

Raman Effect

Sir C.V Raman (1923) found that when a beam of monochromatic light was passed through organic liquids such as benzene, toluene etc., the scattered light contained other frequencies in addition to that of the incident light. This is known as **Raman effect**.

When a monochromatic radiation is scattered by a substance, the scattered radiation will consist of certain discrete frequencies above and below that of incident beam frequency, in addition to that of incident frequency.

Salient features (or) Characteristics of Raman effect:

- (a) Raman effect is observed in gases, vapours, liquids, crystals and amorphous, solids, both organic and inorganic.
- (b) Its spectral character, a more or less diffuse continuous spectrum accompanying the lines or bands.
- (c) It is involving an exchange of energy between the quantum and the molecule, and the equality of the change of frequency.
- (d) The possibility of an improvement in the frequency in addition to the degradation of it.
- (e) The strong polarization of the radiations.
- (f) The distinctness from fluorescence.
- (g) It is considered as an optical analogue to the Compton effect.
- (h) It is also called Incoherent scattering.

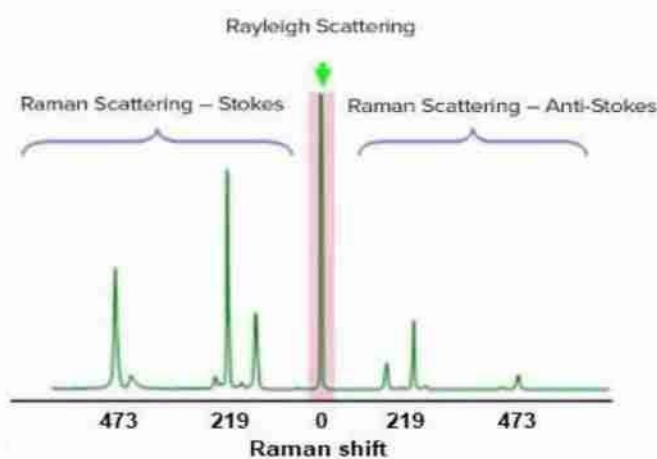
Characteristics of Raman lines:

- a) The stokes lines are more intense than anti-stokes lines. The intensity of anti-stokes lines increases with temperature
- b) Raman lines are symmetrically spaced from the parent line. The intensities of anti-stokes lines decreases rapidly with the increase in separation from the parent line.
- c) The frequency difference between the modified and parent line represents the frequency of the IR absorption line.
- d) The state of polarization of Raman lines varies. This is measured by the depolarization factor.

Stoke's and Anti-stoke's lines:

The original arrangement used by Raman. It was simple in design. A round bottomed glass flask was filled with pure dust-free benzene. The liquid was strongly illuminated by the mercury blue line of wavelength 435.8 nm. The scattered light was examined through a spectrograph in a direction perpendicular to that of the incident beam. It was observed that the spectrum contained, in addition to the incident wavelength of 435.8 nm, some lines of longer wavelength, as well as, shorter wavelength. These lines of modified wavelengths are known as Raman lines.

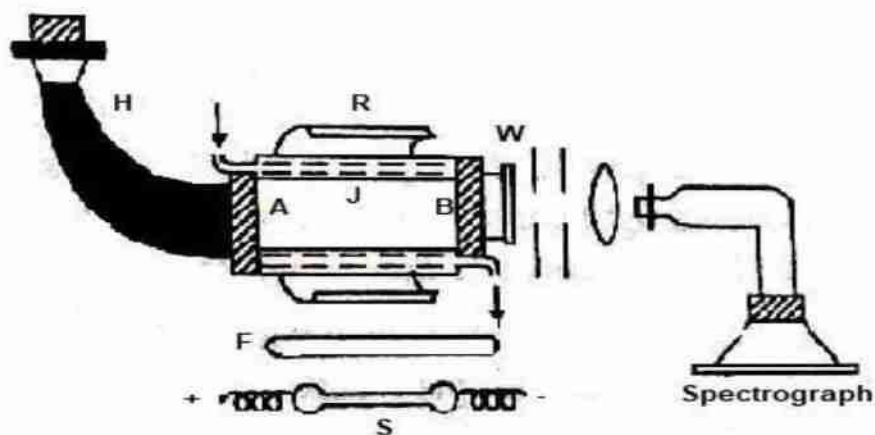
The lines having wavelengths greater than that of the incident wavelength are called Stoke's lines and those having shorter wavelengths are called Anti-stoke's lines. The stokes lines are found to be more intense than anti-stokes lines. Most of the Raman lines are strongly polarized.



The displacement of the modified spectral lines from the existing line, depends only on the scattering substance and is independent of the wavenumber of the existing radiation. Thus, Raman spectrum is characteristic of the scattering substance.

Experimental set up to study Raman effect :

The apparatus shown in fig. is used to study Raman effect in liquids. It was first developed by Wood. It consists of a glass tube AB, containing the pure experimental liquid, free from dust and air bubbles. The tube is closed at one end by an optically plane glass plate W and at the other end it is drawn to a horn (H) and blackened on the outside. (fig.)



Light from a mercury source S is passed through a filter F, which allows only monochromatic radiation of wavelength 435.8 nm to pass through it. The tube is surrounded by a water jacket (J), through which water is circulated to prevent over heating of the liquid. A semi-cylindrical Aluminum reflector (R) is used to increase the intensity of illumination.

The scattered light coming out of the plane glass plate W is condensed on the slit of the spectrograph. A short focussed camera is used to photograph the spectrum. On developing the photographic plate, it exhibits a number of stokes and anti-stokes lines and a strong unmodified line.

Classical theory of Raman effect:

When an Electric field is applied on a molecule, the polarization of molecules taken placed and an induced dipole moment is produced.

The magnitude of induced dipole moment is directly proportional to the strength of the applied electric field.

i.e
$$p \propto E$$

$$p = \alpha E \dots\dots\dots(1)$$

where, α is called polarizability of molecule.

Now strength of the applied electric field is given by $E = E_0 \sin 2\nu_0 t \dots\dots\dots(2)$

Put eq (2) in eq (1), we get

$$p = \alpha E_0 \sin 2\nu_0 t \dots\dots\dots(3)$$

If molecule starts executing vibrational motion in the presence of external electric field then the net polarizability of vibrating molecule is represented by,

$$\alpha = \alpha_0 + \beta \sin 2\nu_{vib} t \dots\dots\dots(4)$$

Where, α_0 = Equilibrium polarizability, β = rate of change of polarizability,

ν_{vib} = vibrational frequency of molecule

Substitute eq (4) in eq (3), we get

$$p = (\alpha_0 + \beta \sin 2\nu_{vib}t) E_0 \sin 2\nu_0t$$

$$p = (\alpha_0 E_0 \sin 2\nu_0t + \beta E_0 \sin 2\nu_{vib}t \sin 2\nu_0t)$$

$$p = \left(\alpha_0 E_0 \sin 2\nu_0t + \frac{\beta E_0}{2} [2 \sin 2\nu_{vib}t \sin 2\nu_0t] \right)$$

$$p = \alpha_0 E_0 \sin 2\nu_0t + \frac{\beta E_0}{2} \cos(\nu_0 - \nu_{vib})2t - \frac{\beta E_0}{2} \cos(\nu_0 + \nu_{vib})2t$$

Above expression conclude that scattered light contains 3 frequencies ν_0 , $(\nu_0 - \nu_{vib})$ and $(\nu_0 + \nu_{vib})$

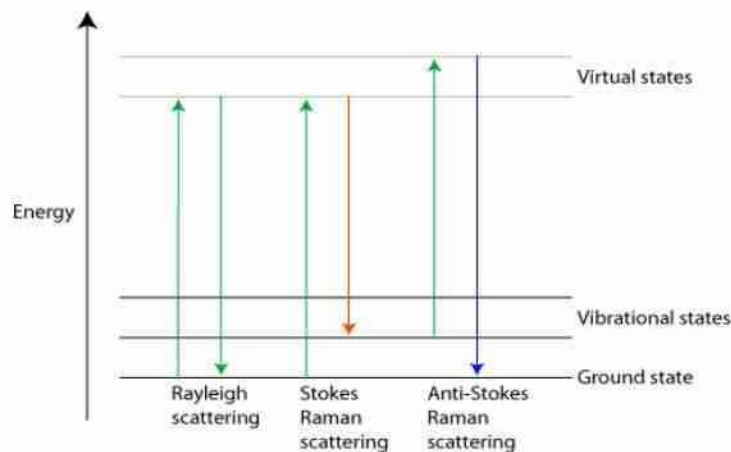
Represents incident light, Stoke's line and Anti-stoke's lines respectively.

Limitations :

1. Stoke's and Anti-stoke's lines are emitted by same moleculesso they must have same intensities which is not true.
2. Vibrational motion of molecule is essential to the mechanism of Raman scattering, but at ordinary temperature, vibrational states are very less.

Quantum theory of Raman effect:

Raman effect is due to the interaction between a light photon and a molecule of the scattering element. 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, ν_1 and ν_2 , its velocities before and after impact. E_1 and E_2 , the intrinsic energies of the molecule, before and after collision, ν_1 be the frequency of the scattered photon.

Applying the principle of conservation of energy,

$$E_2 + 1/2 m\nu_2^2 + h\nu_2 = E_1 + 1/2 m\nu_1^2 + h\nu_1 \dots \dots \dots (1)$$

We assume that the kinetic energy of the molecule remains the same during the process. Hence,

$$\begin{aligned}
 E_2 + h\nu_2 &= E_1 + h\nu_1 \\
 h(\nu_2 - \nu_1) &= E_1 - E_2 \\
 (\nu_2 - \nu_1) &= \frac{E_1 - E_2}{h} \\
 \nu_2 &= \nu_1 + \frac{E_1 - E_2}{h} \dots \dots \dots (2)
 \end{aligned}$$

From eqn. (2), three cases arise:

Case (i): When there is no change in the energy of the molecule, $E_1 = E_2$, then $\nu_1 = \nu_2$. This represents the **Unmodified line**.

Case (ii): If $E_2 > E_1$, then, $\nu_2 < \nu_1$. This represents the **Stokes line**. It means that the molecule has absorbed some energy from the incident photon. Consequently, the incident photon has lower energy or longer wavelength.

Case (iii): If $E_2 < E_1$, then, $\nu_2 > \nu_1$. This represents the **Anti-Stokes 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 higher energy or shorter wavelength.

Since, the molecules possess quantized energy levels, we can write,

$$E_1 - E_2 = nh\nu_c \dots \dots \dots (3)$$

where, $n = 0, 1, 2, 3, \dots$ etc. and ν_c is the characteristic frequency of the molecule.

In the simplest case, $n = 1$, eqn. (2) reduces to,

$$\nu_2 = \nu_1 \pm \nu_c \dots \dots \dots (4)$$

Eqn.(4) shows that the frequency difference ($\nu_2 - \nu_1$) between the incident and scattered photon corresponds to the characteristic frequency ν_c of the molecule.

Factors influencing intensity of Raman lines:

- 1) Intensity of Raman lines is directly proportional to intensity of the light source.
- 2) Intensity of Raman lines is inversely proportional to the fourth power of the wavelength of the source.

- 3) Intensity of Raman lines increases with temperature.
- 4) It depends on the concentration of the sample (or) number of molecules.
- 5) It depends on the scattering properties of the sample.

Applications of Raman effect:

1) A qualitative study of Raman spectrum consists of evaluation of wavelength of the lines, their intensities and the state of polarization. It depends on the number of atoms and the chemical binding force between them. In case of diatomic molecules, the frequency of free vibration of atom is given by,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{F}{\mu}}$$

where F is the restoring force per unit displacement and 'μ' is the reduced mass of the molecule.

From this expression, it follows that: i) A diatomic molecule has only one single vibration frequency, ii) A molecule with lighter atoms has higher frequency than that of a molecule containing heavier atoms iii) The frequency of a molecule with strong chemical bonds is lesser than that having weak chemical bonds.

From the determination of vibrational frequency of Raman spectrum of diatomic molecule, force constant can be calculated. This gives an idea of chemical bonds.

- 2) Raman effect in crystals is complementary to X-ray crystal study and provide information about the binding forces in crystals.
- 3) Various chemical effects like strength of chemical bonds, electrolytic dissociation, hydrolysis etc., have been understood through Raman effect.
- 4) Specific heat capacities of solids, metals and their molecular structure have been explained by Raman effect.
- 5) Raman scanners are used by narcotic squads and airport authorities to detect hazardous chemicals and gases and even for forensic work. These can identify the minute traces of bacteria, chemical pollutants or explosive elements.
- 6) Every molecule has different Raman pattern and so, Raman spectra has been called as finger printing of the universe.

Fluorescence and Phosphorescence:

Fluorescence is a process in which a part of energy absorbed by a substance is released in the form of light as long as the stimulating radiation is continued. The fluorescence emission takes place from a singlet excited states.

Phosphorescence is a process in which energy of light absorbed by a substance is released relatively slowly in the form of light. The phosphorescence emission took place from a triplet excited states.

Fluorescence differs from phosphorescence in that the electronic energy transition that is responsible for fluorescence does not change in electron spin, which results in short-lived electrons ($<10^{-5}$ s) in the excited state of fluorescence.

In Phosphorescence, there is a change in electron spin, which results in a longer lifetime of the excited state (second to minutes). Fluorescence and phosphorescence occurs at longer wavelength than the excitation radiation.

Phosphorescence is a type of photoluminescence related to fluorescence. When exposed to light (radiation) of a shorter wavelength, a phosphorescent substance will glow, absorbing the light and reemitting it at a longer wavelength. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs. Instead, a phosphorescent material absorbs some of the radiation energy and re-emits it for a much longer time after the radiation source is removed.

Comparison between Fluorescence and Phosphorescence:

	Fluorescence	Phosphorescence
1	It is the absorption of energy by atoms or molecules, followed by immediate emission of light or radiation.	It is the absorption of energy by atoms or molecules, followed by delayed emission of light or radiation.
2	The emission of radiation suddenly stops on removal of source of excitation.	The emission of radiation remains for some time even after the removal of source of excitation.
3	The excited atom has comparatively short lifetime before its transition to lower energy state.	The excited atom has comparatively longer lifetime before its transition to lower energy state.
4	The time interval between the absorption and emission of energy is very short.	The time interval between the absorption and emission of energy is comparatively long.
5	Examples: Some corals and fungi are fluorescent. Highlighter pens are also fluorescent.	Examples: Materials with the glow-in-the-dark toys, stickers, paint, wristwatch and clock dials.

1. With an exciting radiation of wavelength 435.8 nm. A substance showed a Raman line at a wavelength of 462.4 nm. Calculate the frequency and wavelength of the corresponding Anti-Stoke's line.

$$\text{frequency of exciting radiation } (\nu_i) = \frac{c}{\lambda_i} = \frac{3 \times 10^8}{435.8 \times 10^{-9}}$$

$$\nu_i = 6.88 \times 10^{14} \text{ Hz}$$

$$\text{frequency of Raman line } (\nu_R) = \frac{c}{\lambda_R} = \frac{3 \times 10^8}{462.4 \times 10^{-9}}$$

$$\nu_R = 6.48 \times 10^{14} \text{ Hz}$$

$$\text{Raman Shift } (\Delta\nu_R) = \nu_i - \nu_R$$

$$\Delta\nu_R = 0.396 \times 10^{14} \text{ Hz}$$

$$\text{frequency of Corresponding Antistoke's line } (\nu_{AS}) = \nu_i + \Delta\nu_R$$

$$\nu_{AS} = (6.88 + 0.396) \times 10^{14}$$

$$\nu_{AS} = 7.28 \times 10^{14} \text{ Hz}$$

$$\text{wavelength of Anti-Stoke's line } (\lambda_{AS}) = \frac{c}{\nu_{AS}}$$

$$\lambda_{AS} = \frac{3 \times 10^8}{7.28 \times 10^{14}}$$

$$\lambda_{AS} = 412.08 \times 10^{-9} \text{ mt}$$

2. A Radiation of wavelength 546.1 nm excites a substance to emit a Raman line of wavelength 538.2 nm. Calculate Raman frequency and wavelength of corresponding Stoke's lines.

$$\text{frequency of Incident radiation } (\nu_i) = \frac{c}{\lambda_i} = 6.49 \times 10^{14} \text{ Hz}$$

$$\text{frequency of Raman line } (\nu_R) = \frac{c}{\lambda_R} = 5.57 \times 10^{14} \text{ Hz}$$

$$\text{Raman Shift } (\Delta\nu_R) = \nu_R - \nu_i$$

$$= (5.57 - 5.49) \times 10^{14}$$

$$\Delta\nu_R = 0.081 \times 10^{14} \text{ Hz}$$

$$\text{frequency of Stoke's line } (\nu_s) = \nu_i - \Delta\nu_R = (5.49 - 0.08) \times 10^{14}$$

$$\nu_s = 5.412 \times 10^{14} \text{ Hz}$$

$$\text{wavelength of Stoke's line } (\lambda_s) = \frac{c}{\nu_s} = \frac{3 \times 10^8}{5.412 \times 10^{14}}$$

$$\lambda_s = 554.9 \times 10^{-9} \text{ mt.}$$