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Pure Rotational Raman Spectra of Diatomic Molecule

For a molecule to be Raman active its molecular rotation or the change in rotational energy must cause some change in the component of the molecular polarizability. The expression for rotational energy levels of a linear diatomic molecule have already been derived ~~is~~ ~~is~~ is given by

$$E = \frac{h^2}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} \quad \text{--- (1)}$$

or  $E = B J(J+1) \text{ cm}^{-1}$  ( $B = \frac{h^2}{8\pi^2 I c}$ )

Here in Raman spectroscopy transition between energy levels is different from transition between rotational levels in microwave spectroscopy. In Raman spectroscopy

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

Selection Rule:-  $\Delta J = 0$  corresponds to no change in rotational energy hence Rayleigh scattering only  $\Delta J = \pm 2$  is the operative part of the selection rule for pure rotational Raman spectrum of a diatomic molecule. It is quite difference from the selection rule for microwave spectroscopy, which is  $\Delta J = \pm 1$ .

Using this selection rule ( $\Delta J = \pm 2$ ) energy level expression (1) for diatomic molecule will be given

$$\Delta E_{rot} = E_{J+2} - E_J \quad \text{--- (1)}$$

$$\text{or } \Delta E_{rot} = \frac{h^2}{8\pi^2 I c} \{ (J+2)(J+2+1) - J(J+1) \}$$

$$= 2B (2J+3) \text{ cm}^{-1} \quad \text{--- (2)}$$

where J is the rotational quantum number in the lower state and (J+2) in the higher state.

Thus if the molecule gains rotational energy from the photon during collision a series of lines

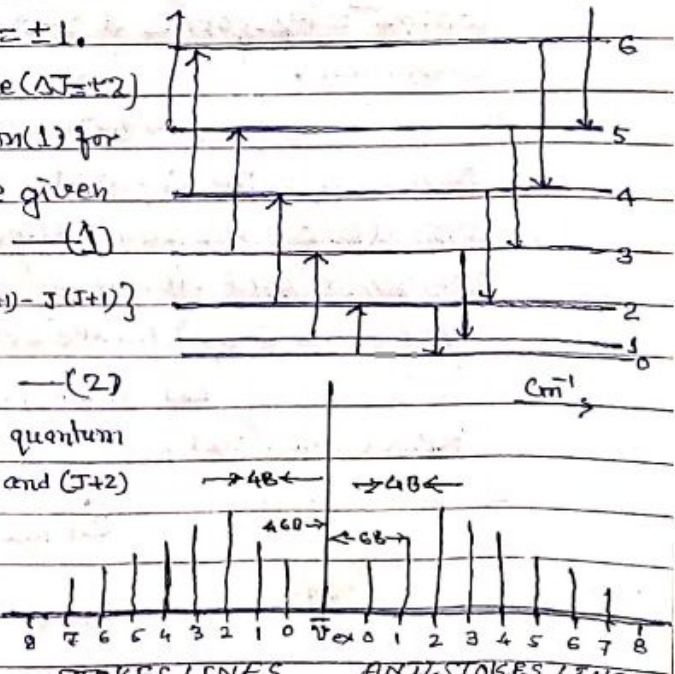


Fig - Upper & Lower Raman Rotational spectra of a diatomic molecule

are produced to the low wave no. or low frequency side of the exciting lines. These lines obtained for  $\Delta J = \pm 2$  are called

S-branch lines or the Stokes lines. For  $\Delta J = -2$  molecule (28)

loses energy to the photon, S-branch lines appear on the high wave no. side of the exciting lines. These are called anti-stokes lines.

The frequency in wave no. of the corresponding spectral lines are given by  $\Delta \bar{\nu} = \bar{\nu}_{ex} \pm B(4J+6) \text{ cm}^{-1}$  a(3)

The allowed transitions and rotational Raman spectrum are shown in Fig —.

### Pure Vibrational Raman Spectra of Diatomic Molecules

The selection rule for pure vibrational Raman spectra of a diatomic molecule is

$$\Delta v = \pm 1 \quad \text{--- (1)}$$

and  $\Delta J = 0, \pm 2$  --- (2)

Above both equations refer to selection rule for vibrational Raman spectra. This shows that transition can take place only to adjacent vibrational levels. It means from one level to next upper level giving Stokes lines or to the next lower level giving anti-stokes lines, anti-stokes lines are weak because in the initial state there are very few excited molecules.

The transition with  $\Delta J = 0$  gives Q-branch those with  $\Delta J = +2$  forms a S-branch and for  $\Delta J = -2$  we get an O-branch.

So far we have considered pure rotational and vibrational Raman spectra separately, but a molecule may rotate and vibrate at the same time therefore we have combined rotational and vibrational Raman spectra.

For such a spectra the selection rules are

$$\Delta J = \pm 1, \Delta J = 0, \Delta J = \pm 2$$

Hence the total energy would be

$$E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}}$$

or  $E_{\text{total}} = \left(v + \frac{1}{2}\right) h\nu_e + BJ(J+1)$

Thus we can obtain vibrational-rotational Raman spectra of linear molecule.