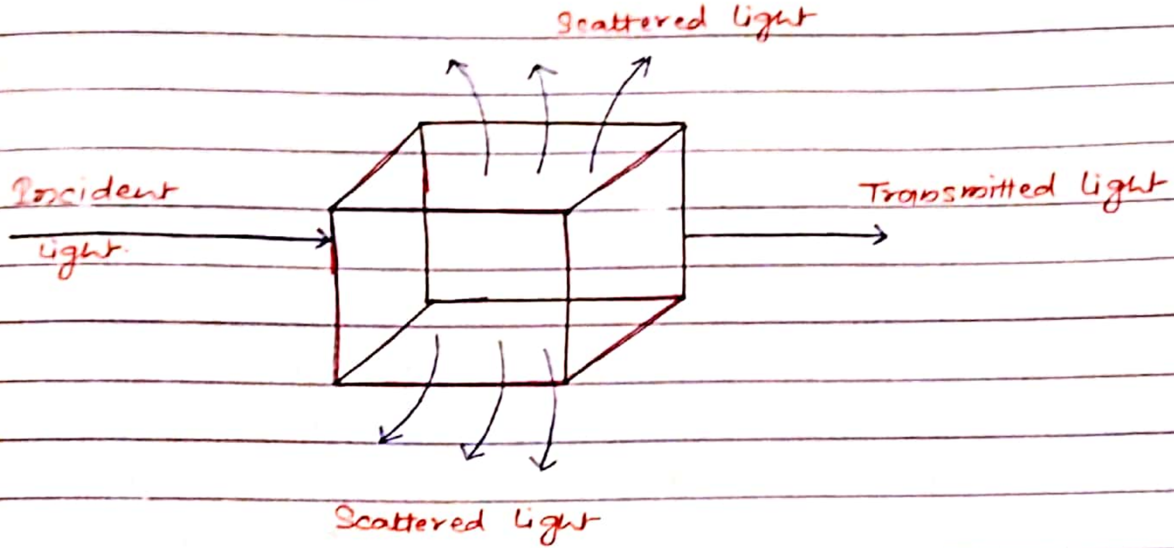
* RAMAN SPECTRA :-

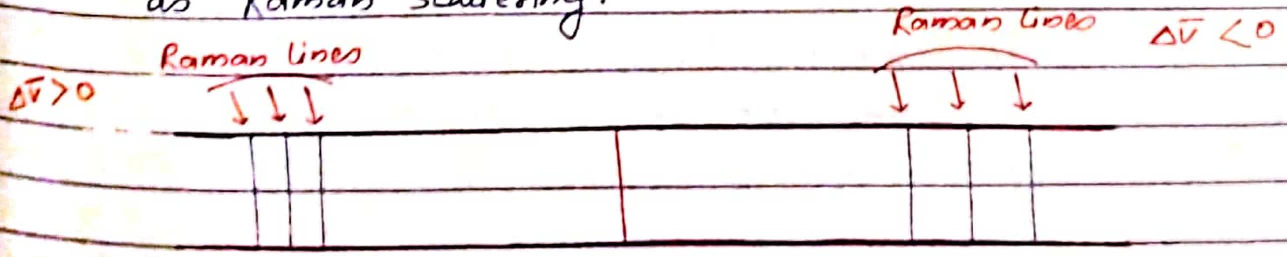
* Introduction :-



-: Scattering of light by non-absorbing Substance :-

* Theory :-

When a beam of light falls on a substance, it may be transmitted, absorbed or scattered. If the substance is transparent and doesnot absorb in the visible region of the electromagnetic spectrum, nearly all of the incident light is transmitted. Small fraction of the incident light emerges in all direction which is due to scattering. If the light is monochromatic, nearly all of the scattered light is observed to be of the same frequency as the incident light. This is known as Rayleigh Scattering. But longer exposure show that light of discreate frequency also scattered. This phenomenon is known as Raman Scattering.



The frequency difference between ~~Rayligh~~ Rayleigh line and Raman lines is independent of the frequency of the incident line but is characteristic of scattering substances. This difference is known as Raman Shift.

*. Classical Theory of Raman effect :—

When a molecule is placed in static electric field it undergoes some deformation. Since, electronic cloud is attracted towards positive pole of the field and positively charged nucleus to the negative pole. This seperation of charge gives rise to an induced dipole moment "μ_i" and the molecule is said to be polarised. The magnitude of 'μ_i' depends on the intensity of electric field E'.

i.e. $\mu_i \propto E$

or $\mu_i = \alpha \cdot E$ ——— ①

where α is the polarizability of the molecule which is a measure of ease of deformability.

When a sample of molecule is subjected to a beam of radiation of frequency 'ν_i' each molecule in it experiences an electric field which varies according to the equation —

$E = E_0 \sin 2\pi \nu_i t$ ——— ②

Thus, the time dependent dipole moment is induced in the molecule and from eqs ① and ② —

$\mu_i = \alpha \cdot E_0 \sin 2\pi \nu_i t$ ——— ③

a/c to electromagnetic theory an oscillating dipole emits radiation whose frequency is same as that of incident frequency so eqn - ③ gives the classical explanation of Rayleigh scattering.

But the molecule itself undergoes some motion like vibration or rotation which changes the ~~polag~~ polarizability periodically and then rotational or vibrational oscillation will superimpose on the dipole.

let us consider a vibrational frequency ν_0 which changes the polarizability in the molecule then the change in polarizability may be written as—

$$\alpha = \alpha_0 + \beta \sin 2\pi \nu_0 t \quad \text{———} \; ④$$

where, α_0 = Polarizability in the equillibrium position.

β = change in polarizability.

Now comparing eqn - ③ and eqn - ④

$$\mu_i = (\alpha_0 + \beta \sin 2\pi \nu_0 t)\, E_0 \sin 2\pi \nu_i t$$

$$[2 \sin A \cdot \sin B = \cos(A-B) - \cos(A+B)]$$

$$\mu_i = \alpha_0 \cdot E_0 \sin 2\pi \nu_i t + \beta E_0 \sin 2\pi \nu_0 t \cdot \sin 2\pi \nu_i t$$

$$\mu_i = \underset{I}{\alpha_0 E_0 \sin 2\pi \nu_i t} + \underset{II}{\tfrac{1}{2} \beta E_0 \cos(\nu_i - \nu_0) 2\pi t} - \underset{III}{\tfrac{1}{2} \beta E_0 \cos(\nu_i + \nu_0)} \cdot 2\pi t \quad \text{———} \; ⑤$$

Thus, the induced dipole moment has three components—

(1). Having same frequency as that of incident frequency (Rayleigh frequency).

$\nu_i \pm \nu_0$ ⟶ Raman shift.

(i). $\nu_i + \nu_0 \longrightarrow$ Anti-Stoke's line.

(ii): $\nu_i - \nu_0 \longrightarrow$ Stoke's line.

* Selection rule for Raman-spectra of Diatomic molecule :-

$\Delta J = 0$ or ± 2 only.

we know that the Rotational energy levels of linear molecule is—

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

where,

$[J = 0, 1, 2 \text{-----}]$

But in Raman spectroscopy we neglect the centrifugal distortion constant then the above expression becomes—

$$\boxed{E_J = BJ(J+1) \text{ cm}^{-1}}$$

where $J = 0, 1, 2 \ldots$

The difference of wave no. between two level is—

$$\boxed{\Delta E_J = BJ'(J'+1) - BJ''(J''+1) \text{ cm}^{-1}} \quad \text{———} ①$$

for the selection rule —

$$\Delta J = J' - J'' = 2$$

$$J' = 2 + J''$$

$$\Delta E_J = B(J''+2)(J''+2+1) - BJ''(J''+1)$$

$$\Delta E_J = B(J''+2)(J''+3) - BJ''(J''+1)$$

$$\Delta E_J = (BJ''+2B)(J''+3) - BJ''(J''+1)$$

$$\Delta E_J = BJ''^2 + 3BJ'' + 2BJ'' + 6B - BJ''^2 - BJ''$$

$$\Delta E_J = 4BJ'' + 6B$$

$$\boxed{\Delta E_J = B(4J''+6)\ cm^{-1}}$$ For S-branch

where $J'' = 0, 1, 2 \ldots\ldots$

Similarly

for the selection rule

$$\Delta J = J' - J'' = -2$$

$$J'' = J' + 2.$$

$$\Delta E_J = BJ'(J'+1) - B(J'+2)(J'+3)$$

$$\Delta E_J = BJ'^2 + BJ' - BJ' + 2B(J'+3)$$

$$\Delta E_J = BJ'^2 + BJ' - (BJ'^2 + 3BJ' + 2BJ' + 6B)$$

$$\Delta E_J = \cancel{BJ'^2} + BJ' - \cancel{BJ'^2} - 5BJ' - 6B$$

$$\Delta E_J = -4BJ' - 6B$$

$$\boxed{\Delta E_J = -B(4J'+6)\ cm^{-1}}$$ for S-branch.

where, $J' = 0, 1, 2 \ldots\ldots$

Thus, the Raman lines will appear at wave number given by the expression.

The existance of the Raman line depends on B. i.e. The change in polazability of the molecule with vibration and the corresponding spectrum ~~and~~ are called vibrational-rotational spectrum. So in order to Raman active a molecular vibration or rotation must cause the change in polazability of the molecule. through the equation — ⑤ is constant with experimental observation of Raman spectra to a considerable extent but still. There is a marked aggrement. The eq — ⑤ pridict that the pair of Raman line with the same absolute value of the frequency shift to be appear in the spectrum with equal intensity but it is observed that the lines on the high frequency side of the Rayleigh line are very weak as compared to the low frequency side.