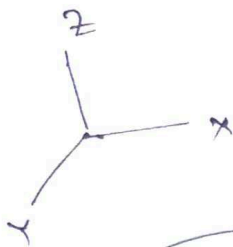


Physical Spectroscopy

Type of Rotational Molecule



Linear

$I_A = 0$
 $I_B = I_C$
 eg. H_2, HCl
 CO_2, O_2, HCN

① C_n axis

$$n \geq 3$$

②

$$C_2\text{-axis} + S_4\text{-axis}$$

Spherical Tops

$(I_A = I_B = I_C)$
 e.g.: perfect Td
 and Oh
 $\Rightarrow CH_4, SF_6$
 \uparrow
 NH_4^+, P_4

Symmetric Tops

Prolate (shuttlecock)




$$I_B = I_C > I_A$$

eg: CH_3F ,
 CH_3CN ,
 $CH_3-C \equiv CH$,
 allene

oblate (disc type)



$$I_B = I_C < I_A$$

eg: BCl_3 ,

 NH_3

Asymmetric Tops

(C_n, C_{2v}, C_s)

$$I_A \neq I_B \neq I_C$$

eg: H_2O , $CH_2 = CHCl$
 NO_2 , anthra.
 H_3BO_3

Rotational Spectroscopy

(microwave)

which of the following are active

$\checkmark SF_4$, $\checkmark H_2S$, $\checkmark SO_2$, $\checkmark O_3$

$\checkmark H_2O$, $\checkmark SCO$, $\times CO_2$, $\times HC \equiv CH$

$\times H_2C = CH_2$, $\checkmark HOCl$, $\checkmark NH_3$, $\checkmark ClF_3$, $\checkmark BF_3$

$\times CH_4$, $\times N_2$

$O=C=O$
 $\leftarrow + + \rightarrow$
 perfect molecule
 \Rightarrow inactive
 sp, sp^2

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{Joule}$$

$$\frac{\text{Joules}}{hc}$$

$$= \frac{J}{J \cdot s \times \text{cm/s}}$$

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

$$J \rightarrow \text{cm}^{-1}$$

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

$I =$ moment of inertia.

$$\therefore \frac{E}{hc} = \frac{h^2}{8\pi^2 I} \frac{J(J+1)}{hc}$$

$$\Rightarrow E' (\text{cm}^{-1}) = \frac{h}{8\pi^2 I c} J(J+1)$$

B

rotational constant

$$\therefore B = \frac{h}{8\pi^2 I c} \rightarrow \text{cm}^{-1}$$

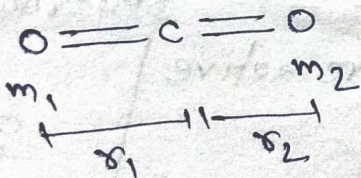
$$B = \frac{h^2}{8\pi^2 I} \rightarrow \text{Joule}$$

$$E = BJ(J+1) \rightarrow J$$

$$E' = BJ(J+1) \rightarrow \text{cm}^{-1}$$

#

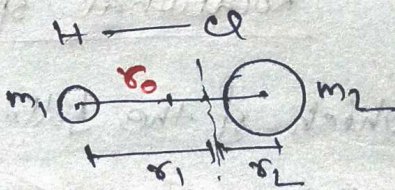
$$\begin{matrix} r_1 = r_2 \\ m_1 = m_2 \end{matrix}$$



$$\therefore I = m_1 r_1^2 + m_2 r_2^2$$

$$= m_1 r_1^2 + m_1 r_1^2$$

$$I = 2m_1 r_1^2$$



$$\therefore I = \mu r_0^2 \rightarrow \text{bond length}$$

$\mu =$ reduced mass

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

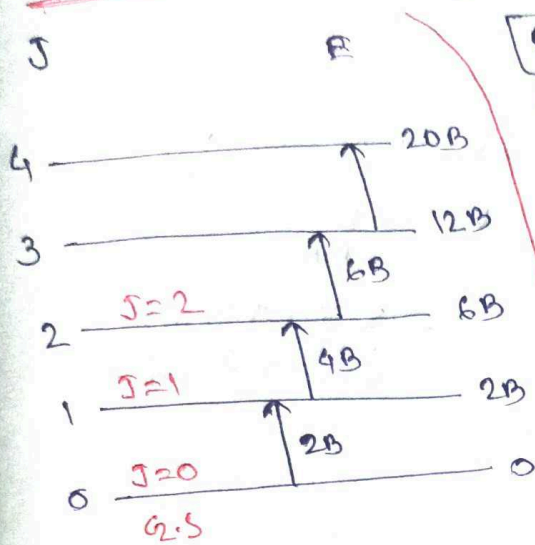
$$= \frac{m_1 + m_2}{m_1 m_2}$$

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

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

rigid rotator

$$E = BJ(J+1)$$



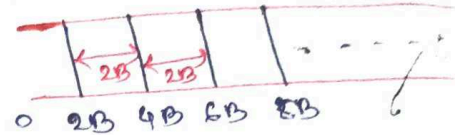
$$E = 0 \text{ at } J=0$$

$$E_1 = B(1)(1+1) = 2B$$

$$E_2 = 6B$$

$$E_3 = 12B$$

$$E_4 = 20B$$



$$J \rightarrow (J+1)$$

$$J=1$$

$$J=0$$

$$\Delta E = 2B(0+1) = 2B$$

$$\begin{aligned} \Delta E &= B(J+1)(J+1+1) \\ &\quad - BJ(J+1) \\ &= B(J+1)(J+2-J) \end{aligned}$$

$$\Delta E = 2B(J+1)$$

lowers level.

$$J=10 \rightarrow J=11$$

$$\therefore \Delta E = 2B(10+1) = 22B$$

$$8. \quad J=10 \rightarrow J=11$$

$\Delta E = 2207 \text{ cm}^{-1}$, calculate ΔE & B .

$$\therefore \Delta E = 2B(J+1) = 2B(10+1) = 22B$$

$$B = \frac{2207}{22} \text{ cm}^{-1}$$

Intensity

$$43 = \pm 1$$

$J=0$	3
	2
	1
	0

Population difference

$$\frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-\frac{4B}{kT}}$$

Degeneracy

$$P \propto e^{-\frac{4B}{kT}} \cdot (2J+1)$$

$$\Rightarrow \frac{dP}{dJ} = \frac{d}{dJ} \left[e^{-\frac{4B(2J+1)}{kT}} (2J+1) \right]$$

$$\frac{dP}{dJ} = 0$$

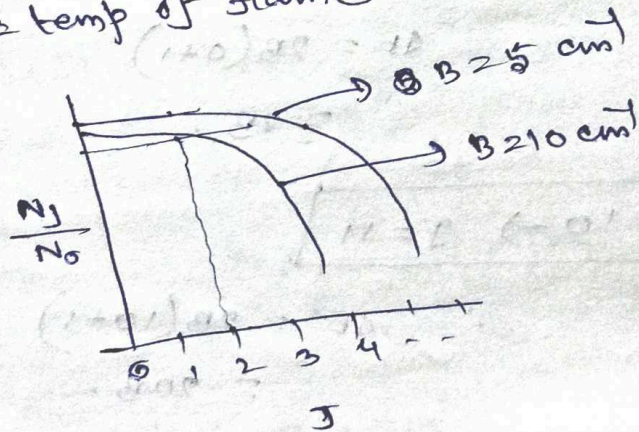
$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

$T = \text{temp of flame}$

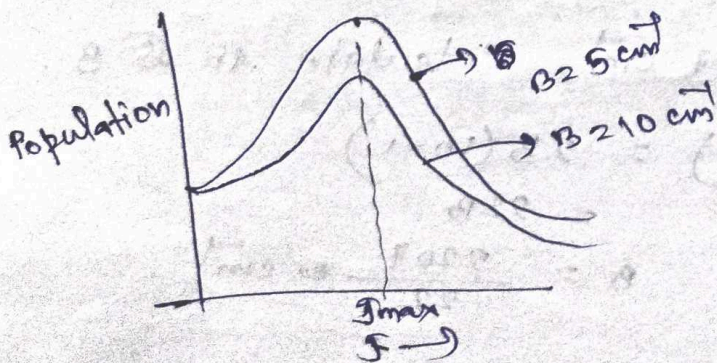
$$\frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-\frac{4B}{kT}}$$

$B \uparrow, 4B \uparrow,$

$\frac{N_J}{N_0} \rightarrow \downarrow$



$B = 10 \text{ cm}$
 $B = 5 \text{ cm}$



$$(2J+1) e^{-\frac{4B}{kT}}$$

Isotopic substitution

^{12}CO ^{13}CO

- i) electron distribution doesn't change
- ii) Internuclear distance does not change.

$\Rightarrow m \uparrow, I \uparrow$
 $B \downarrow$

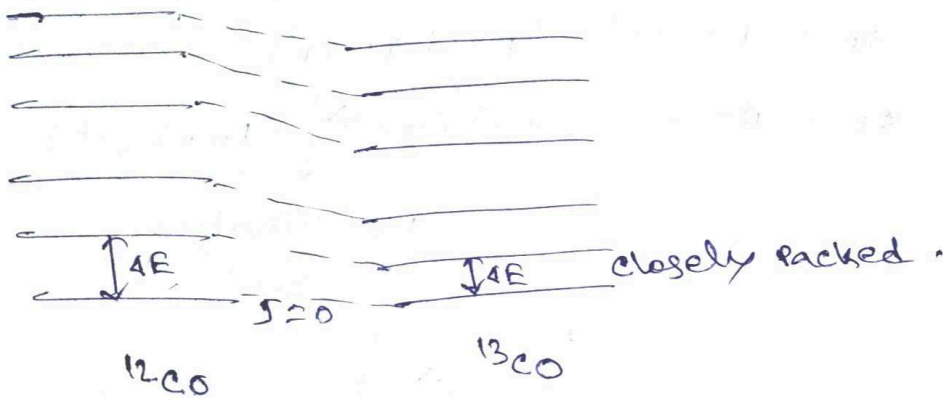
$$\Delta E = 2B J(J+1)$$

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

$$I \propto m$$

$$B = \frac{h}{8\pi^2 I c} \text{ cm}^{-1}$$

$$B \propto \frac{1}{I}$$



3.

^{12}CO

^{13}CO

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

$$B' = \frac{h}{8\pi^2 I_{13} c}$$

$$\therefore \frac{B}{B'} = \frac{h}{8\pi^2 I_c} \times \frac{8\pi^2 I_{13} c}{h}$$

$$\frac{B}{B'} = \frac{I_{13}}{I_c}$$

$$= \frac{B}{B'} = \frac{\mu_2}{\mu_1}$$

$$\Rightarrow \frac{B}{B'} = \frac{\mu_2}{\mu_1}$$

$$\therefore B > B'$$

With increasing I , B decreases
 so always $B > B'$



microwave inactive.

\Rightarrow $^{18}\text{O} = \text{C} = ^{16}\text{O}$ is it active or inactive

\Rightarrow inactive because for isotopic substitution no change in internuclear distribution so it is also inactive.

#

Non-rigid rotor

$$E = BJ(J+1) \quad (\text{rigid rotor})$$

$$E = BJ(J+1) - DJ^2(J+1)^2 \quad (\text{Nonrigid})$$

$D \rightarrow$ distortion constant.

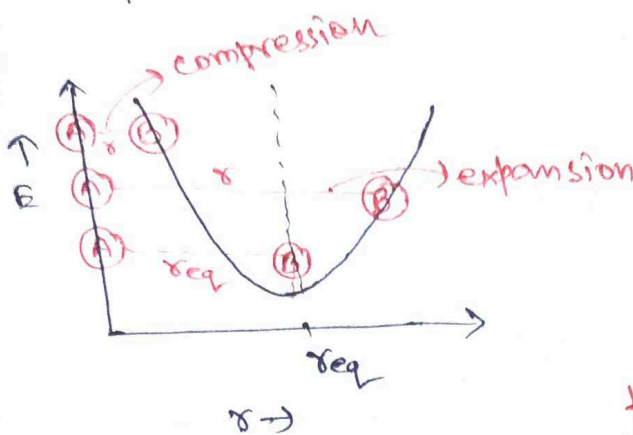
$$D = \frac{4B^3}{\omega^2}$$

$\omega \rightarrow$ vibrational frequency.

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

Vibrational Spectroscopy

→ dipole moment should change during vibration.



Hooke's law

restoring $\propto x$
 $\propto (r - r_{eq})$

~~F~~ $F = kx$

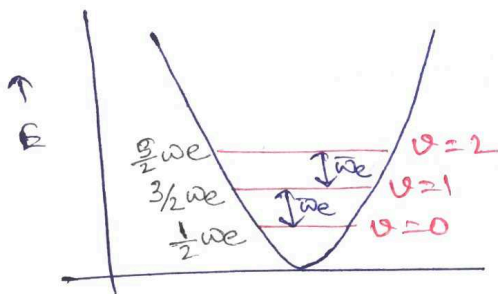
$\therefore F = -kx$
 $= -k(r - r_{eq})$

(-)ve sign indicate restoring force is always opposite direction of x .

$\therefore E = \frac{1}{2} kx^2$

$\therefore P.E = \frac{1}{2} k(r - r_{eq})^2$
 (v)

SHO



$E = (v + \frac{1}{2}) h \nu_e$
 $\nu = 0, 1, 2, \dots$
 $\nu \Rightarrow H_2 \equiv \delta^1$
 $\nu \Rightarrow J.S$

$\therefore E = J$

$\therefore \left(\frac{E}{hc} \right) = (v + \frac{1}{2}) \frac{h \nu_e}{hc} \frac{1}{cm^{-1}}$

$E' (cm^{-1}) = (v + \frac{1}{2}) \frac{\nu_e}{c} cm^{-1}$

$E' = (v + \frac{1}{2}) \bar{\omega}_e cm^{-1} \Rightarrow SHO.$

$\therefore v=0, E_0 = (0 + \frac{1}{2}) \bar{\omega}_e = \frac{1}{2} \bar{\omega}_e = E_0 \rightarrow$ zero point energy.
 $v=1, E_1 = \frac{3}{2} \bar{\omega}_e, E_2 = \frac{5}{2} \bar{\omega}_e$

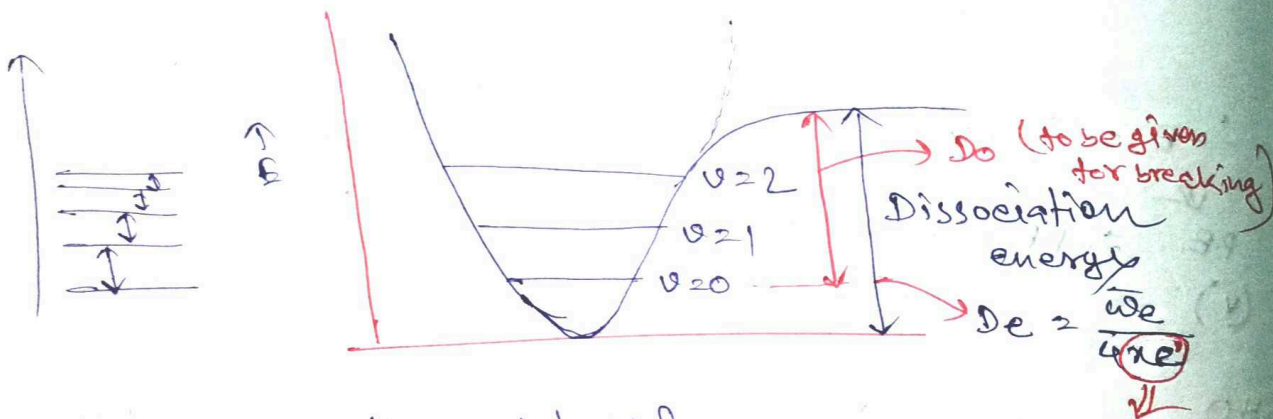
$$\begin{aligned} \Delta E &= E_1 - E_0 \\ &= \frac{3}{2} \bar{\omega}_e - \frac{1}{2} \bar{\omega}_e \\ &= \bar{\omega}_e \end{aligned}$$

$$\begin{aligned} \Delta E &= E_2 - E_1 \\ &= \frac{5}{2} \bar{\omega}_e - \frac{3}{2} \bar{\omega}_e = \bar{\omega}_e \end{aligned}$$

Selection rule

$$\Delta v = \pm 1$$

Anharmonic oscillator



Morse potential

Depth of Morse potential $\equiv D_e$

anharmonic-
needs
constant

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

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

if ξ_e not given then $\xi_e = 1$
or 0.01

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

$$\begin{aligned} \therefore \Delta E &= E_1 - E_0 \\ &= \frac{3}{2} \bar{\omega}_e - \frac{3}{4} \bar{\omega}_e x_e - \frac{1}{2} \bar{\omega}_e + \frac{1}{4} \bar{\omega}_e x_e \\ &= \bar{\omega}_e - 2 \bar{\omega}_e x_e \end{aligned}$$

$$\Delta E = \bar{\omega}_e (1 - 2x_e) \quad \rightarrow \text{transition from } v=0 \text{ to } v=1$$

fundamental vibration.

For SHO, selection rule $\Delta v = \pm 1$

For AHO, selection rule $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

Population is very low in higher energy level so intensity is very low.

① $v=0 \rightarrow v=1$ fundamental transition

$$(E_1 - E_0) \leftarrow \Delta E = \bar{\omega}_e (1 - 2x_e)$$

② $v=0 \rightarrow v=2$ first overtone.

intensity is less in comparison to fundamental transition.

$$\therefore \Delta E = E_2 - E_0$$

~~$$= (2 + \frac{1}{2}) \bar{\omega}_e$$~~

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

③ $v=0 \rightarrow v=3$ second overtone.

intensity very low.

$$\Delta E = E_3 - E_0$$

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

$(v=1 \rightarrow v=2) \rightarrow$ Hot band (temp involve)

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

$$\Delta E = \bar{\omega}_e (1 - 6x_e) \rightarrow \text{Hot band}$$

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

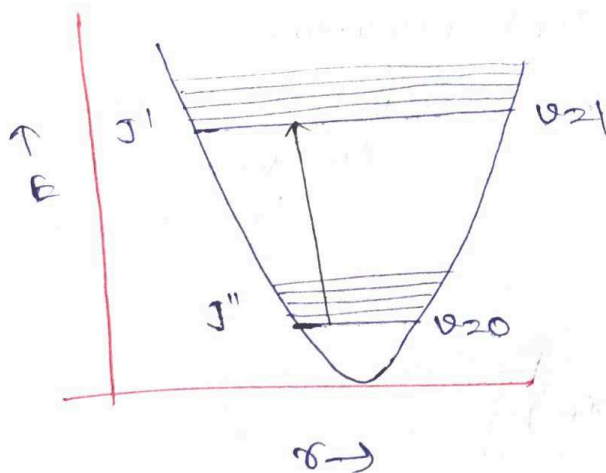
Hot band is nearly close to fundamental band

Vibrating Rotator

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

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

$D \approx 0.01 \gamma$ of B . ignore



vibration \rightarrow IR

rotation \rightarrow microwave

IR \supset microwave

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

$$\Delta J = \pm 1$$

when vibration occurs

rotation must sub

vice versa not always possible.

possible
 $\Delta v = 0 \rightarrow$ vib \times
 $\Delta J = \pm 1$ rot \checkmark

$\Delta v = \pm 1$
 $\Delta J = 0$
 not possible.

Diatomic Molecules

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

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

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

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

$$= \underbrace{\bar{\omega}_e}_{\frac{1}{2} \bar{\omega}_0} - 2x_e \bar{\omega}_e + B \left[J'(J'+1) - J''(J''+1) \right]$$

$$= \bar{\omega}_0 + B \left[J' + J' - J'' - J'' \right]$$

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

Case-I

$$\Delta J = +1$$

$$J' - J'' = +1$$

$$\therefore J' = J'' + 1$$

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

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

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

Case-II

$$\Delta J = -1$$

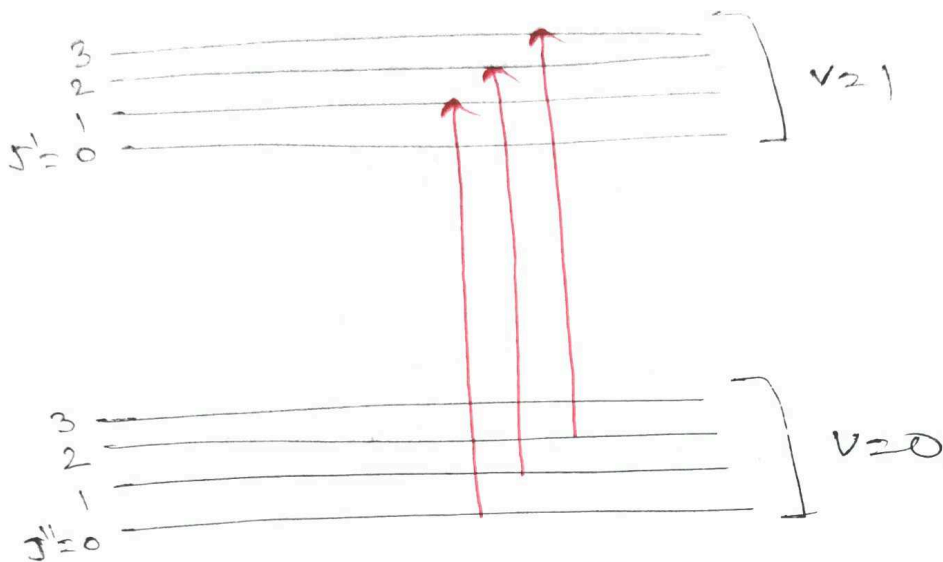
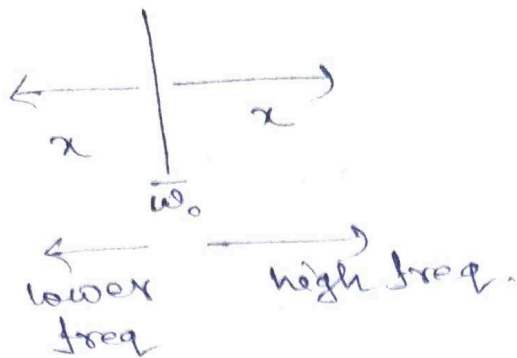
$$\Rightarrow J' - J'' = -1$$

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

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

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

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



$$4J = +1$$

$$J' - J'' = 1$$

$$1 - 0 = 1$$

$$\therefore 4E = \bar{\omega}_0 + 2B(0+1)$$

$$= \bar{\omega}_0 + 2B \quad (\text{when } J''=0)$$

$$4E = \bar{\omega}_0 + 2B(2)$$

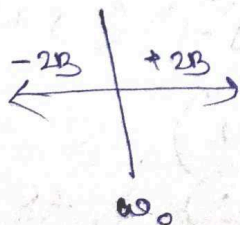
$$= \bar{\omega}_0 + 4B \quad (\text{when } J''=1)$$

$$4E = \bar{\omega}_0 + 6B \quad (\text{when } J''=2)$$

$$4E = \bar{\omega}_0 - 2B \quad \text{when } J'=0$$

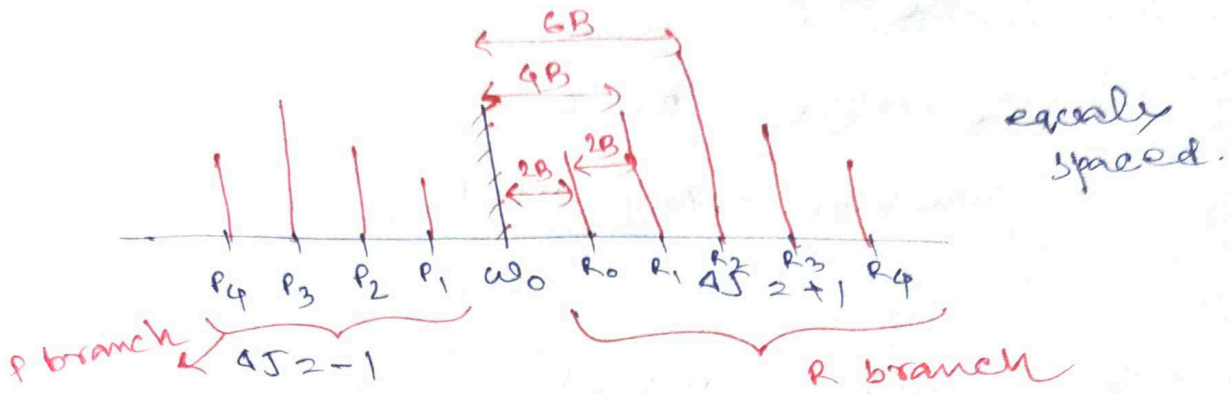
$$4E = \bar{\omega}_0 - 4B \quad J'=1$$

$$4E = \bar{\omega}_0 - 6B \quad J'=2$$



$$\Delta J = \quad -2 \quad -1 \quad \quad 0 \quad \quad 1 \quad 2$$

$$\text{Branch} = \quad 0 \quad \quad P \quad \quad Q \quad \quad R \quad S$$



no P_0 band because for this we need $J''=0 \rightarrow 0$
 $J''=0$ level where
 $J'=2-1$ level not possible.

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

$\Delta E = \bar{\omega}_0$ when $J''= -1$
 which is not possible of $J''= -1$ level.

so no peak in $\bar{\omega}_0$.

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

$$R_0 - P_1 = 4B$$

$$\bar{\omega}_0 \rightarrow \text{band centre}$$

- g.
 $P_1 = 2140.1 \text{ cm}^{-1}$
 $R_0 = 2143.2 \text{ cm}^{-1}$

$$\therefore R_0 - P_1 = 4B$$

$$\therefore B = \frac{R_0 - P_1}{4} = \frac{2143.2 - 2140.1}{4} \text{ cm}^{-1}$$

$$\bar{\omega}_0 \rightarrow ? \quad \frac{2140.1 + 2143.2}{2} = \bar{\omega}_0$$

linear diatomic molecule \rightarrow PR branch

8. fundamental $\rightarrow 2000 \text{ cm}^{-1}$
 First overtone 24100 cm^{-1}
 $x_e \rightarrow ?$

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

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

Polyatomic Molecule

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

Degree of freedom $\rightarrow 3N$, where $N \rightarrow$ total no of atoms.

\therefore For H_2O ,

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

(T+R+V) modes.

\hookrightarrow Translational

\hookrightarrow Rotational

\rightarrow Vibrational

	Linear (CO_2)	non linear (H_2O)
T \rightarrow	3	3
R \rightarrow	2	3
V \rightarrow	$3N - 5$	$3N - 6$

Vibration

\hookrightarrow Stretching $\begin{cases} \text{Asymmetric} \\ \text{Symmetric} \end{cases}$
 \rightarrow Bending

$\omega = \text{Assy} > \text{Sym} > \text{Bending}$

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

$$\text{Total atoms} = N$$

$$\therefore \text{Total number of stretching} = (N-1)$$

$$\text{vibration} = 3-1 = 2$$

$$\therefore \text{Total bending modes of vibration} =$$

$$\text{Total} = \text{str} + \text{bending}$$

$$(3N-6) = (N-1) + \text{bending}$$

$$\Rightarrow (3N-6) - (N-1) = \text{bending modes of vib}^n$$

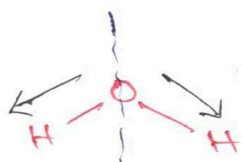
For H_2O molecule,

$$\text{Bending} \rightarrow (3 \times 3 - 6) - (3 - 1) = 3 - 2 = 1$$

For CO_2 molecule,

$$(3N-5) - (3-1) =$$

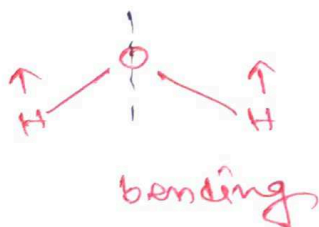
$$\text{Bending} = (3 \times 3 - 5) - (3 - 1) = 2$$



Symmetric
stretching
Parallel vib. (||)



Asymmetric
stretching,
Perpendicular vibⁿ (\perp)



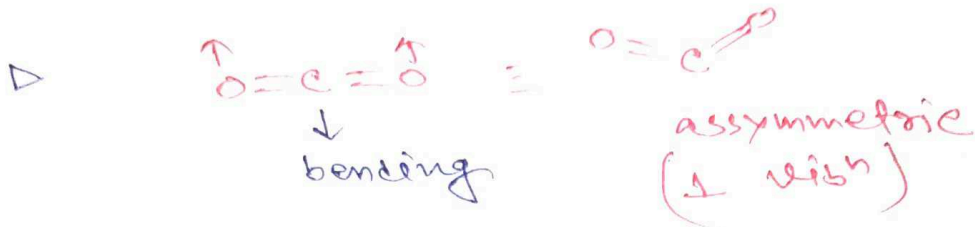
Parallel vib.

Parallel vibⁿ \rightarrow Sym to principal axis
Perpendicular vibⁿ \rightarrow Asym to principal axis



▷ $O=C=O \rightarrow Ca$
 (1) to principle axis

▷ $O=C=O \rightarrow Ca \rightarrow$ (1) to principle axis



(Linear polyatomic molecules)

e.g. CO_2

Parallel vib

$$\hookrightarrow \Delta J = \pm 1$$

$$\hookrightarrow \Delta J = \pm 1$$

Similar to diatomic molecules.

PR branch.

Perpendicular vib

$$\Delta J = \pm 1$$

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

$$\Delta J = 0 \rightarrow Q$$

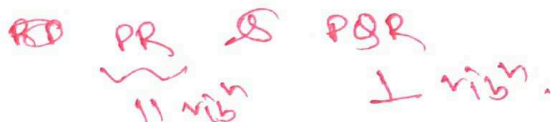
$$\Delta J = +1 \rightarrow R$$

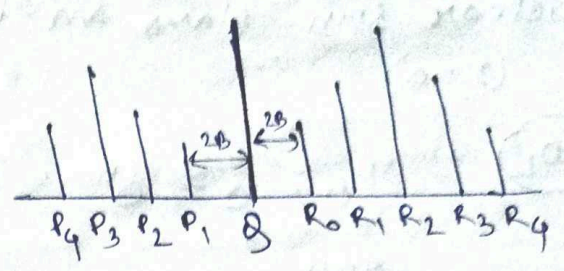
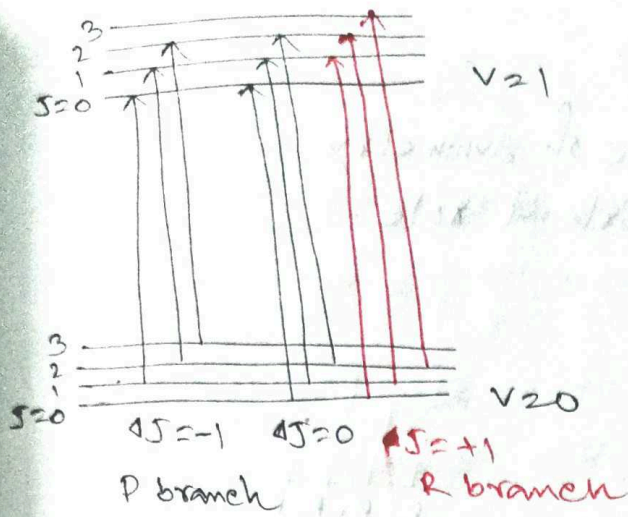
$$\Delta J = -1 \rightarrow P$$

PQR branch

Linear diatomic \rightarrow PR Branch

Linear polyatomic \rightarrow e.g. CO_2





$$\Delta E = E_J', v=1 - E_J'', v=0$$

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

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

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

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

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

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

ω_0 this peak is independent on J value so all peaks comes in one position so peak is very intense & sharp.

Diatomic

- ↳ always linear
- ⇒ PR branch

Polyatomic

- ↳ linear
 - e.g. CO2
 - PR (||) branch
 - PQR (⊥)
- ↳ non linear
 - e.g. H2O
 - PQR branch for both case.

Q. **AB₂**

890 (cm^{-1})
 972 (cm^{-1})

PR
 PQR

two bands present so diatomic not possible polyatomic molecule, linear polyatomic molecule

Rule of Nuclear Inclusion.

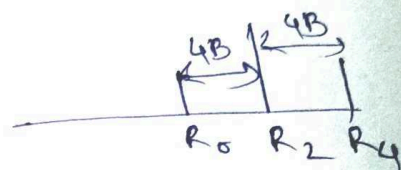
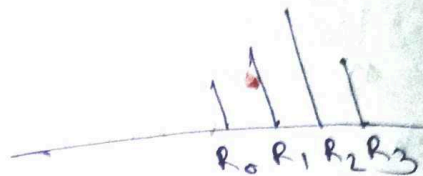
⇒ Molecule having centre of symmetry.
nuclear spin plays an important role.

($I=0$)

(CO_2)



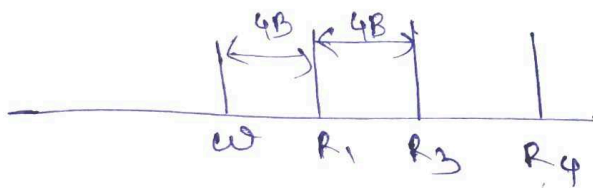
odd
(alternate lines missing)



(O_2)



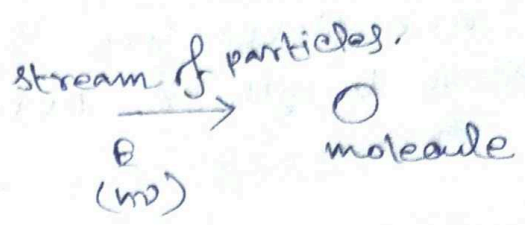
(even lines missing)



Raman Spectroscopy

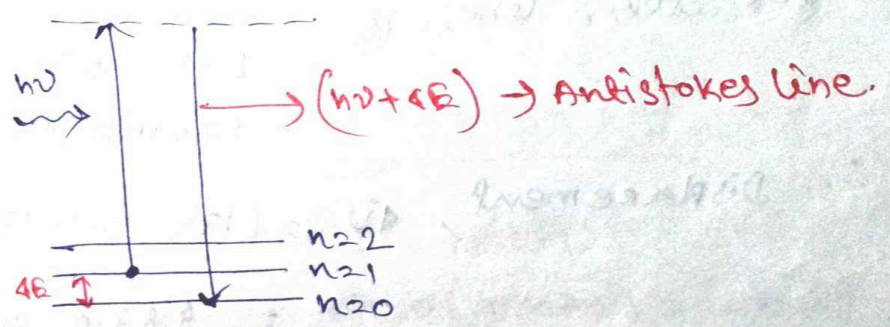
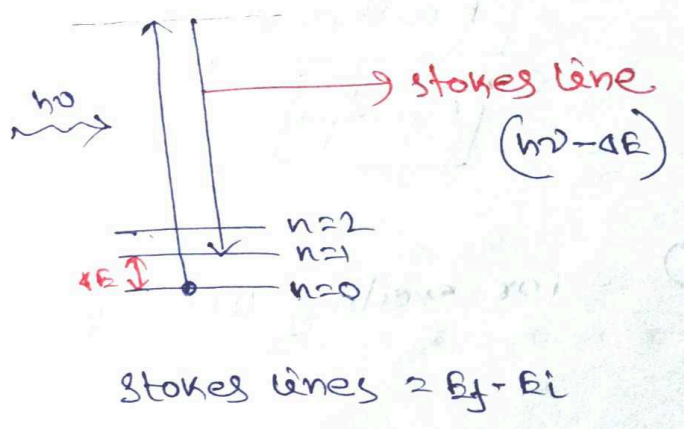
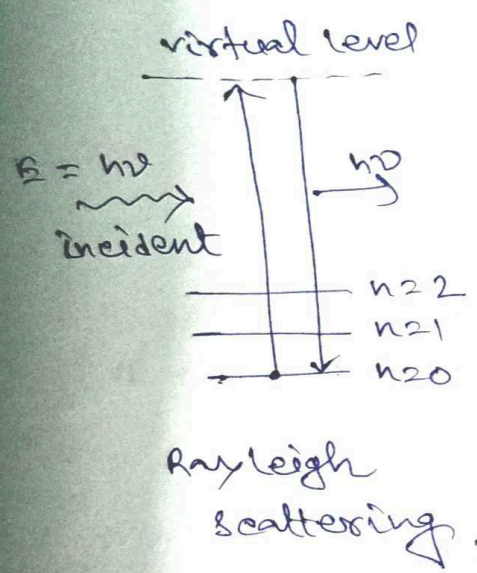
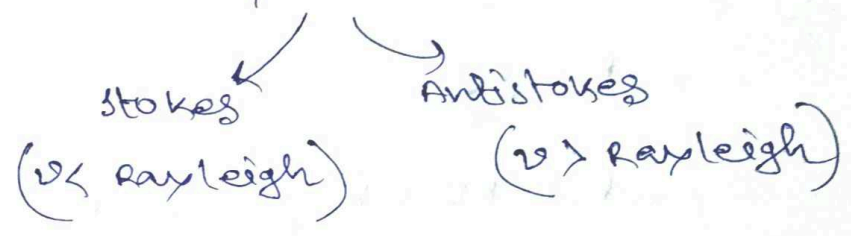
LASER

Scattering



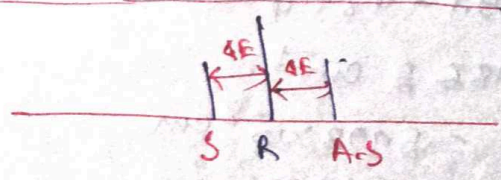
1) elastic collision (no change in energy)
i.e. Rayleigh scattering.

2) Inelastic collision
 \Rightarrow Raman scattering.



$\Delta E \rightarrow$ Raman shift (wave number displacement)

AntiStokes



Energy order

A-S $>$ R $>$ S.

order

S $>$ R $>$ A-S

Q.1. The exciting line in an exp is 5650 \AA and Stokes line is 5810 \AA . calculate wave length of Anti Stokes line.
(Ans $\rightarrow 5498.5 \text{ \AA}$)

Q.2. when a substance is irradiated with 4365 \AA lines, a Raman line attributed to the symmetrical stretching vibration is found to 4814 \AA . calculate the fundamental frequency for the vibration.
(Ans $\rightarrow 6.61 \times 10^{13} \text{ Hz}$)



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

$$E = h\nu = h \frac{c}{\lambda} = hc\bar{\nu}$$

$$\therefore E \propto \nu \propto \bar{\nu}$$

$$E \propto \frac{1}{\lambda}$$

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

① For exciting line, $\bar{\nu} = \frac{1}{5650 \times 10^{-8}}$
 $= 17699.1 \text{ cm}^{-1}$

for Stokes line, $\bar{\nu}_s = \frac{1}{5810 \times 10^{-8}}$
 $= 17211.7 \text{ cm}^{-1}$

\therefore Displacement, $4\bar{\nu} = (17699.1 - 17211.7)$
 $= 487.4 \text{ cm}^{-1}$

\therefore wave no. of anti Stokes line $= \bar{\nu} + 4\bar{\nu}$
 $= 17699.1 + 487.4$
 $= 18186.5 \text{ cm}^{-1}$

\therefore corresponding $\lambda = \frac{1}{18186.5} = 5498 \times 10^{-8} \text{ cm}$
 $= 5498.5 \text{ \AA}$

② exciting line $\bar{\nu} = \frac{1}{4365 \times 10^8} = 22909.5 \text{ cm}^{-1}$.

wave no. of Raman line = $\frac{1}{4814 \times 10^8}$

= 20772.7 cm^{-1} .

Displacement $\Delta \bar{\nu} = 22909.5 - 20772.7$

= 2136.8 cm^{-1} .

Corresponding freq = $2136.8 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm}^{-1} \text{ s}^{-1}$

= $6.41 \times 10^{13} \text{ s}^{-1}$

= $6.41 \times 10^{13} \text{ Hz}$.

Rotational Raman Spectroscopy

$E_J = BJ(J+1)$

$\Delta J = 0, \pm 2$

$\Delta J = 0 \Rightarrow$ Rayleigh line.

$\Delta E = E_{J+2} - E_J \rightarrow$ in general.

$E = BJ(J+1)$

$\therefore \Delta E = B(J+2)(J+2+1) - BJ(J+1)$

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

= $B[\cancel{J} + 3J + 2J + 6 - \cancel{J} - J]$

= $B[4J+6] = \underline{2B[2J+3]}$

$\therefore \Delta E (J \rightarrow J+2)$

$0 \rightarrow 2$

$\Delta E_{0 \rightarrow 2}$

= $B(4 \times 0 + 6) = 6B$.

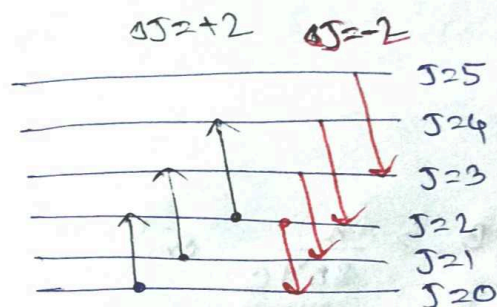
$\Delta J = +2$

$\Delta E_{1 \rightarrow 3}$

= $B(4 \times 1 + 6) = 10B$

$\Delta E_{2 \rightarrow 4}$

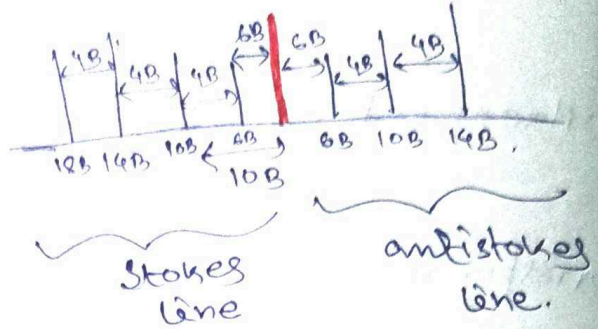
= $B(2 \times 4 + 6) = 14B$.



$$\Delta J = -2$$

$$\begin{aligned} \square \quad h\nu - \Delta E_0 &\rightarrow 2 \\ &= h\nu - 6B \end{aligned}$$

$$\begin{aligned} \square \quad h\nu - \Delta E_1 &\rightarrow 3 \\ &= h\nu - 10B \end{aligned}$$



Q. In the Raman spectra of a triatomic molecule, the first three lines are at 4.86 , 8.14 , 11.36 cm^{-1} . Determine the rotational constant B and moment of inertia.

$$B = 0.81 \text{ cm}^{-1}$$

$$I = 34.45 \times 10^{-40} \text{ gm cm}^2$$

$$B = \frac{h}{8\pi^2 I c} \text{ cm}^{-1}$$

$$h \rightarrow 3.5$$

$$4B = 8.14 - 4.86$$

$$\therefore B = 0.81 \text{ cm}^{-1}$$

$$\begin{aligned} I &= \frac{h}{8\pi^2 B c} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8 \times (3.14)^2 \times 0.81 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm}\cdot\text{s}^{-1}} \\ &= 34.45 \times 10^{-40} \text{ g}\cdot\text{cm}^2 \end{aligned}$$

$$3.5 \rightarrow$$

$$W = F \times d$$

$$W = m \times a \times d$$

$$\begin{aligned} \Rightarrow J &= \text{kg} \times \text{m}\cdot\text{s}^{-2} \times \text{m} \\ &= \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2} \end{aligned}$$

$$\begin{aligned} \therefore J \cdot \text{s} &\Rightarrow \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2} \cdot \text{s} \Rightarrow \text{kg}\cdot\text{m}^2 = 1000 \text{ g} \times (100 \text{ cm})^2 \\ &= 10^7 \text{ g}\cdot\text{cm}^2 \end{aligned}$$

$$\begin{aligned} J \cdot \text{s} &\times 10^7 \\ &\rightarrow \text{g}\cdot\text{cm}^2 \\ &= \text{kg}\cdot\text{m}^2 \end{aligned}$$

Q. Bond length of H_2 molecule is 0.7417 \AA .
 Determine the position of first three Raman lines.
 given mass of $H = 1.67 \times 10^{-24} \text{ g}$.

$$I \propto r_0^2$$

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

$$r_0 = 0.7417 \text{ \AA}, \quad m = 1.67 \times 10^{-24} \text{ g}$$

$$r_{H_2} = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.67 \times 10^{-24} \text{ g})^2}{1.67 \times 10^{-24} \text{ g} + 1.67 \times 10^{-24} \text{ g}}$$

$$= 0.8365 \times 10^{-24} \text{ g}$$

$$B = \frac{h}{8\pi^2 r_{H_2}^2 c} = \frac{6.626 \times 10^{-34} \text{ J.s}}{8 \times (3.14)^2 \times 0.8365 \times 10^{-24} \text{ g} \times (0.7417 \times 10^{-8} \text{ cm})^2}$$

$$\times 3 \times 10^{10} \text{ cm.s}^{-1}$$

$$= 60.73 \text{ cm}^{-1}$$

First three lines at $6B \rightarrow 364.4 \text{ cm}^{-1}$
 $10B \rightarrow 607.3 \text{ cm}^{-1}$
 $14B \rightarrow 850.2 \text{ cm}^{-1}$

Vibrational Raman Spectroscopy

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

$$\Delta v = 0, \pm 1, \pm 2, \dots$$

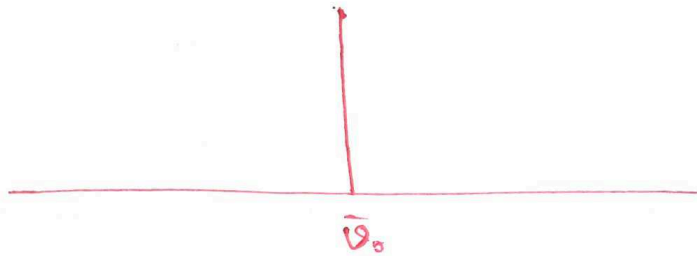
$$\Delta B = B(4J+6)$$

$$v \geq 0 \rightarrow v \geq 1$$

fundamental

$$\Delta B_{v=0 \rightarrow 1} = \bar{\omega}_e (1 - 2x_e)$$

$$\begin{aligned} \therefore \Delta E &= E_1 - E_0 \\ &= \omega_e (1 - 2x_e) \end{aligned}$$



A.S

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

↓ ↓
final initial

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

$$\bar{\nu} = \bar{\nu}_0 \rightarrow \text{R.S.}$$

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

Rule of Mutual Exclusion Principle :-

□ For molecules containing centre of symmetry

IR active mode will be Raman inactive

and

IR inactive mode will be Raman active

Structure Determination

①

Modes of vibr	Raman	IR
* Sym. stretching	Active	Inactive
* Sym. bending	Inactive	Active
* Asy. stretching	Inactive	Active.

CO₂

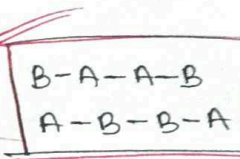
②

Modes	Raman	IR
* Sym. stretch	A	A
* Bending	A	A
* Asy stretch	A	A

H₂O

③

A ₂ B ₂	Raman	IR
* 2374 cm ⁻¹	strong	-
* 2287	-	very strong PR (II) ΔS = ±1
* 1973	very strong	-
* 729	-	very strong PGR (±) ΔS = 0, ±1
* 612	weak	-



centre of symmetry
 PR, PGR present.
 so linear molecule

④

AB ₂	IR	Raman
* 2756	very strong	-
* 3052	strong parallel	strong polarised
* 1595	very strong	-

Non-linear
 no PR absent.
 no PGR absent

