

Lecture 30 Title : Raman Scattering :

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In previous lectures we have learnt that the Infrared spectroscopy is used to record the absorption spectrum of vibrational and rotational states of diatomic molecules.

The origin of this absorption is the change of the dipole moment due to the vibrational and rotational motion.

However, homonuclear diatomic molecules neither possess the permanent dipole moment nor induce dipole moment due to the vibration. Thus these levels are inactive or forbidden in case of Infra red absorption.

Raman spectroscopy is a tool to overcome this problem. Here we will learn the origin of the Raman spectrum and its applications.

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Raman Effect

This inelastic scattering by molecules was first discovered by Sir C. V. Raman in 1928.

He was awarded Nobel Prize for this fundamental work in 1930.

It was predicted by Adolf Smekal in 1923 but named after one of its discoverers in 1928, the Indian scientist Sir Chandrasekhara Venkata Raman

Raman scattering is the inelastic scattering of a photon – change in photon energy

By nature weak effect (approximately 1 in 10^7 photons)



Sir Chandrasekhara Venkata Raman

When strong light of 19436 cm^{-1} is scattered by a material consisting of molecules containing carbonyl group, its spectrum exhibits two rather weak lines at 17786 cm^{-1} and 21086 cm^{-1} apart from the line at 19436 cm^{-1} .

Nature of Raman Effect:

When a parallel beam of monochromatic light goes through a gas or liquid or transparent solid, a part of light is scattered in all directions.

The intensity of scattered light is inversely proportional to the fourth power of wavelength.

It is found that the scattered light contains exactly the same wavelength as the incident light. This scattering is called as Rayleigh scattering.

Apart from this wavelength, the scattered light also contains some weak additional lines. As said earlier that this phenomenon was first discovered by Raman and his collaborators and is known as Raman Effect.

A comparison of the wave numbers of these additional lines shows that these Raman lines are independent of the wavelength of the incident light but depends on the nature of scattering substance.

For different scattering substance, the displacements of the Raman lines from the incident light are different. Thus, the displacements are characteristics of the scattering substance.

Classical theory of Raman Effect:

As discussed in module 1 that when an atom or molecule is brought into an electric field \vec{E} , an electric dipole moment $\vec{\mu}$ is induced in the system. The magnitude of this induced dipole moment is proportional to the electric field,

$$|\vec{\mu}| = \alpha |\vec{E}| \dots\dots\dots(30.1)$$

where α is known as the polarizability.

Except for the case of spherical symmetry, the magnitude of the induced dipole moment depends on the direction of the electric field.

For example, in case of a diatomic molecule, the induced dipole moment will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis.

In general, the direction of $\vec{\mu}$ does not coincide with the direction of \vec{E} . So for a non isotropic molecule, we can write,

$$\mu_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$

$$\mu_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$

$$\mu_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

$$\text{Where } E^2 = E_x^2 + E_y^2 + E_z^2$$

α_{ij} is known as polarizability tensor and this tensor is symmetric i.e. $\alpha_{ij} = \alpha_{ji}$.

Using principle axis transformation, we can write,

$$\mu'_x = \alpha_{x'x'}E_{x'}$$

$$\mu'_y = \alpha_{y'y'}E_{y'}$$

$$\mu'_z = \alpha_{z'z'}E_{z'}$$

x' , y' and z' are principle axes

If we draw lines in any direction from the origin of the principle axes coordinate system, of length proportional to $\frac{1}{\sqrt{\alpha}}$, then the locus of the points of lines will form a surface known as polarizability ellipsoid whose principle axis are x' , y' and z' .

The equation of the ellipsoid as shown in figure-30.1 is given by,

$$\alpha_{x'x'}x'^2 + \alpha_{y'y'}y'^2 + \alpha_{z'z'}z'^2 = 1$$

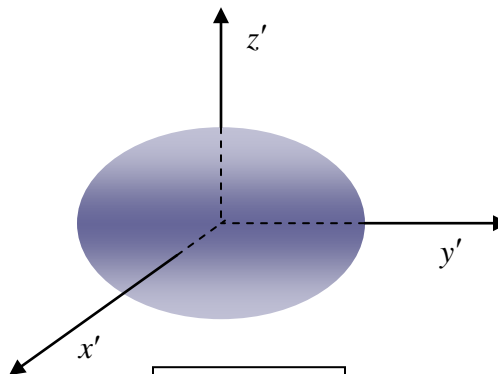


Figure-30.1

For diatomic molecule

$$\alpha_{x'x'} = \alpha_{z'z'}$$

If a light of frequency ν_0 is incident then $\vec{E} = \vec{E}_0 \sin 2\pi\nu_0 t$, then the dipole moment will be from equation 30.1,

$$|\vec{\mu}| = \alpha |\vec{E}_0| \sin 2\pi\nu_0 t \dots\dots\dots(30.2)$$

So the dipole will also oscillate with frequency ν_0 . According to classical electromagnetic theory, when a dipole oscillates, it radiates with the same frequency of oscillation. This is nothing but the Rayleigh scattering as discussed before.

Now, if the molecule vibrates i.e., the internuclear distance changes. And also this polarizability depends on the orientation of the molecule. So the rotation of the molecule also changes the polarizability.

Now we can write the polarizability for vibration

$$\alpha = \alpha_{0v} + \alpha_{1v} \sin 2\pi\nu_v t$$

Where α_{0v} the polarizability in the equilibrium position is, ν_v is the vibrational frequency and α_{1v} is the proportionality constant ($\alpha_{1v} \ll \alpha_{0v}$).

Similarly, for rotation we can write,

$$\alpha = \alpha_{0r} + \alpha_{1r} \sin 2\pi 2\nu_r t$$

Here the frequency with which the polarizability changes during rotation is twice the rotational frequency (figure-30.2). The reason for this is that, the polarizability is same for that of the opposite field.

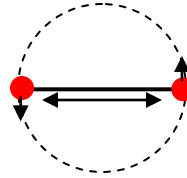


Figure 30.2

Now,

$$\vec{\mu}_v = \alpha \vec{E}$$

$$= (\alpha_{0v} + \alpha_{1v} \sin 2\pi\nu_v t) \vec{E}_0 \sin 2\pi\nu_0 t$$

$$= \alpha_{0v} \vec{E}_0 \sin 2\pi\nu_0 t + \alpha_{1v} \vec{E}_0 \sin 2\pi\nu_v t \sin 2\pi\nu_0 t$$

$$= \alpha_{0v} \vec{E}_0 \sin 2\pi\nu_0 t + \frac{\alpha_{1v}}{2} \vec{E}_0 [\cos 2\pi(\nu_0 - \nu_v)t - \cos 2\pi(\nu_0 + \nu_v)t] \dots\dots\dots(30.3)$$

Similarly for rotation

$$\vec{\mu}_r = \alpha_{0r} \vec{E}_0 \sin 2\pi\nu_0 t + \frac{\alpha_{1r}}{2} \vec{E}_0 [\cos 2\pi(\nu_0 - 2\nu_r)t - \cos 2\pi(\nu_0 + 2\nu_r)t] \dots\dots\dots(30.4)$$

Thus we see from equation-30.3 that the induced dipole moment not only oscillates with frequency ν_0 but also with other displaced frequency $(\nu_0 - \nu_v)$ and $(\nu_0 + \nu_v)$ in case of vibration.

For rotation, the displaced frequencies are $(\nu_0 + 2\nu_r)$ and $(\nu_0 - 2\nu_r)$.

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So the scattered light contains displaced lines on both the sides of undisplaced line and the separations in both cases are same.

Frequency on lower side is known as Stokes lines and on higher side is known as anti stocks lines as shown in figure-30.3.

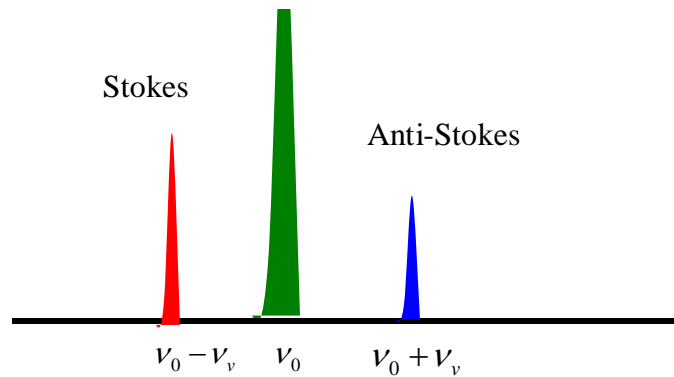


Figure-30.3

The experimental Raman spectrum shows that the intensities of the Stokes lines are higher than that of the anti-Stokes lines.

Classical explanation does not provide information about intensity for both the lines and thus inadequate for explaining the experimental spectrum.

Quantum theory of Raman Effect:

Let us consider for a system, E_0 is the ground electronic state and $\nu'' = 0, 1, \dots$ are the vibrational states of the ground electronic state. If the light frequency ν_0 incident on this system, three cases may arise.

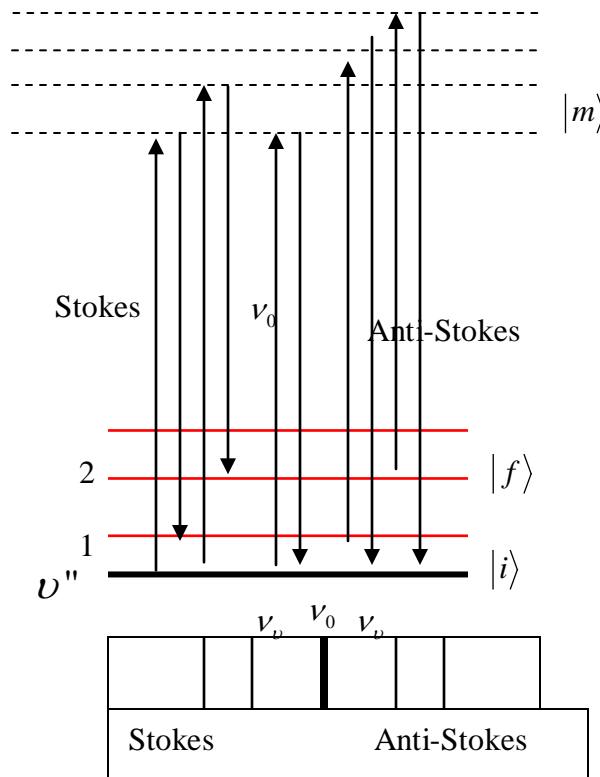


Figure-30.4

Case-I:

Molecules absorb the light of frequency $h\nu_0$ and go to the vibrational state as shown by dashed line in the figure. The vibrational state is created by the light and molecular interaction and exists as long as the light exists. It is not the eigen state of the system but is a linear combination of all the eigen states of the molecule. Thus by definition, the lifetime of the virtual state is very very small. Now the molecules will back to the ground vibrational state ($\nu = 0$) and will emit the same frequency ν_0 . This is the same Rayleigh scattering.

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Case II

Molecules are transferred to the vibrational state by light ν_0 and these excited molecules may come back to the higher vibrational state ($\nu'' = 1$). In this case the emitted frequency is $\nu_0 - \nu_\nu$. According to the energy conservation, the energy will be lost from the incident photon energy $h\nu_0$ to excite the vibrational frequency of the molecule and thus, the emitted photon energy

$$h\nu_{\text{stokes}} = h\nu_0 - h\nu_\nu = h(\nu - \nu_\nu)$$

Case III

In thermal equilibrium, the excited vibrational levels are also populated and molecules there can also absorb light and go to the virtual state. While coming back to the same vibrational state, this will emit frequency ν_0 . But if molecules come back to ground vibrational state ($\nu = 0$) then the emitted frequency will be $(\nu_0 + \nu_\nu)$. Again, according to the energy conservation, the photon energy adds up the vibrational energy and emitted

energy will be

$$h\nu_{\text{antistokes}} = h\nu_0 + h\nu_\nu$$

A typical experimental set up for Raman spectroscopy is shown in figure 30.5

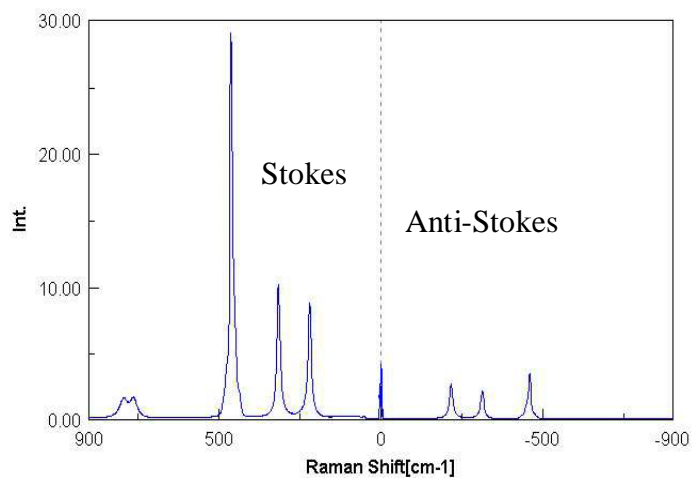
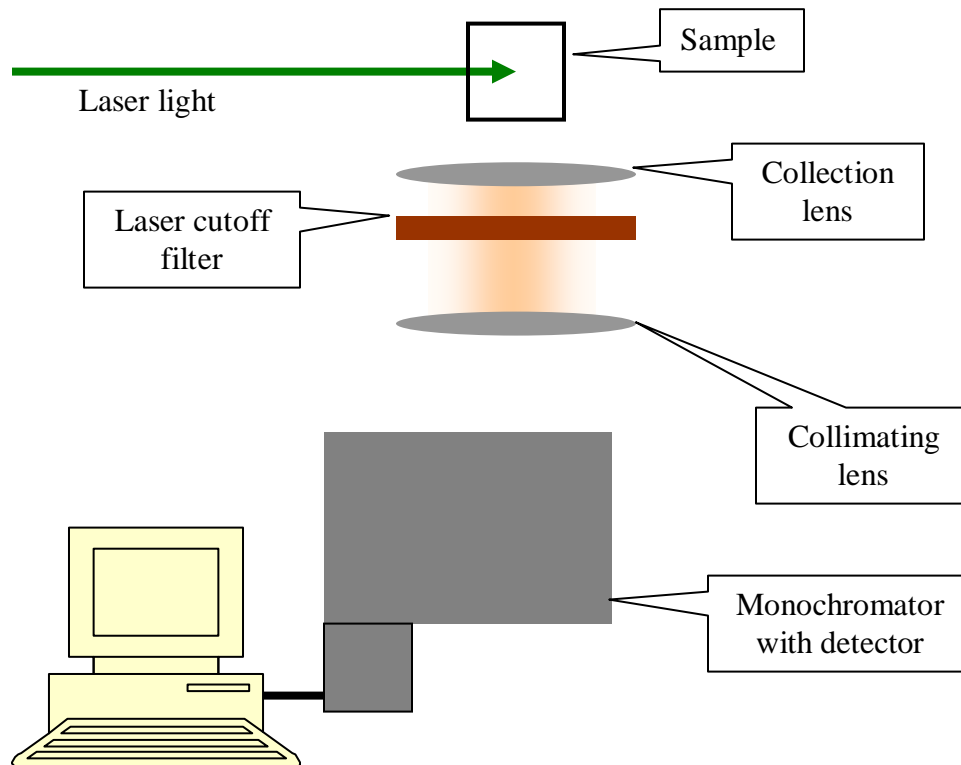


Figure-30.5

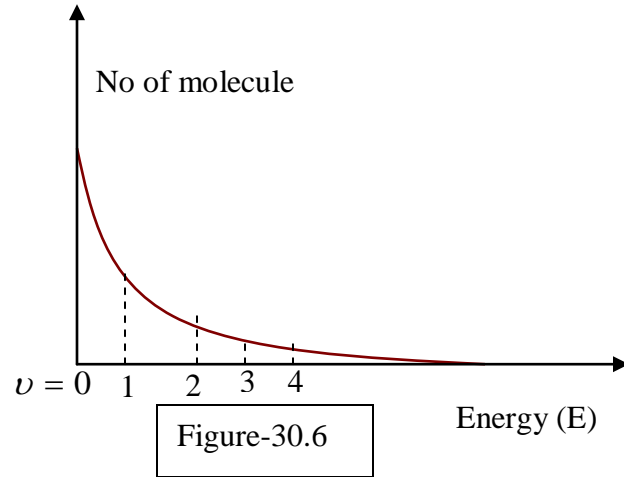
A typical Raman spectrum of CCl_4 is shown in figure 30.5

Now we will discuss why the Stokes lines are higher in intensity than the anti-Stokes lines.

As mentioned earlier, the population to these vibrational states depends on the Maxwell Boltzmann distribution

$$N_v = \frac{N}{Q_v} e^{-G_0(v)hc/kT}$$

The figure-30.6 gives the relative distribution of the no. of molecules in a given vibrational state.



The origin of anti-Stokes lines is from the higher vibrational levels and the population is lower in those states than the ground vibrational level.

As discussed earlier lecture that intensity of transitions lines not only depend on the transition probability, but also depend on the population of the initial state.

This is the reason for the lower intensity of anti-Stokes lines than the Stokes lines.

For vibrational Raman transitions, the selection rule is $\Delta v = \pm 1$. But the parity selection rule is that it connects the same parity states. This can be understood by considering the Raman process as two-photon process. Referring to figure-30.4, the two-photon transition can written as

$$\langle f | e\vec{r} | m \rangle \langle m | e\vec{r} | i \rangle$$

Where $|i\rangle$, $|m\rangle$ and $|f\rangle$ are the initial, middle and final states respectively. Since middle state $|m\rangle$ is not an eigen state of the system (virtual state) we have to define as sum of all eigen states. Thus the transition probability is defined as

$$R \propto \sum_m \langle f | e\vec{r} | m \rangle \langle m | e\vec{r} | i \rangle$$

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Since the electric dipole operator $e\vec{r}$ connects only opposite parity states, it is clear from the above equation that for a nonzero transition probability $|i\rangle$ and $|f\rangle$ will be having the same parity whereas $|m\rangle$ has to be opposite parity states.

So the parity selection rules for which the Raman transitions are allowed

Symmetric \leftrightarrow Symmetric

Antisymmetric \leftrightarrow Antisymmetric

On the other hand, for Infra red spectroscopy as discussed in the previous lecture that the transition probability

$$R \propto \langle f | e\vec{r} | i \rangle$$

So $|i\rangle$ and $|f\rangle$ will be having the opposite parity states. So IR spectroscopy is the complementary of the Raman spectroscopy.

For symmetric molecules such as H_2 , N_2 all the vibrational states are symmetric. Thus it is forbidden in IR transition but allowed only in Raman transition. Hence for this kind of symmetric molecule, Raman spectroscopy is the only tool to get the information of the vibrational levels of the ground electronic state.

For diatomic molecules with identical nuclei such as H_2 , N_2 , for an exchange of the nuclei, the rotational wavefunctions will either remain unchanged or changes its sign. In the electronic ground state, either positive sign rotational levels are symmetric and negative sign levels are antisymmetric or positive sign rotational levels are antisymmetric and negative sign levels are symmetric. In both the cases, Raman selection rule is $\Delta J = 0, \pm 2$.

For the rotational Raman spectra

$\Delta J = 0$ gives the undisplaced Rayleigh line

$\Delta J = 0, \pm 2$ gives the displaced Raman lines.

The transition energy in the spectrum is given by

$$\begin{aligned}\bar{\nu} &= F(J+2) - F(J) \\ &= B(J+2)(J+3) - BJ(J+1) \\ &= 6B + 4BJ\end{aligned}$$

So in the Rotational Raman spectrum, the first undisplaced lines are at $6B$ and the separation between the other Stokes and anti-Stokes lines are $4B$.

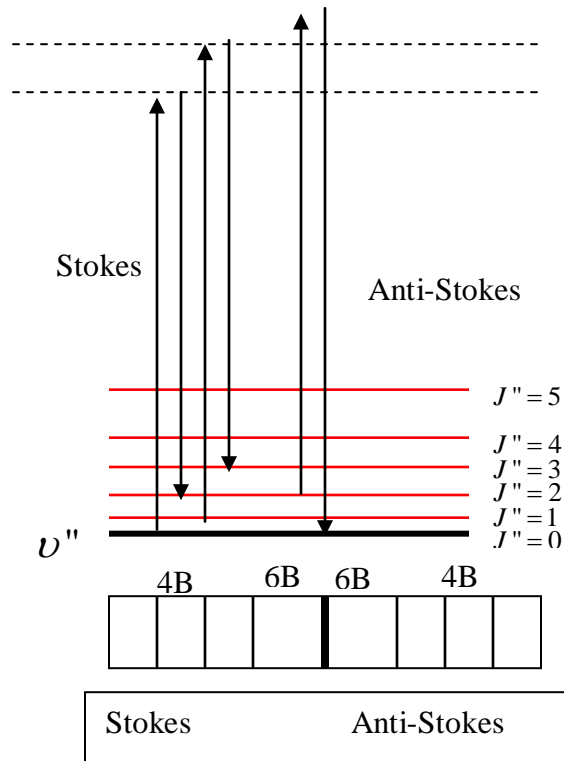
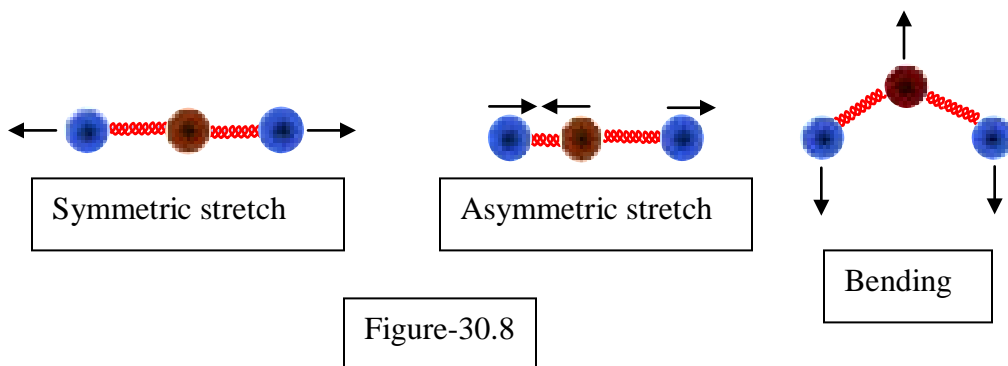


Figure-30.7

For the vibrational Raman spectra, let us take an example of carbon dioxide CO_2 .

The molecule Carbon dioxide is a triatomic molecule.

It has 3 modes of vibrations as shown in figure-30.8. They are (i) symmetric stretch, (ii) asymmetric stretch and (iii) bending.



Note: For linear molecules the no. of vibrational modes is $(3 \times \text{no. of atoms} - 5)$ and others are having the vibrational modes $((3 \times \text{no. of atoms} - 6))$.

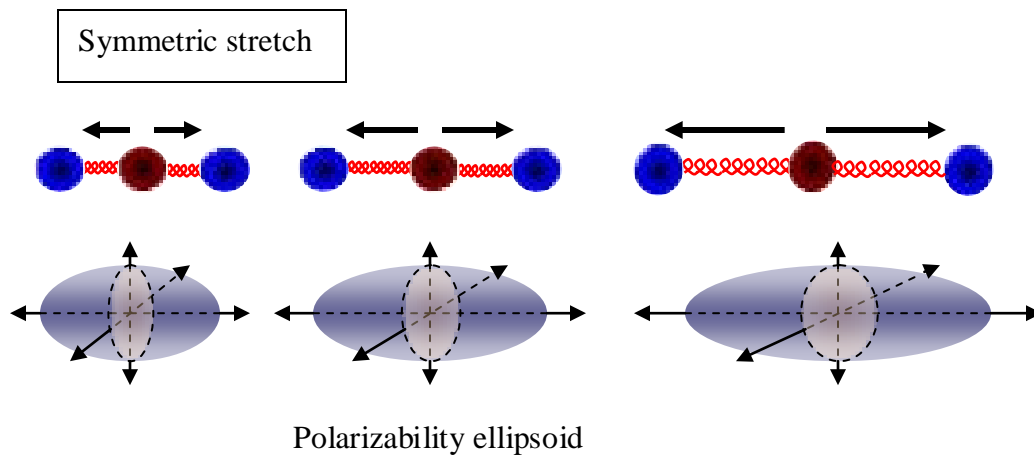


Figure-30.9

The symmetric stretch vibration ν_1 of CO_2 is shown in figure-30.9. During this vibration, the dipole moments of $C=O$ bonds are equal and opposite as shown by arrow, and thus no induced dipole moment for ν_1 vibration. So, this ν_1 vibration will be inactive in IR spectrum. But the polarizability tensor changes due to the vibration. So ν_1 will be active in Raman spectrum. This ν_1 vibration is observed in the Raman spectrum at 1335 cm^{-1} from the excitation laser line.

The second vibration ν_2 is asymmetric stretch. For this vibration the net dipole moment changes as shown by arrow in figure 3.10. So ν_2 will be active in IR spectrum. However, the polarizability ellipsoid does not change due to this vibrational motion. So it will be Raman inactive. This ν_2 is seen in IR spectrum at 667 cm^{-1} .

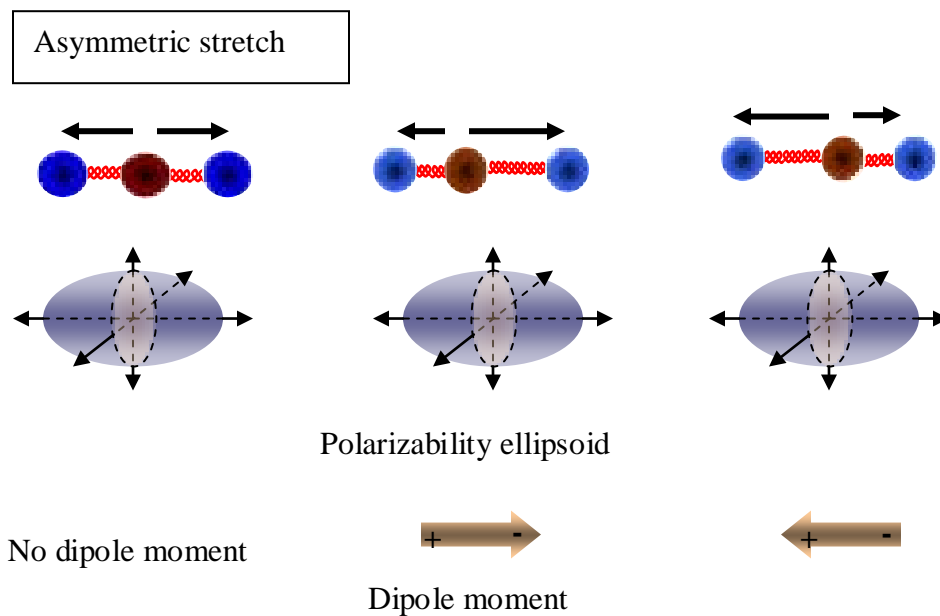


Figure-30.10

The third vibration ν_3 is bending. For this bending vibration the net dipole moment changes as shown by arrow in figure 3.11. So ν_3 will be active in IR spectrum. However, the polarizability ellipsoid does not change due to this vibrational motion. So it will be Raman inactive. This ν_3 is seen in IR spectrum at 2350 cm^{-1} .

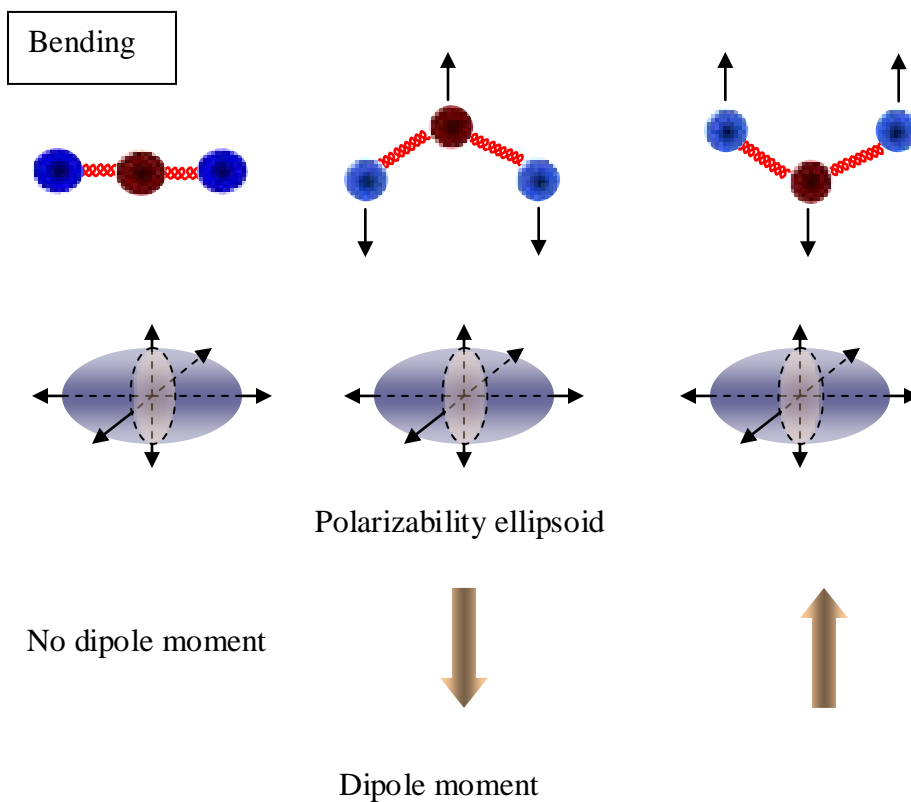
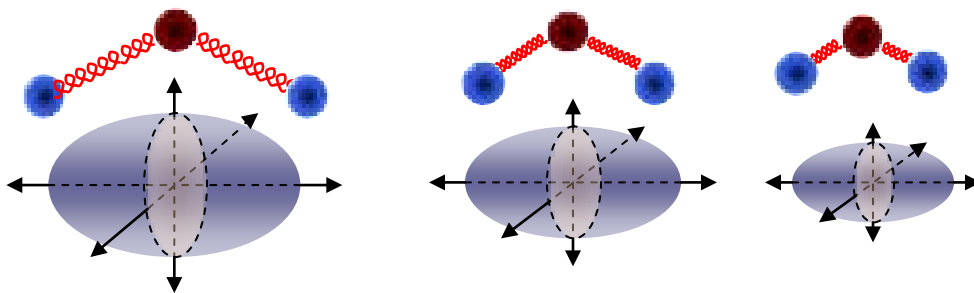


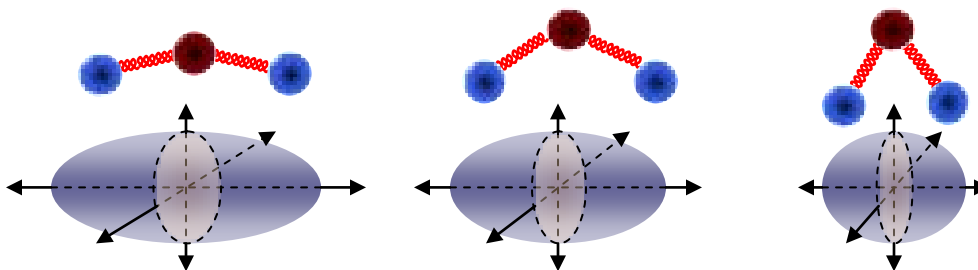
Figure-30.11

Let us take another example of Sulphur dioxide SO_2 . Figure-3012 shows the three normal modes of vibrations. As can be seen from the figure that for all three modes the polarizability ellipsoid changes. Thus all three modes will be Raman active. Not only this, the dipole moment also changes due to these three vibrations. Thus all these mode will be IR active. For SO_2 , $\nu_1 = 1150\text{ cm}^{-1}$, $\nu_2 = 520\text{ cm}^{-1}$, $\nu_3 = 1360\text{ cm}^{-1}$.

Symmetrical stretching ν_1



Bending ν_2



Asymmetrical stretching ν_3

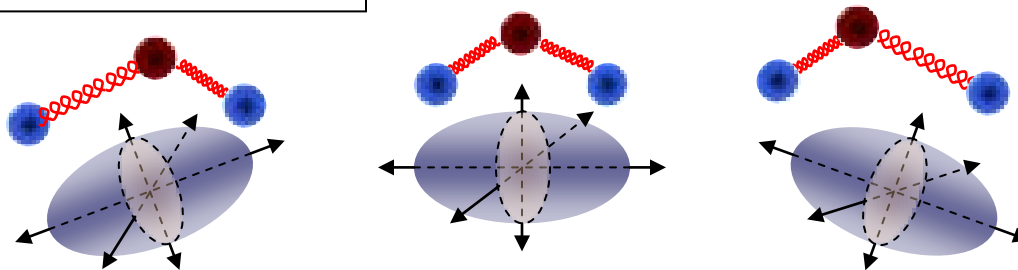


Figure-30.12

Note:

Comparison between Infra red and Raman spectroscopy:

For a given bond, the energy shifts observed in a Raman experiment should be identical to the energies of its infrared absorption bands, provided that the vibrational modes involved are active toward both infrared absorption and Raman scattering.

Infrared absorption requires that a vibrational mode of the molecule have a change in dipole moment or charge distribution associated with it.

On the other hand, scattering involves a momentary distortion of the electrons distributed around a bond in a molecule, followed by reemission of the radiation as the bond returns to its normal state.

In its distorted form, the molecule is temporarily polarized; that is, it develops momentarily an induced dipole that immediately disappears upon relaxation and reemission.

Recap

1. We have described spontaneous Raman effect that originates from the modulation of the polarizability by the molecular vibrations.
2. We have shown the inadequacy of the classical picture to account for the Stokes and anti-Stokes Raman line intensities.
3. In terms of the quantum mechanical picture, it has been described qualitatively as a two-photon process.
4. Cause of the experimentally observed unequal intensities of the Stokes and anti-Stokes Raman line has been traced to the difference in the population densities of the excited and ground vibrational states of the molecule at thermal equilibrium.
5. It has been shown that it provides access to those vibrational states of the molecule which cannot be addressed in IR absorption spectroscopy and hence complements the latter.