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B.Sc II - Sem Chemistry

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(24)

Raman Spectroscopy

1928, Prof. C.V. Raman – Raman effect.

When definite frequency of light was passed through a transparent substance (gas, liquid or solid) and the scattered radiations were observed at right angle to the direction of the incident beam, the scattered radiation was found to consist of not only incident frequency, but also of some lower or some higher frequency than that of the frequency of incident beam. This is known as Raman effect.

The lines of lower frequencies than that of the lines of incident light frequency are called '<u>Stokes</u>' lines and those of higher frequencies are called "<u>Anti-Stokes</u>" lines.

Suppose ν_i and ν_s are the frequencies of incid. and scattered light, then $\Delta\nu = \nu_i - \nu_s$ is called characteristic Raman frequency and the difference $(\nu_i - \nu_s)$ is called the Raman shift, and range 100-4000 cm^{-1}

Mechanism of Raman Effect

Raman effect arises from an exchange of energy between the incident photon and the molecule which scatter this photon on collision.

We know quantum theory.- $E = h\nu$

where h is Planck's constant

Such collision are called inelastic collision. In such a collision two things may happen:-

(i) The molecule may gain energy from the photon, or

and (ii) The molecule may lose energy and give it to photon

This change of energy of the molecule ΔE must be the difference in energy between the two allowed energy levels say $E_1 - E_2$ of the molecule. If the molecule loses ΔE energy the photon will gain and therefore the scattered photon will have frequency greater than the frequency of incident photon i.e. $h\nu + \Delta E$ or $\nu + \Delta E/h$ and if the molecule gain energy ΔE, then it will scatter with energy $h\nu - \Delta E$ or $\nu - \Delta E/h$.

In Raman effect the scattered radiations are only 0.1% of the incident radiation, therefore to show Raman effect the intensity of incident radiation must be very great.

Concept of Polarizability

Raman effect gives a physical picture i.e. polarizability of a molecule. Classical theory is also known as the polarizability theory.

When a molecule is placed in a static electric field it suffers some distortion. Positively charged nuclei are attracted towards the negative pole of the field and the negatively charged electrons to the positive pole. This separation of charge centres induces an oscillating dipole moment in the molecule and this distortion of molecule is given by

$$\mu \propto F \quad \text{---(i)}$$

$$\mu = \alpha F \quad \text{---(ii)}$$

where, α is the polarizability of the molecule and μ is the induced dipole moment.

Thus for rotational and vibrational Raman effect the ellipsoid must have a shape of a squashed sphere. If the axis of ellipsoid is least the polarizability is greatest and vice-versa. In eq(ii) F is the strength of the electric component of electromagnetic radiation which is given by

$$F = F_0 \sin 2\pi \nu t \quad \text{---(iii)}$$

where, F_0 is the equilibrium value of field strength and ν is the frequency of incident light radiation

From eq(ii) and (iii)

$$\mu = \alpha F_0 \sin 2\pi \nu t \quad \text{---(IV)}$$

It was assumed while arriving at eq(iv) that the vibrational and rotational motions are not taking place in the molecule. However if these motions are considered polarizability will vary slightly, and therefore it has to be considered. During vibration change in polarizability with small displacement from the equilibrium position is given by

$$\alpha = \alpha_0 + \beta \frac{x}{A} \quad \text{---} (V)$$

where α_0 is the equilibrium polarizability, β = rate of change of polarizability with displacement x and A is amplitude.

If the vibrational motion of the molecule is treated as simple harmonic motion then displacement x can be written as

$$x = A \sin 2\pi \nu_{vib} t \quad \text{---} (vi)$$

Combining eq. (V) and (vi.) we get

$$\alpha = \alpha_0 + \beta . \sin 2\pi \nu_{vib} t \quad \text{---} (vii)$$

put the values of α and F in eq. (ii) then

$$\mu = (\alpha_0 + \beta \sin 2\pi \nu_{vib} t) E_0 \sin 2\pi \nu t$$

$$= \alpha_0 E_0 \sin 2\pi \nu t + \beta E_0 \sin 2\pi \nu t . \sin 2\pi \nu_{vib} t \quad \text{---} (viii)$$

On expanding and using trigonometric relation than

$$\mu = \alpha_0 E_0 \sin 2\pi \nu t + \frac{1}{2} \beta E_0 \{\cos 2\pi (\nu - \nu_{vib}) t - \cos 2\pi (\nu + \nu_{vib}) t\}$$

$$\text{---} (ix)$$

Thus we see that oscillating dipole has three frequence components:

(i) Induced dipole oscillates with exciting frequency ν which is equal to the frequency of the incident radiation and

(ii) The oscillating induced dipole has another two frequency components as $(\nu \pm \nu_{vib})$.

The line corresponding to frequency ν are Rayleigh lines and the lines corresponding to $(\nu - \nu_{vib})$ are called stokes lines whereas lines corresponding to $(\nu + \nu_{vib})$ are called anti-Stokes lines.

Then $\beta = 0$ and under this condition the dipole oscillates only at the frequency of the incident radition. Some effect will be observed if rotation does not alter the polarizability. Thus we can formulate the general rule.

Rule:- In order to be Raman active, a molecule rotation or vibration must cause some change in a component of the molecular polarizability. A change in polarizability is reflected by a change in either direction or magnitude of the polarizability ellipsoid.