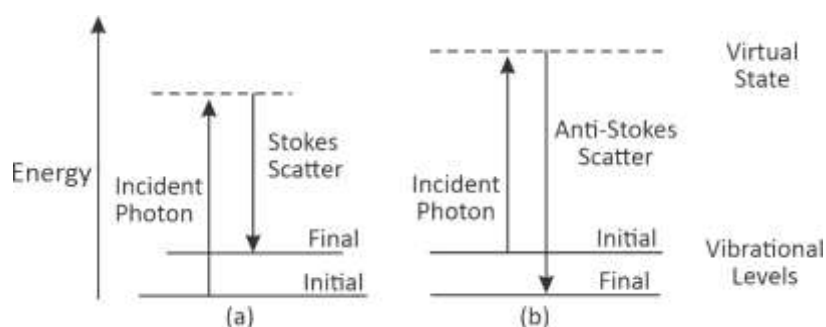


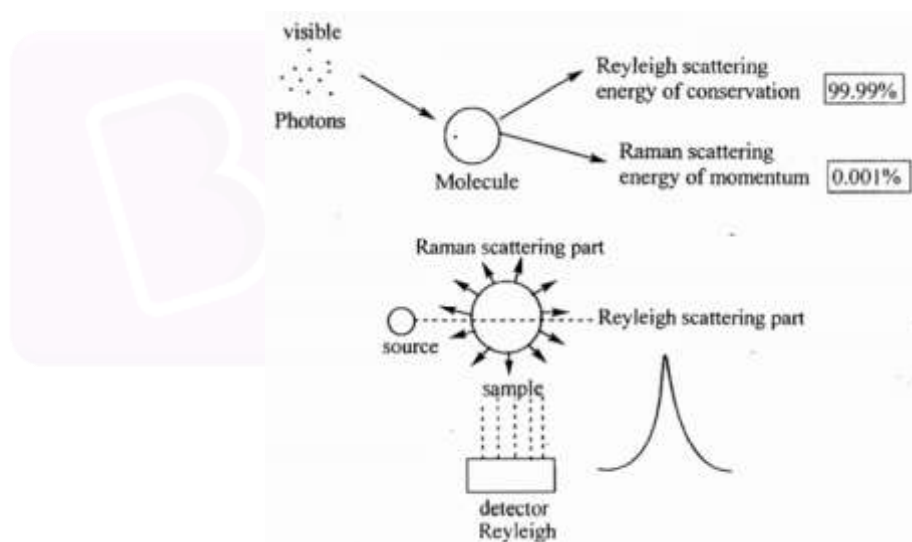
# Study Notes On Raman Spectrum

## Raman Spectrum

The Raman effect takes place when a photon is incident on a molecule and undergoes an interaction with the electric dipole of the molecule. In quantum mechanics, scattering refers to an excitation to a virtual state lower in energy than a real electronic transition with nearly coincident de-excitation and a change in vibrational energy. The energy level diagram which depicts the Stokes and Anti-stokes Raman scattering is given below as:



### Scattering of Photons:



Source, sample, and detector are situated at 90° of each other.

**Raman Activity:** For a molecule to be Raman active, there must occur some change in a component of molecular polarizability. This entity is an anisotropic property and can be expressed as:

$$\mu = \alpha E$$

Here,

$\alpha$  = Polarizability

E = Electric field of radiation

$\mu$  = induced dipole moment.

All the molecules with center of symmetry show mutual exclusion between I.R. and Raman activity.

If a molecule has a center of symmetry, then its IR active vibrations will be Raman inactive, and Raman active vibration will be IR inactive.

### RAMAN EFFECT AND RAMAN SCATTERING

When an electromagnetic radiation with frequency  $\nu$  and energy  $h\nu$  strikes the molecule of sample, then two possibilities are:

(1). In the case of a perfectly elastic collision, the photon will deflect as such without any change in energy. This phenomenon is known as Rayleigh scattering.

(2). In case of inelastic collision, molecules can either gain or lose energy related to vibrational and rotational energy levels. This phenomenon is known as Raman scattering. If there is a gain of energy takes place, then energy of scattered photon will be as:

$$h\nu - \Delta E.$$

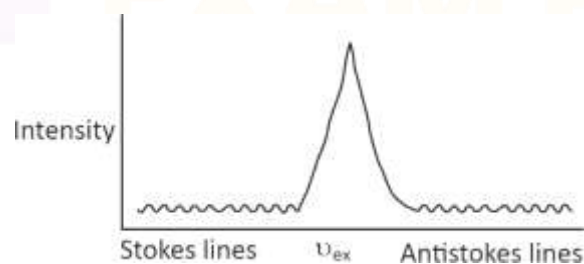
Here,  $\Delta E$  is the Raman shift.

For pure rotational Raman spectra, the value of Raman shift  $\Delta E$  will be equal to the separation in rotational energy levels.

For vibrational Raman spectra, the value of Raman shift will be equal to the separation in vibrational energy levels.

The radiation that scatters with a frequency lower than that of incident frequency is known as Stokes radiation.

Radiation scattered with a frequency higher than that of incident frequency is known as Anti Stokes radiation.



In Raman scattering, if photons get scattered by a ground state molecule, then loss in energy takes place which is equal to rotational or vibrational energy level separation and scattered photons have energy less than incident photons. This is known as Stokes radiation. If a scattered photon has higher energy than that of the incident photon, then radiation is anti-stoke.

Since the population of molecules in the ground state of rotational and vibrational energy levels are always higher than that of the excited state, as a result, the intensity of stoke lines will always be higher than anti stokes lines.

The position of stoke and anti-stokes lines are a mirror image of each other from the position of incident radiation.

**Pure Rotational Raman Spectra (For linear molecule):**

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1}$$

On neglecting D, the above expression will become:

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

**Selection Rule:**

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

If  $\Delta J = 0$ , it means no rotation will take place due to which there will be no change in the energy of the photon.

In the rotational spectrum, the selection rule was:

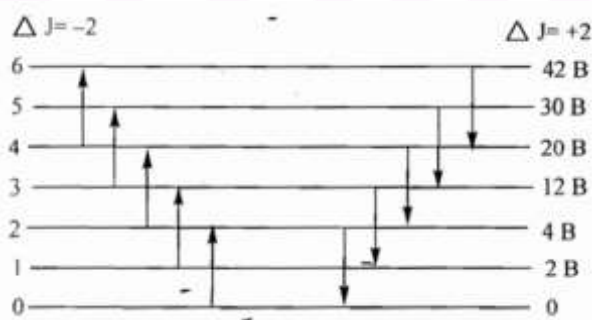
$$\Delta J = +2$$

During  $\frac{m}{n}$  rotation, the polarizability ellipsoid appears two times in a complete rotation.

Calculation  $J \rightarrow J + 2$

$$\epsilon_{J+2} - \epsilon_J = B(J+2)(J+2+1) - BJ(J+1)$$

$$\epsilon_{J+2} - \epsilon_J = B(4J+6) \text{ cm}^{-1}$$



**Vibrational Raman Spectra:**

$$E_v = \left( v + \frac{1}{2} \right) \bar{\omega}_e - x_e \bar{\omega}_e \left( v + \frac{1}{2} \right) \text{ cm}^{-1}$$

Selection Rule:

$$\Delta v = 0, \pm 1, \pm 2 \dots$$

For,

$$\Delta v = \pm 1$$

$$\Delta_{\epsilon v} = \omega_e(1 - 2x_e)$$

$$\text{Raman shift} = \nu_{\text{ex}} \pm \omega_e(1 - 2x_e)$$

**Rotational Vibrational Raman Spectra or, Raman Spectrum of Rotating Vibrator**

$$\epsilon_{Jv} = \left( v + \frac{1}{2} \right) \bar{\omega}_e - x_e \bar{\omega}_e \left( v + \frac{1}{2} \right) + BJ(J+1) \text{ cm}^{-1}$$

**Selection Rule:**

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

$$\Delta v = \pm 1, \pm 2, \pm 3 \dots\dots$$

For,

$$\Delta J = \pm 2$$

$$\Delta v = \pm 1$$

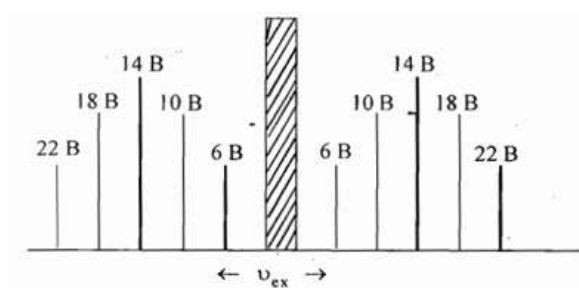
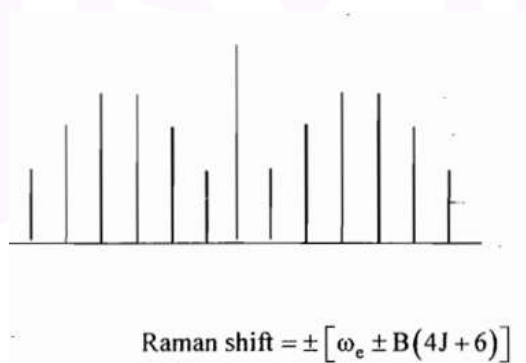
$$\Delta v = 0 \text{ to } \Delta v = 1$$

Then,

$$\Delta J = + 2, \Delta E = \omega_e^- + B(4J+6) \text{ S lines}$$

$$\Delta J = -2, \Delta E = \omega_e^- - B(4J+6) \text{ O lines}$$

$$\Delta J = 0, \Delta E = \omega_e^- \text{ Q lines}$$



$$\Delta J = B(4J + 6)$$

$$J = 0 \Rightarrow 6 B$$

$$J = 1 \Rightarrow 10 B$$

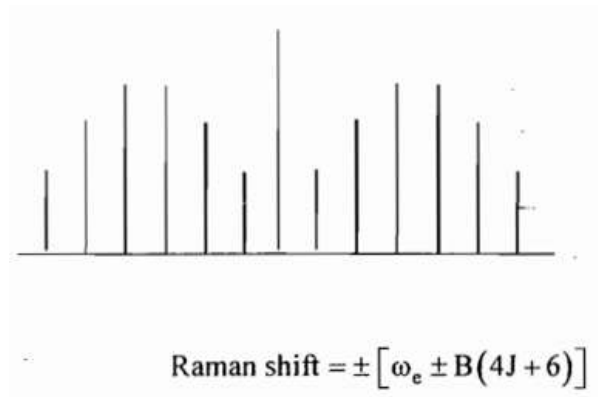
$$J = 2 \Rightarrow 14 B$$

$$J = 3 \Rightarrow 18 B$$

$$J = 4 \Rightarrow 22 B$$

$$\text{Raman shift} = \nu_{\text{ex}} \pm B(4J + 6)$$

For (-), Stoke lines will be there and for (+), Anti stokes lines will be there.



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