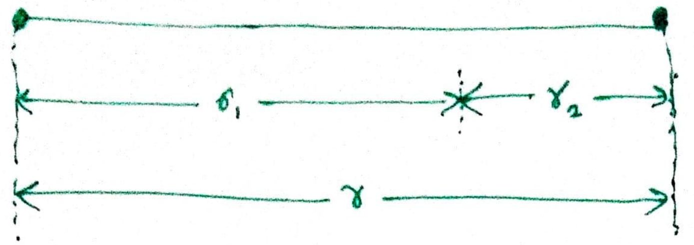
Rotational Spectra of Diatomic molecule



Consider a diatomic molecule in which m_1 and m_2 are the masses of two atoms and r is the equilibrium bond length, rotating about an axis passing through its centre of gravity c.g.

The centre of gravity is defined by the equality of the moments about it i.e.

$$m_1 r_1 = m_2 r_2 \quad — ①$$

The moment of inertia I of a molecule (rotating as a rigid rotor, not subject to centrifugal forces that tend to distort the molecular ~~gravity~~ geometry and change the moment of inertia) is defined as

$$I = \sum_i m_i r_i^2 \quad — ②$$

where r_i is the distance of the ith particle of mass m_i from the centre of gravity. Since a diatomic molecule has two atoms,

$$I = m_1 r_1^2 + m_2 r_2^2 \quad — ③$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad — ④ \text{ (Eqn. ①}$$

$$= r_1 r_2 (m_1 + m_2) \quad — ⑤$$

and $r = r_1 + r_2 \quad — ⑥$

$$\therefore \; m_1 r_1 = m_2 r_2 = m_2 (r - r_1) \quad — ⑦$$

Hence $r_1 = \frac{m_2 r}{m_1+m_2}$ and $r_2 = \frac{m_1 r}{m_1+m_2}$

substituting these values in eq. ③

$$I = m_1\left(\frac{m_2 r}{m_1+m_2}\right)^2 + m_2\left(\frac{m_1 r}{m_1+m_2}\right)^2$$

$$= \frac{m_1 m_2 (m_1+m_2)}{(m_1+m_2)^2}\, r^2$$

$$\boxed{I = \frac{m_1 m_2}{m_1+m_2}\, r^2 = \mu r^2} \quad — ⑧$$

Here $\mu = \left(\frac{m_1 m_2}{m_1+m_2}\right)$ and reduced mass of molecule.

Angular momentum L of a rotating molecule is given by $L = I\omega$ where ω is the angular velocity. Since Angular momentum is quantized,

$$L = \sqrt{J(J+1)}\,\hbar \; ; \; J = 0, 1, 2 \ldots. \quad — ⑨$$

where J is the rotational quantum number.

The energy of rotating molecule is given by $\frac{1}{2} I\omega^2$. The quantized rotational energy levels of a rigid diatomic rotor (rotating molecules) are given by

$$E_J = \frac{1}{2} I\omega^2 = (I\omega)^2/2I = L^2/2I \quad — ⑩$$

using the expression for L from eq. ⑨

$$E_J = J(J+1)\frac{\hbar^2}{2I} \; ; \text{ where } J = 0, 1, 2 \ldots.$$

This equation is also obtained from solution of Schrodinger wave equation.

$$\frac{E_J}{hc} = F(J) = \frac{J(J+1)\hbar}{4\pi c I} \; ; \; J = 0, 1, 2, 3 \ldots. \quad — ⑪$$

F(J) is called rotational term.

$B = \frac{\hbar}{4\pi C I}$ cm^{-1} — ⑫

this is known as rotational constant.

$F(J) = BJ(J+1)$; $J = 0, 1, 2 \dots$ — ⑬

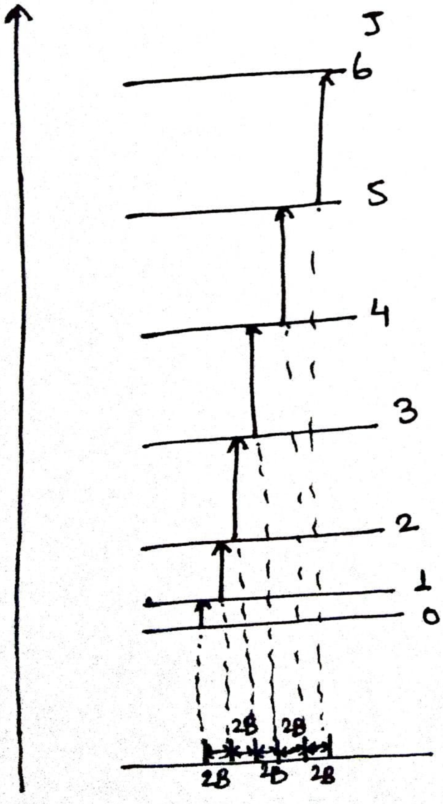
$E_J = hcBJ(J+1)$; $J = 0, 1, 2 \dots$ — ⑭

Taking centrifugal distortion whose effect on the diatomic rotor is to stretch the bond and hence to reduce the rotational constant and hence bring the energy levels closer than in rigid-rotor approximation, the energy levels expression becomes

$F(J) = BJ(J+1) - D_J J^2 (J+1)^2$ — ⑮

D_J → centrifugal distortion constant given by

$D_J = \frac{4B^3}{\bar{\nu}^2}$ — ⑯



where $\bar{\nu}$ is the vibrational frequency of molecule.

There is need of selection rule to determine the radiative transitions between the rotational energy levels. The rotational transitions are governed by

$\Delta J = \pm 1$

For a transition taking place between J and J+1

$\nu_{J \to J+1} = B(J+1)(J+2) - BJ(J+1)$

$= B(J^2 + 3J + 2) - B(J^2 + J)$

$= 2B(J+1)$ cm^{-1} — ⑰

$$\nu_{(0\to1)} = 2B$$
$$\nu_{(1\to2)} = 4B$$
$$\nu_{(2\to3)} = 6B$$
$$\nu_{(3\to4)} = 8B$$

The lines are equally spaced by a difference of 2B, & called frequency separation.

Q1: The internuclear distance (i.e. bond length) of a carbon monoxide molecule is 1.13 Å. Calculate the energy (in joules and eV) and angular velocity of this molecule in the first excited rotational level. The atomic masses are $^{12}C = 1.99 \times 10^{-26}$ kg, $^{16}O = 2.66 \times 10^{-26}$ kg.

Relative Intensities of Rotational Spectral lines:

The relative intensities of spectral lines depend upon the relative population of energy levels. Even at room temperature many of the diatomic molecules are present in the excited state energy levels. Since the energy level population is given by the Boltzmann distribution of molecules in the rotational energy levels i.e.

$$\text{Intensity} \propto \frac{N_J}{N_0} = e^{-E_J/kT} \quad \text{——} \quad (18)$$

Rotational energy levels are degenerate their degeneracy (g_J) for a diatomic molecules being given by

$$g_J = (2J+1) \quad \text{——} \quad (28)$$

In other words the energy level is $(2J+1)$ fold degenerate. For $J=0$, $g_J=1$; for $J=1$, $g_J=3$; for $J=2$ $g_J=5$ and so on.

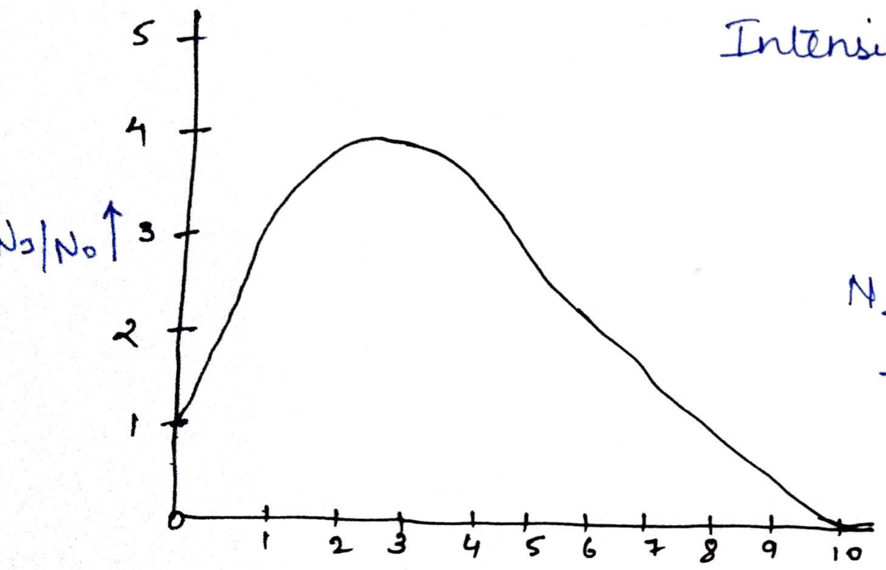
Thus intensity of spectral line is determined by the product of the degeneracy factor and the Boltzmann exponential factor. Hence,

$$\text{Intensity} \propto N_J/N_0 = (2J+1)e^{-E_J/kT}$$

$$E_J = hc\,F(J)$$

$$F(J) = BJ(J+1)$$

$$N_J/N_0 = (2J+1)\,e^{-BJ(J+1)hc/kT}$$



The quantity N_J/N_0 is plotted vs J for a diatomic molecule at room temperature.

As from the graphical interpretation the relative intensity passes through a maximum. A value of J corresponds to maximum in population is given by

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

J_{max} should be rounded off the nearest integral value.