Introduction

The properties and structure of the molecules can be studied by analysing the spectrum of the molecules. The energy of a diatomic molecule is due to (i) the electronic configuration of electrons in the molecule (electronic energy E_e) , (ii) the vibration of the atoms about the equilibrium position (Vibrational energy E_v) and (iii) the rotation of the molecules as a whole about the centre of mass (rotational energy E_r). Thus the total energy of a molecule is expressed as sum of these three independent terms, i.e. $E = E_e + E_v + E_r$

These energies are quantized. If the molecule remains in the ground state level of electronic and vibrational energies, and if there is transitions between the rotational energy levels, then we get **pure rotational spectrum**. The spectrum lies in the microwave and far infrared regions.

If the molecule remains in the ground state level of electronic energies, and if there is transitions between the rotational and vibrational energy levels, then we get **rotation - vibration spectrum**. The spectrum lies in the near infrared regions.

If there is transitions in the electronic, rotational and vibrational energy levels, then we get electronic **spectrum**. The spectrum lies in the visible and ultraviolet regions.

Theory of Pure Rotational Spectrum

Consider a diatomic molecule with atoms of masses m_1 and m_2 separated by a distance R. The molecule can rotate about the centre of mass as shown.
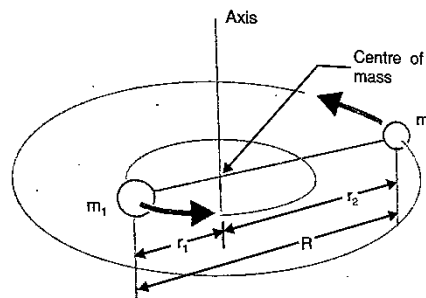
The moment of inertia of this molecule about an axis passing through its centre of mass and perpendicular to the line joining the atoms is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad ....(1)$$

where r_1 and r_2 are the distances of m_1 and m_2 respectively from the centre of mass.

From the definition of centre of mass $m_1 r_1 = m_2 r_2$ ......(2).

Also $R = r_1 + r_2$ ...(3) Thus $r_2 = R - r_1$

Substituting for r_2 in (2) $m_1 r_1 = m_2 (R - r_1)$ or $m_1 r_1 + m_2 r_1 = m_2 R$

Thus $m_1 r_1 + m_2 r_1 = m_2 R$ or $r_1 = \dfrac{m_2}{m_1 + m_2} R$ Also $r_2 = \dfrac{m_1}{m_1 + m_2} R$

Putting these values in equation (1), we get $I = \dfrac{m_1 m_2^2}{(m_1 + m_2)^2} R^2 + \dfrac{m_2 m_1^2}{(m_1 + m_2)^2} R^2$

or $I = \frac{m_1 m_2}{(m_1 + m_2)} R^2$ Thus $I = \mu R^2$ ....(4)   where $\mu = \frac{m_1 m_2}{(m_1 + m_2)}$.

The magnitude of the angular momentum of the molecule is $L = I\omega$

The angular momentum of the rotating diatomic molecule is quantized according to

$L = \sqrt{J(J+1)}\, \hbar$ where $J = 0, 1, 2, 3 .....$ where J is called the rotational quantum number.

The rotational kinetic energy of a diatomic molecule is $E_J = \frac{1}{2} I\omega^2$

As $L = I\omega$, $\omega = \frac{L}{I}$.   Thus $E_J = \frac{L^2}{2I}$ As $I = \mu R^2$ we get $E_J = \frac{L^2}{2\mu R^2}$

Since the angular momentum is quantized, $L = \sqrt{J(J+1)}\, \hbar$ where $J = 0, 1, 2, 3...$

We get $E_J = \frac{\hbar^2}{2I} J(J+1)$ ....(5)

The rotational energy levels of the molecules are found by using the selection rule $\Delta J = \pm 1$. **For two successive energy levels corresponding to** J and $J + 1$. The energy difference is given by $\Delta E = \frac{\hbar^2}{2I} (J+1)(J+2) - \frac{\hbar^2}{2I} J(J+1)$

$$= \frac{\hbar^2}{2I} (J+1)[J + 2 - J]$$

or $E_{J+1} - E_J = \Delta E = \frac{\hbar^2}{I}(J+1)$ ....(6)

The frequencies associated with the transitions between these adjacent states are

$\nu = \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h} = \frac{\hbar^2}{I}(J+1) \times \frac{1}{h}$

or $\nu_{J \to J+1} = \frac{\hbar}{2\pi I}(J+1)$ $\left(\text{since } \hbar = \frac{h}{2\pi}\right)$

The spectrum of a rigid molecule therefore consists of equally spaced lines as shown.

Pure rotational spectra fall in the microwave regions or far infrared regions of the spectrum with frequencies of the order of 10^{12} Hz or energies of 10^{-4} eV .
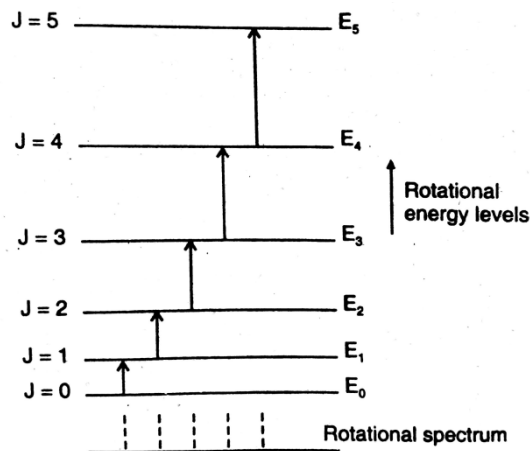
Note : 1. Rotational transitions are found to occur only in molecules that have permanent dipole moment. This is the reason that non-polar diatomic molecules (like H_2) and symmetric polyatomic molecules (like CO_2) do not exhibit rotational spectra.

2. In the pure rotational spectrum $\Delta v = \dfrac{\hbar}{2\pi I}$ (between two successive levels). If Δv is known, I *(moment of inertia)* and hence R can be calculated which is the length of the chemical bond between the atoms.

Theory of origin of Vibration-Rotation spectrum of a molecule

Vibrational spectrum : When a molecule is sufficiently excited, it can vibrate as well as rotate. The graph shows the variation of potential energy of a diatomic molecule with interatomic distance R. The potential energy of a diatomic molecule can be expressed as $V = V_0 + \dfrac{1}{2}k(R - R_0)^2$ ...(1)

where R_0 is the equilibrium separation of the atoms.
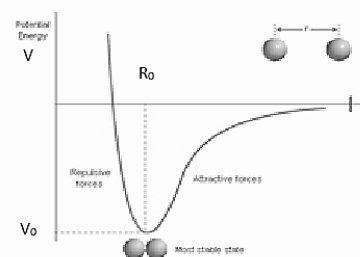
The interatomic force that give rise to potential energy is $F = -\dfrac{dV}{dR} = -k(R - R_0)$ (by differentiating the above equation). This force is the restoring force like in the case of spring and an excited molecule can undergo simple harmonic oscillations. Classically the frequency of oscillation is $v_0 = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$ ...(2) where μ is the reduced mass of the diatomic molecule.

When the quantum mechanical analysis of the harmonic oscillator is considered, the enrgy of the oscillation is found to be $E_V = \left(v + \dfrac{1}{2}\right)hv_0$ ....(3) where v is the vibrational quantum number. It takes values $v = 0, 1, 2, 3, ...$

Substituting for v_0 from (2) in (3), we get $E_V = \left(v + \dfrac{1}{2}\right)h\dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$

or $E_V = \left(v + \dfrac{1}{2}\right)\hbar\sqrt{\dfrac{k}{\mu}}$ .....(4) The vibrational energy levels are equally spaced and the zero point energy is given by $\dfrac{1}{2}hv_0$. The energy difference between adjacent levels is v and $v + 1$ is $\Delta E_V = hv_0$. The frequency of the absorbed of emitted ration is $v_0 = \dfrac{\Delta E_V}{h}$. The allowed transitions are between neighbouring energy levels based on the

selection rule $\Delta v = \pm 1$. The vibrational frequencies of most diatomic molecules fall in the infrared region with frequencies of the order of 10^{14} Hz or energies of about 0.1 eV.

The molecular energy due to both rotation and vibration is obtained by combining the energies of the two cases. It is given by $E_{VR} = E_V + E_R$ $(E_V \gg E_R)$

$$E_{VR} = \left(v + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} +$$

$$\frac{\hbar^2}{2I} J(J+1) \quad \ldots(5)$$

E_V is very large compared to E_R. Even at high temperatures only the vibrational states corresponding to $v = 0$ and $v = 1$ are excited. The diagram (for HBr molecule) shows the $J = 0, 1, 2, 3, 4$ levels of a diatomic molecule for the $v = 0$ and $v = 1$ vibrational states. It also shows that the spectral lines in absorption. The selection rules are $\Delta v = +1$ and $\Delta J = \pm 1$. The transition with $\Delta J = 0$ is not allowed.

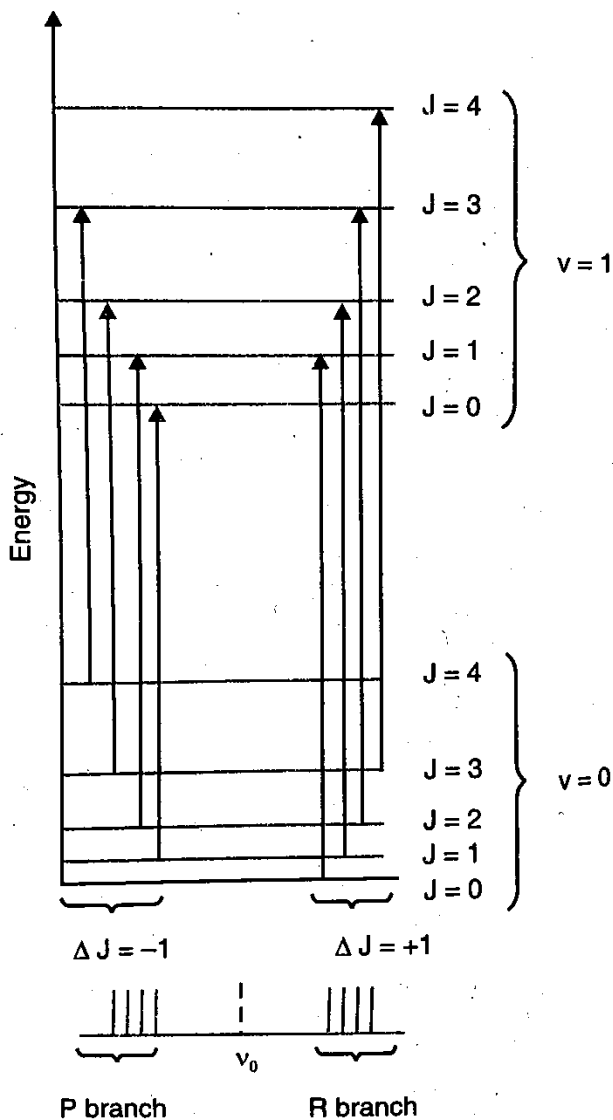The $v = 0 \rightarrow v = 1$ transitions fall into two categories,

(i) P Branch :

Here $\Delta J = -1$ $(i.e. \ J \rightarrow J - 1)$

From equation (4) the frequencies of the spectral lines in the P branch are given by

$$\nu_P = \frac{E_{1,J-1} - E_{0,J}}{h}$$

$$\nu_P = \frac{1}{h} \left\{ \left[\left(1 + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} + \frac{\hbar^2}{2I} (J-1)(J-1+1) \right] - \left[\left(0 + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} + \frac{\hbar^2}{2I} J(J+1) \right] \right\}$$

$$v_P = \left\{ \left[\left(1 + \tfrac{1}{2}\right) \tfrac{1}{2\pi} \sqrt{\tfrac{k}{\mu}} + \tfrac{\hbar^2}{2hI}(J-1)(J-1+1) \right] - \left[\left(0 + \tfrac{1}{2}\right) \tfrac{1}{2\pi} \sqrt{\tfrac{k}{\mu}} + \tfrac{\hbar^2}{2hI}J(J+1) \right] \right\}$$

$$v_P = \tfrac{1}{2\pi} \sqrt{\tfrac{k}{\mu}} + [\,(J-1)J - J(J+1)\,]\tfrac{\hbar}{4\pi I} \quad \text{or} \quad \boldsymbol{v_P = v_0 - J\tfrac{\hbar}{2\pi I}} \quad (J = 1, 2, 3, ...)$$

(ii) R Branch :

Here $\Delta J = +1 \ (i.e. \ J \to J + 1)$

From equation (4) the frequencies of the spectral lines in the P branch are given by

$$v_R = \frac{E_{1,J+1} - E_{0,J}}{h}$$

$$v_R = \tfrac{1}{h} \left\{ \left[\left(1 + \tfrac{1}{2}\right) \hbar \sqrt{\tfrac{k}{\mu}} + \tfrac{\hbar^2}{2I}(J+1)(J+1+1) \right] - \left[\left(0 + \tfrac{1}{2}\right) \hbar \sqrt{\tfrac{k}{\mu}} + \tfrac{\hbar^2}{2I}J(J+1) \right] \right\}$$

$$v_R = \tfrac{1}{2\pi} \sqrt{\tfrac{k}{\mu}} + [\,(J+1)(J+2)J - J(J+1)\,]\tfrac{\hbar}{4\pi I}$$

or $\quad \boldsymbol{v_R = v_0 + (J+1)\tfrac{\hbar}{2\pi I}} \quad (J = 0, 1, 2, 3, ...)$

There is no line at $v = v_0$ (the Q Branch) because transitions for which $\Delta J = 0$ are forbidden in the diatomic molecules. The spacing between the lines in the in both the P and R branch is $\Delta v = \tfrac{\hbar}{2\pi I}$. Hence by measuring the frequencies of these lines, the moment of inertia of the molecule and the length of the chemical bond can be calculated.

Electronic spectra of molecules

When the molecules possess sufficiently large amount of energy, the electronic states of the molecule can be excited. This gives rise to the most general type of transitions, *rotation-vibration-electronic* transitions. These produce photons of frequency

$v = \dfrac{E_{e1} - E_{e2}}{h} + \dfrac{E_{v1} - E_{v2}}{h} + \dfrac{E_{r1} - E_{r2}}{h}$. It is the outermost electrons of the atoms compsing the molecule that are involved. These transitions are energetic enough that they produce electronic bands in the visible and ultraviolet regions. All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule.

Scattering of light

The phenomenon in which the particles of the medium deviate light in a lateral direction is called scattering of light. The particles of the medium absorb light and then emit light in all directions.

Types of scattering

1. Coherent scattering or elastic scattering   2. Incoherent scattering or inelastic scattering

Coherent scattering

The phenomenon of scattering in which the scattered light has the same wavelength as that of incident light is called coherent scattering. In coherent scattering, the incident light does not suffer any change in its energy. Hence it is also called as elastic scattering. Eg. Rayleigh scattering and Tyndall scattering.

Rayleigh scattering : When the dimensions of the scattering particles is very small compared to the wavelength of the incident radiation, the scattering is called Raleigh scattering. According to Raleigh, the intensity of the scattered radiation is inversely proportional to the fourth power of the wavelength of the incident light. i.e, $I \, \alpha \, \dfrac{1}{\lambda^4}$

Let **a** be the size of the particle scattering light and λ the wavelength of the incident light.

If a << λ, Rayleigh's scattering takes place and light of shorter wavelengths get scattered to greater extent.

If a >> λ, Tyndall scattering takes place and light of all wavelengths get scattered nearly equal

Blue colour of sky : The blue colour of the sky is due to Rayleigh scattering of sunlight by the air molecules in the atmosphere. Sunlight contains all colours, from violet to red. According to Raleigh, the intensity of the scattered radiation is inversely proportional to the fourth power of the wavelength of the incident light.

Thus in the daytime when sun light enters earth's atmosphere, violet and blue colours are the most scattered since wavelength is small. Red and orange are the least scattered since wavelength is large. When we look at the sky far away from the sun, the sky appears blue because we receive the most scattered colours, namely, violet and blue.

Note : 1.Near the sun it appears white because we get direct light from the sun.

2.The blue colour of the sea is due to reflection of light from the sky. Raman proved that the blue colour of sea water is due to the scattering of incident sunlight by water molecules.

3.In the absence of the atmosphere, the sky would appear black.

Red colour at sunrise and sunset

The orange red colour of the sky at sunrise and at sunset is due to Rayleigh scattering of light by air molecules in the atmosphere. According to Raleigh, the intensity of the scattered radiation is inversely proportional to the fourth power of the wavelength of the incident light. At sunrise and sunset, the light from the sun travels a longer distance through the earth's atmosphere before reaching the observer. Therefore much of the blue is taken away by scattering. The light that reaches the earth's surface is orange red colour. Thus sky appears orange red colour.

Incoherent scattering : The phenomenon of scattering in which the scattered light has different wavelength compared to that of incident light is called incoherent scattering. In incoherent scattering, the incident light suffers a change in its energy. Hence it is also called as inelastic scattering. Eg. Raman scattering and Compton scattering.

Raman effect

The phenomenon in which there is a change in wavelength of the incident light due to scattering by particles of material medium is called Raman effect.
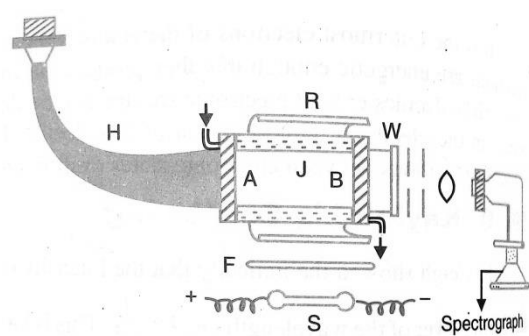
Raman in the year 1928 observed that when a beam of monochromatic light is passed through organic liquids such as benzene, toluene etc, the scattered light was found to consist of lines corresponding to the higher wavelengths as well as lower wavelengths in addition to the incident wavelength. These lines are called Raman lines.

When photons are scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering), such that the scattered photons have the same energy (frequency and wavelength) as the incident photons. A small fraction of the scattered photons (approximately 1 in 10 million) are scattered by an excitation, with the

scattered photons having a frequency different from, and usually lower than, that of the incident photons.[4] In a gas, Raman scattering can occur with a change in energy of a molecule due to a transition to another (usually higher) energy level. The spectrum of the scattered light is called Raman spectrum as shown.

Experimental study of Raman Effect

The apparatus used for the study of Raman effect in liquids was first developed by Wood. It consists of a glass tube AB containing the pure liquid under study. The tube is closed at one end by an optically plane glass plate Wand at the other end end it is drawn into a horn Hand blackened on the outside.Light from a Mercury arc S is passed through a filter Fwhich allows only monochromatic radiation of $\lambda = 4358$ Å to pass through it. The tube is surrounded by a water jacket J through which water is circulated to prevent overheating of the liquid. A semi cylindrical aluminium reflector R is used to increase the intensity of illumination. The scattered light coming out of W is condensed on the slit of a spectrograph. A short focus camera is used to photograph the spectrum. The spectrum appears as shown.
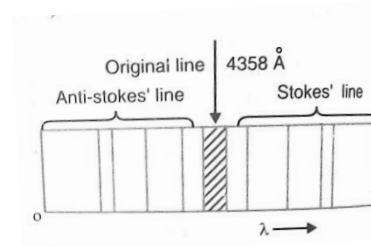
Features of Raman lines

1. The spectrum consists of intense central line of wavelength λ_0 same as that of incident light called Raleigh line.
2. It consists of a number of low intensity lines of linger wavelength called stokes lines.
3. It also consists of very faint lines of lower wavelengths called antistokes line.
4. The Raman lines are almost symmetrically placed wavelengths both above and below the incident light wavelengths.
5. Stokes lines were found to be more intense than the antistokes lines.
6. Raman lines are polarised.
7. The change in wavelength are characteristic of the scattering material and does not depend on the wavelength of incident light.

Quantum theory of Raman Effect

Raman effect is due to the interaction between a light photon and a molecule of the scatterer. Quantum theory is applied to explain Raman effect.

Suppose a photon of frequency ν_1 is incident on a molecule and there is a collision between the two. Let m be the mass of the molecule, v_1 and v_2 its velocities before and after impact, E_1 and E_2 the intrinsic energies of the molecule before and after collision. Let ν_2 be the frequency of the scattered photon. Applying the principle of conservation of energy, $E_2 + \frac{1}{2}mv_2^2 + h\nu_2 = E_1 + \frac{1}{2}mv_1^2 + h\nu_1$ .....(1)

Assuming that the kinetic energy of the molecule is unaltered during the process, the above equation becomes $E_2 + h\nu_2 = E_1 + h\nu_1$ or $\nu_1 = \nu_2 + \frac{E_2 - E_1}{h}$ ...(2)

Three cases arise

1. When the incident photons undergo elastic scattering with the molecules of the medium, the scattered photons have the same energy as that of the incident photons. This results in **unmodified line** of same wavelength as that of the incident light. Here $E_1 = E_2$. Thus $\nu_2 = \nu_2$.

2. Some photons are absorbed by molecules in the lower energy state. When the photons are reemitted, their energy will be less than that of the incident photons. This gives rise to lines having longer wavelength or shorter frequency called **stokes lines**. Here $E_2 > E_1$. The molecule gains energy from the photon and jumps to higher state so that $E_2 - E_1$ is positive. Thus equation (2) is $\nu_1 = \nu_2 + \frac{E_2 - E_1}{h}$. Thus the frequency of the scattered photon is $\nu_2 = \nu_1 - \frac{E_2 - E_1}{h}$. Thus $\nu_2 < \nu_1$. The collision is inelastic.

3. Some photons are absorbed by molecules which are already in the excited state. When the photons are reemitted, their energy will be more than that of the incident photons. This gives rise to lines having shorter wavelength or higher frequency called **antistokes lines.** Here $E_2 < E_1$. The molecule loses energy to the photon and jumps to a lower energy state so that $E_2 - E_1$ is negative. From equation (2), we have $\nu_1 = \nu_2 - \frac{E_2 - E_1}{h}$. The frequency of the scattered photon is $\nu_2 = \nu_1 + \frac{E_2 - E_1}{h}$. Thus $\nu_2 > \nu_1$. Here also the collision is inelastic.

Since the molecules possess quantized energy levels, we can write $E_1 - E_2 = nh\nu_c$ where n = 1, 2, 3…… and ν_c is called the characteristic frequency of the molecule. In the simplest case *n = 1*, the equation (2) reduces to $\nu_2 = \nu_1 \pm \nu_c$.

This equation shows that the frequency difference $\nu_1 - \nu_2$ between the incident and the scatterd photon correspond to the characteristic frequency ν_c of the molecule.

Comparison between coherent scattering and incoherent scattering

Coherent scattering (Elastic or Rayleigh scattering)	Incoherent scattering (Inelastic or Raman scattering)
1. There is no change in wavelength of the light.	1. There is a change in wavelength of the light
2. The incident light does not undergo any change in its energy	2. The incident light undergoes a change in its energy.
3. Intensity of scattered light consisting of shorter wavelengths is more than that of longer wavelengths.	3. Intensity of scattered light consisting of shorter wavelengths is less than that of longer wavelengths.

Applications of Raman effect

1. Raman effect is used in the study of molecular structure.
2. The geometrical configuration of a molecule of the substance can be determined using Raman spectra and infrared spectra of a substance,
3. The study of Raman spectra gives information about the nature of the chemical bond existing between the atoms.
4. Raman spectrum gives information about the structure of water (H_2O) molecule which is non linear or bent having angle of bend as 120^0.
5. Raman effect gives information about the binding forces in crystals.