$$\lambda(\text{in Å}) = \frac{\quad}{\bar{\nu}(\text{cm}^{-1})} = \frac{\quad}{2.341\times10^4}$$

Pure Rotational Raman Spectra. The energy of a rigid rotator will be given by

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \tag{4.17}$$

The selection rule for rotational Raman spectrum is as follows :

$$\Delta J = 0, \pm 2 \tag{4.18}$$

When $\Delta J = 0$, the scattered Raman radiation will be of the same frequency as that of incident light (Rayleigh's scattering). The transition $\Delta J = \pm 2$ gives Stoke's lines (longer wavelength) whereas $\Delta J = -2$ gives the anti-Stoke's lines (shorter wavelength).

When $\Delta J = +2$, the values of rotational Raman shifts (Stoke's lines) will be given by

$$\Delta\bar{\nu} = \frac{h}{8\pi^2 Ic}\left[(J+2)(J+3) - J(J+1)\right]$$

$$= 2B(2J+3) \text{ where } B = \frac{h}{8\pi^2 Ic} \tag{4.19}$$

When $\Delta J = -2$, the values of rotational Raman shifts (anti-Stoke's lines) will be given by

$$\Delta\bar{\nu} = -2B\,(2J+3)$$

On combining equations (4.19) and (4.20), the Raman shift can be put in the form of

$$\Delta\bar{\nu} = \pm 2B(2J+3) \text{ where } J = 0,\ 1,\ 2,\ 3\ldots$$

The wave numbers of the corresponding spectral lines will be given by

$$\bar{\nu} = \overline{\nu_{ex}} + \Delta\nu$$

Where ν_{ex} is the wave number of exciting radiation,

The transitions and the Raman spectrum are shown in Fig. 4.5.

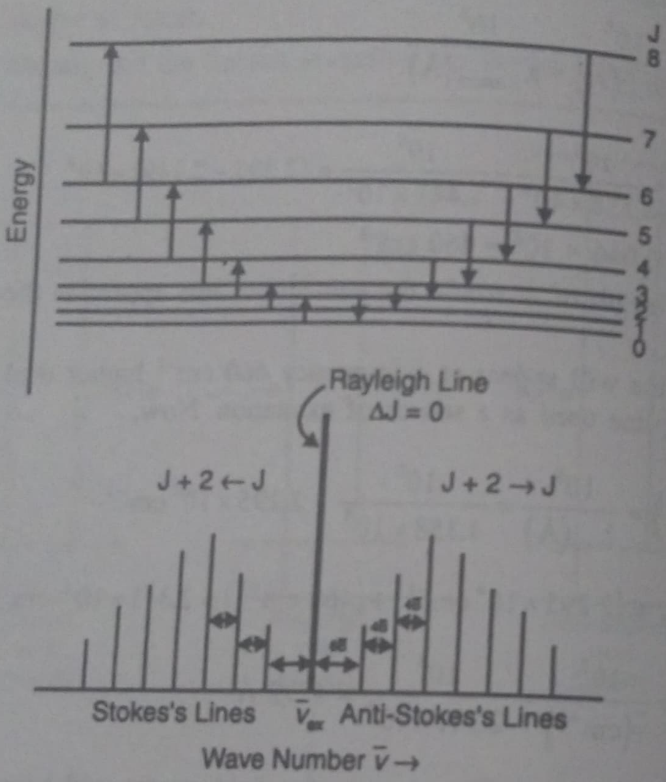


Fig. 4.5 : Rotational Raman Spectrum of a Rigid Diatomic Molecule.

From the Fig. 4.5 it can be seen that the frequency separation of successive lines is 4B cm^{-1} whe it is 2B cm^{-1} in the far-infrared spectra while on substituting J=0 in equation (4.21) we observe that t separation of the first line from the exciting line will be 6B cm^{-1}.

4. *Vibrational-Rotational Raman Spectra.* It is possible to predict theoretically that vibrational a rotational transitions may occur simultaneously in a Raman transition. In such a case, the selectio rules governing such simultaneous changes in rotational and vibrational energy will be

$$\Delta J = 0,\ \pm 2 \text{ and } \Delta v = \pm 1$$

For a diatomic molecule, the vibration-rotational energy levels are given by

$$E_{rv} = hc\left[\overline{w_e}\left(v+\tfrac{1}{2}\right) - \overline{w_e x}\left(v+\tfrac{1}{2}\right)^2\right] + Bhc\ J(J+1)$$

where $v = 0,\ 1,\ 2,\ldots\ldots$

and $J = 0,\ 1,\ 2,\ldots\ldots$

Or, in terms of frequency,

$$\bar{\nu} = \overline{w_e}\left(v+\tfrac{1}{2}\right) - \overline{w_e x}\left(v+\tfrac{1}{2}\right)^2 + B\ J(J+1)$$

Applying selection rules for Raman effect, *i.e.*, $J = 0, \pm 2$, we get

$$\Delta J = 0; \Delta \bar{v}\,(Q) = \bar{v}_0 \text{ (for all J)}$$

$$\Delta J = +2; \Delta \bar{v}\,(S) = \bar{v}_0 + B(4J+6) \text{ (for J = 0,1,2,...)}$$

$$\Delta J = -2; \Delta \bar{v}\,(O) = \bar{v}_0 - B(4J+6) \text{ (for J = 2,3,4,...)}$$

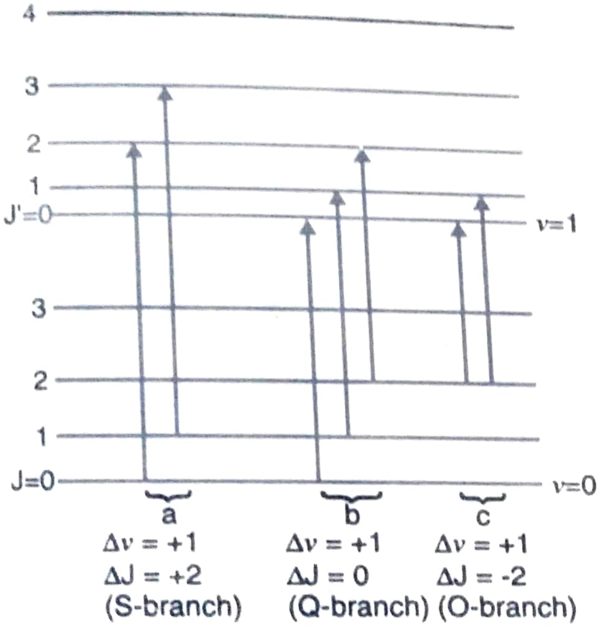
where $\bar{v}_0$ is written for $\bar{w}_e$ (1–2*x*). O, Q and S refer to the O branch lines, Q branch lines, and S branch lines, respectively. The corresponding Stoke's lines will occur at wave numbers represented by

(*i*) $\bar{v}(Q) = \bar{v}_{ex} - \bar{v}(Q) = \bar{v}_{ex} - \bar{v}_0$ (for all values of J)

(*ii*) $\bar{v}(S) = \bar{v}_{ex} - \bar{v}(S) = \bar{v}_{ex} - \bar{v}_0 - B\,(4J+6)$, where J = 0,1,2,...

(*iii*) $\bar{v}(O) = \bar{v}_{ex} - \bar{v}(O) = \bar{v}_{ex} - \bar{v}_0 + B\,(4J+6)$, where J = 2,3,4,...

The various Raman rotation-vibrations transitions are shown in Fig. 4.5. In the Raman spectrum Q branch will be present whereas it is absent in infrared spectrum. Both S and O branches are somewhat similar to the R and P branches in infrared spectroscopy.



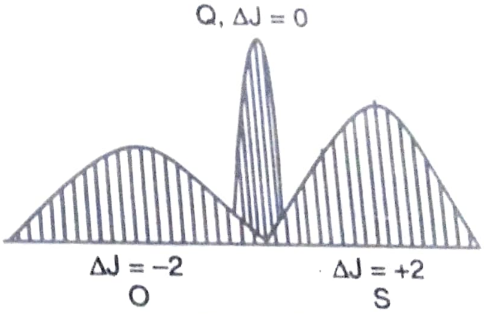


Fig. 4.6A **Fig. 4.6B**

Let us now briefly consider the rotational transitions accompanying a vibrational Raman transition of a diatomic molecule. The selection rules now involve the changes in both the vibrational and the rotational quantum numbers. For a diatomic molecule, the selection rules are

$$\Delta v = +1 \tag{87}$$

$$\Delta J = 0, \pm 2$$

Since at room temperature most of the molecules are in the ground vibrational state (v=0), only the vibrational transition, v=0 to v=1, is of interest. The transitions which ΔJ=0 form a *Q-branch*; those with ΔJ=+2 form an *S-branch* and those with ΔJ=–2 form an *O-branch*. The rotational Raman transitions accompanying a 0→1 vibrational transition are shown in Fig. 4.6. Here, $\Delta\bar{v}$ measures the displacement from the exciting mercury line. The *Q*-branch exhibits an intense 'narrow line' at $\bar{v}_{ex}$ that is usually unresolved while the *S* and *O* branches form weak wings which extend to lower and higher were numbers, respectively, from the intense narrow line.