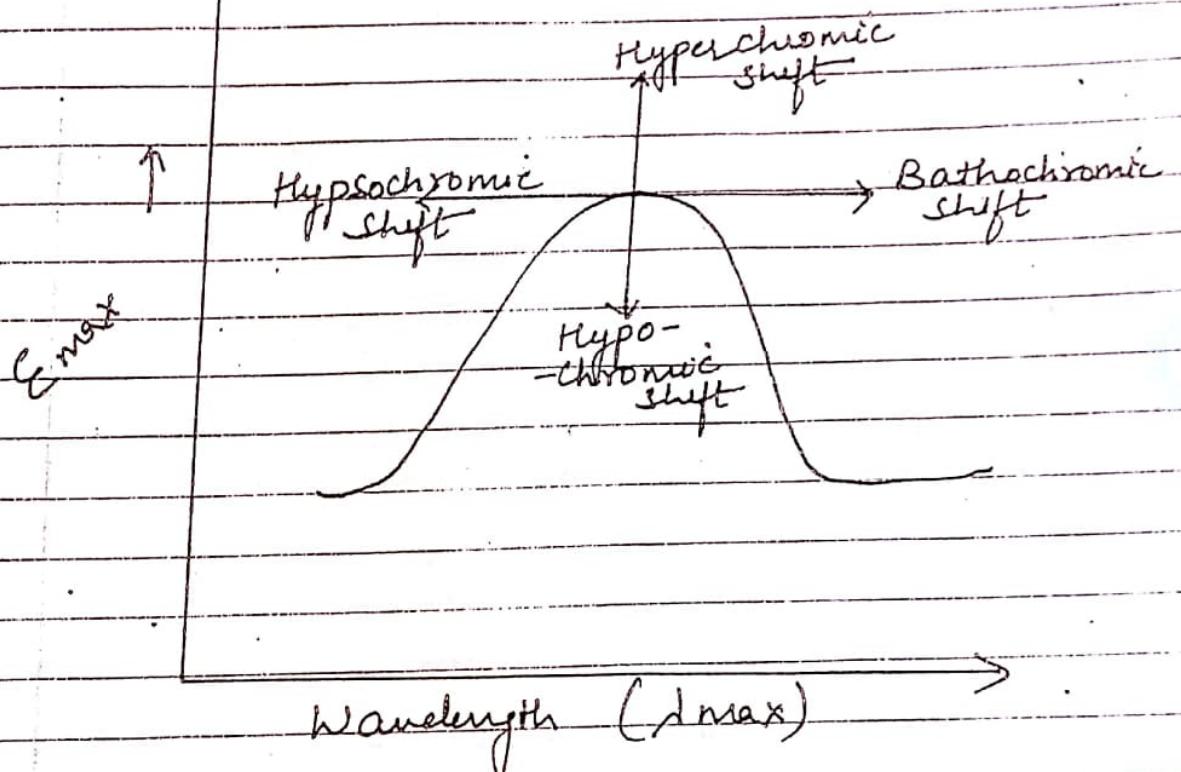
Ques: What is Hyperchromic effect?

Ans: It is an effect due to which the intensity of absorption maximum increases i.e. E_{\max} increases. The introduction of an auxochrome usually increases the intensity of absorption.

Ques: What is Hypochromic effect?

Ans: It is an effect due to which the intensity of absorption maximum decreases i.e. extinction coefficient decreases E_{\max} decreases. The

introduction of group which distorts the geometry of molecule causes hypsochromic effect.

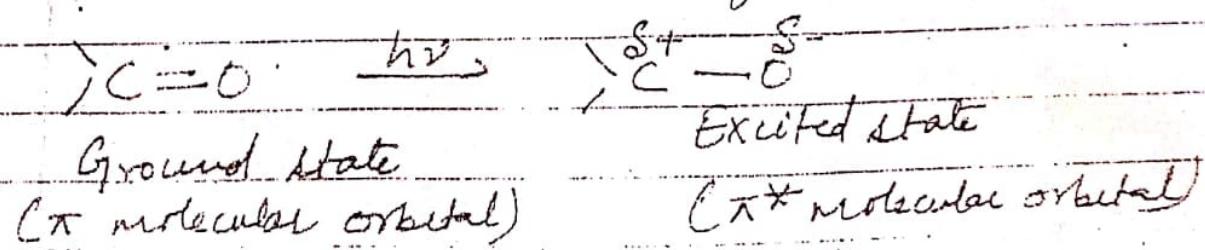


Ques:- what is the effect of solvent on Electronic transitions?

Answer:- The polarity of solvent influences the extent of electronic transition in U.V spectroscopy.

The solvent can shift a particular absorption band either towards longer wavelength or towards shorter wavelength.

Let us consider example of Carbonyl group



If the solvent is polar, π^* molecular orbital

become more solvated due to dipole-dipole interactions or hydrogen bonding. π^* relatively will be more stabilized as compared to π . So energy of the π^* molecular orbital decreases and smaller energy will be required for $\pi - \pi^*$ transitions. And λ_{max} will be shifted towards longer wavelength. On the other hand, $n - \pi^*$ transitions are shifted towards shorter λ_{max} (blue shift)

Applications of U.V. Spectroscopy +

1. Structure elucidation + It is used in identification of functional groups. Identification of an unknown compound can be made by comparing its spectrum with that of known compound.
2. Purity determination + If impurities are present, in a pure compound, additional peaks due to impurities will be present.
3. Reaction kinetics + This technique is used to determine change in concentrations of reactant or product as a function of time.
4. Effect of conjugation + A compound having higher no. of double bonds absorb at higher wavelength. The increase being about 10nm per extension by one double bond.
5. Determination of Molecular Mass can be done by this technique.
6. Determination of calcium in blood serum can be done.

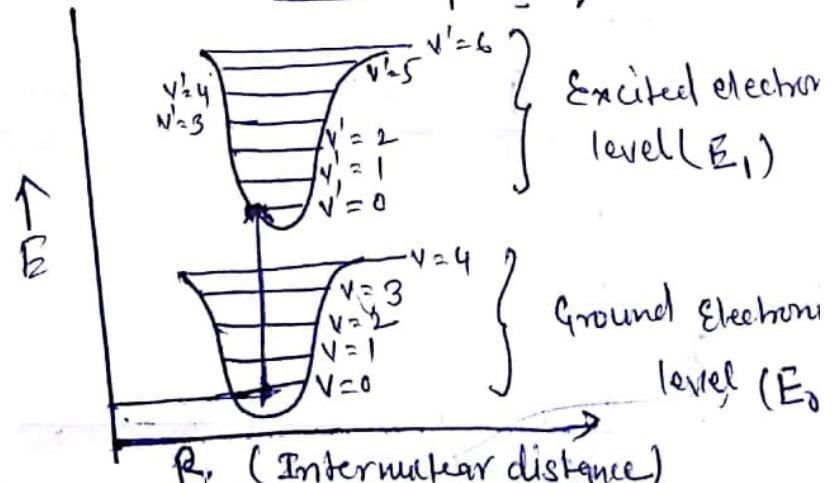
The Franck-Condon Principle

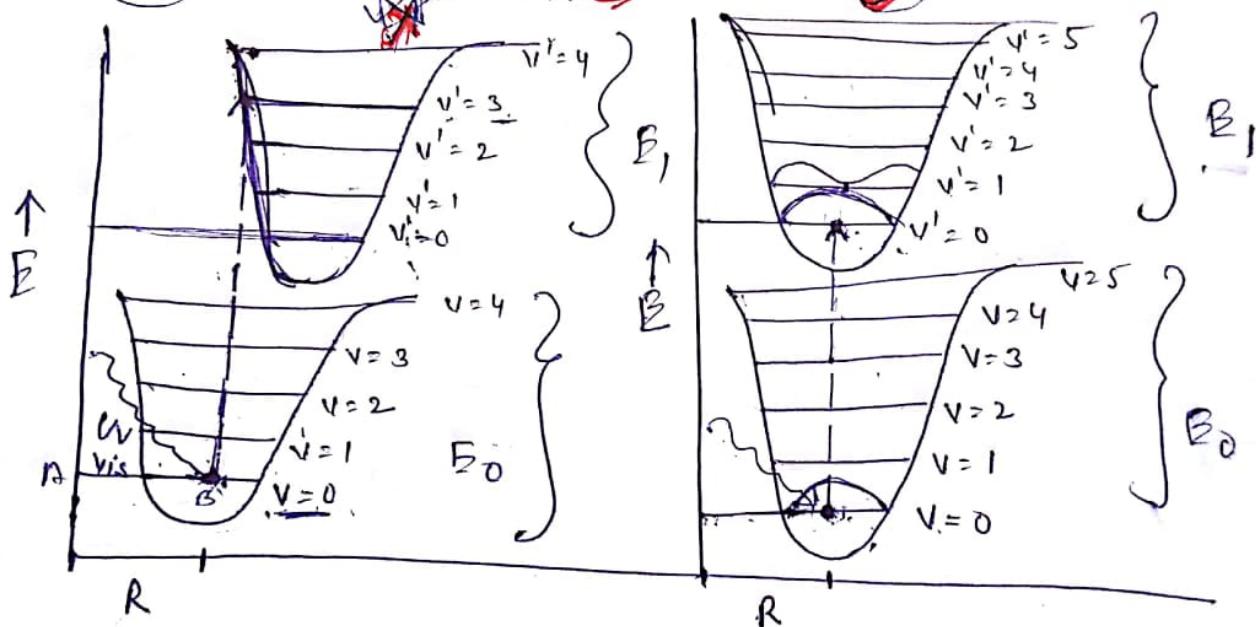
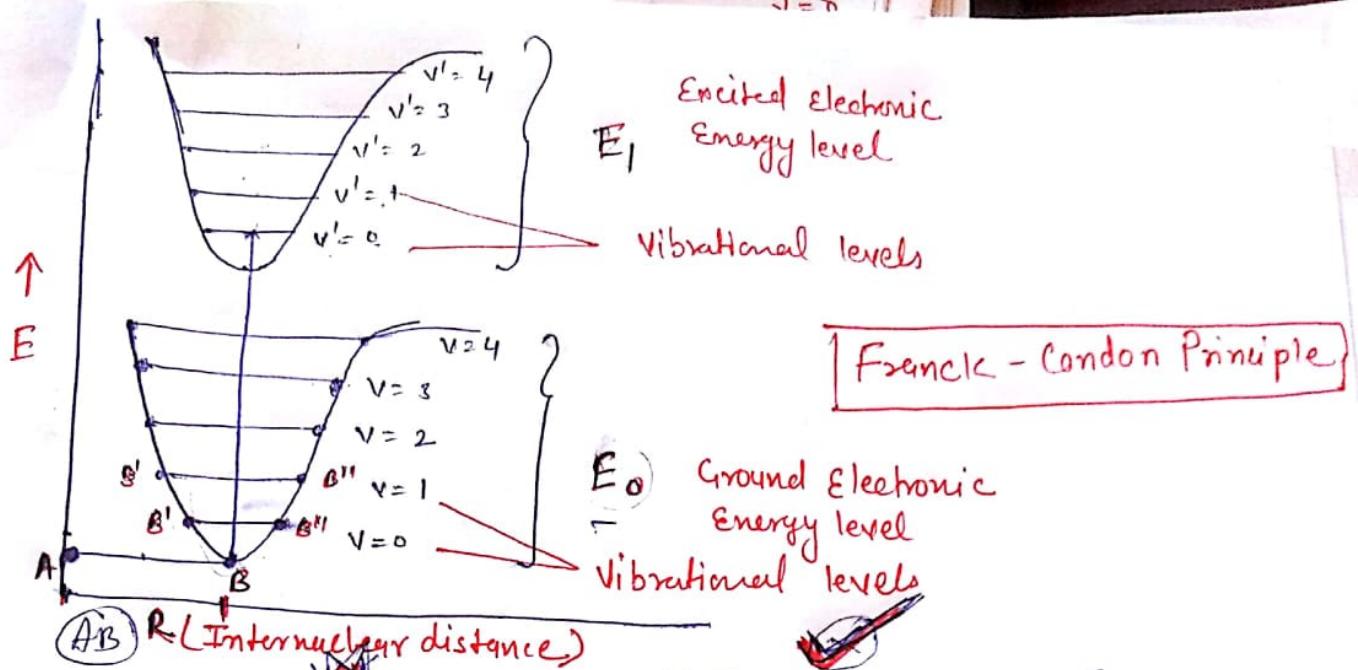
- It is the fundamental principle for absorption spectroscopy.
- According to Franck-Condon Principle, position and velocities of nuclei do not change during the electronic transitions which occur more quickly than the period of vibration of the nuclei as they are heavier compared to electrons.

OR

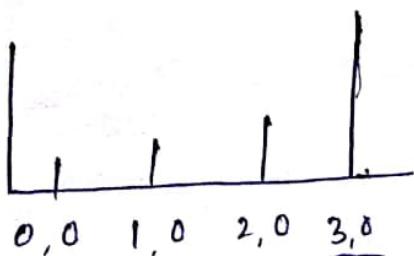
A \rightleftharpoons B

- The Franck-Condon Principle states that as electrons move very much faster than nuclei, the nuclei are effectively stationary during an electronic transition. electronic transition of e^- requires 10^{-15} s time
 - The electron excitation is effectively instantaneous, the nuclei do not have a chance to move. The transition is represented by a ~~vertical~~ vertical arrow on the diagram. (R does not change)
- R = internuclear distance (bond length)
- This principle is used for represent the intensity of vibronic spectra (Vibrational-electronic spectra)

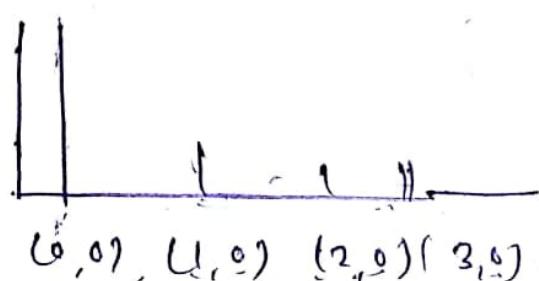




(3, 0) Transition
 higher level, lower level



(No change in internuclear distance)
 (0, 0) Transition



Selection Rule
OR
Transition Rule

Unit - II
Spectroscopy

(1)

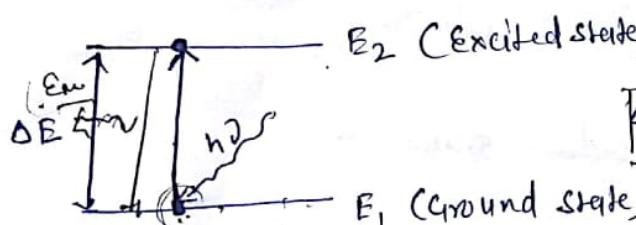
Basic concept of spectroscopy

The electromagnetic radiation provides energy equal to the energy difference (ΔE) b/w the energy levels corresponding to excited state + ground state.

$$\Delta E = h\nu$$

ν = frequency of radiation

h = Planck's constant



$$\boxed{\Delta E = h\nu} \text{ OR } \boxed{\Delta E = E_2 - E_1 = h\nu}$$

Selection Rule or Transition Rule

Selection rule decides whether transition is allowed or not allowed (forbidden).

1) allowed Transition

2) Forbidden Transition

Rule I

Change in energy level OR (Principle Q-N)

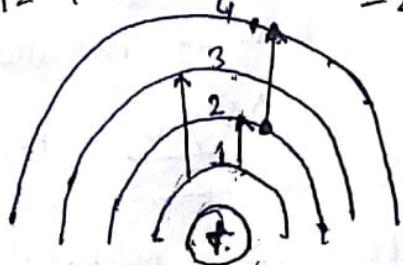
Transition in any energy level

$\Delta n =$ anything.

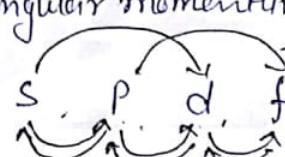
$= \pm 1, \pm 2, \pm 3, \pm 4, \dots$

e^- can jump to any energy level

$$\Delta n = 4 - 2 = +2$$



Rule -2 Laporte's Selection Rule Azimuthal Q. No.

Change in Orbital angular momentum (Δl)
 orbital changes like  forbidden

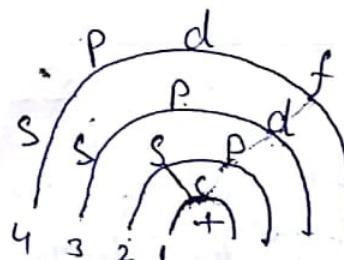
$S \leftrightarrow P$ }
 $P \leftrightarrow d$ } allowed
 $d \leftrightarrow f$ } Transition

$S \leftrightarrow d$ } forbidden
 $P \leftrightarrow f$ } Transition

$\boxed{\Delta l = \pm 1}$ only \rightarrow allowed

$\Delta l \neq \pm 1 \Rightarrow$ forbidden transition

e^- can jump only to next energy level orbital



Rule 3

spin selection rule (Δs) spin Q. No

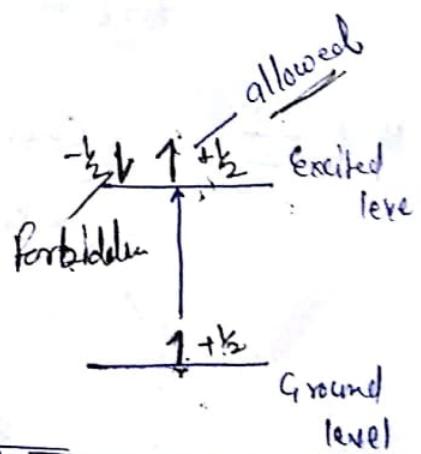
spin angular momentum (s)

$\boxed{\Delta s = 0}$ - allowed

spin multiplicity of e^- should not change

then it is allowed transition

$\boxed{\Delta s \neq 0}$ forbidden transition



NOTE Spin multiplicity (S) = $(2s+1)$

$s = \text{spin of } e^-$

$$\begin{array}{|c|c|c|} \hline & k_2 & k_2 \\ \hline 1 & 1 & 1 \\ \hline \end{array} = s = k_2 + k_2 = 1$$

(2)

Rule 4 Any Total Angular momentum change Rule

$$\boxed{\Delta J = 0, \pm 1} - \text{allowed}$$

$\Delta J \neq 0, \pm 1 \Rightarrow$ forbidden Transition

Total angular momentum = Orbital angular momentum (L)
+ Spin angular momentum (S)

$$J = (\underline{L} + \underline{S}) - \underline{(L-S)}$$

Term Symbol → Extra Study → Not required acc. to Syllabus

$$\boxed{(2s+1)} \begin{matrix} L \\ \vdots \\ J \end{matrix}$$

② $(2s+1) = S$ (Spin angular momentum)

L = Orbital angular momentum

J = Total angular momentum

P^2 (at Represent in Term symbol)

$$s = \begin{matrix} +\frac{1}{2} & +\frac{1}{2} \\ \hline 1 & 1 \end{matrix}$$

$$s = (+\frac{1}{2}) + (+\frac{1}{2})$$

$$m_s = +1 \quad 0 \quad -1$$

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

$$[S] = (2s+1)$$

$$(2 \times 1 + 1) = [3] \checkmark$$

$$\text{Orbitals} = \begin{matrix} s \\ p \\ d \\ f \end{matrix} \quad \begin{matrix} 1 \\ 2 \\ 3 \end{matrix}$$

$$L = \overbrace{1}^{+1}$$

$$L = m_{l_1} + m_{l_2} + m_{l_3} - \dots$$

$$\begin{matrix} 1 & 1 & - \\ m_l & +1 & 0 & -1 \end{matrix}$$

$$L = (+1 + 0) = (1) \checkmark$$

$$J = L+S - L-S$$

$$J = (1+1) - (1-1)$$

2 1 0

(1, 0)

When e's in orbitals are less than half filled

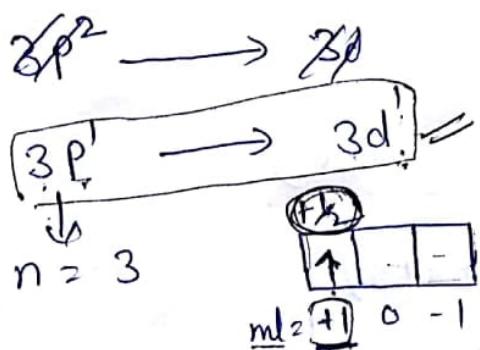
When e's in orbitals are less than half filled then we consider smallest 'J' value and if e's in orbital are more than half filled then we consider highest value of 'J'.

Here $J = \underline{0}$

Extra study

So Term symbol of $\underline{P^2}$ is

$$\alpha (2s+1) L_J = \boxed{3 P_0}$$



$\boxed{3 P_0}$

$$3d^1$$

s_2	z^2				
$m_L = +2, +1, 0, -1, -2$	$\boxed{1}$				

$$S_2 = 2s+1 = 2 \times \frac{1}{2} + 1 = 2$$

$$S = 2s+1$$

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

$L = S$

$J = 0$

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

$$J = L+S - L-S$$

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

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

$\boxed{2 P_{\frac{1}{2}}}$

$$L = 2$$

$$J = L+S - L-S$$

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

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

$\boxed{2 D_{\frac{5}{2}}}$

$\Delta S = 0$

$\Delta L = \pm 1$

$\Delta J = \pm 1$

Rule 5

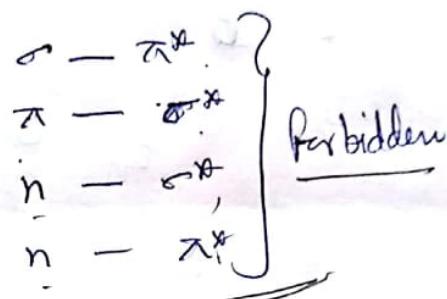
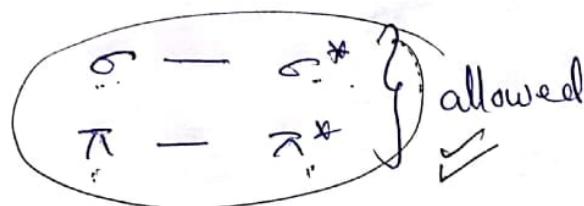
(3)

Symmetry Selection Rule

Bonding orbital = σ π

Anti-bonding orbital = σ^* π^*

Non-bonding orbital = n



Summary of Selection Rule

- ① $\Delta n =$ anything ✓
 $0, \pm 1, \pm 2, \dots$
- ② $\Delta l = \pm 1$ ✓
- ③ $\Delta s = ?$ ✓
- ④ $\Delta J = 0, \pm 1$ ✓
- ⑤ Symmetry Selection Rule

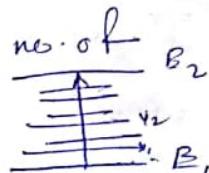
Vibrational-Rotational Spectroscopy (IR spectroscopy)

①

Infra-Red spectroscopy

Basic Introduction:-

- IR spectroscopy is one of the most powerful analytical techniques which gives sufficient information about the structure of a compound.
- It is a valuable tool for the determination of functional group present in organic compounds.
- Unlike the UV spectrum which comprise very few absorption peaks, IR spectrum provides a large no. of absorption bands.
- It is a type of absorption spectroscopy.
- Infra Red radiations are used for the determination of the structure of a compound.
- Vibrational-rotational spectra occur in this spectroscopy hence it is also call Vibrational-Rotational spectroscopy.



Scale to
Sludge.

Principle of IR Spectroscopy

- IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy difference in the possible vibrational & rotational states.
- For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule.
- IR active → must change the dipole moment of molecule like CO_2 , H_2O , HCl etc.
- IR Inactive → No change in dipole moment like O_2 , N_2 , Cl_2 etc.

Principle of IR spectroscopy

- In any molecule it is ~~not~~ known that atoms or group of atoms are connected by bonds.
- These bonds are analogous to springs and not rigid in nature.



Vibration

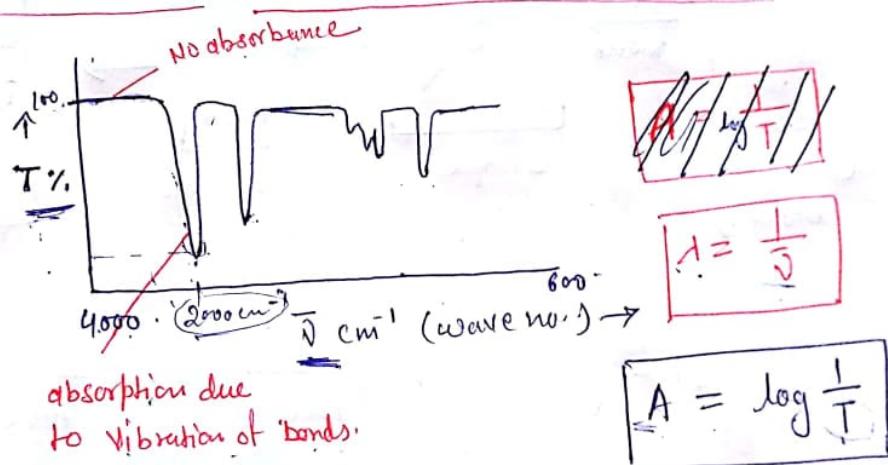
- Because of the continuous motion of the molecule they maintain some vibrations with some frequency characteristic to every portion of the molecule. This is called the natural frequency of vibration.
- When energy in the form of IR radiation is applied then it causes the vibration between the atoms of the molecule and when

Applied infrared frequency \approx Natural frequency of vibration
Then, Absorption of IR radiation take place and a peak is observed.

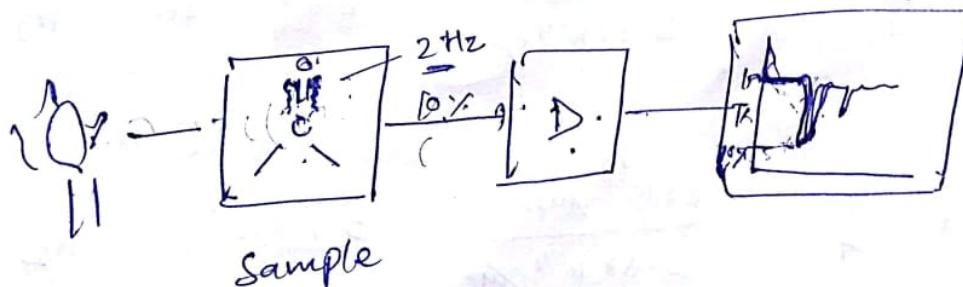
③

- Different functional group absorbs characteristic frequencies of IR radiation. Hence gives the characteristic Peak value.
- Therefore, IR spectrum of a chemical substance is a finger print of a molecule for its determination.
- Band Intensities in IR spectrum may be expressed as Transmittance (T)

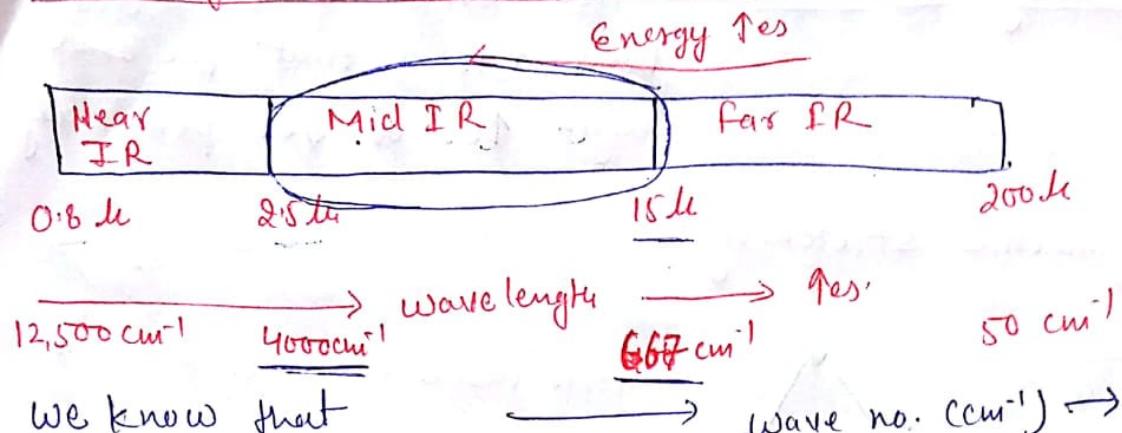
In general, the IR spectra of compounds are plotted as Percentage Transmittance ($T\%$) vs Wave number ($\bar{\nu}$)



Working / Instrumentation



IR region of electromagnetic spectrum



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

IR Radiation

wave no.

c = speed of light

Mid IR

ν = frequency

$(4000 \text{ cm}^{-1} - 667 \text{ cm}^{-1})$

λ = wave length

Mid IR region (4000 cm^{-1} to 667 cm^{-1}) → functional

group determination and molecular vibrations can be detected

In MID IR region. This region is called functional gp region. and Far IR region is called fingerprint region

As to the nature of vibration, It can be divided into two principal groups.

Vibration Types of vibration

Stretching Vibration

Symmetrical stretching

Asymmetrical stretching

Bending Vibration

Scissoring
Rocking

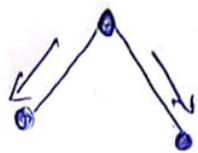
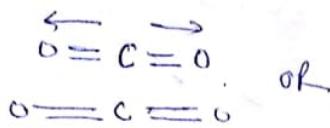
Wagging
Twisting

(5)

I Stretching vibration:-

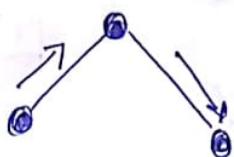
The atoms moves along the bond axis, so that the bond length increases or decreases periodically.

i) Symmetric stretching:-

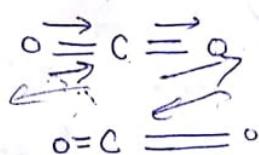


atoms move in same direction

ii) Asymmetric stretching:-



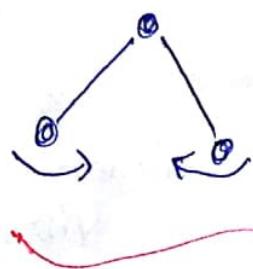
one atom approaches towards the central atom while the other departs from it.



II Bending vibration:-

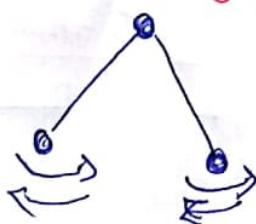
In this type of vibration the position of the atom changes with respect to the original bond axis leading to change in bond angle.

(i) Scissoring

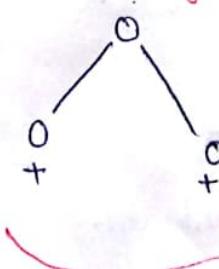


In the plane vibration

Rocking

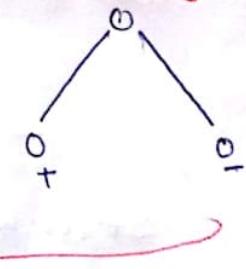


Wagging



out of the plane

Twisting

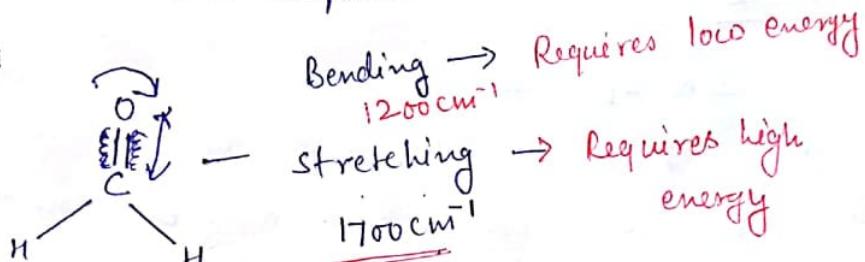


⑥ or

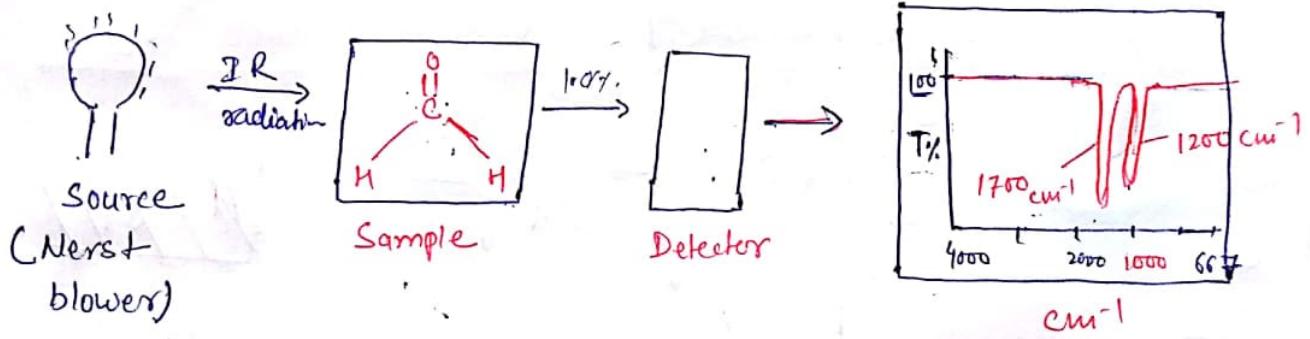
Working / Instrumentation of IR Spectroscopy

IR Spectroscopy is used to detect functional groups present in the compound.

for eg:



Formaldehyde



Frequency calculation

$$\nu = \frac{c}{\lambda} = \nu = \frac{1}{1200 \text{ cm}^{-1}} + \frac{1}{1700 \text{ cm}^{-1}} \Rightarrow [5.8 \times 10^4 \text{ cm}]$$

extra
 For 1200 cm^{-1} $= [8.3 \times 10^4 \text{ cm}]$

$$v = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{ cm/s}}{8.3 \times 10^4 \text{ cm}} = 3.6 \times 10^{13} \text{ sec}^{-1} \text{ or H}_2$$

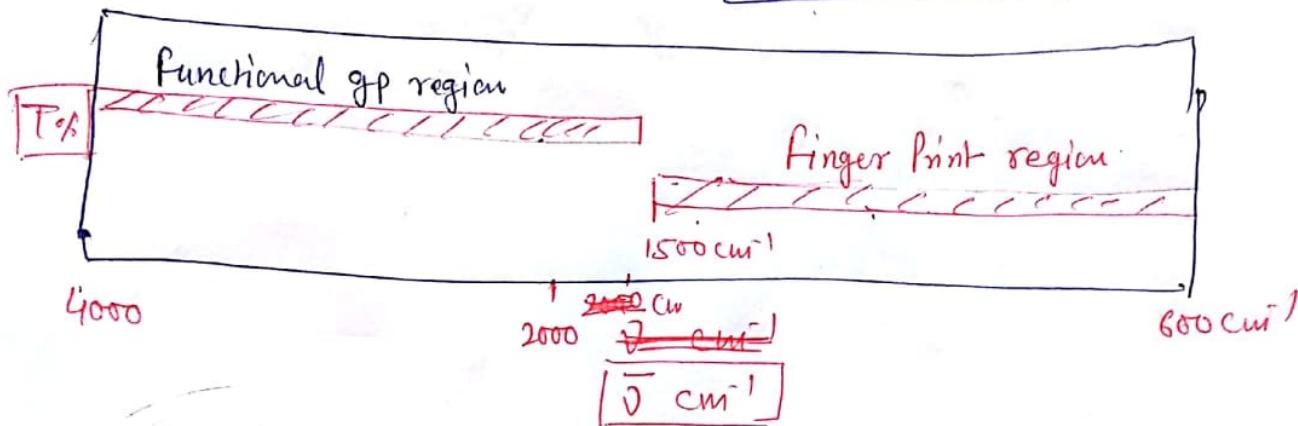
for 1700 cm^{-1}

$$v = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{ cm/s}}{5.8 \times 10^4 \text{ cm}} = 5.1 \times 10^{13} \text{ sec}^{-1} \text{ or H}_2$$

F

Bending vibration require lesser energy than stretching vibration and hence bending vibration occur at higher i (wavelength) or lower wave no. compared to stretching vibration.

MID IR range



Functional group region \rightarrow $4000 - 1500 \text{ cm}^{-1}$

Finger print region \rightarrow $1500 - 600 \text{ cm}^{-1}$



Application of IR Spectroscopy:-

IR spectroscopy is used to determine :-

1. Type of group present in the compound
2. The environment around a group.
3. Whether the compound is aromatic or aliphatic
4. Whether conjugation is present or not.
5. What kind of isomers are present
6. Molecular structure, chemical kinetic, detection of Impurities etc.

Rotational - Vibrational spectra of diatomic molecules

The radiation energy absorbed in IR region brings about the simultaneous change in the rotational and vibrational energies of the molecule.

This is observed in the fine structure of rotation bands. This combined spectrum is called vibrational-rotational spectrum.

The rotational and vibrational changes are considered as independent events and there is no interaction between them.

Thus, the net energy change of ~~the~~ is the algebraic sum of rotational and vibrational energy changes.
i.e

$$\Delta E_{\text{total}} = \Delta E_{\text{vib}} + \Delta E_{\text{rot.}} \quad \text{--- } ①$$

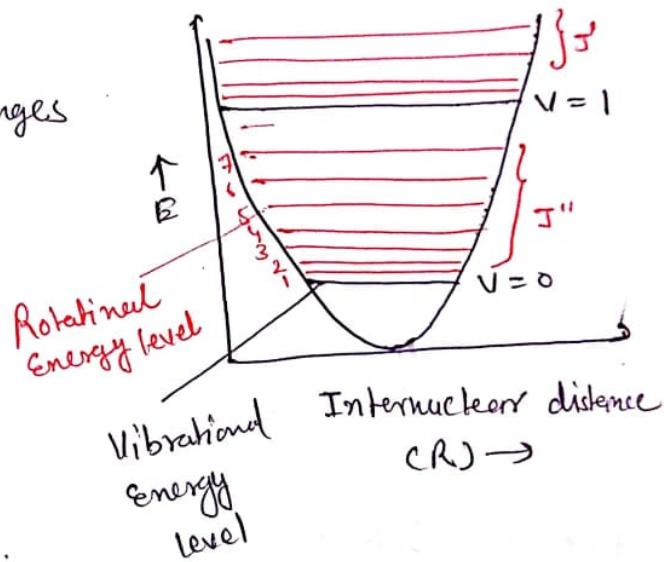
Or, Energy in terms of wave no. -

$$\bar{J}_{J,V} = (\bar{J}_J + \bar{J}_V) \text{cm}^{-1} \quad \text{--- } ②$$

and we know that Energy in terms of wave no. for rotational level (The energy of rotation is quantized and given by) -

$$\bar{J}_J = BJ(J+1) \quad \text{--- } ③$$

we treat the molecular rotation as those of a rigid rotor-



Where - J = rotational Q. no
 B = rotational constant
 $B = \frac{\hbar}{8\pi^2 I C}$

Energy in terms of wave no. for vibrational energy level
 (The energy of vibration is also quantized)

$$\bar{J}_v = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 \omega_e \chi_e \quad \text{--- (4)}$$

Where

ω_e = angular velocity or equilibrium oscillation frequency (or wave no.) of the anharmonic system.

χ_e = anharmonicity constant

v = Vibrational quantum no.

Total energy in terms of wave no.

Put the value of eqn (3) + (4) in eq (2)

$$\bar{J}_{J,v} = BJ(J+1) + (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 \omega_e \chi_e \quad \text{--- (5)}$$

Acc to Selection Rule

$$\Delta v = \pm 1$$

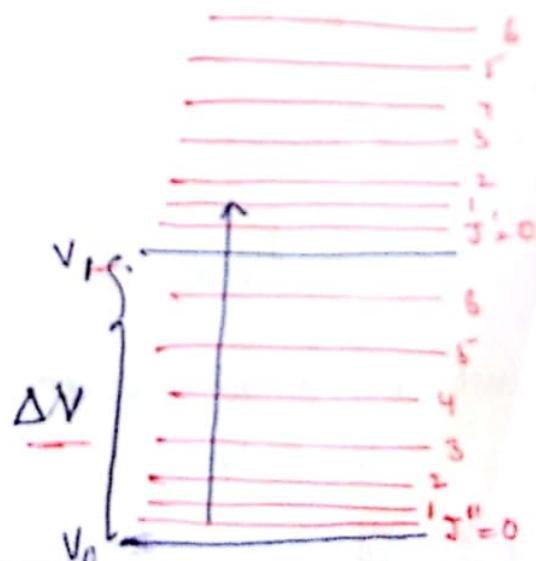
$$\Delta J = \pm 1$$

for vibrational level transition
 of molecule from $v=0$ to $v=1$

for rotational level, Transition
 of molecule from $J'' \rightarrow J'$

$$\underline{\Delta \bar{J}} = \bar{J}_{J', v=1} - \bar{J}_{J'', v=0} \quad \text{--- (6)}$$

Excited level - Ground level



Now, put the value to eq^⑤ in eq^⑥

②

$$\Delta \bar{V} = [BJ'(J'+1) + (1+\frac{1}{2})w_e - (1+\frac{1}{2})^2 w_e x_e] - [BJ''(J''+1) + (0+\frac{1}{2})w_e - (0+\frac{1}{2})^2 w_e x_e]$$

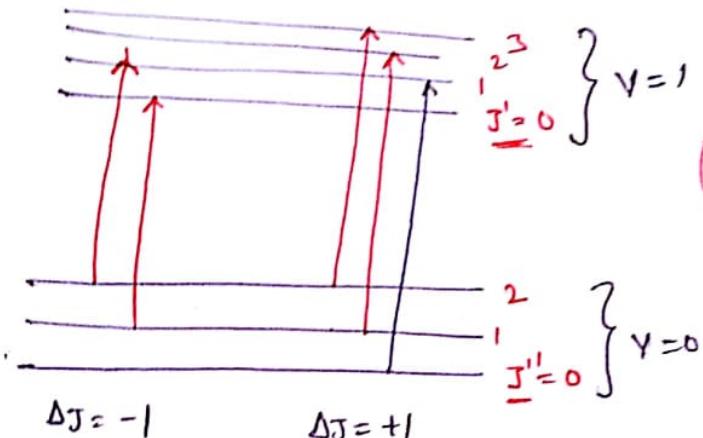
$$= [BJ'(J'+1) + \frac{3}{2}w_e - \frac{9}{4}w_e x_e] - [BJ''(J''+1) + \frac{1}{2}w_e - \frac{1}{4}w_e x_e]$$

$$= \underline{BJ'(J'+1)} - \underline{BJ''(J''+1)} + \underline{w_e} - \underline{2w_e x_e}$$

let $w_e - 2w_e x_e = \omega_0$

then

$$= \boxed{B(J' - J'') [J' + J'' + 1] + \omega_0} \quad \text{--- } ⑦$$



Now, we have two cases,

Selection Rule $\Delta J = \pm 1$
 $\textcircled{1} \quad \underline{\Delta J = +1}$
 $\underline{J'} - J'' = +1$

or $\textcircled{2} \quad \underline{J'} = 1 + \underline{J''} - \underline{\Delta J = -1}$

Substitute

Substitute the value of $J + J''$

from eq ⑧ to eq ⑦.

$$= B(1) [1 + J'' + J'' + 1] + \omega_0$$

$$= B [2J'' + 2] + \omega_0$$

$$= \underline{\omega_0} + \underline{2B(J'' + 1)}$$

$$\boxed{\Delta \bar{V} = \omega_0 + 2BM} \quad \text{--- } ⑨ \quad \text{Where } M = J'' + 1$$

(a) When $\Delta J = -1$

$$\Delta J = \boxed{J' - J'' = -1}$$

$$J'' = J' + 1 \text{ or } \boxed{J' + 1 = J''}$$

Substitute the value to $J' + 1$ to eqn (8).

$$\Delta \bar{v} = B(-1) (2J' + 2) + \omega_0$$

$$= \omega_0 - 2B(J' + 1)$$

$$\text{or } \boxed{\Delta \bar{v} = \omega_0 + 2BM} \quad \boxed{m = -(J' + 1)}$$

~~10~~ (10)

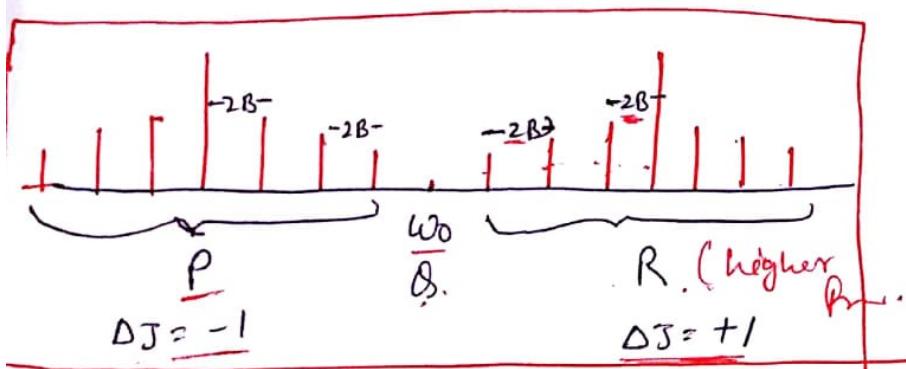
$$\Delta \bar{v} = \omega_0 + 2B \quad (\text{where } m = 1)$$

$$\Delta \bar{v} = \omega_0 - 2B \quad (m = -1)$$

$$\Delta \bar{v} = \omega_0 + 4B \quad (m = 2)$$

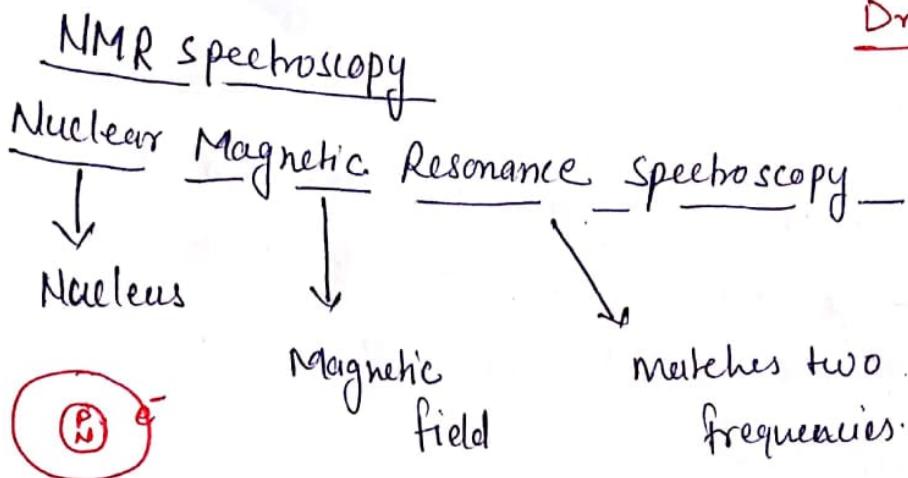
$$\Delta \bar{v} = \omega_0 - 4B \quad (m = -2)$$

separation b/w two spectral line
will be $2B$



* of ω_0 are called
R branch lines.

Thus, the vibrational rotational spectrum would consist of a series of lines with equal spacing of $2B \text{ cm}^{-1}$ on either side of band origin ω_0 . The lines corresponding to -ve value of m , i.e. at lower frequency side of ω_0 are called 'P' branch lines, while those at higher frequency side *

Introduction

- NMR is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the radio frequency region 4 to 900 MHz by nuclei of the atoms.
- ^1H NMR spectroscopy is one of the most powerful tools for elucidating the no. of H or proton in the compound.
- It is used to study a wide variety of nuclei

^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P , etc.

NMR active nucleiAtomic massAtomic no.

odd

 ^1H ✓

even

 ^{14}N ..

odd

even

 ^{13}C ✓NMR inactive nucleiAtomic massAtomic no.

even

eg:- ^{16}O , ^{12}C

even

Elements with either odd mass or odd atomic no.

have the property of Nuclear spin → NMR active

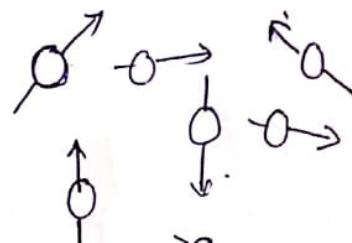
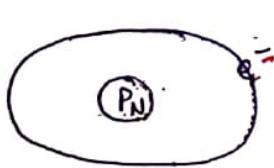
spin q. no. $\neq 0$ - Active, spin q. no. (I) = 0.

(I)

Inactive

Principle of NMR

→ The theory behind NMR comes from the spin of a nucleus and it generates a magnetic field. Without an external applied magnetic field, the nuclear spins are random in direction.

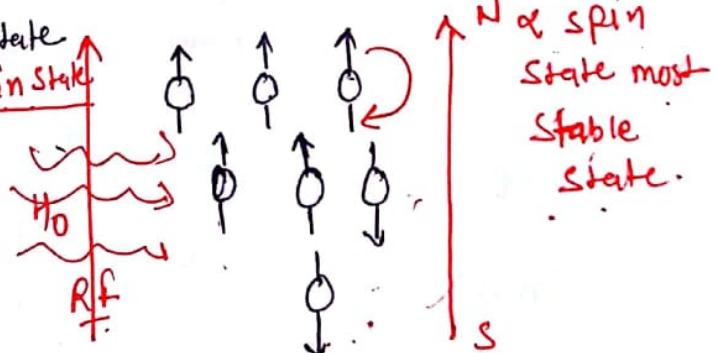


without external magnetic field.

Nuclear spin

A proton like e^- possess property of spin. It is likely to have spin of $+\frac{1}{2}$ or $-\frac{1}{2}$. Both spin state have same energy (in absence of external magnetic field). So ~~do~~

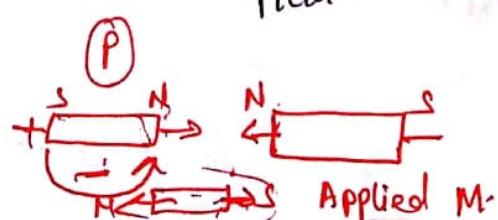
→ When an external magnetic field (B_0 or H_0) is applied the nuclei align themselves either with or against the field of the external magnet. At this state proton is in of spin state



→ If radiofrequency energy is applied, an energy transfer (ΔE) is possible between ground state to excited state, only when the radio frequency energy matches ~~with~~ energy difference (ΔE).
 ~~the~~

$[\Delta E = h\nu]$. This is called Resonance!

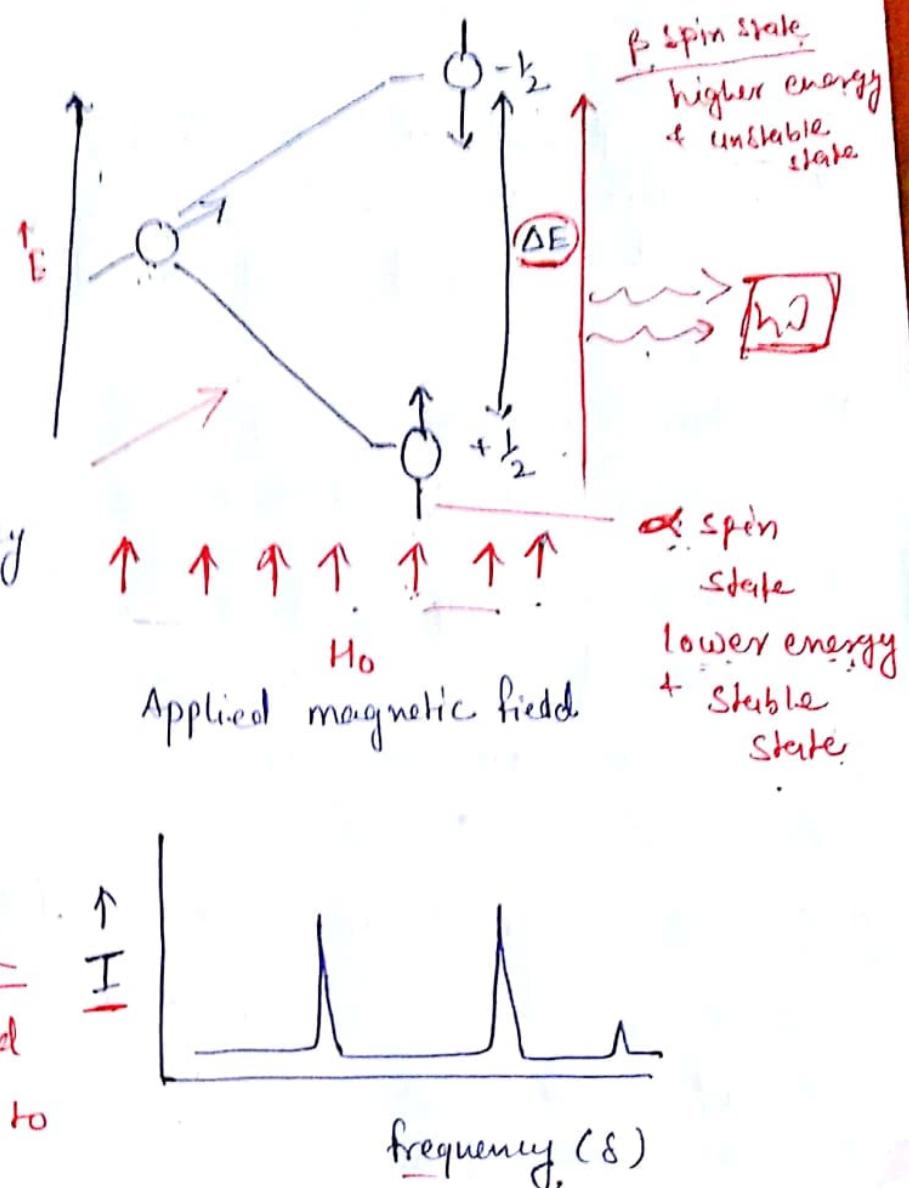
with Applied external magnetic field.



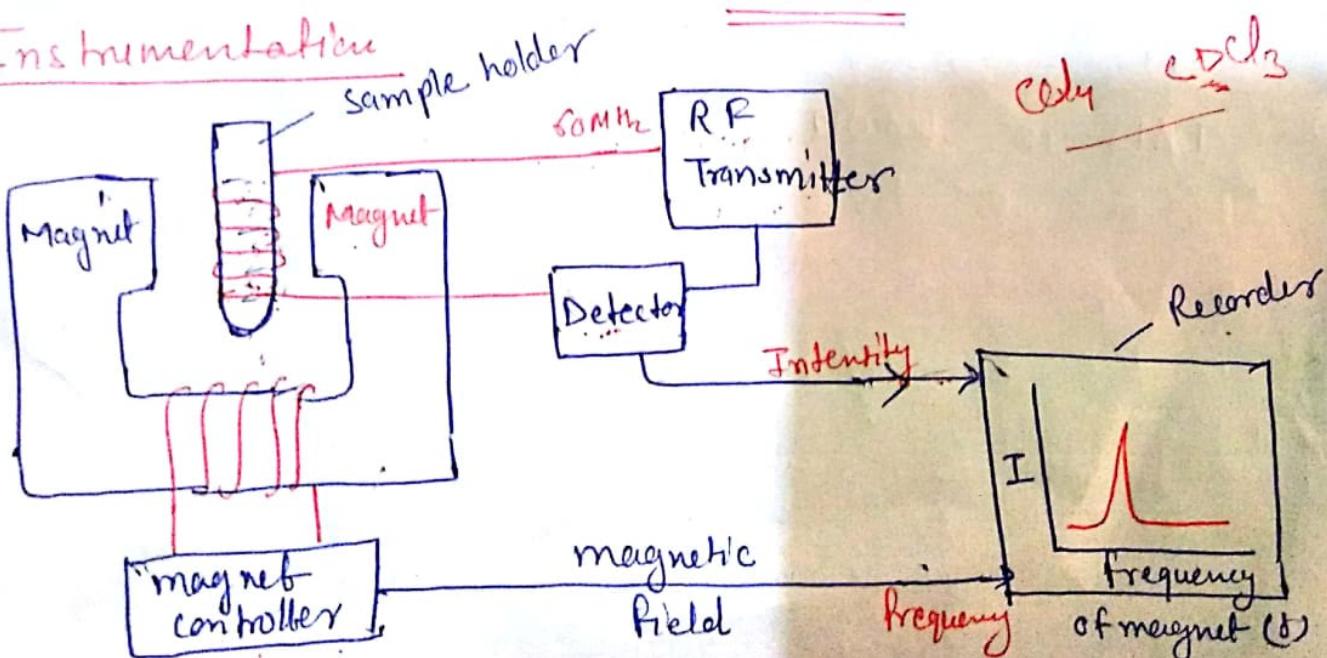
When the spin returns to its ground state level, the absorbed radiofrequency energy is emitted at the same frequency level.

The emitted radiofrequency signal that gives the NMR spectrum of the concerned nucleus.

The NMR spectrum is a plot of Intensity of NMR signal Vs magnetic field (frequency) in reference to TMS.



Instrumentation



NMR spectrophotometer

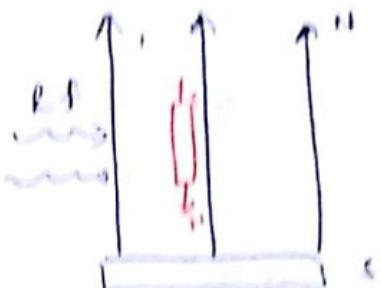
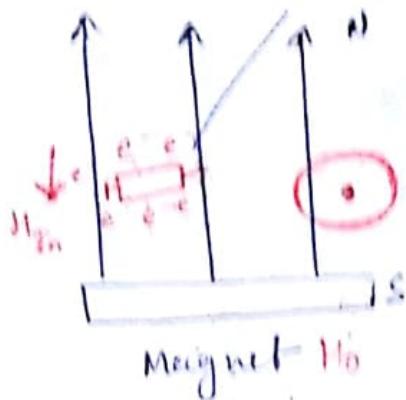
Working

- Sample placed in long cylindrical glass tube
- Dissolved the sample in proton free solvent like CDCl_3 or CCl_4 and add small amount of TMS as internal reference.
- Placed the sample in gap b/w two magnetic poles where coil is attached to a specific RF generator.
- This coil supply radio frequency wave (energy) required to change spin orientation of proton.
- Then detector coil detects RF signal when resonance occurs.
- As magnetic field \uparrow goes, the ~~pen~~.
- As as magnetic field \uparrow goes linearly the recorder pen travels from left to right thus protons which achieve resonance faster, i.e. (Deshielded) appears on left side (downfield), whereas those protons (shielded) appears on right side (upfield) in the form of peaks.
- TMS is shown at a peak value of $\delta = 0 \text{ ppm}$.

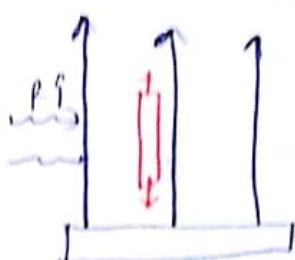
Chemical Shift (Position of Signals)

- The utility of NMR is that all protons do not show resonance at same frequency b/c as it is surrounded by particular no. of valence e⁻s which vary from atom to atom so, they exist in slightly different electronic environment from one another.
- Position of signals in spectrum help us to know nature of proton, i.e. aromatic, aliphatic etc. Thus they absorb at different field strength.
- When ~~molecule~~^{nucleus} placed in magnetic field, so its surrounding electron circulate & generates counter field which opposes the applied magnetic field on proton so that field feels by proton is reduced and that proton called as the shielded proton. So, shielded proton requires less ΔE energy to flip and shifts absorption signal to right side (upfield) of spectrum. This is called shielding.
- If the e⁻ density around a nucleus, decrease the opposing magnetic field becomes small and therefore the nucleus/~~proton~~ proton feels high magnetic field (H_0) strength and such proton is called as Deshielded proton. It needs a higher frequency to achieve resonance and signal appears at left side (down-field) of spectrum. This is called deshielding.

shielded proton

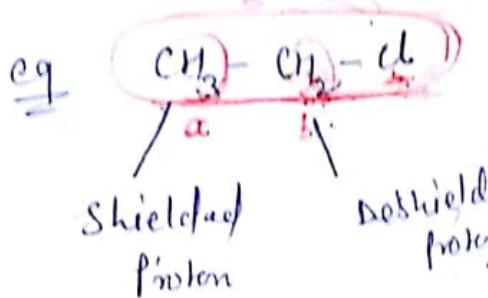
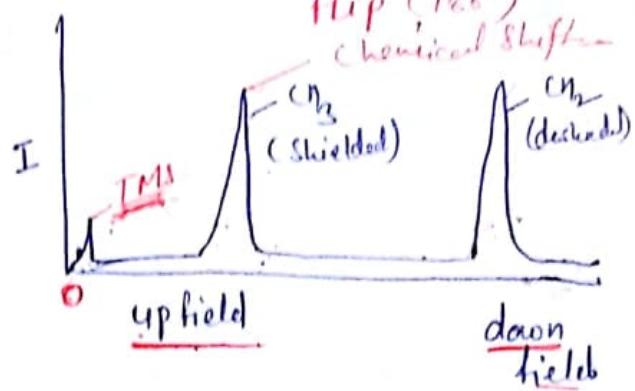


less energy/
frequency is
required to flip
at resonance.



more energy/
frequency is
required to
resonate at
flip (180°)

chemical shift



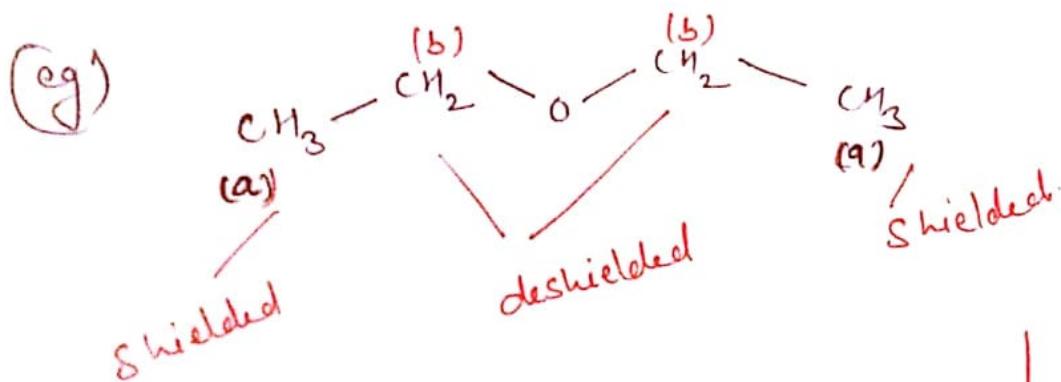
TMS → Tetrabutyl
silane

Such shifting of the position of NMR spectrum of signals which arises due to the shielding or deshielding of proton by surrounding electrons are called as chemical shift

$$\text{chemical shift } (\delta) = \frac{\text{frequency of signal} - \text{freq. of ref. (TMS)}}{\text{spectrometer frequency}} \times 10^6$$

Spin - Spin coupling - (splitting)

- The interaction between the spins of neighbouring nuclei in a molecule may cause the splitting of NMR spectrum. This is known as spin-spin coupling or Splitting.
- The splitting pattern is related to the no. of equivalent H-atoms at the nearby nuclei.
- Splitting of signals indicates the no. of nearby nuclei (usually protons).
- Splitting takes place by (n+1) rule where n = no. of neighbouring nuclei (proton)



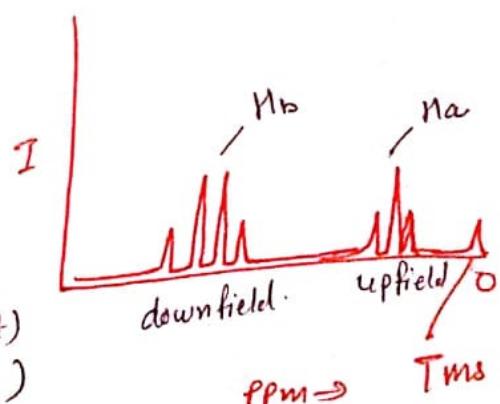
$$\text{For } \text{H}_a = \underline{(n+1)}$$

no. of neighbouring protons = 2

$$\text{spin-spin splitting} = 2+1 = 3 \quad (\text{Triplet})$$

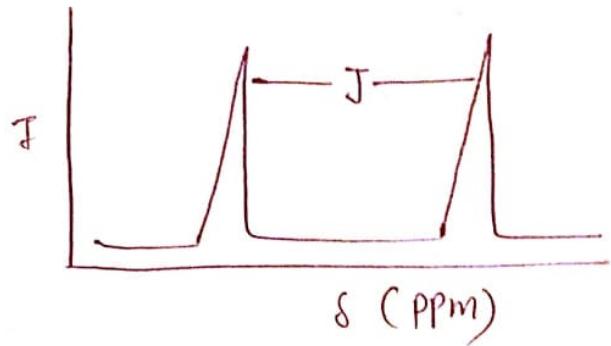
for H_b equivalent protons: — $(n+1)$

$$\text{no. of neighbouring protons} = 3+1 = 4 \quad (\text{Quartet})$$



Coupling constant (J)

- The distance b/w the peaks in a given multiplet is a measure of the splitting effect & is called Coupling constant. It is denoted by ' J ', expressed in Hz.
- Coupling constants are a measure of the effectiveness of spin-spin coupling and very useful in $^1\text{H-NMR}$ of complex structures.



Magnetic Resonance Imaging (MRI)

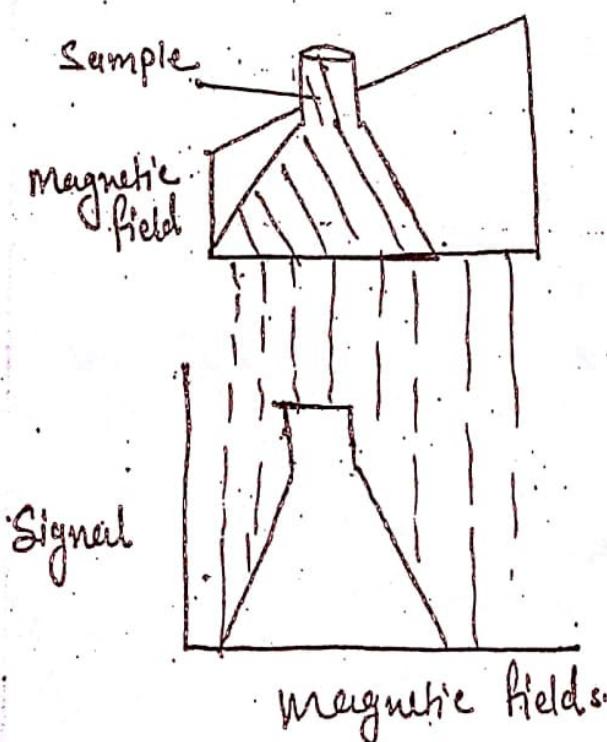
MRI is one of the applications of NMR spectroscopy.

In MRI nuclear magnetic resonance of protons is utilized to ~~dis~~ produce proton-density maps (or images) of the human body.

Thus, MRI is utilized to discriminate b/w healthy and diseased tissues of the body. It is based on the principle that the protons present within water, lipids, fats etc. resonate at a given frequency.

Since the human body contains about 75% water and each water molecule (H_2O) has two ~~H atom~~ nuclei, so images of the different parts of the body can easily be taken.

In a diseased condition of a body part the distribution of water, fats, lipids etc, alters. Hence by using MRI, one can detect the diseased part(s) of the body.



Arrangement for MRI

(8)

Procedure:- For getting an image in MRI, a varying magnetic field is applied across the body part under consideration. The protons in various regions of the body come to resonance at different radio frequencies and the intensity of signal is proportional to the no. of protons at that magnetic field. The body part is then rotated into a different orientation and another projection is made. Finally, the data obtained from different projections is computer combined by Computer to get 3D Image of the body parts. MRI requires very small time for scanning a particular body part.

Application:-

- i) For investigating the functioning of Myocardium, heart etc.
- ii) To identify the regions of excessive fat deposition in different body organs, blood vessels etc.
- iii) For the analyses of blood, by using (^{23}Na) MRI.
- iv) For estimation of Fluorine concentration in different body parts, by using (^{19}F) MRI.

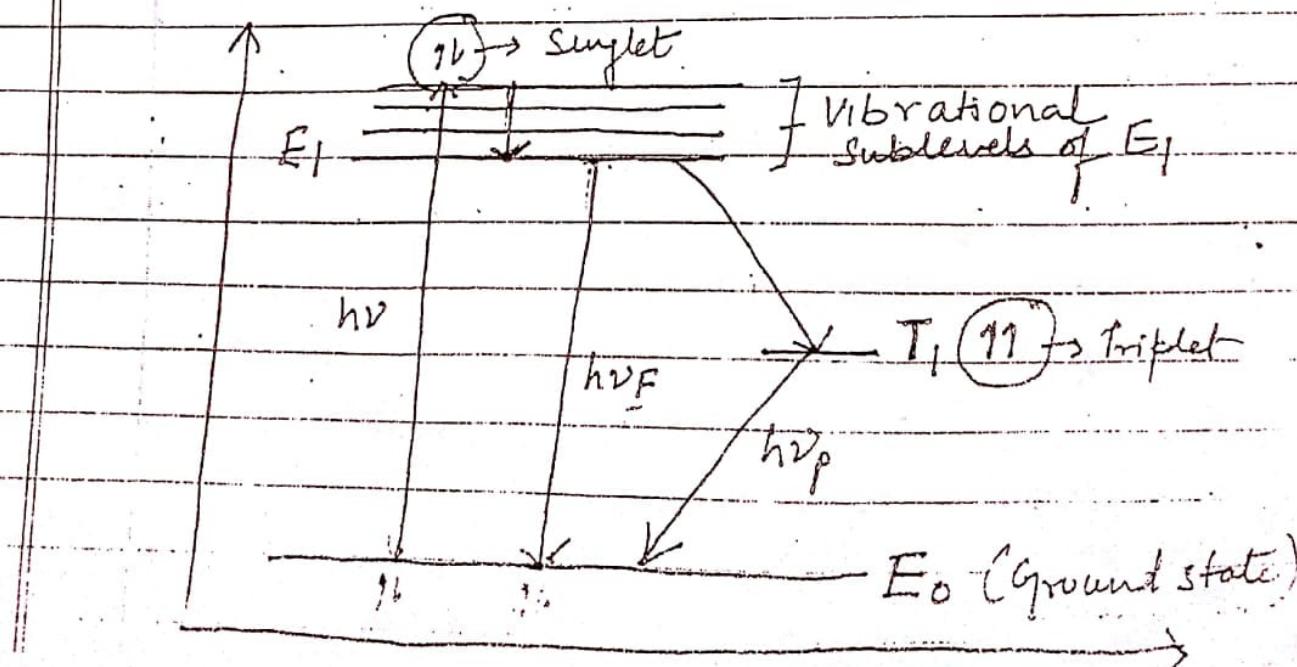
NMR is very sensitive to changes in the physical and chemical environments of the nuclei, especially the protons, which are the most abundant and widely distributed entities in the human body; and the energy involved in NMR Imaging techniques is so low that health risks are eliminated. Consequently, NMR imaging methods for the human body are now being rapidly developed and improved and are widely used.

Fluorescence and Phosphorescence:

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

Anthracene is a colourless substance and its electronic absorption spectrum lies in the ultra-violet region. But it is found that pure samples of anthracene when viewed in the ultraviolet light gives off a blue-visible light. This light is called Fluorescence. The emission of light or fluorescence stops at once when irradiating light is removed. On the other hand, the phenomenon of Phosphorescence is said to occur when the substance continues to emit the radiation of longer wavelength even when the irradiating light is removed.

To study the phenomenon of fluorescence and phosphorescence, let us study the electron excitation process.



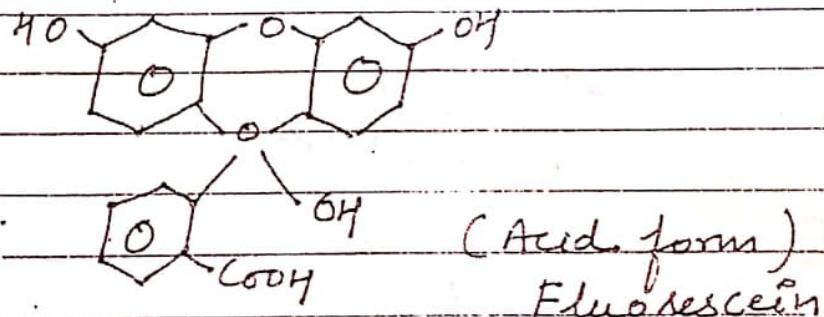
When the molecule in ground state absorb light ($\text{h}\nu$), its one electron gets promoted from ground state molecular orbital to one of the vibrational sub-level of the first excited molecular state (E_1) or to higher excited state E_2, E_3 etc. When the electron returns from E_1 to E_0 , it emits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

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

emitting the radiation of energy hν. It is called phosphorescent radiation.

Applications

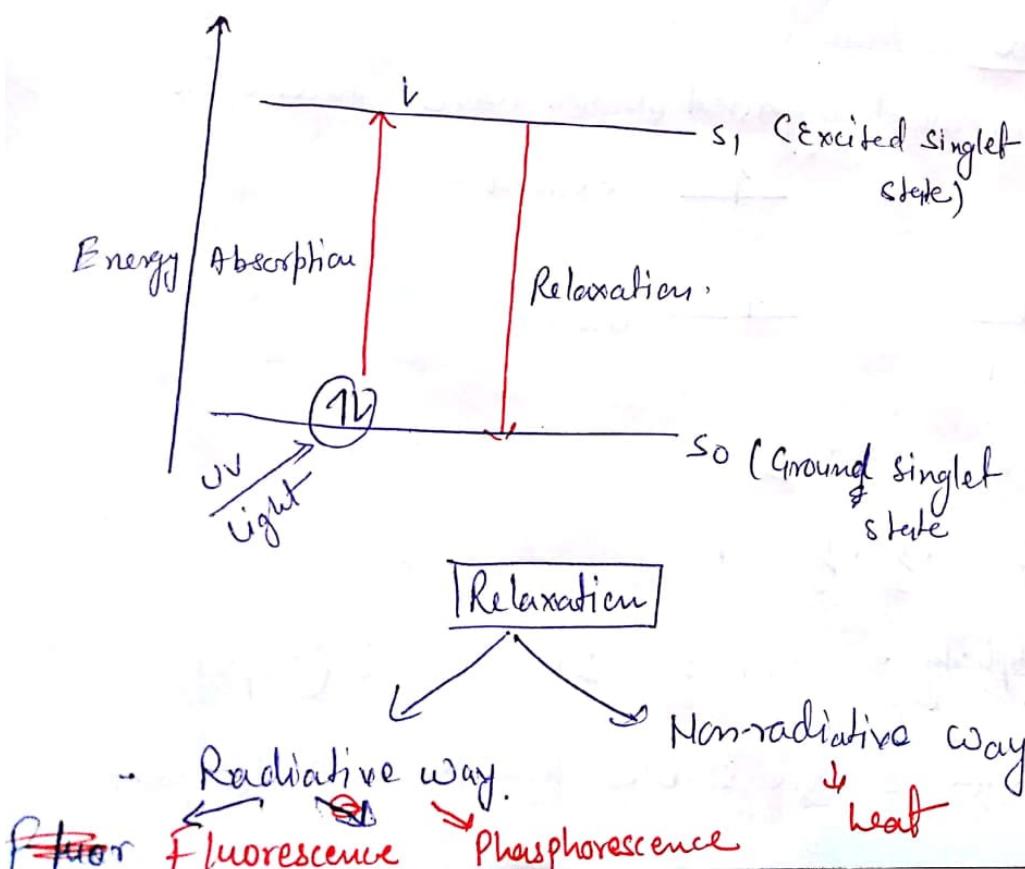
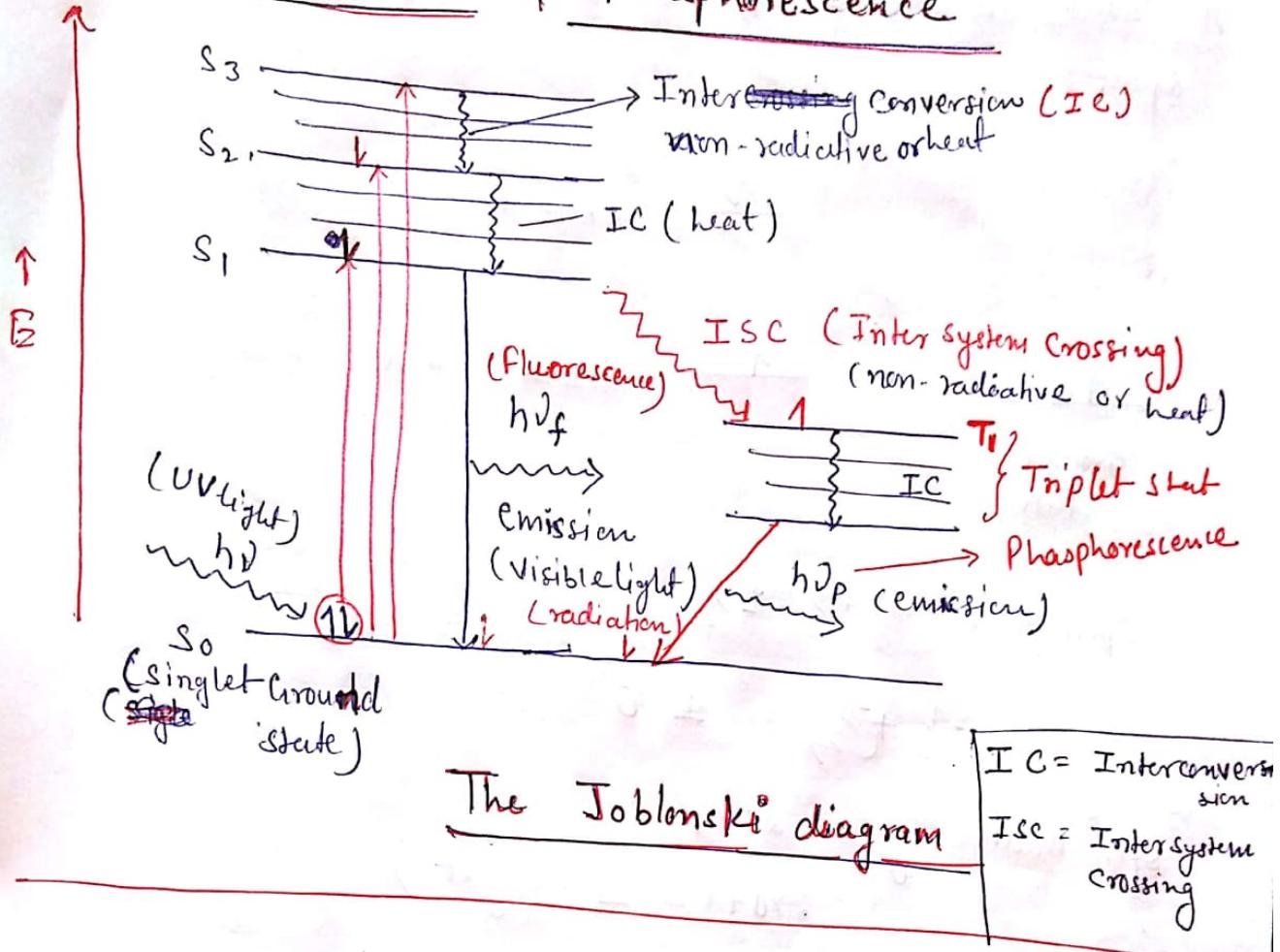
- (1) The intense green fluorescence of aqueous fluorescein solution makes it an excellent material for leak detection and excellent marker for sea rescue operations etc.



- (2) The property of fluorescence is applied in polymer chemistry to detect and identify plasticizers or in study of impurities.
- (3) Phosphorescence seen at night in the sea is due to several species of marine micro-organisms which when agitated by an splash undergo an enzymatic reaction which liberates energy in the form of green light. This phenomenon is called Bio-luminescence.

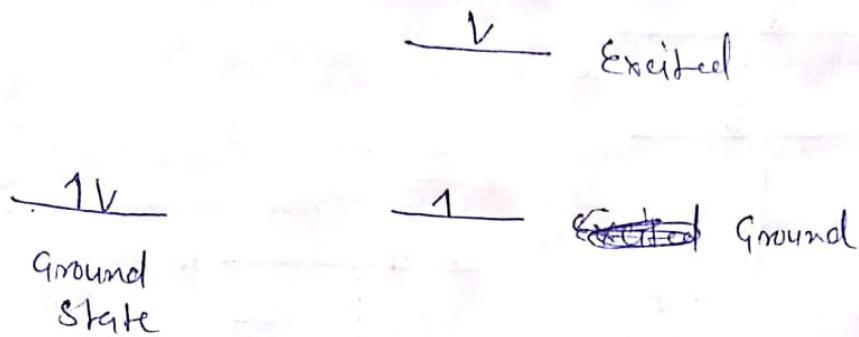
Some Important Points Related to -

Fluorescence & Phosphorescence



→ Singlet state

A State in which all the unpaired e^- have opposite spin



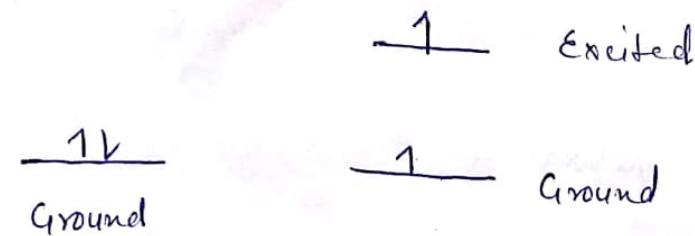
$$\text{Spin Q. no.} = +\frac{1}{2}, -\frac{1}{2}$$

$$S = +\frac{1}{2} + \left(-\frac{1}{2}\right) = 0$$

$$\begin{aligned}\text{spin multiplicity} &= 2S+1 \\ &= 2 \times 0 + 1 = 1 \text{ (singlet)}\end{aligned}$$

→ Triplet state

A State in which unpaired electron have same spin



$$\text{Spin Q. no. } +\frac{1}{2} + \frac{1}{2}$$

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

$$\text{Spin multiplicity} = 2S+1 \Rightarrow 2 \times 1 + 1 = 3 \text{ (Triplet state)}$$

Triplet state is more stable than Singlet state

$$\Delta V = \pm 1$$

→ Fluorescence :-

- * It is the phenomenon of emission of radiation when there is transition from ~~singlet~~ singlet excited state to Singlet Ground state.

Singlet excited state $\xrightarrow{\text{emission of radiation}}$ Singlet ground state
(longer ~~λ~~)

- * In this process the absorbed energy is released in the form of light as long as the excitation continued.
- * It is ~~singlet~~ Singlet to Singlet Transition
- * Avg. lifetime - 10^{-10} to 10^{-7} sec.

→ Phosphorescence

- * The emission of radiation when there is transition from Triplet excited state to Singlet ground state.

Triplet excited state $\xrightarrow{\text{emission of radiation}}$ Singlet ground state.
(longer ~~λ~~ or visible light)

- * In this process the absorbed energy released relatively slow in the form of light.
- * It is a triplet to Singlet transition.
- * Avg. lifetime 10^{-5} to 10^3 sec.

→ Internal Conversion (IC) :-

- * Transition from higher electronic state to the lower excited electronic state is called internal conversion.
- * In this transition no radiation are emitted.

Intersystem Crossing (ISC)

- * It is a non-radiative transition between two iso-energetic vibrations levels belonging to electronic state of different multiplicities.

(11)

Diffraction & Scattering

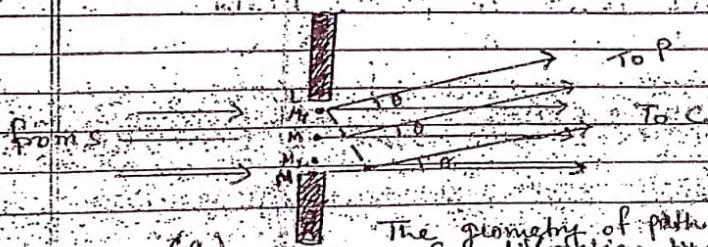
Diffraction :- When light falls on a small slit or hole, the energy of the light wave spreads out. This phenomenon is called diffraction of light.

The bending of light waves around the corners of an opening or an obstacle and spreading of light waves into geometrical shadow is called diffraction.

Diffraction effect depends upon the size of obstacle.

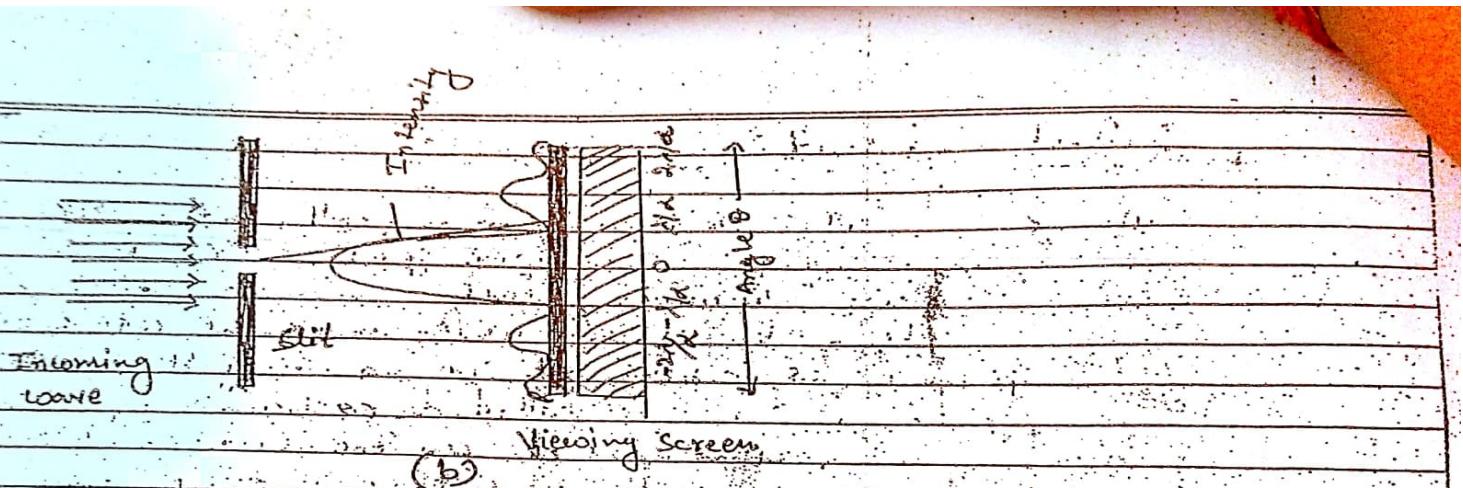
After diffraction of light takes place if the size of obstacle is comparable to the wavelength of light, light waves are very small in wavelength i.e. from 10^{-10} m to 10^{-7} m. If the size of opening or obstacle is near to this limit only then we can observe the phenomenon of diffraction.

Example of diffraction in nature is diamond rays in the solar eclipse.



(a).

The geometry of path difference
for diffraction by a single slit



(b)

The variation of intensity with angle in single slit diffraction. The first secondary maximum is only 4% of the central maximum so it is not to scale in the figure.

The above Figure (a) shows that a parallel beam of light falling normally on a single slit MN of width a . The diffracted wave goes on to meet a screen. The mid-point of the slit is M. A straight line through M perpendicular to the slit plane meets the screen at C. At the central point C on the screen, the angle θ is zero. All path difference are zero and hence all the

parts of the slit contribute in phase. This gives maximum intensity at C (fig. (a)). Now choose an angle θ such that the path difference b/w the edges L & N (slit P) is λ . This angle is given by

$$\alpha \theta = \lambda \quad \text{or} \quad \theta = \frac{\lambda}{\alpha} \quad \text{--- (1)}$$

Further, divide the slit into two equal halves LM & MN each of size $\alpha/2$. eq. (1) gives the angles at which null intensity (zero intensity) occurs with n being any integer (except zero). Notice that the angular size of the central maximum is either the slit width α or zero.

The graph in fig. (b) shows how the intensity on the screen varies with the angle θ . It shows the central maximum at $\theta = 0$, zero intensity at $\theta = \pm n\lambda/\alpha$ ($n \neq 0$) and secondary maxima at $\theta = \pm (n+1)\lambda/\alpha$ ($n \neq 0$).

Types of diffraction

Fraunhofer Diffraction

- source and screen are far away from each other
- Incident wave fronts on the diffracting obstacle are plane.
- Diffraction obstacle give rise to wave fronts which are also plane.
- Plane diffracting wave fronts are converged by means of a convex lens to produce diffraction patterns.

Bragg's Fresnel Diffraction

- Source and screen are not far away from each other
- Incident wave fronts are spherical
- Wave fronts leaving the obstacle are spherical
- Convex lens is not needed to converge the spherical wave fronts.

Scattering

Q Explain the term scattering. What are its applications?

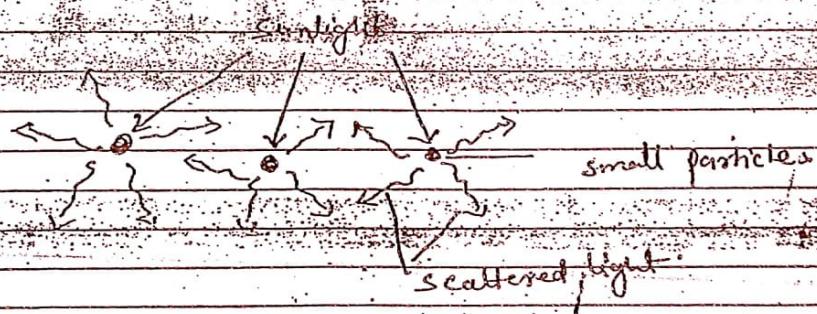
Ans: Scattering is a general physical process where some forms of radiation such as light, sound or moving particles are forced to deviate from a straight line by one or more paths due to irregularities non-uniformities in the medium through which they pass. Scattering may also



(b)

refers to particle-particle collisions b/w molecules, atoms, electrons, photons and other particles. For example \rightarrow cosmic ray scattering in the Earth's upper atmosphere; particle collision trials; particle accelerators; electron scattering by gas atoms in fluorescent lamps; and neutron scattering inside nuclear reactors.

The types of particles or non-uniformities found which have ability to scatter solar radiation in all directions are called scatterers or scattering centres. e.g. - particles, bubbles, droplets and can also include particulates made by human industries.



Types of scattering

Selective scattering (Rayleigh scattering) \rightarrow This type of scattering occurs when certain particles

are more effective at scattering a particular wavelength of light. Air molecules like oxygen and nitrogen for example are small in size and thus more effective at scattering shorter wavelengths of light (blue & violet). The sole effective scatterer by air molecules is responsible for producing our blue sky on a clear sunny day.

Mie Scattering - This type of scattering is responsible for the orange glow of a sunset. Cloud droplets with a diameter of 20 micrometers or so are large enough to scatter all visible wavelengths more or less equally. This means that almost all of the light from the sun enters clouds will be scattered because all wavelengths are scattered, clouds appear to be white. When clouds become very deep, less and less of the incoming solar radiation makes it through to the bottom of the cloud, which gives them a darker appearance.

Applications

- Some of the areas where scattering is significant include:
 - Radar sensing
 - medical ultrasound

- semiconductor wafer inspection
- polymerization process monitoring
- free space communications
- Particle-particle scattering theory is important in areas such as particle physics, atomic molecules and optical physics, nuclear physics and astrophysics.