

radiation. 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.

Quantum theory of Raman effect :

The occurrence of Raman scattering may be most easily understood by considering radiation of frequency ν as consisting of a stream of particles called photons having energy $h\nu$. Photons can be imagined to undergo collisions with molecules and, if the collision is perfectly elastic, they will be deflected unchanged. A detector placed to collect energy at right angles to an incident beam will thus receive photons of frequency ν . This gives rise to "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.

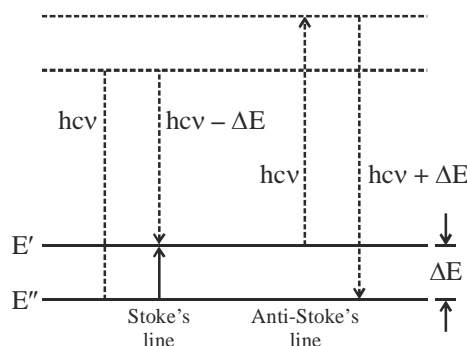
- The molecule before the collision occupies a lower vibrational or rotational energy level and after the emission of the photon, it may be present in anyone of the higher energy levels as permitted by selection rule. In this case, the molecule gains energy equivalent to the energy difference between 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. Such a Raman line is called a "Stoke's line".
- 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, energy is gained by photon and hence its energy is increased and thus a Raman line on high frequency side is observed. Such a Raman line is called an "anti-Stoke's" line.

Stoke's line is generally more intense than anti-stokes line.

The Stoke's lines frequency is $\frac{h\nu - \Delta E}{hc}$.

The anti-stoke's lines frequency is $\frac{h\nu + \Delta E}{hc}$.

The wave number shift in each case being $\frac{\Delta E}{hc}$.



Pure rotational Raman spectra of diatomic molecules:

The rotational energy levels of linear molecules is $\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} (J = 0, 1, 2, 3, \dots)$. But in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving D , the centrifugal distortion constant.

So we take $\boxed{\epsilon_J = BJ(J+1)}$ ($J = 0, 1, 2, \dots$)

The selection rule for the pure rotational Raman spectra of diatomic molecules are $\Delta J = 0$ or ± 2 only.

The selection rule $\Delta J = 0$ gives rise to the Rayleigh scattering only. The selection rule $\Delta J = \pm 2$ gives rise to the Raman lines. The factor 2 is due to the fact that the polarizability ellipsoid rotates twice as fast as the rotation of the molecule.

The difference in wave number between two levels is $\Delta\varepsilon = BJ'(J'+1) - BJ''(J''+1)$

For the selection rule, $\Delta J = J' - J'' = +2$, we have $\Delta\varepsilon = \varepsilon_{J'=J''+2} - \varepsilon_{J''}$

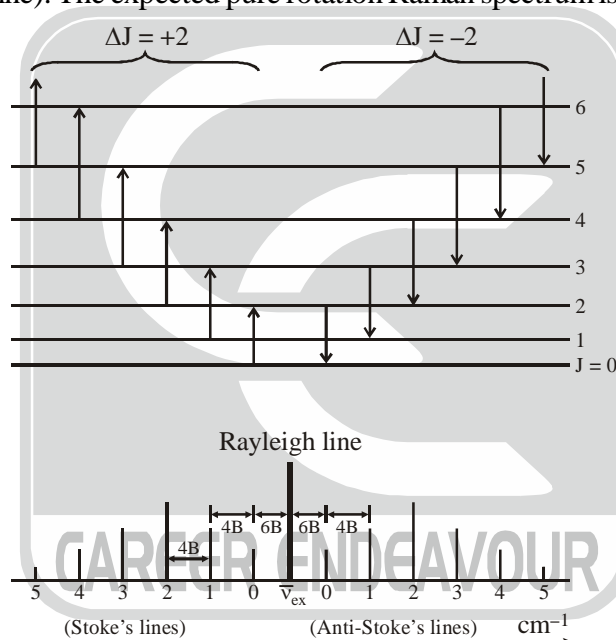
$$\boxed{\Delta\varepsilon = B(4J'' + 6)} \quad J'' = 0, 1, 2, \dots$$

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

$$\Delta\varepsilon = \varepsilon_{J'=J''} - \varepsilon_{J''=J'+2} = -B(4J' + 6) \quad J' = 0, 1, 2, \dots$$

Thus Raman lines will appear at wave number given by expression $\bar{\nu} = \bar{\nu}_{\text{ex}} \pm B(4J + 6)$.

Here, the plus sign refers to anti-stokes lines and minus to stokes line and $\bar{\nu}_{\text{ex}}$ is the wavenumber of the exciting radiation (i.e. Rayleigh line). The expected pure rotation Raman spectrum is shown in figure below.



The first stokes and anti-stokes line will lie at a separation of $6B$ from the Rayleigh line. The remaining lines will lie at a constant spacing of $4B$.

Each transition is labelled according to its lower J value and the relative intensities of the lines are indicated

assuming that the population of the various energy levels varies according to the $\frac{N_J}{N_0} = (2J + 1) e^{-(E_J - E_0)/kT}$.

Here we must note that stokes and anti-stokes lines have comparable intensity because many rotational levels are populated and hence downward transitions are approximately as likely as upwards ones.

It should be mentioned that, if the molecule has a center of symmetry (as, for example O_2 , H_2 , CO_2) then the effects of nuclear spin will be observed in the Raman as in the infrared. Thus for O_2 and CO_2 (since the spin of oxygen is zero) every alternate rotational level is absent. In case of H_2 , and other molecules composed of nuclei with non-zero spin, the spectral lines show an alternation of intensity.

The pure rotational Raman spectra provides the value B , and hence the moment of inertia and bond lengths for molecules. Homonuclear diatomic molecules do 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 the Raman spectra.

Vibrational Raman spectra

For every vibrational mode we can write an expression of the form :

$$\varepsilon = \bar{\omega}_e \left(v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2 \text{ cm}^{-1} \quad (v = 0, 1, 2, 3, \dots)$$

where, $\bar{\omega}_e$ is the equilibrium vibrational frequency and x_e is the anharmonicity constant. Such an expression is perfectly general, whatever the shape of the molecule or the nature of the vibration.

The selection rules for the vibrational Raman spectra are the same as those for pure vibrational spectra i.e. $\Delta v = 0, \pm 1, \pm 2, \pm 3, \dots$ decreases rapidly.

Particularizing, now to Raman active modes, we can apply selection rule to the energy level expression given above, so

$$v = 0 \rightarrow v = 1; \quad \Delta \varepsilon_{\text{fundamental}} = \bar{\omega}_e (1 - 2x_e) \text{ cm}^{-1}$$

$$v = 0 \rightarrow v = 2; \quad \Delta \varepsilon_{\text{overtone}} = 2\bar{\omega}_e (1 - 3x_e) \text{ cm}^{-1}$$

$$v = 1 \rightarrow v = 2; \quad \Delta \varepsilon_{\text{hot}} = \bar{\omega}_e (1 - 4x_e) \text{ cm}^{-1}$$

Since the Raman scattered light is, in any case, of low intensity we can ignore completely all the weaker effects such as overtones and 'hot bands', and restrict our discussion merely to the fundamentals.

We would expect Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibration. So we can write

$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \Delta \varepsilon_{\text{fundamental}} \text{ cm}^{-1}$$

$$\bar{\nu}_{\text{fundamental}} = \bar{\nu}_{\text{ex}} \pm \bar{\omega}_e (1 - 2x_e)$$

where the minus sign represents the Stokes line and the plus sign refers to the anti-Stokes line. Since the latter refers to the transitions $v = 1 \rightarrow v = 0$, it is expected to be very weak as very few molecules exist in the $v = 1$ state at the room temperature. On increasing temperature the population of $v = 0$ state is decreased whereas that of $v = 1$ state is increased, it is thus expected that the intensity of Stokes's line will decrease whereas that of anti-Stokes's line will increase on increasing the temperature of the sample.

The vibrational Raman spectrum of a molecule is then basically simple. It will show a series of reasonably intense lines to the low frequency side of the exciting line with a much weaker, mirror image series on high frequency side. The separation of each line from the center of the exciting line gives immediately the Raman active fundamental vibration frequencies of the molecule.

The vibrational Raman spectra of homonuclear diatomic molecules are of special interest because they yield force constant and rotational constant that are not available from infrared absorption spectroscopy.

Intensity of the anti-Stokes's Raman line is much smaller than that of Stokes's Raman line.

$$\frac{\text{Anti-stoke's intensity}}{\text{Stoke's intensity}} = e^{-\Delta \varepsilon_{\text{fundamental}} \cdot hc/kT}$$

where, $\Delta \varepsilon_{\text{fundamental}} = \bar{\omega}_e (1 - 2x_e)$ is the Raman shift in vibration.

Raman activity of vibrations :

If a molecule has little or no symmetry it is a very straightforward matter to decide whether its vibrational modes will be Raman active or inactive : in fact, it is usually correct to assume that all its modes are Raman active. However, when the molecule has considerable symmetry it is not always easy to make the decision, since it is somewhat not clear, without detailed consideration, whether or not the polarisability changes during the vibration.