

Raman Spectra

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Let a beam of monochromatic light from the visible portion of the spectrum be chosen such that it is not absorbed by the substance under study. If such a light is passed through the substance, nearly all of it is transmitted and a very small fraction of it is scattered in all directions (Figure1). If the scattered light in a direction perpendicular to the incident beam is spectrographed, it is found not only to contain a line corresponding to the frequency of incident light, but also a pattern of relatively weak lines on the low-frequency side of the incident light and a similar pattern of still more weak lines on the high frequency side (Figure2)

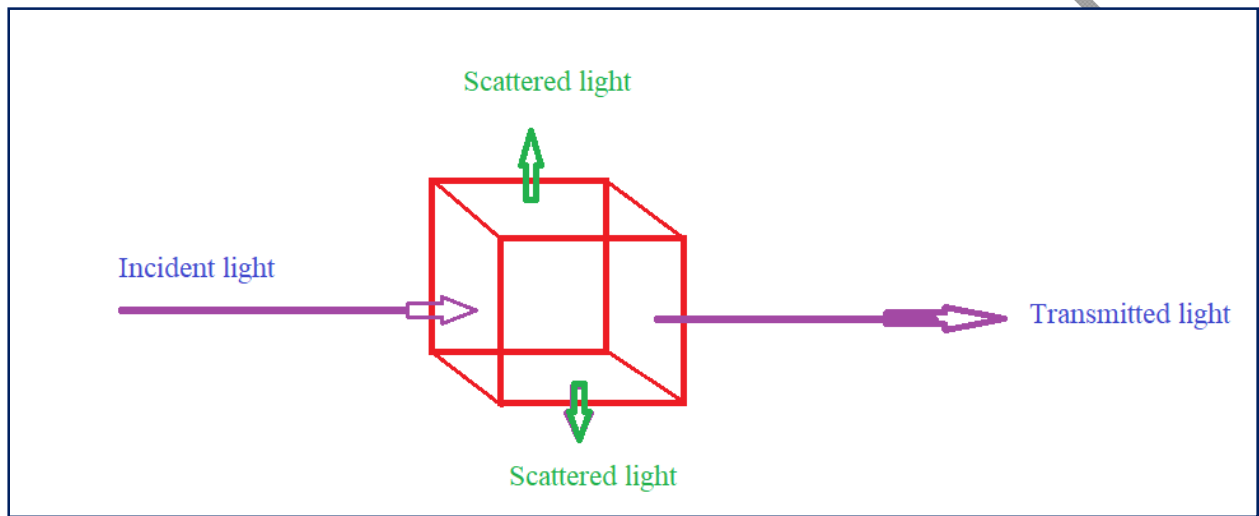


Figure 1: Scattering of light by nonabsorbing substance

The line at the incident frequency is known as Rayleigh line (after Lord Rayleigh who did much pioneering study in the field of light scattering). The other weak lines are called the Raman lines (after C.V.Raman who was the discover of these lines). The difference between the frequencies (or wavenumbers) of the Rayleigh line and a Raman line is known as the **Raman Shift** ,and may be expressed as

$$\Delta\nu = |\nu_0 - \nu_R| \dots\dots\dots(1a)$$

$$\Delta\bar{\nu} = |\bar{\nu}_0 - \bar{\nu}_R| \dots\dots\dots(1b)$$

where the subscripts 0 and R stand for incident and Raman lines, respectively.

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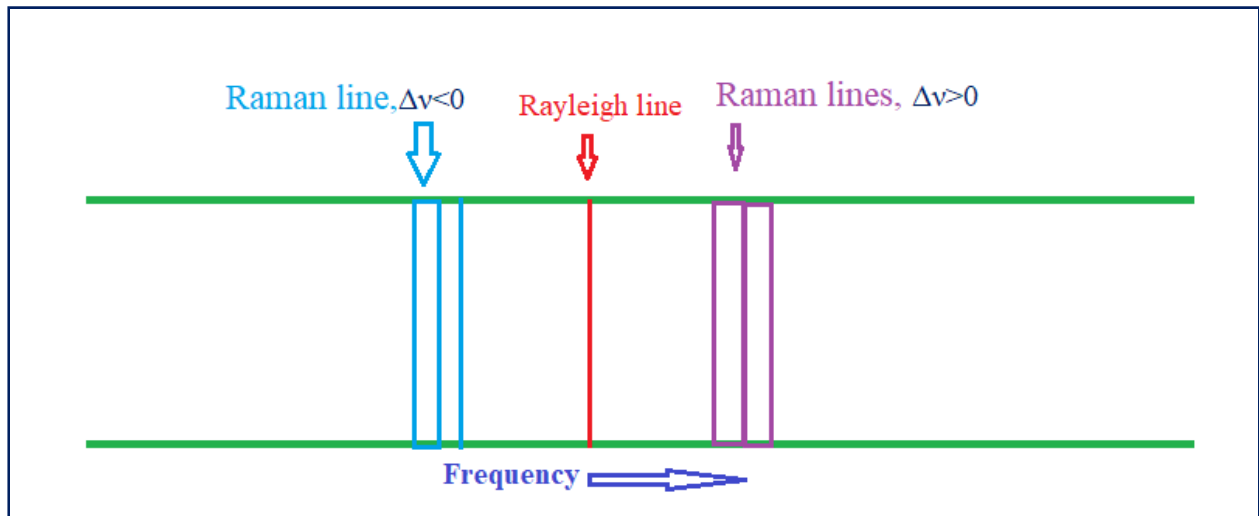


Figure2: Schematic representation of a Raman Spectrum

For a given substance, the Raman shift is found to be independent of the frequency of the incident radiation, i.e it has the same value for different frequency of the incident light. This difference is a characteristic of the substance and is found to be equal to its vibrational or rotational transition.

Essential Criterion For a Molecule to be Raman Active

The Raman Spectroscopy is observed only when there occurs a periodic change in the polarizability of molecule due to its vibrational or rotational oscillation. From the classical point of view the above fact may be understood as follows.

In the presence of a static electric field, a molecule is polarized, i.e., the positively charged nuclei and the negatively charged electron cloud is attracted towards the respective oppositely charged pole of the electric field. Consequently, the molecule acquires an induced dipole moment which is given by

$$p_{ind} = \alpha E \dots\dots\dots (2)$$

where α is the polarizability of the molecule.

In the presence of a beam of radiation, the molecule also acquires an induced dipole moment due to the electrical components of the incident light. This electrical component is not static but varies as the sine (or cosine) wave according to the equation

$$E = E_0 \sin(2\pi vt) \dots\dots\dots (3)$$

where v is the frequency of radiation and t is the time in seconds. This variation is illustrated in Figure 3. Consequently, the induced dipole moment also oscillates according to the equation

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$$p = \alpha E = \alpha E_0 \sin(2\pi\nu t) \dots\dots\dots(4)$$

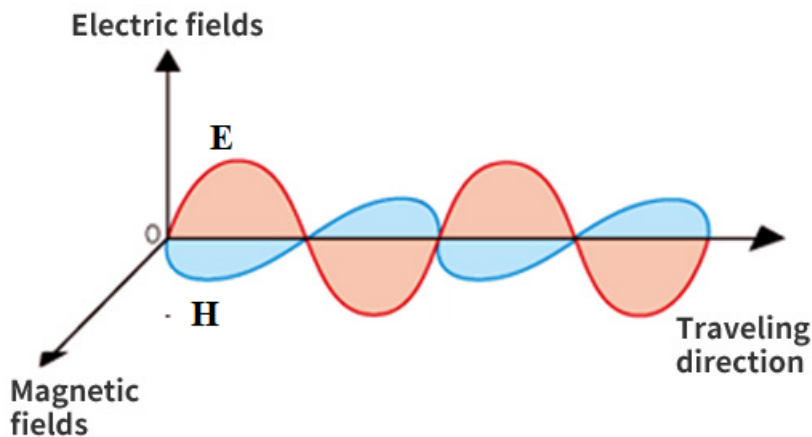


Figure 3: The variation of electric component of the radiation with time

According to the electromagnetic theory, an oscillating dipole emits radiation of its own frequency. This explains the occurrence of Rayleigh line in the light scattered by the substance. The presence of Raman lines due to the periodic change in the value of α due to the internal vibrational or rotational motion according to the equation.

$$\alpha = \alpha_0 + (\partial\alpha/\partial\zeta) \zeta_0 \sin(2\pi\nu_i t) \dots\dots\dots(5)$$

where $(\partial\alpha/\partial\zeta)$ is the change in polarizability with the displacement coordinate ζ , ν_i is the frequency of internal motion, and α_0 is the polarizability in the equilibrium position ζ_0 .

The periodic change in the polarizability will also change periodically the induced dipole moment (Eq.2). When this periodic change is superimposed upon the periodic oscillation due to the electrical component of light (Eq.4),

$$\begin{aligned} \text{We get, } p_{ind} &= \{ \alpha_0 + (\partial\alpha/\partial\zeta) \zeta_0 \sin(2\pi\nu_i t) \} E_0 \sin(2\pi\nu t) \\ &= \alpha_0 E_0 \sin(2\pi\nu t) + (\partial\alpha/\partial\zeta) \zeta_0 E_0 \sin(2\pi\nu_i t) \sin(2\pi\nu t) \dots\dots\dots(6) \end{aligned}$$

$$\text{Since } 2\sin\theta\sin\phi = \cos(\theta-\phi) - \cos(\theta+\phi)$$

$$\begin{aligned} \text{We get, } p_{ind} &= \alpha_0 E_0 \sin(2\pi\nu t) + 1/2(\partial\alpha/\partial\zeta) \zeta_0 E_0 \cos\{(2\pi(\nu - \nu_i)t\} \\ &\quad - 1/2(\partial\alpha/\partial\zeta) \zeta_0 E_0 \cos\{(2\pi(\nu + \nu_i)t\} \dots\dots\dots(7) \end{aligned}$$

That is , induced dipole moment of the molecule not only oscillates with frequency ν , but also with frequency $\nu - \nu_i$ and $\nu + \nu_i$. It is thus expected that besides the frequency ν , the oscillating



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dipole will also emit radiations of frequencies $\nu - \nu_i$ and $\nu + \nu_i$. These radiations appear as the Raman lines in the light scattered by the substance.

Note that if $\partial\alpha/\partial\zeta$ is zero, i.e., there occurs no change in the polarizability during the small displacement from the equilibrium position of the internal motion, then the induced dipole moment of the molecule oscillate with only one frequency corresponding to the frequency of incident light. In such a case, the molecule emits only Rayleigh line and hence Raman lines are not observed, i.e., the molecule is Raman inactive. Thus, the essential criteria for a molecule to be Raman active is that *a molecular vibration or rotation must cause a change in the component of molecular polarizability*. This criterion may be compared with those of rotational and vibrational spectroscopy which respectively are ; (1) the molecule must have a permanent dipole moment , and (2) there should occur a change in dipole moment during the vibration motion.

Since the polarizability has a dimension of volume in gaussian units it may be considered that only those vibrations which are associated with the change in the volume will be Raman active.