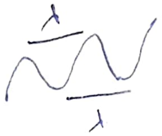
Molecular Spectroscopy

spectrum. → array of waves arrayed in order of wave length and frequency.



wave length → 1 A° = 10^{-8} cm
= 10^{-10} m.

frequency no. of waves that passes thro' point in one sec. denoted by ν expressed in hertz, MHz, KHz etc.

mol. sp
interaction of E. mag. radⁿ with matter.

at. sp.	mol. sp.
1) arise due to energy change ~~from~~ → transition of e^- b/w one energy level to another in an atom.	arise due transition b/w rot. levels (or) vib levels (or) in addition to electronic transition.
2) at. sp are simple and gives sharp lines	mol. sp are complicated. & broad bands are obtained.
3)	

Uses → helps to give informⁿ about
1) Size, shape of molecules, bond lengths, strength of bonds,
2) determⁿ of str. of cpds.

Classification
1) Rotational.
2) Vib. rot.
3) electronic sp.

Let us see **Rotational sp**

↓

arises due to change of energy in rotational

$$\bar{\nu}_{rot} = \frac{\Delta E_J}{hc} = \frac{h^2}{8\pi^2 I hc}\left[J''(J''+1) - J'(J'+1)\right] \quad ⑤$$

$$= \frac{h}{8\pi^2 I c}\left[J''(J''+1) - J'(J'+1)\right]$$

$$\bar{\nu}_{rot} = B\left[J''(J''+1) - J'(J'+1)\right]$$

B = rotational constant

$= h/8\pi^2 I c$

iv) Selection rule for Rotational spl.

i) change in dipole moment.

(ii) Q.M. permits rot. transition to adjacent rot. levels (ie) either increase (or) ↓ by one unit. in Rot. Q. NO (J)

$J'' - J' =$ (ie) $\Delta J = \pm 1$

Thus acco. to. S. Rule

$J = 0 \rightarrow 2$

$= 1 \rightarrow 3$

$2 \rightarrow 0$ etc are not Possible ∵ $\Delta J \neq \pm 1$

(V) Rotational spectrum

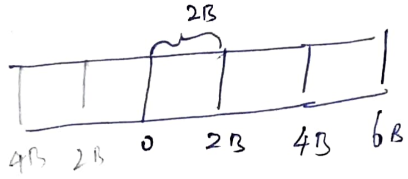
It consists of equidistant sp lines.

We know that $\bar{\nu}_{rot} = B\left[J''(J''+1) - J'(J'+1)\right]$

When $J' = 0$, $J'' = 1$ $\bar{\nu}_{rot} = 2B \text{ cm}^{-1}$

$J' = 1$, $J'' = 2$ then $\bar{\nu}_{rot} = 4B \text{ cm}^{-1}$

$J' = 2$, $J'' = 3$ then $\bar{\nu}_{rot} = 6B \text{ cm}^{-1}$ and so on



rot. sp consist of series of sp. line with fre. Sepn of $2B \text{ cm}^{-1}$

∴ A general eqn $\bar{\nu}_{rot} = 2(J+1)B \text{ cm}^{-1}$

$(J \rightarrow J+1)$ $J = 0, 1, 2, 3 \ldots$

$\Delta\bar{\nu} = 2B$.

[illegible] for a rigid rotator is given

$$E_{rot} = \frac{1}{2} m_1 . v_1^2 + \frac{1}{2} m_2 . v_2^2$$

v_1, v_2 - linear V of masses m_1 & m_2

r_1, r_2 = d/s fro C.G

The above eqn can be written in terms of angular velocity i.e

$$\omega = \frac{v}{r}$$

$$\therefore \quad E_{rot} = \frac{1}{2} m_1 (\omega . r_1)^2 + \frac{1}{2} m_2 (\omega . r_2)^2$$

$$= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2)$$

$$= \frac{1}{2} I \omega^2$$

Since the molecule is rigid rotator, its P.E = 0

the rotational energy values are obtd by solving Schrodinger equation

$$\nabla^2 \psi + \frac{8\pi^2 I E_{rot}}{h^2} \psi = 0$$

When this eqn is solved for E_{rot} or E_J

we get $\quad E_J = \frac{h^2}{8\pi^2 I} [J(J+1)]$ ergs

J = Rot. Q.No. can takes values 0, 1, 2, 3 ...

(III) Frequency of sp. lines

When Transition from lower rotational level → higher rot.l

$J' \rightarrow J''$

The diff in rot. E is given by

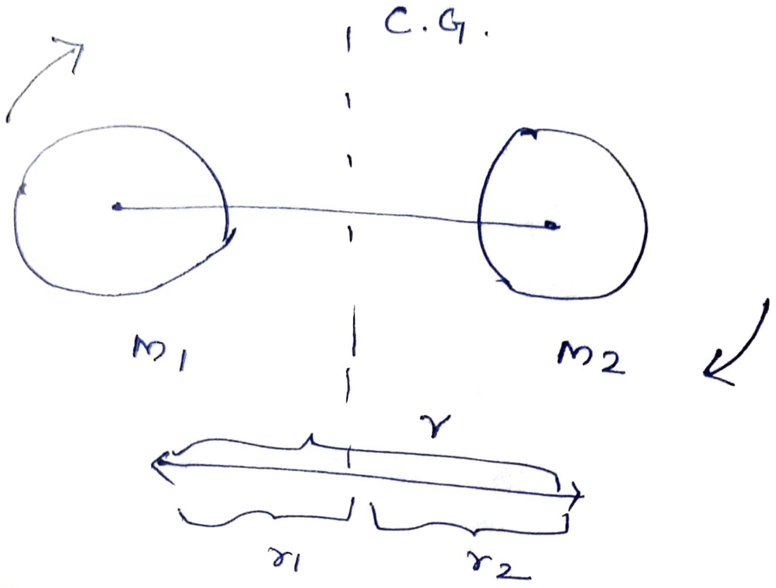
$$\Delta E_J = E_{J''} - E_{J'} = \frac{h^2}{8\pi^2 I^2} [J''(J''+1) - J'(J'+1)]$$

During low → high energy absorbed

high → low " evolved - This appears as

sp. lines. The fre. of sp lines is given ~~in~~ in terms of wave no. $\bar{\nu}_{rot}$ or $\bar{\nu}_J$

Q. Consider a diatomic molecule ③
about its axis thro' its centre of gravity



Moment of Interia.

$$I = m_1 r_1^2 + m_2 r_2^2 \quad —①.$$

System balanced about C.G ∴

$$m_1 r_1 = m_2 r_2 \quad —② \qquad (r = r_1 + r_2) \quad —③$$

$$= m_2 (r - r_1)$$

On solving eqns ② & ③ we get

$$r_1 = \frac{m_2 r}{m_1 + m_2} \; ; \quad r_2 = \frac{m_1 r}{m_1 + m_2} \quad —④$$

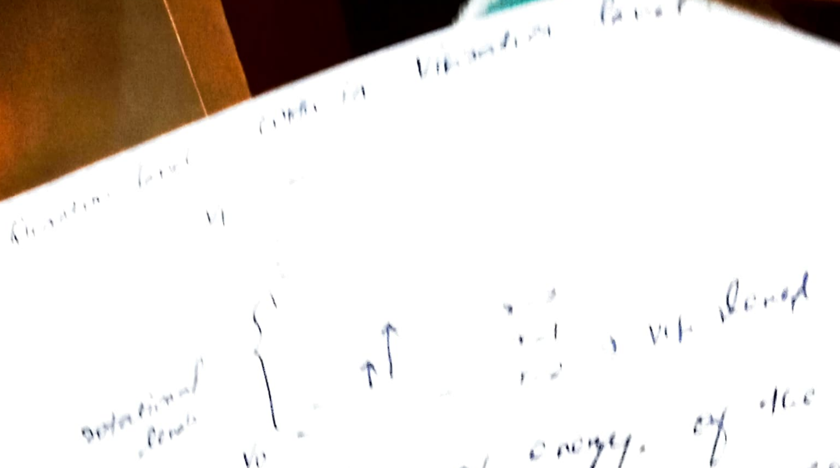
Substitute ④ in ① we get

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

$$I = \frac{m_1 m_2 (m_1 + m_2) r^2}{(m_1 + m_2)^2} = \frac{m_1 m_2}{(m_1 + m_2)} r^2 = \mu r^2 \rightarrow ⑤$$

$$\mu = \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$

$\boxed{I = \mu r^2}$ this eqn defines m. Interia in tems of masses and bond length.



It involves small change of energy of the order of 0.005 eV. The frequency of rot sp line is given by $h\nu = \Delta E$

$$\therefore \nu = \frac{\Delta E}{h} = \frac{0.005 \times 1.6 \times 10^{-12}\ \text{ergs}}{6.6 \times 10^{-27}}$$

$$\lambda = c/\nu = \frac{3 \times 10^{10} \times 6.6 \times 10^{-27}}{0.05 \times 1.6 \times 10^{-12}}$$

$$= 25 \times 10^{5}\ \text{Å}$$

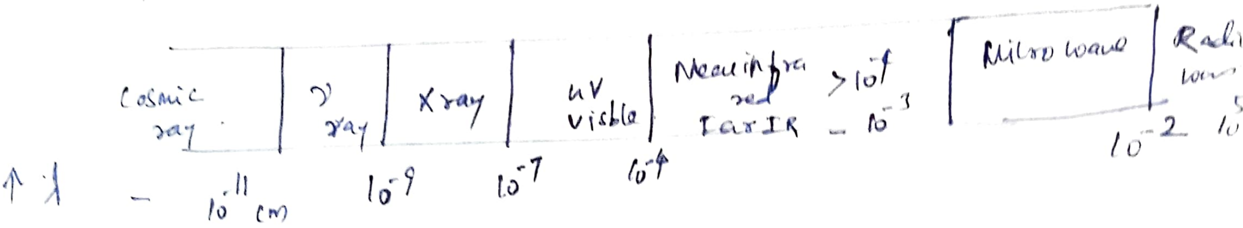
$$= 25 \times 10^{5} \times 10^{-8}\ \text{cm}$$

$$= 250 \times 10^{-4}\ \text{cm} \qquad \boxed{10^{-4}\ \text{cm} = 1\ \text{m}\mu}$$

$$\lambda = 250\ \text{m}\mu$$

Thus rot^n sp appears in far infrared or Microwave region. ($10^{4}\mu - 10^{2}\mu$).

Hence it is otherwise known as Microwave sp. or far infrared sp/.



R. sp/. caused by rotation of the molecule. Molecules having permanent dipole → rot. sp.

∴ ① condition. molecule possess change in dipole moment.

∴ ⑪ Molecules must be polar → rot. sp (HCl, CO) ∴ Micro wave active. Where as N_2, Cl_2 N_2, M. inactive ∵ $\mu = 0$

rot. sp. lines.

it is governed by population of various levels. intensity varies with population. ⑩ The intensity first ↑ reach Max. and then ↓. The position of most intense sp line is given by eqn.

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

k = Boltzmann. c , T = Temp $B = \frac{h}{8\pi^2 I c}$

C = velocity of light h = planks. c I = m. of Intertia.

vii) **Isotopic effect ~~of~~ on Rot. Spectra:**

If diatomic molecule has diff. ~~atoms~~ isotopes of the same element such as HCl, DCl they show. diff. rot. spectra. This is because masses of the isotopic atoms are different & hence the reduced mass, m. of Intertia, frequency of rotn. would be different. &

$$B \propto 1/\mu.$$

The sp. of heavier species will show smaller B value. hence small sepn b/w sp lines

~~It~~ Use : This fact used for evaluation of Precise atomic weights. of atoms

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Vibrational spectroscopy

The sepⁿ of vib. energy levels is greater as compared to rotational levels. This transition b/w vib. levels involves energies of the order of 0.1 eV.

$$\lambda = \frac{c}{\nu} = \frac{c \times h}{\Delta E} = \frac{3\times10^{10} \times 6.6\times10^{-27}}{0.1\times1.6\times10^{-12}\ \text{ergs}}$$

$$= 1.25000\times10^{0}$$

$$= 1.25000\times10^{-8} = 12.5\times10^{-4}\ \text{cm.}$$

$$\downarrow \mu$$

$$= 12.5\,\mu.$$

Vib. spectra would therefore appear in mid infrared region $(10^{2}\mu - 1\mu)$. Vib. ~~[illegible]~~ change accompanies rotational changes and therefore

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

Hence infrared spectroscopy is called Vib. rotational spectroscopy.

Vib. sp/. shown by molecules with permanent dipole mo

O_2, N_2, Cl_2 → Zero dipole moment → donot show Vib. rot. spectra.

In polyatomic molecules E. mag. radⁿ induces dipole moment and give vib. rot. transitions.

Uses: It is highly useful in the determⁿ of mol. str.

<u>Theory of Vib. Rotⁿ. Sp/.</u> Diatomic molecule may rotate and vibrate simultaneously. so the total energy is partially rotⁿ and partly vibration.

$$E_{vib\text{-}rot} = E_{vib} + E_{rot}.$$

We will first consider sp. arising due to vib. changes (Pure vib. sp) and then vib. changes on which rot. changes are super imposed.

Diatomic molecules

Harmonic ↙ Oscillator ↘ Anharmonic Oscillator

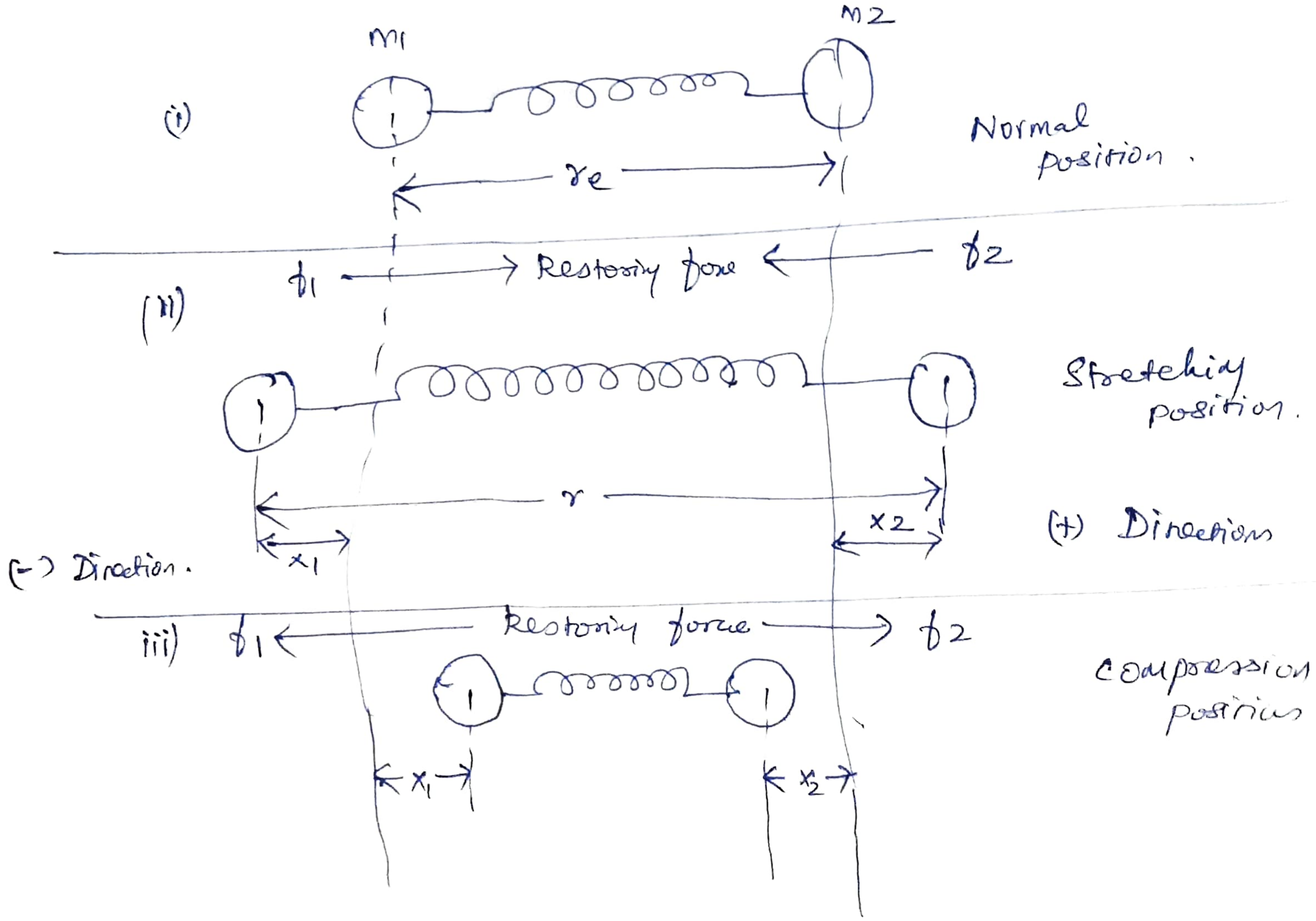
scillator model.

In this Model, the diatomic molecule consist of 2 atoms connected by a spring capable of executing vibrations ∥r to vib of a linear harmonic Oscillator. about their positions.

Let m_1, m_2 be the masses of two atoms A & B. Both oscillate against one another harmonically.

(i) Hook's law is obeyed during oscillation. in other words the force tending to restore an atom to its original State is the force ∝ to displacement of vib. atom from original position.

Let r_e = eq. at. d/s (Bond length)
r = New Bond length when the molecule is stretched.
$x = r - r_e$ ——— ①



atoms shift (displace) by $-x_1$ & $+x_2$ in ③ two directions.

$$x = -x_1 + (+x_2)$$

$$= -x_1 + x_2 \quad \text{———} \ ②$$

By Hook's law

Restoring force ∝ displacement

$f = -kx$ where x = displacement of each atom

restoring force on each atom of diatomic molecule would be

$f_1 = -k_1 x_1$ and $f_2 = -k x_2$.

Where k = force constant of the spring (bond)

The net restoring force on the whole molecule would be algebraic sum of f_1 & f_2 Hence

$$f = f_2 + (-f_1)$$

$$= f_2 - f_1$$

$$f = (-kx_2) - (-kx_1)$$

$$f = -k(x_2 - x_1) \quad \text{———} \ ③$$

From equations ② & ③ we get

$$f = -kx \quad \text{—} \ ④$$

The acceleration of the two particles are respectively

$$-\frac{d^2 x_1}{dt^2} \quad \text{and} \quad +\frac{d^2 x_2}{dt^2}$$

Now force = Mass × acceleration.

$$\therefore \ -k(x_2 - x_1) = m_1\left(\frac{-d^2 x_1}{dt^2}\right)$$

$$= -m_1\left(\frac{d^2 x_1}{dt^2}\right) \quad \text{—} \ ⑤$$

$$-k(x_2 - x_1) = m_2\left(\frac{d^2 x_2}{dt^2}\right)$$

$$= m_2 \left(d^2 x_2 \right) \quad \text{—} \ ⑥$$

~~displacement of~~ both atoms are harmonic &

equations for displacement of both the atoms are

$$x_1 = A_1 \sin 2\pi\nu_0 t \quad \text{—} ⑦$$

$$x_2 = A_2 \sin 2\pi \nu_0 t \quad \text{—} ⑧$$

A_1, A_2 = Amplitudes of vib. of both atoms.

ν_0 = fundamental frequency of vib.

Double diff eqns ⑦ & ⑧ w.r.t t we get

$$\frac{d^2x_1}{dt^2} = -4\pi^2\nu_0^2 A_1 \sin 2\pi\nu_0 t \quad \text{—} ⑨$$

$$\frac{d^2x_2}{dt^2} = -4\pi^2\nu_0^2 A_2 \sin 2\pi\nu_0 t \quad \text{—} ⑩$$

From ⑤, ⑦ and ⑨ we get

$$-k \cdot \sin 2\pi\nu_0 t\,(A_2 - A_1) = -m_1(-4\pi^2\nu_0^2 A_1 \sin 2\pi\nu_0 t)$$

$$-k(A_1 - A_2) = m_1 4\pi^2\nu_0^2 A_1 \quad \text{—} ⑪$$

Illy from ⑥, ⑧ and ⑩

$$-k(A_2 - A_1) = 4\pi^2\nu_0^2 A_2 m_2 \quad \text{—} ⑫$$

Simplifying eqns ⑪ & ⑫

$$kA_2 = -A_1(4\pi^2\nu_0^2 m_1 - k) \quad \text{—} ⑬$$

$$kA_1 = -A_2(4\pi^2\nu_0^2 m_2 - k) \quad \text{—} ⑭$$

Multiply eqns ⑬ and ⑭ and Cancelling $A_1 A_2$

$$k^2 = (4\pi^2\nu_0^2 m_1 - k)(4\pi^2\nu_0^2 m_2 - k) \quad \text{—} ⑮$$

$$4\pi^2\nu_0^2\left[4\pi^2\nu_0^2 m_1 m_2 - k(m_1+m_2)\right] = 0$$

$$4\pi^2\nu_0^2 m_1 m_2 - k(m_1+m_2) = 0.$$

$$4\pi^2\nu_0^2 m_1 m_2 = k(m_1+m_2)$$

$$4\pi^2\nu_0^2 = k\left(\frac{m_1+m_2}{m_1 m_2}\right)$$

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

$$4\pi^2\nu_0^2 = k$$

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{— (16)}$$

The restoring force is related to the P.E (V)

$$f = -\frac{dV}{dx} \quad \text{(or)} \quad V = \frac{1}{2}kx^2$$

Vib energy may be determined by schrodinger wave eqn (one direction)

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left[E_{vib} - P.E\right]\psi = 0$$

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left[E_{vib} - \frac{1}{2}kx^2\right]\psi = 0.$$

The solutions of the above equation

$$\boxed{E_{vib} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right) \text{ergs}} \quad \text{— (17)}$$

Combining equations (16) & (17)

$$\boxed{E_{vib} = h\nu_0\left(v+\frac{1}{2}\right) \text{ergs}} \quad \text{— (18)}$$

v = Vib. Q. No and it takes the value = 0, 1, 2, 3 . . . .

When $v = 0$ from eqn (18)

$$E_0 = h\nu_0\left(0+\frac{1}{2}\right)$$

$$\boxed{E_0 = \frac{1}{2}h\nu_0 \text{ ergs}} \quad \text{— (19)}$$

This is known as Zero point Energy. ie energy of lowest Vib. level. (ie) the molecules never have zero Vib. energy (or) Vib. motion still persists.

Vib. transition from $v' \rightarrow v''$ energy change.

$$\Delta E = E''_{vib} - E'_{vib} = \left(v''+\frac{1}{2}\right)h\nu_0 - \left(v'+\frac{1}{2}\right)h\nu_0$$

$$\Delta E = (v'' - v)h\nu_0$$

ction rule is for vib. transition $\Delta V = \pm 1$

$V'' - V = 1$ hence under this condition eqn ⑳ becomes

$$\Delta E = h\nu_0 \quad — ㉑$$

Let the frequency of vib. transition be ν then.

$$\Delta E = h\nu \quad — ㉒$$

from ㉑ & ㉒

$$\boxed{\nu = \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}} \rightarrow$$ frequency of absorbed or emitted rad" during vib. transition.

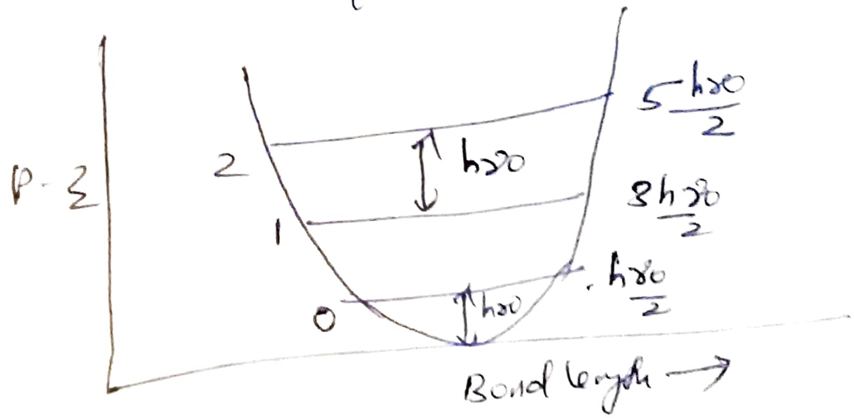
when $V = 0$ $\quad E_{vib} = \frac{h}{2}\nu_0$

$V = 1$ $\quad = \frac{3}{2} h\nu_0$

$V = 2$ $\quad = \frac{5}{2} h\nu_0$

$V = 3$ $\quad = \frac{7}{2} h\nu_0$ & so on.

the spacing b/w the adjacent vib levels is always equal to $h\nu_0$ ie vib. levels of simple harmonic oscillator are equidistant



Raman Spectroscopy

In 1928 Sir C.V. Raman discovered that when a beam of monochromatic light was allowed to pass thro' some org. substances such as benzene, toluene etc., the scattered light continued some additional frequencies over and above that of incident frequency. This is known as Raman effect.

The lines whose wave lengths have been modified in Raman effect are called Raman lines. The lines having wave length ↑ than that of the incident light are called stokes' lins

$$\Delta\nu_R = \nu_i - \nu_s$$ = Positive — Stokes lins

and those having shorter wave length are called antistokes lins

$$\nu_R = \nu_i - \nu_s$$ = negative — Antistokes lines

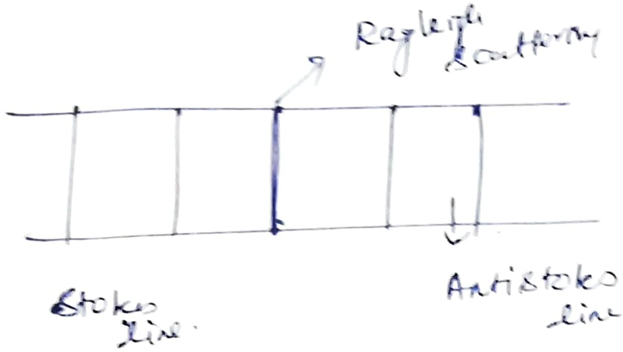
※ Raman effect depends upon characteristic of the substance causing Raman effect and not on the frequency of the incident light

Characteristics of Raman lines

i) Intensity of stoke's lines always greater than the corresponding antistoke's lines. with rise of temp, intensity of anti stoke's lines ↑

ii) Raman shift generally lies in the range of $100 - 3000\ cm^{-1}$ which lies in far and near infrared region of the spectrum

iii) Raman lines are symmetrically displaced about the parent line When the temp, the separation from parent line ↓



The intensity of antistoks lines falls off much rapidly with the ↑ in separation from the parent line

iv) The frequency diff between the modified and parent line represents the frequency of the absorption band of the material.

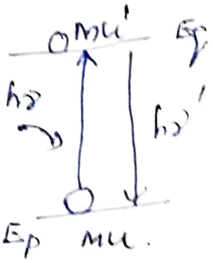
	Raman Spectrum	Infrared Spectrum
1)	It is obtained by studying the light scattered by the vib. molecules.	It is obtained by studying the light absorbed by the vib. molecule.
2	It arises due to a change in polarizability of the vibrating molecules	It arises due to change in dipole moment of the vibrating molecule
③	Concentrated ~~lines~~ solutions are usually preferred	Dilute solution are preferred

water can be used as solvent because it is studied in visible region	Water can't be used as solvent because water is opaque to IR
⑤ Raman spectra are accurate but not sensitive	~~IR~~ IR spectra is accurate as well as sensitive.
⑥ optical systems are made of glass (or) quartz	optical systems are made up of special crystals such as CaF_2, NaBr.

Mechanism of Raman effect: Quantum approach:

Raman effect cannot be explained on the basis of classical electromag. theory. So it is essential to apply the quantum principles for the proper explanation.

Raman effect may be regared as the outcome of the collision between the light photons and the molecules of the substance.



Suppose molecule of mass m in the energy state E_p (sum of electronic, vib, rot. energy) is moving with a velocity u and is colliding with a light of photon. hν. Suppose the molecule undergoes a change in its energy state as well as in its velocity. Let the new energy state be E_q and the velocity be u' after suffering a collision. If we apply principle of conservation of energy then.

~~$E_p + h\nu = E_q + h\nu'$~~

④

$$E_p + \tfrac{1}{2}mv^2) + h\nu = E_q + \tfrac{1}{2}mv'^2 + h\nu' \quad \text{—} ①$$

The change in velocity of the molecule is practically ~~negligible~~ negligible then.

$$E_p + h\nu = E_q + h\nu' \quad \text{—} ②.$$

(or)

$$\nu' = \nu + \frac{E_p - E_q}{h}$$

$$\nu' = \nu + \Delta\nu \quad \text{—} ③ \quad \left(\frac{E_p - E_q}{h} = \Delta\nu \right)$$

There are three cases for eqn ③

Case 1) $E_p = 1$ then the frequency shift $\Delta\nu$ (ie $\frac{E_p - E_q}{h} = 0$) hence $\nu' = \nu$ and this refers to the unmodified line. (ie) the molecules simply deflects the Photon without receiving any energy from it. this Collision being elastic and analogous to Rayleigh scattering.

Case: 2) If $E_p > E_q$ then $\nu' > \nu$ which refers to Stokes Lines. . it means that the molecule is Previously in the excited state and it handed over some of its energy to the incident photon. Thus scattered Photon has greater enenergy.

Case: 3) If $E_p < E_q$ then $\nu' < \nu$ which corresponds to the antistokes lines. The molecule has absorbed some energy from the incident photon and Consequently the scattered photon will possess lower energy.

As the change in the energy of the molecule is governed by quantum rules, we can write

$$E_p - E_q = + nh\nu \quad \text{—} ④$$

where n = 1, 2, 3 etc. and ν_e the characteristic frequency of the molecule. In the simplest case when n = 1 eqn ④ becomes

$$\nu' = \nu \pm \nu_e \quad -⑤$$

$E_p - E_f = h(\nu' - \nu)$

$h(\nu' - \nu) = \pm h\nu_e$

$\nu' = \nu \pm \nu_e$

from the eqn ⑤ we can say that the frequency diff. $(\nu - \nu')$ between the incident and scattered light in Raman effect corresponds to the characteristic frequency (ν_e) of the molecule.

Intensity of spectral lines

Acco. to Boltzman's law, No. of molecules (N_p) having particular energy state E_p is given by

$$N_p = C N g_p e^{-E_p/kT}$$

C = Constant
N = total no. of molecule
g_p = Statistical weight of the state
k = Boltzmann's constant
T = absolute temp

At room temp, the energy E_p of a molecule will be small & therefore the $e^{-E_p/kT}$ will be high. Hence the no. of molecules possessing this low energy E_p will be high. As a consequence of this, stoke's transition will occur more frequently than anti stoke's. Hence Stokes' lines are more intense than the anti Stoke's lines.

As the temp, is raised, the K.E of the molecules ↑ and more molecules are raised to the higher energy state. As a result the antistokes lines will gradually grow in their intensities and become more prominent.

Rotational Raman Spectra.

The selection rule for rotational Raman spectra is $\Delta J = 0, \pm 2$ where in IR $\Delta J = \pm 1$.

When $\Delta J = 0$ - Raman rad^n will be same as incident light (Rayleigh scattering).

When $\Delta J = +2$ gives stokes lines (longer wave length than incident light)

When $\Delta J = -2$ gives antistokes lines (shorter wavelength than incident light)

utilising the relation for the energy of a rigid rotator.

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad — ①$$

When $\Delta J = +2$ then rotational Raman shift (Stokes lines) will be

$$\overline{\Delta\nu}_{1\to2} = \frac{h}{8\pi^2 Ic}\left[(J+2)(J+3) - J(J+1)\right]$$

$$\boxed{\begin{aligned} &\cancel{J^2} + 2J + 3J + 6 - \cancel{J^2} - J \\ &= 4J + 6 \\ &= 2(2J+3) \end{aligned}}$$

$$= 2B(2J+3) \quad — ② \quad \text{where } B = \frac{h}{8\pi^2 Ic}$$

When $\Delta J = -2$, the values for rotational Raman shift (Anti Stokes lines) will be.

$$\overline{\Delta\nu} = -2B(2J+3) \quad — ③$$

On combining ② & ③ the Raman shift will be

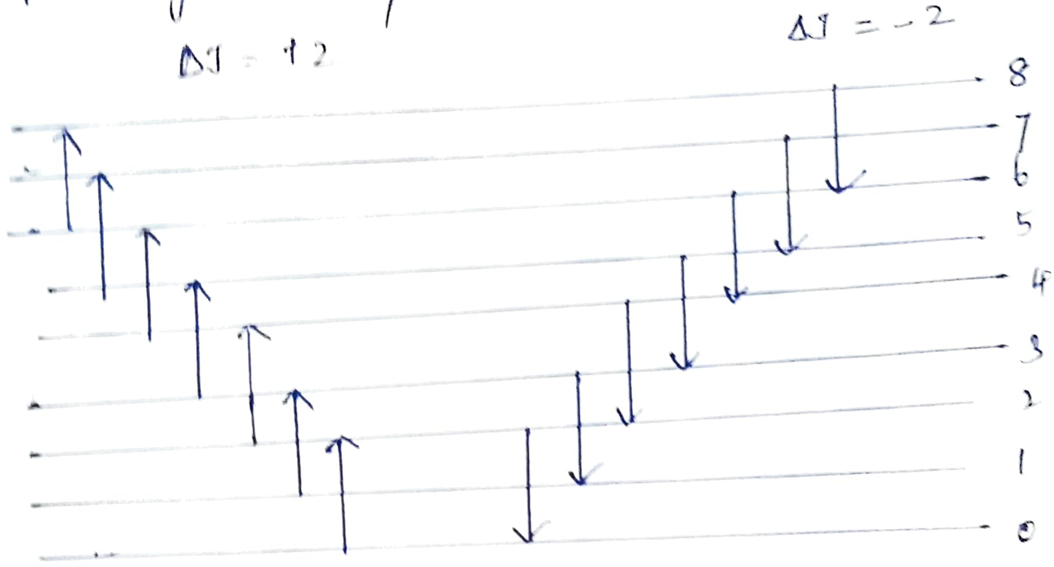
$\Delta\bar{\nu} = \pm 2B(2J+3)$ where $J = 0, 1, 2$

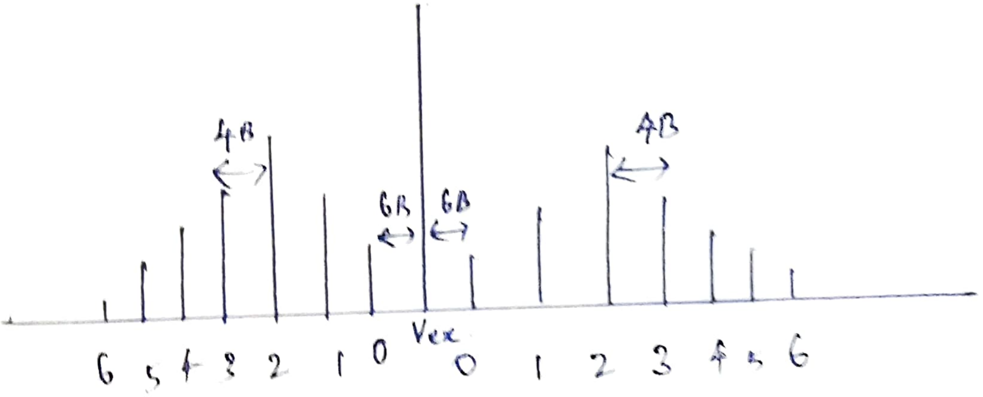
The wave number of the corresponding spectral lines will be

$$\bar{\nu} = \bar{\nu}_{ex} \pm \Delta\bar{\nu} \quad \text{—} ④$$

Where $\bar{\nu}_{ex}$ is the wave number of exciting radiation.

The transition and the Raman spectrum arising are shown diagrammatically as





It can be seen that the frequency sepn of successive lines is $2\bar{B}$ cm^{-1} (Microwave) whereas it is $4B$ cm^{-1} in ~~the~~ Raman (for IR). When $J=0$ in eqn ④ the first line from exciting line will be $6\bar{B}$ cm^{-1}.

rotational Raman Spectra:

If both vibrational and rotational transitions occur simultaneously, then the selection rule will be

$\Delta J = 0, \pm 2$ and $\Delta v = \pm 1$

For a diatomic molecule vib-rot energy levels are given by

$$\overline{\Delta\nu_0} = hc[\overline{\omega}_e(v+\tfrac{1}{2}) - \overline{\omega}_e x(v+\tfrac{1}{2})^2 - \overset{BhcJ}{\cancel{BJhc}}(J+1)]\,cm^{-1} \quad \text{—①}$$

Where $v = 0, 1, 2$ and $J = 0, 1, 2$

In terms of frequency equation ① modifies to

$$\bar{\nu} = \overline{\omega}_e(v+\tfrac{1}{2}) - \overline{\omega}_e x(v+\tfrac{1}{2})^2 + BJ(J+1) \quad \text{—②}$$

When we apply selection rules to equation ② then

i) When $\Delta J = 0$ $\overline{\Delta\nu} = \bar{\nu}_0$ (for all values of J) – Q branch.

ii) When $\Delta J = +2$ $\overline{\Delta\nu} = \overline{\nu_0} + B(4J+6)$ [where $J = 0, 1, 2$] → S branch

iii) When $\Delta J = -2$ $\overline{\Delta\nu} = \overline{\nu_0} - B(4J+6)$ (where $J = 2, 3, 4$) → O branch

Where in the above eqns, $\overline{\nu_0} = \omega_e(1-2x)$

The corresponding wave numbers are represented by.

i) $\bar{\nu}(Q) = \overline{\nu_{ex}} - \overline{\Delta\nu}(Q)$

$= \bar{\nu}_{ex} - \bar{\nu}_0$ (for all values of J)

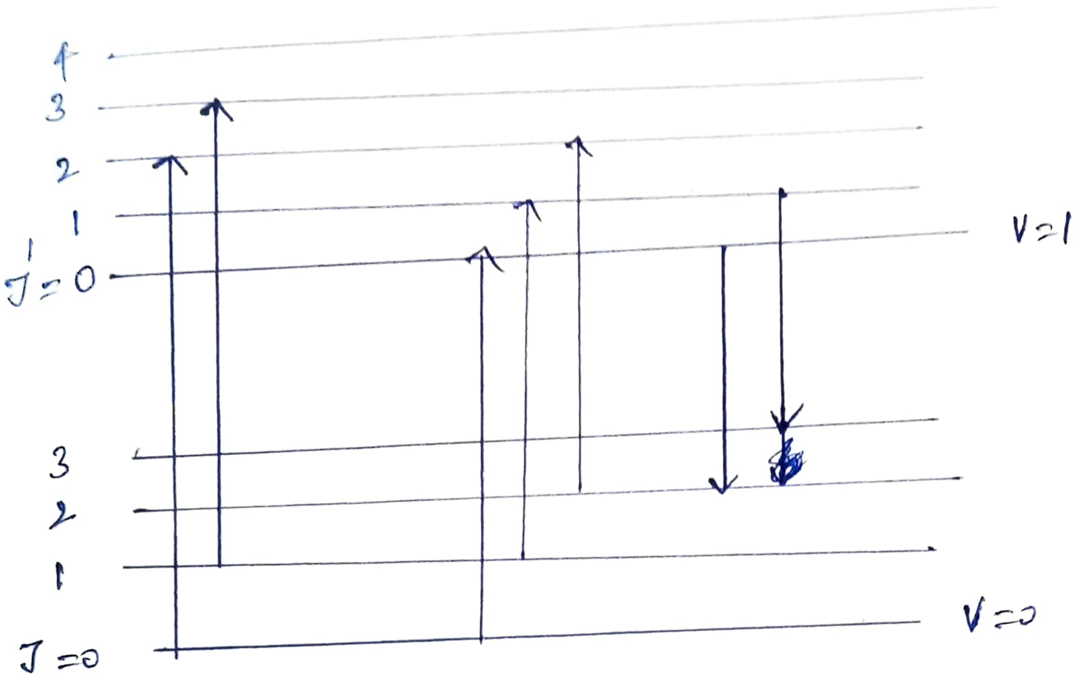
ii) $\bar{\nu}(O) = \bar{\nu}_{ex} - \overline{\Delta\nu}(O)$

$= \bar{\nu}_{ex} - \overline{\nu_0} + B(4J+6)$ where $J = 2, 3, 4$)

iii) $\bar{\nu}(S) = \bar{\nu}_{ex} - \overline{\Delta\nu}(S)$

$= \bar{\nu}_{ex} - \bar{\nu}_0 - B(4J+6)$ where $J = 0, 1, 2\ldots$)

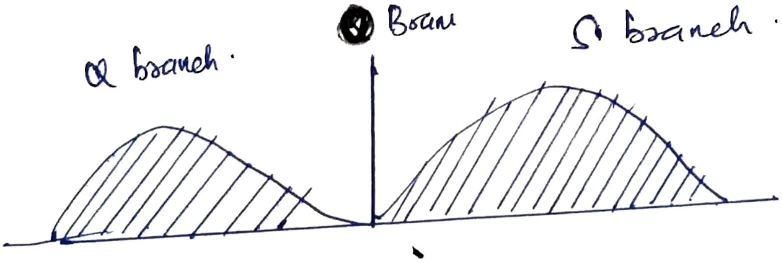
various Raman rot. vib. transitions are shown in the following figure.



ΔV = +1
ΔJ = 2
(S branch)

ΔV = +1
ΔJ = 0
(Q branch)

ΔV = +1
ΔJ = -2
(O branch)



In Raman Sp. Q branch will be present whereas in IR it is absent. All the lines are very close & it can't be resolved. On the other hand S & O branches are very weak, & their lines not superimposed. Both S & O branches are llr to R & P branch in IR.

ual exclusion principle:

It states that if a molecule has a centre of symmetry, the Raman active vibrations are IR inactive and vice versa. If a molecule is not centrosymmetric, some of the vibrations are both Raman and IR active.

This rule provides valuable information about the str. of any molecule.

ex. CO_2 has one strong band in Raman at 1389 cm^{-1} and 2 strong band in IR at 668 & 2349 cm^{-1}. None of these occur both in Raman and IR spectra. This is because CO_2 has centre of symmetry.

H_2O shows both IR & Raman active lines ~~show~~ It shows that H_2O has a bent structure and has no centre of symmetry.

Electronic spectroscopy

(or)

ultraviolet and visible spectroscopy

The electronic spectra are studied in ultraviolet region, arise due to transition of an e^- from one electronic state to another.

absorption spectrum

Emission spectrum.

E. spectra involve large amount of (10^2 kcal/mole) of energy change. Hence it is observed in UV-visible region.

During electronic excitation, vibrational and rotational transition also occur. Hence ele. sp. is very complex and band obtd consists of no. of fine lines due to simultaneous changes in vibrational and rotational energies.

Advantages over microwave and infrared spectra:

i) Handling of experimental technique is much easier than microwave and mid infrared methods.

② Information about excited state of the molecule and heat of dissociation can be easily obtd.

③ In case of Homonuclear molecules, the dipole moment is zero. Hence they do not give IR and microwave spectra. But they show electronic spectra. This is the greatest advantage of ele. spectroscopy.

→ electronic spectra:

When an electronic transition takes place, there are usually a large no. of changes in vibrational levels, each of which give rise to a band. In each of these band, again there are innumerable lines, due to rot. transition. Hence the whole rot- vib spectrum is superimposed on the electronic spectrum and this process produce a band system.

The total energy of molecule is given by

$$E_{total} = E_{ele} + E_{vib} + E_{rot}$$

the change in the total energy can be expressed as

$$\Delta E_{Total} = \Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot} \quad ①$$

But

$$\Delta E_{ele} > \Delta E_{vib} > \Delta E_{rotational}$$

Hence the vib. changes will produce a coarse structure and the rotational change a fine str. in an electronic spectrum.

The frequency of the radiation emitted or absorbed during electronic transition is given by

$$\bar{\nu} = \frac{\Delta E_{Total}}{hc} = \frac{\Delta E_{ele} + \Delta E_{vib} + \Delta_{rotational}}{hc}$$

$$\bar{\nu} = (\bar{\nu}_{Ele} + \bar{\nu}_{vib} + \bar{\nu}_{rot})\ cm^{-1}$$

Rotational Structure:

Transition from state (") to state (') the values of rotational constant B, of the two states B'' and B' respectively.

$$\text{Rotational energy of state (')} = \frac{h}{8\pi^2 I c}\left[J'(J'+1)\right]$$

$$= B'\left[J'(J'+1)\right] cm^{-1}$$

…ional energy of state (") $= \frac{h}{8\pi^2 I'' c}\left[J''(J''+1)\right]$ cm⁻¹

$= B''\left[J''(J''+1)\right]$ cm⁻¹

$$V_{rot} = \left[B''J''(J''+1) - B'J'(J'+1)\right] \text{ cm}^{-1}$$

$$\bar{\nu} = \bar{\nu}_{ele} + \bar{\nu}_{vib} + B''J''(J''+1) - B'J'(J'+1)$$

$\boxed{\bar{\nu}_{ele} + \bar{\nu}_{vib} = \bar{V}_0}$. fre. of the centre of a band

$$\bar{V} = \bar{\nu}_0 + \left[B''J''(J''+1) - B'J'(J'+1)\right] \text{ cm}^{-1}$$

The three permitted transitions

$\Delta J = +1, 0, -1$ then there are 3 cases

Case: 1. $\Delta J = +1$ (or) $J'' - J' = +1$. this transition would give P-branch of the rotational line. The frequency of P-branch is given by.

$$\bar{V}_P = \bar{V}_0 + B''J''(J''+1) - B'(J''-1)J'' \text{ cm}^{-1}$$

$$= \bar{V}_0 + B''J''^2 + B''J'' - B'J''^2 + B'J''$$

$$= \bar{V}_0 + \left[(B''-B')J''^2 + (B''+B')J''\right] \text{ cm}^{-1}$$

Case: 2 For $\Delta J = 0$ ie $J'' - J' = 0$ (or) $J'' = J'$. This transition would give Q-branch of the rotation line, the frequency of which is given by

$$\bar{V}_Q = \bar{V}_0 + \left[B''J''(J''+1) - B'J''(J''+1)\right] \text{ cm}^{-1}$$

$$= \bar{V}_0 + \left[B''J''^2 + B''J'' - B'J''^2 - B'J''\right] \text{ cm}^{-1}$$

$$= \bar{V}_0 + \left[(B''-B')J''^2 + (B''-B')J''\right] \text{ cm}^{-1}$$

Case: 3 For $\Delta J = -1$ (or) $J'' - J' = -1$. This transition would give rise to R-branch of the rotational line. the frequency is given by

$$\bar{V}_R = \bar{V}_0 + \left[B''J''(J''+1) - B'(J''+1)(J''+1+1)\right] \text{ cm}^{-1}$$