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# UNIT 6 : RAMAN SPECTROSCOPY

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## Structure

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## 6.1 INTRODUCTION

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The origin of Raman spectrum lies in the scattering of radiation by molecules. During the scattering of radiation, there is a change in the direction of the photon. For example, the blue colour of the sky is the result of scattering of light by air molecules. The interaction of monochromatic radiation with matter may result in an (i) elastic collision or (ii) inelastic collision. The resultant radiation after an elastic collision will have the same frequency as that of the incident radiation and is known as **Rayleigh scattering**. Thus, in Rayleigh scattering, the frequency of the resultant radiation is the same as that of the incident radiation but the direction of the radiation is changed. On the other hand, if there is an inelastic collision, then the direction as well as the frequency of the resultant radiation would be different from that of the incident radiation. Thus due to inelastic collision, there is a transfer of energy between the electromagnetic radiation and the molecules of the medium. Although the energy thus available for exchange may be stored in the molecule in electronic, vibrational or rotational modes, it is the exchange with the vibrational modes that is of the greatest interest to chemists. The transfer of energy consequent to inelastic collision is of the order of  $3-3000\text{ cm}^{-1}$  which lies in the far infrared to infrared region of the electromagnetic spectrum. These inelastic collisions can, therefore, give us information about the rotations and vibrations of the molecules. The study of such radiation arising out of inelastic collisions is called Raman spectroscopy. In this unit, we shall study the basic concepts related to Raman spectroscopy and its applications.

## Objectives

After studying this unit you should be able to:

- explain the origin of Raman spectrum in terms of classical and quantum mechanical concepts,
- differentiate between infrared and Raman spectroscopy,
- write the selection rules for rotational, vibrational and vibration-rotation Raman spectra,

- describe the rule of mutual exclusion and explain its use in the determination of structure of molecules, and
- illustrate the applications of Raman spectra.

## 6.2 ORIGIN OF RAMAN SPECTRUM

In 1923, Smekal predicted that on irradiation of a substance with a monochromatic light, scattering of radiation will take place and some of the scattered radiation should have different frequencies from that of the incident radiation. In 1928, Raman experimentally established the existence of such frequencies above and below that of the incident beam. However, molecules gain or lose energy according to quantum laws. When the molecules gain energy, the scattered photons will be of lower energy or frequency and appear in the spectrum as Stokes lines. On the other hand, if the molecules lose their energy to the photons, the scattered radiation will appear with higher frequency than the incident radiation, and the resultant lines are called anti-Stokes lines. The main bulk of the scattered radiations will appear unaltered in energy and is termed as Rayleigh scattering.

### 6.2.1 Classical Theory of Raman Spectrum

We can consider the molecules of a substance as a sea of electrons in which the positively charged nuclei are embedded. If such a system is subjected to a static electric field, the electrons will be attracted to the positive pole and the positively charged nuclei will be attracted towards the negative pole. The separation of charges gives rise to induced dipole moment in the molecules. The molecules are then said to be polarized. The magnitude of the induced dipole moment depends on the strength of the applied field ( $E$ ) and the polarizability ( $\alpha$ ) of the molecule.

Polarizability has the dimension of volume and it is considered to be proportional to the volume of the molecule.

$$\mu = \alpha E \quad \dots(6.1)$$

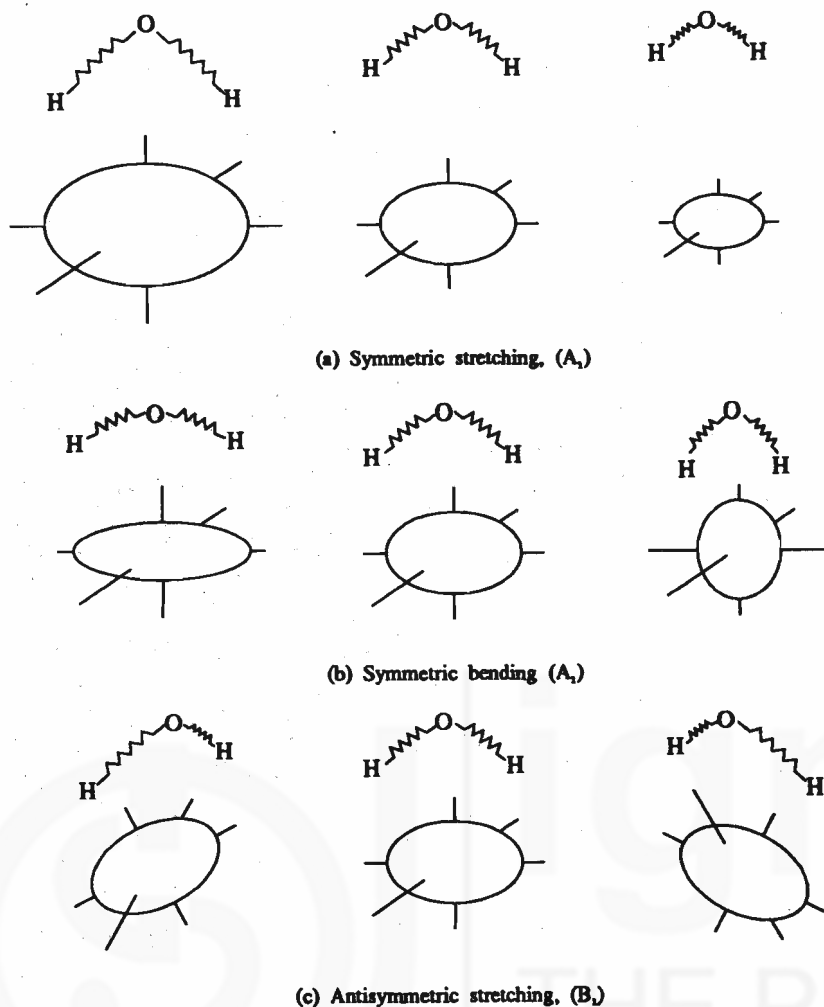
The polarizability of a molecule is a measure of the ease with which a molecule can be distorted. Some molecules may get distorted or deformed much more easily than the others. Polarizability has already been explained in Unit 6 of Block 1 of Atoms and Molecules course. Polarizability of any molecule need not be the same in all directions. For example, even for a simple homonuclear diatomic molecule, the electrons forming the bond can easily be displaced by an electric field applied along the bond axis as compared to the case when the field applied is at right angles to bond axis. In other words, polarizability of molecules is an anisotropic property. The anisotropic nature of molecular polarizability facilitates activity in Raman spectra.

Isotropic property has the same value in all the directions. Density of a substance is an example for isotropic property, since it is same for any portion of a substance, irrespective of the directions.

An anisotropic property has different values along different directions of applications of a force field. X-ray diffraction by crystals is an instance of anisotropic property. The anisotropic nature of polarizability is the main factor deciding the activity in Raman spectra.

Polarizability of a spherical species is an isotropic property. For instance, the polarizability of atoms is isotropic. Polarizability of spherical top molecules (like  $\text{CH}_4$ ,  $\text{SF}_6$ ) is also isotropic.

Using classical theory it is possible to prove that in order to obtain Raman spectrum, the molecular vibration (or rotation) must cause some change in the polarizability of the molecule. We shall just take this result without trying to prove the same. It is possible to depict polarizability changes in terms of polarizability ellipsoids where we represent the polarizability in various directions. The ellipsoid is a three dimensional surface for which the distance from the electrical centre of the molecule is inversely proportional to the square root of the polarizability (i.e.,  $1/\sqrt{\alpha}$ ). Thus where the polarizability is the greatest, the distance from the axis of the ellipsoid is the least and vice versa. During each of the three modes of vibrations of  $\text{H}_2\text{O}$ , symmetric stretching mode ( $\nu_1$ ), bending mode ( $\nu_2$ ) and antisymmetric stretching mode ( $\nu_3$ ), the polarizability changes and hence all the three are Raman active (Fig.6.1).

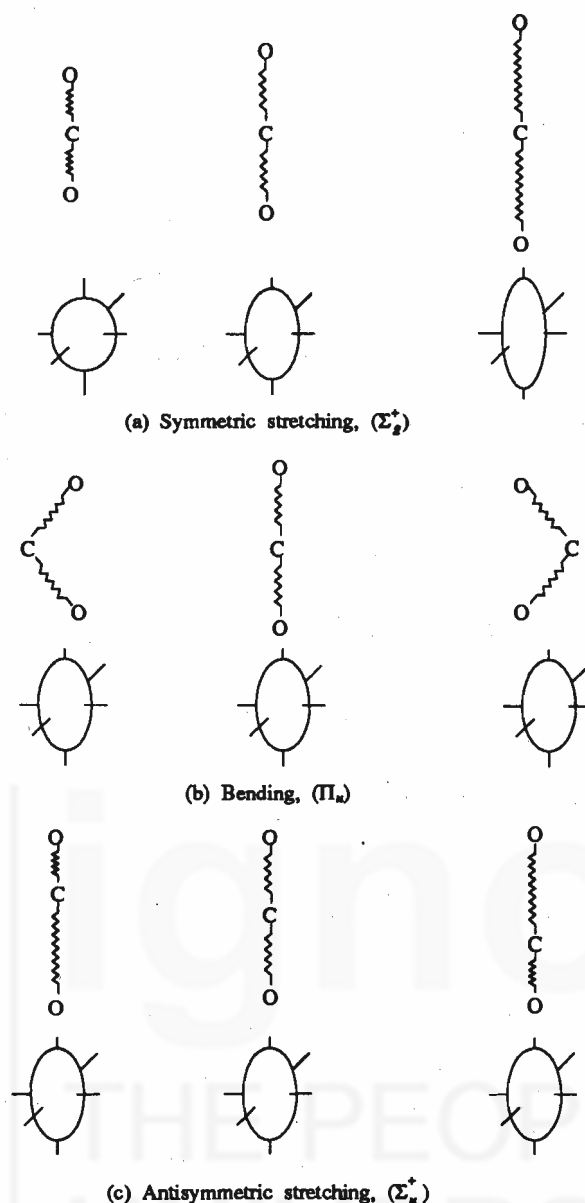


A periodically changing polarizability is the requirement for a Raman band.

In Figs. 6.1 and 6.2, the symmetry species of vibrations (such as  $A_1$ ,  $B_1$ ,  $\Sigma_g^+$ ,  $\Sigma_u^+$  and  $\Pi_u$ ) are mentioned in terms of group theory symbols. In this connection, go through Table 6.2 in Sec 6.7, the marginal matter given along with it and the character tables at the end of the Appendix of this unit.

**Fig.6.1 :** The shapes of the polarizability ellipsoids of  $H_2O$  molecule during three vibrational modes; the centre column shows the equilibrium position of the molecule while those in the right and left are extremes of vibration. (a),(b) and (c) stand for symmetric stretching mode ( $\nu_1$ ), the bending mode ( $\nu_2$ ) and the antisymmetric stretching mode ( $\nu_3$ ), respectively. All the three vibrations of  $H_2O$  involve a change at least in one of the three aspects of polarizability ellipsoids, namely, size, shape or direction.

In the case of  $CO_2$  molecule, it is seen that during symmetric stretching ( $\nu_1$ ), polarizability changes because of the change in ellipsoid size and this mode is Raman active. For the bending ( $\nu_2$ ) and antisymmetric stretching modes ( $\nu_3$ ), there is no overall change in polarizability ellipsoid (Fig.6.2). Hence the bending and antisymmetric stretching modes of  $CO_2$  are Raman inactive. This aspect can be explained as follows. The molecular polarizability of a molecule can be thought of in terms of bond polarizabilities. We can assume that a net periodic polarizability change facilitates activity in Raman spectra. The symmetric stretching mode of  $CO_2$  is Raman active since the polarizability changes in each bond during stretching or compression add up to give a net periodic polarizability change. For the antisymmetric stretching mode of  $CO_2$ , the polarizability change in one bond cancels that for the other bond and this mode is Raman inactive. Similarly during the bending vibrations of  $CO_2$ , the net polarizability change is zero, since the two C-O bonds are bent in opposite directions during each of the bending vibrations of bond angle expansion or compression and hence, the bending mode is also Raman inactive.



**Fig.6.2 :** The shapes of polarizability ellipsoids of  $\text{CO}_2$  molecule during (a) symmetric stretching ( $\nu_1$ ) (b) bending ( $\nu_2$ ) and (c) antisymmetric stretching ( $\nu_3$ ) modes. Of these three, only symmetric stretching accounts for overall change in the ellipsoid and only this is Raman active.

In Units 3 and 4, we have studied that in the infrared (or microwave) region, a vibration (or rotation) is active only when it brings about a change in the dipole moment of the molecule. We can generalise that any vibration (or rotation) which causes a change in the polarizability of the molecule will be Raman active whereas any vibration (or rotation) which brings about a change in the electric dipole moment of the molecule will be infrared (or microwave) active. Some vibrations may be both Raman and infrared active. Group theory can be elegantly used to find out whether a vibration will be Raman active or not. A brief discussion along these lines is given in the Appendix of this unit.

### 6.2.2 Quantum Theory of Raman Spectrum

Let us discuss the quantum mechanical treatment of Raman spectrum. Consider the interaction of a photon of frequency  $\nu$  with an isolated molecule. The oscillating electric field associated with the photon of energy  $h\nu$  interacts with the molecule and deforms the electronic configuration of the molecule. For some infinitesimally small period of time, the photon and the molecule may be considered to constitute a new state, which may be called a virtual state. The molecule has reached this new state through interaction with the photon; this state is higher in energy to the extent of the energy of the incident beam,  $h\nu$ . The virtual state is an unstable state and a photon is immediately emitted as scattered radiation, while the molecule returns to one of the

states associated with the molecule. Let  $E_a$  and  $E_b$  be the initial and final energy states of the molecule. If  $\nu$  and  $\nu'$  are frequencies of the incident and the scattered radiations, we can write using the law of conservation of energy,

$$h\nu + E_a = h\nu' + E_b \quad \dots(6.2)$$

$$E_a - E_b = h(\nu' - \nu) \quad \dots(6.3)$$

If  $E_a = E_b$ , then the scattered radiation will have the same frequency as the incident radiation ( $\nu' = \nu$ ) as evident from the above equation. Thus the collision between the photons and the molecules is an elastic one and the scattering is of Rayleigh type.

If  $E_a < E_b$ , then the frequency of the scattered radiation  $\nu'$  will be less than the frequency of the incident radiation  $\nu$  (or the wavelength of the scattered radiation ( $\lambda'$ ) will be more than that of the incident radiation ( $\lambda$ ) i.e. in Stokes lines,  $\nu' < \nu$  or  $\lambda' > \lambda$ . In other words, some portion of the energy is transferred from the incident radiation to the molecules and thus scattered radiation appears at a lower frequency (or at longer wavelength) in the spectrum. The scattered radiation appears as Stokes lines in the Raman spectrum.

Finally if  $E_a > E_b$ , the scattered radiation will appear at higher frequency (or at shorter wavelength) than the incident radiation and it is known as anti-Stokes lines, i.e., in anti-Stokes lines,  $\nu' > \nu$  and  $\lambda' < \lambda$ . The origin of Stokes lines, Rayleigh lines and the anti-Stokes lines are shown in Fig. 6.3a. The schematic diagram of Raman spectra of a diatomic gas is shown in Fig. 6.3b.

While working problems using Eq. 6.4, you have to remember the following:

- (i)  $\bar{\nu}$  is the wavenumber ( $1/\lambda$ ) of the incident radiation.
- (ii)  $\bar{\nu}'$  is the wavenumber ( $1/\lambda'$ ) of the scattered radiation;  $\bar{\nu}'$  is also called the absolute wavenumber at which a band will be observed in the Raman spectrum or the position of the Raman line.
- (iii)  $\Delta\bar{\nu}$  corresponds to the wavenumber of the vibration band in the vibrational Raman spectrum or the spacing between a particular set of lines in the rotational Raman spectrum.

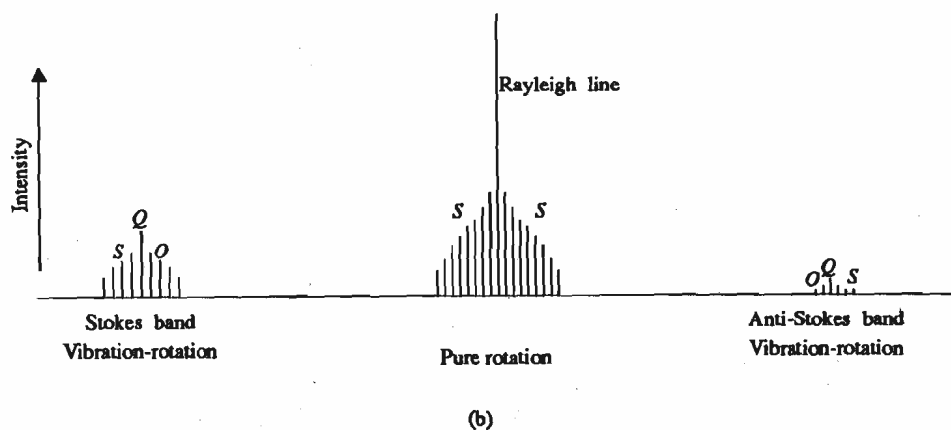
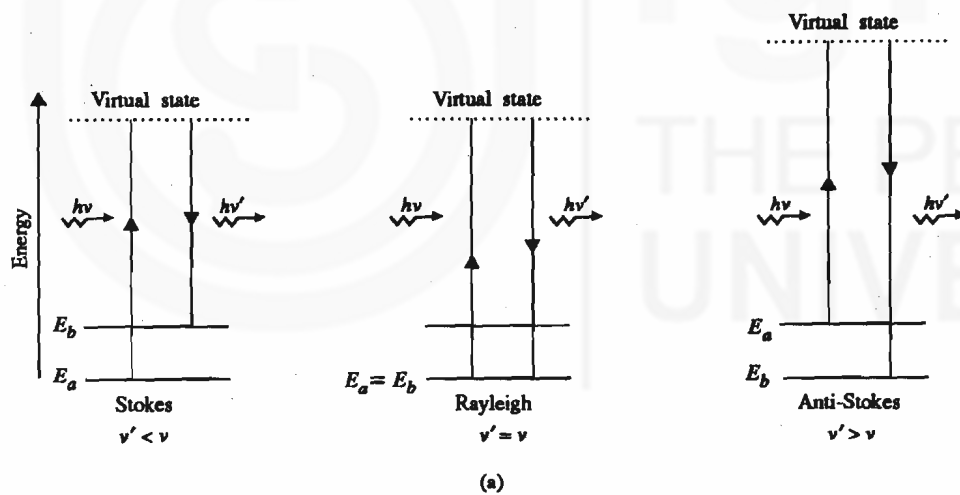


Fig. 6.3: (a) The interactions that give rise to the Stokes, anti-Stokes and Rayleigh lines. (b) The schematic diagram of Raman spectrum of a diatomic gas.

## IR and Raman Spectra

Raman spectrum is a plot of intensity of scattered radiation as a function of wavenumber. The band corresponding to  $\bar{\nu}$  constitutes the Rayleigh line. The bands to the left of  $\bar{\nu}$  are Stokes lines since  $(\bar{\nu}' - \bar{\nu})$  for these are negative. The bands to the right of  $\bar{\nu}$  have positive  $(\bar{\nu}' - \bar{\nu})$  values and these are anti-Stokes lines. The intensity of the lines depends on the population at different energy levels (Fig. 6.3b). The relative heights of lines are indicative of relative intensities.

The experimental details of obtaining Raman spectra will be discussed in Unit 9 of this course.

Since the transfer of energy to and from the molecules follow the same quantum laws, both Stokes and anti-Stokes lines appear at equal spacing from the Rayleigh line. In order to give a common expression for Stokes and anti-Stokes lines, we can write in terms of wavenumbers,

$$\bar{\nu}' - \bar{\nu} = \pm \Delta \bar{\nu} \quad \dots(6.4)$$

where  $\bar{\nu}'$  and  $\bar{\nu}$  are wavenumbers of the scattered and incident radiation, respectively and,  $\Delta \bar{\nu}$ , is the rotational or vibrational or rotation-vibration wavenumber of the molecule.  $\Delta \bar{\nu}$  is known as the Raman shift. The plus sign in Eq. 6.4 refers to anti-Stokes lines while the minus sign refers to Stokes lines.

There are more molecules in the ground state than in the excited state and, the former class gives rise to the Stokes lines while the latter gives rise to the anti-Stokes lines; hence, Stokes lines are more intense than the anti-Stokes lines (Fig. 6.3b).

The intensity of Raman scattering in general is very low. Only about  $10^{-5}$  of the incident radiation is Rayleigh-scattered and the total amount of Raman-scattered radiation is about  $10^{-2}$  that of the Rayleigh-scattered radiation. It is customary to observe only Stokes emission, since anti-Stokes emission for vibrational energy transfer is usually too weak to be detected.

From the above discussion you can understand that the ideal source for Raman spectroscopy must be both very intense and highly monochromatic. The development of laser as a source has greatly facilitated the usage of Raman spectroscopy.

It is found that the Raman shift ( $\Delta \bar{\nu}$ ) is generally of the order of  $3-3000 \text{ cm}^{-1}$ . The Raman shift can be observed from far infrared to infrared region but Raman spectroscopy should not be taken as a kind of infrared or microwave spectroscopy. It is important to remember that a "Raman frequency" of  $2 \times 10^5 \text{ m}^{-1}$  is not measured in the infrared region but corresponds to an emission at a wavelength of 540.8 nm for excitation by an Ar laser. You go through the following examples.

### Example 1

The Raman spectrum of  $\text{C}_2\text{H}_2(\text{g})$  observed using 435.80 nm Hg incident radiation shows one of the lines at 511.00 nm. Determine the wavenumber of the vibration band ( $\Delta \bar{\nu}$ ).

Since  $\lambda' > \lambda$ , the observed band is a Stokes line.

Applying Eq. 6.4 for a Stokes line,

$$-\Delta \bar{\nu} = \bar{\nu}' - \bar{\nu}$$

$$\text{or} \quad \Delta \bar{\nu} = \bar{\nu} - \bar{\nu}' = 1/\lambda - 1/\lambda'$$

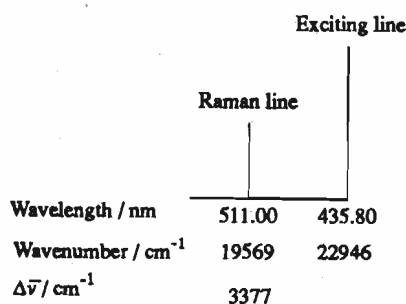
$$= 3.377 \times 10^5 \text{ m}^{-1} = 3377 \text{ cm}^{-1}$$

### Example 2

The Raman spectra of  $\text{CF}_4(\text{g})$  was observed using the 435.80 nm Hg exciting energy. Four bands corresponding to the four fundamental vibrations were observed at 444.25 nm, 448.16 nm, 453.80 nm and 461.64 nm. Determine the wavenumbers ( $\Delta \bar{\nu}$ ) of these fundamental vibrations.

Since  $\lambda' > \lambda$  for all the lines, these are Stokes lines. Applying Eq. 6.4 for Stokes lines,

$$\bar{\nu}' - \bar{\nu} = -\Delta \bar{\nu}$$



we can calculate the wavenumbers of these vibrations as shown below:

Wavelength / nm	461.64	453.80	448.16	444.25	435.80
Wavenumber / $\text{cm}^{-1}$	21662	22036	22313	22510	22946
$\Delta\bar{\nu} / \text{cm}^{-1}$	1284	910	633	436	

In the next three sections, we shall discuss the rotational, vibrational and vibration-rotation Raman spectra of molecules in detail. However, before proceeding to the next section, you may answer the following SAQ.

### SAQ 1

Would all the rotational and vibrational transitions of a molecule be Raman active ?

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## 6.3 ROTATIONAL RAMAN SPECTRA

In Unit 3 of this course while discussing the pure rotational spectra, we classified the molecules under the categories of linear, spherical top, symmetric top and asymmetric top. We also stated mathematical expressions for the calculation of energies of different rotational levels as well as for the energy involved in the transition from one level to another for molecules belonging to these categories. For our discussion on the rotational Raman spectra, we shall follow the same classification.

### Linear molecules

As derived in Unit 3 of this course, the rotational energy levels for a linear molecule are given by Eq. 6.5.

$$\epsilon_J = BJ(J+1) \text{ cm}^{-1} \quad \dots(6.5)$$

where  $J = 0, 1, 2$ , etc,  $B$  is the rotational constant for the molecule and  $\epsilon_J$  is the rotational energy expressed in wavenumbers.

In Eq. 6.5. we have neglected the higher order terms since in Raman spectra, such high precision is generally not obtained. The selection rule for rotational Raman spectra is

$$\Delta\nu = 0 \text{ and} \\ \Delta J = 0, \pm 2 \text{ (in the same vibrational level)}$$

The transition  $\Delta J = 0$  means that the scattered radiation has the same frequency as the incident radiation and it appears as Rayleigh scattering only.

When  $\Delta J = +2$ , we can write for a transition  $J \rightarrow J+2$ ,

It is worth recollecting that the selection rule for microwave spectra is  $\Delta J = \pm 1$ . But in rotational Raman spectra, the selection rule is

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

We know that the rotational changes in the Raman spectrum depend on the polarizability of the molecule. The polarizability in turn is associated with two dipole transitions – one for the incoming, and one for the outgoing photon. Hence, there will be two quantum rotational jumps as given by

$$\Delta J = \pm 2$$

$$\begin{aligned} \Delta \epsilon_{\text{rot}} &= B[(J+2)(J+3) - J(J+1)] \text{ cm}^{-1} \\ &= B(4J+6) \text{ cm}^{-1} \end{aligned} \quad \dots(6.6)$$

where  $J = 0, 1, 2, 3, \dots$  and it is the rotational quantum number in the lower state.

$\Delta \epsilon_{\text{rot}}$  stands for the rotational energy change in  $\text{cm}^{-1}$  unit during the transition. We shall use the term  $\Delta \bar{\nu}_{\text{rot}}$  instead of  $\Delta \epsilon_{\text{rot}}$  and write,

$$\Delta \bar{\nu}_{\text{rot}} = B(4J+6) \text{ cm}^{-1} \quad \dots(6.7)$$

Eq. 6.4 can be rewritten for rotational spectra as follows:

$$\bar{\nu}' - \bar{\nu} = \pm \Delta \bar{\nu}_{\text{rot}} \quad \dots(6.8)$$

$\Delta \bar{\nu}_{\text{rot}}$  is the Raman shift for the rotational Raman spectra or the rotational Raman shift.

Using Eq. 6.7 we can write,

$$\bar{\nu}' - \bar{\nu} = \pm B(4J+6) \text{ cm}^{-1} \quad \dots(6.9)$$

We can understand that  $+\Delta \bar{\nu}_{\text{rot}}$  stands for anti-Stokes lines while  $-\Delta \bar{\nu}_{\text{rot}}$  stands for Stokes lines.

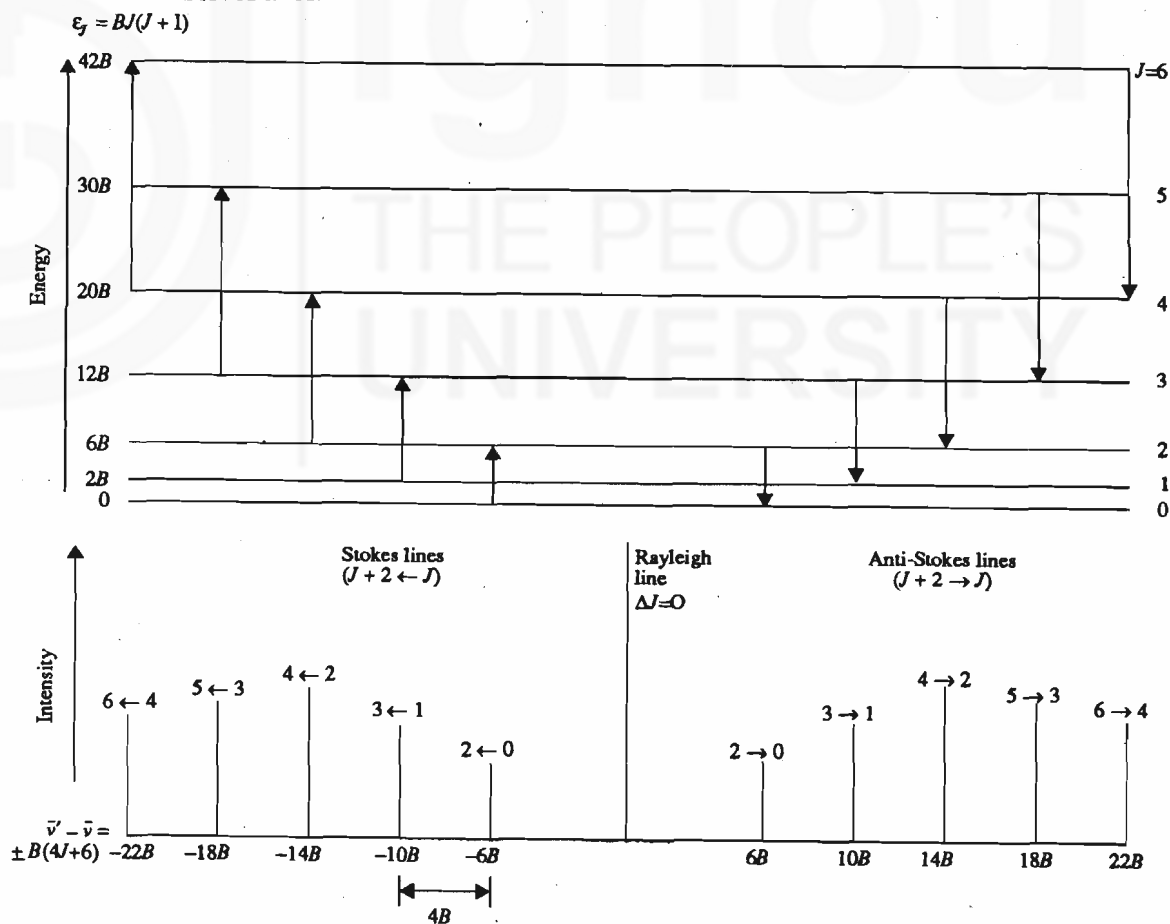


Fig. 6.4: Pure rotational Raman spectrum of a diatomic molecule—schematic diagram.

The schematic Raman rotational spectrum of a diatomic molecule is given in Fig. 6.4. Each transition is labelled according to the transitions. The relative heights of lines are indicative of relative intensities of lines which again depend on the population at various energy levels.



There is a general rule for labelling any series of lines in the spectrum which states that when  $\Delta J = +2, +1, 0, -1, -2$ , the corresponding group of frequencies are called *S*, *R*, *Q*, *P* and *O* branches of the spectrum, respectively. Thus in the above case, when  $\Delta J = +2$ , we shall observe *S*-branch of the spectrum. Notice that when  $J = 0$  is substituted in Eq. 6.9, the separation of the first line from the exciting line is found to be  $6B$ . Once the value of rotational constant  $B$  is known, we can evaluate the moment of inertia of the molecule since,

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

Rotational Raman spectra for molecules like  $H_2, O_2, HCN, CO_2, C_3O_2$  etc. have yielded useful information about their molecular structure. This information is especially useful for homonuclear diatomic molecules which give no infrared or microwave spectra. Raman spectrum with rotational fine structure is generally not obtained for linear molecules having more than three atoms.

It should be mentioned that if the molecule has a centre of symmetry (as in the case of  $H_2, N_2, O_2, CO_2$ ) the nuclear spin exerts its effect in the Raman and IR spectra. The intensity pattern can be explained using nuclear spin effect. We shall not go into the theoretical background of this aspect but state a few examples. The significant conclusion is that the intensity pattern of rotational Raman spectra has a vital role to play while providing data regarding molecular structure.

In order to show the nuclear spin effect on the intensity pattern, let us consider two types of molecules, one having zero nuclear spin and another having nonzero nuclear spin.

- (i) In the rotational Raman spectra of molecules like  $O_2$  (with  $^{16}O$  atoms) and  $CO_2$  (with  $^{12}C$  and  $^{16}O$  atoms, both having zero nuclear spin), every alternate rotational level is absent. One can see an interesting variation between the rotational Raman spectra of  $CO_2$  and  $O_2$ . In  $CO_2$ , every level with odd  $J$  value is missing and thus transitions from  $J = 1, 3, 5, \dots$  levels are completely absent (as shown by dotted lines in Fig. 6.5), while lines of even  $J$  values are observed.

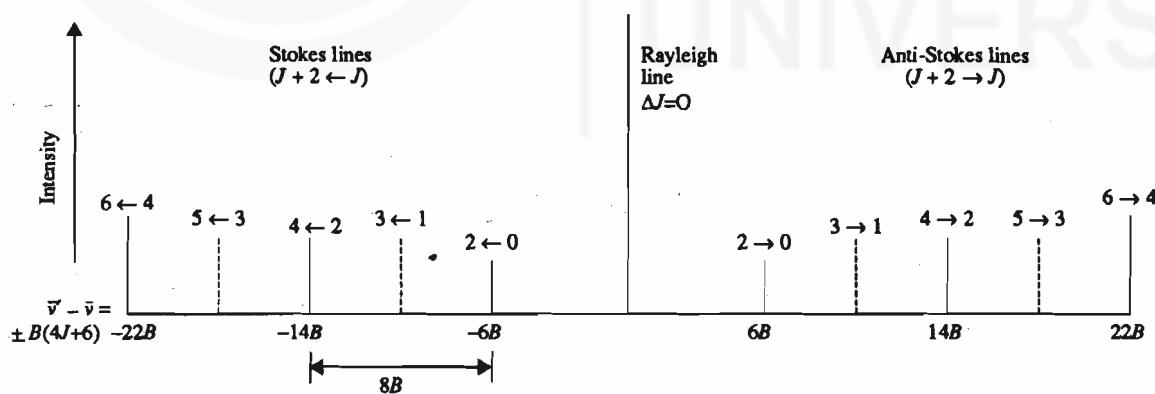


Fig. 6.5: Schematic diagram of pure rotational Raman spectra of  $CO_2$ . Note that all the odd  $J$  lines of  $CO_2$  are absent (as shown by the dotted lines). All the allowed transitions (i.e., those of even  $J$  values) are shown by solid lines.

The average line separation then is equal to  $8B$  (i.e.,  $\Delta \bar{\nu} = 8B$ ) while the difference between the first Stokes line and the first anti-Stokes line is  $12B$ . Similarly in the Raman spectrum of  $^{16}O_2$ , the spectral transitions correspond to energy levels with odd  $J$  values and those from even  $J$  values are missing. The average line separation is equal to  $8B$  while the separation between the first Stokes line, and the first anti-Stokes line is  $20B$ . Let us try to work out the following problem.

**Example 3**

The rotational Raman spectra of  $\text{CO}_2(\text{g})$  showed a series of absorption peaks separated by  $3.16 \text{ cm}^{-1}$  in the  $S$  branch. What is the value of the rotational constant ( $B$ ) for  $\text{CO}_2$  molecule ?

In the case of  $\text{CO}_2$ ,  $\Delta \bar{\nu}_{\text{rot}} = 8B$

$$B = \frac{3.16}{8} \text{ cm}^{-1}$$

$$= 0.395 \text{ cm}^{-1}$$

$$= 39.5 \text{ m}^{-1}$$

- (ii) In the case of molecules like  $^1\text{H}_2$ ,  $^{14}\text{N}_2$  etc. (which have nonzero nuclear spin), the intensity of every alternate line decreases. The intensity ratio of 2:1 in favour of even  $J$  values is observed between the successive lines in the rotational Raman spectra of  $^{14}\text{N}_2$  (Fig. 6.6). In other words, the lines at even  $J$  values have greater intensity than those at odd  $J$  values. In the rotational Raman spectra of  $^1\text{H}_2$ , the intensity ratio of 3:1 is observed between the successive lines.

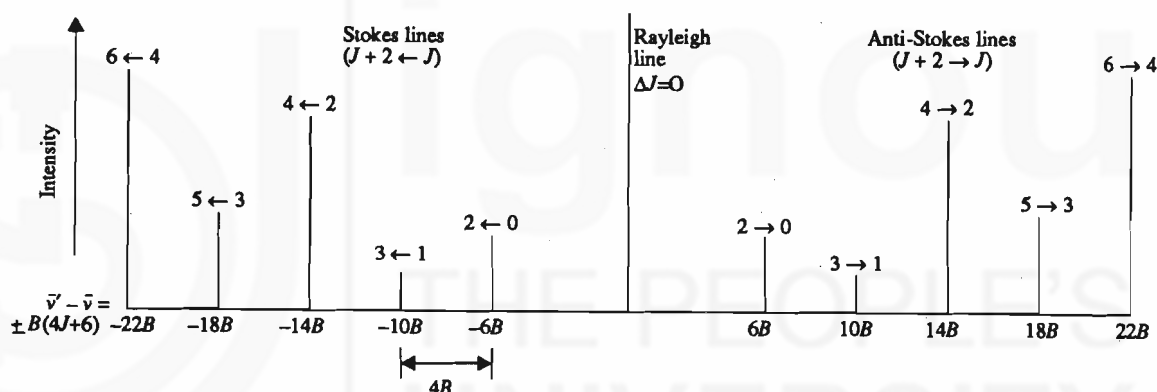


Fig. 6.6: Rotational Raman spectra of  $^{14}\text{N}_2$ .

While using rotational Raman spectra of  $\text{H}_2$ ,  $\text{N}_2$  etc. for obtaining molecular parameters, it should be borne in mind that  $\Delta \bar{\nu} = 4B$ .

**Example 4**

For hydrogen molecule, the spacing between the  $S$ -branch lines in the Raman spectrum is  $243.2 \text{ cm}^{-1}$ . Calculate the bond length of hydrogen.

Mass of hydrogen atom =  $1.673 \times 10^{-27} \text{ kg}$

For hydrogen molecule, the spacing between the lines ( $\Delta \bar{\nu}$ ) =  $4B$

$$4B = 243.2 \text{ cm}^{-1}$$

$$= 2.432 \times 10^4 \text{ m}^{-1}$$

$$B = 6.008 \times 10^3 \text{ m}^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34}}{8 \times (3.143)^2 \times 6.008 \times 10^3 \times 2.998 \times 10^8} \text{ kg m}^2$$

$$= 4.655 \times 10^{-48} \text{ kg m}^2$$

$$\mu = \frac{m_H \cdot m_H}{m_H + m_H} = \frac{m_H}{2}$$

$$= 8.365 \times 10^{-28} \text{ kg}$$

$$r = \left(\frac{I}{\mu}\right)^{1/2} = \left(\frac{4.655 \times 10^{-48}}{8.365 \times 10^{-28}}\right)^{1/2} \text{ m} = 7.46 \times 10^{-11} \text{ m}$$

$$= 74.6 \text{ pm}$$

The spherical top molecules (like  $\text{CH}_4$  and  $\text{SF}_6$ ) on rotation along any axis would not produce a change in the polarizability of the molecules. Hence the spherical top molecules do not exhibit rotational Raman spectra. We shall not discuss the rotational Raman spectra of symmetric top and asymmetric top molecules due to their complexity.

In the next section, we shall discuss the vibrational Raman spectra of molecules. You may try to answer the following SAQ before proceeding to the next section.

### SAQ 2

Calculate  $I$  and carbon-oxygen bond distance ( $r_{\text{C-O}}$ ) for  $\text{CO}_2$  (g), knowing that  $B$  is  $39.5 \text{ m}^{-1}$

Hints:  $I = 2 \times \text{mass of oxygen atom} \times (r_{\text{C-O}})^2$

$$\text{Mass of oxygen atom} = \frac{0.016}{6.023 \times 10^{23}} \text{ kg}$$

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## 6.4 VIBRATIONAL RAMAN SPECTRA

We have seen that the Raman frequencies cover the region of energy which can also bring about the changes in the vibrational energy level of the molecules. Thus, both the infrared and Raman spectra will give us information about the vibrational changes in the molecule. However, since the origin of spectra is different in the two cases, we can get information through Raman spectra about those molecules which are inaccessible to infrared spectra.

Each vibrational change will be accompanied by rotational change. Hence, the vibration spectra is truly a vibration-rotation spectra; but the rotational changes are observed only in the gaseous state, where the molecules are far apart from each other and, have complete freedom of rotation. Thus, only under high resolution, molecules in gaseous state give Raman spectra with rotational fine structure. In this section, we shall deal with the vibrational Raman spectra only.

As discussed in Unit 4 on vibrational spectra, we can express the vibrational energy as

$$\epsilon_{\text{vib}} = (\nu + 1/2) \bar{\nu}_{\text{osc}} - (\nu + 1/2)^2 \bar{\nu}_{\text{osc}} X \text{ cm}^{-1}; (\nu = 0, 1, 2, \dots) \quad \dots(6.10)$$

where  $\nu$  is the quantum number associated with the vibrations of the molecule and  $\bar{\nu}_{\text{osc}}$  is the harmonic frequency in wavenumber which is equal to  $\nu_{\text{osc}}/c$ . You can refer to Eq. 4.28 of Unit 4 for understanding the significance of  $\nu_{\text{osc}}$ . Also  $X$  is the anharmonicity constant.

For any vibrational transition, the selection rule is

$$\Delta \nu = \pm 1, \pm 2, \dots$$

Restricting ourselves to only fundamental vibration, where  $\Delta \nu = +1$ , the transition takes place from  $\nu = 0$  to  $\nu = +1$ . The intensity of other transitions will be very weak and can be neglected.

For vibrational Raman spectrum, we can write an equation similar to Eqs. 6.4 and 6.8,

$$\bar{\nu}' - \bar{\nu} = \pm \Delta \bar{\nu}_{\text{vib}} \quad \dots(6.11)$$

$\Delta \bar{\nu}_{\text{vib}}$  is the vibrational Raman shift.

Eq. 6.11 takes into account only the fundamental band; it ignores overtones for the sake of simplicity.

From Eq. 6.11, we can see that the Raman active vibrational frequencies appear as Stokes and anti-Stokes lines on either side of the central exciting line having a frequency  $\nu$ . The Stokes lines as usual would be more intense than anti-Stokes lines.

### Example 5

Predict the position of the Raman vibration lines for C-H stretching of an alkane at  $2960 \text{ cm}^{-1}$ , if Hg radiation of  $435.8 \text{ nm}$  ( $22946 \text{ cm}^{-1}$ ) is used.

Stokes line: Using Eq. 6.11,  $\bar{\nu}' = (22946 - 2960) \text{ cm}^{-1}$

$$\bar{\nu}' = 19986 \text{ cm}^{-1}$$

Anti-Stokes line: Using Eq. 6.11,

$$\bar{\nu}' = (22946 + 2960) \text{ cm}^{-1}$$

$$= 25906 \text{ cm}^{-1}$$

For molecules having centre of symmetry, there is a generalisation – known as the rule of mutual exclusion – which is quite useful in identifying them. This has been discussed in the following subsection.

### Mutual Exclusion Principle

The mutual exclusion principle states that any molecule which has centre of symmetry will not have any vibrational mode which is both Raman as well as infrared active. A precise way of stating the mutual exclusion principle is as follows:

**For a molecule with centre of symmetry, any given normal vibration may be active in the infrared or in the Raman (or in neither) but not in both.**

The portion written within the brackets 'or in neither' means that some of the normal vibrations may be inactive both in Raman and infrared regions. For example, ethylene, which has centre of symmetry, has twelve modes of vibration. Six of these are Raman active and five are infrared active, the remaining mode is neither infrared active nor Raman active. Such modes of vibrations of molecules with centre of symmetry which are totally inactive in both infrared and Raman spectra are called **spectroscopically silent fundamental vibrations**. In benzene, which has a total of thirty normal modes, twenty two are active either in Raman or in infrared. The remaining eight modes are totally inactive in both Raman and infrared. A simplified statement of mutual exclusion principle is given below:

**"If a molecule has centre of symmetry, then no modes can be both infrared and Raman active".**

As a corollary to the above statement, we can say that if a particular vibration mode of the molecule gives rise to lines at the same frequency in both the infrared and Raman spectra, then the molecule must **not** have centre of symmetry. In the Appendix of this Unit, we shall discuss this principle in relation to group theory.

Let us consider the application of this simple rule in the interpretation of the spectra of two triatomic molecules,  $\text{CO}_2$  and  $\text{SO}_2$ . The two peaks at 2349 and  $667\text{ cm}^{-1}$  in the infrared spectrum of  $\text{CO}_2$  are found to be absent in the Raman spectrum of the molecule. We may expect a single Raman peak for this molecule at  $1340\text{ cm}^{-1}$  due to symmetric stretch. In fact, two peaks of similar intensity appear at  $1388\text{ cm}^{-1}$  and  $1286\text{ cm}^{-1}$  which are due to Fermi resonance between  $\nu_1$  (symmetric stretching frequency) and  $2\nu_2$  (twice the bending frequency) as explained in Sec. 5.3 of the last unit. **The Fermi resonance bands are not covered by mutual exclusion principle since it applies to fundamental modes only.** Thus, it must be noticed that the fundamental modes of  $\text{CO}_2$  which are infrared active are Raman inactive.

Our conclusion is that  $\text{CO}_2$  molecule must have centre of symmetry in accordance with the mutual exclusion principle. This is in agreement with the fact that  $\text{CO}_2$  is a linear molecule with a symmetric structure and its dipole moment is zero.

In the case of  $\text{SO}_2$ , we get three peaks around  $519$ ,  $1151$  and  $1361\text{ cm}^{-1}$  in both the Raman and infrared spectra. These observations indicate that  $\text{SO}_2$  molecule has no centre of symmetry and we shall use this fact in Sec 6.7 in discussing its structure.

It has also been observed that the symmetric vibrations give rise to intense Raman lines but the antisymmetric vibrations produce weaker lines in the spectrum. Frequencies at which these vibrations will occur can be calculated with the help of quantum mechanics which we are not going to discuss in this course.

Answer the following SAQ's before going through Sec. 6.5.

### SAQ 3

$\text{C}_2\text{H}_2$  has two IR bands and three Raman bands, none of them occur at the same wavenumber. Further, one of the IR bands shows a simple PR structure. Comment on the structure of  $\text{C}_2\text{H}_2$ .

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 .....  
 .....

**SAQ 4**

What type of spectral pattern would you expect from IR and Raman spectra, if the structure of  $N_2O$  is  $N-N-O$  but not  $N-O-N$ ? Verify your answer with the case study discussed in Sec. 6.7.

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**6.5 VIBRATION - ROTATION RAMAN SPECTRA**

Relatively a very small number of molecules have been studied for which vibrational Raman spectra show rotational fine structure.

For the simplest case of a diatomic molecule, the selection rules for vibration-rotation Raman spectra are as follows:

$$\Delta J = 0, \pm 2 \text{ and } \Delta v = \pm 1.$$

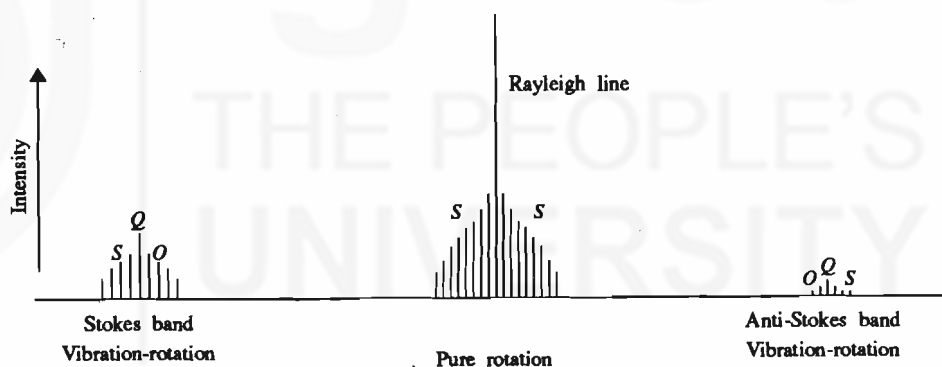


Fig. 6.7: The schematic diagram of the vibration-rotation Raman spectrum of a diatomic gas.

The transitions for which  $\Delta J = -2$  give rise to *O*-branch while those for which  $\Delta J = 0$  give rise to *Q*-branch and finally, if  $\Delta J = +2$ , *S*-branch occurs. In Fig. 6.7, the schematic diagram of the vibration-rotation Raman spectrum of a diatomic gas is shown. The presence of a strong *Q*-branch in the Raman spectra is noteworthy. The lines in *O* and *S*-branches of the Raman spectrum could be analysed to yield *B*, moment of inertia and bond length.

**6.6 POLARIZED RAMAN SPECTRA**

Before explaining polarized Raman spectra, we should understand the terms, plane polarized light and depolarization ratio. You may have studied in Sec. 6.10 of Unit 6 of Atoms and Molecules Course that when monochromatic light is passed through a nicol prism, the outgoing light vibrates in only one particular plane. Such a type of light is called plane polarized light. When plane polarized light is passed through another nicol prism, the intensity of the transmitted light depends on the way the polarizing

axes of the two prisms are oriented towards each other. If the polarizing axes of the two prisms are parallel to each other, the intensity of the transmitted light is maximum. When the two axes are perpendicular, no light passes through the second nicol prism. If the incident light falling on the second nicol prism is only partially polarized, then the intensity of the transmitted light perpendicular to the plane of polarization ( $I_{\perp}$ ) is minimum but not zero. In the case of partially polarized light, it is useful to define the ratio of intensity of light transmitted perpendicular to the plane of maximum polarization ( $I_{\perp}$ ) to the intensity of light transmitted parallel to the plane of maximum polarization ( $I_{\parallel}$ ). This ratio is called depolarization ratio ( $\rho$ ) which is given as

follows: 
$$\rho = \frac{I_{\perp}}{I_{\parallel}} \quad \dots(6.12)$$

The depolarization ratio is quite useful in determining whether a Raman line is polarized or not. A Raman line is said to be polarized, if the value of  $\rho$  lies between 0 and  $6/7$ . If  $\rho$  is more than  $6/7$ , a Raman line is said to be depolarized.

The number of polarized Raman lines can be obtained from the experimental values of  $\rho$  which could help us in assigning the vibrational modes to the experimentally observed frequencies. In general, it can be stated that a symmetric vibration gives rise to a polarized (or partially polarized) Raman line while an antisymmetric vibration gives a depolarized line. The use of polarized Raman lines will be illustrated in Sec. 6.7.

### SAQ 5

Polarized Raman spectra of  $\text{CHCl}_3$  give the following data for three of the bands:

S.No	Raman band/ $\text{cm}^{-1}$	$I_{\perp}$	$I_{\parallel}$
i)	357	5.8	79.2
ii)	660	1.3	83.2
iii)	760	4.7	6.0

Identify those which are polarized.

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## 6.7 APPLICATIONS OF IR AND RAMAN SPECTROSCOPY

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We can derive useful structural information from Raman and infrared spectra of molecules. However, we must realise that Raman and infrared spectra are complementary to each other in many ways as shown in Table 6.1.

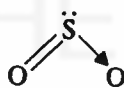
Table 6.1: Characteristics of Raman and Infrared Spectra

Raman	Infrared
1. Raman spectrum is the result of scattering of light by the molecules.	1. Infrared spectrum is because of the absorption of radiation by the molecules.
2. It depends on the changing polarizability of the molecule.	2. It depends on the oscillating dipole moment in the molecule.
3. Homonuclear diatomic molecules are rotationally and or vibrationally active.	3. Homonuclear diatomic molecules are inactive.
4. Water can be used as a solvent.	4. Water is less likely to be used as a solvent since it is opaque to infrared radiations.

Using the case of SO<sub>2</sub> molecule, we now show how the structure of a molecule could be determined using IR and Raman spectra. Let us also explain how the polarized Raman spectra could be used in assigning vibrational modes to the frequencies observed in the spectra.

In sec. 6.4, we have mentioned that SO<sub>2</sub> gives three absorption bands at 519, 1151 and 1361 cm<sup>-1</sup> both in IR spectra and Raman spectra and that it does not have centre of symmetry. Further, a linear polyatomic molecule is expected to show at least some IR bands with P and R branches as exhibited by diatomic molecules (See Fig. 4.11 of Unit 4). These PR bands (or contours) arise due to vibrations causing a dipole change parallel to the principal axis of symmetry. In the IR spectra of SO<sub>2</sub>, no band shows simple PR structure. Hence, SO<sub>2</sub> molecule is not linear and it must have a bent shape.

In the Appendix, we shall examine the Raman activity of the three vibrational modes of triatomic molecules (H<sub>2</sub>O or SO<sub>2</sub>) belonging to C<sub>2v</sub> group.



In Table 6.2, the symmetry species are given in terms of group theory symbols.

Further, the bands at 519 and 1151 cm<sup>-1</sup> are Raman polarized. This indicates that these bands are due to symmetric vibrations. If we make a reasonable assumption that stretching frequencies are larger than bending, then 519 cm<sup>-1</sup> is assigned to symmetric bending vibration while 1151 cm<sup>-1</sup> is assigned to symmetric stretching mode. The band at 1361 cm<sup>-1</sup> is Raman depolarized which indicates that it can be assigned to the antisymmetric stretching mode. Thus we assign the modes of vibration to the observed frequencies of SO<sub>2</sub>; also we infer that it is angular in shape.

The symmetry species of each mode of vibration is denoted in the respective figures. For understanding the characters of these symmetry species, you may consult the character tables for C<sub>2v</sub>, C<sub>3v</sub>, C<sub>∞v</sub> and D<sub>∞h</sub> given at the end of the Appendix of this unit. Even without understanding the basis of group theory symbols, you can try to use them, if you follow the Appendix materials. If by chance you don't follow the Appendix materials, don't lose confidence! You can still follow the main portion of the unit excluding the Appendix.

For a few molecules, IR and Raman active vibrations are discussed in Table 6.2.

Table 6.2: IR Active and Raman Active Vibrations of Some Molecules

Molecule (or ion)	CO <sub>2</sub>	N <sub>2</sub> O	H <sub>2</sub> O or SO <sub>2</sub>	NH <sub>3</sub> (or ClO <sub>3</sub> <sup>-</sup> )
Fig. No.	6.2	6.8	6.1	6.9
Geometry	Linear (symmetric)	Linear (asymmetric)	Angular	Pyramidal
Point group	D <sub>∞h</sub>	C <sub>∞v</sub>	C <sub>2v</sub>	C <sub>3v</sub>



Total number of modes	4	4	3	6
Fundamentals	3	3	3	4
Symmetry species	$\Sigma_g^+$ $\Sigma_u^+$ $\Pi_u$	$2\Sigma^+$ $\Pi$	$2A_1, B_1$	$2A_1, 2E$
IR active species	$\Sigma_u^+$ $\Pi_u$	$2\Sigma^+$ $\Pi$	$2A_1, B_1$	$2A_1, 2E$
Raman active species	$\Sigma_g^+$	$2\Sigma^+$ [ $\Pi$ (bending) too weak to be observed ]	$2A_1, B_1$	$2A_1, 2E$
Polarized vibration	$\Sigma_g^+$ (symmetric stretching)	$\Sigma^+$ (symmetric stretching)	$2A_1$ (symmetric stretching and bending)	$2A_1$ (symmetric stretching and out-of-plane symmetric bending)

N.B:  $\Pi_u$ ,  $\Pi$  and E: Doubly degenerate vibrations

Let us illustrate the use of Table 6.2 in structure determination. Care should be taken to interpret Raman spectra since one or more bands may be missing due to weak intensity (or these bands may be spectroscopically silent).

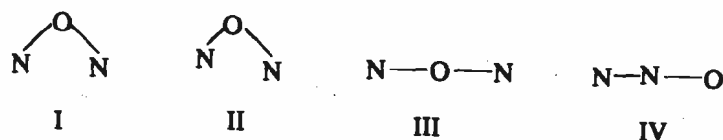
### Case study of $N_2O$

We shall illustrate as to how the structure of  $N_2O$  has been established using infrared and Raman spectral data given in Table 6.3.

Table 6.3: Infrared and Raman Spectral Data of Nitrous Oxide

$\bar{\nu}/\text{cm}^{-1}$	Infrared	Raman
589	strong; PQR band	—
1285	very strong; PR band	very strong
2224	very strong; PR band	strong

The four possible structures of  $N_2O$  are given below:



The presence of two bands with simple PR contours indicate that the molecule is linear. Hence the structures I and II are ruled out.

The appearance of (at least) two bands ( $1285$  and  $2224 \text{ cm}^{-1}$ ) in both infrared and

Raman spectra indicates that the molecule does not have centre of symmetry. As per Table 6.2, we may expect all the three bands to appear in the infrared and Raman spectra. It is possible that the third band at  $589\text{ cm}^{-1}$  is too weak that it is not observed in Raman spectrum. Hence, it is clear that  $\text{N}_2\text{O}$  has the structure IV. Let us try to indicate the vibrational modes of  $\text{N}_2\text{O}$  (Fig. 6.8).

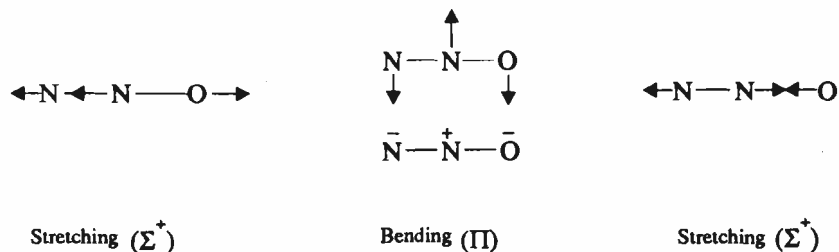


Fig. 6.8: Vibrational modes of  $\text{N}_2\text{O}$

As another example, you may verify the structure of  $\text{ClO}_3^-$  ion as pyramidal using the data given in Tables 6.2 and 6.4. The vibrational modes of  $\text{ClO}_3^-$  ion are given in Fig. 6.9.

Table 6.4: Infrared and Raman Spectra of  $\text{ClO}_3^-$  ion

$\bar{\nu}_{\text{Raman}}/\text{cm}^{-1}$	$\bar{\nu}_{\text{IR}}/\text{cm}^{-1}$
450 (depolarized)	434
610 (polarized)	624
940 (depolarized)	950
982 (polarized)	994

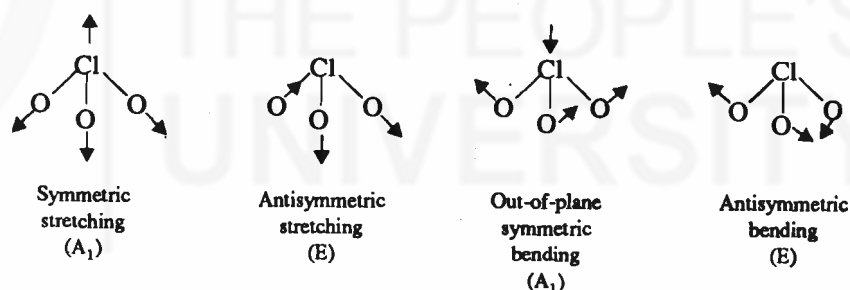


Fig. 6.9: Vibrational modes of  $\text{ClO}_3^-$  ion.

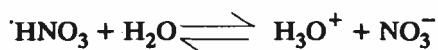
The main advantage of Raman spectroscopy lies in the fact that it can be studied in the visible region of the spectrum unlike microwave or infrared spectroscopy. With the introduction of laser beam as a Raman source, low frequency vibrations can also be easily studied. Rotations and vibrations of molecules which cannot be studied with microwave or infrared techniques are easily handled by Raman spectroscopy. For instance, the structural parameters of homonuclear diatomic molecules can be obtained using Raman spectra.

Raman spectra finds a lot of applications in the structure determination of organic compounds. It can be successfully used for the analysis of a mixture of compounds which are otherwise difficult to identify without separation into constituents. In general, IR is more suitable for molecular vibrations of organic compounds having frequencies above  $650\text{ cm}^{-1}$ . Raman spectra could be studied even upto  $100\text{ cm}^{-1}$  and is therefore, quite suited for studying weak vibrations such as metal-ligand

stretchings, most of which lie below  $600\text{ cm}^{-1}$ . Further, the polar solvents like water can be used in recording Raman spectra. Let us study three more applications of Raman spectra.

### (1) Dissociation constants of mineral acids

By monitoring the intensity of absorption bands due to nitrate ion and nitric acid using Raman spectrum, it is possible to obtain the dissociation constant of nitric acid.



Similarly the dissociation constants of  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$  also have been studied. It has been found that the concentration of  $\text{SO}_4^{2-}$  ion is small in sulphuric acid except in very dilute solutions.

### (2) Structure of complex ions in solution

One of the important applications of Raman spectra is to identify the structure of complex ions of mercury, thallium and silver ions in solution. The existence of mercurous ion as  $\text{Hg}_2^{2+}$  and not as  $\text{Hg}^+$  has been established through the  $\text{Hg}-\text{Hg}$  stretching frequency observed in the Raman spectrum of its ions. Similar results have been obtained for thallos ( $\text{Tl}_2^+$ ) ions also.

### (3) Strength of metal-ligand bonding

The totally symmetric vibrations (Fig. 6.10) of the tetrahedral complex ions (like  $\text{ZnCl}_4^{2-}$ ,  $\text{CdCl}_4^{2-}$ ,  $\text{HgCl}_4^{2-}$ , etc) and the octahedral complexes (like  $\text{SiF}_6^{2-}$ ,  $\text{PF}_6^-$ ,  $\text{SF}_6$ ) can be studied using Raman spectra. These are all IR inactive. From their Raman spectra, metal-ligand bond stretching force constants and hence, information about the strength of the metal-ligand bond can be obtained. It is seen that the oxyanions such as  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  etc. have much larger force constants. This is taken as an evidence that there is  $d\pi - p\pi$  bonding between the central atom and the oxygen atom in addition to the  $\sigma$  bonding.

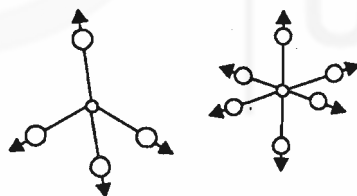


Fig. 6.10: Totally symmetric vibrations of  $\text{ML}_4$  and  $\text{ML}_6$  complexes.

### SAQ 6

A molecule  $\text{AB}_2$  has three prominent IR absorption bands and one Raman band; for the Raman band, the vibrational Raman shift coincides with one of the three IR bands. The rotational fine structure of the IR bands is complex and does not show simple PR contour. What is the shape of the molecule ?

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## 6.8 SUMMARY

In this unit we explained the origin of Raman spectrum in terms of classical as well as quantum mechanical models arriving at the same results. Next we discussed the rotational, vibrational and vibration-rotation Raman spectra in detail. The relevant selection rules were also given. The principle of mutual exclusion was stated and its importance in the elucidation of molecular structure was given. A brief outline of the utility of the study of polarized Raman lines was given. Finally a few applications of Raman spectroscopy were discussed.

## 6.9 TERMINAL QUESTIONS

- 1) If the fundamental vibrational frequency of a particular ketone occurs at  $1730\text{ cm}^{-1}$ , determine the position of Raman lines. The ketone is irradiated with argon laser of wavelength  $514.53\text{ nm}$ .
- 2) As per Table 5.3 of Unit 5, the C–H stretching range is  $2962\text{--}2853\text{ cm}^{-1}$  for an alkane. Assuming that argon laser of wavelength  $514.53\text{ nm}$  ( $19435\text{ cm}^{-1}$ ) is used, find the upper and lower wavenumbers for the positions of the Stokes lines for C–H stretching.
- 3) Why is that the intensity of Stokes lines generally greater than the anti-Stokes lines ?
- 4) How can you differentiate between the following two structures using IR and Raman spectra :



- 5) Which of the following molecules would give pure rotational Raman spectrum :  
 $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SF}_6$ ,  $\text{CH}_4$  and  $\text{N}_2$  ?
- 6) The vibrational Raman shift for C–H bending vibration is  $1460\text{ cm}^{-1}$ . For argon laser of wavenumber  $19435\text{ cm}^{-1}$ , predict the position of Stokes and anti-Stokes lines corresponding to C–H bending vibration.

## 6.10 ANSWERS

### Self Assessment Questions

- 1) A molecular rotation or vibration will be Raman active, only if it is accompanied by polarizability change.

$$\begin{aligned}
 2) \quad I &= \frac{h}{8\pi^2 Bc} \\
 &= \frac{6.626 \times 10^{-34}}{8 \times (3.143)^2 \times 39.5 \times 2.998 \times 10^8} \text{ kg m}^2 \\
 &= 7.08 \times 10^{-46} \text{ kg m}^2
 \end{aligned}$$

But as per the hints given,

$$I = \frac{2 \times 0.016}{6.023 \times 10^{23}} \times (r_{C-O})^2 \text{ kg m}^2$$

$$r_{C-O} = \left[ \frac{(7.08 \times 10^{-46} \times 6.023 \times 10^{23})}{0.032} \right]^{1/2} \text{ m} = 1.15 \times 10^{-10} \text{ m}$$

$$= 115 \text{ pm}$$

- 3) Since none of the bands appear in both IR and Raman spectra at the same wavenumber,  $C_2H_2$  must have centre of symmetry. The presence of an IR band with a simple PR structure brings out the linear structure. Hence  $C_2H_2$  has the linear symmetrical structure as shown below:



- 4) The structure  $N - N - O$  does not have centre of symmetry whereas  $N - O - N$  has. Hence, if the structure  $N - N - O$  is correct, one or more bands must occur at the same wavenumber in both IR and Raman spectra.
- 5)  $\rho$  values at all these three bands are less than  $6/7$  and these bands are polarized.
- 6) The molecule does not have centre of symmetry. It does not have linear structure. Hence,  $AB_2$  must be angular.

### Terminal Questions

- 1) We have to find the position of both Stokes lines and anti-Stokes lines. As per Eq. 6.4,  $\bar{\nu}'$  for Stokes line =  $\bar{\nu} - \Delta \bar{\nu}$

$$= \left( \frac{1}{514.53 \times 10^{-9}} - 1.730 \times 10^5 \right) \text{ m}^{-1}$$

$$= (1.9435 \times 10^6 - 1.730 \times 10^5) \text{ m}^{-1}$$

$$= 1.7705 \times 10^6 \text{ m}^{-1}$$

$$= 17705 \text{ cm}^{-1}$$

Similarly  $\bar{\nu}'$  for anti-Stokes line =  $\bar{\nu} + \Delta \bar{\nu}$

$$= 2.1165 \times 10^6 \text{ m}^{-1}$$

$$= 21165 \text{ cm}^{-1}$$

- 2) As per Eq. 6.4,  $\bar{\nu}'$  for the Stokes lines lie between  $(19435 - 2962) \text{ cm}^{-1}$  and  $(19435 - 2853) \text{ cm}^{-1}$ , i.e., between  $16473 \text{ cm}^{-1}$  and  $16582 \text{ cm}^{-1}$
- 3) There are more molecules in the ground state than in the excited state. The former class gives rise to the Stokes lines, while the latter gives rise to the anti-Stokes lines. Hence, Stokes lines are more intense than the anti-Stokes lines.
- 4) The molecule with angular symmetrical structure can be expected to exhibit three IR bands and three Raman bands, all the three being common; the molecule with linear symmetrical structure has no band appearing in both IR and Raman spectra.
- 5) The spherical top molecules  $SF_6$  and  $CH_4$  could not exhibit pure rotational Raman spectrum; others can.

6) Use Eq. 6.11,

$$\text{Stokes line : } (19435 - 1460) \text{ cm}^{-1} = 17975 \text{ cm}^{-1}$$

$$\text{Anti-Stokes line: } (19435 + 1460) \text{ cm}^{-1} = 20895 \text{ cm}^{-1}$$

## 6.11 APPENDIX

In this Appendix, we shall show how group theory helps in identifying Raman active vibrations and in understanding the mutual exclusion principle.

### Raman active vibrational modes

Group theory can be used to find out whether a particular vibrational mode will be Raman active or not. In the case of vibrational Raman spectra, a particular vibration mode will be active only if the polarizability of the molecule changes during vibration. In terms of the polarizability operator  $\alpha$ , the transition moment integral can be obtained using the term,  $\int \psi_b \alpha \psi_a d\tau$ , where  $\psi_a$  and  $\psi_b$  are the wave functions corresponding to ground state and the excited state, respectively. In this term,  $\alpha$  is one of the following quadratic or binary functions of the cartesian coordinates:

$$x^2, y^2, z^2, xy, yz, zx, (x^2 - y^2).$$

A vibration will be Raman active, if it belongs to the same symmetry species as a component of polarizability. A vibration transition may give rise to a Raman band, only if the symmetry species of the product of the functions  $\psi_a \psi_b$  is the same as one of  $x^2, y^2, z^2, xy, yz, zx$  or any combination of these. In that case, the transition moment integral will have nonzero value and the vibrational mode is Raman active.

This rule can be applied to find out the Raman activity of the vibrational modes of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ .

### $\text{H}_2\text{O}$

In Unit 5, we have mentioned that for  $\text{H}_2\text{O}$  (as also for  $\text{SO}_2$ ) molecule, two of the vibrational modes belong to  $A_1$  symmetry and the third one belongs to  $B_1$  symmetry and all these are IR active. Let us now see whether these are Raman active.

#### (i) Vibrational modes with $A_1$ symmetry

From the  $C_{2v}$  character table, we see that the vibrational modes with  $A_1$  symmetry belong to the same irreducible representation as  $x^2, y^2$  or  $z^2$ . Hence the vibrational modes with  $A_1$  symmetry are Raman active.

#### (ii) Vibrational mode with $B_1$ symmetry

The vibrational mode with  $B_1$  symmetry belongs to same irreducible representation as  $xz$ ; hence this mode also will be Raman active.

### $\text{NH}_3$

In unit 5, we have mentioned that for  $\text{NH}_3$  molecule, two of the vibrational modes belong to  $A_1$  symmetry and the other two to E symmetry. From the  $C_{3v}$  character table, we see that (i) the vibrational modes with  $A_1$  symmetry belong to the same irreducible representation as  $z^2$  or  $x^2 + y^2$ , and (ii) the vibrational modes with E symmetry belong

Since  $\text{SO}_2$  belongs to  $C_{2v}$  group (just like  $\text{H}_2\text{O}$  molecule), two of the vibrational modes belong to  $A_1$  symmetry and the third one belongs to  $B_1$  symmetry. Also all these three modes are active both in infrared and Raman spectra.

to the same irreducible representation as  $(x^2 - y^2, xy)$  or  $(xz, yz)$ . Hence all the four vibrational modes of  $\text{NH}_3$  are Raman active.

Let us next explain the mutual exclusion principle using group theory.

### The mutual exclusion principle

Point groups of molecules with centre of symmetry have two sets of irreducible representations. The representations which are symmetric with respect to inversion are called *g* ('gerade') representations, while those which are antisymmetric to inversion are called *u* ('ungerade') representations. Let us explain as to how to identify a particular representation as *u* or *g*.

By inversion operation, the coordinates *x*, *y* or *z* become  $-x$ ,  $-y$  or  $-z$  i.e., these undergo a sign change on inversion.

$$\begin{array}{l} \text{inversion} \\ x \longrightarrow -x \\ \\ \text{inversion} \\ y \longrightarrow -y \\ \\ \text{inversion} \\ z \longrightarrow -z \end{array}$$

i.e., *x*, *y* and *z* coordinates are antisymmetric with respect to inversion. But the quadratic or the binary functions of coordinates do not undergo a sign change on inversion i.e., these are symmetric with respect to inversion.

$$\begin{array}{l} \text{inversion} \\ x^2 \longrightarrow (-x) \cdot (-x) = x^2 \\ \\ \text{inversion} \\ xy \longrightarrow (-x) \cdot (-y) = xy \end{array}$$

This is true of all binary or quadratic coordinates and their combinations.

In the light of the definition given for *g* and *u* functions, the coordinates *x*, *y* and *z* which are antisymmetric to inversion belong to *u* representation whereas the quadratic and binary coordinates,  $x^2, y^2, z^2, xy$ , etc. belong to *g* representation (since these are symmetric with respect to inversion).

The selection rule for IR active vibration which we have studied in the Appendix of the last unit can be stated as follows:

A vibration will be IR active, if the excited mode has the same symmetry as one of the cartesian coordinates (*x*, *y* and *z*).

Using this, we can infer that in the molecules with centre of symmetry, the vibrational modes belonging to *u* symmetry species are IR active.

Similarly using the selection rule for Raman spectra that a normal vibration will be Raman active if the vibrational mode has the same irreducible representation as one of the quadratic or binary coordinates, we can infer that in case of molecules with centre of symmetry, vibrational modes belonging to *g* symmetry species are Raman active.

In short, in molecules with centre of symmetry, a vibrational mode may be active either in Raman or in infrared but not in both. This is the mutual exclusion principle stated in Sec. 6.4.

You can use Table 6.2, Figs. 6.1, 6.2, 6.8 and 6.9 and the character tables  $C_{2v}$ ,  $C_{3v}$ ,  $C_{\infty v}$  and  $D_{\infty h}$  (given at the end of this Appendix) and verify that

- (i) IR active vibrations belong to the same symmetry species as *x*, *y* or *z*.
- (ii) Raman active vibrations belong to the same symmetry species as any of the quadratic or binary functions of the cartesian coordinates.

For instance, from Table 6.2, Fig. 6.2 and the character table for  $D_{\infty h}$  group, we can infer that the symmetric stretching vibration of  $\text{CO}_2$  is Raman active since it belongs to  $\Sigma_g^+$  symmetry to which also quadratic and binary functions,  $x^2 + y^2$  and  $z^2$ , belong. Similarly, bending and antisymmetric stretching of  $\text{CO}_2$  are IR active since these two belong to  $\Pi_u$  and  $\Sigma_u^+$  to which the cartesian coordinates (*x*, *y*) and *z* also belong. Why don't you verify the entries in Table 6.2 regarding the IR and Raman active vibrations of  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$  and  $\text{ClO}_3^-$  ion also? Use the relevant figures and the character tables of point groups as mentioned in Table 6.2.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$		
$A_1$	1	1	1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	
$E$	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$

$C_{\infty v}$	$E$	$2C_{\infty}^{\phi}$	.....	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	.....	1	$z$	$x^2 + y^2, z^2$
$A_2 \equiv \Sigma^-$	1	1	.....	-1	$R_z$	
$E_1 \equiv \Pi$	2	$2 \cos \phi$	.....	0	$(x, y); (R_x, R_y)$	$(xz, yz)$
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	.....	0		$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	.....	0		
.....	....	.....	.....	.....		

$D_{\infty h}$	$E$	$2C_{\infty}^{\phi}$	.....	$\infty\sigma_v$	$i$	$2S_{\infty}^{\phi}$	.....	$\infty C_2$		
$\Sigma_g^+$	1	1	.....	1	1	1	.....	1		$x^2 + y^2, z^2$
$\Sigma_g^-$	1	1	.....	-1	1	1	.....	-1	$R_z$	
$\Pi_g$	2	$2 \cos \phi$	.....	0	2	$-2 \cos \phi$	.....	0	$(R_x, R_y)$	$(xz, yz)$
$\Delta_g$	2	$2 \cos 2\phi$	.....	0	2	$2 \cos 2\phi$	.....	0		$(x^2 - y^2, xy)$
.....	.....	.....	.....	.....	.....	.....	.....	.....		
$\Sigma_u^+$	1	1	.....	1	-1	-1	.....	-1	$z$	
$\Sigma_u^-$	1	1	.....	-1	-1	-1	.....	1		
$\Pi_u$	2	$2 \cos \phi$	.....	0	-2	$2 \cos \phi$	.....	0	$(x, y)$	
$\Delta_u$	2	$2 \cos 2\phi$	.....	0	-2	$-2 \cos 2\phi$	.....	0		
.....	.....	.....	.....	.....	.....	.....	.....	.....		

### Further Reading

1. J.R.Dyer, Application of Absorption Spectroscopy of Organic Compounds, Eastern Economy Edition, Prentice-Hall of India Pvt.Ltd.
2. D.H.Williams and Ian Fleming, Spectroscopic Methods in Organic Chemistry. Tata Mc Graw Hill Publishing Co. Ltd. 4thEd.
3. C.N Banwell, Fundamentals of Molecular Spectroscopy, 3rd Ed, Tata McGraw Hill Publishing Co. Ltd.