

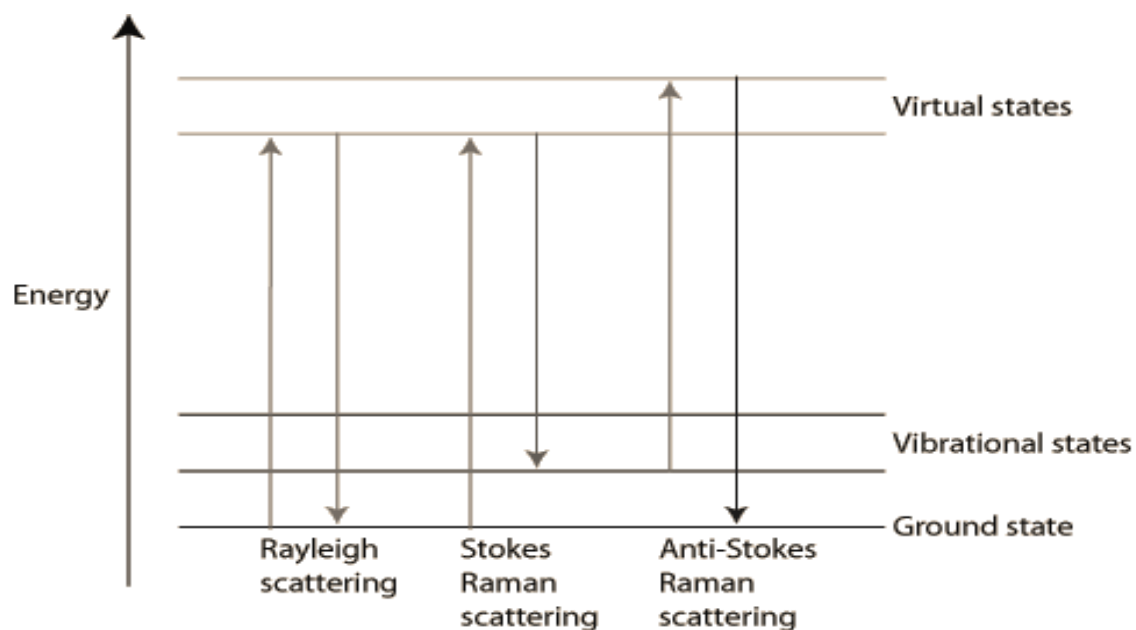
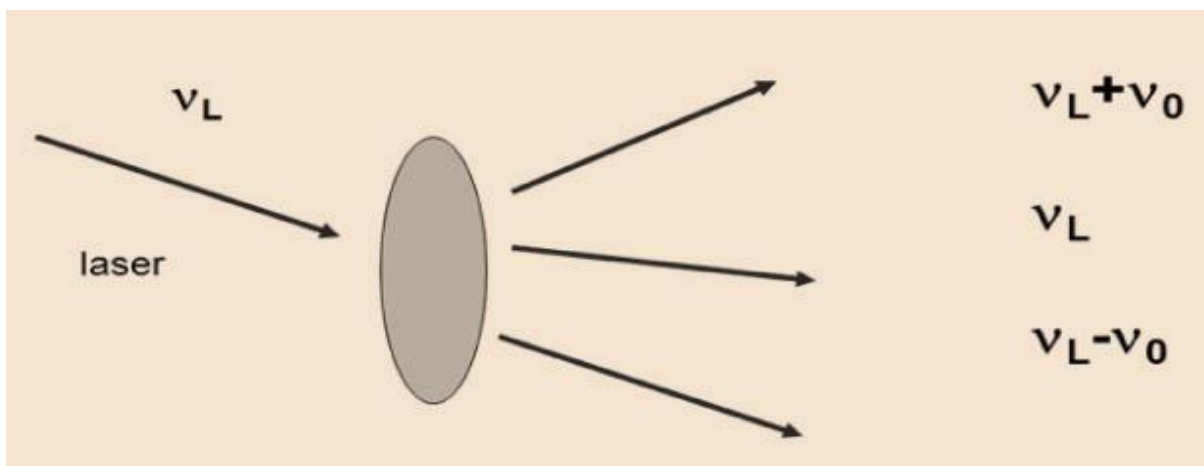
## **UNIT-IV**

### **Raman Spectra**

## 23.1 Raman Effect

When a monochromatic radiations or radiations of very narrow frequency band are scattered by a solid then the scattered radiations not only consists of radiations of incident frequency but also radiations of frequencies above and below that of incident beam frequency. This type of scattering in which the frequency of incident beam undergoes a definite change was observed and was studied by Raman in 1928 and is called as Raman Effect. If  $\bar{\nu}_i$  is the wavenumber of incident wave and  $\bar{\nu}_s$  is the wavenumber of scattered wave then the Raman shift is given by

$$(\Delta\bar{\nu})_{rmn} = \bar{\nu}_i - \bar{\nu}_s$$



This difference is the characteristic of the material which is scattering the waves and it does not depend upon the wavenumber of the incident radiation. If  $(\Delta\bar{\nu})_{\text{Raman}}$  is positive then Raman spectra is said to have Stokes lines and if  $(\Delta\bar{\nu})_{\text{Raman}}$  is negative then the Raman spectra is said to have anti-Stokes lines. The intensity of Stokes lines is higher as compared to anti-Stokes lines. The Raman shift  $(\Delta\bar{\nu})_{\text{Raman}}$  lies within the range 100-3000  $\text{cm}^{-1}$ , which fall in the far and near infra-red region of the spectrum. This shift suggests that the changes in the energy of scattered radiations in the Raman Effect correspond to the energy changes accompanying rotational and vibrational transition in the molecules of the materials.

## 23.2 Classical Theory of Raman Effect

If an atom or a molecule is placed in an electric field then the electrons and the nuclei are displaced relative to each other i.e. an electric dipole moment is induced in the molecule due to this relative displacement of electrons and nuclei. It is also called as molecular polarization by the external electric field. Let  $E$  is the intensity of electric field and  $\mu$  is the magnitude of induced dipole moment then

$$\mu = \alpha E$$

Where  $\alpha$  is the polarizability of the molecule. The intensity of the electric field of the electromagnetic wave of frequency  $\nu$  can be expressed as

$$E = E_0 \sin(2\pi\nu t)$$

So the polarizability of the molecule is given by

$$\mu = \alpha E_0 \sin(2\pi\nu t)$$

So the interaction of radiation of frequency  $\nu$  induces a dipole moment in the atom or molecule. This dipole moment oscillates with same frequency  $\nu$ . So from the classical theory this oscillating dipole will scatter or emit radiation of frequency  $\nu$  i.e. frequency of incident radiations. It is called as Rayleigh scattering.

In the above discussion no internal motion i.e. rotation and vibration of the molecule is considered. Let us first consider the effect of vibrational motion of a diatomic molecule. When the two nuclei of the molecule vibrate along the line joining them then the

polarizability of the molecule will change. The change in the polarizability  $\alpha$ , with small displacement  $x$  from equilibrium position is given by

$$\alpha = \alpha_0 + \beta \frac{x}{A}$$

Where  $\alpha_0$  is the equilibrium polarizability  $\beta$  is the rate of variation of polarizability with displacement and  $A$  is the vibrational amplitude. If the molecule executes the simple harmonic motion then the displacement from the mean position is given by

$$x = A \sin(2\pi\nu_v t)$$

Where  $\nu_v$  is the frequency of vibration of the molecule. So the polarizability of the molecule is given by

$$\alpha = \alpha_0 + \beta \sin(2\pi\nu_v t)$$

So the induced dipole moment is given by

$$\mu = \alpha_0 E_0 \sin(2\pi\nu t) + \beta E_0 \sin(2\pi\nu t) \sin(2\pi\nu_v t)$$

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

Thus the induced dipole moment oscillates with frequencies of radiations  $\nu$ ,  $\nu + \nu_v$  and  $\nu - \nu_v$ . The first frequency is same as that of incident radiations i.e. Rayleigh scattering and last two frequencies are due to Raman scattering. The vibrational shift is equal to  $\nu_v$ .

Now let us consider the effect of rotation of molecule on polarizability. During the rotation of the molecule the orientation of the molecule with respect to electric field of radiation changes, therefore the molecule is not isotropic, it shows different polarizability in different directions. The polarizability of the molecule varies with time. The variation of polarizability can be expressed as

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

Where  $\nu_r$  is the frequency of rotation. The polarizability changes at a rate twice the frequency of rotation, therefore in place of  $\nu_r$  we have written  $2\nu_r$ . The induced dipole moment is given by

$$\mu = \alpha_0 E_0 \sin(2\pi\nu t) + \beta' E_0 \sin(2\pi\nu t) \sin(4\pi\nu_r t)$$

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

The Raman lines will have frequencies  $\nu$ ,  $\nu + 2\nu_r$  and  $\nu - 2\nu_r$ . The Raman shift will be  $2\nu_r$  i.e. equal to twice the frequency of rotation.

So we conclude that in the scattered radiation there will be vibrational lines at  $\nu_v$  on either sides of Rayleigh line  $\nu$  and also rotational Raman lines at  $2\nu_r$  on either sides of  $\nu$ . It is not necessary to have a permanent electric dipole moment to show Raman spectra. So the homo-nuclear molecules also show Raman spectra even though they are IR inactive.

### 23.3.1 Quantum Theory of Raman Effect

When electromagnetic waves are incident on the molecules of a substance then due to absorption of these radiations the molecules are raised to higher state. Now if the molecules return to their original state then the frequency of radiation emitted is same as that of incident light, but if they return to a higher or lower state.

Let us consider a molecule in its initial state having energy  $E''$  and it is exposed to incident radiations of wavenumber  $\bar{\nu}_i$ . Due to absorption of this radiation the molecule is raised to higher energy state having energy  $E'' + hc\bar{\nu}_i$ . Now suppose that the molecule returns to a level of energy level of energy  $E'$  lying above  $E''$ , by losing energy  $hc\bar{\nu}_s$  and wavenumber of scattered radiations is  $\bar{\nu}_s$ .

$$E'' + hc\bar{\nu}_i - hc\bar{\nu}_s = E'$$

$$E' - E'' = hc(\bar{\nu}_i - \bar{\nu}_s) = hc(\Delta\bar{\nu})_{\text{ram}} = \Delta E$$

The Raman shift is equal to the difference in energy of two levels represented by  $E'$  and  $E''$ . The sign of  $(\Delta\bar{\nu})_{\text{ram}}$  depends upon  $(E' - E'')$ , if  $E' > E''$  then  $(\Delta\bar{\nu})_{\text{ram}}$  is positive and hence Raman Stokes lines are produced. If  $E' < E''$  then  $(\Delta\bar{\nu})_{\text{ram}}$  is negative and hence Raman anti-Stokes lines are produced. Classically the intensity of Stokes and anti-Stokes

lines should be same but experimentally it is found that the intensity of Stokes lines is higher as compared to anti-Stokes lines.

### 23.3.2 Probability of Transition in Raman Effect

When an atom or molecule is placed in electric field of intensity  $E$  the electrons and nuclei are displaced in such a manner so as to induce electric dipole moment  $\mu$  given by

$$\mu = \alpha E$$

Where  $\alpha$  is the molecular polarizability. Now if the two nuclei vibrate along the line joining them then the polarizability will vary. For small displacement the variation in the polarizability is expressed as

$$\alpha = \alpha_0 + \beta \frac{x}{A},$$

Where  $\alpha_0$  the equilibrium polarizability is  $\beta$  is the rate of variation of polarizability with displacement and  $A$  is amplitude of vibrations. Let us consider the  $x$  components of polarizability and determine the transition probability as

$$P_{mn}(x) = \int \psi_m^* (\alpha_{xx} E_x) \psi_n d\tau \quad (A)$$

Where  $\alpha_{xx}$  is the polarizability in the  $x$  direction when the electric field  $E_x$  is acting in the same directions. The variation of polarizability  $\alpha_{xx}$  during the oscillation of molecule is given by

$$\alpha_{xx} = \alpha_{xx}^0 + \beta_{xx} \frac{x}{A} \quad (B)$$

Therefore from equation (A) and (B) we have

$$P_{mn}(x) = \alpha_{xx}^0 E_x \int \psi_m^* \psi_n d\tau + \frac{E_x}{A} \beta_{xx} \int \psi_m^* \psi_n d\tau \quad (C)$$

So we conclude from equation (C) as

1. The first term of this equation is zero except  $m = n$ . This term gives rise to a transition which does not involve the vibrational or rotational transitions. This term gives the transition probability of Rayleigh scattering.
2. For Raman scattering  $m \neq n$ , the first term is zero, while for non zero of second term  $\beta_{xx}$  must change during the vibrations.
3. For the molecule to be Raman active it is necessary that the molecular polarizability must change in any direction during the rotations of the molecule.

### 23.3.3 Vibrational Raman Spectra

The vibrational Raman spectrum arises due to transition of molecule from one vibrational level to other vibrational level of same electronic state. Quantum mechanically if  $\beta_{xx}$  is not zero, the molecule will show Raman scattering. From the study of matrix element  $P_{mn}(x)$  of the polarizability, it is found that in case of harmonic oscillator the same selection rule holds for Raman scattering as in case of infra-red spectrum i.e.

$$\Delta v = \pm 1$$

The transition take place only adjacent vibrational levels i.e. from one level to next upper level (Stokes lines) or to the next lower level (anti-Stokes lines). Thus in the Raman spectrum there will be one Stokes and one anti-Stokes line which are shifted by an amount  $|\Delta\bar{\nu}|_{vib}$  to both sides of the original line.

$$|\Delta\bar{\nu}|_{vib} = G(v+1) - G(v) = \bar{\nu}$$

At ordinary temperature most of the molecules are in their lowest vibrational state i.e.  $v = 0$ , so majority of transitions will be of the type  $v = 0$  to  $v = 1$ . A small number of molecules occupy the  $v = 1$  level which may undergo the transitions as  $v = 1$  to  $v = 2$  (Stokes line) or from  $v = 1$  to  $v = 0$  level (anti-Stokes line). The intensity of these will be weak because of small number of molecules in this state. Thus the intensity of the Stokes-Raman lines corresponding to transition  $v = 0$  to  $v = 1$  is much greater than that of anti-Stokes Raman lines corresponding to transition  $v = 1$  to  $v = 0$ . At high temperature the number of molecules in higher vibrational levels increases so the intensities of anti-Stokes lines increases.

The vibrational energy of a diatomic molecule is given by

$$E_v = (v + \frac{1}{2})hc\bar{\nu} - (v + \frac{1}{2})^2 hc x \bar{\nu}$$

For transition  $v=0$  ( ) to  $v=1$  ( ) giving very strong vibrational Raman line

$$E' - E'' = (1 - 2x)hc\bar{\nu}$$

The Raman shift is given by

$$(\Delta\bar{\nu})_{vib} = (1 - 2x)\bar{\nu} = \bar{\nu}_0$$

Where  $\bar{\nu}_0$  is equal to the frequency of the centre of the fundamental vibrational band in the infra-red spectrum of the molecule.

### 23.3.4 Rotational Raman Spectra

These spectra arise due to transition of the molecule from one rotational energy state to the other rotational state of the same vibrational state. These lines appear on both sides of Rayleigh line. The selection rule for rotation Raman transition is different from that of purely rotational transitions (for infra-red). For the Raman Effect the selection rules for transition between rotational levels are as

$$\Delta J = 0, \pm 2$$

The transition corresponding to  $\Delta J = 0$  represents no change in the molecular energy i.e. there is same frequency of scattered Raman radiation (Rayleigh scattering). The transition corresponding to  $\Delta J = +2$  gives Stokes lines while  $\Delta J = -2$  gives the anti-Stokes lines.

The rotational energy levels of a linear molecule are represented by

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

For transition  $\Delta J = +2$ , the value of rotational shift of Stokes lines is given by

$$(\Delta\bar{\nu})_{rot} = \frac{h}{8\pi^2 c I} \{(J+2)(J+3) - J(J+1)\}$$

$$(\Delta\bar{\nu})_{rot} = 2B(2J+3), \text{ Where } B = \frac{h}{8\pi^2 c I}$$

For transition  $\Delta J = -2$ , the value of rotational shift of anti-Stokes lines is given by



$$(\Delta\bar{\nu})_{rot} = -2B(2J + 3)$$

In more general for the Raman Shift due to rotational motion of the molecule is as

$$(\Delta\bar{\nu})_{rot} = \pm 2B(2J + 3), \text{ Where } J = 0, 1, 2, 3, \dots \text{ etc.}$$

The wavenumber of the corresponding spectral lines are given by

$$\bar{\nu} = \bar{\nu}_{exc} - (\Delta\bar{\nu})_{rot}, \text{ Where } \bar{\nu}_{exc} \text{ is the wavenumber of exciting radiations.}$$

### 23.3.5. Vibrational-Rotational Raman Spectra

Theoretically it is possible for vibrational and rotational transitions to take place simultaneously in a Raman transition, the selection rule is as  $\Delta v = \pm 1$  and  $\Delta J = 0, \pm 2$ .

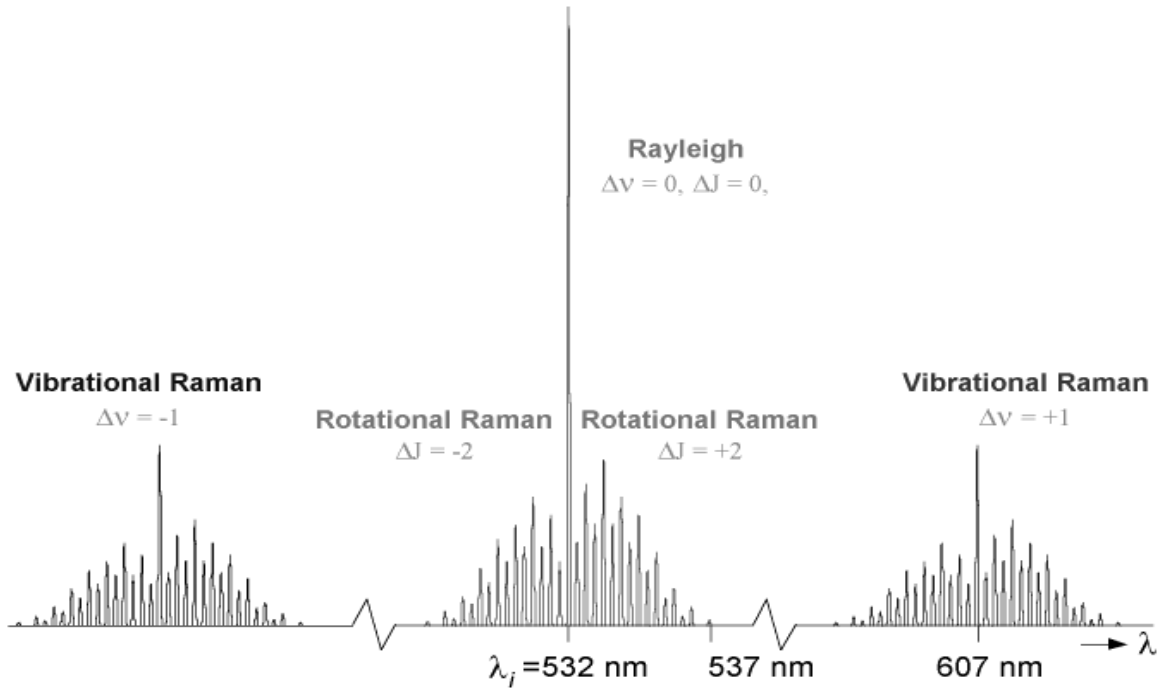
For a diatomic molecule vibrational-rotational energy levels are given by

$$E_{vr} = hc\left\{\bar{\nu}\left(v + \frac{1}{2}\right) - \bar{\nu}x\left(v + \frac{1}{2}\right)^2\right\} + BhcJ(J + 1)$$

Where  $v = 0, 1, 2, 3 \dots$  etc. and  $J = 0, 1, 2, 3, \dots$ , etc.

In terms of wavenumber

$$\bar{\nu}_{vr} = \bar{\nu}\left(v + \frac{1}{2}\right) - \bar{\nu}x\left(v + \frac{1}{2}\right)^2 + BJ(J + 1)$$



Applying selection rules

$$\Delta J = 0 \quad \Delta \bar{\nu}(Q) = \bar{\nu}_0 \text{ cm}^{-1}, \text{ For all } J$$

$$\Delta J = +2 \quad \Delta \bar{\nu}(S) = \bar{\nu}_0 + B(4J + 6) \text{ cm}^{-1}, J = 0, 1, 2, 3, \dots$$

$$\Delta J = -2 \quad \Delta \bar{\nu}(O) = \bar{\nu}_0 - B(4J + 6) \text{ cm}^{-1}, J = 2, 3, 4, \dots$$

Where

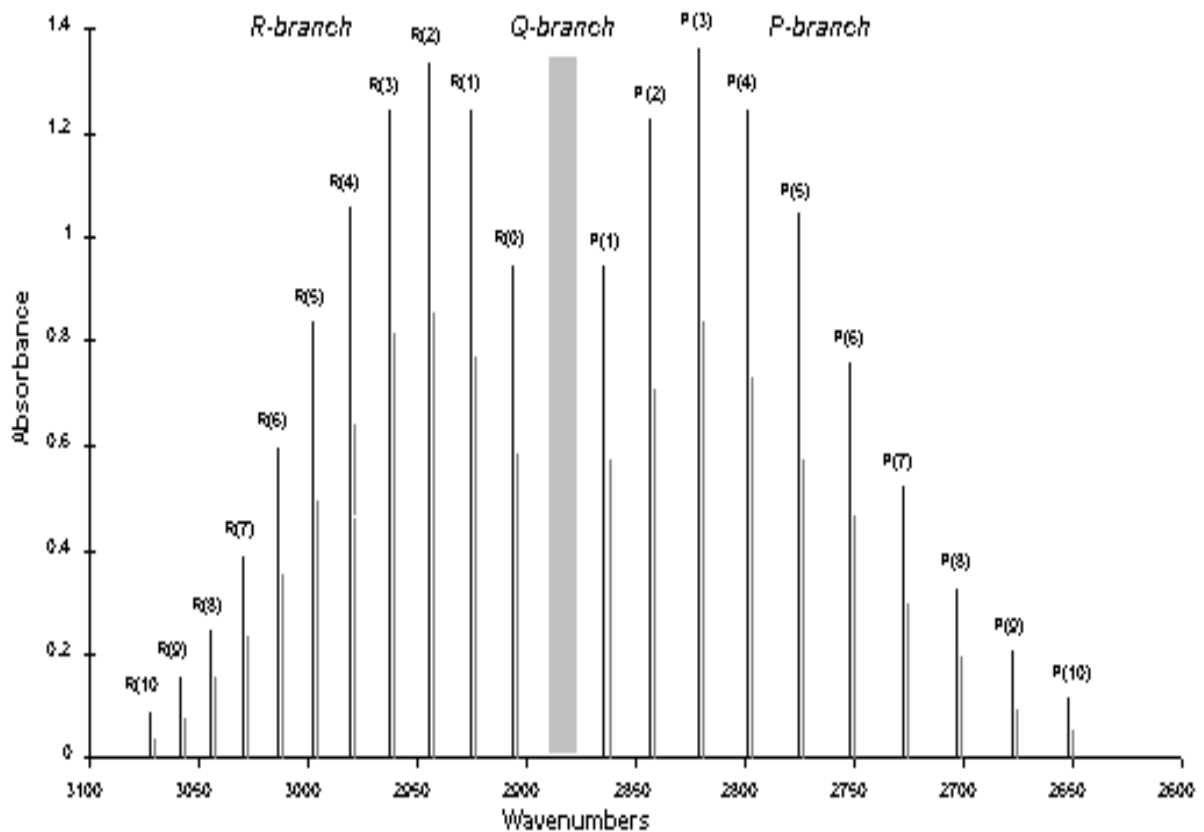
$\bar{\nu}_0 = \bar{\nu}(1 - 2x)$ , and O, Q, S refers to O branch, Q branch, R branch respectively.

The Stokes lines will occur at

$$\bar{\nu}(Q) = \bar{\nu}_{exc} - \Delta \bar{\nu}(Q) = \bar{\nu}_{exc} - \bar{\nu}_0 \text{ cm}^{-1}, \text{ for all value of } J$$

$$\bar{\nu}(O) = \bar{\nu}_{exc} - \Delta \bar{\nu}(O) = \bar{\nu}_{exc} - \bar{\nu}_0 + B(4J + 6) \text{ cm}^{-1}, \text{ for } J = 2, 3, 4, \dots$$

$$\bar{\nu}(S) = \bar{\nu}_{exc} - \Delta \bar{\nu}(S) = \bar{\nu}_{exc} - \bar{\nu}_0 - B(4J + 6) \text{ cm}^{-1}, \text{ for } J = 0, 1, 2, \dots$$



The anti-Stokes lines will occur at

$$\bar{\nu}(Q) = \bar{\nu}_{exc} + \Delta\bar{\nu}(Q) = \bar{\nu}_{exc} + \bar{\nu}_0 \text{ cm}^{-1}, \text{ for all value of } J$$

$$\bar{\nu}(O) = \bar{\nu}_{exc} + \Delta\bar{\nu}(O) = \bar{\nu}_{exc} + \bar{\nu}_0 - B(4J + 6) \text{ cm}^{-1}, \text{ for } J = 2, 3, 4, \dots$$

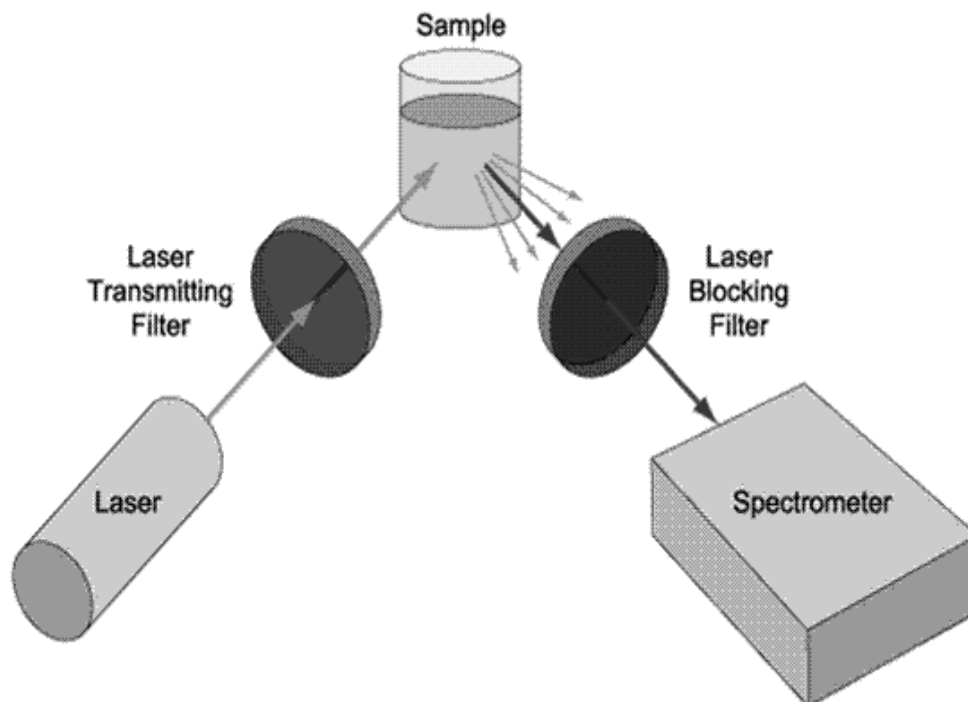
$$\bar{\nu}(S) = \bar{\nu}_{exc} + \Delta\bar{\nu}(S) = \bar{\nu}_{exc} + \bar{\nu}_0 + B(4J + 6) \text{ cm}^{-1}, \text{ for } J = 0, 1, 2, \dots$$

## 23.4 Raman Spectrometer

The instrument required to record the Raman scattering is called as Raman Spectrometer. The recording the Raman spectrum essentially requires illumination of sample with monochromatic radiations and detection of scattered radiations at right angle to incident radiations. The basic components of the Raman Spectrometer are as

- 1. Exciting source:** In the Raman spectrometer we need a monochromatic source of radiations. For this purpose one particular line of mercury arc spectrum is selected. The choice of the wavelength of this line depends upon the intensity

of the line. Nowadays in Raman spectrometer a Helium-Neon laser beam is used.



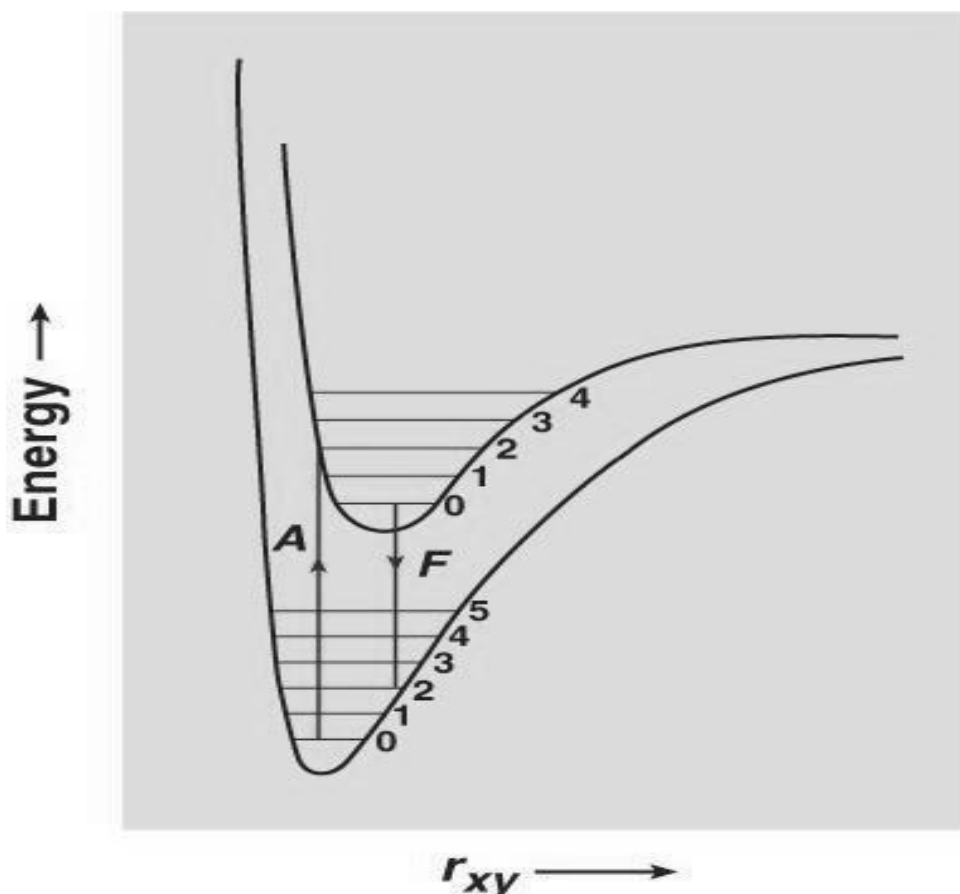
- 2. Sample Tube and Sample:** The material of the sample tube is either glass or quartz. The tube is shaped along with associated reflectors in a way so as to direct much of the incident light into the sample. The length of the tube is 20-30 cm and 12 cm in diameter. To avoid multiple reflections the back of the tube is horn-shaped and blackened. The other end of the tube is made optically flat so that scattered radiations do not suffer any distortion on their exit. The Raman tube is protected from heat generated by lamps by means of a glass jacket through which water circulates. The Raman spectrum can be recorded with solid, liquid and gas phase samples but the liquid sample is more preferred because it is easy to handle it. The quantity of the liquid sample required is between 10-100 mL. Water is a good solvent because of its weak Raman spectrum.
- 3. Filters:** Liquid filters are placed between the source and the sample tube in order to remove high energy radiations that may cause photodecompositions, to isolate single exciting line and to remove the continuous spectrum in the region occupied by the Raman line.
- 4. Optical system:** The optical system is designed so that the maximum amount of scattered Raman radiation is accepted by the spectrometer. A suitable

spectrograph, with prism or grating having wide aperture and medium dispersion is preferred.

### **23.5. Franck Condon Principle**

The Franck Condon principle is related to electronic spectra of the molecules. The electronic spectra of the molecule arise when the electrons in the molecules are excited to higher energy state. The energy involved in this is large so the electronic spectra of the molecules fall in the visible and ultraviolet region of electromagnetic spectrum. The electronic spectra arise due to change in the arrangement of molecular electrons. A small change in electronic energy is accompanied by a large change in the vibrational energy of the molecule and a small change in vibrational energy is accompanied by a large change in rotational energy of the molecule. The vibrational energy changes cause the appearance of various bands and the rotational energy changes cause formation of various lines in each band.

The probability of transition between two given vibrational levels of two different electronic states is given by the Franck-Condon principle. According to this principle “The transition between two vibrational levels should start from extreme position of the levels and they are represented by vertical lines”.



The rearrangement of the electrons in a molecule is 1000 times faster than the time period of vibrations of nuclei. During the electronic transition the inter-nuclear distance does not change appreciably so the transitions are represented by vertical lines. Further, the transitions are most probable when the nuclei in their mean positions. The nuclei spend maximum time in these states because of zero kinetic energy in these states. The square of the vibrational eigen function is maximum at extreme positions implying the probability of finding the nuclei is maximum there. However for lowest vibrational state  $v = 0$ , quantum mechanics predicts that the most probable position for nuclei is the equilibrium position  $r_e$ . Thus the most probable inter-nuclear distance for the vibrational levels other than  $v = 0$ , corresponds to extreme positions and mid-position for  $v = 0$ . So, the transitions will start from extreme position for levels other than  $v = 0$  and for  $v = 0$  the transition will start from mid-point.

## 23.6 Solved Exercises

- Q1. The wavelength of the exciting line in Raman scattering is  $5460 \text{ \AA}$  and Stokes line is observed at  $5520 \text{ \AA}$ . Find the wavelength of anti-Stokes line.

Sol. The Raman shift is given by

$$(\Delta\bar{\nu})_{\text{raman}} = \bar{\nu}_i - \bar{\nu}_s$$

$$\bar{\nu}_i = \frac{1}{5460 \times 10^{-8}} = 18315 \text{ cm}^{-1}$$

$$\bar{\nu}_s = \frac{1}{5520 \times 10^{-8}} = 18116 \text{ cm}^{-1}$$

$$(\Delta\bar{\nu})_{\text{raman}} = 18315 - 18116 = 199 \text{ cm}^{-1}$$

The wavenumber of the anti-Stokes line is given by

$$(\bar{\nu}_s)_{\text{anti-stokes}} = \bar{\nu}_i + (\Delta\bar{\nu})_{\text{raman}} = 18315 + 199 = 18514 \text{ cm}^{-1}$$

The wavelength of anti-Stokes line is given by

$$\lambda = \frac{1}{18514} = 5401 \text{ \AA}$$

Q2. The exciting radiations has wavelength  $4358 \text{ \AA}$  in Raman spectrum of a substance which show lines at  $(\Delta\bar{\nu})_{\text{raman}} = 608, 846, 995, 1599$  and  $3064 \text{ cm}^{-1}$ . At what wavelength these lines will appear if the exciting source has wavelength  $5461 \text{ cm}^{-1}$

Sol. The wavenumber of the exciting line

$$\bar{\nu}_i = \frac{1}{5461 \times 10^{-8}} = 18312 \text{ cm}^{-1}$$

Since the difference remain the same then the wavenumber of Raman lines are as

$$\bar{\nu}_s = \bar{\nu}_i - (\Delta\bar{\nu})_{\text{raman}}$$

So the wavenumbers are as

$$\bar{\nu}_{s1} = 18312 - 608 = 17704 \text{ cm}^{-1}$$

$$\bar{\nu}_{s2} = 18312 - 846 = 17466 \text{ cm}^{-1}$$

$$\bar{\nu}_{s3} = 18312 - 995 = 17317 \text{ cm}^{-1}$$

$$\bar{\nu}_{s4} = 18312 - 1178 = 17134 \text{ cm}^{-1}$$

$$\bar{\nu}_{s5} = 18312 - 1599 = 16113 \text{ cm}^{-1}$$

$$\bar{\nu}_{s6} = 18312 - 3064 = 15248 \text{ cm}^{-1}$$

Q.3 A substance shows a Raman line at  $4567 \text{ \AA}^0$  when exciting line  $4358$  was used. Find the positions of Stokes and anti-Stokes lines for the same substance when exciting line  $4047 \text{ \AA}^0$  is used.

Sol. The Raman shift is given by

$$(\Delta\bar{\nu})_{\text{rm}} = \bar{\nu}_i - \bar{\nu}_s$$

$$\bar{\nu}_i = \frac{1}{4358 \times 10^{-8}} = 22946 \text{ cm}^{-1}$$

$$\bar{\nu}_s = \frac{1}{4567 \times 10^{-8}} = 21896 \text{ cm}^{-1}$$

$$(\Delta\bar{\nu})_{\text{rm}} = 22946 - 21896 = 1050 \text{ cm}^{-1}$$

The wavenumber of the other exciting line is

$$\bar{\nu}'_i = \frac{1}{4047 \times 10^{-8}} = 24710 \text{ cm}^{-1}$$

So the wavenumber of Stokes line is as

$$\bar{\nu}_{\text{stoke}} = 24710 - 1050 = 23660 \text{ cm}^{-1}$$

And the wavenumber of anti-Stokes line is

$$\bar{\nu}_{\text{anti-stoke}} = 24710 + 1050 = 25760 \text{ cm}^{-1}$$

The wavelengths of Stokes and anti-Stokes lines are

$$\lambda_{\text{stoke}} = \frac{1}{23660} = 4226.5 \text{ \AA} \quad \lambda_{\text{anti-stoke}} = \frac{1}{25760} = 3882 \text{ \AA}$$

Q.4 In the rotational Raman spectrum of a molecule the displacement from exciting line is represented by  $(\Delta\bar{\nu})_{\text{rot.}} = \pm(62.4 + 41.6J) \text{ cm}^{-1}$ . Calculate the moment of inertia of the molecule.

Sol. The rotational Raman shift is given by



$$(\Delta\bar{\nu})_{rot.} = 2B(2J + 3)$$

$$(62.4 + 41.6J) = 2B(2J + 3)$$

$$41.6(J + \frac{3}{2}) = 4B(J + \frac{3}{2})$$

$$B = \frac{41.6}{4} = 10.4 \text{ cm}^{-1}$$

The rotational constant B is related to moment of inertia I as

$$B = \frac{h}{8\pi^2 Ic} \quad \text{so} \quad I = \frac{h}{8\pi^2 Bc}$$

$$I = \frac{6.62 \times 10^{-27}}{8 \times (3.14)^2 \times 10.4 \times 3 \times 10^{10}} = 2.7 \times 10^{-40} \text{ gm.cm}^2$$

### 23.7 Self Learning Exercises

- Q1. What is Raman Effect?
- Q2. What is Rayleigh line?
- Q3. Explain Stokes and anti-Stokes lines?
- Q4. Explain the origin of Stokes and anti-Stokes lines.
- Q5. Explain the variation of polarizability of molecule with the electric field of electromagnetic radiations.
- Q6. Explain why the intensity of Stokes and anti-stokes lines is not same?
- Q7. Write the selection rules for Raman vibrational-rotational transitions.
- Q8. Write the basic components of Raman spectrometer.
- Q9. Explain the Franck-Condon principle.
- Q10. Discuss the classical theory of Raman Effect.
- Q11. Discuss the quantum theory of Raman Effect.
- Q12. Explain the fine structure of Raman spectral lines.

## 23.8 Summary

The aim of this unit is to study the spectroscopy technique known as Raman Effect. This technique can be used in place of IR spectroscopy technique but this technique is more versatile as compared to IR technique. The IR technique fails to provide information when the molecules are homo-nuclear in the materials. Since the principle of Raman Effect involves the polarization of molecules by the radiations so the information can also be obtained from this technique. Here first the definition of Raman Effect is discussed and then its classical and quantum theories are developed. The quantum theory is useful to provide the information about the intensity of Stokes and anti-Stokes lines. The selection rules for transitions among the various vibrational levels as well between rotational levels are discussed. The basic components of Raman spectrometer are discussed. Finally there is the discussion on the Franck-Condon principle which predicts the transition probability between two electronic states.

## 23.9 Bibliography

Homo-nuclear:	Same type of nucleus
Hetero-nuclear:	Different type of nucleus
Polar:	Having +ive and -ive charge
Oscillating:	Periodically varying
Polarizability:	measurement of tendency to be polarized
Band:	Group of energy levels or spectral lines
Shift:	Kind of displacement
Accompanying:	Simultaneously
Photodecomposition:	Dissociation by radiations
Scattering:	Absorption and re-emission of radiations

Inter-nuclear:           Between two nucleus.

### **23.10 References and Suggested Readings**

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