

Chapter-III

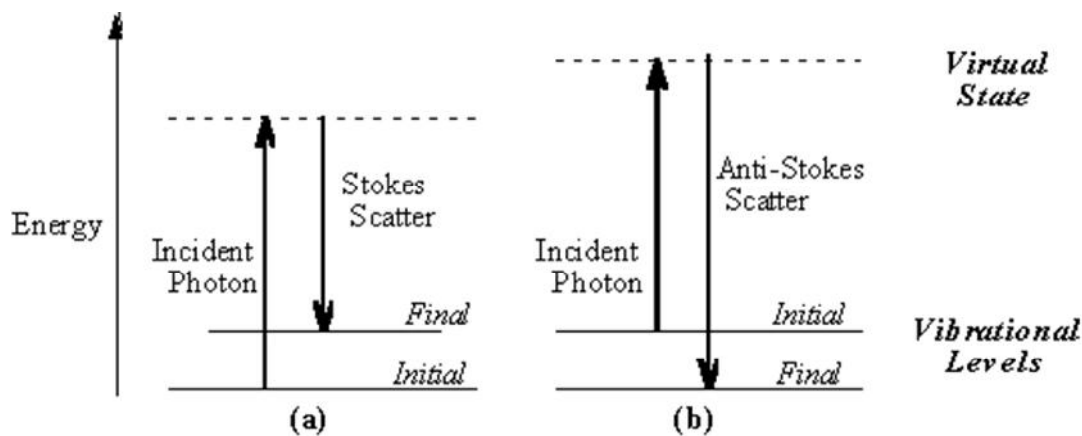
THEORY OF RAMAN EFFECT

1. The Raman Effect:-

The Raman effect was first theoretically predicted by A. Smekal, (1923); followed by quantum mechanical descriptions by Kramers and Heisenberg, (1925) and Dirac, (1927). The first experimental evidence for the inelastic scattering of light by molecules such as liquids was observed by Raman and Krishnan, (1928). It was recognized immediately by Raman that he was dealing with a new phenomenon of a fundamental character in light scattering, something analogous to the Compton effect. In order to establish its identity, Raman employed a mercury arc and a spectrograph to record the spectrum of the scattered light. He then made the startling observation that when any transparent substance (be it solid, liquid, or gas) was illuminated by a mercury arc lamp, and the light scattered by the medium was analyzed with the aid of a spectrograph, the spectrum of the scattered light exhibited over and above the lines present in the spectrum of the mercury arc light; either new lines or, in some cases, bands and generally also unresolved continuous radiation shifted from the present line to different extents. The unmodified radiation constituted the Rayleigh scattering.

The first announcement of the discovery of this phenomenon, namely the appearance of modified radiation in scattering, was made by Professor C.V. Raman on March 16, 1928 at meeting of the South Indian Science Association at Bangalore. In the very first announcement Raman drew special attention to the universality of the phenomenon and its importance for the elucidation of the structure of matter. He further showed that each line of the incident radiation, provided it was of sufficient intensity, gave rise to its own modified scattering and the frequency shifts the relative intensities, the state of polarization and other features of the new lines and bands were independent of the excitation radiation. The new lines were shown to be characteristic of the substance under investigation. After Raman and Krishnan announcement, and almost

simultaneously by Landsberg and Mandelstam, (1928) from solid. After the experimental verification of the Raman Effect, the new scattering technique was mainly used for the investigation of organic and inorganic compounds in liquids or solids state or in solution (Kohlrausch, 1931). With the development of the laser in the 1960's and the appropriate detection devices such as multichannel arrays and charge-coupled devices (CCD cameras), Raman spectroscopy experienced a dramatic growth in analytical applications. Apart from the spectroscopy of phonons Raman effect has been used for studying other quasi particles in solids such as Plasmons and polaritons (Schrotter, 1970). The development of high intensity laser system also led to the discovery of several new nonlinear light-scattering Processes (Long D.A., 1982, Woodbury, E.J., 1962, and Yuratich, M.A., 1977). If light interacts with matter without changing its frequency, the process is called elastic scattering because the photons change only their direction and not their energy. The scattered light has the same frequency as the incident light. Rayleigh scattering is one particular elastic scattering process. The key assumption in Rayleigh's theory is that the scattering particles are small enough as compared to the wavelength of the incident light to consider the electric field independent of space within the particles. Scattering process in which the interaction of the incident photons with the scattering particles (atoms, molecules) causes a change of direction of the photons and a change in energy are called inelastic (scattering) processes, Raman scattering, where the energy change is caused by interaction with the vibrational and rotational movement of the scattering molecules, is such an inelastic scattering process. The Raman effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies. In classical terms, the interaction can be viewed as a perturbation of the molecule's electric field. In quantum mechanics, the scattering is described as an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The scattering event occurs in 10⁻¹⁴ seconds or less. The virtual-state description of scattering is shown in Figure 3.1 a, b.



(a) Stokes Raman scattering

(b) Anti-Stokes Raman scattering

Figure 3.1 a, b Energy level diagram for Raman scattering

The energy difference between the incident and scattered photons is represented by the arrows of different lengths in Figure 3.1a. Numerically, the energy difference between the initial and final vibrational levels, or Raman shift in wavenumbers (cm^{-1}), is calculated through equation (1)

$$V = \frac{1}{\lambda_{\text{Incident}}} - \frac{1}{\lambda_{\text{Scattered}}} \quad \text{--- (1)}$$

in which incident and scattered are the wavelengths (in cm) of the incident and Raman scattered photons, respectively. The vibrational energy is ultimately dissipated as heat. Because of the low intensity of Raman scattering, the heat dissipation does not cause a measurable temperature rise in a material. At room temperature, the thermal population of vibrational excited states is low, although not zero. Therefore, for the majority of molecules, the initial state is the ground state, and the scattered photon will have lower energy (longer wavelength) than

the exciting photon (called Stokes shift). This Stokes shifted scatter is what is usually observed in Raman spectroscopy and is depicted in figure 3.1a.

According to the Boltzman population of states, a small fraction of the molecules are in vibrationally excited states. Raman scattering from vibrationally excited molecules leaves the molecule in the ground state. The scattered photon appears at higher energy, as shown in figure 3.1b. This anti-Stokes-shifted Raman spectrum is always weaker than the Stokes-shifted spectrum, but at room temperature it is strong enough to be useful for vibrational frequencies less than about 1500 cm^{-1} . The Stokes and anti-Stokes spectra contain the same frequency information. The ratio of anti-Stokes to Stokes intensity at any vibrational frequency is a measure of temperature. Anti-Stokes Raman scattering can be used for contact-less thermometry. Furthermore, the anti-Stokes spectrum can also be used when the Stokes spectrum is not directly observable, for example because of poor detector response or spectrograph efficiency.

2. Classical Theory of Raman Effect:-

Most of the experimental results obtained by Raman spectroscopy can be interpreted by simple classical theory, because many of the mathematical expression used are valid under certain conditions even in a quantum mechanical treatment (Placzek, G., 1934). In this classical approach the molecules are described as an ensemble of atoms performing simple harmonics vibrations, without taking into account the quantization of the rotational and vibrational energy levels. According to the classical theory, the incident electromagnetic field induces an electric dipole moment of scattering system (molecule or solid). Such an induced dipole moment is oscillating with the frequency of the incident radiation and is acting as a secondary source for electromagnetic radiation. The light is scattered into a solid angle of 4π . The intensity of the scattered radiation can be deduced from the classical theory as shown in figure 3.2.

The classical description of Raman scattering depicted in above figure is that of a polarization induced in the molecule by the oscillating electric field of

the incoming light, with or without exchanging energy with vibrations in the molecules.

The incident electric (time-dependent) field vector is given by equation (1).

$$\bar{E} = \bar{E} \cos \alpha_L t \quad \text{--- (1) [Since } \omega = 2\pi \nu$$

Which induces the electric dipole moment $\bar{\mu}$, as in equation (2)

$$\mu = \epsilon \alpha E \quad \text{--- (2)}$$

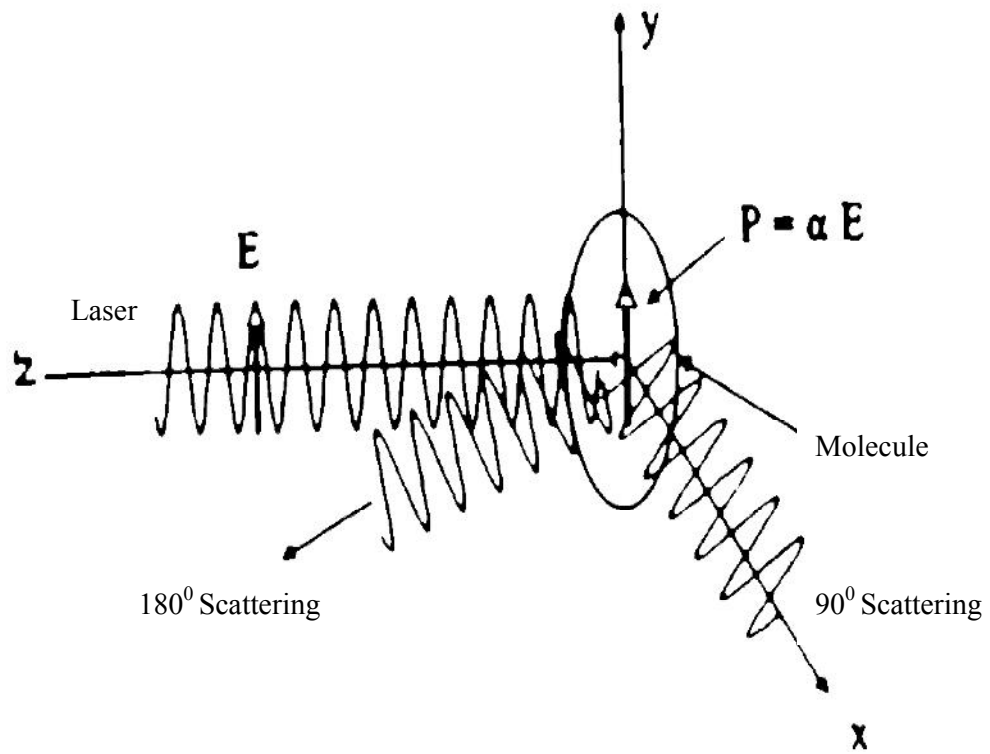


Figure 3.2 Polarization (p) induced in a molecule's electron cloud by an incident Optical Electric field (E)

The proportionality quantity 'α' is the polarizability of the scattering system, E₀ is the amplitude and [ω_L] is the angular frequency of the incident field

' α ' represents a second rank tensors and equation (2) is the short notation of the following linear equation system given in equation (3)

$$\begin{cases} \mu_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\ \mu_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \\ \mu_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \end{cases} \quad (3)$$

According to these equations, the three components of the electromagnetic fields in Cartesian coordinates and the nine components of the polarizability tensors generates three components of the induced dipole moment

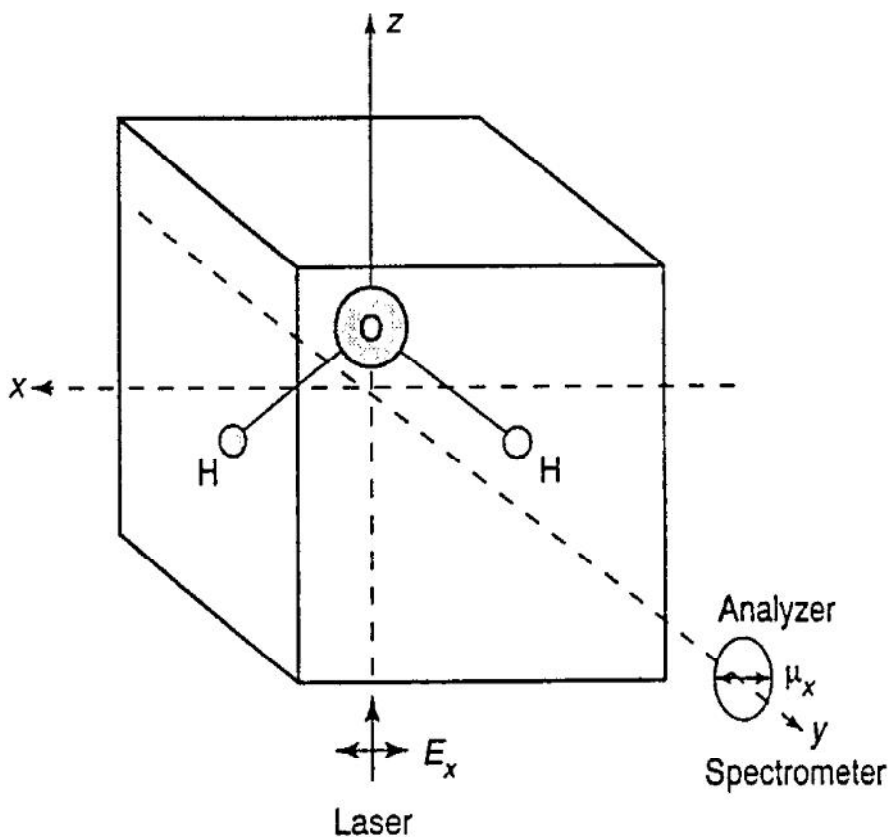


Figure 3.3 Raman scattering geometry of the molecule

(The scattering intensity is collected in the 90° direction)

' α ' is in many cases a symmetric matrix, and thus there are only six independent components for most molecules [$\alpha_{\rho\sigma} = \alpha_{\sigma\rho}$].

First we consider the earliest case that only one component of \bar{E} [e.g. E_x] does contribute to one component of $\bar{\mu}$ [e.g. μ_x]. This corresponds to a Raman scattering geometry, which is depicted in figure 3.3. A water molecule or a crystal is fixed to the xz plane of the Cartesian coordinate system.

The incident radiation propagates in the z -direction and is polarized in the x -direction. According to the interaction of the molecules, different dipole components may be excited inside the molecule. The scattered light is observed at 90° in the y -direction. Using a polarizer, which allows only the observation of x -polarized light, the observed dipole moment is given in scalar form by equation (4)

$$\mu_x = \alpha_{xx} E_x \quad \text{--- (4)}$$

In a simple short notation, without using any indices, equation (4) can be written as equation (5)

$$\bar{\mu} = \alpha \bar{E} \quad \text{--- (5)}$$

Or in combination with equation (1), it becomes equation (6)

$$\mu = E_0 \cos \omega_L t \quad \text{--- (6)}$$

In this case, E_0 represents the amplitude of electric field component, which oscillates in the x -direction and induces the corresponding dipole moment. According to the laws of classical electrodynamics an oscillating electric dipole emits radiation of the same frequency at which the dipole oscillates. If the polarizability ' α ' does not change with time [$\alpha = \text{constant}$], then the induced dipole will re-emit the incident radiation of the angular frequency ω_L [Rayleigh scattering]. However, if the polarizability consists of terms, which depends upon vibrational frequencies, these terms will modulate the incident field. According to such time dependent change in the Polarizability [$\alpha = \alpha\{t\}$] of vibrating

molecules, new frequency components will be observed in the scattered radiation. In order to describe a certain lattice vibration or normal mode of a molecule, a harmonic oscillator with the angular frequency ω_R is considered its time dependent amplitude is given by equation (7)

$$q = q_0 \cos\{\omega_R\} t \quad \text{--- (7)}$$

In the case that the molecular vibration affects the polarizability and if the vibrational amplitude is small, the polarizability can be expanded in a Taylor series around its equilibrium position $q = 0$, to give equation (8).

$$\alpha\{q\} = \alpha_0 + \left\{ \frac{\partial \alpha}{\partial q} \right\}_0 q + \dots \quad \text{--- (8)}$$

Where only terms up to first order are considered. Introducing equation (7), (9), and equation (8) in (2) results in equation (9):

$$\mu = \left[\alpha_0 + \left\{ \frac{\partial \alpha}{\partial q} \right\}_0 q_0 \cos\{\omega_R\} t \right] E_0 \cos(\omega_L) t \quad \text{--- (9)}$$

$$\mu = \alpha_0 E_0 \cos(\omega_L) t + \left\{ \frac{\partial \alpha}{\partial q} \right\}_0 q_0 \cos\{\omega_R\} t E_0 \cos(\omega_L) t$$

OR, alternatively, equation (10):

$$\mu = \underbrace{\alpha_0 E_0 \cos(\omega_L) t}_{\text{Rayleigh scattering}} + \underbrace{\frac{1}{2} \left\{ \frac{\partial \alpha}{\partial q} \right\}_0 q_0 E_0 \cos\{\omega_R - \omega_L\} t}_{\text{Stokes-Raman scattering}} + \underbrace{\frac{1}{2} \left\{ \frac{\partial \alpha}{\partial q} \right\}_0 q_0 E_0 \cos\{\omega_R + \omega_L\} t}_{\text{Anti-stokes Raman scattering}} \quad \text{--- (10)}$$

After assuming [classically] that the polarized electrons will radiate light at the frequency of their oscillations, equation (10) demonstrates that light will be scattered at three frequencies. The first term corresponds to scattering without change of frequency and in phase with the incident light; i.e. coherent Rayleigh scattering its intensity depends only on the molecular polarizability and so this phenomenon will be expected to arise with all substances. The second and

third terms corresponds to scattering with change of frequency i.e. Raman scattering: the low frequency term by analogy with fluorescence is called the stokes-Raman scattering and the high frequency term, the anti-stokes Raman scattering. According to equation (10) the scattered radiation of the induced dipole moment consists of three components with the angular frequencies ω_L , $\omega_S = (\omega_L - \omega_R)$, and $\omega_{AS} = (\omega_L + \omega_R)$, which corresponds to Rayleigh, stokes-Raman and anti-stokes scattering, respectively as in equation (11)

$$\mu = \mu^R + \mu^S + \mu^{AS} \quad \text{---(11)}$$

From this simple derivation one can also deduce that μ^S and μ^{AS} will contribute to the induced dipole moment only, if the polarizability does change during the vibration [$\{\delta\alpha/ \delta q\}_0 \neq 0$]. In order to derive an expression for the Raman intensities, we consider an oscillating electric dipole with angular frequency ‘ ω ’ in equation (12)

$$\mu = \mu_0 \cos \omega t \quad \text{---(12)}$$

Where μ_0 is the amplitude. The total emitted power derived by classical theory is given by Gerthsen, et al (1997), according to equation (13)

$$P = \frac{1}{4\pi\epsilon_0 c^3} |\ddot{\mu}|^2 \quad \text{---(13)}$$

Where $\ddot{\mu}$ is the second derivatives of the dipole moment in respect to time, p is the emitted power, ϵ_0 is the permittivity of vacuum, and ‘ c ’ is the speed of light. Since an optical detector cannot resolve optical frequencies in the order of $\approx 10^{15}$ Hz, an intensity averaged over time will be detected using equation (12) and averaging over time [$\cos^2 (\omega t) = 1/2$] gives the average (over the solid angle of 4π) rate of the total emitted power, as in equation (14)

$$\bar{P} = \frac{1}{4\pi} \frac{2}{3} \frac{1}{4\pi\epsilon_0 c^3} (\mu_0)^2 \quad \text{---(14)}$$

Where \bar{P} is the total emitted power. Thus, the scattered intensity per solid angle in 90° direction [such as depicted in figure 3.3]. Yields equation (15) (Alonso, M., et al, 1977).

$$I = \frac{\bar{P}}{(8\pi/3)} = \frac{[4/12 \cdot \mu_0^3](\mu_0)^2}{(8\pi/3)}$$

After simplification we obtain,

$$I = \frac{\mu^4}{32 \cdot 2 \cdot \mu_0^3} (\mu_0)^2$$

Where 'I' is the scattered intensity per solid angle in the 90° direction. Now, consider a dipole ' μ ' which is located at the origin of a Cartesian coordinate system and does vibrate along a fixed direction from such an oscillating dipole a detector which is located in the y-direction without any polarizer in front, will detect the μ_x and μ_z but not the μ_y component of the scattered intensity, caused by the transverse ness of radiation, shown as in equation (16)

$$I = \frac{\mu^4}{32 \cdot 2 \cdot \mu_0^3} \{(\mu_x)^2 + (\mu_z)^2\} \quad \text{--- (16)}$$

i) Polarizability:-

In the same way as an oscillating induced dipole can be treated as classical electromagnetic emitters. Because of equation (2) and (3), various components of the induced dipole moment contribute to Raman scattering. First, the different contributions to Raman scattering of molecules with fixed orientation in a Cartesian coordinate system (such as crystals) are considered, followed by randomly oriented molecules (such as gases, liquids and amorphous solids). The most common geometry in Raman spectroscopy is a 90° arrangement depicted in figure 3.4. The incident electromagnetic radiation with electric field vector either in the x or y direction propagates along the z-axis. For both polarization cases the induced dipole moments will consist of

three components. Detecting the scattered light in the y-direction allows only the observation of the components μ_x and μ_z , according to equations (17).

$$\begin{array}{l}
 \mu_x = \alpha_{xx} E_x \\
 \mu_z = \alpha_{zx} E_x \\
 \mu_x = \alpha_{xy} E_y \\
 \mu_x = \alpha_{zy} E_y
 \end{array}
 \quad \left. \vphantom{\begin{array}{l} \mu_x = \alpha_{xx} E_x \\ \mu_z = \alpha_{zx} E_x \\ \mu_x = \alpha_{xy} E_y \\ \mu_x = \alpha_{zy} E_y \end{array}} \right\} \text{-----(17)}$$

Therefore, the entire scattering intensity (including the scattered Rayleigh intensity at $\omega = \omega_L$, the Stokes-Raman intensity at $\omega = \omega_S$, and the anti-Stokes Raman intensity at $\omega = \omega_{as}$ in the y-direction for x-polarized light is given by equation (18).

$$I_{x(x+z)} = \frac{\omega^4}{32 \pi^2 \epsilon_0 c^3} \{(\mu_x)^2 + (\mu_z)^2\}$$

$$I_{x(x+z)} = \frac{\omega^4}{32 \pi^2 \epsilon_0 c^3} [(\alpha_{xx})^2 + (\alpha_{zx})^2] (E_x)^2 \text{----- (18)}$$

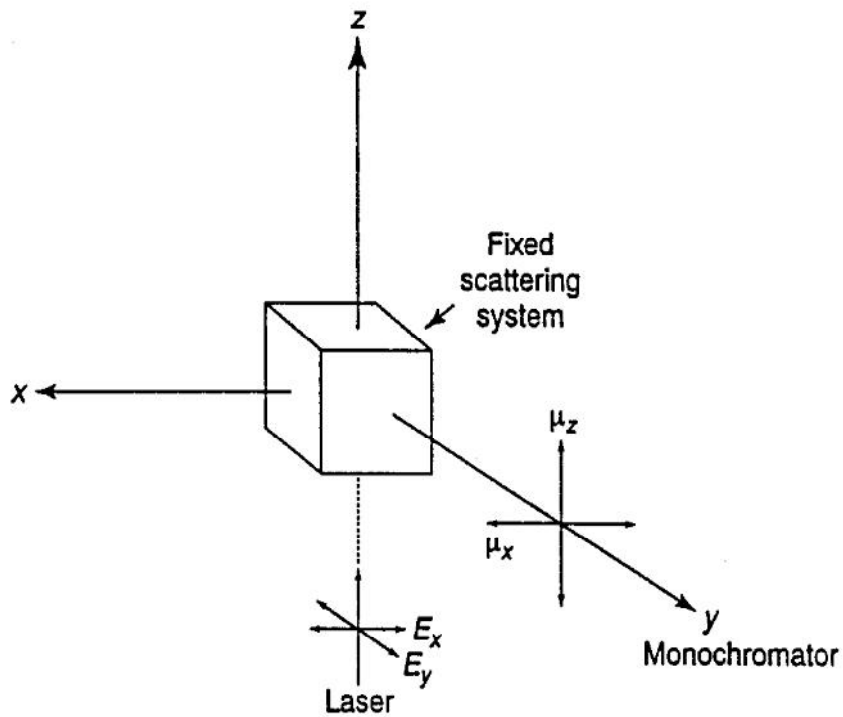


Figure 3.4 Illustration of three mutually perpendicular components of dipole moments μ_x , μ_y and μ_z

And for y- polarized light, equation (19)

$$I_{y(x+z)} = \frac{\omega^4}{32 \pi^2 \epsilon_0 c^3} [(\alpha_{xy})^2 + (\alpha_{zy})^2] (E_y)^2 \quad \text{--- --- --- (19)}$$

Using the incident field intensity ' I_0 ' instead of the field amplitude, (Alonso, M. et al, 1977), gives equation (20)

$$I_0 = \frac{c\epsilon_0}{2} (E_x)^2$$

And similarly we can write

$$I_0 = \frac{c \epsilon_0}{2} (E_y)^2 \quad \text{--- (20)}$$

$$(E_y)^2 = (E_z)^2 = \frac{2I_0}{c\epsilon_0}$$

Combining equation (20) with equations (18) and (19) yields equations (21) and (22)

$$I_{x(x+z)} = \frac{k^4}{16 \pi^2 (\epsilon_0)^2 c^4} I_0 [(\alpha_{xx})^2 + (\alpha_{zx})^2] \quad \text{--- (21)}$$

And

$$I_{y(x+z)} = \frac{k^4}{16 \pi^2 (\epsilon_0)^2 c^4} I_0 |(\alpha_{xy})^2 + (\alpha_{zy})^2| \quad \text{--- (22)}$$

Where the first index indicates the polarization of the incident laser beam and the second index characterizes the polarization of the observed scattering. Since in the example above no polarizer was used in the detection line both components (x and z) of the induced dipole are observed. The use of a polarizer in front of the detector results in the suppression of one component and thus, only one component has to be considered in equation (21) and (22). In the case of a parallel polarized analyzer in front of the detector equations (21) and (22) changes, as given by equations (23) and (24).

$$I_{xx} = \frac{k^4}{16 \pi^2 (\epsilon_0)^2 c^4} I_0 (\alpha_{zy})^2 \quad \text{--- (23)}$$

And similarly,

$$I_{yx} = \frac{I_0^4}{16 \cdot 2 \cdot (\cdot)_0^2 C^4} I_0 (\alpha_{zy})^2 \text{ --- (24)}$$

If a perpendicular polarized analyzer is used the following components of equations (21) and (22) are observed (equations 25 and 26).

$$I_{xz} = \frac{I_0^4}{16 \cdot 2 \cdot (\cdot)_0^2 C^4} I_0 (\alpha_{zx})^2 \text{ --- (25)}$$

$$I_{yz} = \frac{I_0^4}{16 \cdot 2 \cdot (\cdot)_0^2 C^4} I_0 (\alpha_{zy})^2 \text{ --- (26)}$$

Analyzing scattered light from a crystal whose main axes have been oriented parallel with respect to the axes of the chosen scattering geometry allows directly the investigation of the different components of the polarizability tensors. Since the main axes of a crystal can be oriented in different ways the Porto notation (Porto, S.P.S, 1966), has been introduced: a (bc) d, where a and b indicate the propagation direction and the polarization of the incident light wave respectively, and d and c characterize the direction of observation and the polarization of the scattered light respectively. In this section the Raman scattering of randomly oriented molecules such as gases, liquids and amorphous solids is discussed. The scattered Raman intensity can be calculated by averaging over all components of every single molecule over the solid angle of 4π . In those cases one cannot distinguish experimentally between the different components $\alpha_{\rho\sigma}$ of the polarizability tensors. However, there are two invariants of the tensors components $\alpha_{\rho\sigma}$, which are constant regardless of the orientation of the molecules (Long, D.A., 1977). The first invariant is the mean values, which can be expressed as equation (27)

$$\bar{\alpha} = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \text{ --- (27)}$$

And Second, the anisotropy, as in equation (28)

$$\gamma^2 = \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \{(\alpha_{xy})^2 + (\alpha_{yz})^2 + (\alpha_{zx})^2\}] \text{---(28)}$$

According to Wilson, et al (1955), the average squared scattering tensors elements can be written as equations (29) and (30)

$$\overline{(\alpha_{xx})^2} = \overline{(\alpha_{yy})^2} = \overline{(\alpha_{zz})^2} = [45 \sigma^2 + 4 \tau^2/45] \text{---(29)}$$

$$\overline{(\alpha_{xx})^2} = \overline{(\alpha_{yy})^2} = \overline{(\alpha_{zz})^2} = [2 \tau^2/15] \text{---(30)}$$

For a scattering system like in figure 3.4, the scattering intensity of randomly oriented molecules results then in equations (31) and (32)

$$I_{x(x+z)} = \frac{\sigma^4}{16 \pi^2 (r_0)^2 C^4} I_{0N} [45 \sigma^2 + 7 \tau^2/45] \text{---(31)}$$

$$I_{y(x+z)} = \frac{\sigma^4}{16 \pi^2 (r_0)^2 C^4} I_{0N} [2 \tau^2/15] \text{---(32)}$$

Where 'N' is the number of molecules in the scattering volume.

ii) Depolarization Ratio :-

A very useful quantity for the investigation of randomly oriented molecules (gases, liquids, and amorphous solids) is the depolarization ratio 'ρ'. The determination of 'ρ' yields information about the symmetry of vibrations, which makes easier the assignment of experimentally observed Raman vibrations to normal modes of the molecules. The depolarization ratio 'ρ' is calculated from the ratio of two intensities, which can be obtained from Raman measurements with different polarization of incident laser light or the scattered geometry depicted in figure 3.4, where the incident laser beam propagates in the z-direction and is polarized either in the x or y direction, the scattered light is observed at 90° in the y-direction. Depending on the position of a polarizer in front of the detector, the observed dipole moment is either x

or z polarized. This notation can be replaced by using the terms parallel or perpendicular; for example I_{\parallel} (I_{\perp}) indicates that the Raman intensity is measured using a polarizer in front of the detector which is oriented parallel (perpendicular) to the polarization of the incident laser light. The scattering intensity can be obtained by equations (33) and (34)

$$I_{xx} = I_{\parallel} \frac{4}{16 \cdot 2 \cdot (\cdot)_0^2 c^4} I_{0N} [45 \bar{\alpha}^2 + 7 \nu^2/45] \text{ --- --- (33)}$$

$$I_{yx} = I_{\perp} \frac{4}{16 \cdot 2 \cdot (\cdot)_0^2 c^4} I_{0N} [2 \nu^2/15] \text{ --- --- (34)}$$

The depolarization ratio is then defined as equation (35)

$$\rho = \frac{I_{\parallel}}{I_{\perp}} = \frac{3 \nu^2}{[45 \bar{\alpha}^2 + 4 \nu^2]} \text{ --- --- (35)}$$

Since both components $\bar{\alpha}$ and γ can be equal to zero, the value of ' ρ ' can vary between 0 and $3/4$. A Raman band with $\rho = 3/4$ is called depolarized and those with $0 \leq \rho < 3/4$ polarized. Only for totally symmetric vibrations those which maintain all of the symmetry elements of the molecules can α be nonzero resulting in a depolarization ratio $< 3/4$. All other modes have $\rho = 3/4$. Thus, totally symmetric vibrations can be easily distinguished from those, which are not.

We have seen, therefore, that the simple classical treatment of Rayleigh and Raman scattering leads to a fair insight into the phenomenon, showing how stokes and anti-stokes lines arise, how the shifts are related to molecules frequencies and how polarization phenomena arise, and how these are related to the molecular symmetry. However, within the field of classical physics, no explanation is forthcoming as to why anti- stokes lines are weaker than their stokes companions or why certain selection rules holds or what factors governs the intensities of Raman lines. Clearly to proceed further quantum physics will be necessary, and this can be applied in two stages. We

can think of an electromagnetic field interacting with the molecule and then either deal with a classical field and a fully quantized molecule; or go the whole hog and consider a quantized field interacting with quantized molecules (Kiefer, W., 2000).

3. Quantum Theory of Raman Effect:-

D) Vibrational Raman spectra:-

According to this theory, the Raman effect may be regarded as the outcome of the collision between the light photons and molecules of the substance.

Suppose,

v = Velocity of the molecule

m = Mass of the molecule before collision with photon

E_{β} = Energy of the molecule before collision

$h\nu$ = Energy of the incident photon

This molecule will undergo change in its energy after the collision. Then the new energy state of the molecule after the collision will be described on the basis of law of conservation of energy,

$$E_{\beta} + \frac{1}{2} mv^2 + h\nu = E_q + \frac{1}{2} mv'^2 + h\nu' \text{ -----(1)}$$

Where,

v' = Velocity of the molecule after the collision

E_q = Energy after the collision

ν' = Frequency of the photon after the collision

It can be easily proved that the change in velocity of the molecule is practically negligible. Thus, above equation may be written as

$$E_{\beta} + h\nu = E_{\alpha} + h\nu' \quad \text{--- (2)}$$

$$\nu' = \frac{\nu + (E_{\beta} - E_{\alpha})}{h} \quad \text{--- (3)}$$

$$\nu' = \nu \pm \nu_c \quad \text{--- (4)}$$

From equation (3), three cases may arise

- 1) If $E_{\beta} = E_{\alpha}$, the frequency difference (Raman shift), $\Delta\nu$ [i.e. $(E_{\beta} - E_{\alpha}) / h$] = 0. It means that $\nu' = \nu$ and this refers to the unmodified line, where the molecule simply deflects the photon without receiving the energy from it. This collision is elastic and analogous to Rayleigh scattering.
- 2) If $E_{\beta} > E_{\alpha}$ then $\nu' > \nu$ which refers to the anti-stokes 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.
- 3) If $E_{\beta} < E_{\alpha}$ then $\nu' < \nu$. This corresponds to Stokes lines. The molecule has absorbed some energy from the photon and consequently the scattered photon will have lowest energy. From the equation (4), it follows that the frequency difference $(\nu - \nu')$ between the incident and scattered photon in Raman effect corresponds to the characteristic frequency ' ν_c ' of the molecule. Therefore, the characteristic frequency is expressed by the relation.

$$\nu' - \nu = \pm \nu_c \quad (\nu) \quad \text{--- (5)}$$

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.

II) Pure Rotational Raman Spectra :-

The energy of the rigid rotator is given by

$$E_r = \frac{h^2}{8 \cdot 2I_c} J(J + 1)$$

The selection rule for rotational Raman spectrum is as follows,

$$J = 0, \pm 2$$

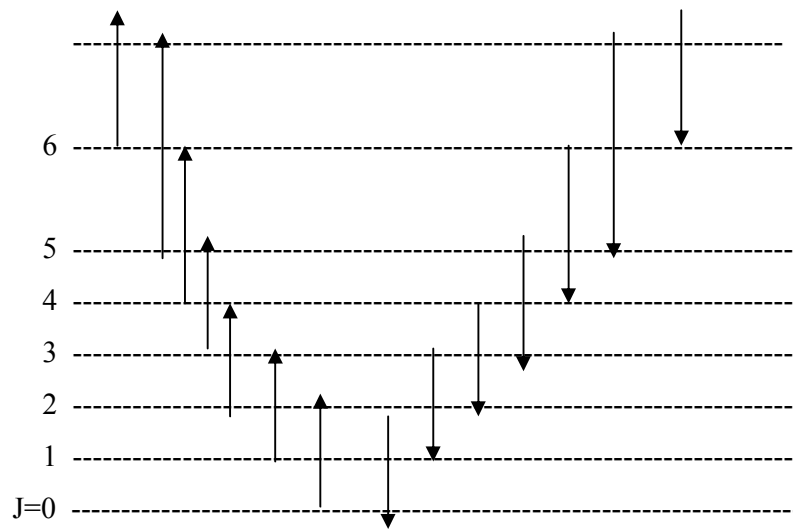
When, $\Delta J = 0$, the scattered Raman radiation will be of the same frequency as that of incident light (Rayleigh's scattering).

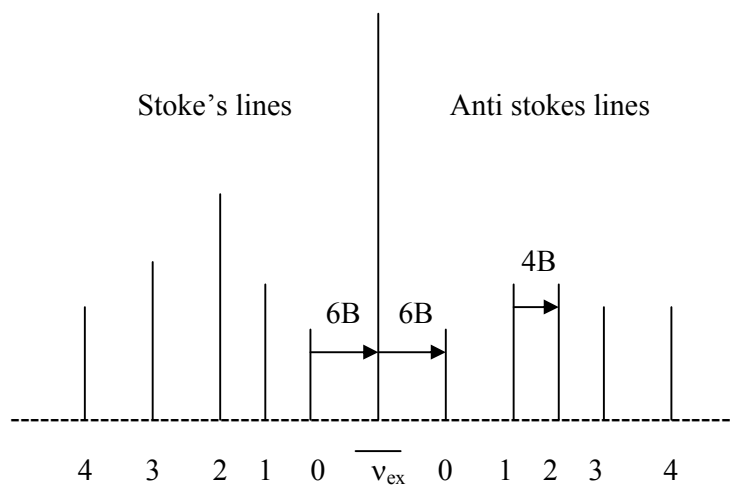
The transition,

$\Delta J = +2$; gives Stoke's lines (longer wavelength) whereas,

$\Delta J = -2$; gives the antistoke's lines (shorter wavelength).

When $\Delta J = +2$, the values of rotational Raman shifts (stoke's lines) will be given by





$$\bar{\nu} = \frac{h^2}{8\pi^2 I_c} [(J + 2)(J + 3) - (J + 1)]$$

$$\bar{\nu} = 2B(2J + 3) \text{ --- --- --- (6)}$$

Where,

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

I_c = moment of inertia of the molecule

When ,

$\Delta J = -2$, the values of rotational Raman shifts (antistoke's lines) will be

given by

$$\bar{\nu} = -2B(2J + 3) \text{ --- --- --- (7)}$$

On combining equations (6) and (7), the Raman shifts can be put in the form of,

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

Therefore, the corresponding Raman shift in terms of wave number $\Delta\nu$ (cm^{-1}) is given by

$$\nu = \bar{\nu}_s - \bar{\nu}_{\text{ex}} \text{ --- --- --- --- --- (8)}$$

Where,

$\bar{\nu}_{\text{ex}}$ = Wave number of exciting radiation

$\bar{\nu}_s$ = Wave number of scattered radiation

The transition and the Raman spectrum are shown in figures (3.5)

From the above figure, it can be seen that frequency separation of successive lines is $4B \text{ cm}^{-1}$ whereas it is $2B \text{ cm}^{-1}$ in the far infrared spectra while on substituting $J=0$ in equation (8). We observe that the separation of the first line from the exciting line will be $6B \text{ cm}^{-1}$ (Chatwal, G., 1987)

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