# BSc-TY. Semester-VI

## Paper-XIV :- Atomic and Molecular physics

## Unit-II :- Molecular spectra

- Ⓘ Regions of Electromagnetic Spectra
- Ⓘⓘ Classification of molecular spectra
- Ⓘⓘⓘ Theory of pure rotational spectra
- Ⓘⓥ Theory of rotation Vibration spectra
- ⓥ Raman Effect
- ⓥⓘ Experimental study.

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## * Regions of Electromagnetic spectra :-

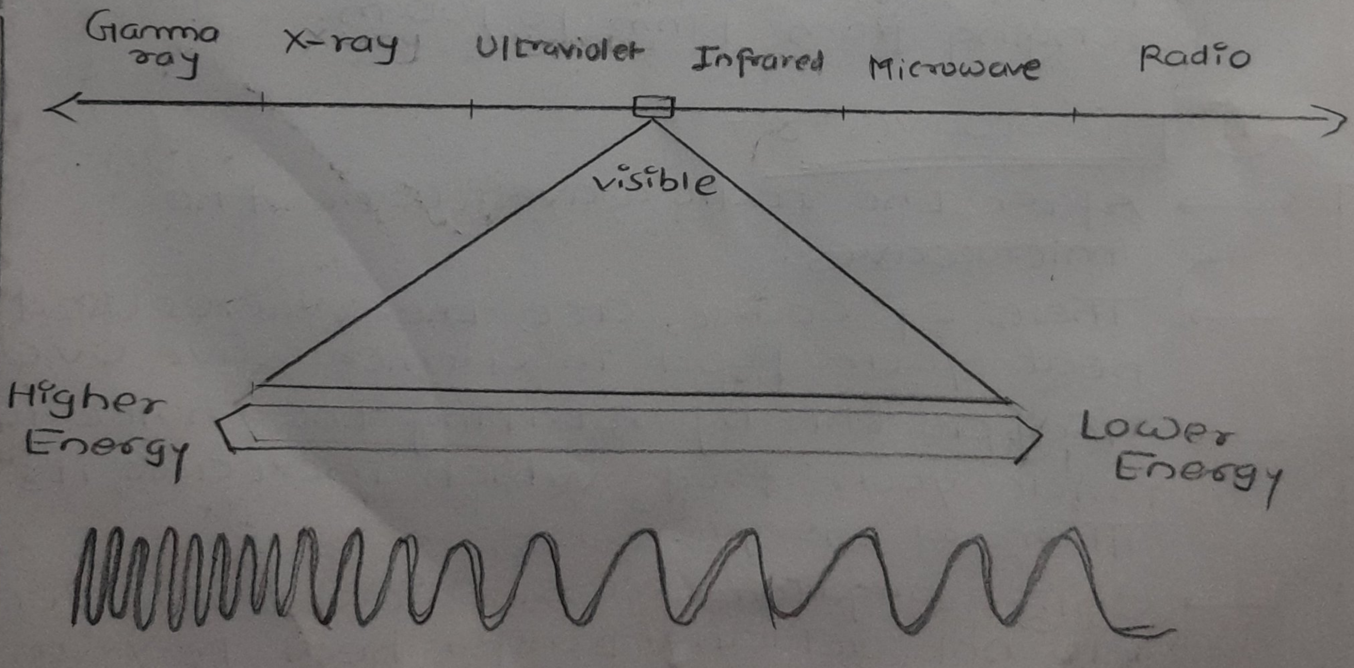


fig :- Electromagnetic spectrum

→ The entire range (Electromagnetic spectrum) is given by radio waves, microwaves, infrared radiation, visible light, UV ~~ray~~ radiation, X-rays, gamma rays.

## (I) Radio waves :-

- → The lowest frequecy waves on out EM spectrum are the radio waves. ($< 3\times10^{11}$ Hz)
- → These are the waves that televisions and radio stations use to transmit data.
- → By exciting the $e^{\ominus}$ on a conducting antenna, these stations create radio waves that can be received by other devices.
- → The data is created by modulating the parameters of the oscillations for instance by changing the amplitude and the wavelength.
- → Radio waves have the longest wavelength, ranging from 1 mm to 100 m.

## (II) Microwaves :-

- → After the radio waves come the microwaves.
- → These, of course, are the waves used to heat your food in a microwave oven.
- → They do this by rotating the molecules inside your food, which increases its Thermal energy.
- → Unlike regular ovens, microwave ovens do not actually transfer heat to your food.
- → They heat the food directly by exciting the molecules.
- → Microwaves also used in wi-fi technology but only at low intensities.

→ Microwaves have the wavelength ranging from 1mm to 25 µm.

→ Microwaves have the frequency ranging from $3 \times 10^{11} \rightarrow 10^{13}$ Hz.

## Ⅲ Infrared Region :-

→ frequency range $3 \times 10^{12} - 3 \times 10^{14}$ Hz.

→ We call it as a infrared region because it's just 'below the red part of the visible spectrum.

→ Infrared region have the wavelength ranging from 25µm - 2.5µm.

## Ⅳ Visible light :-

→ The region of visible light waves is pretty small compared to most other regions.

→ This part of spectrum is defined as the range of light frequencies to which the human eye is most sensitive.

→ Visible light spans from 760 to 380 nm.

## Ⅴ Ultraviolet :-

→ Sun is the main source of ultraviolet radiation.

→ It causes skin tanning and burns

→ Hot materials that are in space also emit UV radiations.

→ frequency range in this region $10^{15} - 10^{17}$ Hz and wavelength ranging from 400 nm - 1 nm.

## (vi) X-rays :-

→ X-rays have the frequency ranging from $10^{17} - 10^{20}$ Hz and wavelength ranging from 1nm – 1pm.

## (vii) gamma rays :-

→ It has wide application in the medical field.

→ Gamma ray imaging is used to see ~~an~~ inside our bodies.

→ Interestingly, the universe is the biggest gamma ray generator of all.

→ Gamma rays have the frequency ranging from $10^{20} - 10^{24}$ Hz and wavelength ranging from $< 10^{-12}$ m.

# Introduction :- Molecular spectra :-

→ The Atomic spectra which is the spectra emitted by atoms (when the emitting substance is in atomic state) due to energy changes in their electronic system.

→ There is another class of spectra called the molecular spectra which is the spectra emitted by molecules (when the emitting substance is in molecular state) containing two or more atoms.

→ Molecular spectra is also known as Band spectra.

→ Because, the component lines of spectra were found indistingushible which appeared merged together into strips of shaded intensity.

→ Thus under low dispersion, molecular spectra appears as continuous bands usually a band has a sharp intense ~~on~~ edge on one side called 'band head'. which gradually decreases in intensity toward the other side.

→ Thus the continuous spectrum appears to be divided into several bands.

→ With high resolving power instruments the band spectra is found to have threefold structure :-

Ⓘ Each band is ~~called as~~ composed of a Large no. of lines which are crowded together at the long wavelength side. Called "band head". The lines become more widely separated & weaker as they recede from the band.

(II) Several bands follows one another in regular sequence consistituting a group of bands.

(III) Different groups of band are quite close and because of their regular arrangement they form a band system.

## * Classification of Molecular spectra :—

Band spectra produced by molecules are found to occur in different spectral regions.

Accordingly, molecular spectra is divided into three spectral ranges corresponding to the different type of transition betn molecular energy levels.

(I) Pure Rotational spectra
(II) Vibrational- Rotational spectra
(III) Electronic spectra.

### (I) Pure Rotational spectra :—

→ Molecular energy states arising from the rotation of a molecule as a whole are separated by quite small energy interval ($\approx 10^{-3} eV$)

→ Spectra arising from transition betn these states are observed in absorption in the far infra red region ($10^2 \mu$ to $10^3 \mu$ where $1 \mu = 10^{-6}$ m $= 10^4 A^\circ$) or in the microwave region ($10^3 \mu - 10^4 \mu$)

→ Only those molecules which have permanent electric dipole moment can give rise to a pure rotational spectra.

→ Thus pure rotational spectra are observed only for the Heteronuclear molecule diatomic molecule such as HCl, HBr, HF etc.

→ Homomoleculer diatomic molecule such as $H_2$, $O_2$, $N_2$ etc. do not exhibit pure rotational spectra.

## (II) Vibrational-Rotational spectra :-

→ Rotation vibration bands arise from the vibration of the atoms inside the molecule upon which are suspended the rotational motion of molecules.

→ The spectra so obtained are observed in absorption in the near infrared region ($1\mu$ to $10^2\mu$).

→ They are observed like pure rotational spectra, only for the Heteronuclear molecule like HCl, HBr, HF etc.

→ The Homonuclear diatomic molecules like $H_2$, $O_2$, $N_2$ etc do not produce vibrational rotational spectra.

## (III) Electronic Spectra :-

→ The most complex molecular spectra is the electronic spectra which is observed in both emission and absorption. in the visible and UV region.

→ All diatomic molecules Homonuclear as well as Heteronuclear exhibit electronic spectra.

→ Thus, Homonuclear molecule such as $H_2$, $N_2$, $O_2$ etc which ~~are~~ give neither rotational nor vibrational-rotational spectra.

→ Because they do not have permanent dipole moment, give electronic spectra.

→ The molecular ~~spectra~~ electronic spectra involves a change in all the three electronic, vibrational and rotational energy.

→ The change in electronic energy is accompanied by a change in vibrational energy which gives rise to vibrational transitions forming group of various bands.

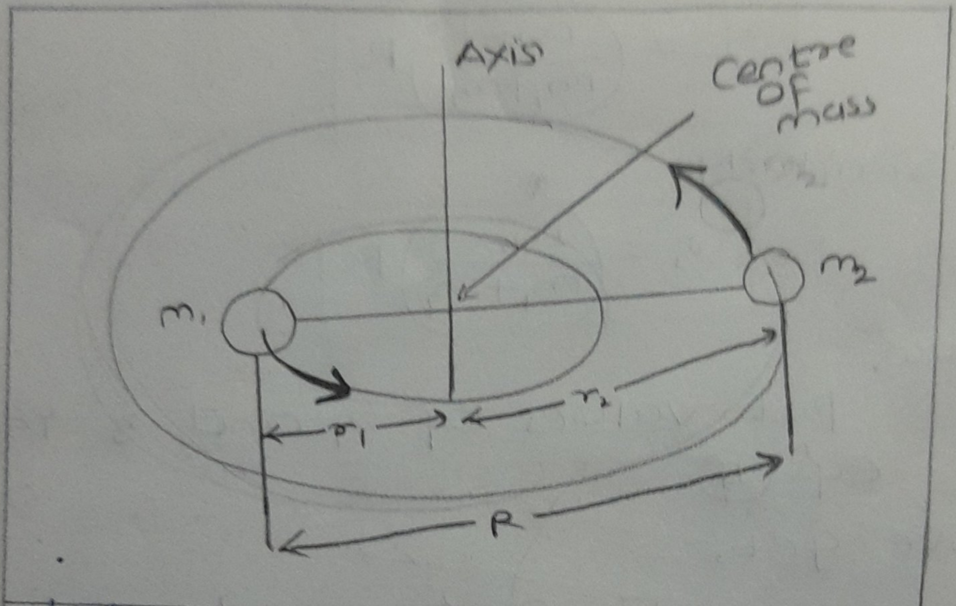
→ The change in vibrational energy in turn is accompanied by changes in rotational energy of the molecule giving rise to rotational transitions forming a series of lines in each band.

→ Thus, the bands of electronic spectra show a fine structure

## * Theory of the Origin of Pure Rotational Spectrum of a Molecule :

Consider,

A diatomic molecule Consisting of two atoms of masses $m_1$ and $m_2$ joined together by a weightless rigid rod of Length R. The Centre of mass of the system lies at a point on the rod.



Let,

$r_1$ and $r_2$ be the distances of atoms from the Centre of mass

So we have,

$$\boxed{R = r_1 + r_2} \quad \text{——} \quad (I)$$

The Moment of Inerentia of this molecule about an axis passing through its Centre of mass and perpendicular to a line joining the atoms is

$$\boxed{I = m_1 r_1^2 + m_2 r_2^2} \quad \text{——} \quad (II)$$

By defination of centre of mass,

$$m_1 r_1 = m_2 r_2$$

$$r_1 = \frac{m_2 r_2}{m_1} \quad \text{——} \quad (III)$$

Using (III) in (I)

we get,

$$R = \left(\frac{m_2 r_2}{m_1}\right) + r_2 \quad \cdots\cdots \text{(From Ⅲ)}$$

$$= \left(\frac{m_2}{m_1} + 1\right) r_2$$

$$= \left(\frac{m_2 + m_1}{m_1}\right) r_2$$

$$\boxed{r_2 = \left(\frac{m_1}{m_1 + m_2}\right) R}$$

Similarly,

$$\boxed{r_1 = \left(\frac{m_2}{m_1 + m_2}\right) R}$$

Now,

put values of $r_1$ and $r_2$ into the eq$^n$ Ⅱ

we get,

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

$$I = m_1 \left(\frac{m_2 R}{m_1 + m_2}\right)^2 + m_2 \left(\frac{m_1 R}{m_1 + m_2}\right)^2$$

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

$$= \frac{m_1 m_2 R^2 \cancel{(m_2 + m_1)}}{(m_1 + m_2)^{\cancel{2}}}$$

$$\boxed{I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) R^2} \quad \text{—— Ⅳ}$$

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$$\boxed{I = m'R^2} \text{ ——— } ⓥ$$

where,

$m' = \frac{m_1 m_2}{(m_1+m_2)}$ is called reduced mass.

Rotational K.E of the diatomic molecule is given as,

$$E = \frac{1}{2} I\omega^2 \text{ ——— } (VI)$$

The Angular momentum L of the molecule is,

$$L = I\omega$$

$$\text{so, } \omega = \frac{L}{I}$$

Put, $\omega = \frac{L}{I}$ into eq$^n$ (VI)

we get,

$$E = \frac{1}{2} I \left(\frac{L}{I}\right)^2$$

$$= \frac{L^2}{2I}$$

$$\boxed{E = \frac{L^2}{2I}} \text{ ——— } (vii)$$

The angular momentum of the rotating diatomic molecule is quantised according to,

$$L = \sqrt{J(J+1)}\,\hbar \text{ ——— } (viii)$$

where,

J = rotational Quantum number

J = 0, 1, 2, 3 . . . . .

Now,

using eq$^n$ (viii) in (vii)

$$E = \frac{\left[\sqrt{J(J+1)}\,\hbar\right]^2}{2I}$$

$$\boxed{E_J = \frac{J(J+1)\hbar^2}{2I}}$$

For $J=0$

$E_0 = 0$

For $J = 1$

$$E_1 = \frac{1(1+1)\hbar^2}{2I} = \frac{2\hbar^2}{2I} = \frac{\hbar^2}{I}$$

$$\boxed{E_1 = \frac{\hbar^2}{I}}$$

for $J = 2$

$$E_2 = \frac{2(2+1)\hbar^2}{2I} = \frac{6\hbar^2}{2I} = \frac{3\hbar^2}{I} = 3E_1$$

$$\boxed{E_2 = 3E_1}$$

for $J = 3$

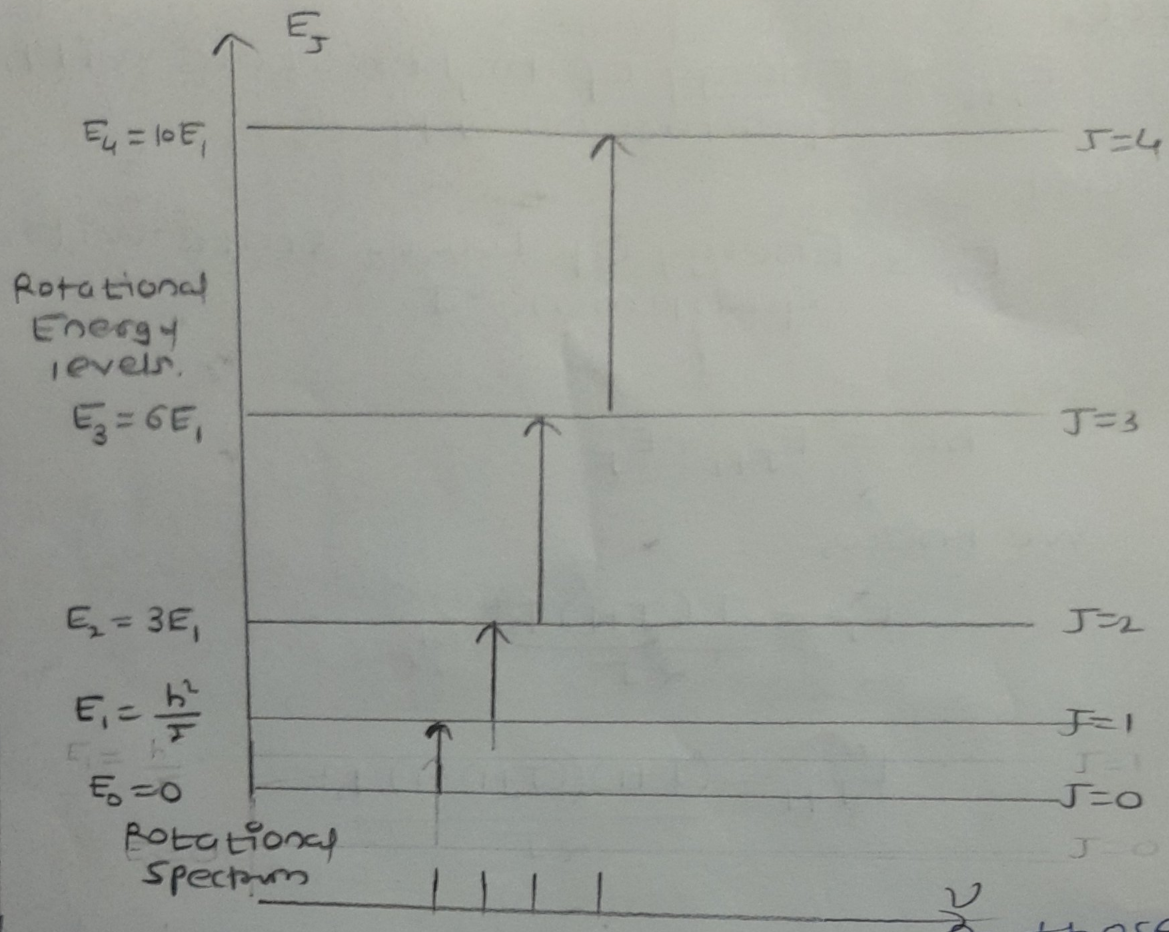
$$E_3 = \frac{3(3+1)\hbar^2}{2I} = \frac{12\hbar^2}{2I} = \frac{6\hbar^2}{I} = 6E_1$$

$$\boxed{E_3 = 6E_1}$$

Similarly,

for $J = 4$

$$\boxed{E_4 = 10E_1}$$



→ Rotational Transition occurs in those molecules which possess a permanent electric dipole moment.

→ For this reason, non polar diatomic molecules such as $H_2$ and symmetric polyatomic molecules such as $CO_2$ and $CH_4$ do not exhibit rotational spectra.

⊙ Selection Rule:- For a given molecule only those tranistion are possible bet$^n$ allowed rotational Energy levels for which $\Delta J = \pm 1$

⊙ Frequency of Spectral line:-

In Practical situation, the rotational spectra is alway obtained in absorption. When a molecule makes a transition from Initial state of quantum number J to next Higher state of quantum number J+1.

Let,

$E_{J+1}$ = Energy of higher state with quantum no. $J+1$

and,

$E_J$ = Energy of lower state with quantum no. $J$.

So,

$$h\nu = E_{J+1} - E_J$$

We know,

$$E_J = \frac{J(J+1)\hbar^2}{2I}$$

$$\therefore E_{J+1} = \frac{(J+1)((J+1)+1)\hbar^2}{2I}$$

$$\therefore h\nu = E_{J+1} - E_J$$

$$h\nu = \frac{(J+1)(J+1+1)\hbar^2}{2I} - \frac{J(J+1)\hbar^2}{2I}$$

$$\nu_{J\to J+1} = \frac{(J+1)\hbar^2}{\cancel{2}I}\left[\cancel{J}+\cancel{2}-\cancel{J}\right]$$

$$\nu_{J\to J+1} = \frac{(J+1)\hbar^2}{2Ih}\times 2$$

$$= \frac{(J+1)\hbar^2}{Ih} \quad \ldots\ldots \left(\hbar = \frac{h}{2\pi}\right)$$

$$\ldots\ldots \therefore \left(h = \hbar\, 2\pi\right)$$

$$= \frac{(J+1)\hbar^{\cancel{2}}}{I(\cancel{\hbar}\cdot 2\pi)}$$

$$\boxed{\nu_{J\to J+1} = \frac{\hbar}{2\pi I}(J+1)}$$

$$\boxed{\nu_{J \to J+1} = \frac{\hbar}{2\pi I}(J+1)}$$

$J=0$

$\nu_{0 \to 1} =$

The spectrum of a rigid molecule therefore consists of equally spaced lines.

* Importance of the pure rotational spectrum for determining the properties of a molecule :-

The frequency difference bet$^n$ two succesive lines in the pure rotational spectrum of a diatomic molecule is given by ,

$$\Delta\nu = \nu_{J+1 \to J+2} - \nu_{J \to J+1}$$

$$\Delta\nu = \frac{\hbar}{2\pi I}$$

By Measuring $\Delta\nu$, the moment of Inertia $I$ of the molecule can be calculated.

Now,

$$I = m' R^2$$

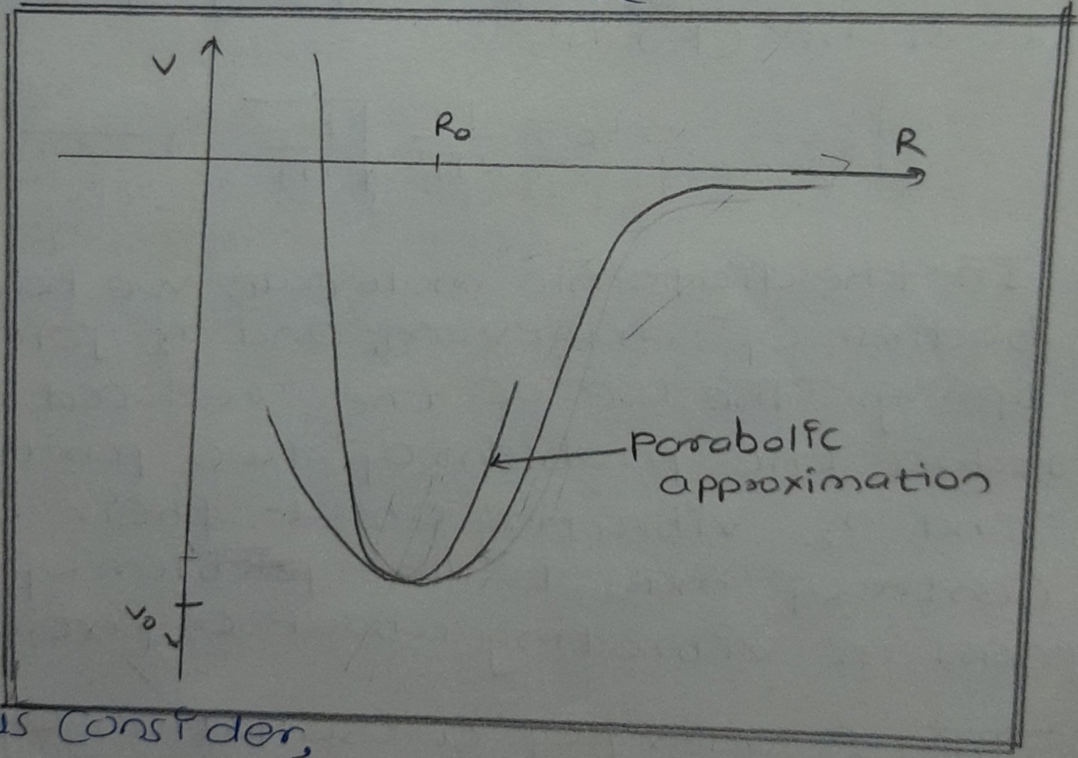
$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) R^2$$

Thus, the distance R between the nuclei can be calculated. This gives the length of the chemical bond between the atoms.

# Theory of the Origin of the Vibration-Rotation Spectrum of a Molecule :-

In the study of rotational spectra we deal with the diatomic rigid rotator possessing rotational motion. In fact the atoms in a molecule do not remains in fixed relative positions but vibrate about some mean position i.e. molecule can oscillate as well as rotate.

The vibrations of molecule may be harmonic or anharmonic depending on which the spacing between the energy levels also changes. for simplicity here we consider, simple harmonic oscillations of a diatomic molecule.



Let us consider,

Vibration of a P.E. (V) of a diatomic molecule with internuclear distance R. as shown in above fig.

In neighbourhood of eqn. separation (R₀). the curve is almost parabolic in Nature. Therefore, the P.E in this region is,

∴ Restoring force is responsible for this potential is,

$$F = -\frac{dV}{dR}$$

$$= \frac{-d}{dR}\left(V_0 + \frac{1}{2}k(R-R_0)^2\right)$$

$$F = -k(R-R_0) \quad \text{———} \; \text{(II)}$$

where,

F is the restoring force of harmonic oscillator and k is the spring constant

Therefore,

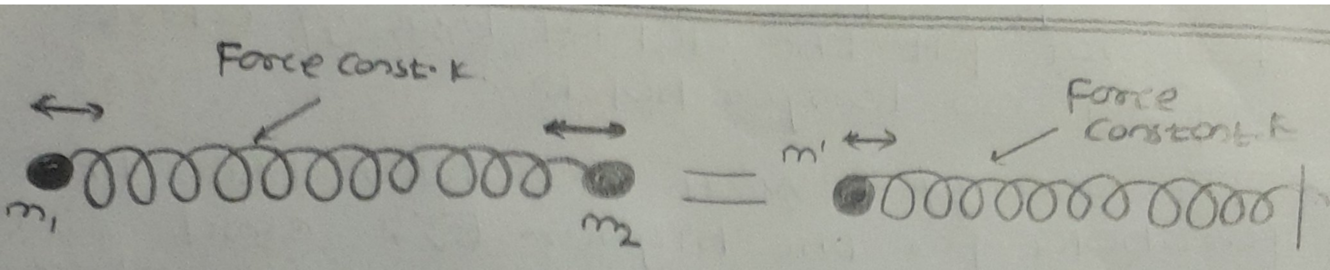
The frequency $\nu_0$ of oscillation of mass connected to a spring of force constant (k) is,

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad \text{———} \; \text{(III)}$$

→ In the diatomic molecule we have two bodies of masses $m_1$ and $m_2$ joined by a spring. The use of the "reduced mass" reduce the problem of two particles $m_1$ and $m_2$ vibrating about their common centre of mass to the problem of single mass $m'$ vibrating about a fixed point.

The frequency of a oscillation of such a two body oscillator is

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m'}} \quad \text{———} \; \text{(IV)}$$



$$m' = \left(\frac{m_1 \cdot m_2}{m_1 + m_2}\right)$$

According to Quantum mechanics, the Vibrational Energy ($E_v$) is also quantised such that,

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0 \quad \text{———} \quad ⓥ$$

Where,

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

The Lowest Energy state with $v=0$, also possess a finite energy $\frac{1}{2} h\nu_0$ Called Zero point energy.

Substitute value of $\nu_0$ from eqⁿ (IV) into ⓥ

$$\boxed{E_v = \left(v + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{m}}} \quad \text{----} \left(\hbar = \frac{h}{2\pi}\right)$$

——— (vi)

eqⁿ (vi) gives vibrational Energy levels.

It is seen that, vibrational energy levels are equispaced.

since,

$$E_v \propto \left(v + \frac{1}{2}\right)$$

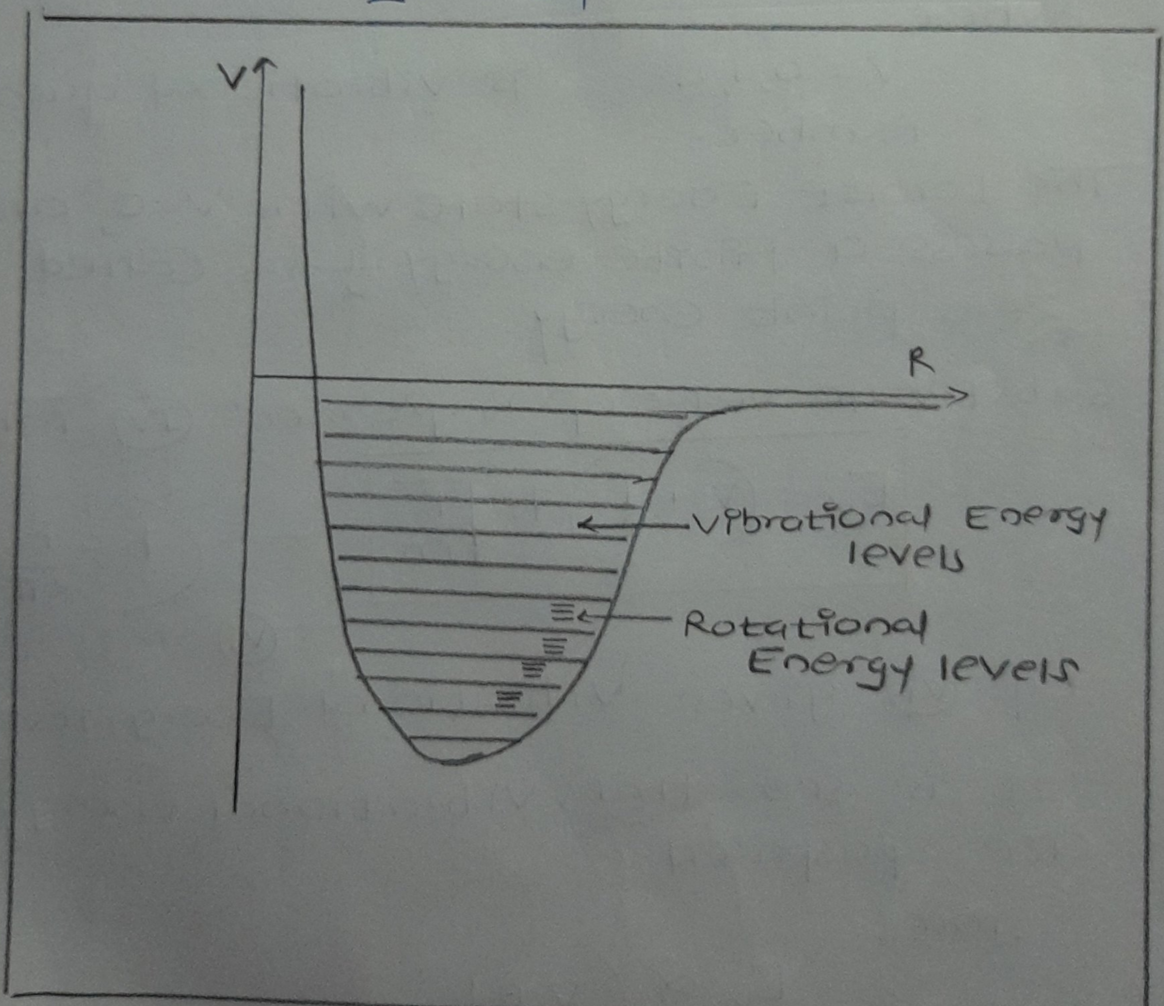
→ For large amplitude vibrations, the parabola does not fit the actual Energy curve eq? ⓥⓘ no longer holds.

→ The energy is well is wider than the parabola for the higher $E_v$'s and therefore these energy levels are closer together than the lower $E_v$'s.

→ This diagram also shows that the fine structure in the vibrational levels caused by the simultaneous excitation of rotational levels.

→ The selection rule for the transition bet? the vibrational state is

$$\Delta v = \pm 1$$



→ Pure rotational spectra are observed only in liquids. This is because, interaction betn neighbouring molecules prevent their rotational motion.

→ The vibrations and rotations of a molecule take place independently of each other. Thus neglecting the interaction betn rotational and vibrational motions the Total Energy of a molecule may be given by,

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

$$E_{v,J} = E_v + E_J$$

$$\boxed{E_{v,J} = \left(v+\frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}} + J(J+1)\frac{\hbar^2}{2I}}$$

→ $E_v$ is very much larger than $E_{rot}$. Even at High temp. only the vibrational states corresponding to $v=0$ $v=1$ are excited.

→ Below fig. shows the $J=0,1,2,3$ and 4 levels of a diatomic molecule for the $v=0$ and $v=1$ vibrational states.

→ It also shows the spectral lines in absorption. The selection rules are $\Delta v = 1$ and $\Delta J = \pm 1$.

→ The transition with $\Delta J = 0$ is not allowed.

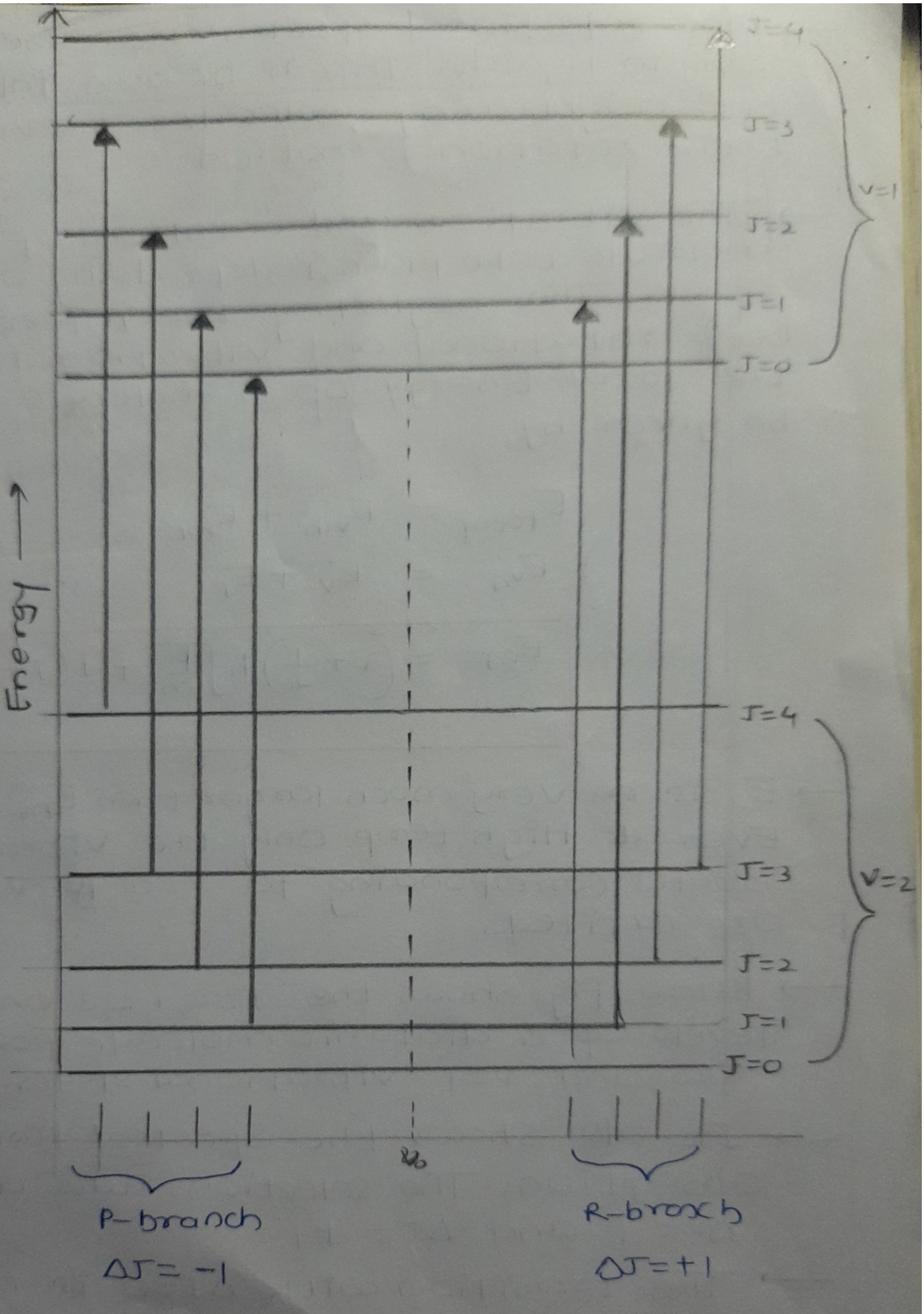


fig:- Vibrational rotational transition
(fine structure of vibrational specra.

The selection rules for the transition are

$\Delta v = \pm 1$ and $\Delta J = \mp 1$

Thus $\nu$ transitions can be grouped into two parts

i.e.

Ⓘ P-Branch

Ⓘⓘ R-Branch

Ⓘ P-Branch :-

Here, $\Delta J = -1$ (i.e. $J \to J-1$)

Since, transitions are $v = 0 \to 1$ and $J \to J-1$ the corresponding frequencies are

from eq^n^ (vii)

$$E_{v,J} = \left(v + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{m'}} + J(J+1)\frac{\hbar^2}{2I}$$

$$E_{1,J-1} = \left(1 + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{m'}} + (J-1)(J-1+1)\frac{\hbar^2}{2I}$$

$$= \frac{3}{2}\hbar\sqrt{\frac{K}{m'}} + J(J-1)\frac{\hbar^2}{2I}$$

$$E_{0,J} = \left(0 + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{m'}} + J(J+1)\frac{\hbar^2}{2I}$$

$\nu_p = E_{\cancel{1,J-1}}$

$$\nu_p = \frac{E_{1,J-1} - E_{0,J}}{h}$$

$$= \frac{1}{h}\left[\frac{3}{2}\hbar\sqrt{\frac{K}{m'}} + J(J-1)\frac{\hbar^2}{2I} - \frac{1}{2}\hbar\sqrt{\frac{K}{m'}} - J(J+1)\frac{\hbar^2}{2I}\right]$$

$$= \frac{1}{h}\left[\hbar\sqrt{\frac{K}{m'}} + J\frac{\hbar^2}{2I}\left[J-1-J-1\right]\right.$$

$$= \frac{1}{h}\left[\hbar\sqrt{\frac{K}{m'}} - J\frac{\hbar^2}{I}\right]$$

$$= \left[\frac{\hbar}{h}\sqrt{\frac{K}{m'}} - \frac{J\hbar^2}{hI}\right]$$

$=$ ~~$h = \frac{\hbar}{2\pi}$~~

~~$\hbar = \hbar \cdot 2\pi$~~

$$\therefore \nu_P = \frac{\hbar}{\hbar \cdot 2\pi}\sqrt{\frac{K}{m'}} - \frac{J\hbar^2}{2\pi\hbar I} \quad \ldots\ldots \left[\hbar = \frac{h}{2\pi}\right] \quad \left[h = \hbar 2\pi\right]$$

$$\nu_P = \frac{1}{2\pi}\sqrt{\frac{K}{m'}} - \frac{J\hbar}{2\pi I}$$

$$\boxed{\nu_P = \nu_0 - \frac{J\hbar}{2\pi I}} \quad \ldots \quad J = 1, 3, 3 \ldots\ldots$$

## (II) R- Branch :-

Here, $\Delta J = +1$ (ie. $J \rightarrow J+1$)

$$\nu_R = \frac{E_{1,J+1} - E_{0,J}}{h}$$

$$E_{1,J+1} = \left(1 + \frac{1}{2}\right)\hbar\sqrt{\frac{K}{m'}} + (J+1)(J+1+1)\frac{\hbar^2}{2I}$$

$$E_{0,J} = \frac{1}{2}\hbar\sqrt{\frac{K}{m'}} + J(J+1)\frac{\hbar^2}{2I}$$

$$\nu_R = \frac{E_{1,J+1} - E_{0,J}}{h}$$

$$\nu_R = \frac{1}{h}\left[E_{1,J+1} - E_{0,J}\right]$$

$$= \frac{1}{h}\left[\left(\frac{3}{2}\hbar\sqrt{\frac{k}{m'}} + (J+1)(J+2)\frac{\hbar^2}{2I}\right) - \left(\frac{1}{2}\hbar\sqrt{\frac{k}{m'}} - J(J+1)\frac{\hbar^2}{2I}\right)\right]$$

$$= \frac{1}{h}\left[\hbar\sqrt{\frac{k}{m'}} + (J+1)\frac{\hbar^2}{2I}\left[J+2-J\right]\right]$$

$$= \frac{1}{h}\left[\hbar\sqrt{\frac{k}{m'}} + (J+1)\frac{\hbar^2}{I}\right] \cdots \left(\hbar = \frac{h}{2\pi}\right)$$

$$= \frac{1}{2\pi}\sqrt{\frac{k}{m'}} + \frac{(J+1)\hbar^2}{2\pi I}$$

$$\nu_R = \nu_0 + \frac{(J+1)\hbar^2}{2\pi I}$$

$$\therefore \boxed{\nu_R = \nu_0 + \frac{(J+1)\hbar^2}{2\pi I}} \qquad J = 0, 1, 2, 3 \cdots\cdots$$

There is no line at $\nu = \nu_0$ (the Q branch) because transition for which $\Delta J = 0$ are forbidden in diatomic molecules.

The spacing between the line in both P and the R branch is $\Delta\nu = \frac{\hbar}{2\pi I}$.

Hence,

By measuring these lines ~~in both the p~~ ~~and~~ the moment of inertia of the molecules and the length of the chemical bond can be calculated.

# * Electronic spectra of a Diatomic molecule :-

A

→ When there is enough Available energy, the electronic states of the molecules can be excited.

→ This gives rise to the most general type of transitions, rotation-vibration-electronic transitions.

→ These produce photons of frequency

$$\nu = \frac{E_{e_1} - E_{e_2}}{h} + \frac{E_{v_1} - E_{v_2}}{h} + \frac{E_{rot_1} - E_{rot_2}}{h}$$

→ It is the outermost electrons of the atoms composing the molecules that are involved.

→ These transitions are energetic enough that they produce electronic bands is the visible and ultraviolet regions.

→ All molecules exhibit electronic spectra, since a dipole moment change alway accompanies a change in the electronic configuratis of a molecule.

→ In molecular spectra, relative transitions between electronic states of different total spin are forbidden.

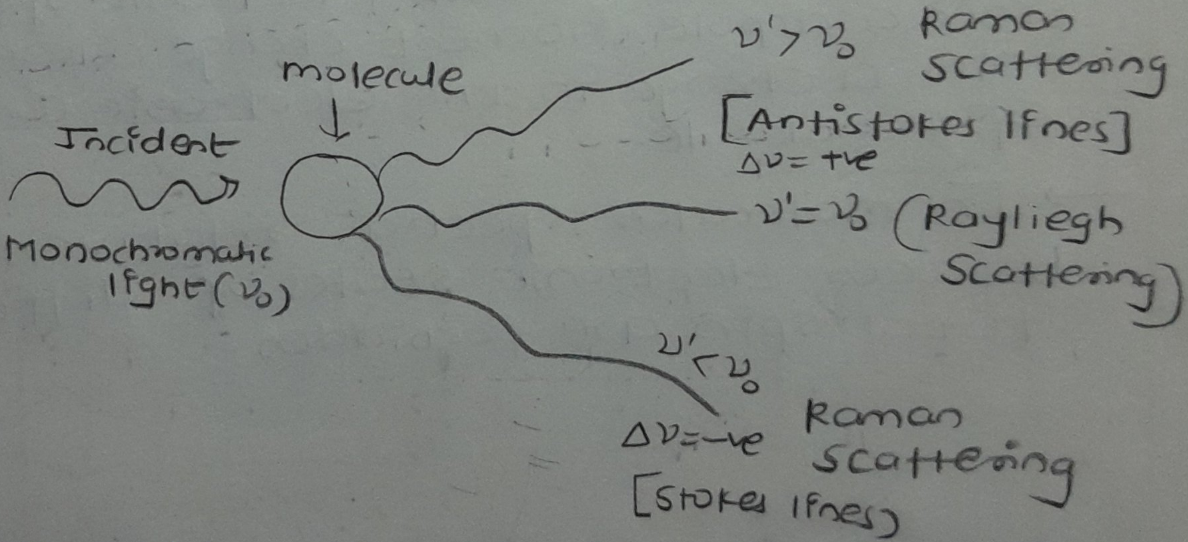
## * Raman Effect :-

→ In 1928, Sir C.V. Raman, while studying the scattering of light by liquids found that when a beam of monochromatic light was passed through organic liquids such as Benzene, toluene etc.

→ The scattered light contained other frequencies in addition to that of incident light.

→ Such a scattering is called Raman Scattering.

→ "The scattering of light from molecules with a change in frequency" is called Raman Effect.



→ Raman observed that, the spectrum of a scattered light contains a line of same frequency as that of the incident light which is called Rayliegh line. & weak lines on each side of Rayliegh line.

→ The lines on the Low frequency side are called Stokes lines and the lines on the high frequency side are called Anti-stokes

→ stokes lines are more intense than Anti-stokes lines.

Let,

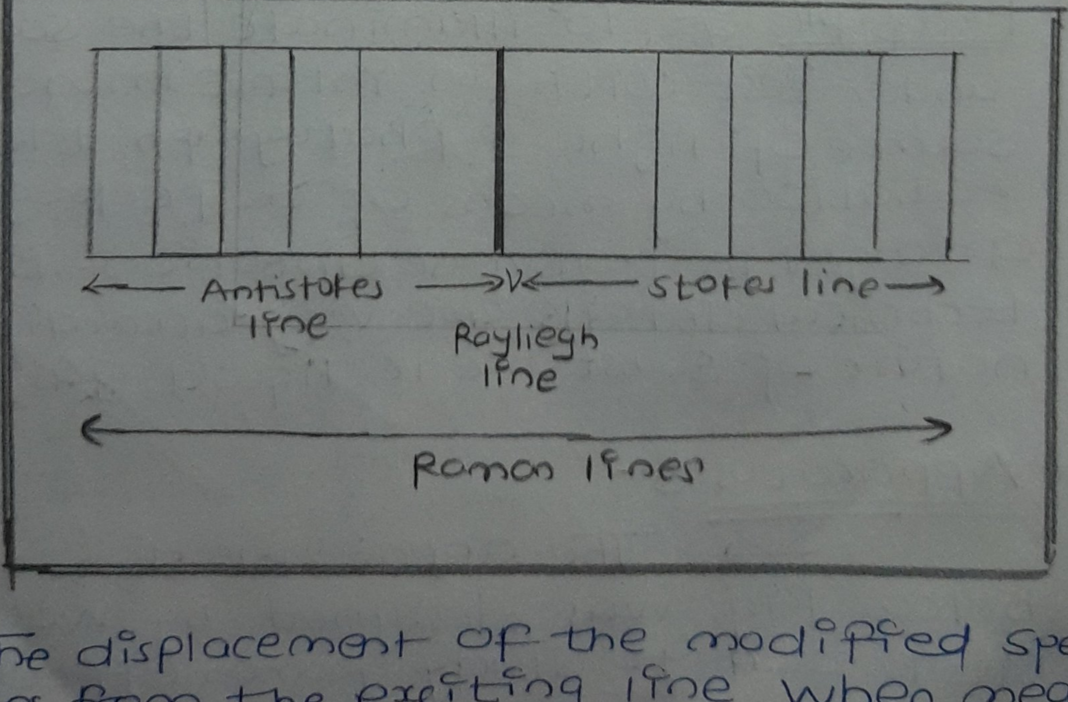
$\nu_0$ is frequency of incident radiation and $\nu'$ is frequency of scattered radiation then Raman shift ($\Delta\nu$) is given by

$$\Delta\nu = \nu_0 - \nu'$$

① when $\nu' < \nu_0$ then $\Delta\nu = -ve$ ; Raman spectrum is said to be consisting of stokes lines.

Ⅱ when $\nu' > \nu_0$, then $\Delta\nu = +ve$ , Raman spectrum is said to be consisting of Antistokes lines.

Ⅲ when $\nu' = \nu_0$, then $\Delta\nu = 0$ Raman spectrum is said to be consists of Rayliegh line only.



→ The displacement of the modified spectral lines from the exciting line, when measured in wavenumbers, depends only on scattering of substance

→ and it is independent of the wavenumber of the exciting radiation.

→ The Raman spectrum is thus charac
of the scattering substance.

→ Raman spectrum is thus characteristics of the scattering substance.

→ Raman effect is quite different from Rayliegh scattering.

→ In Rayleigh or coherent scattering there is no change in wavelength.

→ But in Raman scattering, the scattered light contains modified wavelength as well as the original wavelength.

→ for this reason, Raman effect is also called incoherent scattering and is considered as the optical analogue of the compton effect.

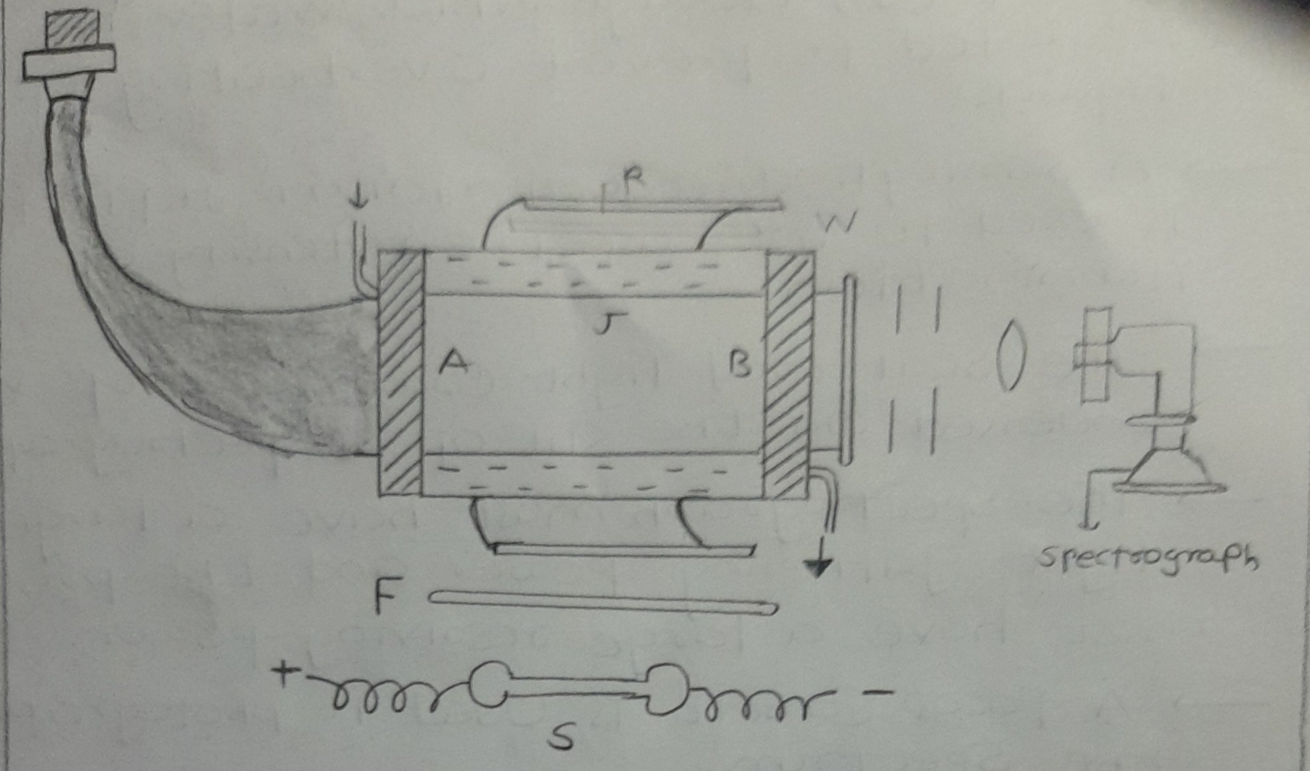
## * Experimental Study of Raman Effect :

⊙ Principle :- To illuminate the substance under test with an intense monochromatic source of light & photograph the scattered radiation by means of a spectrograph arranged in transverse direction. But the technical details are vary according to nature of substance i.e. liquid, gas, solid.

⊙ Apparatus :-

→ The apparatus shown in below fig. was designed by wood & it is used to study Raman effect in liquids.

→ ~~Fi~~



Experimental study of Raman effect

AB → glass tube
W → Optical plane glass tube
H → Horn
F → Filter
R → Reflector
J → Water Jacket

## ⊙ Experimental Study :-

→ It Consists of glass tube AB about 1 to 2 cm in diameter & 10 to 15 cm long, Containg the pure experimental liquids from dust and air bubbles.

→ The tube is closed at one end by an Optically plane glas plate W and at the other end it is drawn into a horn(H) and blackened on the outside.

→ Light from a mercury arc S is passed through a filter F which allows only monochromatic radiation of $\lambda = 4358\,\text{Å}$ to pass through it.

→ The tube is surrounded by a water jacket (J) through which water is circulated to prevent overheating of the liquids.

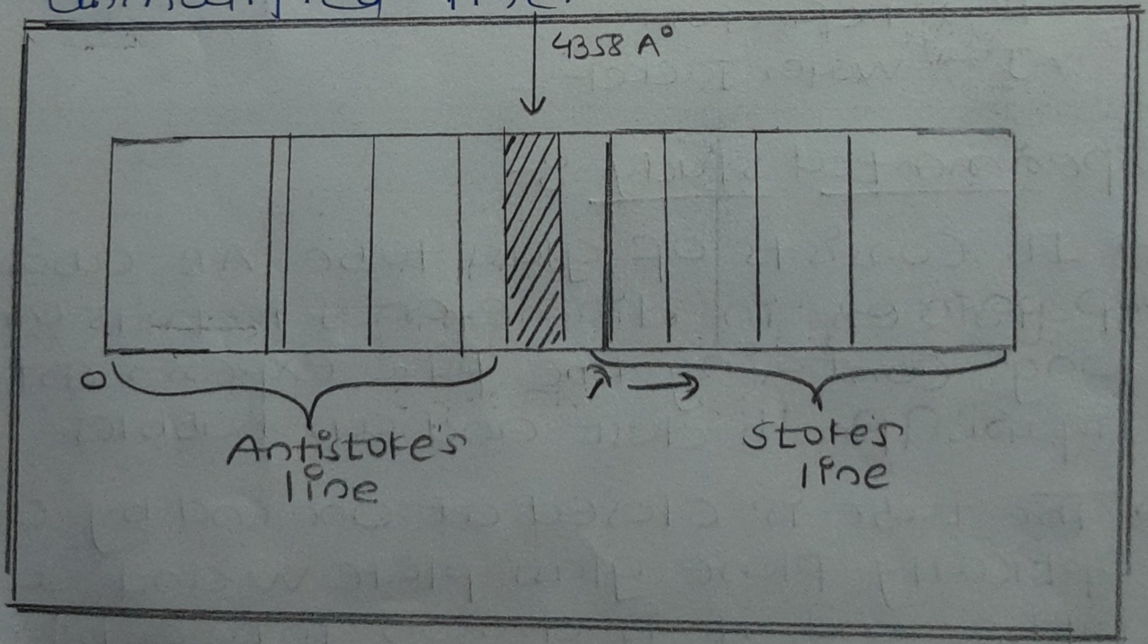
→ A semicylindrical aluminium reflector R is used to increase the intensity of illumination.

→ The scattered light coming out of W is condensed on the slit of a spectrograph

→ The spectrograph must have a large light gathering power and the prism must have a large resolving power.

→ A focus camera is used to photograph the spectrum.

→ On developing the photographic plate, it exhibits a number of stokes's lines, a few antistokes's lines and a strong unmodified line.



* characteristics of Raman Lines :-

(I) The stokes lines are always more intense than antistokes lines.

(I) The Raman lines are symmetrically displaced about the parent line.

(II) The frequency differences between the modified and the parent line represents the frequency of the corresponding infrared absorption line.