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Topic - Raman Spectra

Raman Spectroscopy

When a monochromatic light of definite frequency is passed through any substance (gas, liquid or solid) and the scattered light is observed at right angle to the incident beam, the scattered light may contain lines of frequency lower or higher than original frequency. This is called Raman effect. The lines of lower frequency than original are called Stokes lines and that of higher frequency as anti-Stokes lines.

If ν_i and ν_s are frequency of incident and scattered radiation then $\nu_i - \nu_s = \Delta\nu$ is called Raman shift. It is characteristic of the substance irradiated and quite independent of frequency of incident radiation. $\Delta\nu$ corresponds to IR region.

Quantum theory of Raman effect — consider a photon of frequency ν falling on a molecule. For elastic collision, the scattered photon will have same energy as incident photon. For inelastic collision, the scattered photon will have higher or lower energy than incident photon. If we assume that K.E. of photon and molecule remains unchanged before and after the collision. Then

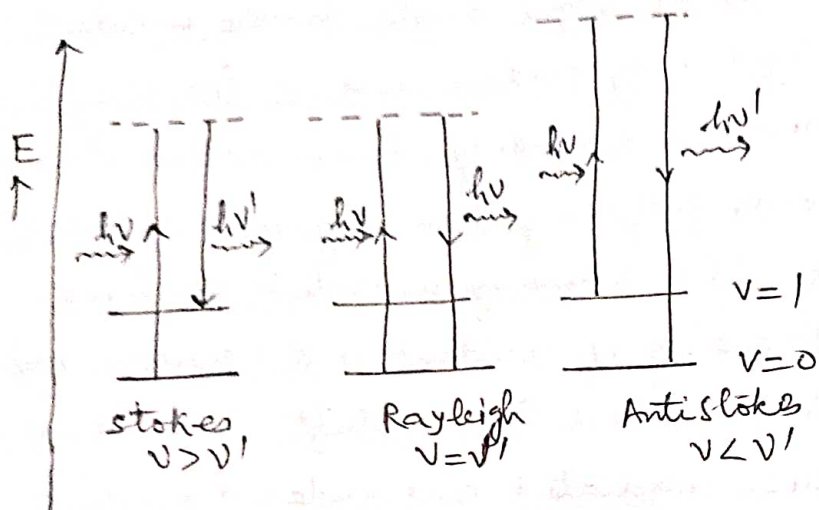
$$h\nu + E = h\nu' + E' \quad \text{--- (1)}$$

where E is the energy of molecule (rot, vib and electronic). The prime represent after the collision value.

From (1) we have, $(E' - E) / h = \nu - \nu'$ --- (2)

- | | |
|--|---------------------|
| case I, $\nu = \nu' \Rightarrow E = E'$ | Rayleigh Scattering |
| case II (a), $\nu < \nu' \Rightarrow E > E'$ | } Raman Scattering |
| (b), $\nu > \nu' \Rightarrow E < E'$ | |

So in Raman scattering, when the photon collides with the molecule, the energy is either transferred to, or taken away from the molecule. It is as shown in the figure -



So when the molecule is excited to higher unstable vibrational state, returns to original state, we get Rayleigh scattering. If it returns to a different vibrational level, this gives Raman scattering (Stokes lines). When the molecule in $v=1$ is promoted to higher unstable vibrational state and returns to ground state, this also gives Raman scattering (anti-Stokes lines). Thus Raman spectrum of a molecule consists of Stokes and anti-Stokes lines, which are symmetrically situated about the Rayleigh line.

Intensity of the lines - Let the molecules distributed among the diff. quantum states of energy E_1, E_2, \dots etc.

If N_p is the no. of molecules having energy E_p then by Boltzmann's law, $N_p = c N g_p e^{-E_p/kT}$ where c is constt, N is total no. of molecules and g_p is the statistical weight of the state.

At room temp, E_p is small so $e^{-E_p/kT}$ will be high and N_p is high.

This means Stokes transitions will occur more frequently than anti-Stokes. So Stokes lines are more intense comparative to anti-Stokes. This is because the anti-Stokes lines correspond to return of a molecule from unstable excited vibrational state to ground state and initially there are very few molecules in excited vibrational state. But as the temp. rises, the intensity of anti-Stokes lines gradually rises and become more prominent.

Pure Rotational Raman spectra — The selection rule for pure rotational spectra (Raman) of a diatomic molecule is, $\Delta J = 0, \pm 2$. The operative part is $\Delta J = +2$ because $\Delta J = 0$ is Rayleigh scattering and $\Delta J = -2$ is ignored because rotational q . number of upper state must be greater than lower state.

$$\text{Now } \bar{E}_J = BJ(J+1) \text{ cm}^{-1} \quad (J=0, 1, 2, 3, \dots) \quad \text{--- (1)}$$

$$\text{So } \Delta \bar{E}_J = \bar{E}_{(J+2)} - \bar{E}_J = B(4J+6) \text{ cm}^{-1}$$

It is customary to call $\Delta J = +2$ transitions as S-branch lines

$$\text{Thus } \Delta \bar{E}_S = B(4J+6) \text{ cm}^{-1} \quad (J=0, 1, 2, 3, \dots) \quad \text{--- (2)}$$

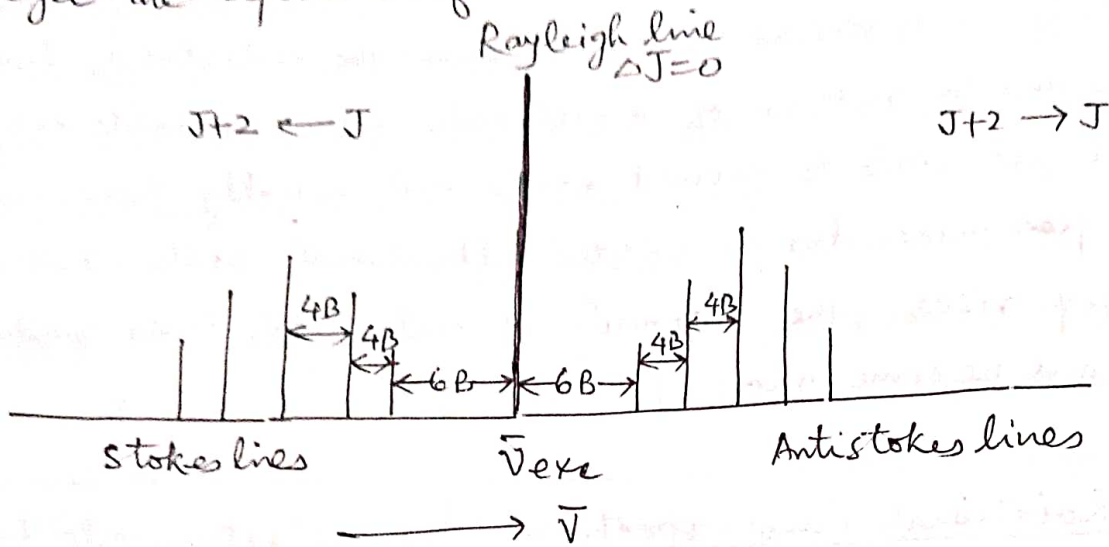
where J is the q . number of lower rotational energy level.

Hence the Raman spectral lines appear at the wave numbers given by, $\bar{\nu}_R = \bar{\nu}_{exc} \pm \Delta \bar{E}_S = \bar{\nu}_{exc} \pm B(4J+6) \text{ cm}^{-1}$

The -ve sign refers to Stokes lines and +ve sign to the anti-Stokes lines.

From equation (2) if $J=0$, $\Delta \bar{E}_S = 6B$, so the first Stokes or anti-Stokes lines will appear at a distance $6B$ from exci-

ting Rayleigh line. Now by putting $J=1, 2, 3, \dots$ etc in equation (2) we get the separation of successive Raman lines as $4B$.



Since many rotational levels are equally populated, the Stokes and anti-Stokes lines in Rotational Raman spectra are of comparable intensity.

For molecules having centre of symmetry and atoms of non-zero nuclear spin eg, H_2 ; $CH \equiv CH$ etc., the spectral lines show an alternation of intensity. For linear molecules with centre of symmetry, and having atoms of zero nuclear spin the alternate rotational level remain empty, so the alternate line in the spectrum is missing. So the first line occurs at $10B$ distance and spacing b/w any two adjacent successive lines on either side is $8B$.

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vibrational Raman spectra — The vibrational energy of anharmonic oscillator is given by,

$$\bar{E}_V = \bar{\nu}_e \left(V + \frac{1}{2} \right) \left[1 - x \left(V + \frac{1}{2} \right) \right] \text{ cm}^{-1}$$

The selection rule is, $\Delta V = \pm 1, \pm 2, \dots$

The transition from $V=0$ to $V=1$ is most probable at room temperature. So corresponding wave number is given by,

$$\bar{\Delta E} (0 \rightarrow 1) = \bar{\nu}_e (1 - 2x) \text{ cm}^{-1}$$

So the frequency of Raman lines is given by,

$$\bar{\nu}_R = \bar{\nu}_{exc} \pm \bar{\nu}_e (1 - 2x) \text{ cm}^{-1}$$

where +ve sign refers to anti-stokes and -ve sign to Stokes' lines.

Since population of $V=1$ at room temp. is much lower, so anti-stokes lines are much weaker than Stokes lines. Since the Raman scattered light is of low intensity, hence it is generally difficult to observe overtones and hot bands.

Polarizability and Raman spectra — when a molecule is placed in an electric field, the field distorts the electronic structure and changes the equilibrium positions of the nuclei. In this way electric field induces a dipole moment (M_{ind}) which is proportional to electric field E . i.e. $M_{ind} = \alpha E$ — (1)

Here proportionality constt. α is called polarisability of molecule. By equation (1), α can be defined as induced dipole moment generated by unit electrical field strength.

It is observed that for a molecular vibration or rotation to be active in Raman spectrum, it must cause a change

in the molecular polarisability. The homonuclear diatomic molecules eg, H_2 , N_2 , O_2 etc. do not show IR spectra because they do not have a permanent dipole moment. But they show Raman spectra because their vibration is accompanied by change in polarisability of the molecules. Hence there occurs a change in the induced dipole moment at the vibrational frequency.

Q. A sample was excited by 4358 \AA line of Hg. A Raman line was observed at 4447 \AA . What is Raman shift in cm^{-1} ? What is the wavelength of antistokes line?

Ans.
$$\Delta \bar{\nu}_R = \frac{10^8}{\lambda_{exc}(\text{A}^\circ)} - \frac{10^8}{\lambda_R(\text{A}^\circ)} = \frac{10^8}{4.358 \times 10^3} - \frac{10^8}{4.447 \times 10^3} = 460 \text{ cm}^{-1}$$

The antistokes line appears on a higher frequency side. Hence

$$\bar{\nu}_{\text{antistokes}} = \bar{\nu}_{exc} + 460 \text{ cm}^{-1}$$

$$\text{Now } \bar{\nu}_{exc} = \frac{10^8}{4.358 \times 10^3} = 2.295 \times 10^4 \text{ cm}^{-1}$$

$$\text{So } \bar{\nu}_{\text{antistokes}} = 2.295 \times 10^4 + 460 = 2.341 \times 10^4 \text{ cm}^{-1}$$

$$\bar{\nu}(\text{antistokes}) \text{ in } \text{A}^\circ = \frac{10^8}{\lambda(\text{cm}^{-1})} = \frac{10^8}{2.341 \times 10^4} = 4272 \text{ A}^\circ$$