

RAMAN EFFECT

While studying the scattering of light, Sir C. V. Raman 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 or Raman scattering.

EXPERIMENTAL STUDY OF RAMAN EFFECT

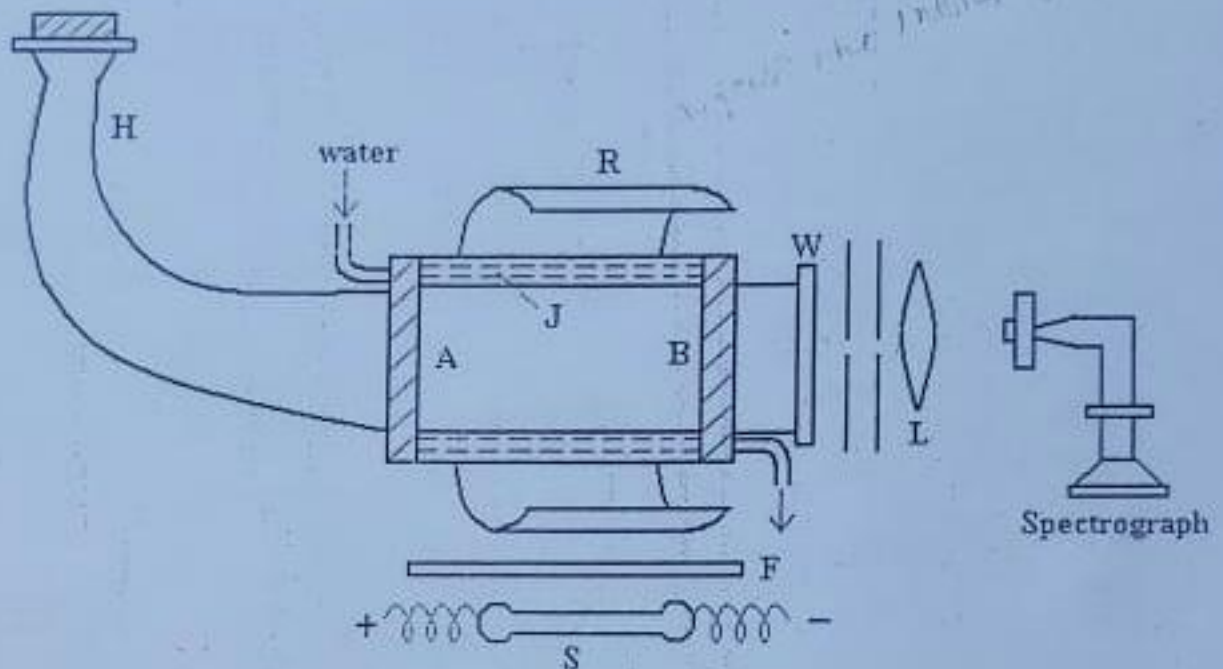


Figure 1: Experimental arrangement to study Raman effect

The basic instrumentation for obtaining Raman spectrum is shown in Figure 1. The basic instrumentation consists of a glass tube AB containing pure experimental liquid. The tube is closed at one end by an optically plane glass plate which forms the window W and the other end is drawn into the shape of a horn H and blackened on the outside.

Light from a mercury arc source S is first passed through a suitable filter F, which allows only monochromatic radiation of wavelength $\lambda = 4358 \text{ \AA}$ 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 because of the proximity of the heated arc. A semi-cylindrical aluminum reflector R is used to increase the intensity of illumination. The scattered light coming out of W passes through a lens L, which directs the scattered radiation upon the slit of the spectrograph and the Raman lines are obtained on the photographic plate, after a long time exposure. This photograph shows in addition to the incident line, faint lines on either side of it as shown in Figure 2. The lines of frequency longer than that of incident radiations are called antistoke's lines and the lines of frequency shorter than the incident radiations are called stoke's lines. A strong unmodified line is also present.

It is seen in Raman spectrum that:

1. The Stoke's lines are always more intense than antistoke's lines.

- The Raman lines are symmetrically displaced with respect to the parent or original line.
- The frequency difference between the modified lines and the parent line represents the frequency of the corresponding infra-red absorption line.
- Scattered wavelengths in the Raman effect are strongly polarized.

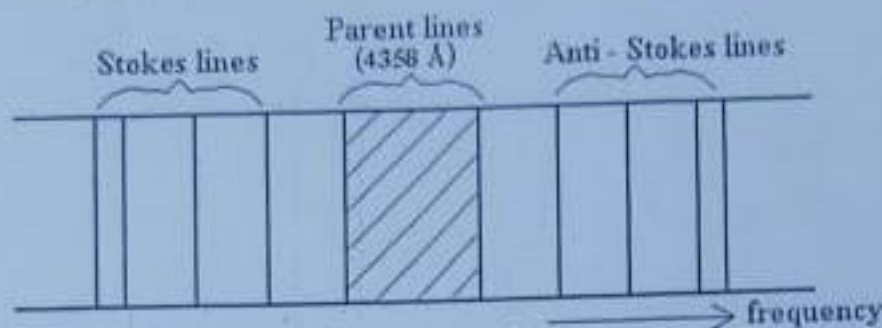


Figure 2: Raman lines

Theory of Raman Effect:

Raman Effect is explained using quantum theory.

According to quantum theory of light, a wave of frequency ν consists of photon, each of energy $h\nu$. When light falls on the molecules of a solid, liquid or gas; the photon undergoes a collision with the molecule. There are two possibilities:

- If the collision is elastic, there is no transfer of energy from the photon to the molecule and vice-versa. The photon is therefore scattered without any change of energy and the frequency of the scattered photon is same as that of the incident photon. This explains the presence of unmodified lines in Raman Effect.
- If the collision is inelastic, there is an exchange of energy between the photon and the molecule.

Let a photon of frequency ν collide with a molecule of energy E_1 . After collision, let the energy of the molecule be E_2 and the frequency of the scattered photon be ν' . Here, change in kinetic energy of the molecule is assumed to be negligible. According to the law of conservation of energy,

$$h\nu + \frac{1}{2}mv^2 + E_1 = h\nu' + \frac{1}{2}mv'^2 + E_2$$

Since there is no change in temperature during collision, there is no change in kinetic energy

$$\text{i.e. } \frac{1}{2}mv^2 = \frac{1}{2}mv'^2$$

$$\therefore h\nu + E_1 = h\nu' + E_2$$

$$\text{or } h\nu' = h\nu + E_1 - E_2$$

$$\text{or } \nu' = \nu + \frac{E_1 - E_2}{h} \dots\dots\dots(1)$$

Now, three cases arise depending on the values of E_1 and E_2 .

- If $E_1 = E_2$ i.e., there is no change in the energy of the molecule, then $\nu = \nu'$ i.e. the collision becomes elastic [Case(i)]
- If $E_1 > E_2$ then equation (1) becomes

$$\nu' = \nu + \frac{E_1 - E_2}{h}$$

$$\text{or } \nu' = \nu + \Delta\nu \text{ where } \Delta\nu = \frac{E_1 - E_2}{h}$$

Then, $\nu' > \nu$ i.e., the frequency of the scattered photon is higher than that of the incident photon. This explains the presence of antistoke's lines on the higher frequency or shorter wavelength side of the Raman spectrum.

c) If $E_2 > E_1$ then equation (1) becomes

$$\nu' = \nu - \frac{E_1 - E_2}{h}$$

$$\text{or } \nu' = \nu - \Delta\nu \text{ where } \Delta\nu = \frac{E_1 - E_2}{h}$$

Then, $\nu' < \nu$ i.e., the frequency of the scattered photon is less than that of the incident photon. This explains the presence of modified stoke's lines on the lower frequency or longer wavelength side of the Raman spectrum.

Intensity of Raman lines

The molecules of a medium may be in different quantum states possessing different energies E_1, E_2, E_3 etc. Assuming the validity of Boltzmann energy distribution in the case of molecules, we may represent the number of molecules N_1 in energy state E_1 by

$$N_1 = CN g_p e^{-E_1/kT}$$

where C is a constant, N is the total number of molecules, g_p is statistical weight of a state, k is Boltzmann constant and T is absolute temperature.

At room temperature the energy E_1 of a molecule is small and thus $e^{-E_1/kT}$ will be very high. Hence the number of molecules N_1 with low energy E_1 will be large in number. As a result, stokes transitions occur more frequently than antistokes. Thus stokes lines appear more intense than antistokes lines.

However, with the rise in temperature, the kinetic energy of the molecules increases and more molecules are raised to higher energy states. On account of this, the intensity of antistokes' lines gradually increases with increase of temperature.

Factors affecting the intensity of Raman lines are:

1. **Intensity of parent line:** Intensity of Raman line can be expressed as a power of intensity of parent line. For example, in gases, intensity of Raman line is $(1/1000)^{\text{th}}$ of that of parent line and in liquids, it is $(1/100)^{\text{th}}$ of that of parent line.
2. **Nature of photographic plate used:** To obtain good intensity, photographic plates with uniform sensitivity should be used.
3. **Wavelength of incident light:** Scattered intensity is proportional to $(1/\lambda^4)$ where λ is the wavelength of incident light. Thus, it is desirable to use light of shorter wavelength.
4. **Temperature:** Stokes lines are always more intense than antistokes lines. However, the intensity of anti Stokes' lines gradually increases with the rise in temperature.
5. **Polarization:** The polarized lines are sharp and intense while unpolarized lines are diffuse and weak.

Polarization of Raman lines

Some lines in Raman spectra are found to be plane polarized to different extent even though the exciting radiation is unpolarised. Polarized light can be detected using analyser.

The analyser is held in front of Raman tube and is rotated. If intensity undergoes complete extinction in a certain position, then it can be concluded that scattered light is plane polarized. If light intensity varies between certain maximum to a minimum not equal to zero, then scattered light is partially polarized.

The state of polarization of a Raman line is measured by a quantity known as depolarization factor P. The depolarization factor is the ratio of intensities of horizontal and vertical components, when incident light is vertically polarized. P varies from 0 to 1 for partially polarized light. It varies from 0 to 0.86 in Raman spectra.

The polarized lines are sharp and intense while unpolarized lines are diffuse and weak.

Applications of Raman Effect:

1. A qualitative identification of Raman spectrum consists in the evaluation of the wavelength of the lines, their intensities and state of polarization. Investigation of bond angles, bond stiffness and other structural confirmation require Raman data in addition to infrared spectroscopy. Some vibrations which do not show up in IR spectra appear in Raman spectra and vice versa. This enables cross-checking. Further Raman lines show characteristics polarization effects. This enables one to obtain additional information about molecular structure.

The combined use of IR and Raman spectroscopy enables the determination of the shape of the molecules. For instance, it can be found out whether triatomic molecules of the type AB_2 are symmetrical ($B-A-B$) or asymmetrical ($B-B-A$). Two examples are given below:

i) CO_2 has two very strong bands in its IR absorption spectrum at 66800 m^{-1} and 234900 m^{-1} while only one strong band in its Raman spectrum at 138900 m^{-1} . None of these bands occur both in Raman and IR spectra. This implies that the molecule is linear and symmetric and hence it should be represented by $O-C-O$.

ii) Nitrous oxide (N_2O) has two strong bands at 222400 m^{-1} and 128500 m^{-1} in Raman spectrum and three strong bands at 222400 m^{-1} , 128500 m^{-1} and 58900 m^{-1} in IR spectrum. Thus the molecule cannot have a centre of symmetry though it is linear.

Hence the molecule has asymmetrical structure $N-N-O$.

Thus the study of Raman spectra of different substances enables us to classify them according to their molecular structure.

2. Diatomic molecules such as H_2 and O_2 do not give IR spectra but give Raman spectra. The study of Raman spectra of these molecules gives information about the nature of chemical bond existing between the atoms. By measuring the characteristic frequency of the molecule, the force constant of the bond can be found.
3. Various chemical effects like strength of chemical bonds, electrolytic dissociation, hydrolysis, etc. have been understood through Raman Effect.
4. Specific heat capacity of solids and brilliance of metals and their molecular structure have been explained by Raman effect.
5. Raman effect is used to determine the binding force in crystals.
6. It is used to study certain aspects of nuclear physics such as nuclear spin and isotopic constitution of the nucleus.
7. It is used to find out qualitative as well as quantitative identity of a particular substance in a mixture.
8. It is widely employed in the analysis of aromatic oils.