

# Infra-Red Spectroscopy —

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Range —  $400 - 4000 \text{ cm}^{-1}$

Principle — The absorption of IR radi<sup>n</sup> causes an excitation of molecule from a lower to the higher vibrational level. All the bonds in a molecule are not capable of absorbing IR energy but only those bonds which are accompanied by a change in dipole moment will absorb in the infra-red region.

Such vibrational transitions which are accompanied by a change in the dipole-moment of the molecule are called infra-red active transitions. Thus, these are responsible for absorption energy in the IR region. On the other hand, the vibrational transitions which are not accompanied by a change in dipole-moment of the molecule are not directly observed and these are IR-inactive.

We know that each vibrational level is associated with a number of closely spaced rotational levels. Clearly, the IR-spectra is considered as vibrational-rotational spectra.

In the IR-spectroscopy, the absorbed energy brings about predominant changes in the vibrational energy which depends upon :-

- (i) masses of the atoms present in a molecule,
- (ii) Strength of the bonds,
- (iii) The arrangement of atoms within the molecule.

" It has been found that no two compounds except 2 the enantiomers can have similar IR spectra."

## Degree of freedom for molecular vibrations

If a molecule has  $N$ -atom, then

$$\text{Total number of degree of freedom} = 3N$$

$$\text{Degree of freedom for translational motion} = 3.$$

$$\text{Remaining degree of freedom for Rotational Vibrational motion} = 3N - 3.$$

Degree of freedom for rotational motion,

$$\text{if molecule is linear} = 2$$

$$\text{if molecule is non-linear} = 3.$$

Remaining degree of freedom for vibrational motion.

$$\text{Linear} = 3N - 3 - 2 = 3N - 5$$

$$\text{Non-linear} = 3N - 3 - 3 = 3N - 6.$$

# Vibrational Energy Levels of a Simple Harmonic 3

## Oscillator

A SHO is the one in which the restoring force is proportional to displacement in accordance with Hooke's law —

$$f = -kx$$

where  $k$  — force constant.

Using the concepts of quantum mechanics, it can be seen that if the vibratory motion of the nuclei of a diatomic molecule is taken as equivalent to that of a Simple Harmonic Oscillator, then the vibrational energy is given by the equation —

$$E_v = \left(v + \frac{1}{2}\right) h \omega_{osc} \quad \text{Joules ; } v = 0, 1, 2, 3, \dots$$

$v$  — vibrational quantum number.

$$\bar{\nu}_v = \left(v + \frac{1}{2}\right) \frac{hc}{\lambda_{osc}}$$

where  $\omega_{osc}$  — Oscillator frequency.

$$\frac{E}{h\nu} = \left(v + \frac{1}{2}\right) \frac{E}{h\nu_{osc}}$$

$$\bar{\nu}_v = \left(v + \frac{1}{2}\right) \bar{\nu}_{osc} \quad \text{cm}^{-1}$$

where  $\omega_{osc}$  — vibrational frequency or  
[ $\omega$ ] Oscillation frequency. 4

- At absolute zero [0K] — translational and rotational motion ceases in a crystal.
- Residual energy of vibrations  $E_0$  still remains i.e. vibrational motion still exist.

### Selection rule

Schrodinger wave equation leads to the simple selection rule for the Harmonic oscillator undergoing vibrational changes —  $\Delta v = \pm 1$

### Relation b/w force constant and wave number

$\omega_{osc}$   
↑  
Oscillatory frequency

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Hz}$$

where  $k$  — force constant  
 $\mu$  — reduced mass —  $\frac{m_1 m_2}{m_1 + m_2}$

or

$$\frac{c}{\lambda_{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\bar{\omega}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where —  $\bar{\omega}_{osc}$  — wave number.

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for Simple Harmonic Oscillator, the vibrational energy given by,

$$E_v = \left(v + \frac{1}{2}\right) h \omega_{osc} \quad \text{Joules}$$

where  $v = 0, 1, 2, 3, \dots$

or

$$\bar{\nu}_v = \left(v + \frac{1}{2}\right) \bar{\omega}_{osc} \quad \text{cm}^{-1}$$

and selection rule  $\Delta v = \pm 1$

Apply the selection rule we have immediately—  
suppose transition takes place from  $v$  to  $v+1$ .

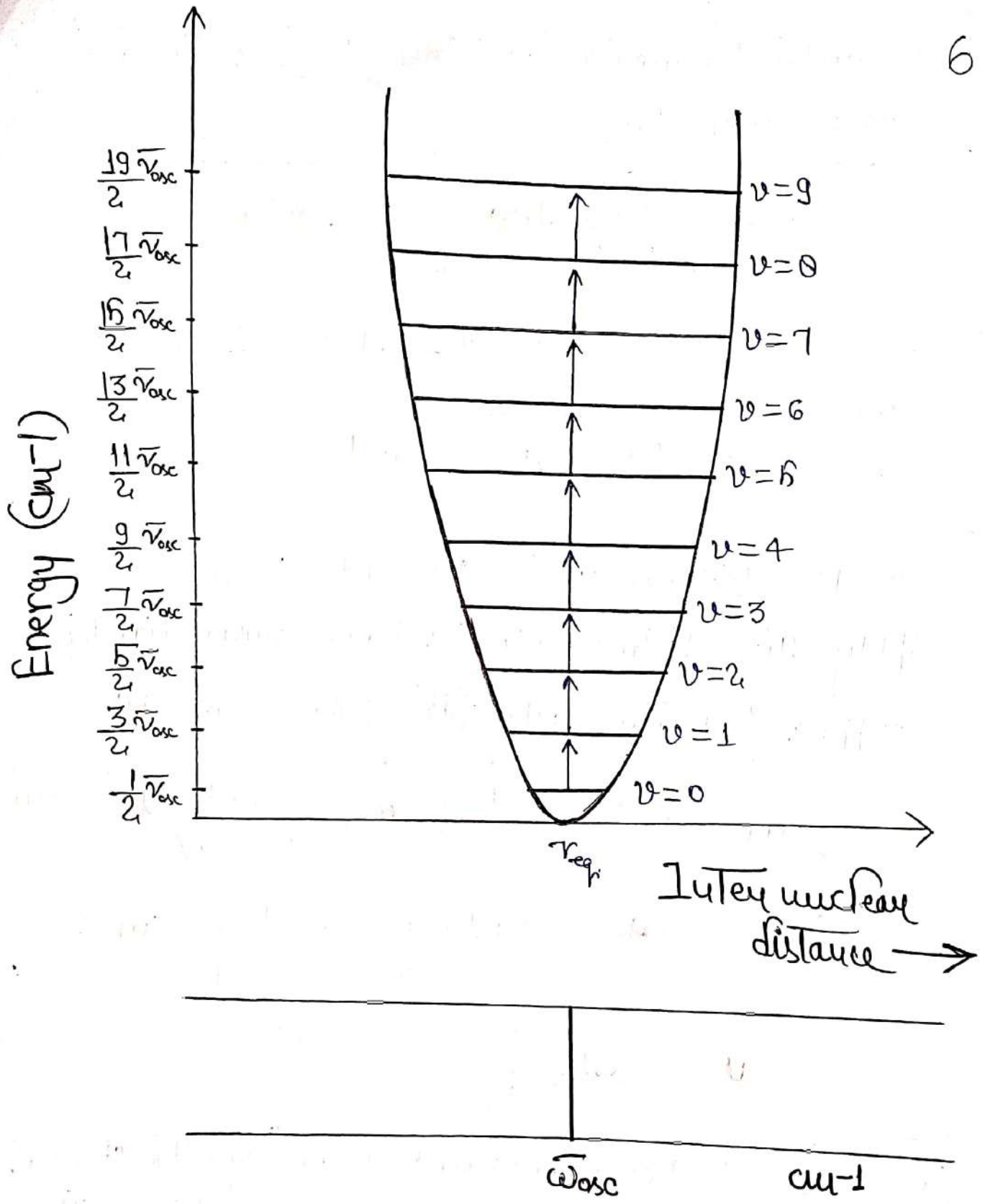
$$\bar{\nu}_{v+1} - \bar{\nu}_v = \left(v+1 + \frac{1}{2}\right) \bar{\omega}_{osc} - \left(v + \frac{1}{2}\right) \bar{\omega}_{osc} \quad \text{cm}^{-1}$$

$$\Delta \bar{\nu} = \bar{\omega}_{osc} \left[ \cancel{v} + 1 + \frac{\cancel{v}}{2} - \cancel{v} - \frac{1}{2} \right] \text{cm}^{-1}$$

$$\boxed{\Delta \bar{\nu} = \bar{\omega}_{osc}} \quad \text{cm}^{-1}$$

Since the vibrational energy levels are equally spaced, transitions between any two neighbouring states will give rise to the same energy change.

Further, since the difference between energy levels expressed in  $\text{cm}^{-1}$  gives directly the wave number of the spectral line.



The only one line [absorption line] will be obtained in the vibrational spectrum whose wave number is equal to the equilibrium vibrational frequency of the diatomic molecule.

As the vibrational levels are equally spaced, any transition from  $v$  to  $(v+1)$  will give rise to the same energy change and hence only one line is expected. 7

### Zero point Energy —

Consider the diatomic molecule as Simple Harmonic Oscillator, the vibrational energy is given by the equation —

$$E_v = \left(v + \frac{1}{2}\right) h\nu$$

$$\because \nu = \frac{c}{\lambda} = c\bar{\omega}_{osc}$$

$$E_v = \left(v + \frac{1}{2}\right) hc\bar{\omega}_{osc}$$

where

$v = 0, 1, 2, 3, \dots$  vibrational quantum number.

for lowest vibrational level;  $v = 0$ .

$$E_0 = \frac{1}{2} hc\bar{\omega}_{osc}$$

This is called zero point energy.

It implies that at absolute zero [i.e. 0K] when all translational & rotational motion ceases in crystal, the residual energy of vibration  $E_0$  still remains. i.e. vibrational energy [motion] still exists.

# Vibrational Energy Levels of an Anharmonic

## Oscillator —

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When a molecule is undergoing SHOs, the restoring force of the harmonic vibrations is directly proportional to the displacement and the energy of the harmonic oscillation is given by —

$$E_v = \left(v + \frac{1}{2}\right) h c \bar{\omega}_{osc} \quad \text{--- (1)}$$

But the movement of a real oscillator is not perfectly harmonic. This is because as displacement increases, the restoring force becomes weaker and for large enough amplitude of vibration, the atoms of the molecule must fall apart i.e. the molecule must dissociate into atoms. Such a real oscillator is said to be an anharmonic oscillator. And Energy can be given by —

$$E_v = \left(v + \frac{1}{2}\right) h c \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 h c x_e \bar{\omega}_e^2 \quad \text{--- (2)}$$

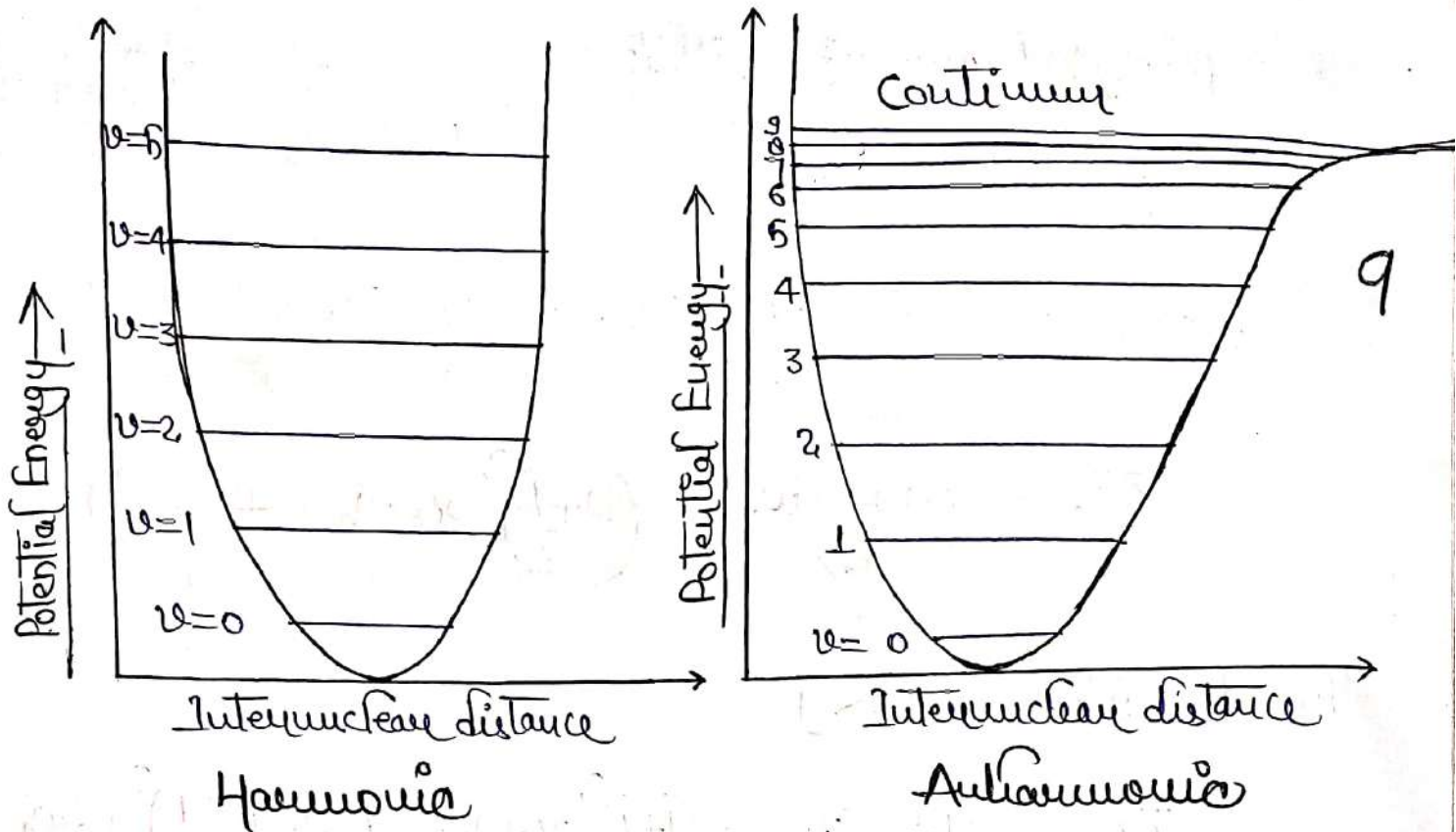
where

$x_e$  — Anharmonicity constant.

$\bar{\omega}_e$  — Equilibrium oscillation frequency.

Putting  $v = 0, 1, 2, 3, \dots$  in eq<sup>n</sup> (1) & (2) we get Potential energy curve & energy levels for harmonic & Anharmonic oscillator —





selection rule for the vibrational transition of an harmonic oscillator

for simple harmonic oscillator,

$$\Delta v = \pm 1$$

for Anharmonic oscillator,

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

$0 \rightarrow 1$  - Fundamental transition [most intense]

$0 \rightarrow 2$  - First overtone

$0 \rightarrow 3$  - Second overtone

$1 \rightarrow 2$  - Hot band [At higher temperature only]

for Anharmonic oscillator —

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$$E_v = \left(\nu + \frac{1}{2}\right) h c \bar{\omega}_e - \left(\nu + \frac{1}{2}\right)^2 h c \bar{\omega}_e x_e$$

$$h c \bar{\nu}_v = h c \left[ \left(\nu + \frac{1}{2}\right) \bar{\omega}_e - \left(\nu + \frac{1}{2}\right)^2 \bar{\omega}_e x_e \right]$$

$$\bar{\nu}_v = \left(\nu + \frac{1}{2}\right) \bar{\omega}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \bar{\omega}_e \quad \text{--- (1)}$$

for transition,  $0 \rightarrow 1$

$$\bar{\nu}_v = \left(1 + \frac{1}{2}\right) \bar{\omega}_e - \left(1 + \frac{1}{2}\right)^2 x_e \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e + \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e$$

$$\bar{\nu}_v = \frac{3}{2} \bar{\omega}_e - \left(\frac{3}{2}\right)^2 x_e \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} x_e \bar{\omega}_e$$

$$= \frac{3}{2} \bar{\omega}_e - \frac{9}{4} x_e \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} x_e \bar{\omega}_e$$

$$= \left(\frac{3}{2} - \frac{1}{2}\right) \bar{\omega}_e - \left(\frac{9}{4} - \frac{1}{4}\right) x_e \bar{\omega}_e$$

$$\bar{\nu}_v = \frac{2}{2} \bar{\omega}_e - \frac{8}{4} x_e \bar{\omega}_e$$

$0 \rightarrow 1$

$$\boxed{\bar{\nu}_v = (1 - 2x_e) \bar{\omega}_e} \text{ cm}^{-1} \text{ Fundamental transition.}$$

for transition,  $0 \rightarrow 2$  ; from eq<sup>n</sup> (i)

$$\bar{\nu}_e = \left(\nu + \frac{1}{2}\right) \bar{\omega}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \bar{\omega}_e$$

$$\Delta \bar{\nu}_e = \left(2 + \frac{1}{2}\right) \bar{\omega}_e - \left(2 + \frac{1}{2}\right)^2 x_e \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e + \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e$$

$$= \frac{5}{2} \bar{\omega}_e - \left(\frac{5}{2}\right)^2 x_e \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e + \left(\frac{1}{2}\right)^2 x_e \bar{\omega}_e$$

$$= \frac{5}{2} \bar{\omega}_e - \frac{2.5}{4} x_e \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} x_e \bar{\omega}_e$$

$$= \left(\frac{5}{2} - \frac{1}{2}\right) \bar{\omega}_e - \left(\frac{2.5}{4} - \frac{1}{4}\right) x_e \bar{\omega}_e$$

$$= \frac{2.4}{2} \bar{\omega}_e - \frac{2.4}{4} x_e \bar{\omega}_e$$

$$\Delta \bar{\nu}_e = 2 \bar{\omega}_e - 6 x_e \bar{\omega}_e$$

$0 \rightarrow 2$   $\Delta \bar{\nu}_e = 2 \bar{\omega}_e (1 - 3 x_e) \text{ cm}^{-1}$  First Overtone

Similarly,

$0 \rightarrow 3$   $\Delta \bar{\nu}_e = 3 \bar{\omega}_e (1 - 4 x_e) \text{ cm}^{-1}$  Second Overtone

$1 \rightarrow 2$   $\Delta \bar{\nu}_e = \bar{\omega}_e (1 - 4 x_e) \text{ cm}^{-1}$  Hot Band

## Types of molecules showing vibrational spectra

The condition required is only the change in dipole moment and the molecule need not have a permanent dipole moment.

eg. in case of homonuclear diatomic molecules like  $H_2, O_2, N_2$  etc. which have only stretching motion/vibrations and no bending motion/vibration, the dipole moment does not change during vibration. Hence these molecules do not give vibrational spectra i.e. they are said to be infrared-inactive.

On the other hand, heteronuclear diatomic molecules like  $HCl, CO, NO$  etc. and polyatomic molecules like  $CO_2, H_2O, CH_4, C_2H_4$  etc. which show change in dipole moment in some mode of vibration give vibrational spectra and are said to be infrared active.

# Vibrational-Rotational Spectra

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Pure vibrational spectra are obtained only for liquids where rotational motion is hindered due to interactions between the liquid molecules. However in case of gaseous molecules, as the energy required for rotation is much less than that required for vibration, the vibrational motion is always accompanied by rotational motion and hence we don't have a pure vibrational spectra; instead we have a vibrational-rotational spectra lying in the infrared region.

As rotational motion and vibrational motion take place independent of each other, applying Born-Oppenheimer approximation, the total energy of molecule may be taken as the sum of the rotational energy and the vibrational energy (which is much larger than the former). Thus

$$E_{\text{Total}} = E_r + E_v \quad \text{--- 1}$$

or  
it can be written as,

$$E_{v,J} = E_J + E_v \quad \text{--- 2}$$

expressing in terms of wave numbers it can be written as-

$$\bar{\nu}_{v,J} = \bar{\nu}_J + \bar{\nu}_v \quad \text{--- 3}$$

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

$$\bar{\nu}_v = \left(\nu + \frac{1}{2}\right) \bar{\omega}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \bar{\omega}_e$$

substituting these values in eq<sup>n</sup> 3 - 14

$$\bar{\nu}_{v,J} = BJ(J+1) + \left(\frac{v+1}{2}\right)\bar{\omega}_e - \left(\frac{v+1}{2}\right)^2 x_e \bar{\omega}_e$$

when a transition takes place from a level with quantum number  $v$  and  $J$  to a level with quantum numbers  $v'$  and  $J'$ , the energy change -

$$\Delta\bar{\nu} = BJ'(J'+1) + \left(\frac{v'+1}{2}\right)\bar{\omega}_e - \left(\frac{v'+1}{2}\right)^2 x_e \bar{\omega}_e - BJ(J+1) - \left(\frac{v+1}{2}\right)\bar{\omega}_e + \left(\frac{v+1}{2}\right)^2 x_e \bar{\omega}_e$$

$$= B[J'(J'+1) - J(J+1)] + \bar{\omega}_e \left[ \frac{v'+1}{2} - \frac{v+1}{2} \right] - x_e \bar{\omega}_e \left[ \left(\frac{v'+1}{2}\right)^2 - \left(\frac{v+1}{2}\right)^2 \right]$$

$$= B[J'^2 + J' - J^2 - J] + \bar{\omega}_e [v' - v]$$

$$- x_e \bar{\omega}_e \left[ \frac{v'^2 + \frac{1}{4} + 2v' \times \frac{1}{2}}{4} - \frac{v^2 + \frac{1}{4} + 2v \times \frac{1}{2}}{4} \right]$$

$$= B[(J'^2 - J^2) + (J' - J)] + \bar{\omega}_e [v' - v] - x_e \bar{\omega}_e [v'^2 + v' - v^2 - v]$$

$$= B[(J' - J)(J' + J) + (J' - J)] + \bar{\omega}_e [v' - v] - x_e \bar{\omega}_e [v'^2 + v' - v^2 - v]$$

now restricting to the transition from  $v=0$  to  $v'=1$ , we get

$$= B[(J'-J)(J'+J+1)] + \overline{\omega}_e[1-0] - \mu_e \overline{\omega}_e[1+1-0-0]$$

$$= B[J'-J][J'+J+1] + \overline{\omega}_e - 2\mu_e \overline{\omega}_e$$

$$\Delta \overline{\nu} = \overline{\omega}_e(1-2\mu_e) + B(J'-J)(J'+J+1)$$

Putting  $\overline{\omega}_e(1-2\mu_e) = \overline{\omega}_0$

$$\Delta \overline{\nu} = \overline{\omega}_0 + B(J'-J)(J'+J+1) \quad \text{cm}^{-1}$$

(i) for transition with  $\Delta J = +1$ ;

i.e.  $J'-J = +1 \Rightarrow J' = J+1$

$$\Delta \overline{\nu} = \overline{\omega}_0 + 2B(J+1) \quad \text{--- 4}$$

(ii) for transition with  $\Delta J = -1$

i.e.  $J'-J = -1 \Rightarrow J = J'+1$

$$\Delta \overline{\nu} = \overline{\omega}_0 - 2B(J'+1) \quad \text{--- 5}$$

combining eq<sup>n</sup> 4 & 5.

$$\Delta \overline{\nu} = \overline{\omega}_0 + 2Bm \quad \text{--- 6}$$

where  $m = (J+1)$  in eq<sup>n</sup> 4

&  $m = -(J'+1)$  in eq<sup>n</sup> 5.

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

$$m = 1, 2, 3, 4, \dots \text{ for eq<sup>n</sup> 4}$$

$$m = -1, -2, -3, -4, \dots \text{ for eq<sup>n</sup> 5.}$$

or  $m = \pm 1, \pm 2, \pm 3, \pm 4, \dots$  for eq<sup>n</sup> 6.

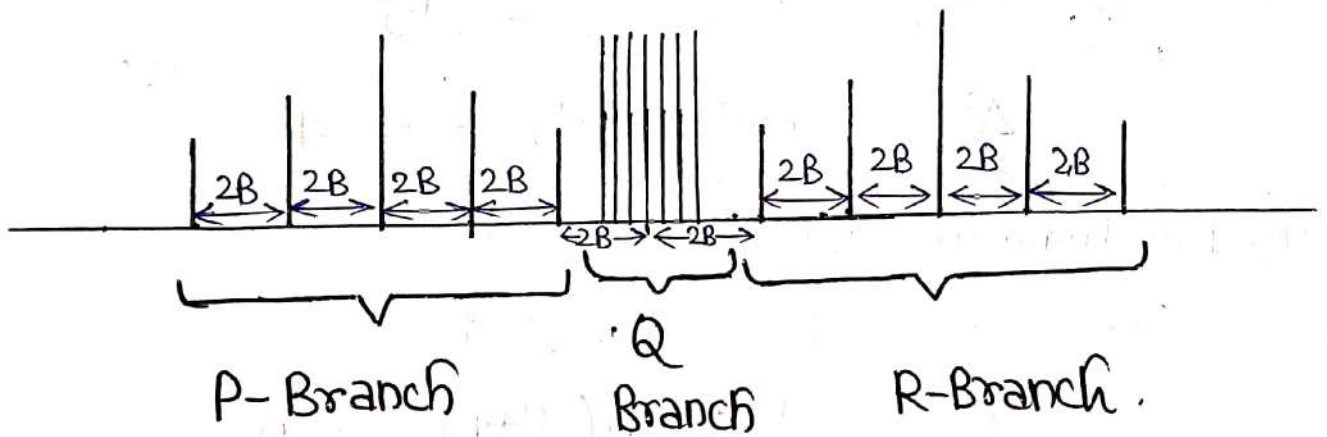
+ sign for  $\Delta J = +1$  & - sign for  $\Delta J = -1$

(i)  $\omega \neq 0$ ;  $\Delta \nu = \omega_0 + 2Bm$   $\because m \neq 0$ ; we always get value of  $\Delta \nu$   $\neq \omega_0 + m$ ; if  $m=0$ ; then  $\Delta \nu = \omega_0$ ;  $m=0$  is not possible. 16

Therefore, line corresponding to the frequency  $\omega_0$  will not appear in the spectrum. This wave number is called the band centre or band origin.

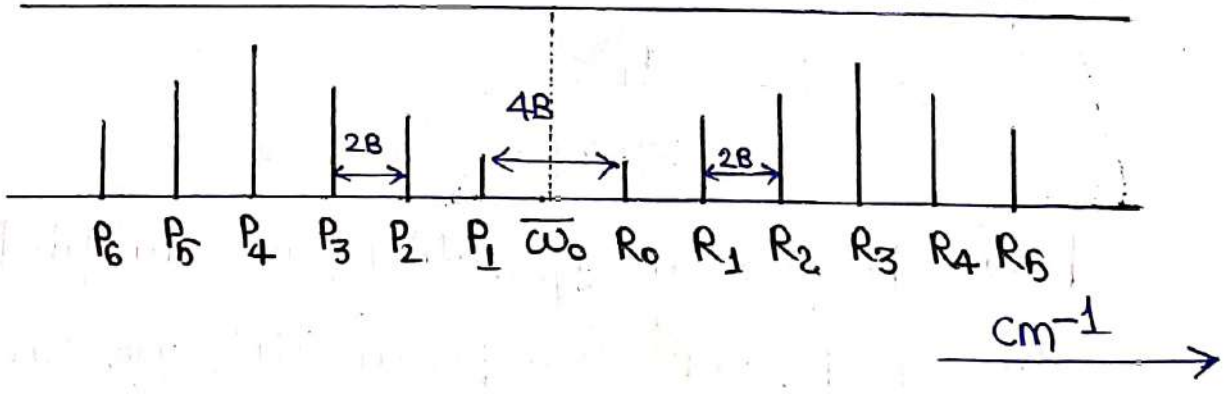
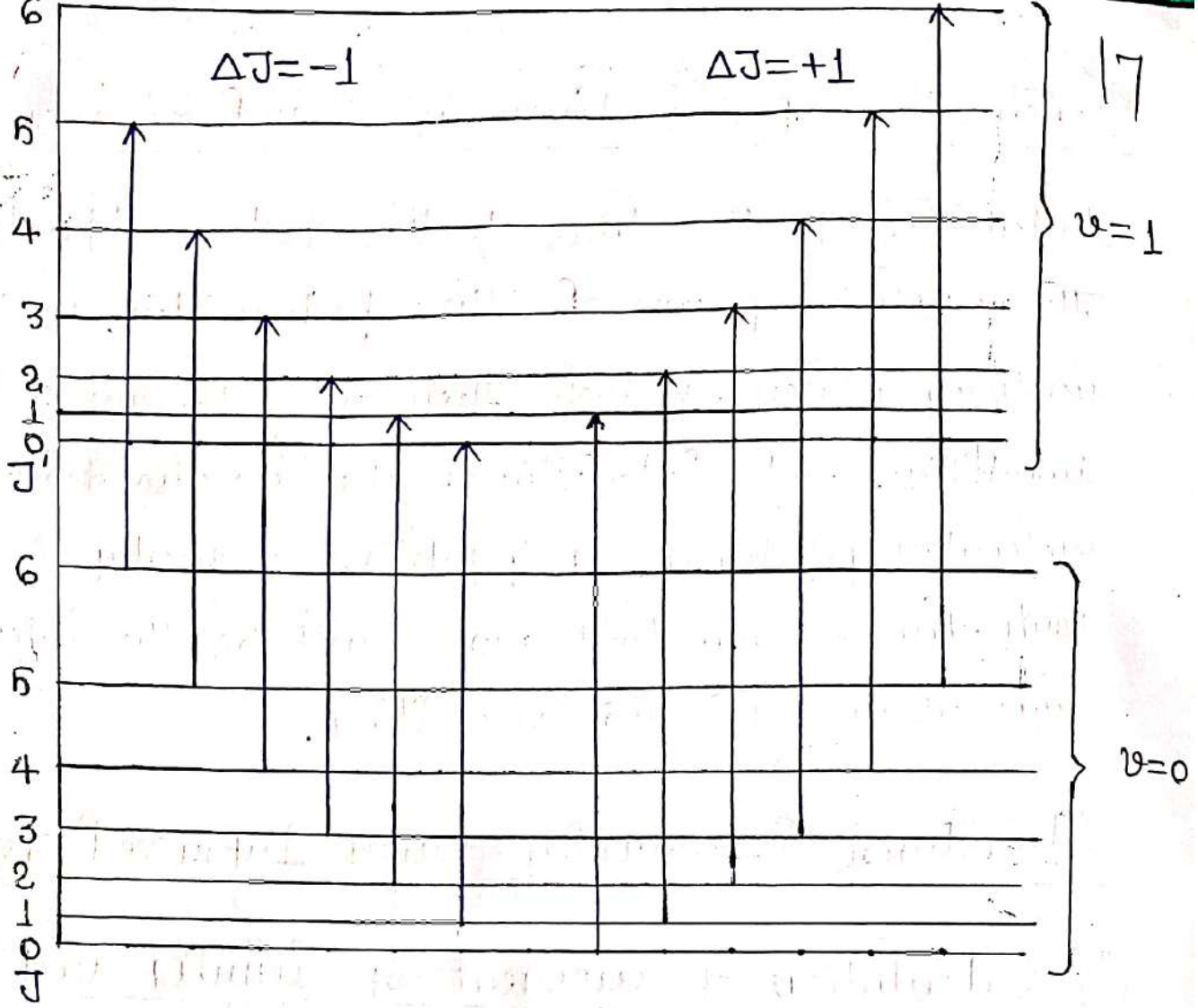
(ii) As  $m = \pm 1, \pm 2, \pm 3, \pm 4, \dots$

it follows that the spectrum will consist of equally spaced lines on each side of the band centre, with spacing equal to  $2B$  b/w any two adjacent lines.



for  $\Delta J = -1$  — P Branch  
 $\Delta J = +1$  — R Branch  
 $\Delta J = 0$  — when vibrational transition occurs without accompanied by rotational transition  
 [eg. in case of NO]





## Intensities of the lines in P and R branches—

Intensities of the lines of the spectrum depends on the resolving power of the spectrometer. If its resolving power is high then we get lines of high intensities. And intensities of the lines also depends on molecular population. If population is greater in particular energy level more will be the intense line observe for that transition.

## Structural information from Infrared spectra

### (i) Calculation of moment of inertia and bond length—

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

From frequency separation, we can find the value of B, and then from this we can calculate moment of inertia. i.e.

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

From moment of inertia we can calculate the bond length of diatomic molecule. i.e.

$$I = \mu r_0^2$$

$$r_0^2 = \frac{1}{\mu}$$

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$$r_0 = \sqrt{\frac{1}{\mu}}$$

(ii) Calculation of force constant—

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

On Squaring

$$\omega_{osc}^2 = \frac{1}{4\pi^2} \frac{k}{\mu}$$

$$k = 4\pi^2 \omega_{osc}^2 \mu$$

(iii) Calculation of equilibrium dissociation energy—

The equilibrium dissociation energy of a diatomic molecule is given by

$$D_e = \frac{w_e}{4x_e}$$

This is the dissociation energy when it is measured from the bottom of the Morse potential energy curve. The true dissociation energy is however, measured from the ground level ( $v=0$ ) and is given by—

$$D_0 = \frac{w_e}{4x_e} - \frac{1}{2} w_e \left(1 - \frac{1}{2} x_e\right)$$

## Isotopic effect on the vibration-rotation spectrum

For vibration-rotation spectrum of HCl, it is found that if the resolving power of the spectrometer is high, each individual line of the spectrum is found to consist of doublets having a wavelength difference of about  $27 \text{ \AA}$ .

This splitting is due to presence of the two isotopes of Cl vizually  $^{35}\text{Cl}$  &  $^{37}\text{Cl}$  in HCl. These isotopes with different masses result into different moment of inertia  $I$  and the fundamental frequency of vibration ( $\omega$ ) for  $\text{HCl}^{35}$  &  $\text{HCl}^{37}$ . Hence they produce splitting of lines.

## Vibrational frequency for different functional groups

The vibration spectra of [IR spectra] of polyatomic molecules are very useful for the identification of organic compounds or for testing the purity of a compound by comparing its IR spectrum with that of the pure compound.

A molecule made up of  $N$  atoms has  $(3N-6)$  or  $(3N-5)$  normal modes of vibration. These vibrations may be divided into two parts—skeletal vibrations and group vibrations.

It is observed that skeletal vibrations takes place when the absorption of energy is upto  $1500\text{ cm}^{-1}$ . They are characteristic of the molecule as a whole i.e. whether it is linear, branched or has benzenoid structure etc. This part of the spectrum is called fingerprint region.

However, certain groups of atoms, irrespective of the molecule in which they are present, absorb at a particular wave number ( $>1500\text{ cm}^{-1}$ ) to exhibit group vibrations. Thus, they give rise to characteristic absorption bands in the spectrum.

Characteristic IR absorption frequencies for some common functional groups [ $\text{in cm}^{-1}$ ]

$\text{>C=O}$	Aldehyde	- 1740-1720	(s)
	Ketone	- 1725-1705	(s)
	Carboxylic acid	- 1725-1700	(s)
	Ester	- 1760-1730	(s)
	Amide	- 1680-1630	(s)
	Anhydride	- 1810 & 1760	(s)
	Acid-anhydride	- 1800	(s)

C-H	Alkane	2850-2960
	Alkenes	3000-3100
	Alkynes	3300
	Aromatics	3050-3150
C=C	Alkene	1600-1680
	Aromatics	1475 & 1600
C≡C	Alkynes	2100-2260
C-O	Alcohols, ethers, esters, carboxylic acids, sulfoxides	1000-1300
	O-H	Alcohols & Phenols
O-H	Free	3600-3650
	H-bonded	3200-3400
	Carboxylic acids	2400-3400
N-H	Primary Amines, Secondary Amines, Amides	3100-3500
	C-N	Amines
C≡N	Nitriles	2240-2260
N=O	Nitro R-NO <sub>2</sub>	1350-1650

C-X

Fluoride

1000-1400 23

Chloride

640-785

Bromide & Iodide

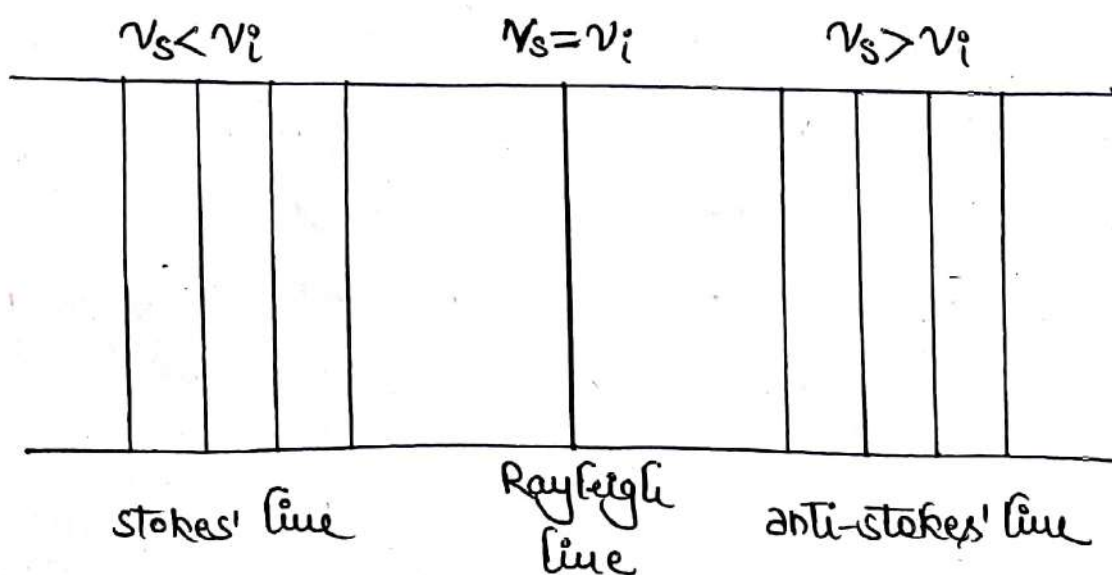
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# Raman Spectra

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Introduction— When a beam of light is passed through a transparent substance, a small amount of the radiation energy is scattered, the scattering persisting even if all dust particles or other extraneous matter are rigorously excluded from the substance. If monochromatic radiat<sup>n</sup>, or radiation of a very narrow frequency band, is used, the scattered energy will consist almost entirely of radiation of the incident frequency (the so-called Rayleigh scattering) but, in addition, certain discrete frequencies above and below that of the incident beam will be scattered, it is this which is referred to as Raman scattering.

The lines with lower frequency are called Stokes lines whereas lines with higher frequency are called anti-stokes line.





The difference between the frequency of the incident <sup>25</sup> light and that of a particular scattered line is depend only upon the nature of the substance being irradiated and is completely independent of the frequency of the incident light.

$$\Delta\nu = \nu_i - \nu_s$$

The difference  $\Delta\nu$  is called Raman frequency or Raman shift. Thus the Raman frequencies observed for a particular substance are characteristic of that substance and the observed spectrum is known as Raman Spectrum.

## Classical Theory of Raman Effect :

### — Molecular Polarizability

The classical Theory of the Raman-effect, while not wholly adequate, is worth consideration since it leads to an understanding of a concept basic to this form of spectroscopy—the polarizability of a molecule.

When a molecule is put into a static electric field it suffers some distortion, the positively charged nuclei being attracted towards the negative pole of the field, the electrons to the positive pole. This separation of charge centres causes an induced electric dipole moment to be set up in the molecule and the molecule is said to be polarized.

The size of the induced dipole  $\mu$ , depends both on the magnitude of the applied field,  $E$ , and on the ease with which the molecule can be distorted.

we may write

$$\mu = \alpha E$$

where —  $\alpha$  — polarizability.

$E$  — applied field

$\mu$  — induced dipole moment

In case of atoms or spherically symmetrical molecules such  $\text{CH}_4$ ,  $\text{SF}_6$  etc same polarizability is induced whatever be the direction of the applied electric field. They are said to be isotropically polarizable. Such molecules are said to be isotropic molecules.

In case of all diatomic molecules (homonuclear or heteronuclear) or non-spherical molecules, the polarizability depends upon the direction of the electric field.

eg. in case of  $\text{H}_2$  molecule, the distortion produced is more when the electric field is applied parallel to the bond than when it is applied perpendicular to it and we write  $\alpha_{\parallel} > \alpha_{\perp}$ .

This fact may be confirmed experimentally (eg. by a study of the intensity of lines in the Raman spectrum of  $H_2$ ), when it is found that the induced dipole moment for a given field applied along the axis is approximately twice as large as that induced by the same field applied across the axis, fields in other directions induce intermediate dipole moments.

Such molecules are, therefore, said to be anisotropically polarizable.

## Types of molecules showing Rotational Raman Spectra

A molecule scatters light because it is polarizable. Hence the gross selection rule for a molecule to give a rotational Raman spectrum is that the polarizability of the molecule must be anisotropic i.e. the polarizability of the molecule must depend upon the orientation of the molecule with respect to the direction of the electric field.

Hence all diatomic molecules, linear molecules and non-spherical molecules give Raman spectra i.e. they are rotationally Raman active.

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On the other hand, spherically symmetric molecules such as  $\text{CH}_4$ ,  $\text{SF}_6$  etc. do not give rotational Raman spectrum, i.e. they are rotationally Raman inactive.

## Quantum theory of Pure Rotational Raman spectra of Diatomic molecules—

The rotational energy levels of linear molecules—

$$\bar{\nu}_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1}$$

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

But in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving  $D$ , the centrifugal distortion constant. Thus we take the simpler expression—

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

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

Transitions between these levels follow the formal selection rule—

$$\Delta J = 0 \text{ or } \pm 2 \text{ only.}$$

which is to be contrasted with the corresponding selection rule for microwave spectroscopy,  $\Delta J = \pm 1$ .

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The fact that in Raman work the rotational quantum number changes by two units rather than one is connected with the symmetry of the polarizability ellipsoid.

The selection rule  $\Delta J = 0$  corresponds to Rayleigh scattering whereas selection rule  $\Delta J = \pm 2$  give rise to Raman lines.

When a transition takes place from a lower rotational level with quantum number  $J$  to a higher rotational level with quantum number  $J'$ , the energy absorbed in terms of wave numbers will be—

$$\Delta \bar{\nu} = B J' (J' + 1) - B J (J + 1) \quad \text{--- (i)}$$

For the selection rule  $\Delta J = +2$ ,

$$J' - J = 2 \Rightarrow J' = J + 2$$

From eq<sup>n</sup> (i)

$$\begin{aligned} \Delta \bar{\nu} &= B (J+2)(J+2+1) - B J (J+1) \\ &= B (J+2)(J+3) - B J (J+1) \\ &= B [J^2 + 5J + 6 - J^2 - J] \end{aligned}$$

$$\Delta \bar{\nu} = B [4J + 6] \quad \text{where } J = 0, 1, 2, 3, \dots \quad \text{--- (ii)}$$

Again for the selection rule,  $\Delta J = -2$

$$J' - J = -2$$

$$J = J' + 2$$

$$\Delta \bar{\nu} = B J'(J'+1) - B(J'+2)(J'+2+1) \quad 30$$

$$= B J'(J'+1) - B(J'+2)(J'+3)$$

$$= B J'(J'+1) - B(J'^2 + 5J' + 6)$$

$$= B[\cancel{J'^2} + J' - \cancel{J'^2} - 5J' - 6]$$

$$= B[-4J' - 6]$$

$$\Delta \bar{\nu} = - B[4J'+6] \quad \text{or} \quad \text{--- (ii)}$$

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

Combining the eq<sup>n</sup> (i) and (ii),  
the wave numbers of the lines obtained in the  
Raman spectrum will be given by,

$$\bar{\nu} = \bar{\nu}_i \pm \Delta \bar{\nu}$$

or  $\boxed{\bar{\nu} = \bar{\nu}_i \pm B[4J+6]} \quad \text{--- (iii)}$

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

Here  $\bar{\nu}_i$  - represents the wave number of Rayleigh  
line.

+ sign gives line with higher wave numbers  
called anti-Stokes' lines

- sign gives lines with lower wave numbers,  
called Stokes' lines.

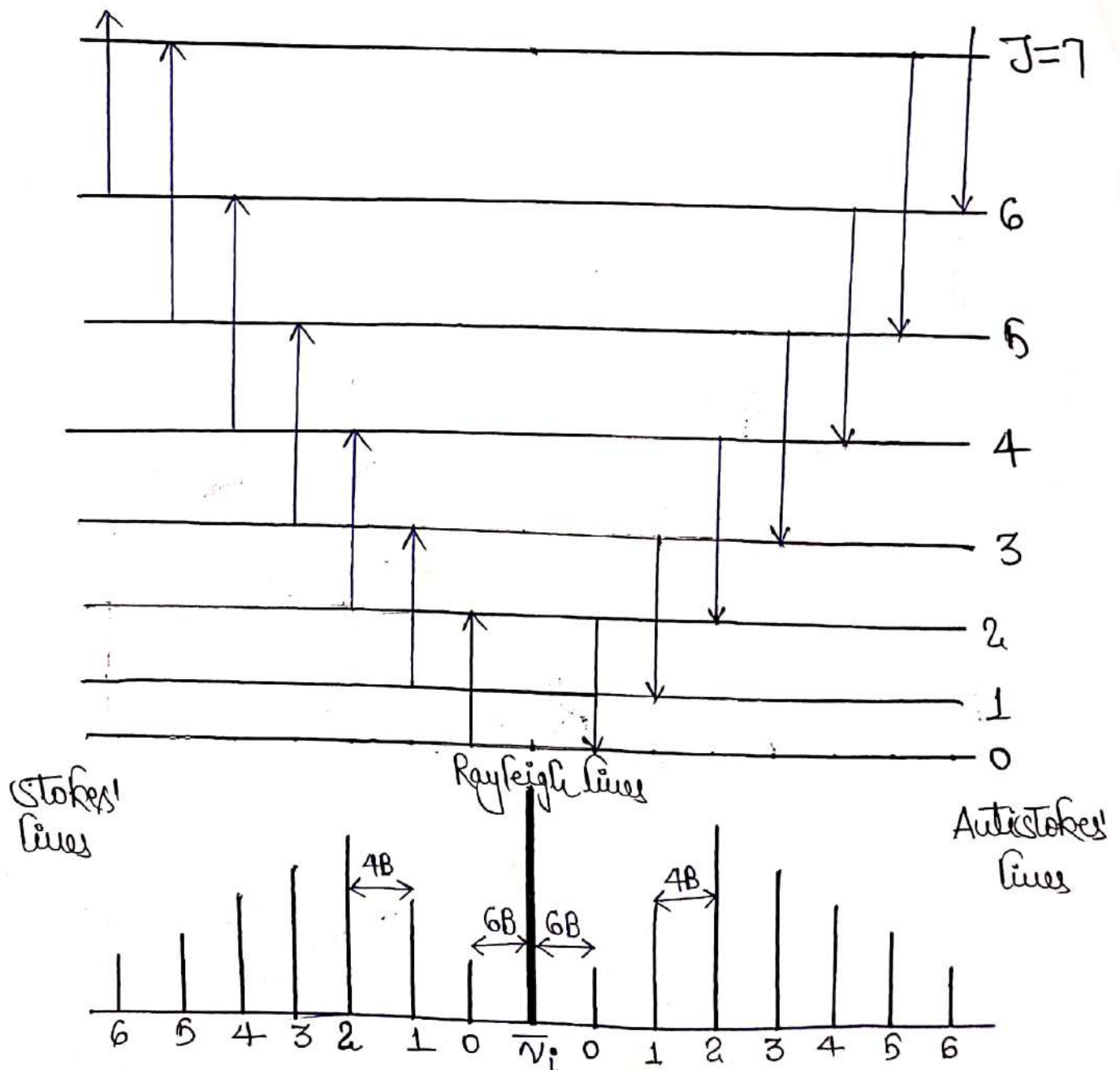
From eq<sup>n</sup> (i)  $J=0$ .

$$\bar{\nu} = \bar{\nu}_i \pm B[4 \times 0 + 6]$$

$$\bar{\nu} = \bar{\nu}_i \pm 6B$$

i.e. the first Stokes' line and anti-Stokes' line will be at a separation  $6B$  from the Rayleigh line.

Further putting  $J=1, 2, 3, \dots$  the separation  $6B$  w any two adjacent Stokes' lines or anti-Stokes' lines will be  $4B$ .



## The Born-Oppenheimer Approximation

According to Born-Oppenheimer Approximation, the total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies.

Or  
Electronic, vibrational and rotational energies [translational energies] of a molecule are completely independent of each other.

Mathematically, we can write Born-Oppenheimer Approximation as -

$$E_{\text{Total}} = E_{\text{electronic}} + E_{\text{vib.}} + E_{\text{rot.}} + E_{\text{trans.}}$$

A change in the total energy of a molecule may then be written -

$$\Delta E_{\text{Total}} = \Delta E_e + \Delta E_{\text{vib}} + \Delta E_{\text{rot.}} + \Delta E_{\text{trans.}}$$

The approximate orders of magnitude of these changes are -

$$\Delta E_e \approx \Delta E_v \times 10^3 \approx \Delta E_r \times 10^6.$$



and so we see that vibrational changes will produce a coarse structure and rotational changes a fine structure on the spectra of electronic transitions.

We should also note that whereas pure rotation spectra are shown only by molecules possessing a permanent electric dipole moment and vibrational spectra require a change of dipole during the motion, electronic spectra are given by all molecules since changes in the electron distribution in a molecule are always accompanied by a dipole change.

This means that homonuclear molecules [eg.  $H_2$  or  $N_2$ ], which show no rotation or vibration-rotation spectra, do give an electronic spectrum and show vibrational and rotational structure in their spectra from which rotational constants and bond vibration frequency may be calculated. [derived].

# Electronic transitions and Band Spectra

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There are no simple formulae available for the energies of electronic levels [except for the hydrogen like atoms].

Electronic spectra are obtained when the electrons in a molecule are excited from a lower electronic energy level to a higher level.

According to Born-Oppenheimer approximation, the energy of the molecule in the initial state

$$E = E_e + E_v + E_r$$

Energy of the molecule in final state,

$$E' = E'_e + E'_v + E'_r$$

∴ Energy change involved in the electronic transition will be given by -

$$\Delta E = E' - E$$

$$= (E'_e - E_e) + (E'_v - E_v) + (E'_r - E_r)$$

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_r$$

But according to Planck's quantum theory -

$$\Delta E = h\nu = hc\bar{\nu}$$

$$hc\bar{\nu} = \Delta E_e + \Delta E_v + \Delta E_r$$

$$\bar{\nu} = \frac{\Delta E_e + \Delta E_v + \Delta E_r}{hc}$$

As for a particular electronic transition 35

[so that  $\Delta E_e$  remains constant], and for a particular vibrational transition [so that  $\Delta E_v$  remains constant],  $\Delta E_r$  can have different values [due to different rotational transitions within the same vibrational energy change of the same electronic energy level], a number of closely spaced lines are obtained.

This constitutes a "band".

For each vibrational transition, separate band will be obtained. Thus due to different vibrational transitions for a particular electronic transition, a set of bands is obtained, called the band group or band system. Each electronic transition will give a band system and hence the complete electronic spectra, involving different electronic transitions gives rise to a series of band groups.

Thus the electronic band spectrum obtained for a gaseous molecule is quite complex.

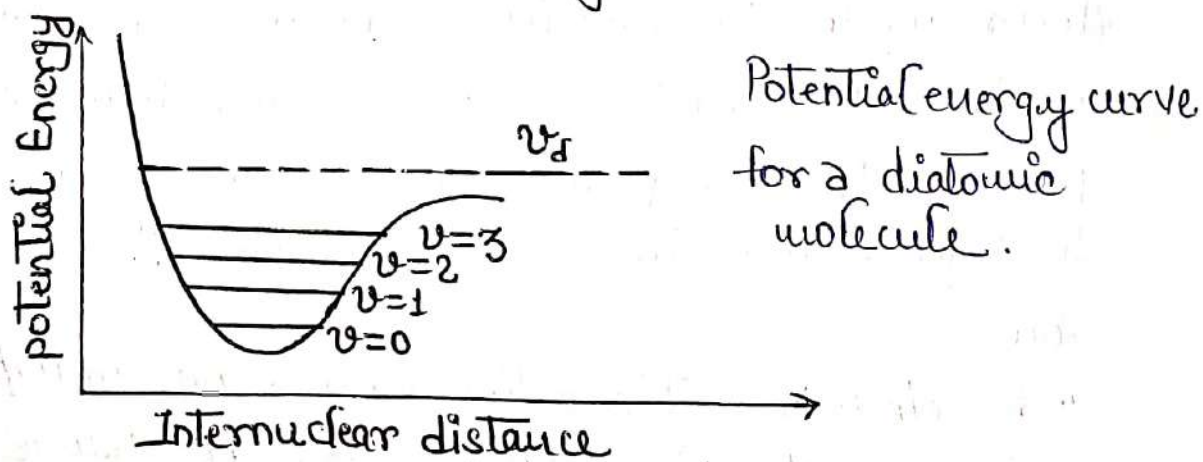
"In spite of the complex nature of the electronic band spectra, these are preferred over the other types because these are obtained in the visible and ultraviolet regions so that these can be easily photographed and studied."

# Franck-Condon Principle

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The explanation of electronic band spectra and dissociation energy can be easily understood in terms of potential energy curves and Franck-Condon principle as follows—

The potential energy curve [The Morse Curve] of a diatomic molecule is obtained by plotting the potential energy of the system versus internuclear distance between the two approaching atoms.



The atoms of system are vibrating when absorb radiation from a source. The vibrational levels of the system may be represented by horizontal lines and indicated by appropriate vibrational quantum numbers.

If sufficient energy is supplied so that system occupies the vibrational level represented by  $v_d$ , the corresponding internuclear distance should become infinity i.e. the molecule should dissociate into atoms.

However, this usually does not happen because before this stage is reached, the  $e^-$  jumps to the higher energy level i.e. electronic transition takes place and the dissociation will take place only of the molecule in the higher energy level.

The transition between the two electronic states takes place according to the Franck-Condon principle explained below—

According to this principle, "Nuclei being much more massive than electrons, an electronic transition takes place much more faster than the nuclei can oscillate to change their internuclear distance."

or

"An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition."

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground electronic state.

There will probably [but not necessarily] be differences in such parameters as vibrational frequency, equilibrium internuclear distance, or dissociation energy between the two states, but this simply means that we should consider each excited molecule as a new, but rather similar, molecule with a different, but also rather similar, Morse curve.

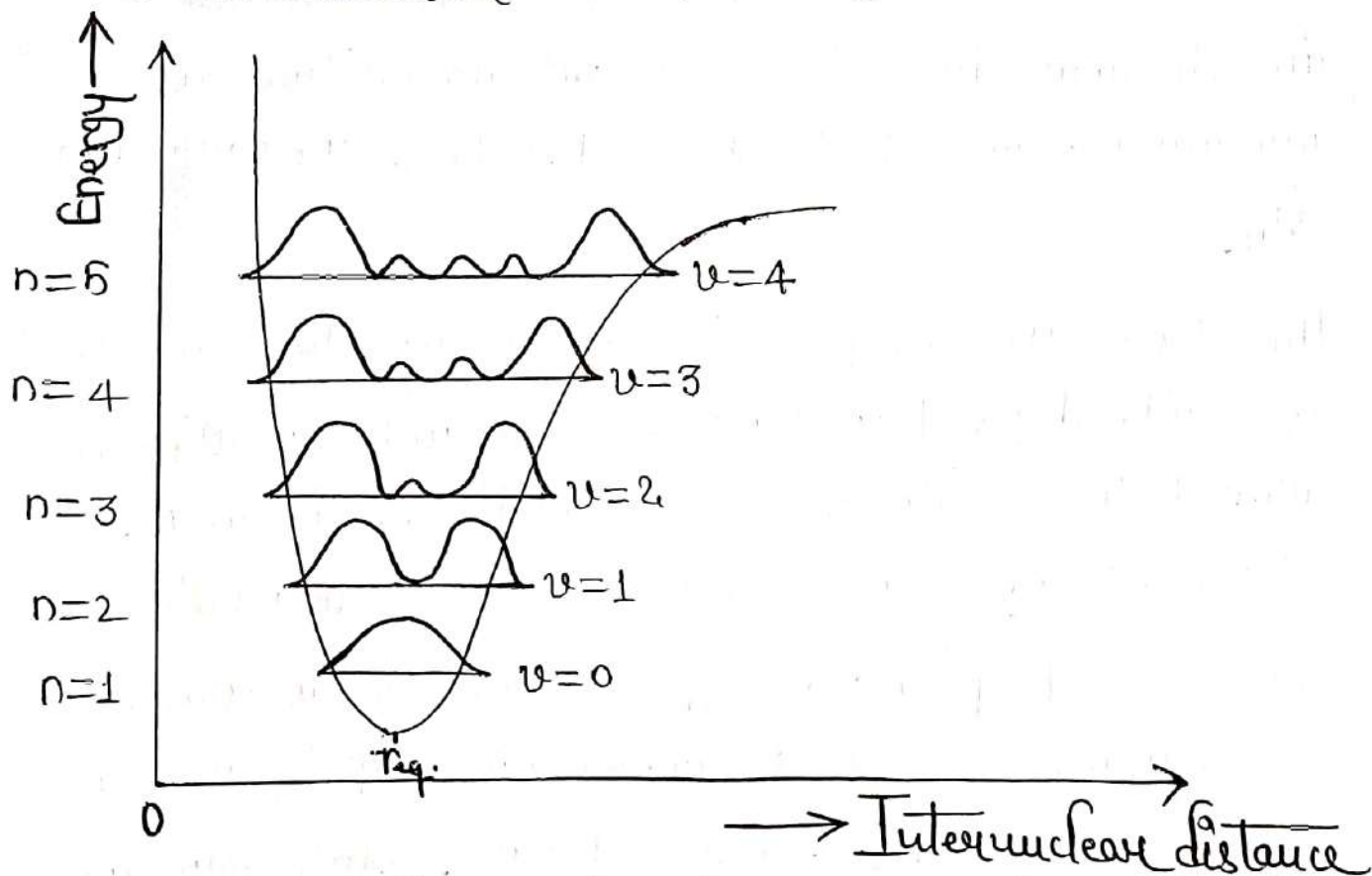
Although quantum mechanics imposes no restrictions on the change in the vibration quantum number during an electronic transition, the vibrational lines in a progression are not all observed to be of the same intensity.

The Morse curve, represents the energy when one atom is considered fixed on the  $r=0$  axis and the other is allowed to oscillate between the limits of the curve.

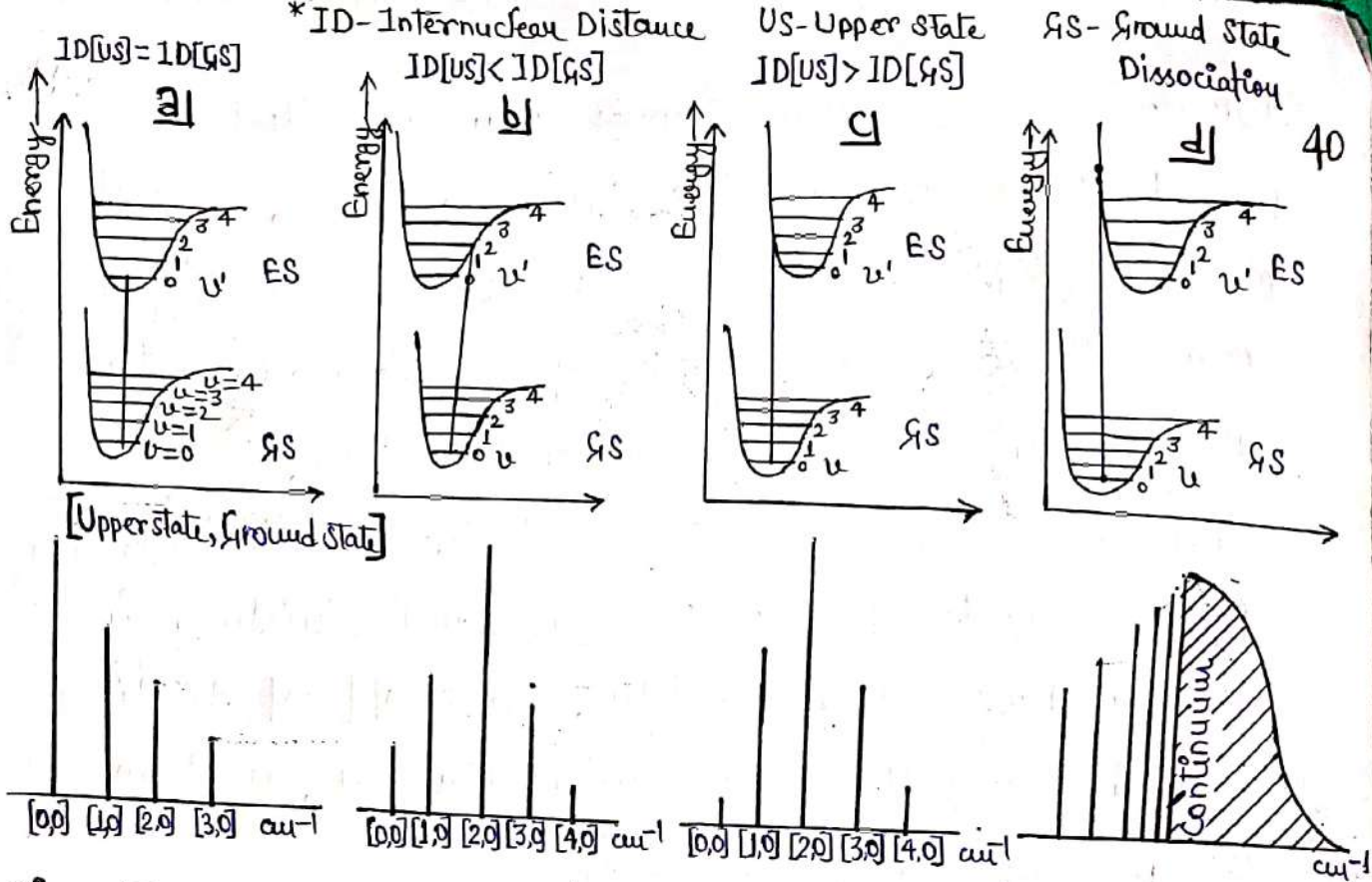
Classical theory would suggest that the oscillating atom would spend most of its time on the curve at the turning point of its motion, since it is moving most slowly there; quantum theory, while agreeing with this view for high values of the vibrational quantum number, shows that for  $v=0$  the atom is most likely to be found at the centre of its motion, i.e. at the equilibrium internuclear distance  $r_{eq}$ .

for  $v=1, 2, 3, \dots$ . The most probable positions steadily approach the extremities until, for high  $v$ , the quantal and classical pictures merge.

This behaviour is shown in fig [6.6] where we plot the probability distribution in each vibrational state against internuclear distance. Following figure the variation of  $\psi^2$  with internuclear distance, where  $\psi$  is the vibrational wave function.



Fig— The probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.



Fig— The operation of the Franck-Condon principle for—

- a) Internuclear distances equal in the upper state & lower state.
- b) Upper state internuclear distance a little less than that in the lower state.
- c) Upper state distance a little greater than in the lower, and
- d) Upper state distance considerably greater.

Above figure shows four possibilities.

a) We show the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Franck-Condon principle suggests that a transition occurs vertically on this diagram, since the internuclear distance does not change, and so if we consider the molecule to be initially in the ground state both electronically & vibrationally, then the most probable transition is that indicated by the vertical line.

Thus the strongest spectral line of the progression will be the [0,0].



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However, the quantum theory only says that the probability of finding the oscillating atom is greatest at the equilibrium distance in the  $v=0$  state - it allows some, - although small, chance of the atom being near the extremities of its vibrational motion.

Hence there is some chance of the transition starting from the ends of the  $v=0$  [gs] and finishing in the  $v'=1, 2, 3, \dots$  etc [upper states]. The  $[1,0]$   $[2,0]$ , etc. lines diminish rapidly in intensity, however, as shown at the foot of fig. [previous page].

6] The case where the excited electronic state has a slightly smaller internuclear separation than the ground state. A vertical transition from the  $v=0$  level will be most likely to occur into the upper vibrational state  $v'=2$ , transitions to lower and higher  $v'$  states being less likely; in general the upper state most probably reached will depend on the difference between the equilibrium separations in the lower and upper states.

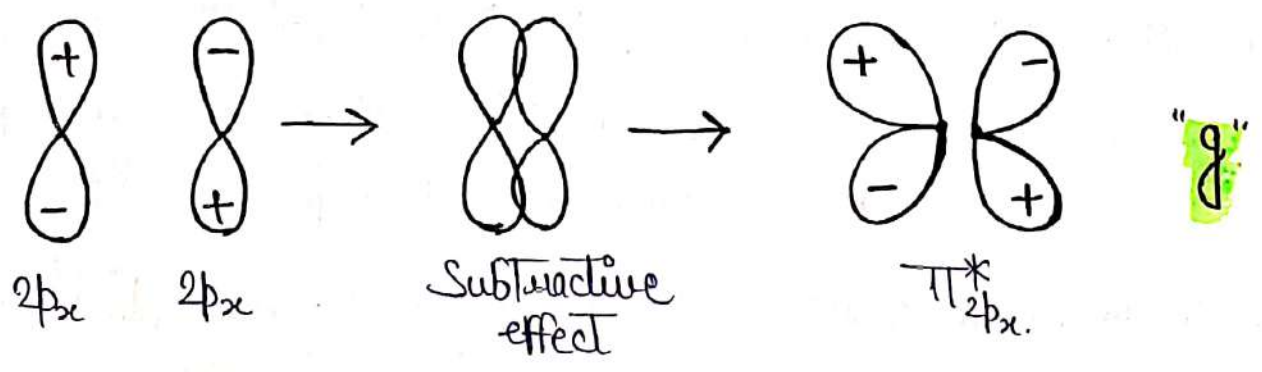
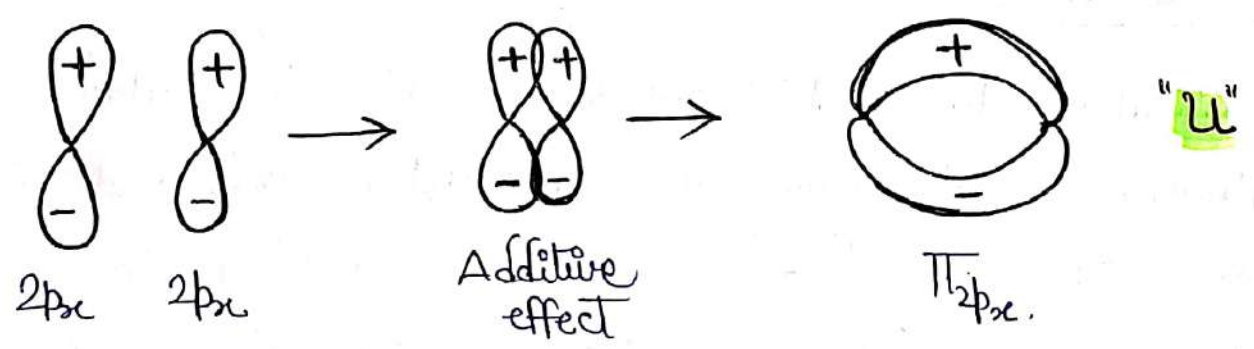
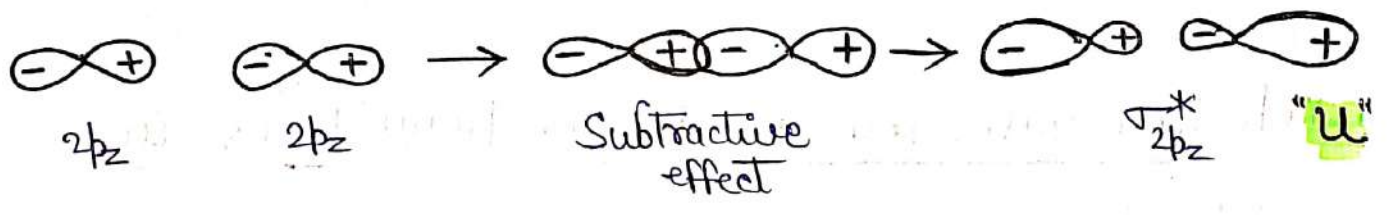
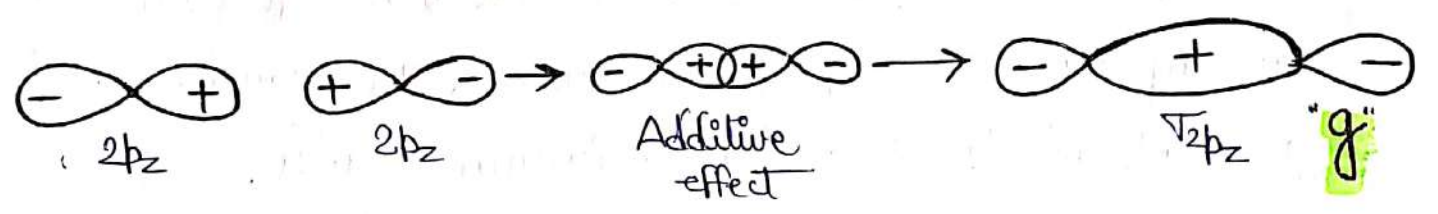
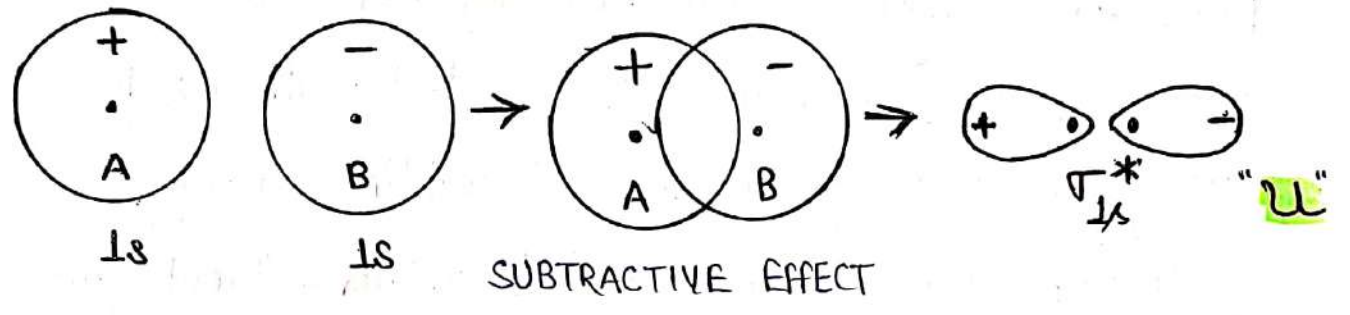
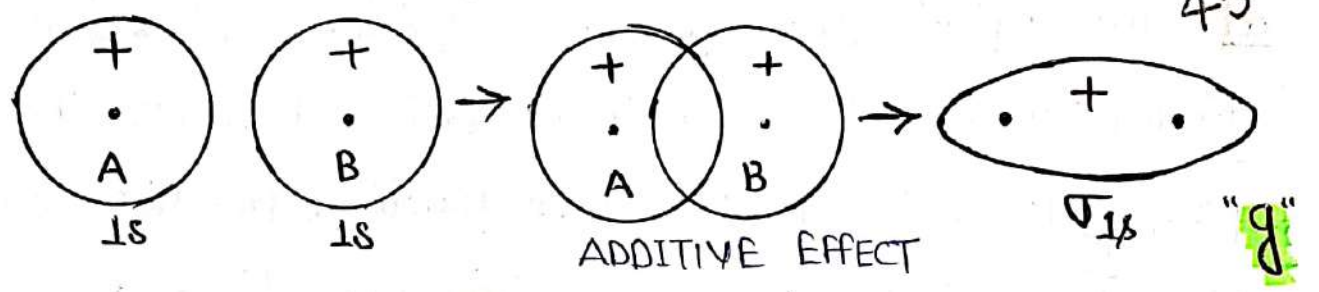
7] The excited electronic state has a slightly larger internuclear separation than the ground state, but the resulting transitions and spectrum are similar.

d) The upper state separation is found to be considerably greater than that in the lower state and we see that, firstly, the vibrational level to which a transition takes place has a high  $v'$  value. Further, transitions can now occur 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 vibrations and, since the atoms which are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum results.

Selection rules for Electronic Transitions in Molecules—

Molecular orbitals which are formed by the overlap of the atomic orbitals along the internuclear axis and which have symmetrical electron charge density about the intermolecular (molecular) axis are called  $\sigma$ -molecular orbital [BMO - Bonding Molecular Orbital] - Additive overlapping.  
 $\sigma^*$ -molecular orbital formed by subtractive overlapping.  
 - [ABMO - Anti bonding molecular orbital]

Similarly, molecular orbitals which are formed by the sideways overlap of atomic orbitals are called  $\pi$ -molecular orbitals if they are bonding and are called  $\pi^*$  molecular orbitals if they are anti bonding.



g-gerade

u-ungerade

Selection rule— In order to understand selection rules for electronic transition in molecules, we should understand a few terms and symbols. 44

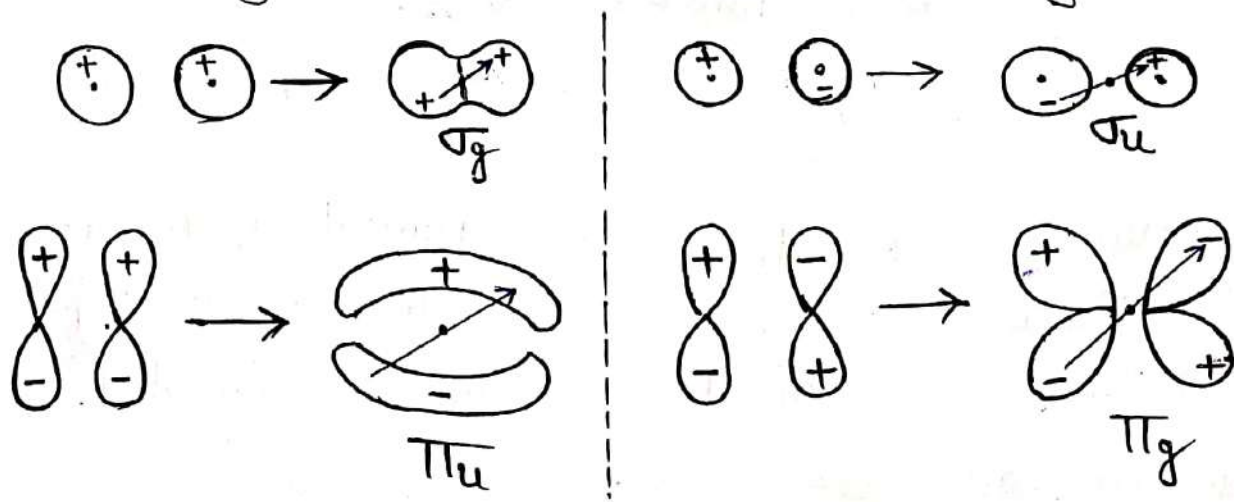
(i) Parity— [gerade and Ungerade]

Parity represents the behaviour of an orbital with respect to inversion.

We consider a point in the molecular orbitals and note the sign of the orbital [wave function]. Then we travel equal distance through the centre of the molecule to a point on the other side. [Centre of inversion]. This operation is called inversion.

If at this point, the orbital has the same sign, it is said to have even parity and is denoted by  $g$  [from gerade].

If the orbital has opposite sign, then it is said to have odd parity and is denoted by  $u$  [for ungerade, uneven].



(ii) Multiplicity of state - If  $S$  represents total spin quantum number, then  $2S+1$  gives the spin multiplicity of the state. 45

If  $S=0$ ,  $2 \times 0 + 1 = 1$  - Singlet state

$S=1$ ,  $2 \times 1 + 1 = 3$  - Triplet state

$S = \frac{1}{2}$ ;  $2 \times \frac{1}{2} + 1 = 2$  - Doublet state

(iii) Term Symbols of Molecule -

$$\therefore \tau = \frac{h}{2\pi}$$

component of the total orbital angular momentum about inter-

nuclear axis :

0

$\pm 1$

$\pm 2$

unit  
[ $\tau$ ]

$\Lambda$

Symbol :

$\Sigma$

$\Pi$

$\Delta$

where

$\Lambda$  - Total electronic orbital angular momentum

$$\Lambda = \sum \lambda_i$$

[ $\Lambda$  is like  $L$  in case of Atomic Term]

$$\text{or } \Lambda = \lambda_1 + \lambda_2 \text{ \& } \lambda_1 - \lambda_2$$

$S$  - Total spin angular momentum :

$$S = \sum s_i$$

- However, for an effective bond formation, the necessary and sufficient condition is that two electrons must pair up [it must follow the Pauli Exclusion principle]. Hence in most cases  $S=0$ .

- However, in cases like  $O_2$  where the unfilled orbitals are antibonding  $\pi$  orbitals,  $S$  is 1. 46

The two quantities  $\Lambda$  &  $S$  combine vectorially to give total resultant angular momentum,  $\Omega$  i.e.

$$\Omega = \Lambda + S$$

- The symmetry of the molecular electronic state in homonuclear diatomic molecules is decided by the following rule -

$$g \times g = g \quad g \times u = u \quad \& \quad u \times u = g$$

where  $g$  &  $u$  are the symmetries of the outermost MO.

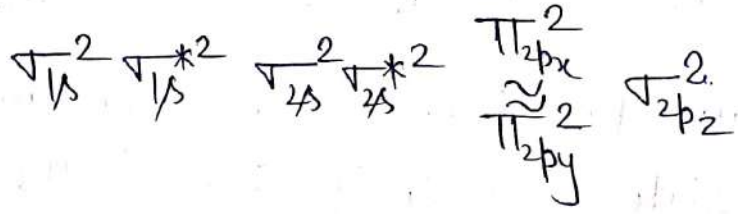
- If wave functions change sign under reflection, it is  $-$  state and if it remains the same it is  $+$  state.

Alternatively, if the total resultant orbital angular momentum,  $\Omega$ , is 0 or an even number, the electronic state is  $+$  and if odd number it is  $-$  state.

In general the electronic states of a molecule can be obtained from direct product of the symmetry of occupied orbitals. A doubly filled orbital always have  $\Sigma$  symmetry.

Orbitals Occupied	$\Lambda = \lambda_1 + \lambda_2$	Molecular States
$\sigma\sigma$	$\Lambda = 0 + 0 = 0$	$\Sigma$
$\sigma\pi$	$\Lambda = 0 + 1 = 1$	$\pi$
$\pi\pi$	$\Lambda = 1 + 1 = 2$	$\Delta$
	$1 - 1 = 0$	$\Sigma$
$\sigma\Delta$	$\Lambda = 2 + 0 = 2$	$\Delta$
$\Delta\pi$	$\Lambda = 1 + 2 = 3$	$\Phi$
	$2 - 1 = 1$	$\pi$
$\Delta\Delta$	$\Lambda = 2 + 2 = 4$	$\Gamma$
	$2 - 2 = 0$	$\Sigma$

all  $N_2 - 14e^-$



$S = 0$

$\Lambda = 0$

$\sigma [BMO] \rightarrow g$

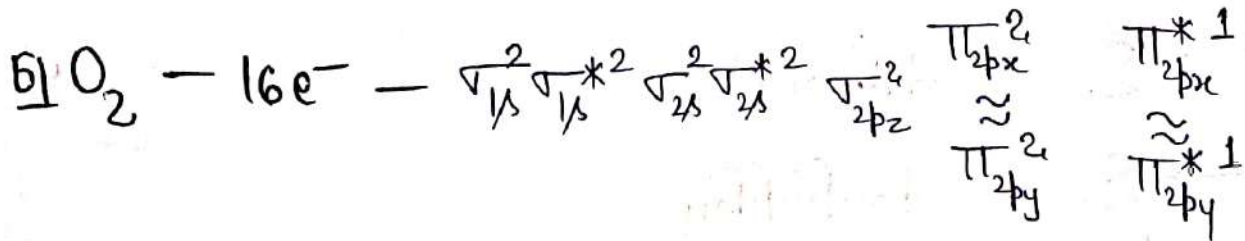
$\Omega = \Lambda + S$

$\Omega = 0 + 0 = 0$  i.e. + state

$2S + 1 =$

$2 \times 0 + 1 = 1$

$1 \Sigma_g^+$

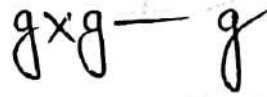


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1	1
+1	-1

$$S=1$$



$$\Lambda = 1 \times 1 + 1 \times (-1)$$

$$= 1 - 1$$

$$\Lambda = 0$$

$$\Omega = \Lambda + S$$

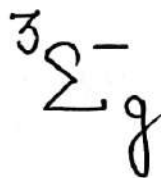
$$= 0 + 1$$

$$= 1 \text{ odd i.e. -ve state}$$

$$2S+1 = 2 \times 1 + 1$$

$$= 3 \text{ Triplet}$$

Term symbol -



The selection rules for transitions between different states of the molecule:

(i)  $\Delta\Lambda = 0, \pm 1$

i.e.  $\Sigma \leftrightarrow \Sigma, \pi \leftrightarrow \Sigma, \Delta \leftrightarrow \pi = \text{Allowed}$

$\Delta \leftrightarrow \Sigma = \text{forbidden}$

(ii) The transitions are allowed only between the states having same multiplicity. i.e.



$${}^3\Sigma \leftrightarrow {}^3\Sigma \quad \text{allowed}$$

$${}^1\Sigma \leftrightarrow {}^3\Sigma \quad \text{forbidden}$$

$${}^1\Sigma \leftrightarrow {}^1\Pi \quad \text{allowed.}$$

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(iii)

$$+ \leftrightarrow + \quad \text{allowed}$$

$$- \leftrightarrow -$$

but

$$+ \leftrightarrow - \quad \text{forbidden.}$$

eg.

$$\Sigma^+ \leftrightarrow {}^+\Sigma \quad \text{Allowed}$$

$$\Sigma^+ \leftrightarrow {}^-\Sigma \quad \text{forbidden}$$

$${}^-\Sigma \leftrightarrow {}^-\Sigma \quad \text{allowed.}$$

(iv) Only those transitions are allowed which are accompanied by a change in parity.

Thus

$$g \leftrightarrow u \quad \text{allowed}$$

$$u \leftrightarrow g \quad \text{allowed}$$

$$g \leftrightarrow g \quad \text{forbidden}$$

$$u \leftrightarrow u \quad \text{forbidden.}$$

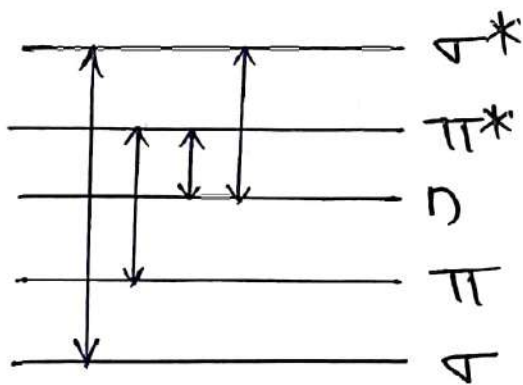
This is known as Laporte selection rule.

# Molecular orbitals [ $\sigma$ , $\pi$ , $n$ ] involved in electronic transitions— 50

The most common MOs present in a molecule are the bonding MOs,  $\sigma$  and  $\pi$  and the corresponding antibonding MOs,  $\sigma^*$  and  $\pi^*$ . Besides these, there may be hetero atoms such as N or O present in the molecule which have orbitals containing lone pairs of electrons. As they are non bonding orbitals, they are designated as  $n$  orbitals.

HOMO — Highest Occupied Molecular Orbital.

LUMO — Lowest Unoccupied Molecular Orbital.



Allowed transitions—

- (i)  $\sigma \rightarrow \sigma^*$
- (ii)  $\pi \rightarrow \pi^*$
- (iii)  $n \rightarrow \pi^*$
- (iv)  $n \rightarrow \sigma^*$

Intensity of electronic bands— Greater the overlap, greater is the intensity.



In presence of an acid, the  $e_s$  of  $n$ -orbital undergo protonation and the  $n \rightarrow \pi^*$  band disappears.