molecules are often found to be active. active. molecules are not found

4.5. Mechanism of Raman Effect

Raman effect is much more complex than ordinary infrared absorption and full quantum theory i being worked out. Once again the classical theory is able to explain the existence of the Raman effect w as the quantum theory is needed to predict selection rules and intensities correctly.

1. *Classical Theory of Raman Effect.* When an electric field is applied to a molecule, its electrons nuclei are displaced. Thus, an induced dipole moment is produced in the molecule due to displacement of the electrons and nuclei, and the molecule is said to be polarized. Suppose E is strength of electronic field and μ is the magnitude of induced dipole moment. Then, we can

$$\mu = \alpha E$$

where α is termed as the polarizability of the molecule.

When a sample of molecules, which can be polarised, is subjected to a beam of radiation of frequen ν, the electric field experienced by each molecule varies according to the following equation

$$E = Eo \sin 2\pi\nu t$$

and, therefore, the induced dipole undergoes oscillations of frequency, ν, *i.e.*,

$$\mu = \alpha E = \alpha Eo \sin 2\pi\nu t$$

Such an oscillating dipole emits radiation of its own frequency, ν. Thus, equation (4.4), explains the Rayleigh's scattering. In deriving equation (4.4), vibration and rotation of molecules have not bee considered.

(a) *Effect of vibration.* If a molecule undergoes vibratory motion, this changes the polarizabil periodically and then the oscillating dipole will have superimposed upon it the vibrational oscillat Suppose a vibration of frequency ν_{vib} changes the polarizability. Then, one can write.

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_{vib}t$$

where α_0 = the equilibrium polarizability and

β = the rate of changes of polarizability with the vibration. Substituting equation (4.5) in (4 we get

$$\mu = \alpha E = (\alpha_0 + \sin 2\pi\ \nu_{vib}t)\ E_0 \sin 2\pi\nu t$$

or $\mu = \alpha_0 E_0 \sin 2\pi\nu t + \frac{1}{2}\beta E_0\ [\cos 2\pi(\nu-\nu_{vib})t - \cos 2\pi(\nu+\nu_{vib})t]$ (4

From the equation (4.6) it is evident that the induced oscillating dipole has frequency components $\nu \pm \nu_{vib}$ as well as the exciting frequency ν. It means that the induced dipole oscillates wit frequencies $(\nu+\nu_{vib})$ and $(\nu-\nu_{vib})$ which are more and less than the frequency of incident radiation and thus predict the existence of Raman effect. Thus, the Raman shift will be as follows :

$$\text{Raman shift} = (\nu+\nu_{vib}) - \nu = \nu_{vib}$$ (4.7

Thus, we find that the oscillating dipole has three distinct frequency components : (i) the exciting frequency ν with amplitude $\alpha_0 E_0$ (ii) $\nu-\nu_m$ and (iii) $\nu+\nu_m$ with very small amplitudes=(½) (∂α ∂q)$q_0 E_0$. Hence, the Raman spectrum of a vibrating molecule consists of a relatively intense band at the incident frequency and two very weak bands at frequencies slightly above and below that of the intense band.

If, however, the molecular vibration does not change the polarizability of the molecule, then $(\partial\alpha/\partial r)=0$ so that the dipole oscillates only at the frequency of the incident (exciting) radiation). The same is true of the molecular rotation. We conclude that *for a molecular vibration or rotation to be active in the Raman spectrum, it must cause a change in the molecular polarizability*

i.e., $\partial\alpha/\partial r \neq 0$ (4.7 A)

Homonuclear diatomic molecules such as H_2, N_2, O_2, which do not show IR spectra since they do not possess a permanent dipole moment, *do show Raman spectra since their vibration is accompanied by a change in polarizability of the molecules*. As a consequence of the change in polarizability, there occurs a change in the induced dipole moment at the vibrational frequency.

(b) *Effect of rotation*. Let us now discuss the effect of rotation of molecule on polarizability. When a diatomic molecule rotates, the orientation of a molecule varies with respect to the electric field of rotation. If the molecule is not optically isotropic (*i.e.*, it is exhibiting different polarizabilities in different directions), the polarization will vary with time. If we express variation of α by an equation identical to equation (4.5), we have

$$\alpha = \alpha_0 + \beta' \sin 2\pi (2\nu_r)t \qquad (4.8)$$

where ν_r is the frequency of rotation. In equation (4.8) it is important to note that $2\nu_r$ is used because a rotation through π angle will bring the diatomic molecule in a position in which the polarization becomes same as initially. On substituting equation (4.8) in (4.4) we get

$$\mu = \alpha_0 E_0 \sin 2\pi\nu t + \tfrac{1}{2}\beta' E_0 [\cos 2\pi (\nu-2\nu_r)t - \cos 2\pi (\nu+2\nu_r)t] \qquad (4.9)$$

From the above equation (4.9), it follows that the frequency of Raman lines will be $(\nu+2\nu_r)$ and $(\nu-2\nu_r)$. In this case the Raman shift would be

$$\text{Raman shift} = (\nu+2\nu_r) - \nu = 2\nu_r \qquad (4.10)$$

From equation (4.10), it follows that the Raman shift would be equal to twice the frequency of rotation of molecule.

2. *The Quantum Theory of Raman Effect*. According to this theory, the Raman effect may be regarded as the outcome of the collisions between the light photons and molecules of the substance.

Suppose a molecule of mass m in the energy state E_p is moving with a velocity v and is colliding with a light photon $h\nu$. Suppose this molecule undergoes a change in its energy state as well as in its velocity. Let this new energy state be E_q and the velocity be v' after suffering a collision. If we apply the principle of conservation of energy, we can write

$$E_p + \tfrac{1}{2}mv^2 + h\nu = E_q + \tfrac{1}{2}mv'^2 + h\nu' \qquad (4.11)$$

In can be easily proved that the change in velocity of the molecule is practically negligible. Thus, equation (4.11) may be written as

$$E_p + h\nu = E_q + h\nu' \qquad (4.12)$$

or
$$\nu' = \nu + \frac{E_p - E_q}{h} \qquad (4.13)$$

or
$$\nu' = \nu + \Delta\nu \qquad (4.14)$$

From equation (4.13) three cases may arise :

(i) If $E_p = E_q$, the frequency difference (Raman shift) $\Delta\nu$ (*i.e.* $(E_p - E_q)/h$ is zero. It means that $\nu' = \nu$ and this refers to the unmodified line where the molecule simply deflects the photon without receiving any energy from it. The collision thus being elastic is analogous to **Rayleigh scattering**.

(ii) $E_p > E_q$, then $\nu' > \nu$ which refers to the anti-Stoke's lines. It means that the molecule was previously in the excited state and it handed over some of its intrinsic energy to the incident photon. Thus, the scattered photon has greater energy.

(iii) If $E_p < E_q$, then $\nu' < \nu$. This corresponds to Stoke's lines. The molecule has absorbed some energy from the photon and consequently the scattered photon will have lower energy.

As the change in the intrinsic energy of the molecule is governed by the quantum rules, one ca write.

$$E_p - E_q = \pm nh\nu_c \qquad (4.1$$

where $n=1, 2, 3,.....$ etc. and ν_c is the characteristic frequency of the molecule. In the simplest case when $n=1$, equation (4.15) becomes as

$$\nu' = \nu \pm \nu_c \qquad (4.$$

From the above equation it follows that the frequency difference ($\nu-\nu'$) between the incident and scattered photon in the Raman effect corresponds to the characteristic frequency ν_c of the molecule. The Raman lines are equidistant from the unmodified parent line on the either side, at distances equal to the characteristic frequency of the molecule and they refer to the infrared absorption lines of the scatterer.

The Rayleigh scattering and the Raman scattering are shown schematically in Fig. 4.4.

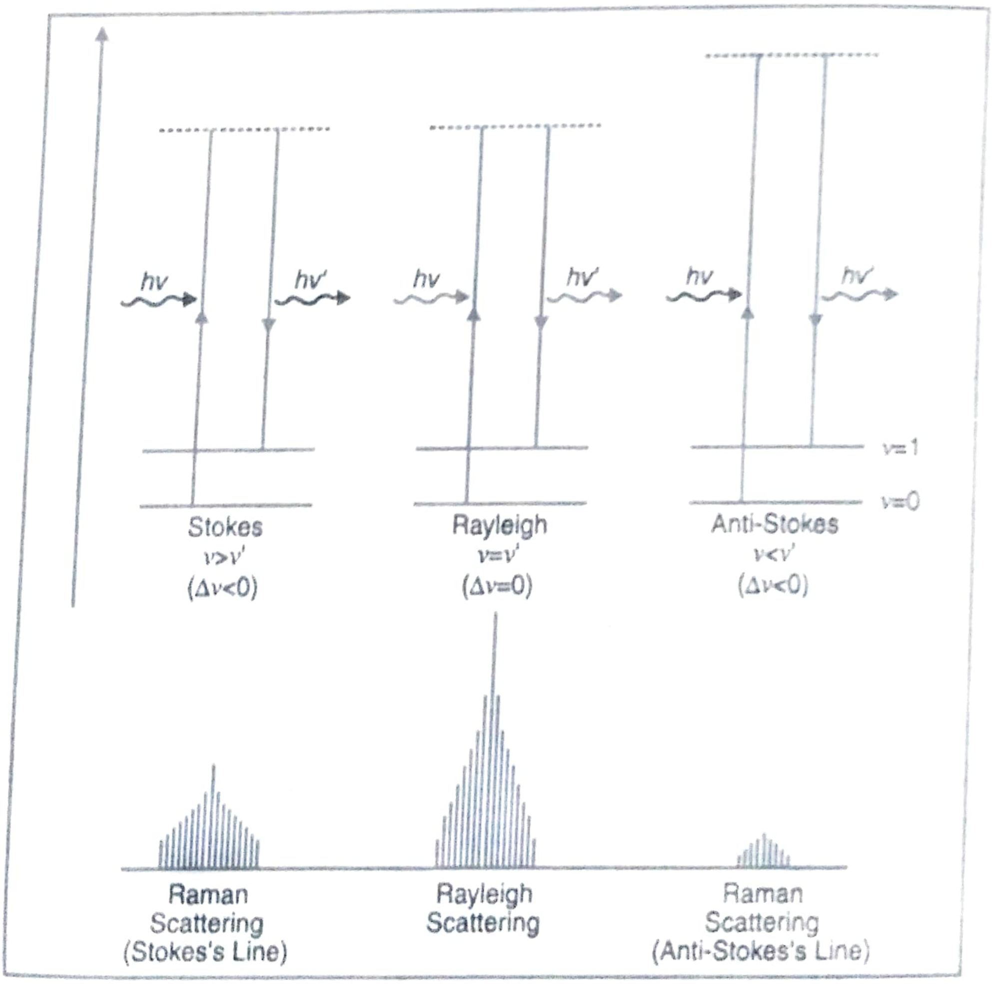

Fig. 4.4 : The Rayleigh Scattering and the Raman Scattering.

We can write Eq. 4.12 as follows :

$$E_p - E_q = h(\nu-\nu') = h\,\Delta\nu_{\text{Raman}} = hc\,\Delta\bar{\nu}$$

This shifts in frequency ($\nu-\nu'$) are called **Raman shifts**. The Raman shifts fall in the range 100–4,000 cm^{-1} for vibrational energy changes. Their values are smaller for rotational energy changes.

Since $\bar{\nu} = 1/\lambda$ we have

$$\bar{\nu}\left(\text{in cm}^{-1}\right) = \frac{10^8}{\lambda\left(\text{in Å}\right)}$$

Hence, Raman shift (in cm^{-1}) is given by

$$\Delta\bar{\nu} = \frac{10^8}{\lambda_{ex}(\text{in Å})} - \frac{10^8}{\lambda_{Raman}(\text{in Å})} \qquad (4.16A)$$

where λ_{ex} is the wave length corresponding to the exciting (incident) frequency.

Example 1. A sample was excited by the 4358 Å line of mercury. A Raman