MOLECULAR SPECTROSCOPY.

Spectrum due to transition between allowed energy states of molecules called Molecular spectrum.

Molecular spectra are produced due to excitation of substance in the molecular state.

The frequency of the spectra is equal ratio of difference between two energy state to planks constant.

$$i.e., \quad v = \frac{\Delta E}{h} = \frac{E \rightleftharpoons E'}{h}$$

If a molecule suffers transition of from lower energy state to higher energy state then the spectra is absorption.

And in emission spectra the transition is from higher energy state to lower energy state.

Nature of molecular spectrum.

1. A molecular spectrum is a band spectrum.
2. Molecular spectra consist of several bands.
3. Each band consists of large number of lines.
4. Longer wavelength side of the band called band head.

Energy of molecule Or Molecular excitation.

When the energy supplied to the molecule the excitation energy of three types.

1. Rotational excitation (E_r): Due to rotational transition, the spectrum lies in far infrared region.
2. Vibrational excitation (E_v): Due to vibrational transition the spectral line are in near infrared region.
3. Electron excitation (E_e): Change in electronic configuration: Due to change in electronic configuration of the molecule nuclei the spectra lies in visible and ultraviolet region.

The total energy of the molecule quantized, and is given by $E = E_r + E_v + E_e$.

Diatomic molecule: A molecule having two atoms separated by a distance which is larger as compared to atomic dimensions is called diatomic molecule.

Molecule consists of similar atoms called Homonuclear molecule.

Example: H_2, O_2, N_2, etc..

Molecule consists of two dissimilar atoms called Hetro-nuclear molecule.

Example: NO, HCl, Co, etc.,

Rigid rotator: A rigid body consists of two point masses joined together by a mass less rod and rotating about common axis passing through the centre of mass and normal to the line joining.

The moment of inertia of a rigid rotator is given by

$$I = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

Where, $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ called reduced mass of the system.

The angular momentum of rigid rotator is $\vec{L} = I \vec{\omega}$

And energy is $E = \dfrac{1}{2} I \omega^2$

According to quantum mechanics the angular momentum is $L = I\omega = n\hbar$

And energy is given by $E = \dfrac{L}{2I} = \dfrac{n^2 \hbar^2}{2I}$

Where is n is quantum number having integral value.

Expression for rotational energy levels and frequency of a diatomic molecule.

Consider a diatomic molecule consisting of atoms of mass m_1 and m_2, separated by a distance R. The atoms are revolving in a circle axis passing through the centre of mass with radius r_1 and r_2 of mass m_1 and m_2 respectively. Then,

$$R = r_1 + r_2 \qquad\qquad ...(1)$$

And $m_1 r_1 = m_2 r_2 \qquad\qquad ...(2)$

Moment of inertia of the diatomic molecule about an axis passing through the centre of mass is given by

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \qquad ...(3)$$

From equation (2) $r_1 = \left(\dfrac{m_2}{m_1}\right) r_2$ and $R = r_1 + r_2$

$$R = \dfrac{m_2}{m_1} r_2 + r_2 \qquad \Rightarrow \qquad R = r_2 \left(\dfrac{m_1 + m_2}{m_1}\right)$$

then $\qquad r_1 = R\left(\dfrac{m_2}{m_1 + m_2}\right) \qquad \qquad ...(4)$

similarly $\quad r_2 = R\left(\dfrac{m_1}{m_1 + m_2}\right) \qquad \qquad ...(5)$

Substituting the values of r_1 and r_2 in equation (3)

$$I = \dfrac{m_1 m_2^2}{(m_1 + m_2)^2} R^2 + \dfrac{m_2 m_1^2}{(m_1 + m_2)^2} R^2$$

$$I = m_1 m_2 \dfrac{m_1 + m_2}{(m_1 + m_2)^2} R^2 = \dfrac{m_1 m_2}{m_1 + m_2} R^2$$

$$I = \mu R^2$$

Where, $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ called reduced mass of the system.

The kinetic energy of rotational of the molecule is given by

$$E = \dfrac{1}{2} I \omega^2 \qquad \qquad ...(6)$$

The angular momentum of the molecule about the axis of rotation is given by

$$\vec{L} = I\vec{\omega} \qquad \qquad ...(7)$$

From equation (6) and (7) $E = \dfrac{L^2}{2I} \qquad \qquad ...(8)$

According to quantum mechanics angular momentum is quantized and is given by,

$$L = \sqrt{J(J+1)}\, \hbar$$

$J = 0, 1, 2, \ldots \ldots$ is known as rotational quantum number.

As the energy depends upon quantum number J,

$$E = \frac{L^2}{2I} = \frac{J(J+1)}{2I}\hbar^2 \qquad \ldots(10)$$

$$E = \frac{J(J+1)}{2\mu R^2}\hbar^2 \qquad \ldots(11)$$

The equation (10) and (11) says the rotational energy is quantized and depends upon the moment of inertia. i.e., mass shape and size of the molecule.

The selection rule for rotational quantum number J is $\Delta J = \pm 1$.

And the energy of emitted photon is given by

$$E = h\nu$$

$$h\nu = E_i - E_f = E_J - E_{(J-1)}$$

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

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

$$h\nu = \frac{Jh^2}{4\pi^2 I} \qquad \left(\because \hbar = \frac{h}{2\pi}\right)$$

$$\nu = \frac{Jh}{4\pi^2 I} = J\nu_o \qquad \left(where,\ \nu_o = \frac{h}{4\pi^2 I}\right)$$

But, in actual practice the rotational spectra is observed due absorption and the frequency is given by

$$\nu = \frac{E_{(J+1)} - E_J}{h} = \frac{h}{4\pi^2 I}(J+1)$$

NOTE:

1. The energy level separations in rotational spectra are not equal.

Substituting the values of $J = 0,1,2,\ldots\ldots$ for E_J becomes $0, \dfrac{3\hbar^2}{I}, \dfrac{6\hbar^2}{I}, \dfrac{10\hbar^2}{I}, \ldots\ldots$ hence the spacing between the energy level is not equal but increasing with rotational quantum number J.

2. The frequency lines are equally spaced in rotational spectra.
   Substitute the values of $J = 0,1,2,\ldots\ldots$
   $\nu = J\nu_o$ becomes $0, \nu_o, 2\nu_o, 3\nu_o, \ldots\ldots$

The differences of consecutive frequencies are equal to ν_o hence the frequencies of rotational spectra are equally spaced.

3. The region of rotational spectra in the electromagnetic spectrum is microwave or fare infra red region, because of very low energy of the order $10^7 \overset{\circ}{A}$

For example consider CO molecule, has a frequency of $1.153 \times 10^{11} Hz$ which corresponds to the wavelength of $2.6 \times 10^{-3} m = 2.6 \overset{\circ}{A}$

4. All molecules do not show rotational spectra.

Because, the molecules which have electric dipole moment they only absorbs emit electromagnetic radiation in transition between rotational energies.

i.e., the emission of rotational spectra is due to dipole moment of molecule.

Expression for vibrational spectra:

Consider a vibrational motion of a diatomic molecule consisting of atoms of mass m_1 and m_2, separated by an equilibrium distance R_o. As the molecule vibrates along the line joining the two atoms the separation between them also change. Let R the separation between two atoms of mass m_1 and m_2 at any instant. The change in distance between the two atoms is equal to $(R - R_o)$.

For the oscillation of small amplitude restoring force is proportional to deviation from the equilibrium position R_o.

$$F \alpha -(R - R_o) \quad \Rightarrow \quad F = -kx \qquad \cdots(1)$$

Where k is force constant. And $R - R_o = x$

But, $F = ma = m\dfrac{d^2 x}{dt^2} \qquad \cdots(2)$

Substitute eq (2) in Eq(1) we get,

$$m\frac{d^2 x}{dt^2} = -kx \quad \Rightarrow \quad \frac{d^2 x}{dt^2} + \frac{k}{m} = 0 \qquad \cdots(3)$$

The system of diatomic molecule consist of can be compare to elastic spring. As there is force acting on the system, oscillation of system is treated as simple harmonic oscillator of mass equal to reduced mass of the system.

Reduced mass of the system is $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

Then the eq(3) becomes, $\dfrac{d^2 x}{dt^2} + \dfrac{k}{\mu} = 0$ $\qquad \cdots (4)$

According to classical mechanics, the frequency of simple harmonic oscillator is given by

$$v_o = \dfrac{1}{2\pi} \sqrt{\dfrac{k}{\mu}} \qquad \cdots (5)$$

According to Quantum mechanics the restoring force is equal to change in potential energy

$$F = -\dfrac{dV}{dx} \qquad \cdots (6)$$

Comparing equation (1) and (6) we get,

$$dV = k \; x \; dx \qquad \cdots (7)$$

Potential energy for a displacement x from the equilibrium position $x = 0$ is given by

$$V = \int_0^x k \; x \; dx = \dfrac{1}{2} kx^2 \qquad \cdots (8)$$

Schrodinger time independent wave equation is given by,

$$\dfrac{d^2 \psi}{dx^2} + \dfrac{2m}{\hbar^2}\left(E - V\right)\psi = 0$$

Put $m = \mu$ and $V = \dfrac{1}{2} kx^2$ equation (8) becomes,

$$\dfrac{d^2 \psi}{dx^2} + \dfrac{2\mu}{\hbar^2}\left(E - \dfrac{1}{2} kx^2\right)\psi = 0$$

$$E\psi = -\dfrac{\hbar^2}{2\mu}\dfrac{d^2 \psi}{dx^2} + \dfrac{1}{2}kx^2 \psi \qquad \cdots (9)$$

Solution of equation (9) for the energy levels of the simple harmonic oscillator is

$$E = \left(n + \frac{1}{2}\right)h v_o \qquad \cdots (10)$$

Where, $n = 0, 1, 2, 3 \ldots$ are vibrational quantum number. and $v_o = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Selection rule for vibrational quantum number is $\Delta n = \pm 1$

The energy of emitted radiation is

$$\Delta E = E_{(n+1)} - E_n$$

$$hv = \left(n + 1 + \frac{1}{2}\right)h v_o - \left(n + \frac{1}{2}\right)h v_o$$

$$hv = \frac{1}{2} h v_o$$

$$v = v_o = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \cdots (11)$$

Equation (10) and (11) represents the energy and frequency of vibrational spectra.

NOTE:

1. Energy levels of vibrational spectra are equally spaced.

   Substitute the values of vibrational quantum number $n = 0, 1, 2, 3 \ldots$

   values of energy level takes $\frac{1}{2} h v_o, \frac{3}{2} h v_o, \frac{5}{2} h v_o, \ldots$ the difference between

   consecutive energy level equal to $\frac{1}{2} h v_o$.

2. The frequency lines are equally spaced in rotational spectra.
   Frequency of vibrational spectra is independent of vibrational quantum number hence frequency lines are equally spaced.

3. The region of rotational spectra in the electromagnetic spectrum is infra red region with wavelength ranging from $8000 A^o - 50,000 A^o$

   For example: consider HCl molecule with a force constant $k = 470 Nm^{-1}$
   Mass of Hydrogen is 1anu and chlorine is 35amu

   Reduced mass, $\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{1 \times 35}{1 + 35} = 1.62 \times 10^{-27} kg$

Frequency, $v = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}} = \dfrac{1}{2 \times 3.142}\sqrt{\dfrac{470}{1.62 \times 10^{-27}}} = 8.6 \times 10^{13}\, S^{-1}$

And the wavelength is $v = \dfrac{c}{\lambda} = \dfrac{3 \times 10^{8}}{8.6 \times 10^{13}} = 35000\, A^{\circ}$

4. The vibrational spectra are observed only in absorption. For the transition of energy between the energy levels the molecule must possess dielectric moment. Hence the homonuclear diatonic molecule like H_2, N_2, O_2 does not show vibrational or rotational spectra.

5. Pure rotational spectra are observed in liquids. Because the energy associated with molecular rotation is negligible.

6. Pure rotational spectra are observed in freely moving molecules like gas or vapor. Here the molecules.

7. The diatomic molecule exhibit both the rotational and vibrational transition of energy the spectral lines are appear as broad peaks called vibration-rotation band.

Electronic spectra:

Consider a diatomic molecule subjected to electromagnetic radiation. The electrons in the different orbit of the atoms of the molecule absorb the energy and jump to high exited state. The spacing between the ground and exited level is much greater than vibrational and rotational levels.

Electronic transition involves much higher energy and spectra lies in visible or ultraviolet region.

Energy is measured in eV. And the separation of energy level is 10^{-2} to $10^{-3} eV$. The electronic levels consist of large number of closely spaced levels. Hence the spectrum consists of closely spaced lines called bands.

All the molecules exhibit electronic spectra because change in dipole moment is associated with electronic configuration of the molecule.

Homo-nuclear molecules like H_2, O_2, N_2, etc., are also exhibit electronic spectra.

Total Energy of the molecule is given by, $E = E_r + E_v + E_e$

Frequency of electronic spectra is given by

$$v = \frac{E_1 - E_2}{h} = \frac{E_{e1} - E_{e2}}{h} + \frac{E_{v1} - E_{v2}}{h} + \frac{E_{r1} - E_{r2}}{h}$$

$$v = \frac{\Delta E_e}{h} + \frac{\Delta E_v}{h} + \frac{\Delta E_r}{h}$$

$$v = \frac{1}{h}\left[\Delta E_e + \Delta E_v + \Delta E_r\right]$$

This most general type of transition and is known as rotational-vibrational – transition. Since $E_e > E_v > E_r$ the frequency or position of electronic spectra is determined by ΔE.
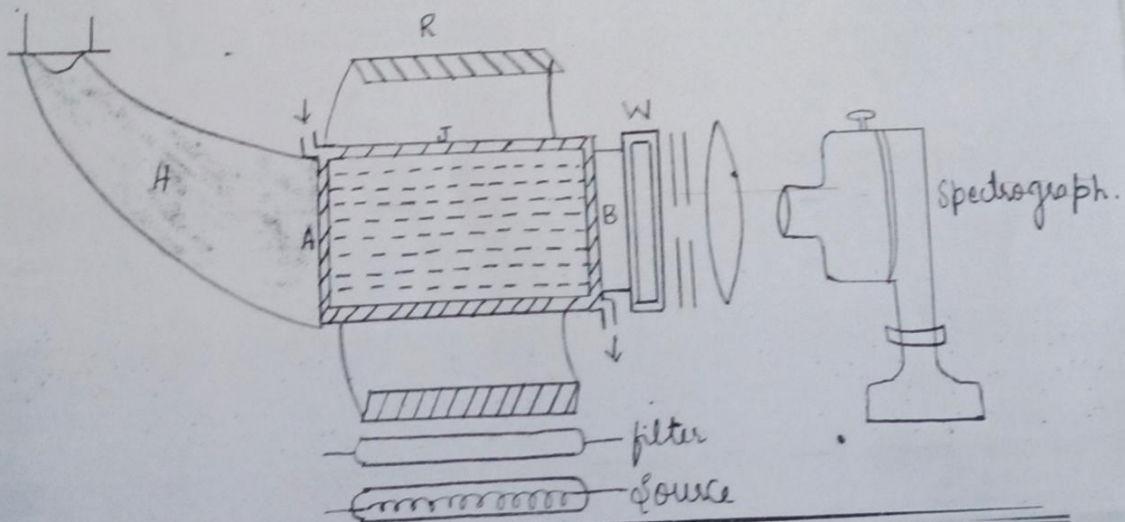
Raman Effect:

The phenomenon of scattering of strong beam of light when passing through the gas, liquid, or transparent solid results in spectrum consist of incident beam along with certain weak and strong changed frequencies.

The lines or frequencies are symmetrical on both sides. The low frequency side lines are called stokes lines and are more intense. The high frequency side line is called anti-stoke line and are less intense. Stokes and anti-stokes lines are called Raman lines and most of Raman lines are strongly polarized.

Experimental arrangement of Raman Spectra:

The modern method of studying Raman Effect was first developed by Wood in 1916. It consists of glass tube AB containing pure experimental liquid, free from dust and air bubble. One of the ends AB is connected with horn shaped tube and coated with black material to prevent reflection of light. Another end of AB is fitted with optically plane glass plate W.

Quantum theory of Ramann Effect.

Raman Effect is the interaction between photon and molecule. Let m be the mass of molecule V_1 and V_2 are velocities before and after collision with the photon of frequency v_1. Let v_2 be the frequency of scattered photon. E_1 and E_2 be the initial energy of molecule.

By law of conservation of energy,

$$E_2 + \frac{1}{2}mV_2^2 + hv_2 = E_1 + \frac{1}{2}mV_1^2 + hv_1 \qquad \cdots(1)$$

Assuming the kinetic energy of the molecule is remain unchanged, then

$$E_2 + hv_2 = E_1 + hv_1$$

$$v_2 - v_1 = \frac{E_2 - E_1}{h} \qquad \Rightarrow \qquad v_2 = v_1 + \frac{E_2 - E_1}{h} \qquad \cdots(2)$$

Equation (2) gives the frequency of scattered photon.

There are three possible types of scattering

Case (i) $E_2 = E_1$ then $v_2 = v_1$ represents unmodified line

Case (ii) $E_2 > E_1$ then $v_2 < v_1$ represents stokes line

Case (iii) $E_2 < E_1$ then $v_2 > v_1$ represents anti-stokes line

All the energy levels of molecular possess are quantized.

$$\text{i.e., } E_1 - E_2 = nhv_C \qquad \cdots(3)$$

$$n = 0,1,2,3,\ldots\ldots\ldots v_C = \text{Characteristic Frequency of molecule}$$

In simplest case n=1 equation (2) becomes

$$v_2 = v_1 + v_C \qquad \cdots(4)$$

Equation (4) represents the difference between incident and scattered photon corresponds to characteristic frequency.

Tube AB is surrounded by a water jacket to prevent increase in temperature. Light from mercury arc S is passed through the filter F which allows only the monochromatic frequency. A semi-cylindrical aluminum reflector R is surrounded by AB to increase the intensity of illumination.

The scattered light coming out of the plate W is focused by the slit. A short focus camera is used to photograph of the spectrum.

Observations:

In developing photograph the number of stokes lines and few anti-stokes lines and strong unmodified line are observed.

Stokes lines are high intense than anti-stokes lines

Stokes and anti-stokes lines are symmetrically displaced from the parent line.

The frequency difference between modified and parent line are represents the frequencies of infrared absorption lines.

Applications:

Structural details of the atom can be studied

Nature of chemical bond exist between the molecules are studied.

Molecular structure, structural symmetry, angle between the molecules can be decided.

Various chemical effect such as electrolytic dissociation, hydrolysis, etc., are been understood by Raman Effect

In X-ray crystallography it is used to provide information about binding force in crystal.