

# ELECTRONIC SPECTROSCOPY

↳ In this spectroscopy electronic transition takes place.

↳ Relies on the quantized nature of energy state.

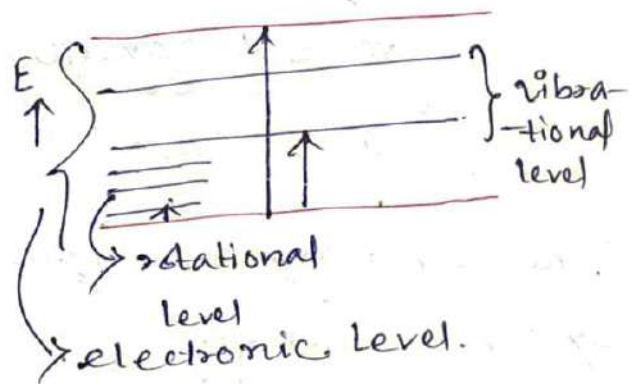
Since,

↳ From Born-Oppenheimer approximation -

$$E_{\text{total}} = E_{\text{rot.}} + E_{\text{vib.}} + E_{\text{elec.}} \quad [E_{\text{trans.}} \text{ is negligible}]$$

$$E_{\text{elec.}} \gg E_{\text{vib.}} \gg E_{\text{rot.}}$$

↳ Along with electronic transition, vibrational as well as rotational transition also take place.



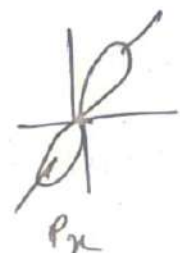
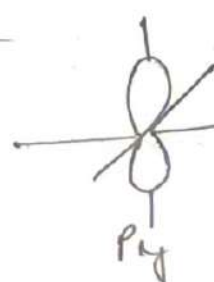
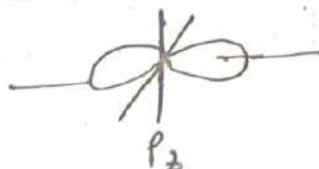
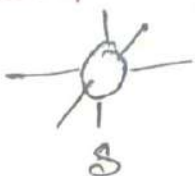
↳ Electronic spectra is a complex spectra  
 ↳ Energy required for electronic transition is 5-10 eV (UV-visible region)

↳ Also known as UV-visible spectroscopy.

↳ It is an analytical technique to study the electronic structure & its dynamics in atoms & molecules.

## Electronic spectroscopy of atoms -

### Shape of Atomic orbitals -



For  $1s$  —  
 $n = 1, l = 0$   
 $m = 0$

For  $2p_z$   
 $n = 2, l = 1, m = +1, 0, -1$

For  $3s$  —  
 $n = 3, l = 0$   
 $m = 0$

For  $3p$   
 $n = 3, l = 1$   
 $m = 0, +1, -1$

where —

$n$  = Principal quantum no. ( $n = 1, 2, 3, \dots$ )

$l$  = Orbital " ( $n-1, n-2, \dots, 0$ )

$m$  = magnetic " ( $\pm 1, \pm(l-1), \dots, 0$ )

$s$  = spin " ( $\pm \frac{1}{2}$ )

### The energy of atomic orbitals —

↳ The energy of each orbital varies considerably from atom to atom.

↳ There are two main contributions —  
i) Attraction between electrons and molecules.

ii) Repulsion between electrons in the same atom.

↳ For Hydrogen atom —

— Inter-nuclear effect is absent

— All orbitals with the same 'n' values have the same energy in hydrogen.

e.g.  $2s$  &  $2p$  are degenerate for hydrogen atom.

↳ For  $s$ -orbital,  $E_n = -\frac{m e^4}{8 h^2 \epsilon_0^2 n^2} \text{ J}$

$$E_n = - \frac{m e^4}{8 h^3 c \epsilon_0^2 n^2} \text{ cm}^{-1}$$

$$E_n = - R/n^2 \text{ cm}^{-1} \rightarrow \textcircled{1} \quad (n=1, 2, 3, \dots)$$

where,

$\epsilon_0$  = vacuum permittivity

$R$  = Rydberg const ( $R = \frac{m e^4}{8 h^3 c \epsilon_0^2}$ )

↳ For hydrogen atom, since p, d... orbitals have the same energies as the corresponding s-orbital, therefore eq<sup>n</sup> ① represents all the electronic energy levels of this atom.

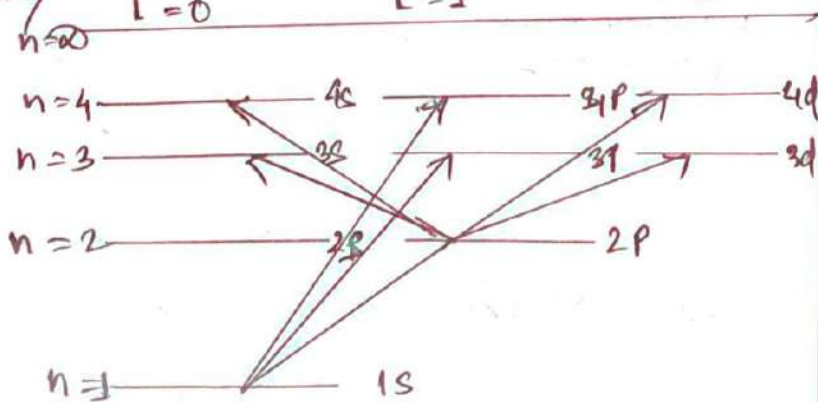
↳ For lowest value of  $E_n$  —

$$E_n = - R \text{ cm}^{-1}, \quad (n=1)$$

Represents the most stable state known as ground state.

↳ The value of  $E_n$  increases with the increasing value of 'n'.

↳  $E_n = 0$  for  $n = \infty$  → the state of ionization.



Selection Rule

$\Delta n = \text{anything}$ ,

$\Delta l = \pm 1$  only

$\therefore 1s \rightarrow np \quad (n \geq 2)$

&  $2p \rightarrow ns \text{ or } nd$

fig: Some lower electronic energy levels and transition between them for hydrogen atom

↳ Since energy of s, p, d orbitals are same in case of hydrogen atom, so energy required for transitions are also same.

↳ In general —

$$\Delta E = E_{n'} - E_{n''} \quad \text{cm}^{-1}$$

$\left\{ \begin{array}{l} \text{If, } n' = \text{higher state \& } \\ n'' = \text{lower state} \end{array} \right\}$

where,  $\Delta E = \text{energy difference.}$

Therefore —

$$\begin{aligned} \text{wave no., } \bar{\nu}_{\text{spectroscopy}} &= \frac{R}{n'^2} - \left( -\frac{R}{n''^2} \right) \\ &= R \left\{ \frac{1}{n'^2} - \frac{1}{n''^2} \right\} \text{cm}^{-1} \end{aligned}$$

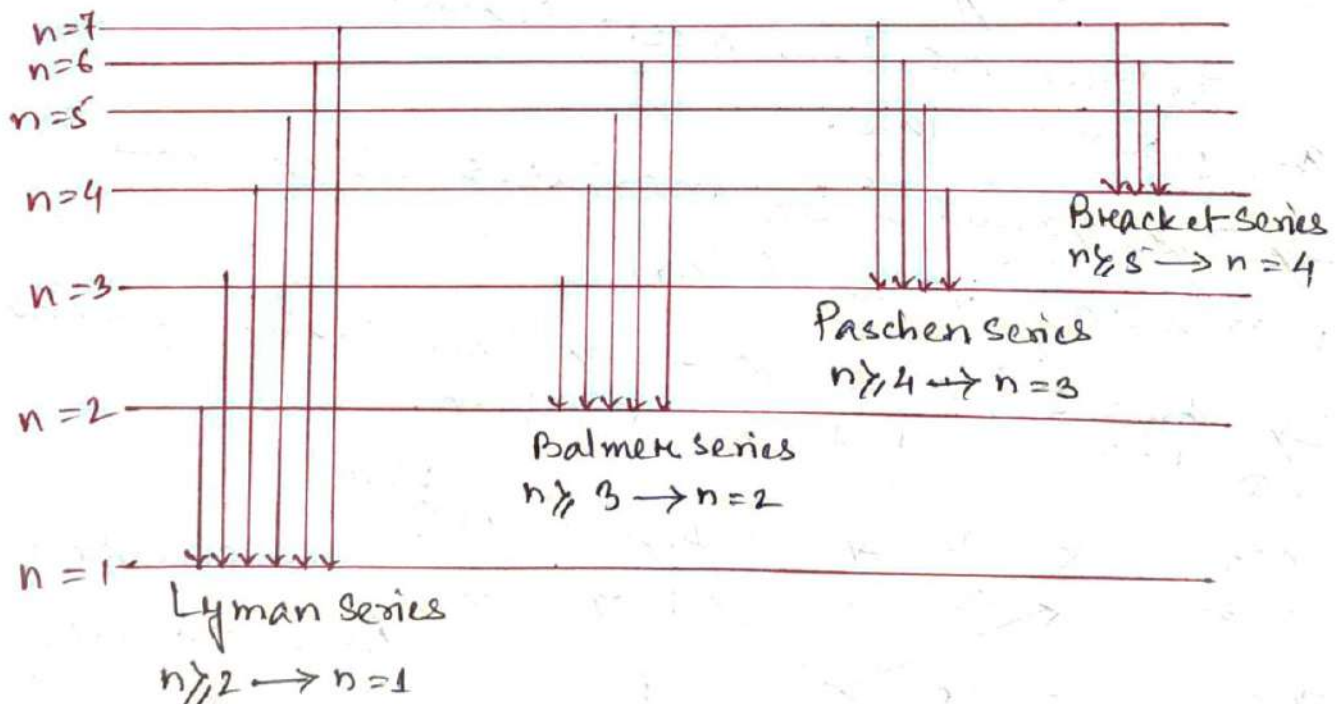


Fig: Spectrum of hydrogen.

↳ The spectrum of hydrogen consists of a large no. of lines.

↳ Each line series of hydrogen spectrum is continuous absorption or emission to high wave numbers of the convergence limits.

↳ Convergence limit represent the situation where the atomic electron has absorbed just sufficient energy from radiation to escape from the nucleus with zero velocity.

↳ Atomic electron may absorb more than this & hence escape with higher velocities.

↳ K.E. of an electron moving in free space is not quantized, any energy above the ionization energy can be absorbed.

↳ Hence the spectrum in this region is continuous.

Electronic Angular Momentum — (For single e<sup>-</sup> states)

↳ Orbital Angular Momentum — ( $l \rightarrow B \cdot a$ )

orbital angular momentum  $l_z$

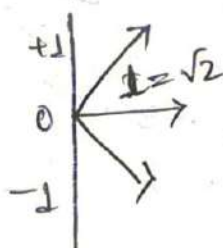
$$l = \sqrt{l(l+1)} \frac{h}{2\pi}$$

$$= \sqrt{l(l+1)} \text{ units}$$

[  $l$  = orbital quantum no. ]

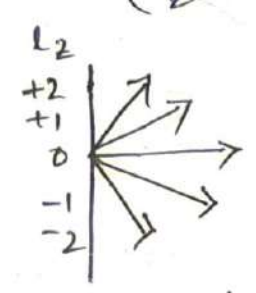
$$\left( \frac{h}{2\pi} \pm l, \pm(l-1), \dots, 0 \right)$$

(  $l_z \equiv m$  )



$l = (p\text{-state})$

$$\therefore l = \sqrt{1(1+1)} = \sqrt{2}$$



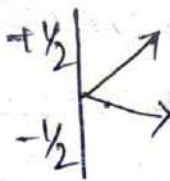
$l = 2$  (d-state)

$$l = \sqrt{2(2+1)} = \sqrt{6}$$

↳ Electron spin angular momentum — ( $S$ )

spin angular momentum  $\vec{S} = \sqrt{s(s+1)} \frac{h}{2\pi}$   
 $= \sqrt{s(s+1)}$  units.  $\left\{ \begin{array}{l} s = \text{spin quantum no.} \end{array} \right.$

↳  $S_z$



$S = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \quad [s = \frac{1}{2}]$   
 $= \sqrt{\frac{1}{2} \times \frac{3}{2}} \quad [S_z = +\frac{1}{2}, -\frac{1}{2}]$   
 $S = \frac{1}{2} \sqrt{3} \quad = \frac{1}{2} \sqrt{3}$

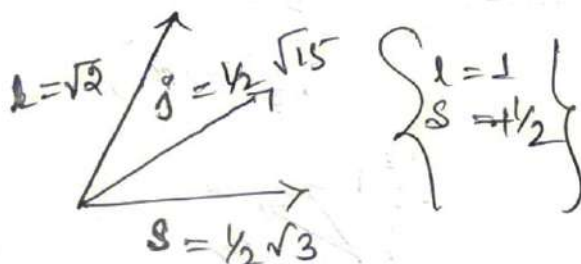
↳ Total electronic Angular Momentum — ( $J$ )

Total angular momentum  $\vec{J} = \vec{l} + \vec{s}$

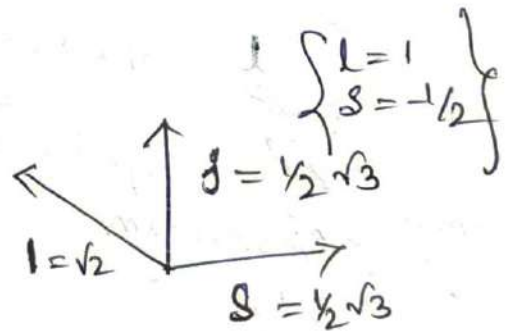
$J = \sqrt{j(j+1)} \frac{h}{2\pi}$   
 $= \sqrt{j(j+1)}$  units.  $\left\{ \begin{array}{l} j = \text{total angular momentum quantum no.} \\ j = l + s \end{array} \right.$

$J_z = \pm j, \pm(j-1), \dots, \frac{1}{2}$

For p electron,  $l=1$



↳  $l$  &  $s$  have the same direction



↳  $l$  &  $s$  oppose each other

↳ Thus total momentum is different in magnitude for the two cases.

↳ Hence have two different energy states depending on whether  $L$  &  $S$  reinforce or oppose for the same electron.

### Term Symbol —

$2S+1$   
 $L_j$  An abbreviated description of the total angular momentum quantum no.

↳ Provides information —

- ↳ ~~Total~~ orbital angular momentum,  $l$
- ↳ Spin multiplicity of the term,  $2S+1$
- ↳ Total angular momentum  $j$

eg:-  
For  $l = 1, S = +1/2, -1/2$

$$\begin{aligned} \therefore 2 \times \frac{1}{2} + 1 & \text{P} \\ & \text{L+S} \\ & = 2 \text{P}_{1+1/2} \\ & = \underline{\underline{2 \text{P}_{3/2}}} \end{aligned}$$

$$\begin{aligned} 2 \times \frac{1}{2} + 1 & \text{P} \\ & \text{L+S} \\ & = 2 \text{P}_{1-1/2} \\ & = \underline{\underline{2 \text{P}_{1/2}}} \end{aligned}$$

↳  $l = 0 \quad 1 \quad 2 \quad 3$

State symbol = S P D F

# Fine structure of Hydrogen Atom Spectrum

Selection rule —

$\Delta n = \text{anything}$ ,  $\Delta l = \pm 1$ ,  $\Delta j = 0, \pm 1$

Allowed transitions between any S level & any P level —

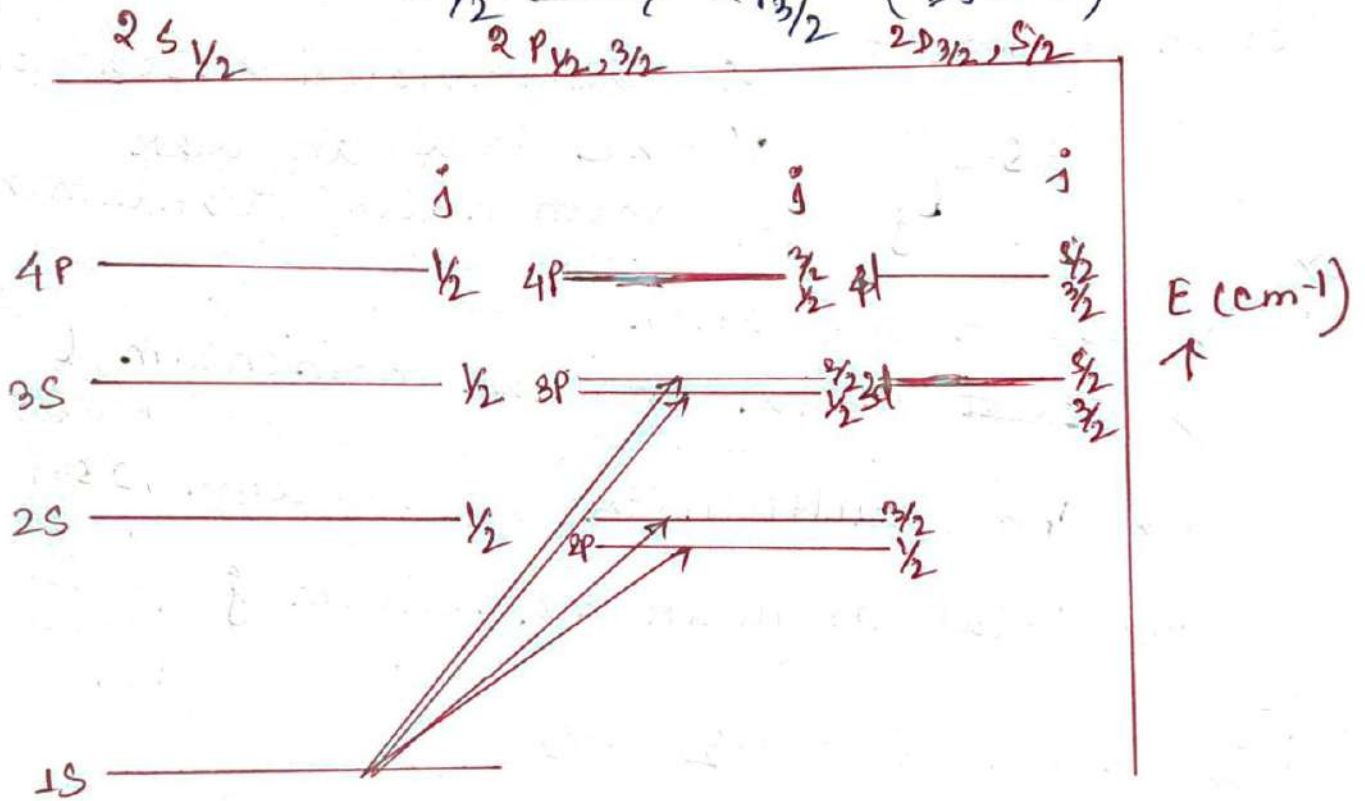
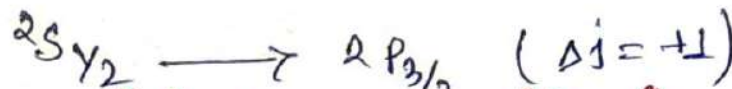
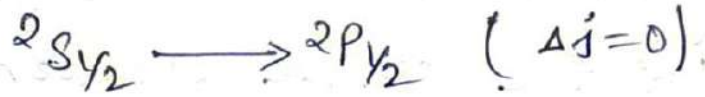
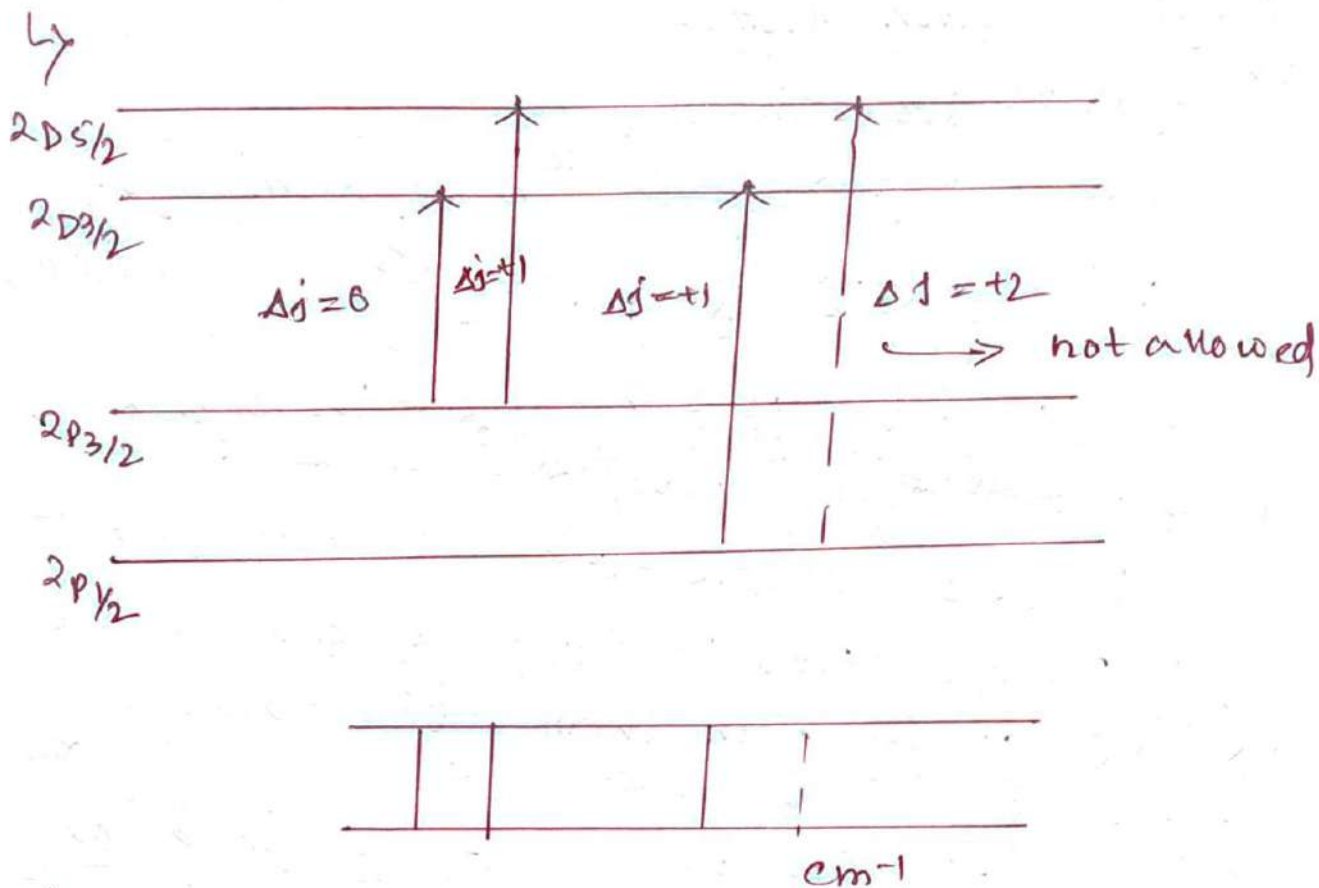


Fig: Transition between some of the lower energy states of the hydrogen atom inclusion of  $j$ -splitting.

$j$ -splitting decreases with increasing  $n$  & with increasing  $l$ .

↳ The inclusion of coupling between orbital and spin momenta has led to a slight increase in the complexity of the hydrogen spectrum.





↳ Fig: Compound doublet spectrum due to transition between  $2p$  &  $2d$  levels in hydrogen atom

↳ All the lines in hydrogen spectrum should be close doublets if the transition involve  $s$ -level or compound doublet if  $s$ -e<sup>-</sup>s are not involved.

↳ Thus in above fig. the spectrum will consist of the three lines shown at the foot of the fig. and this arising from transitions between doublet levels, which is referred to as "Compound doublet" spectrum.

## Multi-electron Atoms

↳ 1) Pauli's Principle —

No two electrons in an atom may have the same set of values for  $n, l, m, s$

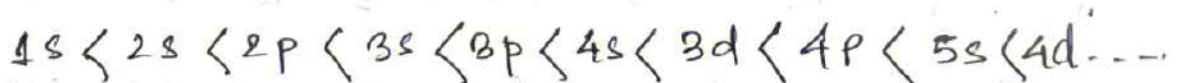
→ 2) Electrons tend to occupy the orbital with lowest energy level

→ Hund's principle —

Electrons tend to occupy degenerate orbitals singly with their spins parallel.

↳ Orbital energies in many-electron atoms increase with increasing  $n$ , as they do for hydrogen, but they also increase with increasing  $l$ .

The order of the energy levels for most atoms is as follows —



↳ When a set of orbitals of given  $n$  &  $l$  is filled it is referred to as a closed

shell. e.g. He  $\rightarrow 1s^2$   
Be  $\rightarrow 2s^2$  etc.

↳ Closed shells make no contribution to the orbital or spin angular momentum of the whole atom & hence they may be ignored when discussing atomic spectra.

# Electronic spectra of Hydrogen like species -

↳ Alkali metals, lithium, sodium,  $\text{He}^+$ ,  $\text{Be}^+$ ,  $\text{B}^+$ , potassium etc.

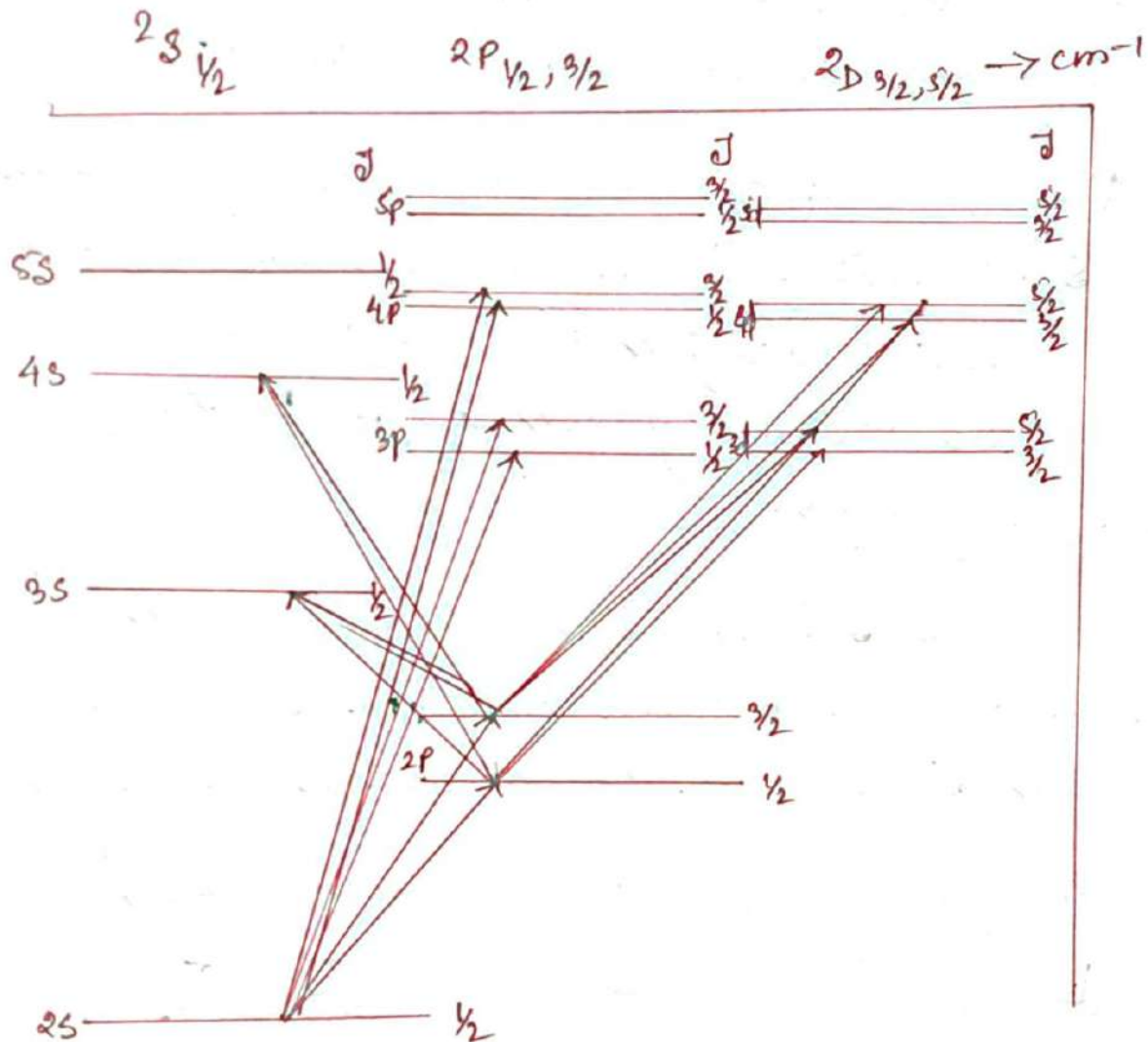


Fig: Some allowed transitions of some of the lower energy levels of the lithium atom.

↳ Selection rules -

$$\Delta n = \text{anything}, \quad \Delta l = \pm 1$$

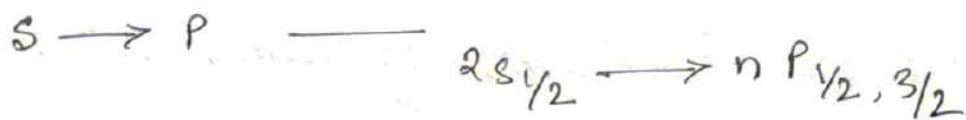
$$\Delta J = 0, \pm 1$$

↳ Two separate series of lines will be seen -

From 2p state } two separate series of lines

- $2 \ 2p_{1/2, 3/2} \rightarrow n \ 2s_{1/2}$
- $2 \ 2p_{1/2, 3/2} \rightarrow n \ 2D_{3/2, 5/2}$

↳ Transition from the ground state —



— A series of doublets similar to the Lyman series will be formed.

↳ The  $j$ -splitting due to coupling between  $L$  &  $S$  increases with the atomic no. Thus the doublet separation of lines in the spectral series for multi-electron atoms are higher than <sup>for</sup> hydrogen.

↳ Any atom which has a single electron moving outside a closed shell will exhibit a spectrum of the type of "hydrogen-like spectra".

Term Symbol — (For multi-electron atom)

$$\begin{matrix} (B.O.D) \\ \hookrightarrow \end{matrix} L = \sqrt{L(L+1)}, \begin{matrix} (B.O.D) \\ \hookrightarrow \end{matrix} S = \sqrt{S(S+1)}, \begin{matrix} (B.O.D) \\ \hookrightarrow \end{matrix} J = \sqrt{J(J+1)}$$

$(B.O.D) \hookrightarrow L$  = Total orbital momentum  
 $2L$  = total " " quantum no.

$(B.O.D) \hookrightarrow S$  = Total spin angular momentum  
 $2S$  = Total " " quantum no.

$(B.O.D) \hookrightarrow J$  = Total angular momentum  
 $2J$  = Total " " quantum no.

∴ Term Symbol —  $2S+1 \underset{J}{L}$  where,  $L = \text{orbital quantum no.}$

For Symbol  $\rightarrow$   $L = 0 \ 1 \ 2 \ 3 \ 4 \ \dots$   
 $\rightarrow \ 3 \ P \ D \ F \ G \ \dots$

# ELECTRONIC SPECTROSCOPY OF MOLECULES

## The Born-Oppenheimer Approximation:-

↳ Implies that electronic, vibrational & rotational energies of a molecule are completely independent of each other.

↳ Total energy of a molecule —

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

∴ change in the total energy —

$$\Delta E_{\text{total}} = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}} \quad \text{J}$$

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

↳ Electronic spectra are given by all molecules since changes in the electronic distribution in a molecule are always accompanied by a dipole change.

## Vibrational Coarse Structure:- (Diatomic molecule)

Ignoring rotational changes —

$$E_{\text{total}} = E_{\text{elec.}} + E_{\text{vib}} \quad \text{J}$$

$$E_{\text{total}} = E_{\text{elec.}} + E_{\text{vib}} \quad \text{cm}^{-1}$$

$$\text{Since, } E_{\text{vib}} = (v + \frac{1}{2}) \bar{\omega}_e - (v + \frac{1}{2})^2 \bar{\omega}_e x_e \quad \text{cm}^{-1}$$

$$(v = 0, 1, 2, \dots)$$

where,  $v$  = vibrational quantum no.

$\bar{\omega}_e$  = Oscillation frequency  
(expressed in frequency)

$x_e$  = Anharmonicity constant.

↳ For bond stretching vibrations, —

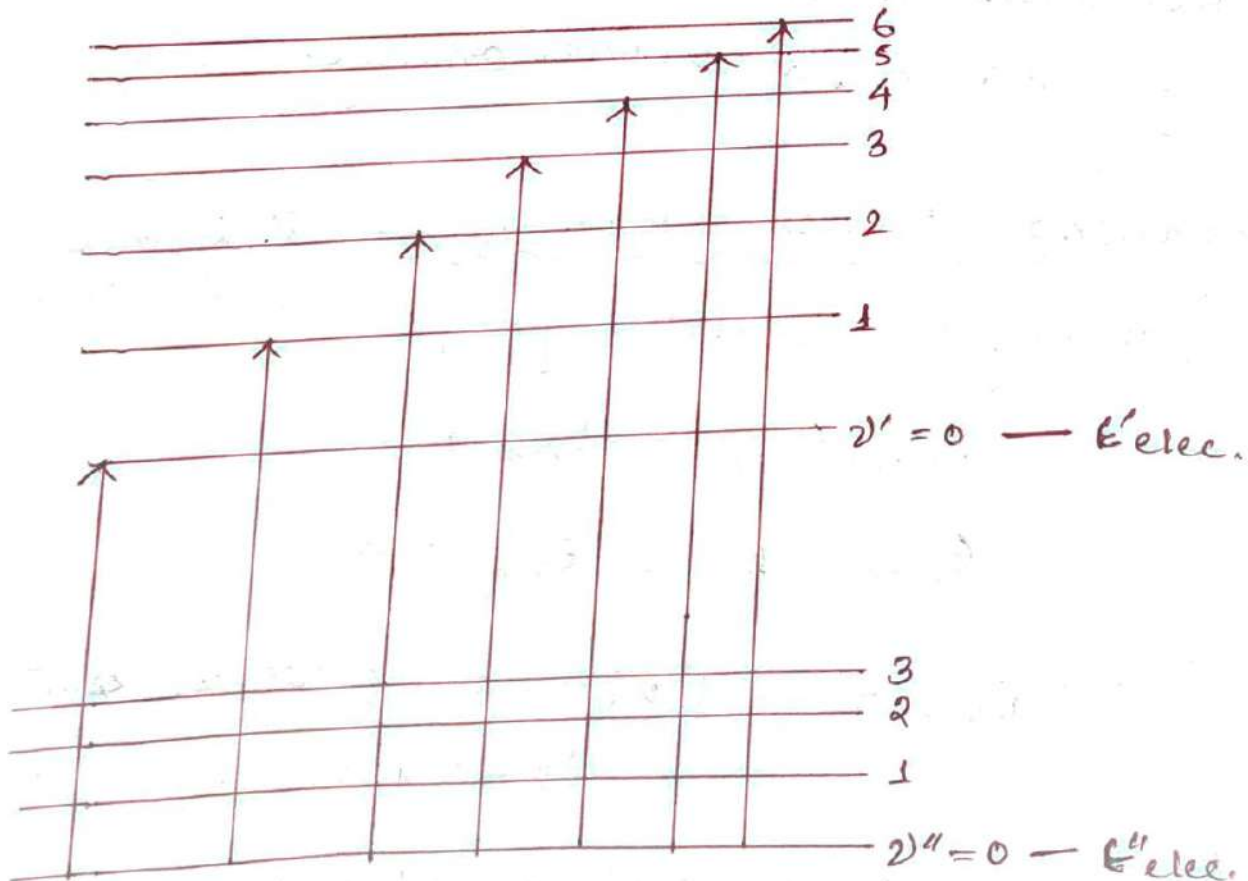
—  $x_e$  is small and positive.

↳ value of  $x_e \approx 0.01$

↳ Indicates that the vibrational levels crowd more closely together with increasing the value of  $v$ .

$$\therefore E_{\text{total}} = E_{\text{elec.}} + (v + \frac{1}{2})\bar{\omega}_e - x_e (v + \frac{1}{2})^2 \bar{\omega}_e \text{ cm}^{-1}$$

( $v = 0, 1, 2, \dots$ )



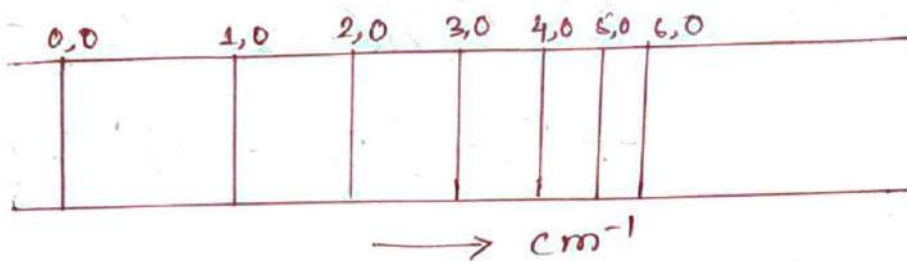


Fig:- Vibrational 'coarse' structure of the band formed during electronic absorption from the ground state ( $v''=0$ ) to a higher state.

↳ When a molecule undergoes an electronic transition, i.e.,  $v'' \rightarrow v'$ , there is essentially no selection rule for  $v$ .

- Hence so many spectral lines would be expected.

↳ Virtually all the molecules exist in the lowest vibrational state, ( $v''=0$ ). So only transitions to be observed with appreciable intensity are  $v''(0) \rightarrow$  higher levels ( $v'(1, 2, 3, \dots)$ )

↳ Set of transition such as ( $v', v''$ ) eq:- (0,0), (1,0), (2,0) - ... are called band.

↳ The lines in a band crowd together more closely at high frequencies. This is due to anharmonicity of the upper state vibration.

Again — 
$$\Delta E_{\text{total}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib.}}$$

$$\therefore \tilde{\nu} \text{ spec.} = (E' - E'') + \left\{ (\nu' + \frac{1}{2}) \bar{\omega}_e' - x_e' (\nu' + \frac{1}{2})^2 \bar{\omega}_e'^2 \right. \\ \left. - \left[ (\nu'' + \frac{1}{2}) \bar{\omega}_e'' + x_e'' (\nu'' + \frac{1}{2})^2 \bar{\omega}_e''^2 \right] \right\} \text{ cm}^{-1}$$

↙  
wave no. of  
spectral lines absorbed  
or emitted.

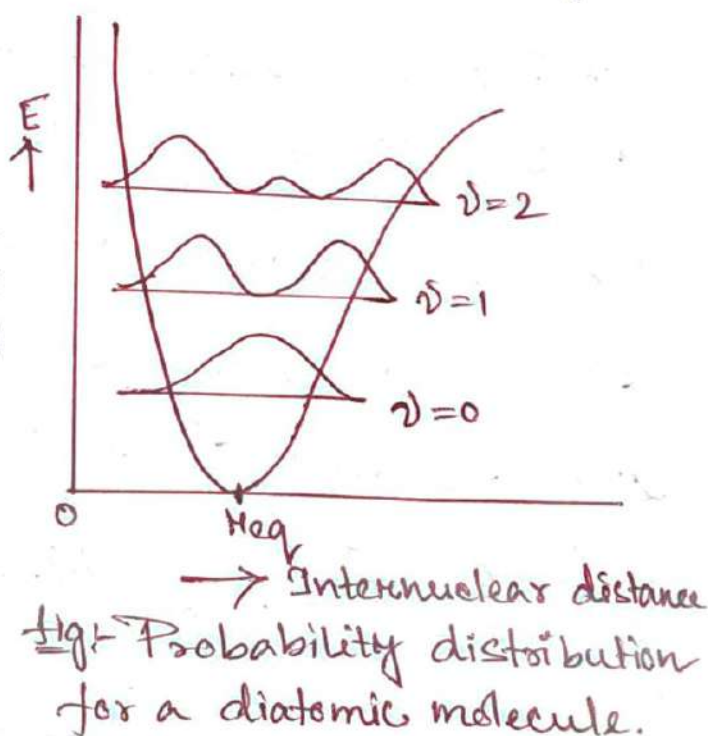
### Frank-Condon Principle -

↳ During an electronic transition, the vibrational lines in a progression are not all observed to be of the same intensity.

↳ This can be explained by Frank-Condon Principle.

This principle states that, an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

↳ In the fig. the Morse curve, represents the energy distribution, when one atom is considered fixed on the  $r=0$  axis & the other is allowed to oscillate between the limits of the curve.





From the fig., it is observed that the nuclei are most likely to be found at a distance apart given by the maxima of the curve for each vibrational state.

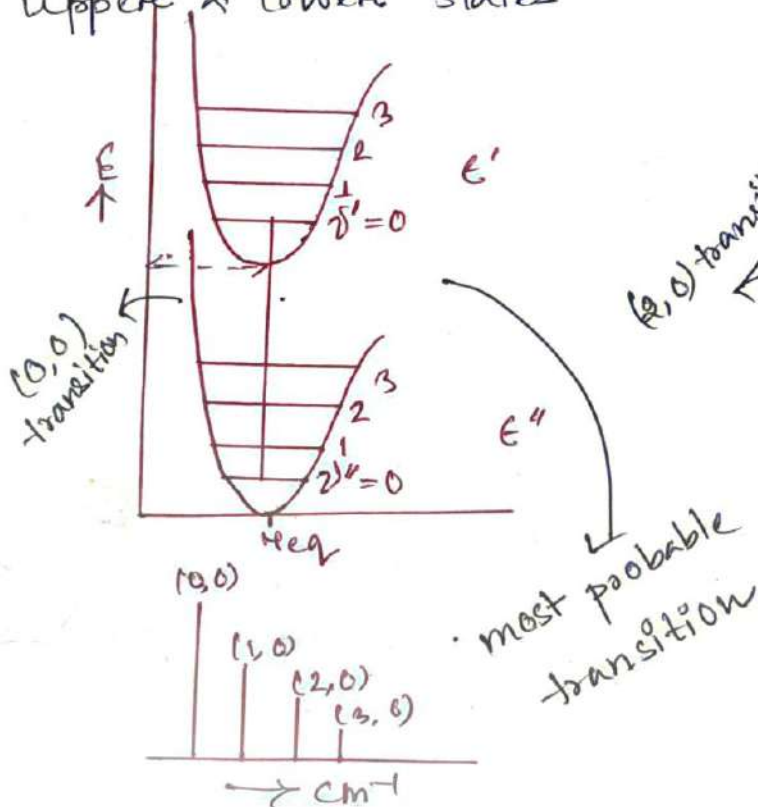
It shows that —

For  $v=0$ , the atom is likely to be found at a centre of its motion, i.e., at the eqm internuclear distance  $r_{eq}$ .

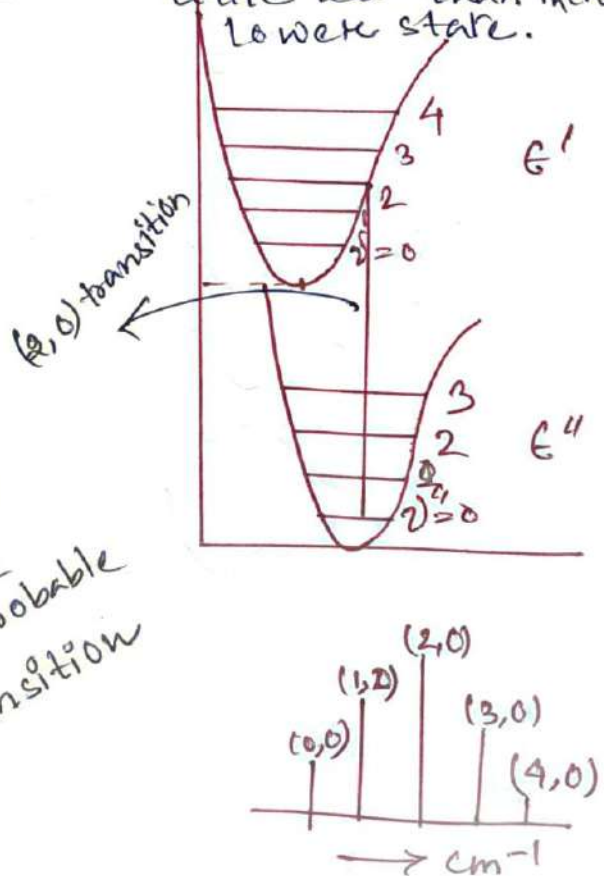
When a diatomic molecule undergoes a transition into an upper electronic state —

There will be four possibilities —  $(0,0)$  = ground state  
 $(v', 0)$  = excited state

i) Internuclear distances equal in the upper & lower states

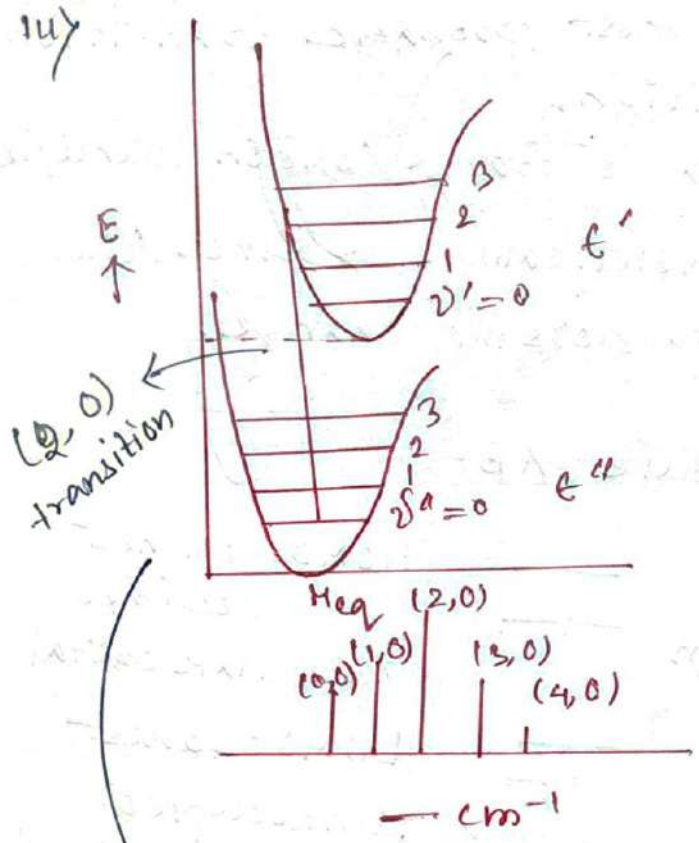


ii) Upper state internuclear distance a little less than in the lower state.



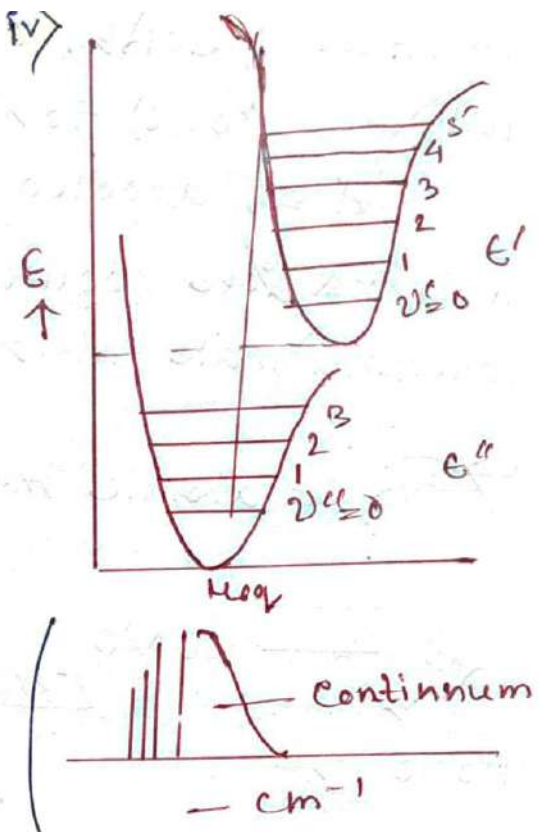
most probable transition

iii)



Upper state distance a little greater than in lower state.

iv)



Upper state distance considerably greater.

In this case, transition occurs to a state where the excited molecule has energy in excess of its own dissociation energy

From such states the molecule will dissociate without any vibration, & the transitions are not quantized & a continuum results.

But according to Franck-Condon Principle - case (i), i.e. (0,0) transition will give highest

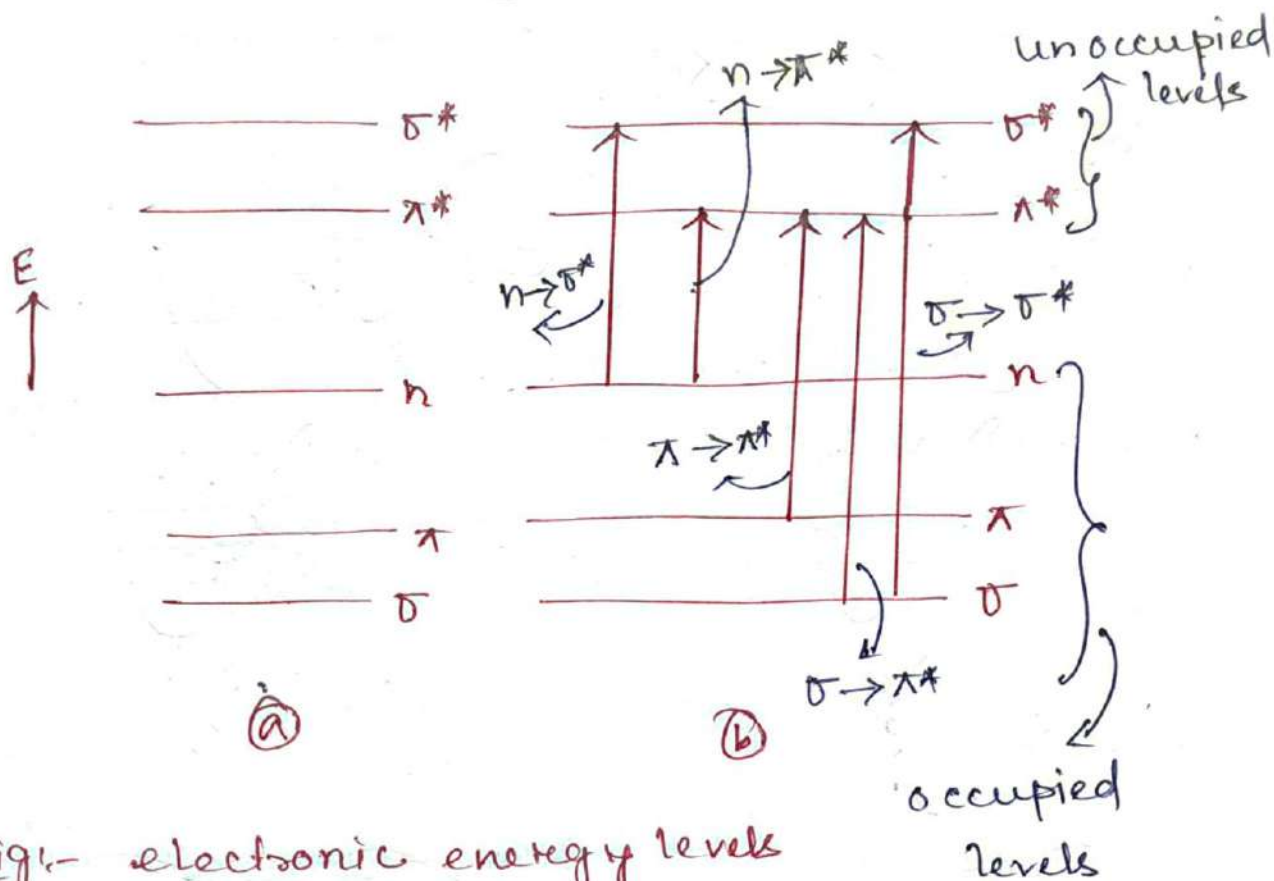


Fig:- electronic energy levels & transitions

↳ All compounds other than alkanes, the  $e^-$ s may undergo several possible transitions of different energies —

- $\sigma \rightarrow \sigma^*$  → In alkanes
- $\sigma \rightarrow \pi^*$  → In carbonyl compounds
- $\pi \rightarrow \pi^*$  → In alkenes, carbonyl compounds, alkynes, azo compounds etc.
- $n \rightarrow \sigma^*$  → In oxygen, nitrogen, sulfur & halogen compounds
- $n \rightarrow \pi^*$  → In carbonyl compounds.

## Selection rule —

### ① $\Delta S = 0$

— Change in spin quantum no. of an  $e^-$  during the transition is not allowed to take place — Forbidden transition if  $\Delta S > 0$ .

eg:- For an  $e^-$ ,  $S = +\frac{1}{2}$  &  $-\frac{1}{2}$

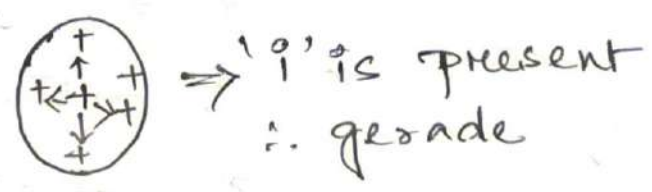
$\therefore \left. \begin{array}{l} (+\frac{1}{2}) \uparrow \longrightarrow \uparrow (+\frac{1}{2}) \\ (-\frac{1}{2}) \uparrow \longrightarrow \uparrow (-\frac{1}{2}) \end{array} \right\} \Rightarrow \Delta S = 0$   
allowed

$(+\frac{1}{2}) \uparrow \longrightarrow \downarrow (-\frac{1}{2}) \rightarrow$  Forbidden  
 $\Delta S = -\frac{1}{2} - (+\frac{1}{2}) = -1$

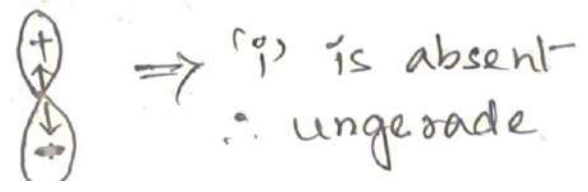
### ② Symmetry ( $\Delta l = \pm 1$ ) OR $g \rightarrow u$ allowed $u \rightarrow g$ allowed

$g$  &  $u$  (gerade)  $\rightarrow$  (ungerade)  $\rightarrow$   $i$  (centre of symmetry absent)  
 $\rightarrow$   $i$  (centre of symmetry present)

eg:- s-orbital —



p-orbital —

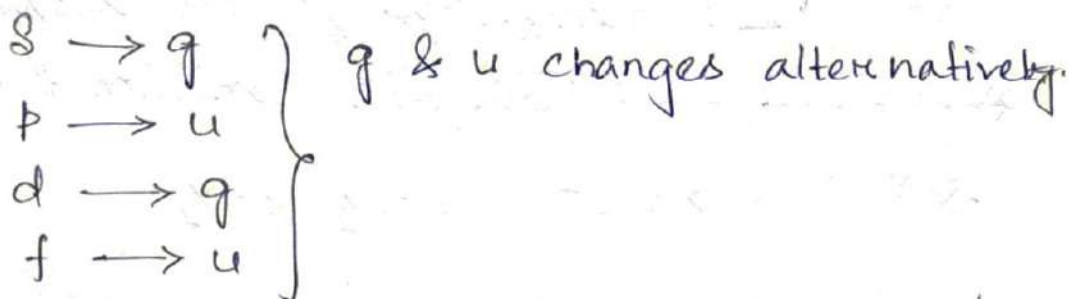


d-orbital —



$\Rightarrow$  'i' is present  
 $\therefore$  gerade.

Trick —



$\hookrightarrow$   $\sigma$ -orbital —

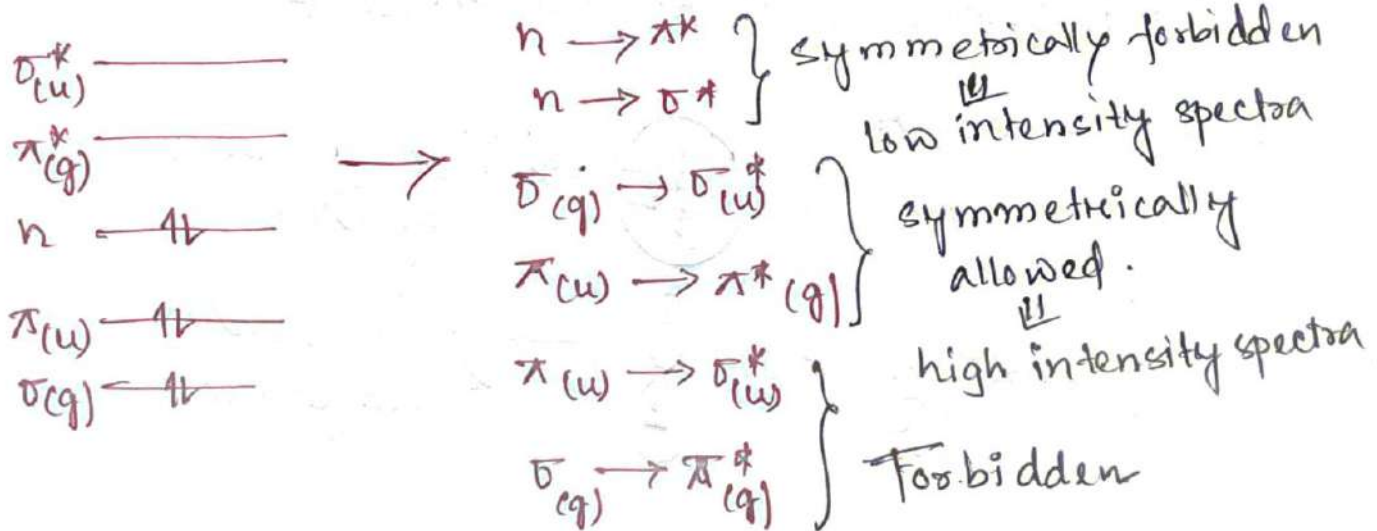
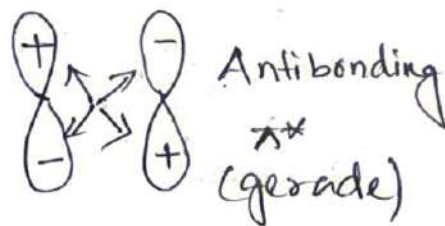
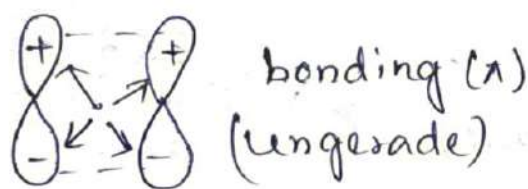


gerade (bonding orbital)

Antibonding orbital ( $\sigma^*$ )

$\hookrightarrow$  ungerade

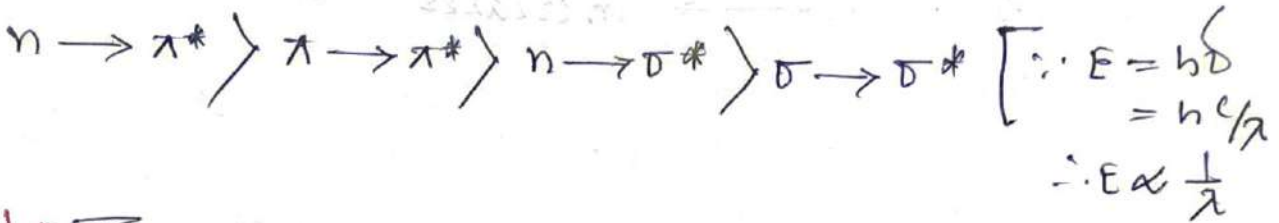
$\pi$ -orbital —



↳ Energy order —



Wavelength order —



↳ For UV —

$\lambda$  range  $\Rightarrow$  200-400 nm

Vacuum  $<$  200 nm

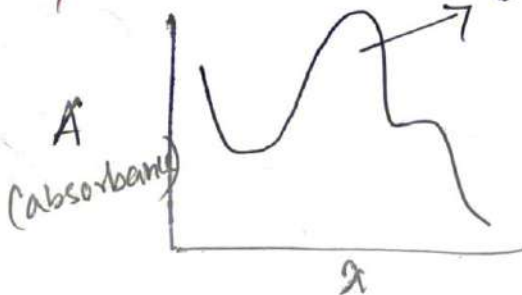


$\rightarrow$  n,  $\pi$ ,  $\sigma$  present

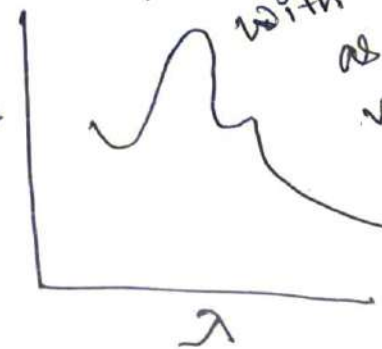
So, spectra recorded in vacuum  $\left\{ \begin{array}{l} - \text{so } O_2 \text{ also absorbs the incident light (radiation)} \end{array} \right.$

$\rightarrow$  Otherwise  $O_2$  will give the spectra along with the molecule for which spectra is recorded

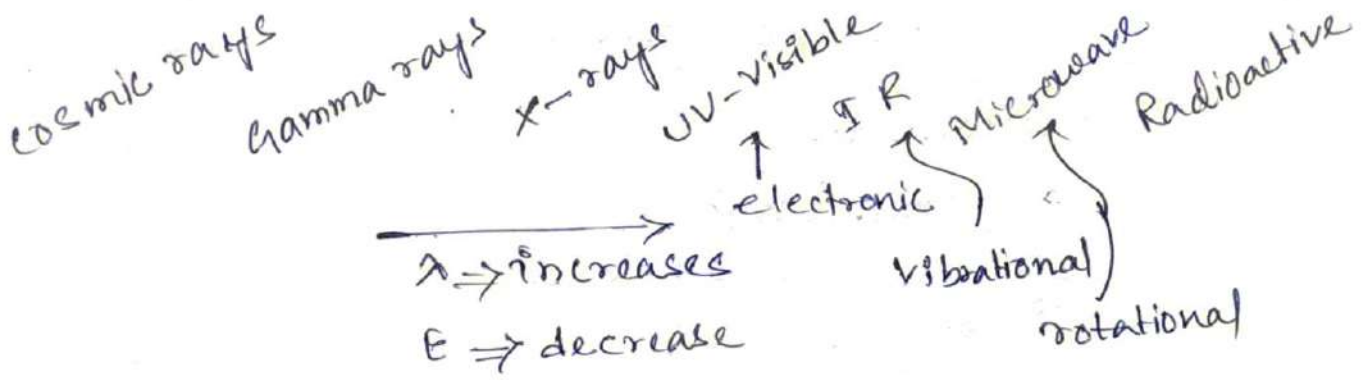
↳ Spectra —



log E



$\Rightarrow$  Since electronic transition associated with rotational as well as vibrational transitions



## Principle of Absorption Spectroscopy:-

- ↳ The greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption.
- ↳ The more effectively a molecule absorbs light of a given wavelength, the greater the extent of light absorption.

Therefore,

According to Beer-Lambert's law —

$$A = \log \left( \frac{I_0}{I} \right) = \epsilon c l \quad (\text{For a given wavelength})$$

Where, —

$A$  = Absorbance / optical density

$I_0$  = Intensity of light incident upon sample cell.

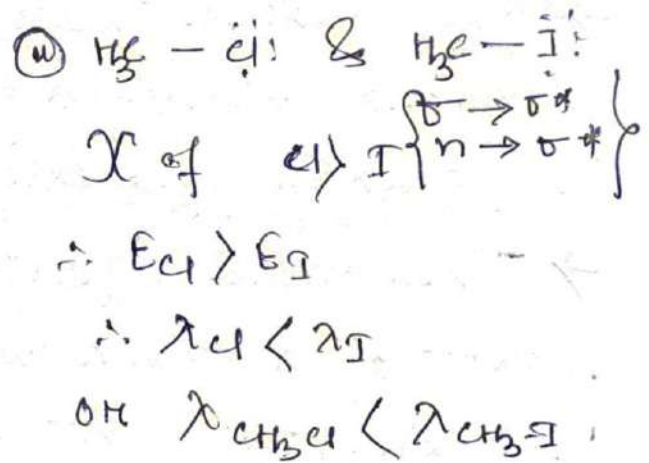
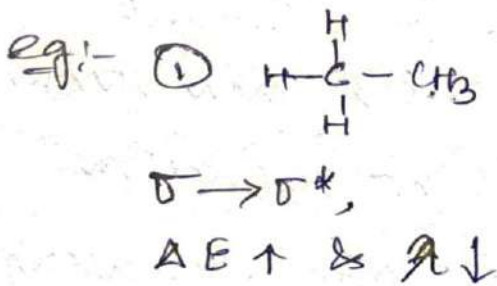
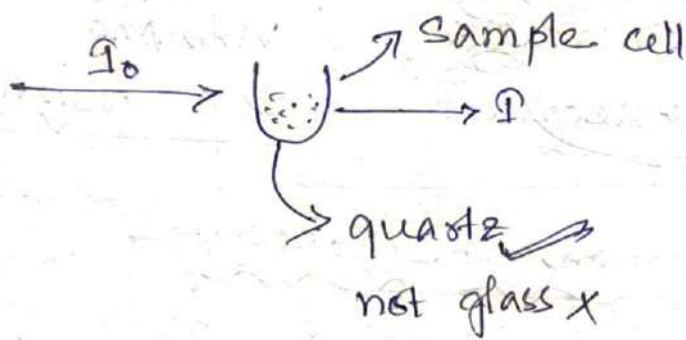
$I$  = Intensity of light leaving sample cell

$c$  = molar concentration of solute

$l$  = length of sample cell (cm)

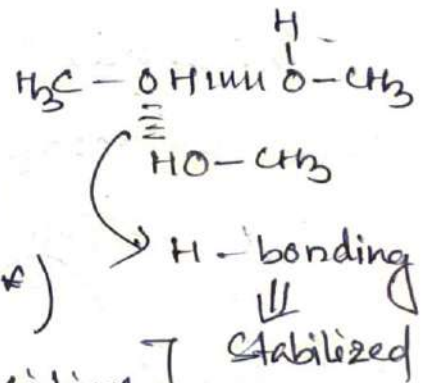
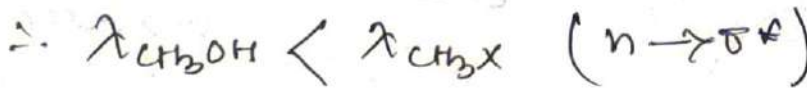
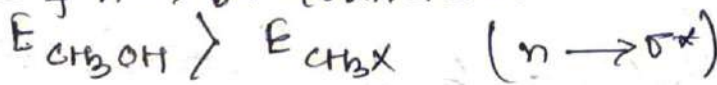
$\epsilon = \text{molar absorptivity}$

intensity depends on  $\lambda$

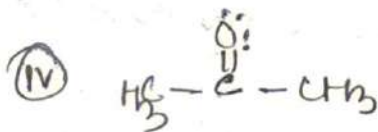


eg: (iii) —

In case of  $n \rightarrow \sigma^*$  transition



$[n \rightarrow \sigma^* \text{ is H-bonding sensitive}]$

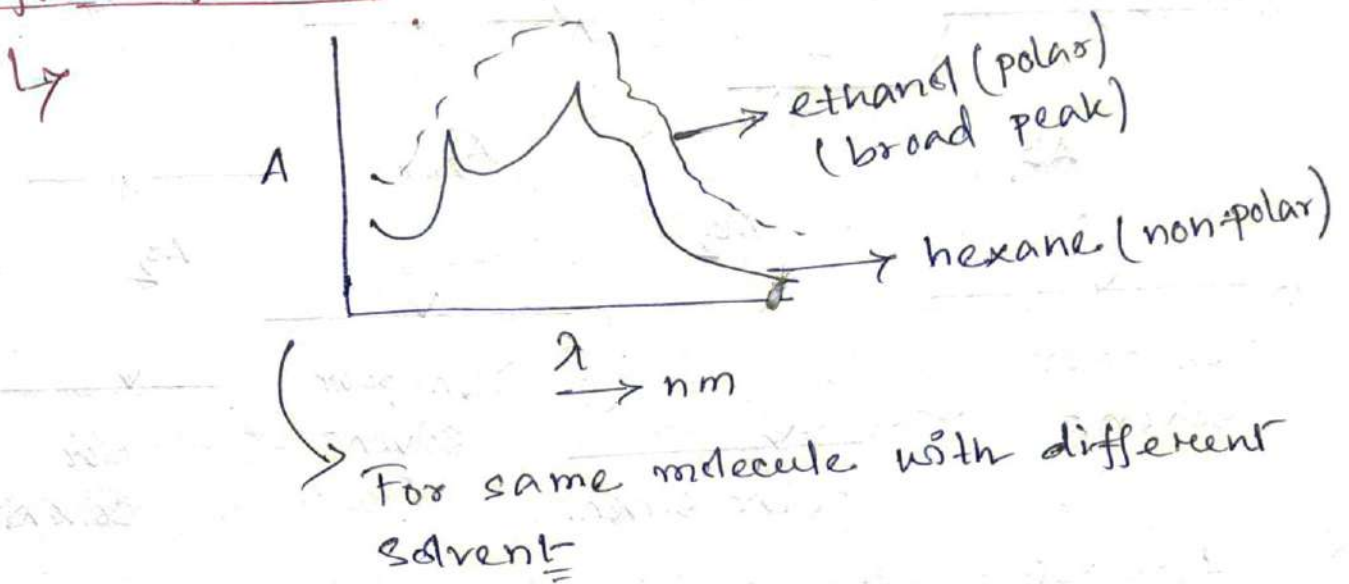


$\pi \rightarrow \pi^*$  (symmetrically allowed)  
 $n \rightarrow \pi^*$  ( " forbidden)

Intensity low



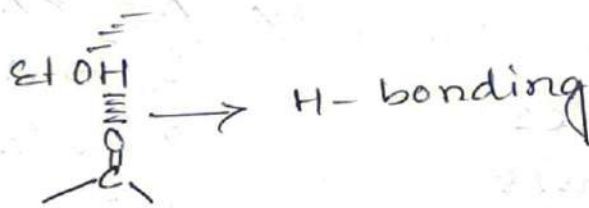
## Effect of solvent



In polar solvent —

solute-solvent interaction takes place.

eg:-



solute-solvent complex stabilized by

π-π-bonding.

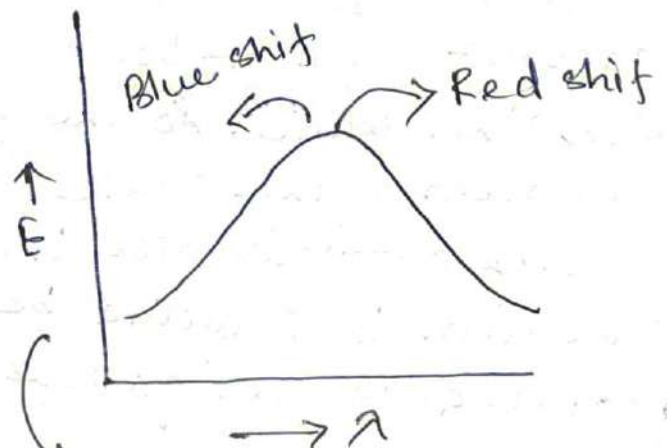
↳ polar solvents —

$H_2O$ ,  $EtOH$ ,  
 $CH_3OH$ ,  $CH_3CH$  etc.

Non-polar solvents —

n-Hexane, Isooctane,  
cyclo-hexane etc.

If solvent changes from  
polar to non-polar



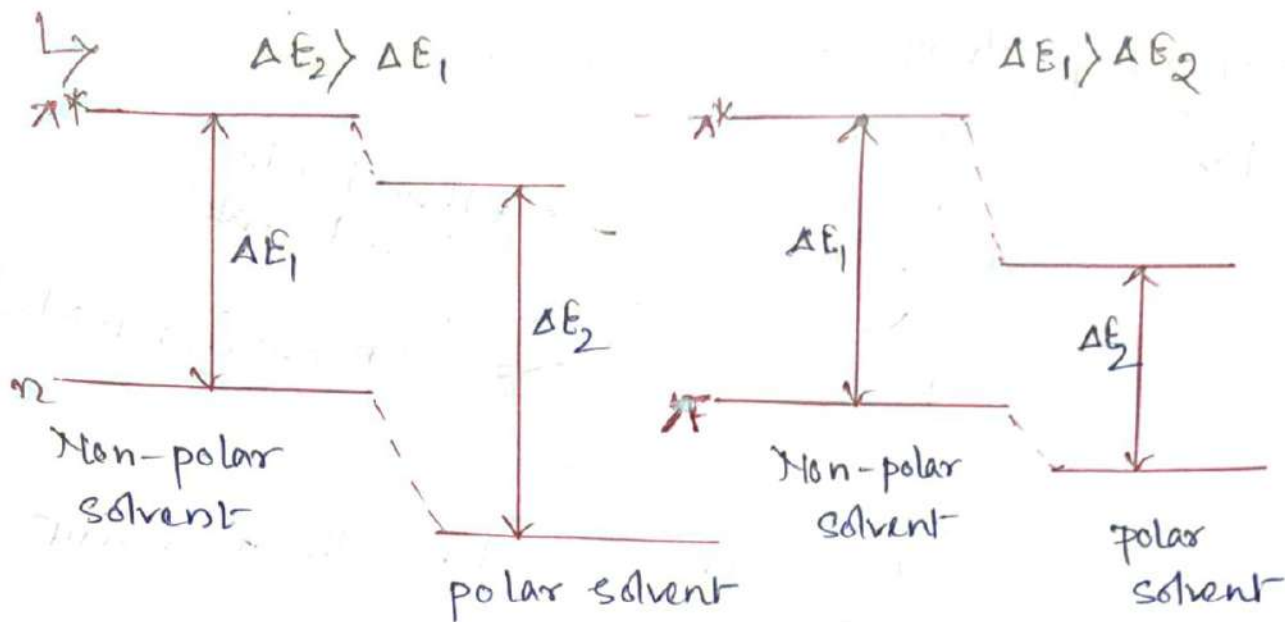


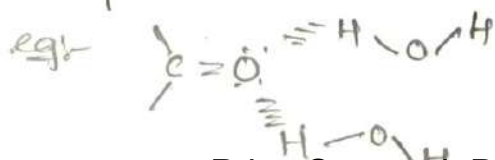
fig: Absorption shift with the change in polarity of the solvent

i)  $n \rightarrow \pi^*$   
 $E \rightarrow$  Increases  
 $\lambda \rightarrow$  decreases

$\therefore$  Blue shift

— A non polar solvent does not form H-bond with the solute, so the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state.

— In polar solvent, H-bonding forms a solute-solvent complex. So, n-orbital is stabilized in polar solvent more than  $\pi^*$



ii)  $\pi \rightarrow \pi^*$   
 $E \rightarrow$  decreases  
 $\lambda \rightarrow$  increases  
 $\therefore$  Red shift

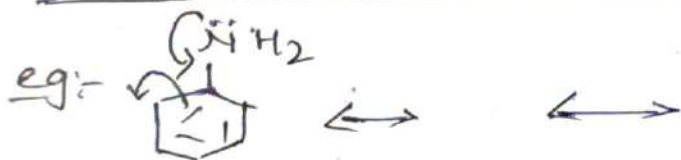
— Due to the transition to  $\pi^*$ -anti-bonding orbital, bond length increase & bond order decreases, so dipole moment of the bond increases —

$\therefore$  dipole moment =  $q \times d$   
 $q =$  charge,  $d =$  distance

Therefore excited state ( $\pi^*$ ) becomes more polar. So, H-bonding formation takes place in  $\pi^*$  & it gets stabilized more than  $\pi$ .

# Chromophore & Auxochrome

<u>Chromophore</u>	<u>Auxochrome</u>
<p>↳ Co-valently unsaturated compound or group</p> <p>eg:- <chem>C1=CC=CC=C1</chem>, <chem>[O-][N+](=O)c1ccccc1</chem>,  <math>(N=0)</math>  <math>(\geq 0)</math>  <chem>CC(=O)C</chem> etc.</p> <p>— Responsible for transitions.</p>	<p>↳ Saturated compound or gr.            eg: alkane  <chem>C</chem>, <chem>CC</chem>, <chem>CCN</chem>, <chem>CCCl</chem> etc.</p> <p>— changes intensity as well as wavelength of chromophores.            (Specially increases the intensity)</p>



↳ resonance occur  $\rightarrow$  Energy decreases.

Compound becomes coloured.  $\leftarrow$   $\lambda$  increases

↳ Bathochromic shift — (Red shift) — If. wavelength increases. or a shift to lower energy

↳ Hypsochromic shift — (Blue shift) — A shift to higher energy or shorter wavelength

↳ Hyperchromic effect



An increase in intensity

↳ Hypochromic effect



A decrease in intensity

↳ The attachment of substituent groups in place of hydrogen on a basic chromophore structure changes the position & intensity of an absorption band of the chromophore.

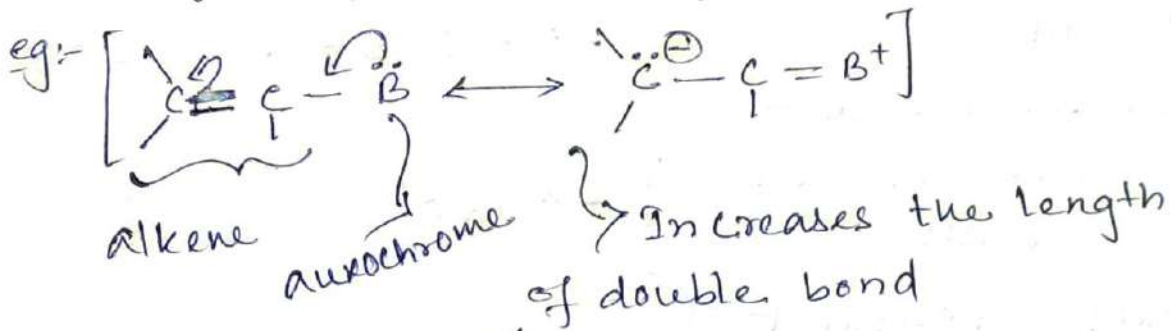
### The effect of Conjugation —

In the presence of conjugated double bonds, the electronic energy levels of a chromophore move closer together. As a result, the energy required to produce a transition from an occupied electronic level to an unoccupied level decreases, & the wavelength of the light absorbed becomes longer.



Bathochromic shift takes place.

→ Many auxochromes exert their bathochromic shifts by means of an extension of the length of the conjugated system.



Due to the interaction of lone pair of auxochrome with  $\pi$ -e<sup>-</sup> of double bond.

So, as a result non-bonded e<sup>-</sup>s become part of the  $\pi$ -system of molecular orbitals, increasing its length by one extra orbital

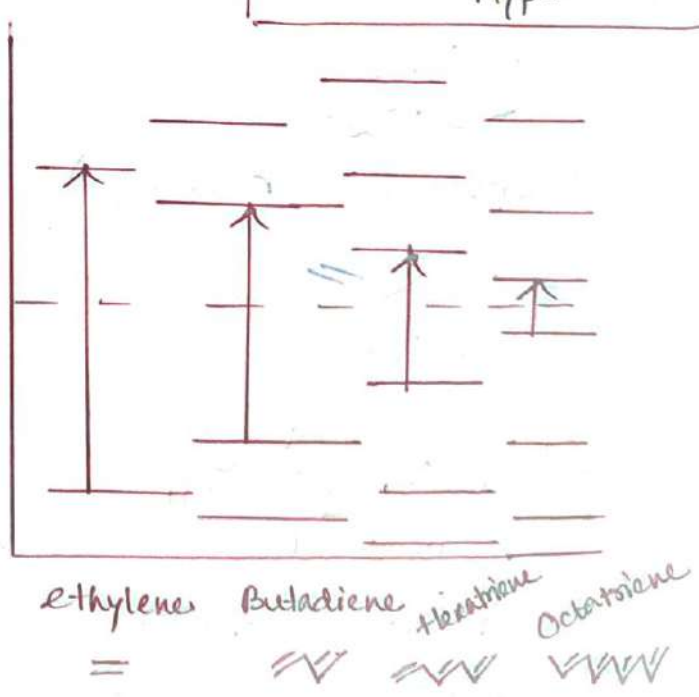
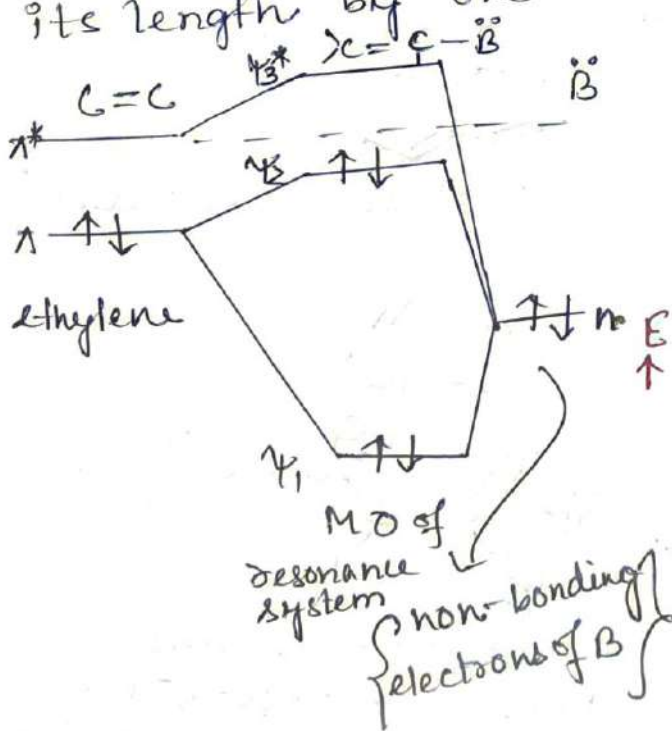
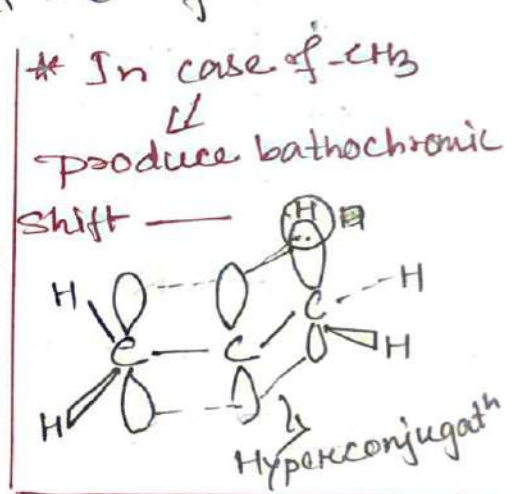


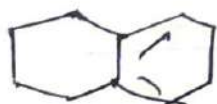
Fig- Energy relationship of new MO & the interacting  $\pi$ -system & its auxochrome

Fig- Comparison of  $\pi \rightarrow \pi^*$  energy gap in a series of polyenes.

# The Woodward - Fieser Rules (Prediction of the wavelength)

↳ For Dienes -

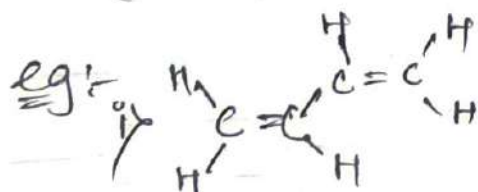
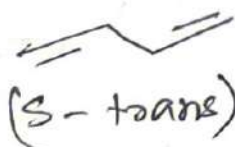
	Homonuclear (cisoid)	Heteronuclear (transoid)
↳ Parent	$\lambda = 253 \text{ nm}$	$\lambda = 214 \text{ nm}$
↳ <u>Increments for</u>		
i) Double bond extending conjugation	→ 30	20
ii) Alkyl substituent on ring residue	→ 5	5
iii) Exocyclic double bond	→ 5	5
↳ <u>Polar grouping</u> -		
- COCH <sub>3</sub>	→ 0	0
- OR	→ 6	6
- Cl, - BH	→ 5	5
- NR <sub>2</sub>	→ 60	60



(Homonuclear diene)

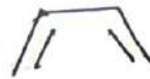


(Heteronuclear diene)

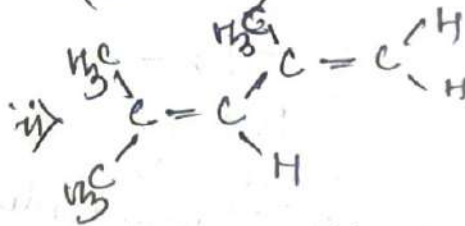


Transoid = 214 nm

observed = 217 nm



(s-cis)

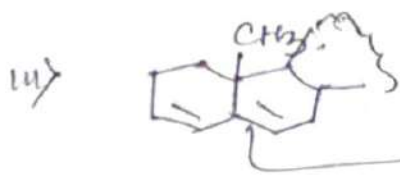


Transoid = 214 nm

Alkyl gps =  $3 \times 5 = 15 \text{ nm}$

$\lambda_{\text{max}} = 229 \text{ nm}$

observed = 228 nm



Transoid = 214 nm

Ring residue =  $3 \times 5 = 15$  nm

Exocyclic double bond = 5 nm

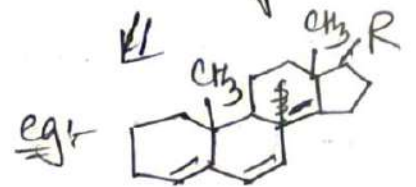
$$\lambda_{max} = 234 \text{ nm}$$

observed = 235 nm

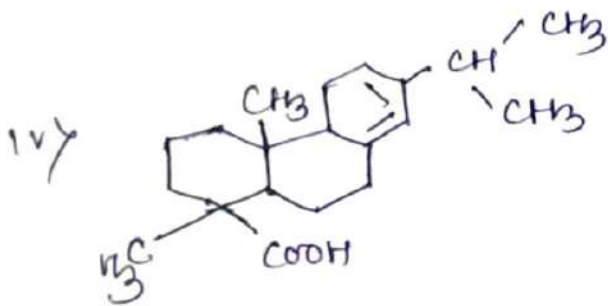
exocyclic double bond

(Lies outside a given ring)

↓  
may lie within one ring even though it is outside another ring.



No. of exocyclic double bonds = 3



Cisoid = 253 nm

Alkyl substituent = 5 nm

ring residues =  $3 \times 5 = 15$  nm

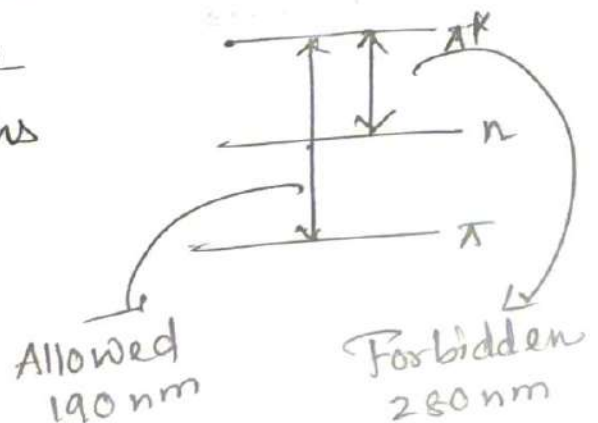
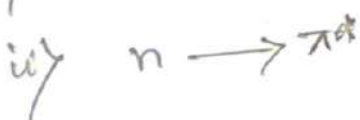
Exocyclic double bond = 5 nm

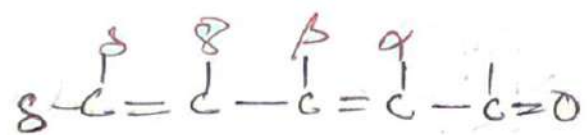
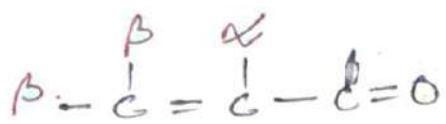
$$\lambda_{max} = 278 \text{ nm}$$

observed = 275 nm

↳ For carbonyl compounds; enones —

↳ Carbonyl compounds have two principal UV-transitions





1) Base values —

- i) Six membered ring or acyclic parent enone → 215 nm
- ii) Five-membered ring parent enone → 202 nm
- iii) Acyclic dienone → 245 nm

2) Increments for —

- i) Double bond extending conjugation → 30
- ii) Alkyl group on ring residue →
  - α 10
  - β 12
  - γ & higher 18

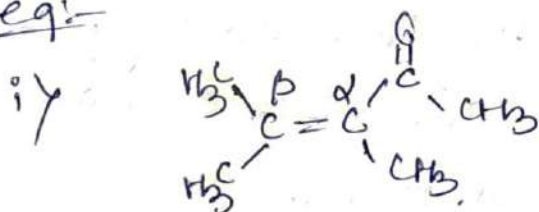
3) Other groups —

- OH →
  - α 35
  - β 30
  - γ 50
- OCOCH<sub>3</sub> → (α, β, γ) 6
- OCH<sub>3</sub> →
  - α 35
  - β 30
  - γ 17
  - δ 31
- Cl →
  - α 15
  - β 12



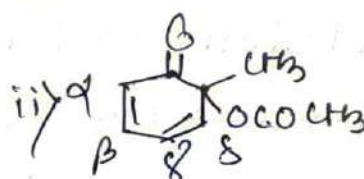
- BH	→	$\alpha$ 25
		$\beta$ 30
-NR <sub>2</sub>	→	$\beta$ 95
a) Exocyclic double bond	→	5
b) Homocyclic diene component	→	39

eg:-



Acyclic enone = 215 nm  
 $\alpha$ -CH<sub>3</sub> = 10

$\beta$ -CH<sub>3</sub> = 2 × 12 = 24  
 $\lambda_{max} = 249$  nm



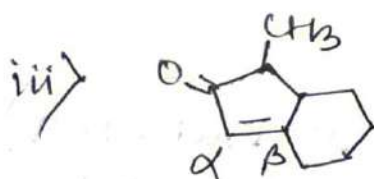
Six-membered enone = 215 nm

Double-bond extending conjugation = 30

Homocyclic diene = 39

$\beta$ -ring residue = 18

$\lambda_{max} = 302$  nm



Five-membered enone = 202 nm

$\beta$ -ring residue = 2 × 12 = 24

Exocyclic double bond = 5

$\lambda_{max} = 231$  nm

## Application of Particle in a box model for conjugated polyenes

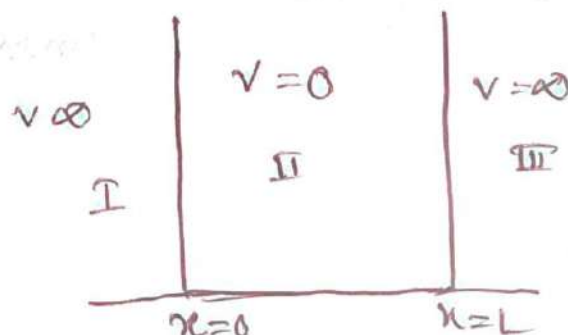
In a conjugated system, the  $\pi$ -e<sup>-</sup>s are delocalized over the framework of that conjugated system.

$\pi$ -e<sup>-</sup>s are mobile throughout the C-atom skeleton containing the alternating double bond.  $\rightarrow$  For such systems, the energy of these e<sup>-</sup>s in the molecule can be compared with the particle in a box model.

$\Downarrow$   
Where the non-interacting  $\pi$ -e<sup>-</sup>s are delocalized over the  $-C=C-C=C-$  framework of length 'L', & minimizes interelectronic repulsion between them.

$\Downarrow$   
In this case, the potential energy (V) of the electron being constant throughout the length of the molecular box & then rising to infinity at each <sup>end</sup> of the conjugated position of the polyene.

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$



An orbital is a wavefunction for a single electron.

If the  $e^-$  is in orbital  $n$ , then the particular wavefunction  $\psi_n$  —

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

& energy,  $E_n = \frac{n^2 h^2}{8mL^2}$

$n = 1, 2, 3, \dots$   
 $L =$  length of 1-D box  
 $m =$  mass of  $e^-$   
 $h =$  Planck's const.

$\therefore$  For a particle in 1-D box —

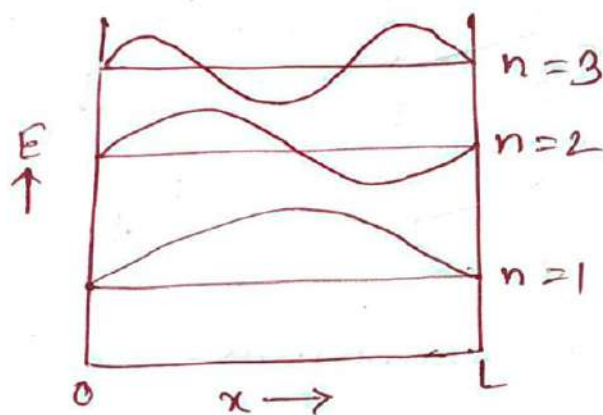


Fig. A particle in 1-D box wave functions.

Let us consider, 1,3-butadiene —



1,3-butadiene

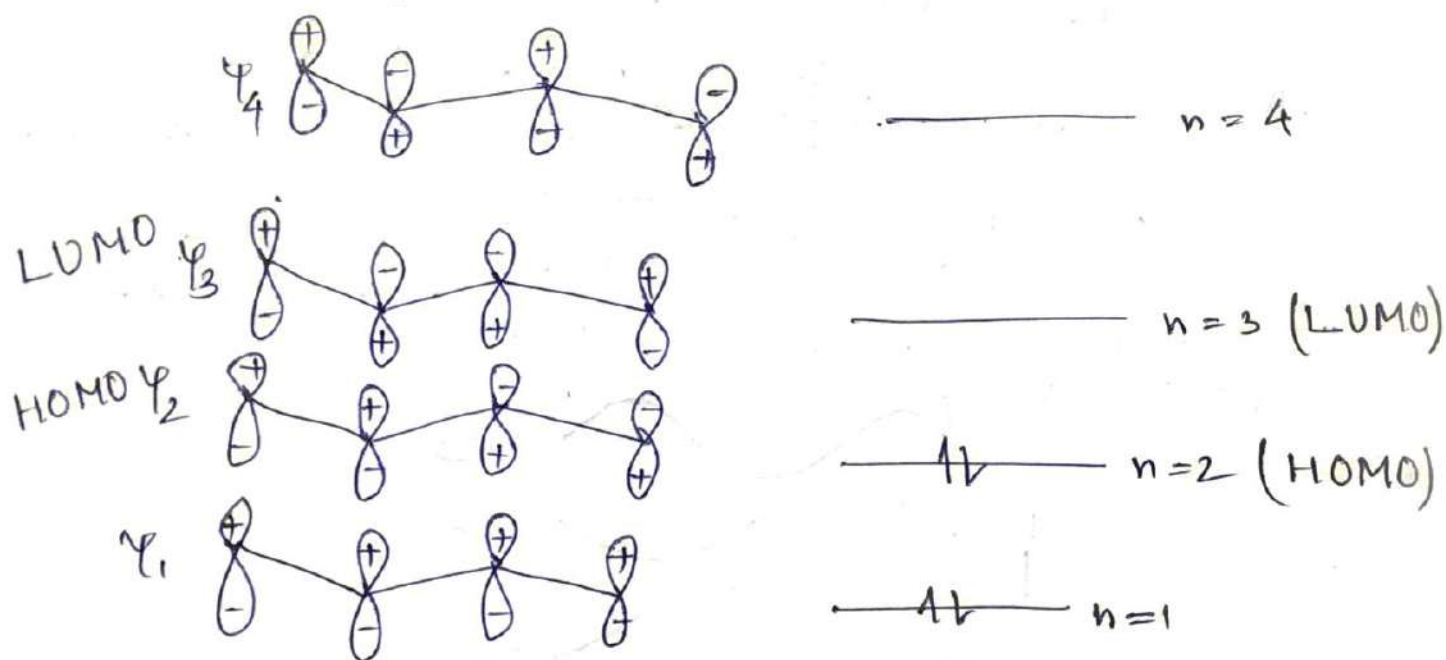
↳ each C is  $sp^2$ -hybridized

↓  
 $s, p_y$  &  $p_z$  orbitals

Involved in  $\sigma$ -bonding.

Therefore, each C-atom has an unused  $2p$ -orbital & one  $e^-$

→ 2p orbitals are parallel to each other & these four 2p-orbitals combine to form the following 4  $\pi$ -orbitals —

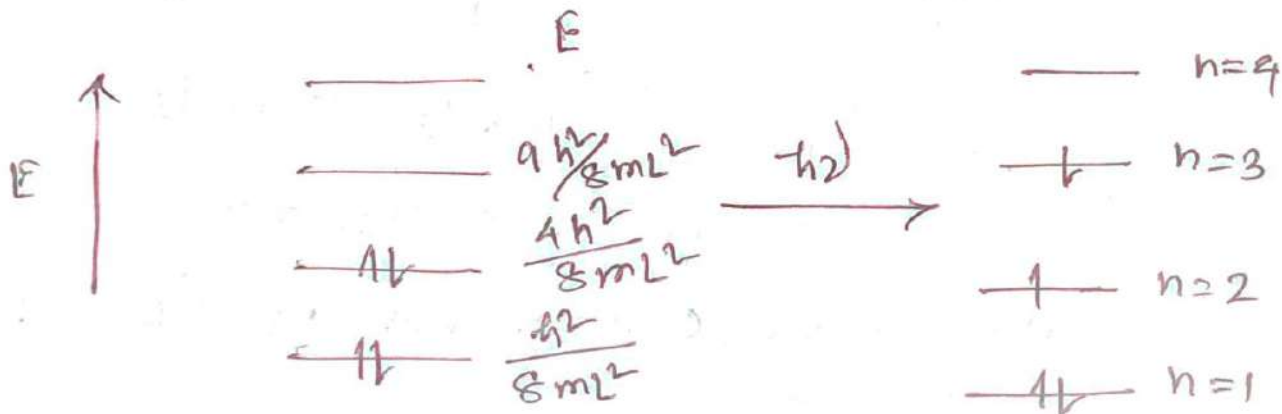
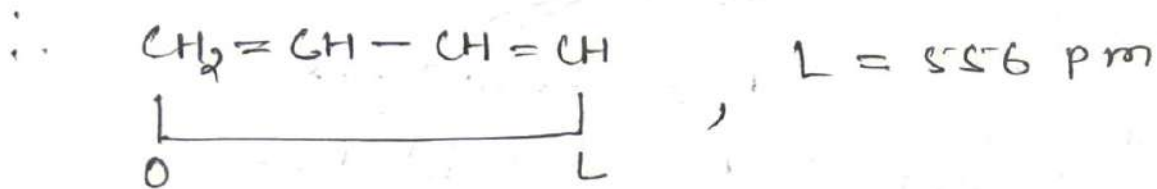


FMO of 1,3-butadiene

Since — 1,3-butadiene



↳ 2- $\pi$ -bonds =  $4\pi e^-$



$$\Delta E = E_3 - E_2 \quad \left[ \because \Delta E_n = E_{\text{excited}} - E_{\text{ground}} \right]$$

$$= \frac{9h^2}{8mL^2} - \frac{4h^2}{8mL^2}$$

$$= (9 - 4) \frac{h^2}{8mL^2}$$

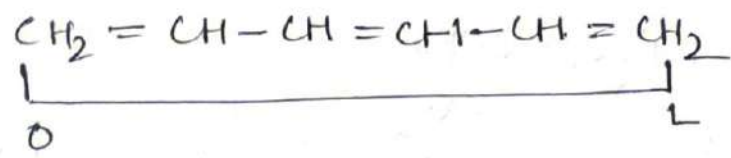
$$= \frac{5h^2}{8mL^2} = \frac{5 \times (6.626 \times 10^{-34} \text{ Js})^2}{8 \times 9.11 \times 10^{-31} \text{ kg} \times (556 \times 10^{-12} \text{ m})^2}$$

$$= 9.74 \times 10^{-19} \text{ J}$$

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

$$= 203 \text{ nm (UV region)}$$

For hexatriene—



$$L = 837 \text{ pm}$$

$$6 \pi e^- = 3 \pi\text{-bonds}$$

$$\psi_n = 3 \rightarrow \psi_n = 4$$

$$\therefore \lambda = 303 \text{ nm (UV-region)}$$

∴ With the increasing conjugation —

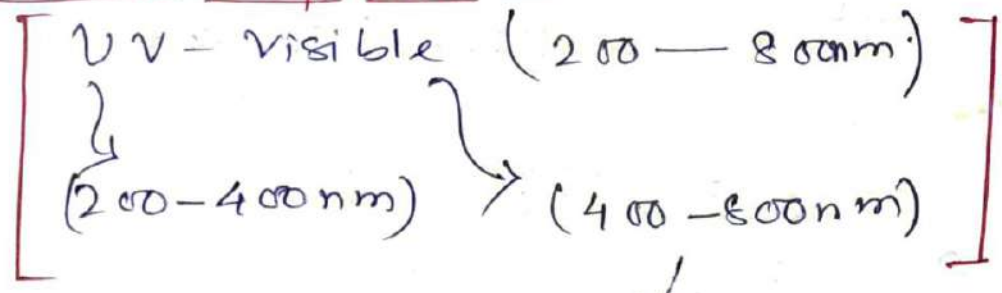
value of  $\lambda$  increases



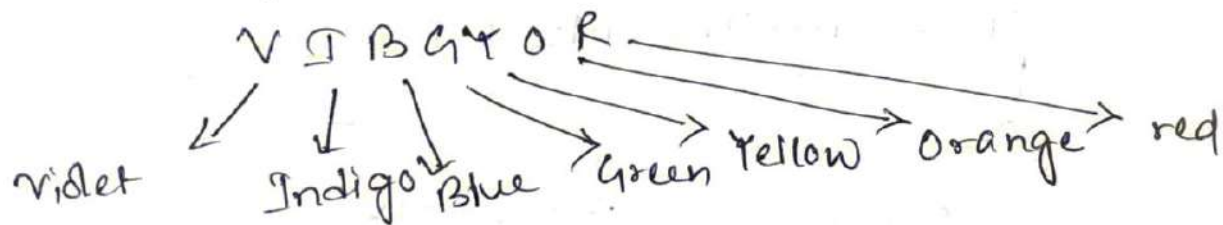
Bathochromic shift.

↳  $\beta$ -Carotene  $\rightarrow$  22 atoms  
 } Pigment  $\rightarrow$  Orange coloured.  
 } Present in carrot  
 $\lambda \sim 2900 \text{ pm}$

Color in compounds —  $\lambda \rightarrow$  Visible region. (400-700 nm)



Light wave with wavelength between this limit appear colored to the human eye.



$\lambda \rightarrow$  Increases  
 $E \rightarrow$  Decreases

— There is an inverse relationship between the observed color & the color absorbed.  
 ↳ When light emitted from source (eg. lamp) we observe a lamp, an emission spectrum we observe the color corresponding to the wavelength of the light being emitted.

eg: a) A light source emitting violet light

↓  
emits light at the high-energy end of visible spectrum.

b) A light source emitting red light

↙  
emits light at the low-energy end of the visible spectrum.

↳ ii) When we observe the color of a particular object or substance, we do not observe that object or substance emitting light.

↳ but we observe the light that is being reflected. (The color that our eye perceives is not the color corresponding to the wavelength of the light absorbed but its complement)

↳ iii) In case of transparent objects & solutions the eye receives the light that is transmitted.

Colour of light absorbed	Wavelength of light absorbed (nm)	observed colour
Violet	400	Yellow
Orange-red	600	Blue green
Blue	450	Orange
Yellow-green	530	Red-violet
Yellow	550	Violet
Red	700	Green
Blue-green	500	Red

### Quantitative estimation by UV- (electronic spectrophotometry):-

A spectrophotometer determines the amount of photons (intensity of light) absorbed after it passes through sample solution.

↳ With the help of spectrophotometer concentration of an analyte can be measured.

↳ A UV-Vis of  $\nu$

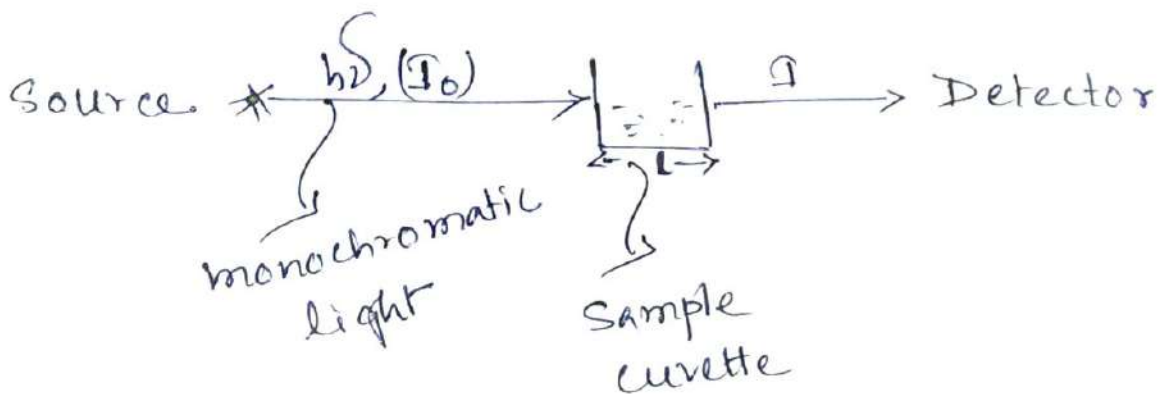
↳ A UV-visible or electronic spectrophotometer measures the intensity of the light ~~before it~~ passing through a sample solution in a cuvette, & compares it to the intensity of the light before it passes through the sample.



↳ Spectrophotometry is a method that ~~measures~~ ~~the~~ concerns the quantitative measurement of the reflection or transmission properties of a material.

↳ The main components of a <sup>electronic</sup> spectrophotometer —

- i) A light source
- ii) A sample holder
- iii) A dispersive device to separate the different wavelengths of the light
- iv) A suitable detector



This instrument measures Transmittance (T)

Defined as —

$$A = -\log T \quad \left| \quad \text{or } T = \frac{I}{I_0} \right.$$

$$\therefore A = -\log \left( \frac{I}{I_0} \right)$$

Absorbance.

From Beer-Lambert's law —

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

## Photoelectron Spectroscopy (PES) :-

Principle — Based on photoelectric effect

↓  
Einstein (1905)


If a sample is irradiated with high energy photons of energy  $h\nu$ ,  $e^-$ s are emitted & part of the energy of the incident radiation is carried off as K.E. of the emitted  $e^-$ s.

$$h\nu = \text{Binding energy} + \text{K.E.} \quad \text{energy}$$

$$\text{Binding energy} = h\nu - \text{K.E.}$$

↓  
can be referred as ionization energy.

(Min<sup>m</sup> energy required to remove an  $e^-$  from an atom)

→ i.e.; from HOMO / 

↓  
Highest occupied atomic orbital

→ Monochromatic radiation is used. (sources →

helium lamp,  $e^-$  bombardment of Ag, Al, or Mg etc.)

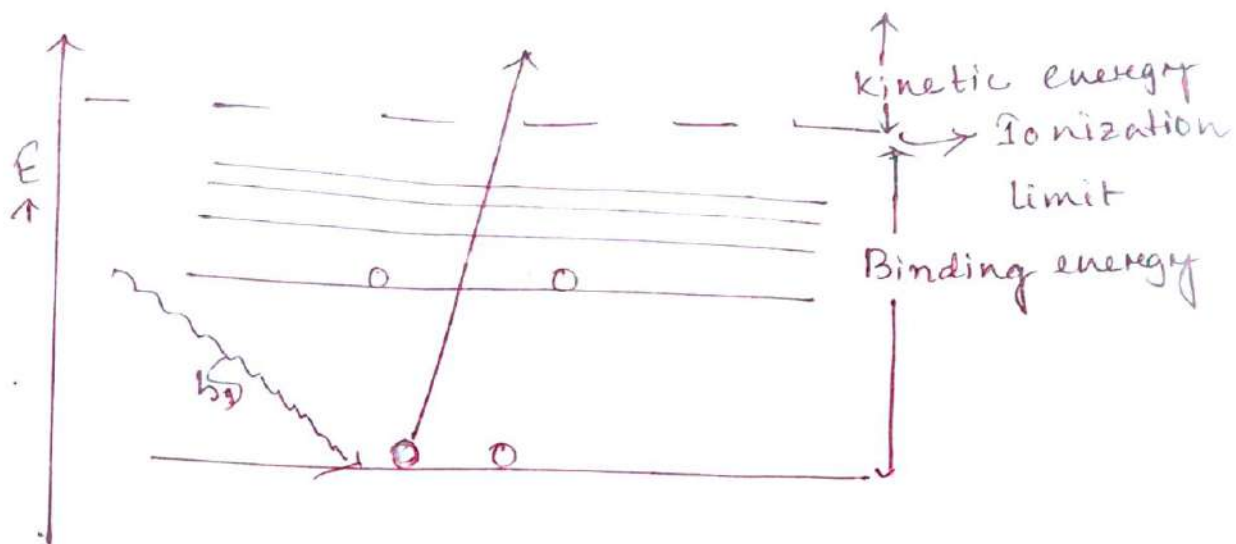
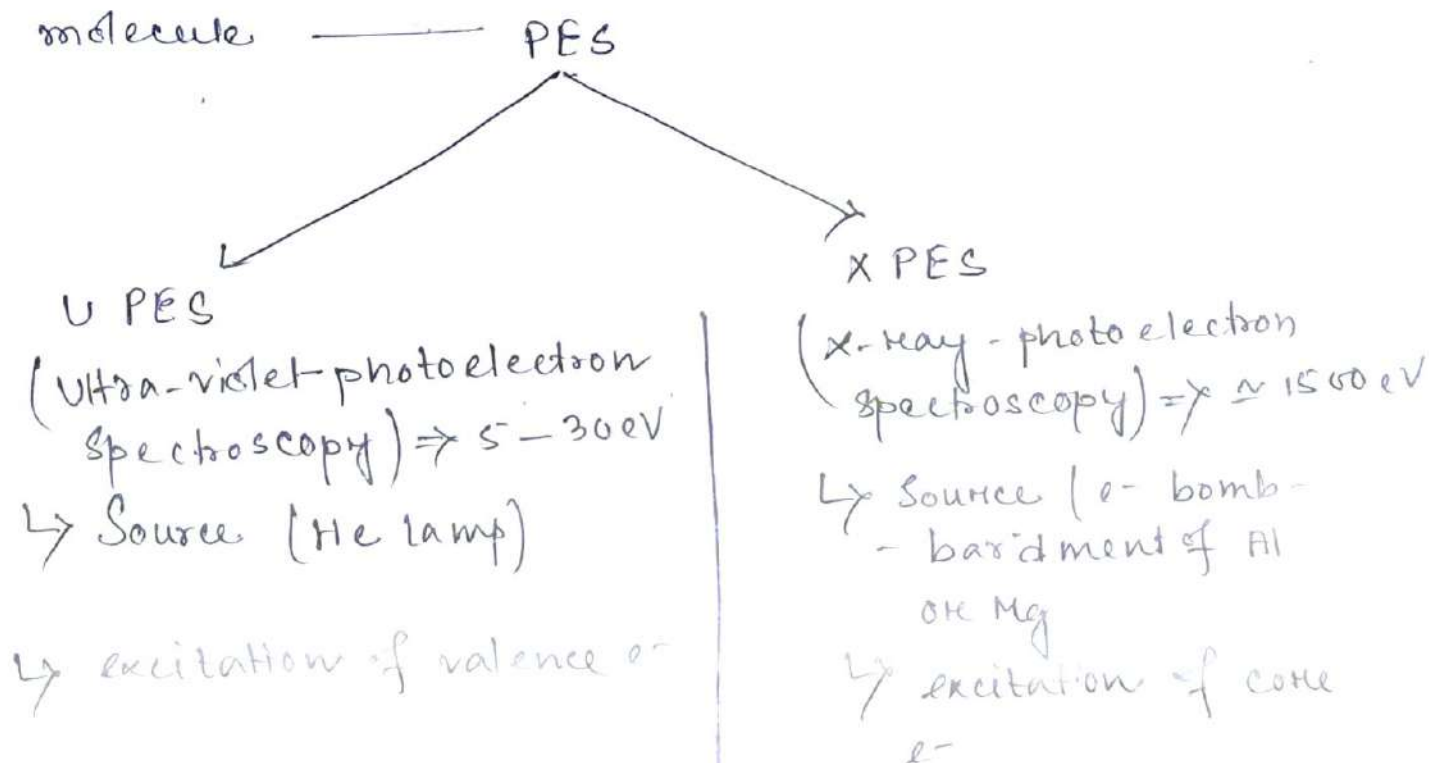


Fig Principle of PES

→ When ionization occurs, k. E. acquired by the emitted  $e^-$ s is not quantized.

↳ Any incident energy higher than ionization energy can be used for excitation.

→ Electrons can be ejected from either the core or the valence levels of atoms or molecules



## Instrumentation -

- i) A suitable source of electromagnetic radiation of high intensity
- ii) A sample chamber
- iii) Analyzer (to analyze the energy distribution of  $e^-$ s emitted from the sample)
- iv) Detector (to detect the  $e^-$ s whose energy has been measured by the analyzer)

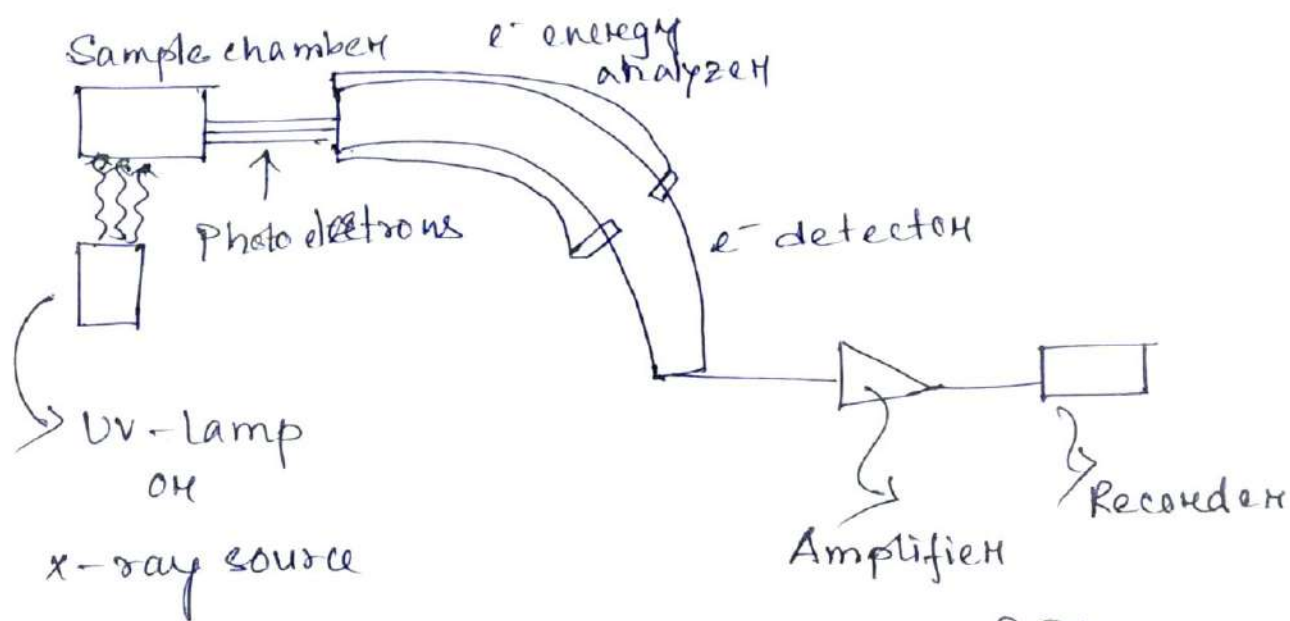


fig. Schematic diagram of a PES.  
Photoelectron spectrometer

→ Plot of a Photoelectron spectrum is -  
the no. of  $e^-$ s emitted against their  
kinetic energy.

D.C.S of Atoms:-  $Ag = 1s^2 2s^2 2p^6 3s^2 3p^6$

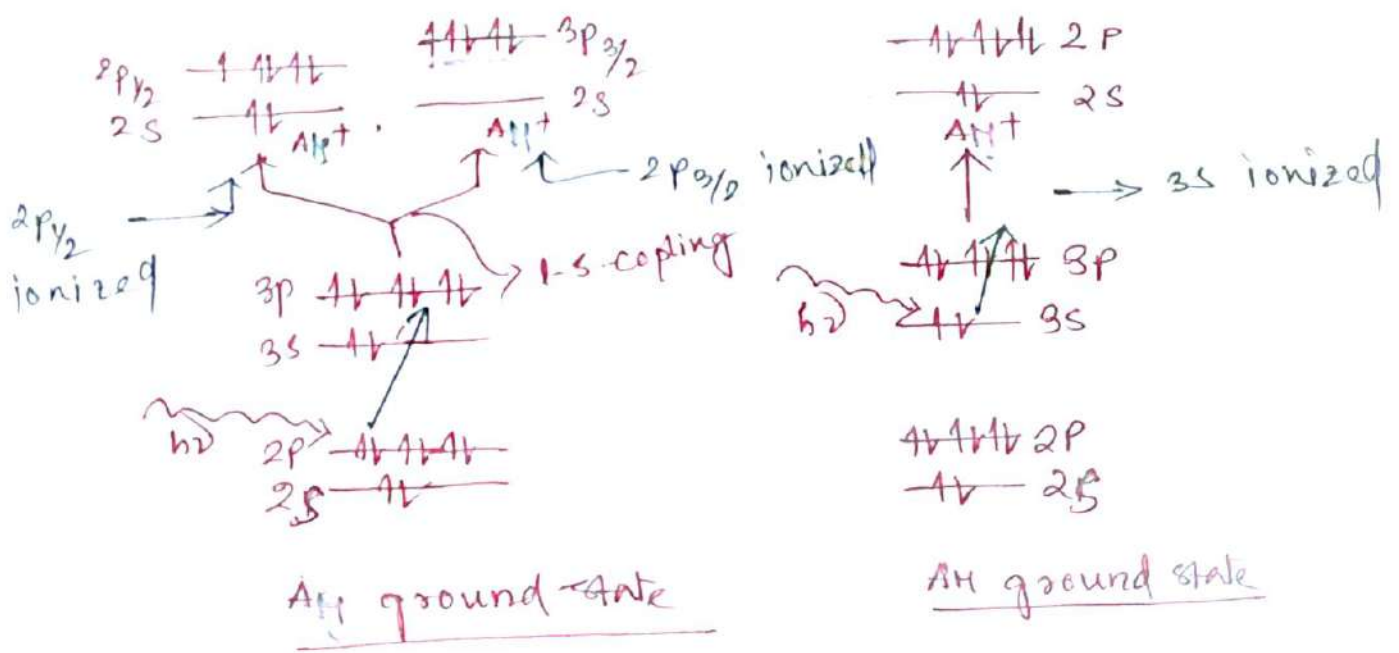
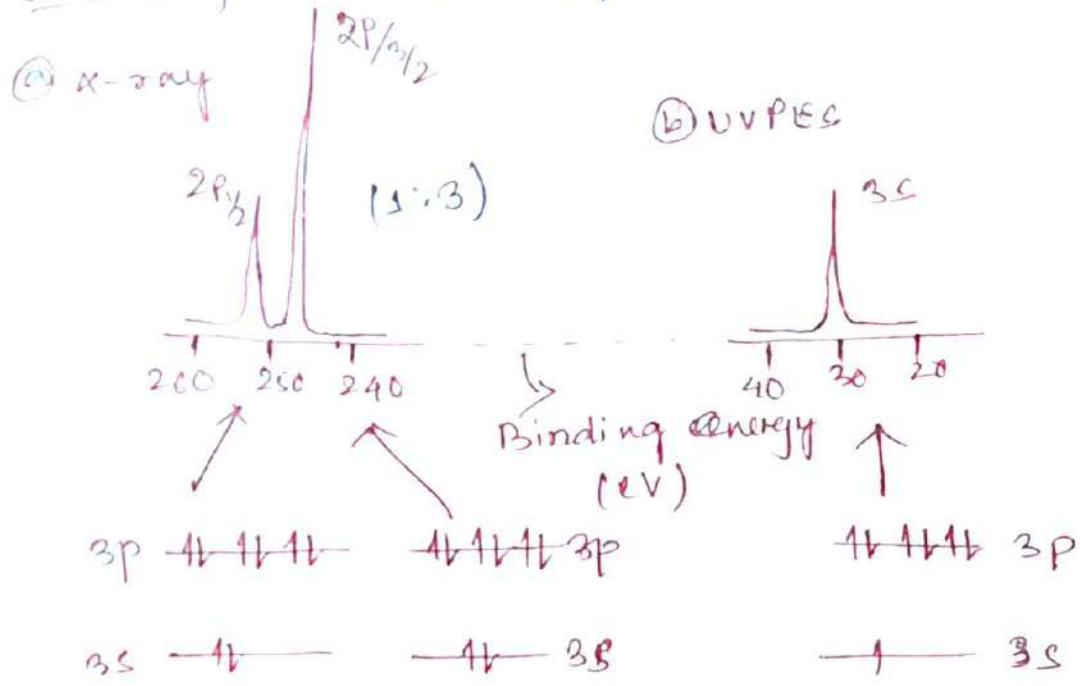


Fig. (a) X-ray & (b) UV-PEC spectra of Ag

Probability of ejecting  $e^-$  from a particular energy level depends on the no. of  $e^-$ s originally present that level  
 $\hookrightarrow$  i.e., degeneracy =  $(2J+1)$

↳ Area under the peaks resulting from excitation of the 3s & 2p e<sup>-</sup>s —

ratio = 1:3 (2 e<sup>-</sup>s in 3s & 6 e<sup>-</sup>s in 2p)

↳ From (a), there is a twice the chance of forming an ion in the  $^2P_{3/2}$  state compared to ion formation in the  $^2P_{1/2}$  state.

↳ since, degeneracy of  $^2P_{3/2} = 2J+1$   
 $= 2 \times 3/2 + 1$   
 $= 4$   
" "  $^2P_{1/2} = 2J+1$   
 $= 2 \times 1/2 + 1$   
 $= 2$

## ~~PES of Molecules~~

### Molecular PES —

(VV-PES) —

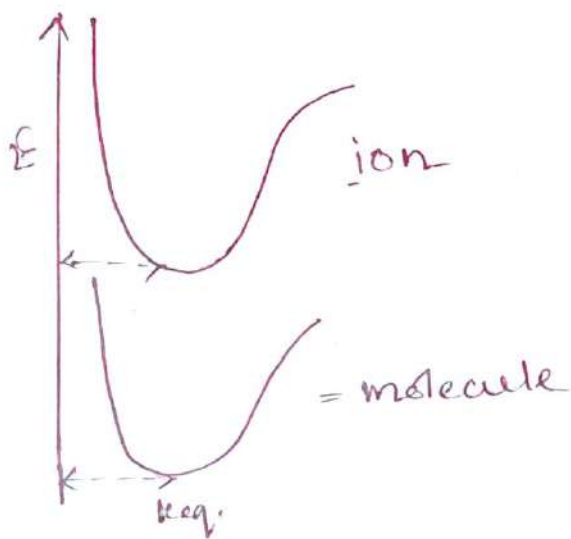
↳ In case of molecules, the nature of the ionization bands produced by the emission of e<sup>-</sup>s from non-bonding, bonding & anti-bonding follow certain patterns as follows —

↳ If the ionized e<sup>-</sup> comes from a non-bonding orbital, the pot. energy

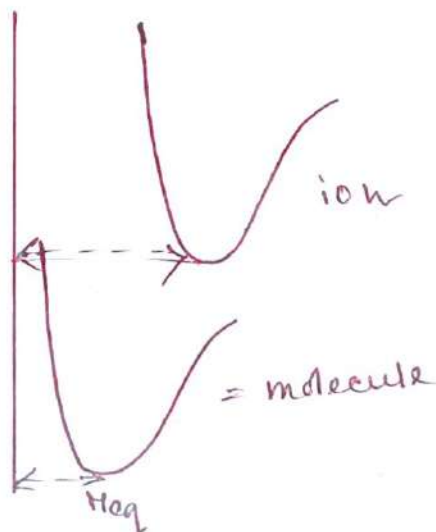
curve for the ion is almost same as the molecule. (since no change in bond length or strength occurs)

ii) If a bonding  $e^-$  is removed, the bonding in the ion is expected to be weaker & longer than that in the molecule. Hence the pot. energy curve of the ion will be shifted to the direction of longer eqm bonds.

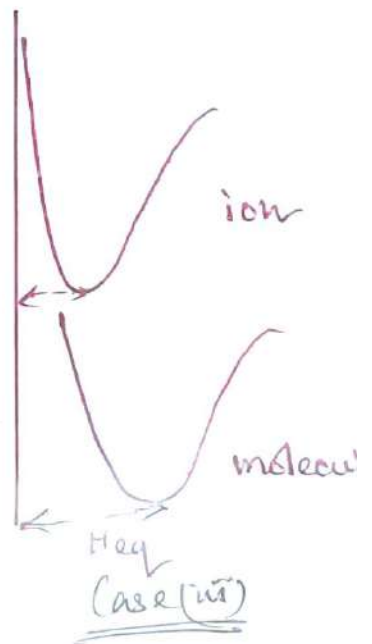
iii) If an  $e^-$  in an antibonding orbital is removed the opposite of the above is expected.



Case (i)

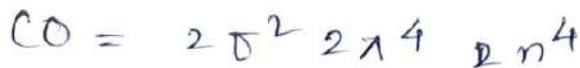
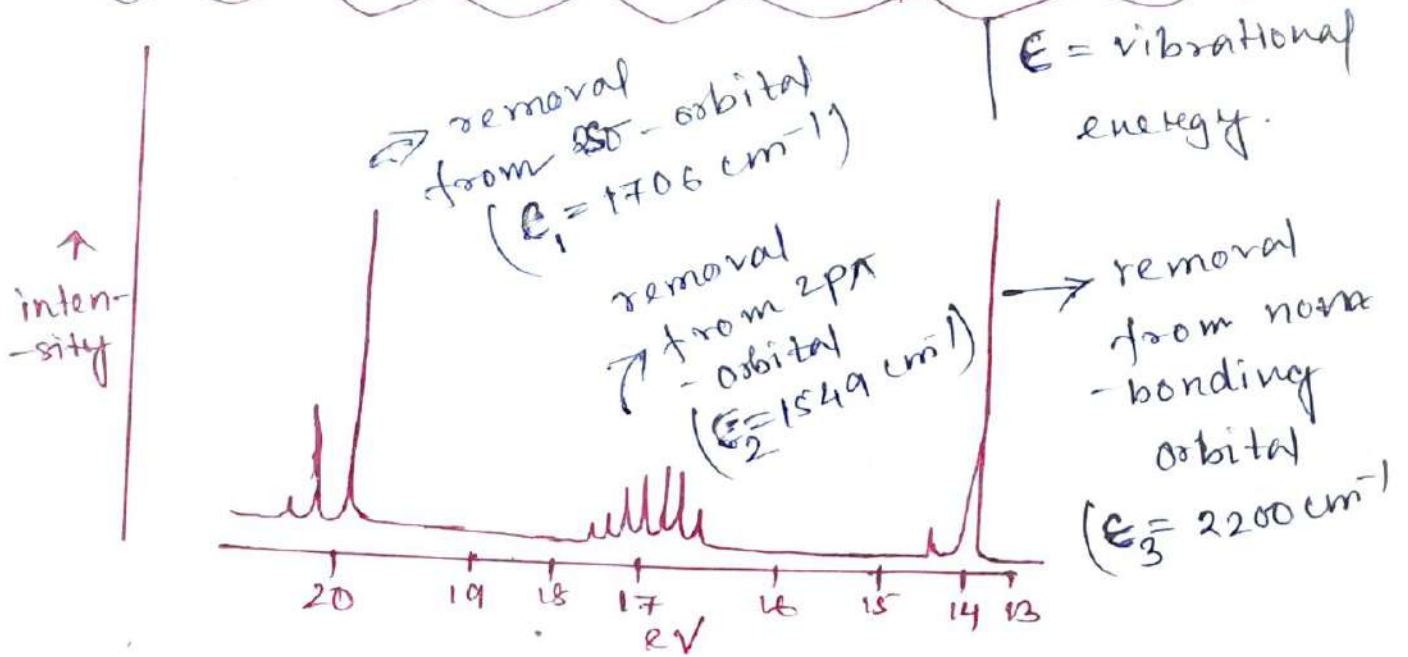


Case (ii)



Case (iii)

# Ultra-violet photoelectron spectrum of CO



}  $n^2 =$  non pair  $e^-$

For free molecule CO —

$$E_0 = 2157 \text{ cm}^{-1}$$

$$\therefore E_1 \& E_2 < E_0$$

indicates removal of  $e^-$  from bonding orbital

$$E_3 \approx E_0$$

removal of  $e^-$  from non-bonding orbital.

Binding energy of  $2p\pi e^- < 2s e^-$   
 $(\approx 18.5 \text{ eV}) \quad (\approx 19.9 \text{ eV})$



X-Ray photoelectron spectroscopy of  $H_2O$

$H_2O$   
 $(\overset{\delta-}{O}=\overset{\delta+}{H}-\overset{\delta+}{H})$

electronegativity -  
 $O > H$   
 $\therefore$  experiences a greater reduction of  $e^-$  density  
 $\Downarrow$   
 More strongly bound core  $e^-$ s than the end atoms of same kind.

(electronic environment of each atom in a molecule is different)  
 $\Downarrow$   
 Hence binding energy of core  $e^-$ s for non-equivalent atoms of the same kind is different in a molecule.  
 chemical shift

$\therefore$  Binding energy of  $N^{1s}$   $>$   $N^{1s}$  in  $H_2O$   
 $(412.6 \text{ eV})$   
 $(408.7 \text{ eV})$

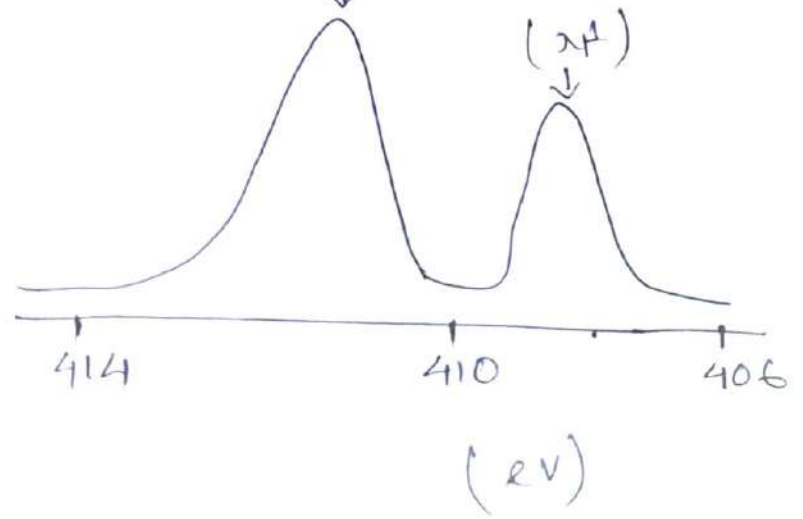


Fig. Photoelectron spectrum of  $H_2O$ .