

# Vibrational Spectroscopy.

# Radiations used in vibrational spectroscopy -

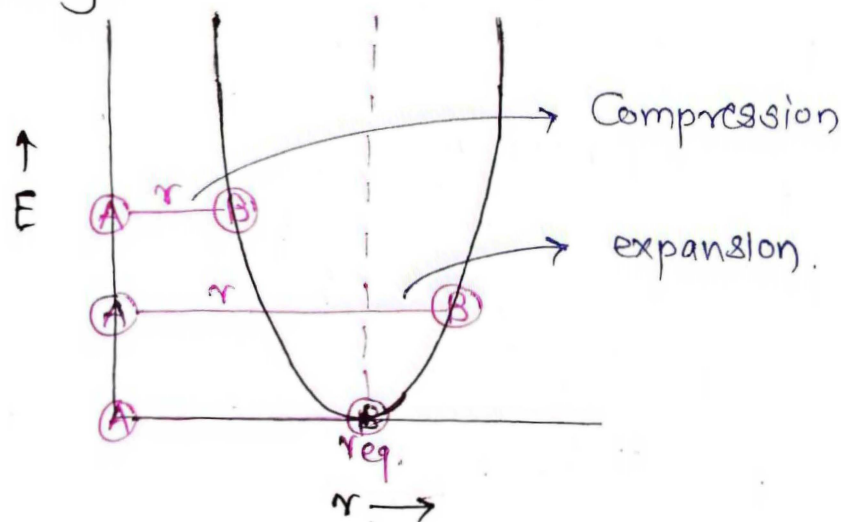
Infrared

⇒ Hence, also called IR spectroscopy.

# Condition -

During vibrations, dipole moment should change.

# Energy diagram -



# Hooke's Law -

⇒ Molecule tries to retain its original / eq<sup>m</sup> position.

restoring force that brings molecule to its eq<sup>m</sup> position.

restoring  $\propto x$

$\rightarrow (r - r_{eq})$

$$f \propto x$$

$$f = -k \cdot x$$

→ -ve sign → force is acting in opposite direction of  $x$ .

$$f = -k \cdot (r - r_{eq})$$

# Energy -

Energy = force  $\times$  displacement.

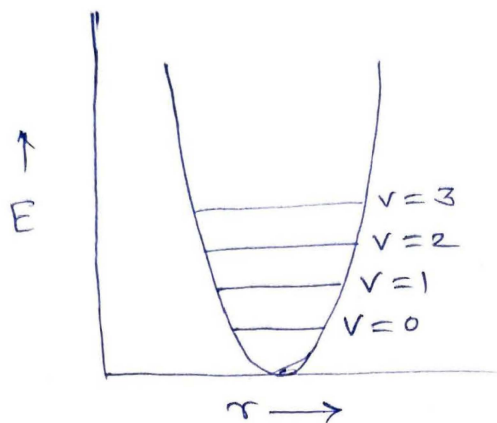
$$E = \frac{1}{2} k \cdot x^2$$

Potential energy (V).

$$V = E = \frac{1}{2} k (r - r_{eq})^2$$

# SHO -

(Simple Harmonic Oscillator)



$$E = \left(v + \frac{1}{2}\right) h\nu \quad \text{Joules unit.}$$

$\downarrow$                        $\downarrow$   
Js                      Hz  $\equiv$  s<sup>-1</sup>

Conversion - Joules  $\rightarrow$  cm<sup>-1</sup>

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

$$\Rightarrow E' = \left(v + \frac{1}{2}\right) \cdot \frac{\nu}{c} \quad \text{cm}^{-1} \text{ unit.}$$

In vibrational spectroscopy,  $\nu \equiv \omega \equiv$  frequency.

$$E' = \left(v + \frac{1}{2}\right) \cdot \frac{\omega}{c}$$

$$\omega \Rightarrow \text{s}^{-1}$$

$$\bar{\omega} \Rightarrow \text{cm}^{-1}$$

$$* E' = \left(v + \frac{1}{2}\right) \cdot \bar{\omega}_e$$

$$\# E = \left(v + \frac{1}{2}\right) \cdot \bar{\omega}_e$$

$$v=0, E_0 = \left(0 + \frac{1}{2}\right) \cdot \bar{\omega}_e = \frac{1}{2} \cdot \bar{\omega}_e$$

$$v=1, E_1 = \left(1 + \frac{1}{2}\right) \cdot \bar{\omega}_e = \frac{3}{2} \bar{\omega}_e$$

$$v=2, E_2 = \left(2 + \frac{1}{2}\right) \cdot \bar{\omega}_e = \frac{5}{2} \bar{\omega}_e$$

$$v=3, E_3 = \left(3 + \frac{1}{2}\right) \cdot \bar{\omega}_e = \frac{7}{2} \bar{\omega}_e$$

$$E_0 = \frac{1}{2} \cdot \bar{\omega}_e$$

Zero point energy.

# Energy difference -

$$\Delta E = E_1 - E_0 = \frac{3}{2} \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e = \bar{\omega}_e$$

$$E_2 - E_1 = \frac{5}{2} \bar{\omega}_e - \frac{3}{2} \bar{\omega}_e = \bar{\omega}_e$$

$$E_3 - E_2 = \frac{7}{2} \bar{\omega}_e - \frac{5}{2} \bar{\omega}_e = \bar{\omega}_e$$

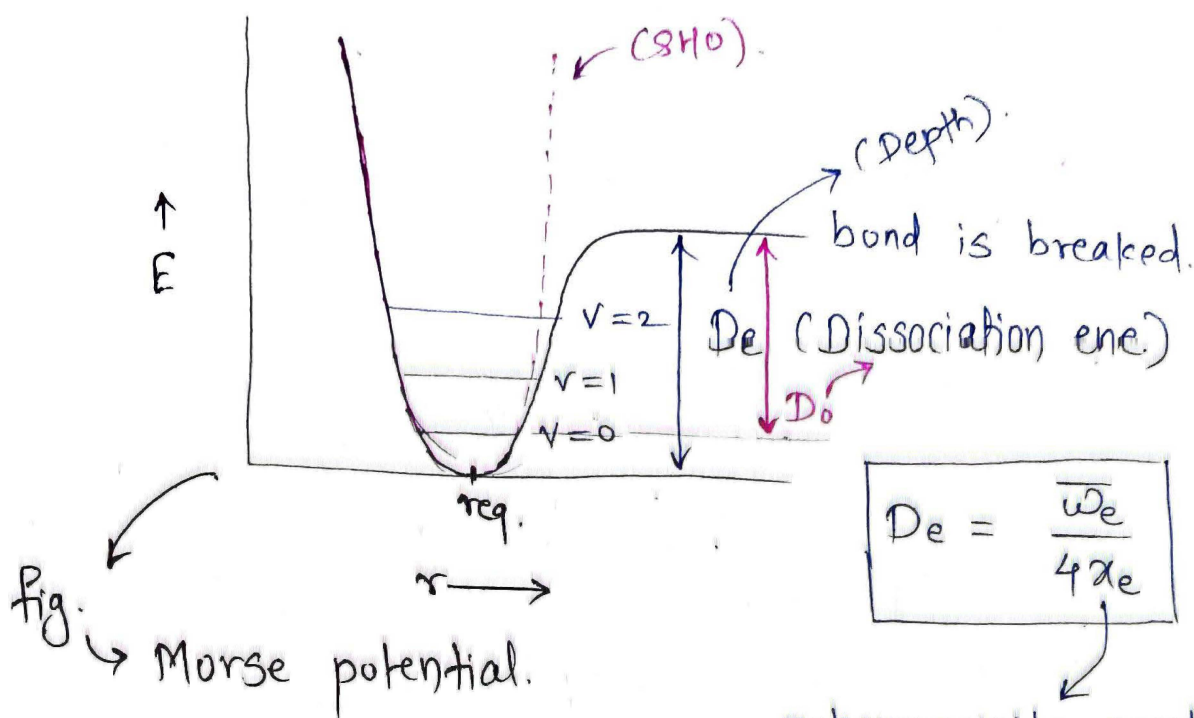
⇒ Lines in energy level diagram are  
equispaced. ⇒ SHO

# Selection rule -

$$\Delta v = \pm 1$$



# # Unharmonic Oscillator -



$$D_e = \frac{\bar{\omega}_e}{4x_e}$$

anharmonicity constant.

⇒ Depth of Morse potential  $\equiv D_e$  (Dissociation ene.)  
 $+ \frac{1}{2} \bar{\omega}_e$   
 ↑ zero pt. ene.

## # Energy. -

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

↑ anharmonicity constant.

⇒  $x_e \approx 0.01$  small & positive.

If value of  $x_e$  is not mentioned in the question take it as 1.

consider 0.01 or 1. acc. to options given.

$$D_0 = D_e - \frac{1}{2} \bar{\omega}_e$$

$$\# E = \left(v + \frac{1}{2}\right) \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e \cdot x_e$$

As,  $v$  goes non increasing,  
 term  $\left(v + \frac{1}{2}\right)^2 \bar{\omega}_e x_e$  increases  
 $\Rightarrow$  resulting in decreasing spacing bet<sup>n</sup> levels.



$\#$  Energy difference -

transition -  $v=0 \rightarrow v=1$ .

$$\begin{aligned} \Delta E &= E_1 - E_0 \\ &= \left[ \left(1 + \frac{1}{2}\right) \bar{\omega}_e - \left(1 + \frac{1}{2}\right)^2 \bar{\omega}_e \cdot x_e \right] - \left[ \left(0 + \frac{1}{2}\right) \bar{\omega}_e - \left(0 + \frac{1}{2}\right)^2 \bar{\omega}_e \cdot x_e \right] \\ &= \left[ \frac{3}{2} \bar{\omega}_e - \frac{9}{4} \bar{\omega}_e \cdot x_e \right] - \left[ \frac{1}{2} \bar{\omega}_e - \frac{1}{4} \bar{\omega}_e \cdot x_e \right] \\ &= \frac{1}{2} \bar{\omega}_e - 2 \cdot \bar{\omega}_e \cdot x_e \end{aligned}$$

$$\boxed{\Delta E = \bar{\omega}_e (1 - 2x_e)}$$

$\hookrightarrow$  Fundamental vibration.

$\#$  Selection rule -

$$\boxed{\Delta v = \pm 1, \pm 2, \pm 3, \dots}$$

## # Intensity -

$v=0 \rightarrow v=1$  shows maximum intensity than all other transitions.

⇒ Reason - population difference.

We know that, As energy increases, population ↓  
Hence  $v=0$  level has maximum population resulting in maximum intensity.

⇒ Population of  $v=1 = 1\%$  of  $P_{v=0}$ .

## # $v=0 \rightarrow v=1$

fundamental transition ⇒ max. intensity.

$$\Delta E = \bar{\omega}_e (1 - 2x_e)$$

## # $v=0 \rightarrow v=2$

first overtone ⇒ Intensity is less.

$$\Delta E = E_2 - E_0$$

$$\Delta E = \left[ \left(2 + \frac{1}{2}\right) \bar{\omega}_e - \left(2 + \frac{1}{2}\right)^2 \bar{\omega}_e x_e \right] - \left[ \frac{1}{2} \bar{\omega}_e - \frac{1}{4} \bar{\omega}_e x_e \right]$$

$$= \frac{5}{2} \bar{\omega}_e - \frac{25}{4} \bar{\omega}_e x_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} \bar{\omega}_e x_e$$

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

$$\Delta E = 2\bar{\omega}_e (1 - 3x_e)$$

$$\# \nu=0 \rightarrow \nu=2$$

Second overtone  $\Rightarrow$  Intensity very low.

$$\Delta E = E_3 - E_0$$

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

$$= \left[ \frac{7}{2} \bar{\omega}_e - \frac{49}{4} \bar{\omega}_e x_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} \bar{\omega}_e x_e \right]$$

$$= 3\bar{\omega}_e - 12\bar{\omega}_e x_e$$

$$\boxed{\Delta E = 3\bar{\omega}_e (1 - 4x_e)}$$



# Hot Band -

$$(v=1 \rightarrow v=2)$$

Condition -

temperature is increased.

⇒ Due to rise in temperature, molecule gets sufficient energy and population in  $v=1$  level becomes considerable.

Hence, transition is possible.

⇒ With increase in temp, intensity goes on increasing of hot band.

$$\# \Delta E = E_2 - E_1$$

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

$$= \left[ \frac{5}{2} \bar{\omega}_e - \frac{25}{4} \bar{\omega}_e \cdot x_e - \frac{3}{2} \bar{\omega}_e + \frac{9}{4} \bar{\omega}_e \cdot x_e \right]$$

$$= \bar{\omega}_e - 4 \bar{\omega}_e \cdot x_e$$

$$\boxed{\Delta E = \bar{\omega}_e (1 - 4 x_e)}$$

$$\text{Fundamental} \Rightarrow \Delta E = \bar{\omega}_e (1 - 2 x_e)$$

# There is not much difference in hot band & fundamental. Hence, hot band lies somewhere nearer to fundamental one.

## # Vibrating Rotator -

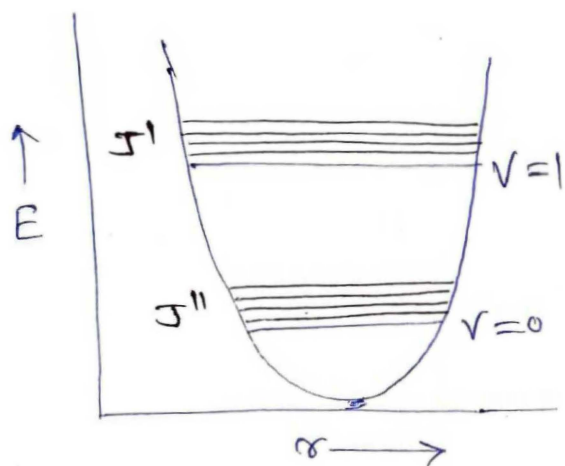
$$\# E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}}$$

$$E_{\text{total}} = \underbrace{\left( v + \frac{1}{2} \right) \bar{\omega}_e - \left( v + \frac{1}{2} \right)^2 \bar{\omega}_e x_e + B J(J+1) - D J^2(J+1)^2}_{}$$

Here we consider only these terms.

$D J^2(J+1)^2$  is neglected  $\Rightarrow D \approx 0.01\%$  of  $B$ .

(Not possible - as we are considering molecule as rigid but it is vibrating).



frequency -  
(IR > Microwave)

## # Selection rule -

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

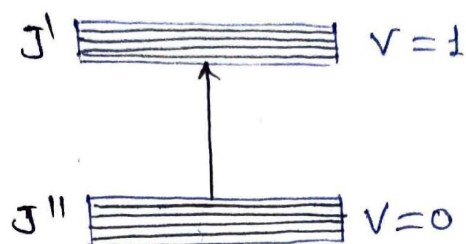
$$\Delta J = \pm 1$$

#  $\Delta J = \pm 1, \Delta v = 0 \Rightarrow$  possible - vibrations  $\times$  rotation  $\checkmark$

But  $\Delta J = 0, \Delta v = \pm 1 \Rightarrow$  Not possible

# # Vibrational spectra of diatomic molecules -

Diatomic molecules are linear always.



$$E = E_{rot.} + E_{vib.}$$

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

$$\Delta E = E_{final} - E_{initial}$$

$$= E_{J', v=1} - E_{J'', v=0}$$

$$= \left[ BJ'(J'+1) + (1 + \frac{1}{2})\bar{\omega}_e - (1 + \frac{1}{2})^2 \bar{\omega}_e x_e \right] - \left[ BJ''(J''+1) + (0 + \frac{1}{2})\bar{\omega}_e - (0 + \frac{1}{2})^2 \bar{\omega}_e x_e \right]$$

$$= \left( \frac{3}{2} - \frac{1}{2} \right) \bar{\omega}_e - \left( \frac{9}{4} - \frac{1}{4} \right) \bar{\omega}_e x_e + B [J'(J'+1) - J''(J''+1)]$$

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

$$= \bar{\omega}_0 + B [ (J'^2 - J''^2) + (J' - J'') ]$$

$$= \bar{\omega}_0 + B [ (J' + J'')(J' - J'') + (J' - J'') ]$$

$$= \bar{\omega}_0 + B [ (J' - J'')(J' + J'' + 1) ]$$

$$\Delta E = \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1)$$

$$\Delta E = \bar{\omega}_0 + B(J' - J'')(J' + J'' + 1)$$

Case I -  $\Delta J = +1$

$$J_{\text{final}} - J_{\text{initial}} = J' - J'' = +1$$

$$\Rightarrow J' = J'' + 1$$

$\therefore$  Expression becomes -

$$\begin{aligned}\Delta E &= \bar{\omega}_0 + B(J'' + 1 - J'')(J'' + 1 + J'' + 1) \\ &= \bar{\omega}_0 + B(1)(2J'' + 2)\end{aligned}$$

$$\Delta E = \bar{\omega}_0 + 2B(J'' + 1)$$

Case II -  $\Delta J = -1$

$$J_{\text{final}} - J_{\text{initial}} = J' - J'' = -1$$

$$\Rightarrow J'' = J' + 1$$

$\therefore$  Expression becomes -

$$\begin{aligned}\Delta E &= \bar{\omega}_0 + B(J' - J' + 1)(J' + J' + 1 + 1) \\ &= \bar{\omega}_0 + B(-1)(2J' + 2)\end{aligned}$$

$$\Delta E = \bar{\omega}_0 - 2B(J' + 1)$$

$$\bar{\omega}_0 = \bar{\omega}_e(1 - 2x_e)$$

$\rightarrow$  Fundamental vibration.



$$\# \quad \Delta E = \bar{\omega}_0 + 2B(J''+1) \leftarrow \Delta J = +1$$

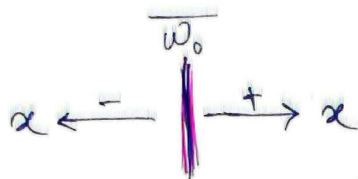
$$\Delta E = \bar{\omega}_0 - 2B(J'+1) \leftarrow \Delta J = -1$$

Now considering  $J'$  and  $J'' \equiv J$

$$\text{and } 2B(J+1) \equiv \alpha.$$

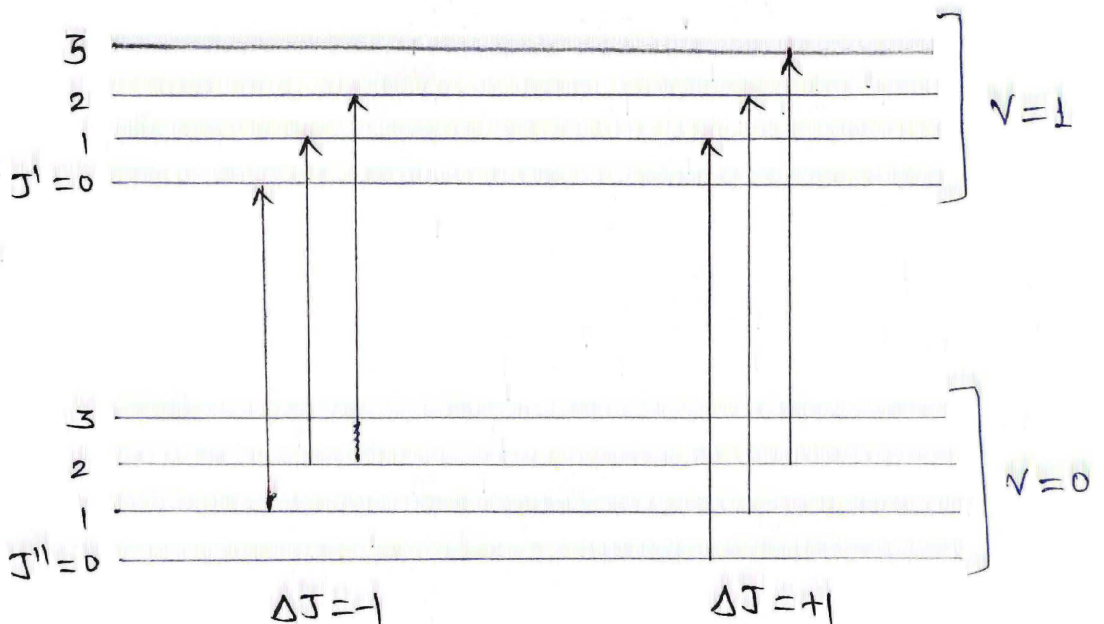
$$\Delta E = \bar{\omega}_0 + \alpha$$

$$\Delta E = \bar{\omega}_0 - \alpha$$



low freq.      high freq.

# Energy diagram -



$$J'=0 \rightarrow \bar{\omega}_0 - 2B$$

$$J'=1 \rightarrow \bar{\omega}_0 - 4B$$

$$J'=2 \rightarrow \bar{\omega}_0 - 6B$$

$$\bar{\omega}_0 + 2B \leftarrow J''=0$$

$$\bar{\omega}_0 + 4B \leftarrow J''=1$$

$$\bar{\omega}_0 + 6B \leftarrow J''=2$$

#  $\Delta J = +1 \Rightarrow \Delta E = \bar{\omega}_0 + 2B(J''+1)$

$J'' = 0, \Delta E = \bar{\omega}_0 + 2B$

$J'' = 1, \Delta E = \bar{\omega}_0 + 4B$

$J'' = 2, \Delta E = \bar{\omega}_0 + 6B$

$J'' = 3, \Delta E = \bar{\omega}_0 + 8B$

$\Delta J = -1 \Rightarrow \Delta E = \bar{\omega}_0 - 2B(J'+1)$

$J' = 0, \Delta E = \bar{\omega}_0 - 2B$

$J' = 1, \Delta E = \bar{\omega}_0 - 4B$

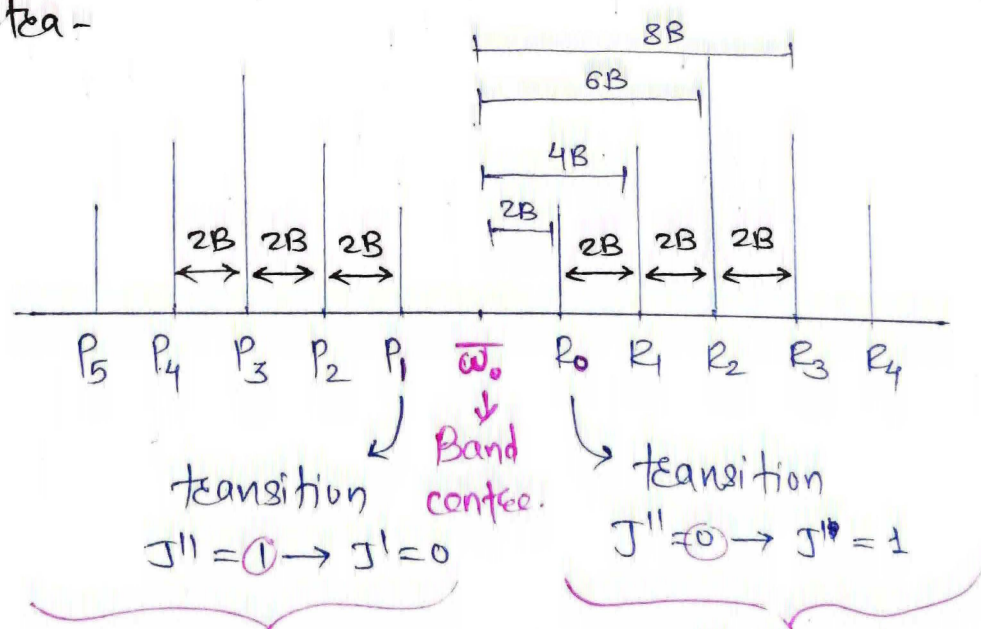
$J' = 2, \Delta E = \bar{\omega}_0 - 6B$

$J' = 3, \Delta E = \bar{\omega}_0 - 8B$

#

$\Delta J$	-2	-1	0	1	2
Branch	O	P	Q	R	S

# Spectra-



P-Branch

R-Branch

# Peak at  $\bar{\omega}_0$  is not possible.

Reason-

$$\Delta E = \bar{\omega}_0 + 2B(J'' + 1)$$

For  $\Delta E = \bar{\omega}_0$ ,  $J''$  must be equal to  $-1$ .

But  $J'' = -1$  is not possible.

$$\Delta E = \bar{\omega}_0 - 2B(J' + 1)$$

For  $\Delta E = \bar{\omega}_0$ ,  $J'$  must be equal to  $-1$ .

But  $J' = -1$  is not possible.

#  $P_1 + R_0 = 4B$

Que.  $P_1 = 2140.1 \text{ cm}^{-1}$

$$R_0 = 2143.2 \text{ cm}^{-1}$$

Find  $B$ ,  $\bar{\omega}_0$ .

Ans.  $P_1 + R_0 = 4B$

$$\Rightarrow B = \frac{2140.1 + 2143.2}{4} = \frac{4283.3}{4} = 1070.8$$

$$B = 1070.8 \text{ cm}^{-1}$$

$$\bar{\omega}_0 = \frac{P_1 + R_0}{2} = \frac{4283.3}{2} = 2141.6$$

$$\bar{\omega}_0 = 2141.6 \text{ cm}^{-1}$$

Linear diatomic molecule  $\equiv$  PR Branch.

Que Fundamental vibration =  $2000 \text{ cm}^{-1}$   
first overtone =  $4100 \text{ cm}^{-1}$   
Calculate  $x_e$ .

Ans -

$$\bar{\omega}_e (1 - 2x_e) = 2000$$

$$2\bar{\omega}_e (1 - 3x_e) = 4100$$

Now,

$$\frac{\bar{\omega}_e (1 - 2x_e)}{2\bar{\omega}_e (1 - 3x_e)} = \frac{2000}{4100}$$

$$40 (1 - 3x_e) = 41 (1 - 2x_e)$$

$$120x_e - 40 + 41 - 82x_e = 0$$

$$38x_e = -1$$

$$x_e = -\frac{1}{38}$$



## # Vibrational Spectra of Polyatomic molecules -

ex.  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{HCN}$ .

Linear or non linear.

## # Degree of freedom -

$$\text{Degree of freedom} = 3N$$

→ total no. of atoms.

ex.  $\text{H}_2\text{O}$

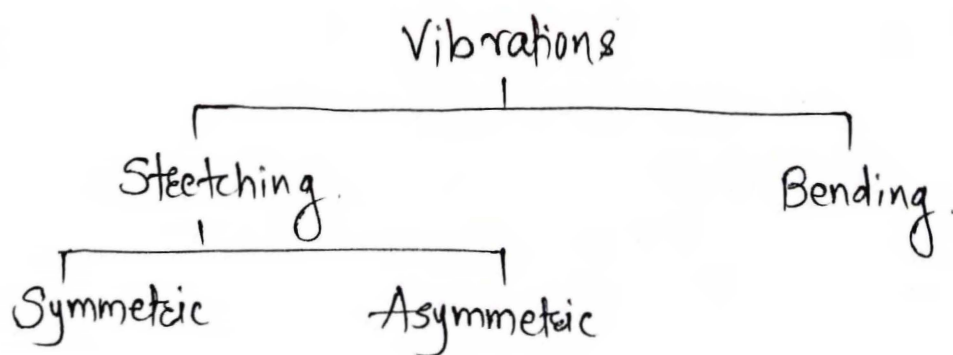
$$\text{DOF} = 3 \times 3 = 9$$

## # Modes of degree of freedom -

	Linear	Non-Linear
Translational	3	3
Rotational	2	3
Vibrational	$(3N-5)$	$(3N-6)$

Degree of freedom = Transl<sup>n</sup> + Rotational + Vibrational.

#



Frequency order -

$$\text{Asymm.} > \text{Symm} > \text{Bending}$$

#

Total degrees of freedom =  $3N$ .

Total atoms =  $N$

Total number of stretching vibrations =  $N-1$

Total bending modes of vibrations =  $(3N-6) - (N-1)$

(total = stretching + Bending)

(for non-linear)

Total bending modes of vibrations =  $(3N-5) - (N-1)$

(for linear)

# Vibrations -

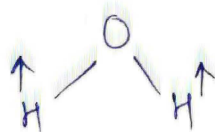
Symmetric stretching -



Asymmetric stretching -



Bending -



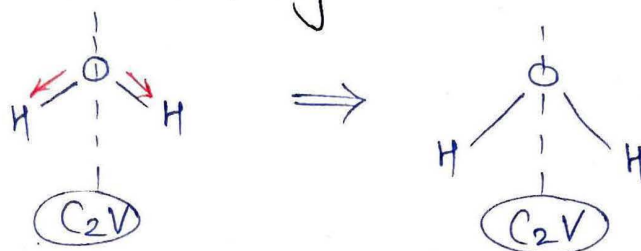
Hydrogen atoms moves front of plane  
or back of the plane.

# # Parallel and perpendicular vibrations -

(II) Parallel - Symm. to principle-axis

(I) Perpendicular - Asymm. to principle-axis.

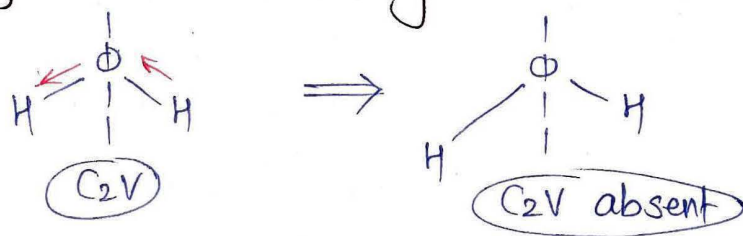
⇒ Symmetric stretching -



Symm. to principle axis.

⇒ Parallel vibration.

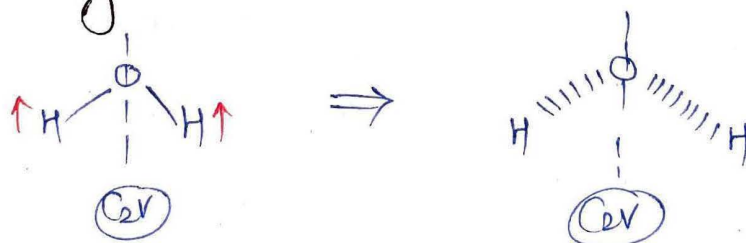
⇒ Asymmetric stretching -



Asymm. to principle axis

⇒ Perpendicular vibration.

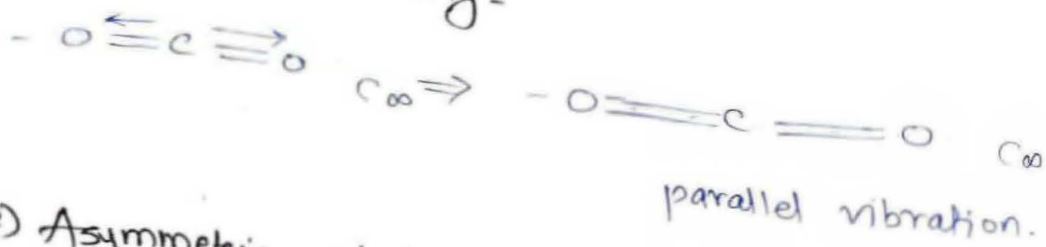
⇒ Bending -



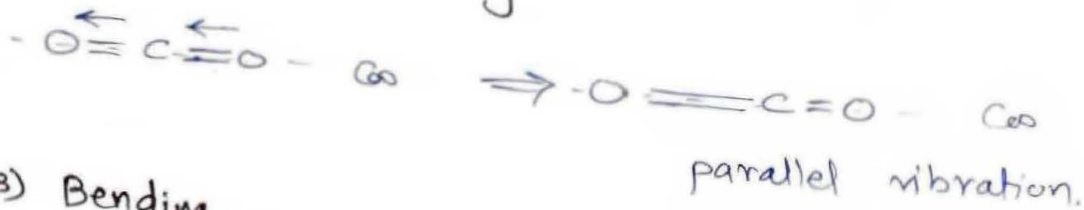
⇒ Parallel vibration.

Ex.  $\text{CO}_2$   $\begin{cases} \rightarrow 2 \text{ stretching} \\ \rightarrow 2 \text{ bending} \end{cases}$

1) Symmetric stretching -

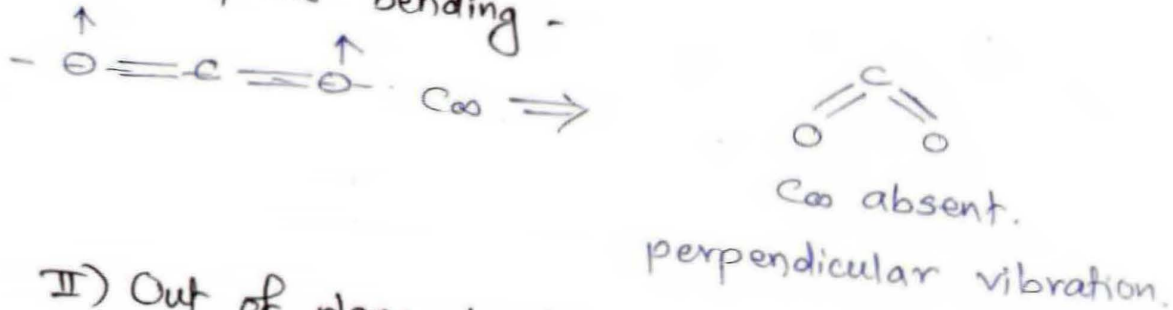


2) Asymmetric stretching -

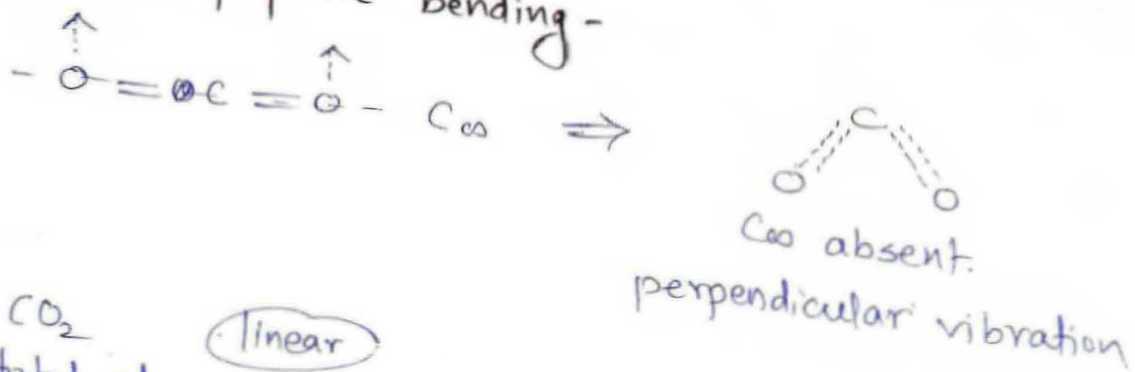


3) Bending -

I) In plane bending -



II) Out of plane bending -



#  $\text{CO}_2$  linear  
total atoms = 3.

Total stretching vibrations =  $N - 1 = 3 - 1 = 2$

Total bending vibrations =  $(3N - 5) - (N - 1)$   
=  $9 - 5 - 3 + 1$   
= 2

$\Rightarrow$  2 stretching and 2 bending.



## # Linear Polyatomic molecules -

ex.  $\text{CO}_2$   
vibrations

parallel

perpendicular

$$\Delta V = \pm 1$$

$$\Delta V = \pm 1$$

$$\Delta J = \pm 1$$

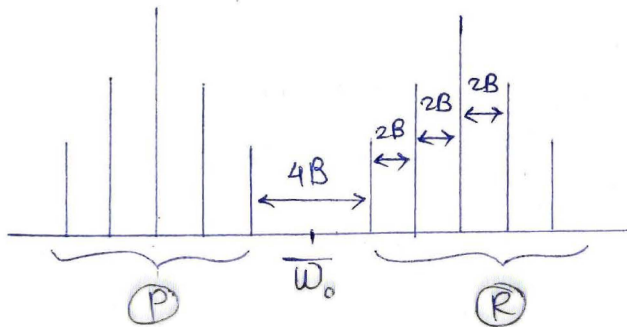
$$\Delta J = 0, \pm 1$$

PQR Branch.

Similar to diatomic molecule.

Hence  $\Rightarrow$  PR Branch.

Selection rules are diff.  
for parallel and  
perpendicular  
vibrations.



Here, value of  $B$  is less than that of diatomic molecule.

Reason - In polyatomic molecule -

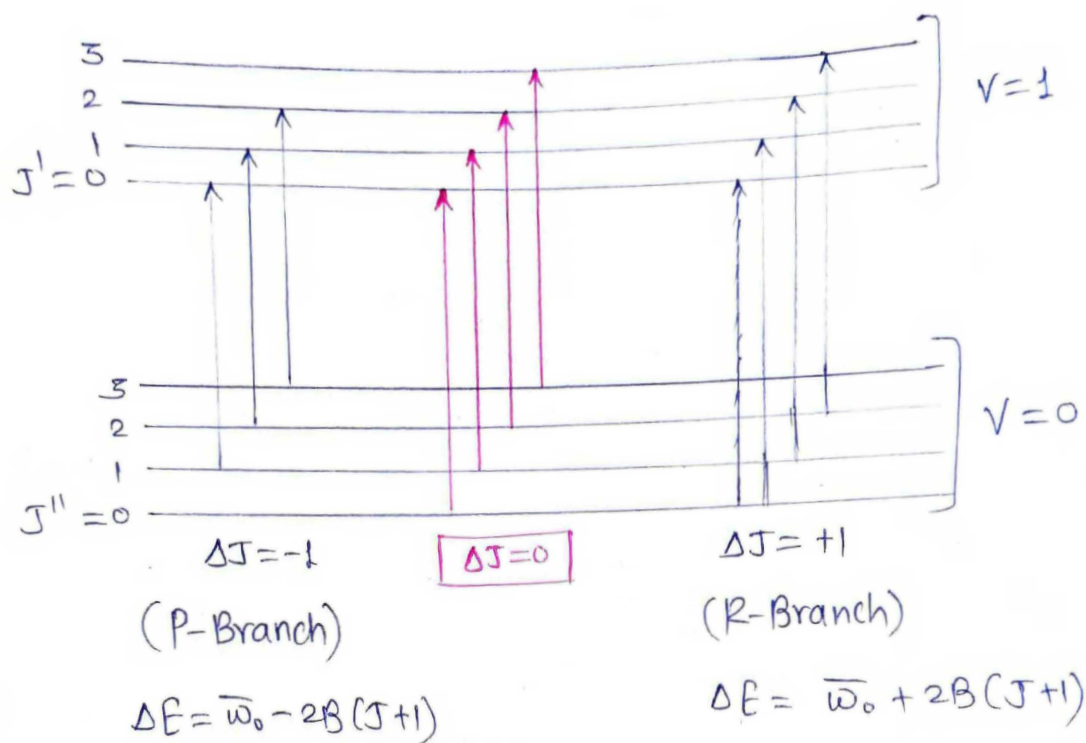
mass  $\uparrow \Rightarrow$  moment of inertia  $\uparrow \Rightarrow B \downarrow$ .

# # PQR Branches -

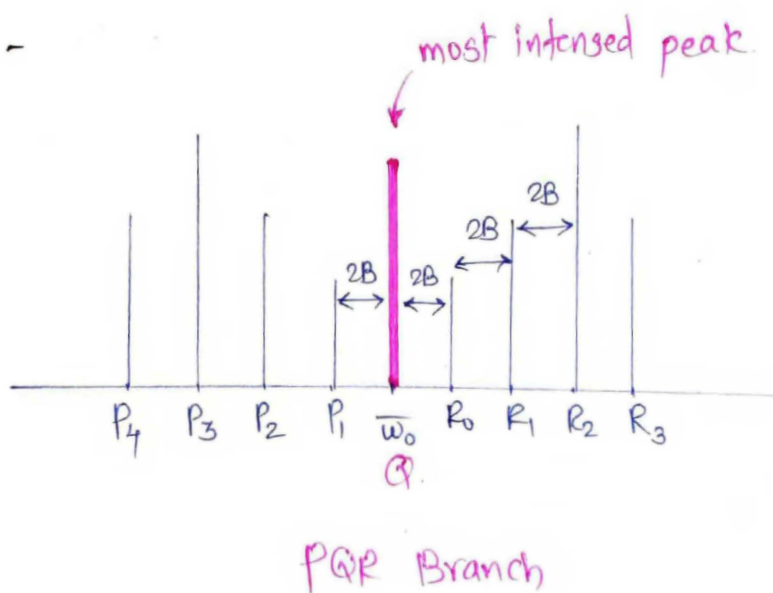
(Due to perpendicular vibrations.)

$$\Delta V = \pm 1$$

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



# # Spectra -



# Most intensified peak - Q Branch.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$= E_{J', v=1} - E_{J'', v=0}$$

$$= E_{J, v=1} - E_{J, v=0}$$

$$= \left[ B J(J+1) + \left(v + \frac{1}{2}\right) \bar{\omega}_0 - \left(v + \frac{1}{2}\right)^2 \bar{\omega}_e \cdot x_e \right]$$

$$- \left[ B J(J+1) + \left(0 + \frac{1}{2}\right) \bar{\omega}_e - \left(0 + \frac{1}{2}\right)^2 \bar{\omega}_e \cdot x_e \right]$$

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

$$= \bar{\omega}_e - 2 \bar{\omega}_e \cdot x_e$$

$$= \underbrace{\bar{\omega}_e (1 - 2x_e)}$$

$$\boxed{\Delta E = \bar{\omega}_0}$$

As, frequency is independent of value of  $J$  from above equation.

The peak becomes sharp & intensified due to

$$\text{transitions } J' = 0 \rightarrow J'' = 0$$

$$J' = 1 \rightarrow J'' = 1$$

$$J' = 2 \rightarrow J'' = 2$$

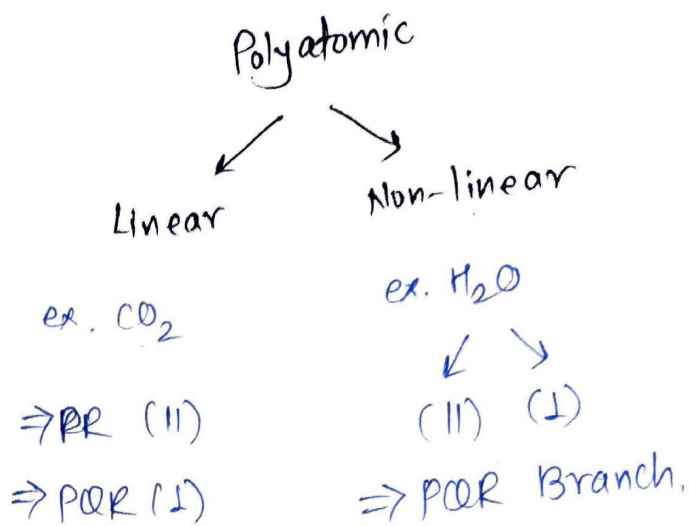
Peaks due to all above transitions overlaps each other

Resulting the intensified peak.

## # Summary -

Diatomic  
(always linear)

⇒ PR Branch.



Que. molecule  $\text{AB}_2$

$890 \text{ cm}^{-1} \rightarrow \text{PR}$

$972 \text{ cm}^{-1} \rightarrow \text{PQR}$

Determine the structure.

Ans. - Since PQR branch - it cannot be diatomic.

⇒ Polyatomic molecule.

In polyatomic, since PR are present.

⇒ Linear polyatomic molecule.

∴ Structure -

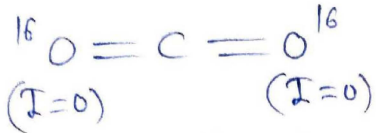


## # Influence of Nuclear Spin -

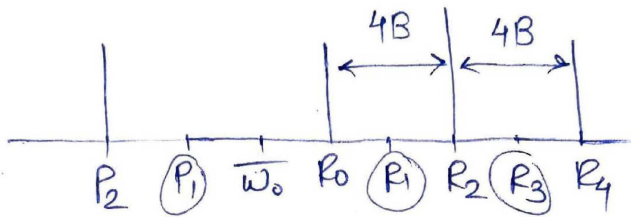
# # Influence of mutual inclusion - nuclear spin -

⇒ Molecule having Centre of Symmetry, nuclear spin plays an important role.

ex.  $\text{CO}_2$



Odd alternate lines are missing in spectra.



ex.  $\text{O}_2$



All even lines are missing.

