## Explanation of Raman Lines From the Quantum Viewpoint

The Raman lines are, in general, of vary weak intensity as compared to the Rayleigh line. From the qualitative quantum vviewpoint, the occurance of Raman lines may be understood as followes:

The photon on colliding with a molecule will constitute either an elastic or inelatic collision. It may be considered that the molecule to form a complex with the photon during the extermely short time of collision ($\approx 10^{-15}$s). The energy of the complex will not correspond to a molecular electronic energy level (Figure 4a) . Now if the collision is elastic, the complex will dissociate to give the molecule and photon of the same energy which it had before the collision. This gives rise to the Rayleigh scattering. On the other hand, if the collision is inelastic, there can occur an exchange of energy between molecule and photon . This exchange of energy can be of two types

(1) Th molecule before the collision occupies a lower vibrational or rotational energy level and aster the emission of the photon, it may be present in any one of the higher energy levels as permitted by the selection rule. In this case, the molecule gains energy equivalent to the energy difference between the two involved levels. This energy is provided by the photon and hence its energy is decreased and thus a Raman line on the low frequency side is observed. (Figure 4b)

(2) The molecule before the collision occupies one of the higher vibrational or rotational energy level and after the emission of the photon may be present in any one of the lower energy levels as permitted by the selection rule. In this case, the molecule loses an energy equivalent to the energy difference between the two involved levels. This is gained by the photon and hence its energy is increased and thus a Raman line on the higher frequency side is observed (Figure 4c).
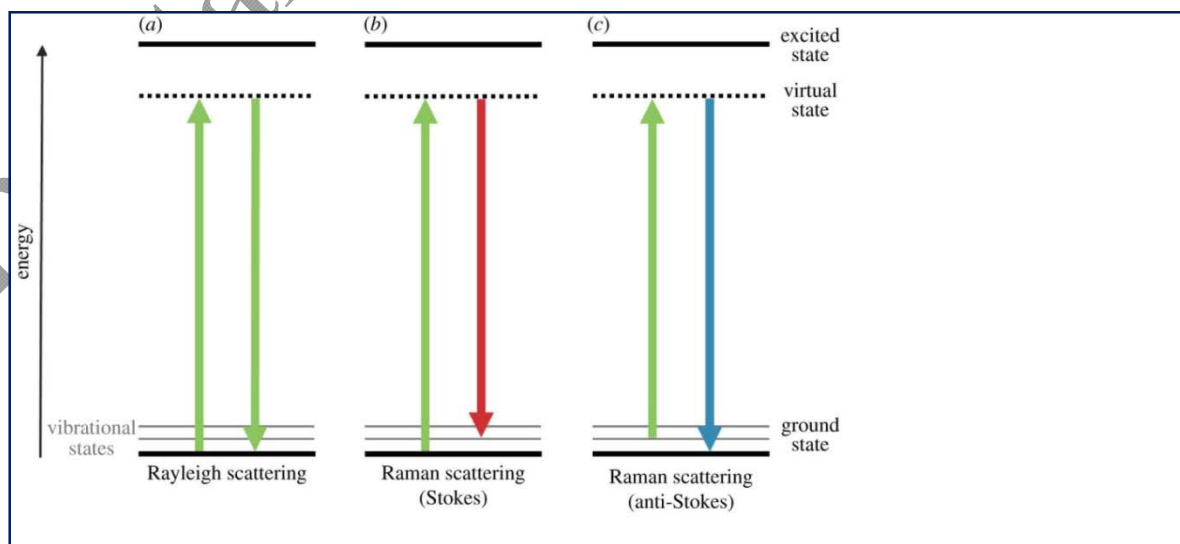
Figure4: (a) Rayleigh scattering with Δv=0. (b)Raman scattering with Δv<0 (c) Raman scattering with Δv>0.

Pure Roattaional Raman Spectra of Diatomic Molecules

The selection rules for the pure rotational Raman spectra of diatomic molecules are

$$\Delta J = 0, \text{ or } \pm 2$$

The selection rule for $\Delta J = 0$ gives rise to Rayleigh scattering only.

The rotational energy expression is

$$\bar{\upsilon} = BJ(J+1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(8)$$

The difference of wavenumber between two level is

$$\Delta\bar{\upsilon} = BJ'(J'+1) - BJ''(J''+1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(9)$$

For the selection rule $\Delta J = J' - J'' = 2$, then

$$\Delta\bar{\upsilon} = BJ''(J''+2)(J''+3) - BJ''(J''+1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots.(10)$$

$$= B(4J''+6) \qquad J'' = 0,1,2\ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

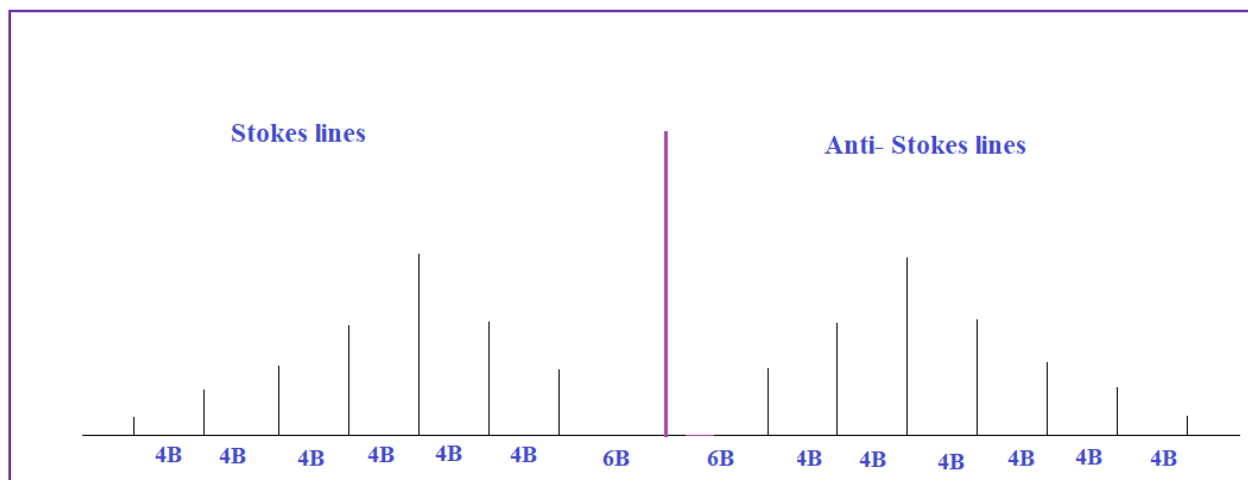Similarly for the selection rule $\Delta J = J' - J'' = -2$, then

$$\Delta\bar{\upsilon} = -B(4J'+6) \qquad J' = 0, 1, 2\ldots..$$

Thus, Raman lines will appear at wavenumber gives by the expression

$$\bar{\upsilon} = \bar{\upsilon}_0 \pm B(4J+6); \qquad J = 0, 1, 2, 3,\ldots\ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(12)$$

where $\bar{\upsilon}_0$ is the wavenumber of Rayleigh line. The lines at wavenumbers less than $\bar{\upsilon}_0$ are known as Stokes' lines. The expected pure rotational Raman spectrum is shown in Figure 5.

Figure 5: An expected pure rotational Raman spectrum for diatomic molecule

The first Stokes' and anti –Stokes' lines will lie at a separation of 6B from the Rayleigh line. The remaining lines will lie at a constant spacing of 4B.

Application of Pure Rotational Raman Spectra

The pure rotational Raman spectra provide the value of B. Thus, the moment of inertia and bond length of the molecule can be determined. The usefulness of Raman spectroscopy may be emphasized here. Homonuclear diatomic molecule does not exhibit pure vibrational or rotational spectra as they possess no dipole moment. But they do exhibit rotational Raman spectra and hence structural parameters which cannot be determined by pure rotational spectra can be determined from Raman spectra.