PRESENTATION

By

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Raman Specrta

When a beam of monochromatic radiation is passed through a substance which do not absorb radiation then nearly all of this light is transmitted. However, a small fraction of the incident light is scattered in all directions. If the scattered light has the same frequency as the incident light, it is referred to as Rayleigh scattering or elastic scattering.

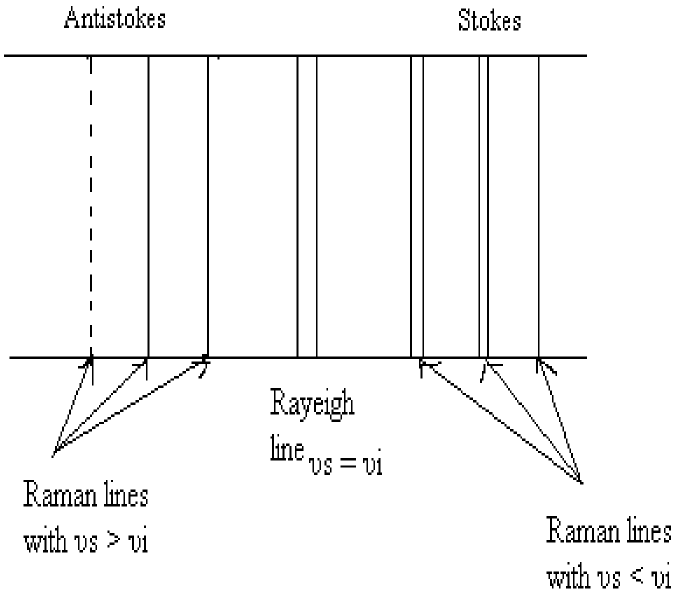
Prof. C.V. Raman in 1928 found that along with Rayleigh frequency the radiations of various frequencies other than incident light are also absorbed. This scattering is referred to as Raman scattering and the phenomenon of the change of frequency is known as Raman effect.

If υ_i = frequency of incident light

υ_s = frequency of scattered light

then, $\Delta\upsilon_R = (\upsilon_i - \upsilon_s)\ s^{-1}$

This is known as Raman frequency or Raman shift.



The line at the incident frequency is called the Rayleigh line, while the pattern of weak lines on the either side is called Raman spectrum of the scattering substance.

The frequency difference between Rayleigh line and Raman is known as Raman shift ($\Delta\upsilon_{R)}$. The Raman shift ($\Delta\upsilon_{R}$) is characteristics of the scattering substance. It is related to the vibrational and rotational transitions of the substance.The Raman lines are always weak with respect to the incident light intensity.

The Raman lines at lower frequency than the incident are called stokes lines. ($\Delta\upsilon < 0$)

while the Raman lines at higher frequencies (high frequencies) are called antistokes lines. ($\Delta\upsilon > 0$). Stokes lines are more intense than the incident light.

♣ Explanation for Raman effect :-

According to the quantum theory. The electromagnetic radiation of frequency υ can be treated as a propagation of photons with energy hυ. When light of frequency υ_i (E = hvi) fall on the molecule following two types of collisions are possible.

1) Elastic collision :-

In this, there is no loss or gain of energy. The photon is deflected with its original energy h υ_i . Therefore, the frequency of scattered light has same frequency as the incident light. This is Rayleigh scattering or elastic scattering.

2) Inelastic collision :-

In this, energy is exchanged between molecule & photon. There is a loss or gain of energy by molecule. The energy change ΔE will be equal to difference in energies in two of its permitted levels. These permitted levels, exist in vibrational & rotational energies. So the energy gain or lost; ΔE will correspond to the change in vibrational or rotational energy. Thus,

(a) The photon will be scattered with energy

$h\upsilon_s = h\upsilon_i - \Delta E$, If the molecules absorbs energy from the photon and

$$\upsilon_s = \frac{h\upsilon_i - \Delta E}{h}$$

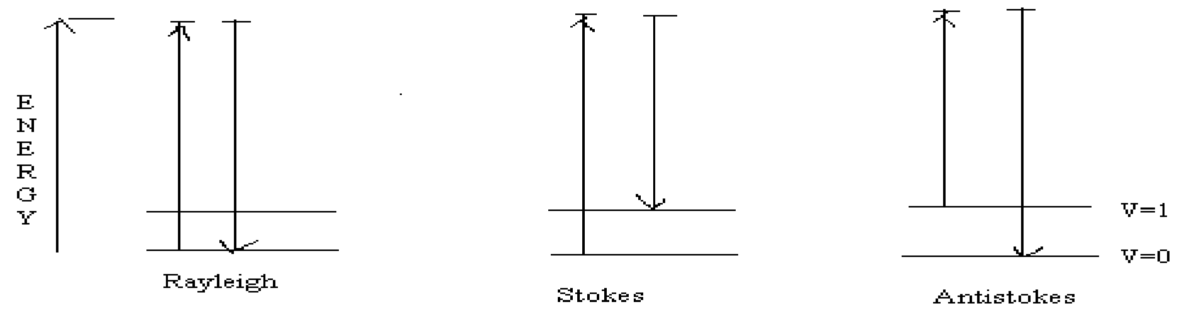
$$\Delta E = \Delta\upsilon_R$$

$$\upsilon_s = \frac{h\upsilon_i - \Delta\upsilon_R}{h}$$

$$\upsilon_s = \upsilon_i - \Delta\upsilon_R$$

$$\Delta\upsilon_R = (\upsilon_i - \upsilon_s)$$

Hence the frequency of scattered light is less than the frequency of incident photon, vs <vi . This corresponds to stoke lines produced when molecule absorbs energy from photon.



(b) The photons will be scattered with energy

$h\,\upsilon_s = h\,\upsilon_i + \Delta E$, if the molecules transfers or loses energy to photon.

Similarlly as the case first, The frequency of scattered radiation will be

$$\upsilon_s = \upsilon_i + \Delta\upsilon_R$$

Hence the frequency of the scattered light is greater than the frequency of incident photon

i.e. $\upsilon_s > \upsilon_i$. This corresponds to anti-stoke lines produced when molecules give up energy to incident photons.

♣ Concept of polarizability :-

When a molecule is placed in an electric field, its electron & nuclei are displaced resulting thereby a separation of charges. This causes an induced dipole momentand molecule is said to be polarized. The extent of separation of charges is determined by polarizability (α) of the molecule.

$$\mu = \alpha E$$

Where μ = induced dipole moment

E = strength of applied field

The magnitude of polarizability varies when the direction of applied field is varied, so it is isotropic property.

The change in polarizability of molecule makes a molecule Raman active. The vibrations and rotation may change the polarizability periodically.

If the vibration or radiation does not change the polarizability of the molecule, the dipole oscillates only with the frequency of the incident radiation (Rayleigh scattering)

Hence to be Raman active, the polarizability of the molecule must change during vibrational and rotational motions. There is essential condition for Raman spectra.

♣ ***Pure rotational pure & vibrational Raman spectra of diatomic molecules.***

If Raman lines are obtained only due to the vibrational motion the spectum is called pure vibrational Raman spectrum. While if the Raman lines are obtained due to the rotational motion, it is referred to as pure rotational Raman spectrum.

♣ **Selection rule :-**

In case of rotationl Raman spectra, the permitted rotational transitions have $\Delta J = \pm 2$ is rotational quantum numbers changes by two units. While in case of vibrational Raman spectra, allound transitions are $\Delta V = \pm 1$,±2, ±3 etc. But ±1 transition icommonly noted probability of higher transition decreases very rapidly.

♣ Applications :-

For homonuclear molecules O_2, H_2, etc, the polarizability changes during rotational motion and hence the give Raman spectra. But there molecules are neither give vibrational spectra (infrared) nor rotational spectra (microwave). from the frequency separation of the spectral lines, rotational constant, moment of inertia and bond length can be obtained.

The fluorescence phenomenon can be compared with the Raman spectrum. fluorescence spectrum is obtained when the molecule absorbs the incident radiation energies and gets exited. Equivalent energy is emitted in the form of radiation when the exited molecules comes back. The Raman spectrum consists of lines having greater and lesser frequencies than the incident radiation while fluorescence spectrum is usually associated with lower frequencies than the incident radiation (stokes phenomenon). the frequencies of Raman lines depends on the frequencies of incident radiation but the fluorescence frequencies are independent. The frequency separation ($\Delta\upsilon$) of spectral line is the characteristics of the substance in Raman spectroscopy while in case of fluorescence spectra, scattered frequencies (υ_s) an characteristics of the scattered.

Raman Spectra can be comp aired with the IR Spectra. Raman spectrum arises due to the changes in the molecular polarisibility during rotational & vibrational motion of the molecules while IR Spectrum is not given by homonuclear non-polar molecules but Raman Spectra are given even by homonuclear molecules. Infrared Spectrum involves generally solution prepared in inert non polar solvents. Which Raman Spectra can be obtained even with solids & liquids.