

Unit-2

(b) Raman Spectroscopy

Introduction

[Vib.-Rotational Spectroscopy]

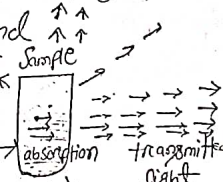
Raman effect was observed by an Indian physicist "Sir C. V. Raman" in 1928.

For which he was awarded by NOBEL PRIZE in physics in 1930.

Basics and Principle :-

Raman effect

When a sample is exposed to a monochromatic light in visible region, the sample absorbs light and major portion of the light gets transmitted monochromatic through the sample. However a minute (very less) part of the light is scattered by the sample in all the directions.



one can observe the scattering at right angle to the incident beam. The incident light has a particular frequency (ν_0).

If the scattered light has the frequency (ν_1)

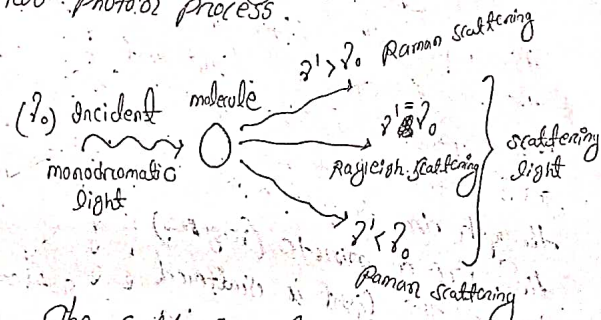
Same as the incident light, then scattering is called "Rayleigh scattering".

$$\nu_0 = \nu_1$$

However, it has been observed that about 1% of total scattered intensity occurs at frequencies different from the incident frequency, this is called as "Raman Scattering".

$$\nu_0 \neq \nu_1$$

Raman scattering can be thought of as a two-photon process.

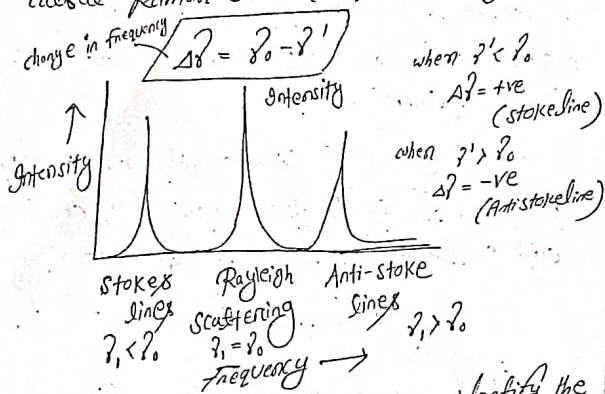


The scattering of light from molecules with a change in frequency is called as "Raman effect".

① If the scattered light frequency is lower than the incident light frequency is called "Stoke lines".

② If the scattered light frequency is higher than the incident light frequency is called "anti-stoke line".

The difference between incident light frequency and scattered light frequency is called Raman shift ($\Delta \nu$) is given by,



By studying the spectra one can identify the rotational levels and thus a particular molecule, this helps in performing qualitative analysis.

Similarly the intensity value of a particular Raman line helps to determine the concentration of a molecule in a sample. In this manner, quantitative analysis can be done.

Thus, Raman spectroscopy can be used to perform both quantitative and qualitative analysis.

Theory :-

Classical theory :-

When an electric field is applied to a molecule, its electrons cloud are displaced. By an induced dipole moment is produced in the molecule due to the displacement of the electrons and nuclei and the molecule is said to be polarized.

Suppose E is the strength of electric field and μ is the magnitude of induced dipole moment. Then we can write,

$$\mu = \alpha \cdot E \quad \text{--- (1)}$$

where α is the polarizability of the molecule.

When a sample of molecules, which can be polarised is subjected to a beam of radiation of frequency ν the electric field experienced by each molecule varies according to the following eqn,

$$E = E_0 \sin 2\pi \nu t \quad \text{--- (2)}$$

therefore, the induced dipole undergoes oscillation of frequency ν that is,

$$\mu = \alpha \cdot E_0 \sin 2\pi \nu t \quad \text{--- (iii)}$$

Such an oscillating dipole emits radiation of its own frequency ν . Thus this eqn (iii) explains the Rayleigh's scattering.

Effect of vibration and rotation

If a molecule undergoes vibration and rotational motion, this changes the polarizability periodically and then the oscillating dipole will be superimposed upon it the vibrational/rotational oscillation.

Suppose a vibration and rotational frequency (ν_1) change the polarizability. Then, overall polarizability

$$\alpha = \alpha_0 + \beta \sin 2\pi \nu_1 t \quad \text{--- (iv)}$$

where, α_0 = equilibrium polarizability
 β = the rate of change of polarizability.

Substituting eqn (iv) in eqn (iii),

$$\mu = (\alpha_0 + \beta \sin 2\pi \nu_1 t) E_0 \sin 2\pi \nu t \quad \text{--- (v)}$$

$$\text{or } \mu = \alpha_0 E_0 \sin 2\pi \nu t + \frac{1}{2} \beta E_0 \left[\cos 2\pi (\nu - \nu_1) t - \cos 2\pi (\nu + \nu_1) t \right]$$

From the above eqn it is evident that the induced oscillating dipole has frequency components $\nu \pm \nu_1$, as well as the exciting (incident) frequency ν . It means that the induced dipole oscillates with frequency $(\nu + \nu_1)$ and $(\nu - \nu_1)$ which are more and less than the incident radiation frequency and thus predict the existence of Raman effect (or) Raman scattering.

If the molecular vibration/rotation does not change the polarizability of molecule then,

$$\beta = 0$$

So that the dipole oscillates only at the frequency of the incident radiation.

Then,

$$\mu = \alpha_0 E_0 \sin 2\pi \nu t$$

This shows Rayleigh scattering only.

So we conclude that for a molecular vibration or rotation to be active in the Raman spectrum, it must be cause a change in the molecular polarizability.

that is,

$$\beta \neq 0$$

Quantum theory :-

According to this theory, the radiant effect may be regarded as the outcome of the collisions between the light photons and molecules of the substance.

Light is nothing but the bundle/packet of energy which called also photon.

The energy of photon $E = h\nu$

where,

h = Planck const.

$h = 6.626 \times 10^{-34}$ J.S

ν = frequency of radiation

Suppose a molecule of mass m in the energy state E_p is ~~moving with a velocity v~~ is colliding (elastically or inelastically) with a light photon $h\nu_0$.

Suppose this molecule undergoes a change in its energy state ~~as well as~~ and after collision frequency is ν' .

Let this new energy state be E_q ~~and~~ ~~velocity~~ after suffering a collision.

then according to conservation of energy, the sum of energy and frequency before collision is equal to after collision.

$$E_p + h\nu_0 = E_q + h\nu'$$

$$E_p - E_q = h\nu' - h\nu_0$$

$$E_p - E_q = h(\nu' - \nu_0)$$

$$\frac{E_p - E_q}{h} = \nu' - \nu_0$$

$$\boxed{\nu' = \nu_0 + \frac{E_p - E_q}{h}}$$

scattered radiation frequency

From this eqn three cases are arise,

Case-(1)

If $E_p = E_q$ then frequency of incident and scattered radiation will equal $\nu_0 = \nu'$.

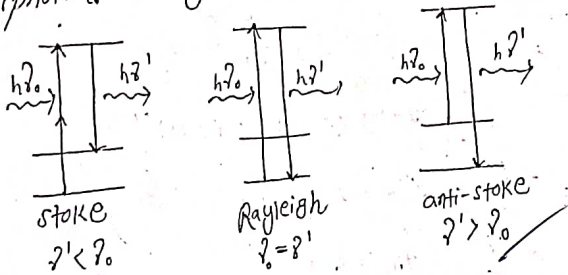
the means the molecule simply deflected photon with out receiving any energy from it. The collision thus being elastic is analogous to Rayleigh scattering.

Case-(2)

If $E_p < E_q$ then $\nu_0 > \nu'$ This corresponds to Stokes line. The molecule has absorbed some energy from the photon and consequently the scattered photon will have lower energy.

Case - (ii)

If $E_p > E_q$ then $J' > J_0$ which refers to anti-stoke's line. It means that the molecule was previously in the excited state and it handed over some of its intrinsic energy to the incident photon. Thus, the scattered photon has greater energy.



Pure Rotational Raman Spectra :-

We know rotational energy of a diatomic molecule is given by $E_J = BJ(J+1) \text{ cm}^{-1}$ (or) $E_J = \frac{J(J+1) \cdot h^2}{2I}$

The selection rule for rotational Raman spectrum is, $\Delta J = 0, \pm 2$

When, $\Delta J = 0$ the scattered Raman radiation will be of the same frequency as that incident light (Rayleigh's scattering).

The transition $\Delta J = \pm 2$ give stoke's lines where as $\Delta J = -2$ gives anti-stoke lines.

When $\Delta J = +2$ the value of rotational Raman shift (stoke line) will be given by,

$$\Delta E = E_{J+2} - E_J$$

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

$$= \frac{h^2}{2I} [(J+2)(J+3) - J(J+1)]$$

$$= \frac{h^2}{2I} [J^2 + 3J + 2J + 6 - J^2 - J]$$

$$= \frac{h^2}{2I} (4J + 6)$$

$$= \frac{2h^2}{2I} (2J + 3) = \frac{h^2}{I} (2J + 3)$$

$$\Delta E = \frac{h^2}{4\pi^2 I} (2J + 3) \quad \left(h = \frac{h}{2\pi} \right)$$

When $\Delta J = -2$ the value of rotational Raman shift (anti-stoke line) will be given by,

$$\Delta E = \frac{h^2}{4\pi^2 I} (2J + 3)$$

We know,

$$\Delta E = h\nu$$

$$E_c - E' = \frac{h^2}{4\pi^2 I} (2J+3)$$

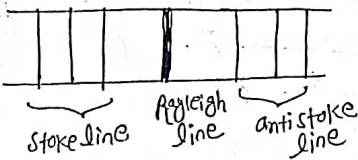
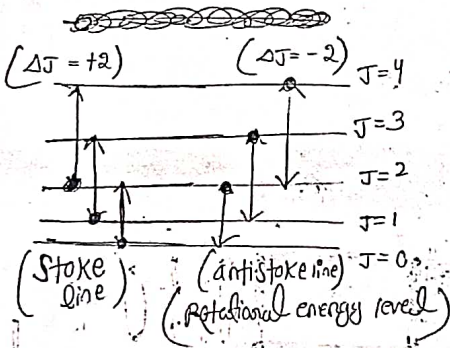
$$h^2 J_0 - h^2 J' = \frac{h^2}{4\pi^2 I} (2J+3)$$

$$h(J_0 - J') = \frac{h^2}{4\pi^2 I} (2J+3)$$

$$J_0 - J' = \frac{h}{4\pi^2 I} (2J+3)$$

$$\Delta J = \frac{h}{4\pi^2 I} (2J+3)$$

Raman shift



Vibrational Raman spectra :-

We know,
$$E_v = (v + \frac{1}{2}) \bar{\omega}_e - (v + \frac{1}{2})^2 \bar{\omega}_e x_e$$

where,

$\bar{\omega}_e$ = frequency

v = vibrational quantum no.

x_e = Anharmonicity constant

($x_e = 0.01$)

Selection rule

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

Since at room temp most of the molecule are in ground vibrational state ($v=0$) so only the vibrational transition ($v=0$ to $v=1$) is of interest [fundamental vib.]

$\Delta v = 0$ (show Rayleigh lines)

When $\Delta v = +1$ the value of vibrational Raman shift (Stoke line) will be given by,

$\Delta E_v = E_{v_1} - E_{v_0}$

$$\Delta E_v = \left[(1 + \frac{1}{2}) \bar{\omega}_e - (1 + \frac{1}{2})^2 \bar{\omega}_e x_e \right] - \left[(0 + \frac{1}{2}) \bar{\omega}_e - (0 + \frac{1}{2})^2 \bar{\omega}_e x_e \right]$$

$$\Delta E_v = \frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e - \frac{1}{2} \omega_e + \frac{1}{4} \omega_e x_e$$

$$\Delta E_v = \omega_e - 2\omega_e x_e$$

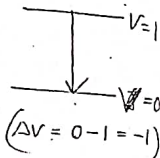
$$\Delta E_v = \omega_e (1 - 2x_e)$$

$$\frac{3}{2} - \frac{1}{2} = \frac{2}{2} = 1$$

$$-\frac{9}{4} + \frac{1}{4} = -\frac{8}{4} = -2$$

Similarly if $\Delta v = -1$ the value of vibrational Raman shift (antistokes line) will be given by,

$$\Delta E_v = E_{v_0} - E_{v_1}$$



$$\Delta E_v = \left[\left(0 + \frac{1}{2}\right) \omega_e - \left(0 + \frac{1}{2}\right)^2 \omega_e x_e \right] - \left[\left(\frac{1}{2} + 1\right) \omega_e - \left(\frac{1}{2} + 1\right)^2 \omega_e x_e \right]$$

$$\Delta E_v = \left[\frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e \right] - \left[\frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e \right]$$

$$\Delta E_v = -\omega_e + 2\omega_e x_e$$

$$\Delta E_v = -\omega_e (1 - 2x_e)$$

$$\frac{1}{2} - \frac{3}{2} = -\frac{2}{2} = -1 \quad v=0$$

$$-\frac{1}{4} + \frac{9}{4} = \frac{8}{4} = 2$$

$$\Delta E_v = \pm \omega_e (1 - 2x_e)$$

$$\nu_{\text{fundamental vibration}} = \nu_0 \pm \Delta E_v = \nu_0 \pm \omega_e (1 - 2x_e)$$

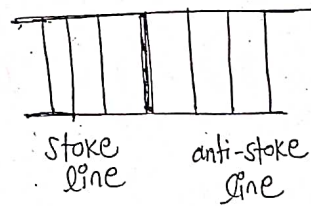
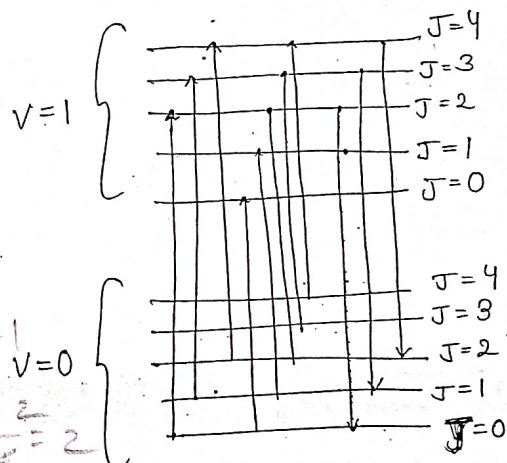
$$\nu_{\text{fundamental vibration}} = \nu_0 \pm \omega_e (1 - 2x_e)$$

Vibrational-Rotational Raman spectra:-

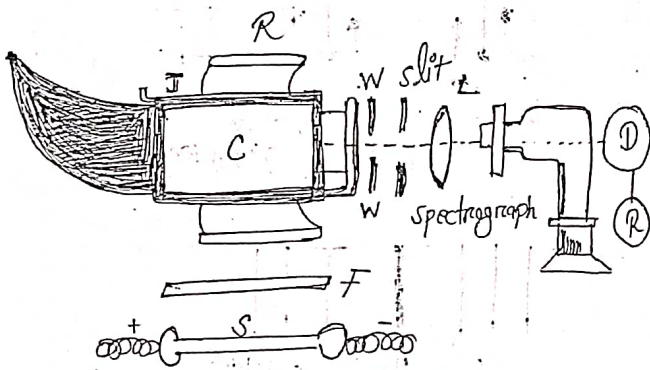
$$\Delta v = \pm 1$$

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

$$E_{J+V} = \left[\bar{\omega}_e \left(v + \frac{1}{2} \right) - \left(v + \frac{1}{2} \right)^2 \bar{\omega}_e x_e \right] + J(J+1) \frac{h^2}{2I}$$



Instrumentation :-



Procedure :-

C is a Ramon tube which acts as a container for sample (liquid/gas/solid) to be investigated. It is made of glass and is 1-2 cm in diameter and 10-25 cm long. The one

end of the tube is drawn like a horn and blackened outside to provide a suitable background. The other end of the tube is closed with an optically plane glass plate. The scattered light emerges through the window W. The Ramon tube C is surrounded by water jacket J in which cold water is circulated in order to prevent the overheating of liquid because of the proximity of the heated arc.

A special helium discharge tube which acts as a source of light and is filtered by nickel oxide filters F to get a monochromatic light. But now a days mercury arc lamp is used as a source of light. The mercury arc (S) is placed quite near to the Ramon tube and a semi-cylindrical aluminium reflector which enhances the intensity of light. A lens L in front of the plane window directs the scattered radiation upon the slit of the spectrograph and then the Ramon lines are obtained on the photographic plate.

Components :-

Source of light :-

- The Ramon effect is relatively weak.
- Therefore, it is essential to have a source of high intensity.

- The mercury arc is the most useful source.
- The line obtained from mercury arc is 4358 \AA is the most commonly used wavelength in Raman Spectroscopy.
- Now in modern Raman spectroscopy Laser used as a light source.
- diff Laser source ^{used} like Helium-neon which produce 6328 \AA line and also use Argon-ion laser.
- The advantage of using laser as source are,
 - 1) No filtering is necessary.
 - 2) Give a single intense frequency source.
 - 3) Resolution high.
 - 4) also can determine small sample.
 - 5) line need small area compare to other source.

2) Filter :-

In case of non-monochromatic incident light there will be overlapping of Raman shifts which will make the interpretation of the Raman spectrum difficult. It is therefore essential to have monochromatic radiations. For getting monochromatic radiation filters are used. They may be made of nickel oxide glass, quartz glass. filter is placed between the source and sample. different filters are used like, mercury vapour, Corning glass No. 5874.

3) Sample holder :- (Sample handling).

- For study of Raman effect the type of sample holder to be used depends on intensity of source and nature of sample.
- Gas sample requires sample holders which are generally bigger in size than those for liquids. sample holder made up of glass/quartz.
- liquid sample requires sample holders whose length 15 cm & diameter 2 cm .
- Solid one dissolved before subjecting to Raman spectrograph. for dissolving solid sample the most suitable solvent is carbon tetrachloride.
- The sample holders in Raman are varied according to the sample form.

4) Spectrograph :-

- It should have large gathering power.
- Special prisms of high resolving power should be used.
- A short focus camera should be used. A lens in front of the plane window directs the scattered radiation upon the slit of the spectrograph and the Raman lines can be obtained on photographic plate.

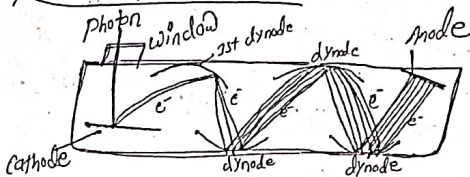
Raman spectrographs have either photographic or automatic recording devices.

High resolving power gratings are not used in spectrograph because of poor luminosity which needed long exposures.

5) Detector :-

Mostly photomultiplier tube are used as detectors for the study of Raman spectra.

Photomultiplier tube :-



PMT is a combination of photoemissive cathode and an internal e^- multiplying chain of dynode. The scattered radiation is transmitted through PMT and fall on photo cathode. A photo e^- released by photo cathode and is attracted to first dynode which is coated with photo emissive material like BeO, Cs and gain energy by its impact release several secondary electrons. These are attracted to the next dynode and release several e^- . The multiplied photocurrent is measured directly via 1st dynode probe and will get a spectrum of high intensity.

Intensity of Raman Peak :-

The intensity of Raman peak has been depend upon,

- 1) Polarizability of molecule
- 2) Intensity of source
- 3) conc. of the active group in sample

Application :-

- 1) Application in Pharmaceuticals
- 2) Application in cosmetics
- 3) Life sciences
- 4) Geology and mineralogy
- 5) Carbon contain materials

Raman Spectra of H_2N , CO , CO_2 , N_2O

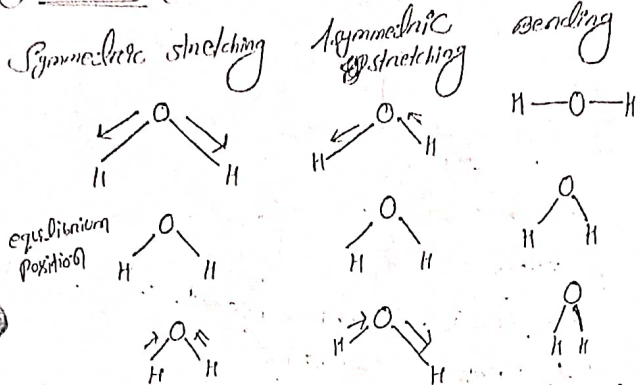
H_2O :-

\rightarrow Raman active there must be change in polarizability in molecule.

\rightarrow And this polarizability either may occur due to change in magnitude and change in direction.

\rightarrow And Raman active molecule can only give Raman spectra.

① H_2O :- (bend shape)

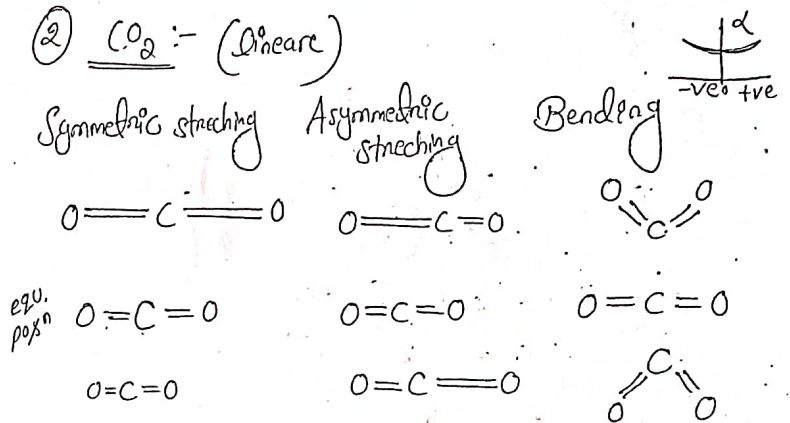


Here due to symmetric stretching increasing and decreasing in bond length so the polarizability of molecule also increase and decreasing from the equilibrium position. So there is change in polarizability due to change in magnitude. So symmetric stretching in H_2O is Raman active.

Here due to asymmetric stretching change in direction of polarizability of molecule. So here polarizability change due to change in direction. So asymmetric stretching of H_2O is Raman active.

Here also change in polarizability occur due to change in direction. So bending of H_2O is also Raman active.

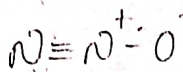
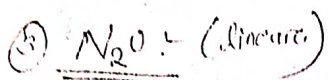
② CO_2 :- (Linear)



due to symmetric stretching there is increasing in bond length and also decrease in bond length from its equilibrium position. So there is change in polarizability due to change in magnitude. So symmetric stretching of CO_2 is Raman active.

Here no change in direction as well as in magnitude. So the polarizability almost same with its equilibrium position. So there is no change in polarizability. So it is Raman inactive.

Here also no change in direction as well as in magnitude. So bending in CO_2 is no change in polarizability. So it is Raman inactive.

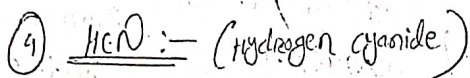


no centre of symmetry

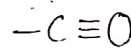
so no rule of mutual exclusion
so all mode will be both Raman & IR active.

(2) Raman line $\leftarrow \begin{matrix} 2224 \text{ cm}^{-1} \\ 1285 \text{ cm}^{-1} \end{matrix}$

(1) IR line $- 589 \text{ cm}^{-1}$



It show 2 lines (Raman) at 2062 cm^{-1} & 2094 cm^{-1} due to two isomers HNC & HNC (hydrogen isocyanide).



It give only one Raman lines at 2155 cm^{-1}

Quantitative analysis :-

- It give information about the composition present sample.
- It give the structure elucidation.
- It give/tell about the stability of co-ordination compound.
- It also give information about organic compound.
- Raman microprobes are used to determine analytes in a single bacterial cells, components in individual particle of smoke and fly ash