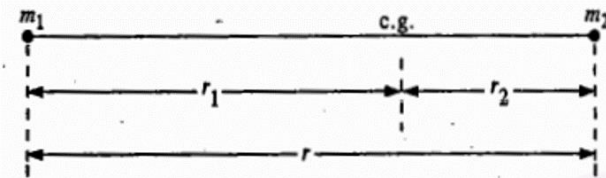# Study Notes on Rotational Spectra

Rotational Spectra

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

Rotation of a diatomic molecule about its centre of gravity.

The centre of gravity is defined by the quality of the momenta about it, i.e.,

$$m_1 r_1 = m_2 r_2 \qquad ..... (1)$$

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

$$I = \sum_i m_i r_i^2 \qquad ..... (2)$$

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

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad ..... (3)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad \text{(using Eq.1)}$$

$$= r_1 r_2 (m_2 + m_1) \qquad ..... (4)$$

Also, $\qquad\qquad\qquad r = r_1 + r_2 \qquad\qquad\qquad ..... (5)$

Therefore, from Eqs. 1 and 5:

$$m_1 r_1 = m_2 r_2 = m_2 (r - r_2) \qquad ..... (6)$$

Hence, $\qquad\qquad r_1 = \dfrac{m_2 r}{m_1 + m_2}$ and $r_2 = \dfrac{m_1 r}{m_1 + m_2}$

Substituting the above values of r_1 and r_2 in equation 3.

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r^2 \qquad ..... (7)$$

$$= \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)} r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2 \qquad ..... (8)$$

Where $\mu = m_1 m_2 / (m_1 + m_2)$ is called the reduced mass of the molecule.

Classically, the angular momentum L, of a rotating molecule is given by L = Iω where ω is its angular velocity. However, the angular momentum is quantized, being given by

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

Where, J is the rotational quantum number. The energy of a rotating molecule is given by $\frac{1}{2} I\omega^2$. Hence, the quantized rotational energy levels of a rigid diatomic rotor (rotating molecule) are given by

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

Using the expression for L from Eq. 9,

$$E_J = J(J+1) \frac{\hbar^2}{2I} ; \text{ where } J = 0, 1, 2, \ldots \qquad \ldots\ldots (11)$$

The expression of total rotational energy is given by:

$$F(J) = E_J / hc = J(J+1) \frac{\hbar}{4\pi cI} ; \; J = 0, 1, 2, \ldots \qquad \ldots\ldots (12)$$

F(J) is called the rotational term. Defining the rotational constant B as:

$$B = \frac{\hbar}{4\pi cI} cm^{-1}, \qquad \ldots\ldots (13)$$

We have, $\qquad F(J) = BJ(J+1) \; ; \; J = 0, 1, 2, \ldots \qquad \ldots (14a)$

and $\qquad E_J = \hbar c \, BJ(J+1); \; J = 0, 1, 2, \ldots \qquad \ldots (14b)$

If we want to consider centrifugal distortion whose effect on the diatomic rotor is to stretch the bond and hence to increase the moment of inertia, and thereby to reduce the rotational constant and hence bring the energy levels closer than in the rigid-rotor approximation, then the energy level expression (14a) becomes

$$F(J) = B J (J + 1) - D_J J^2 (J + 1)^2 \qquad \ldots\ldots (14c)$$

Rotational spectrum of a rigid diatomic molecule.
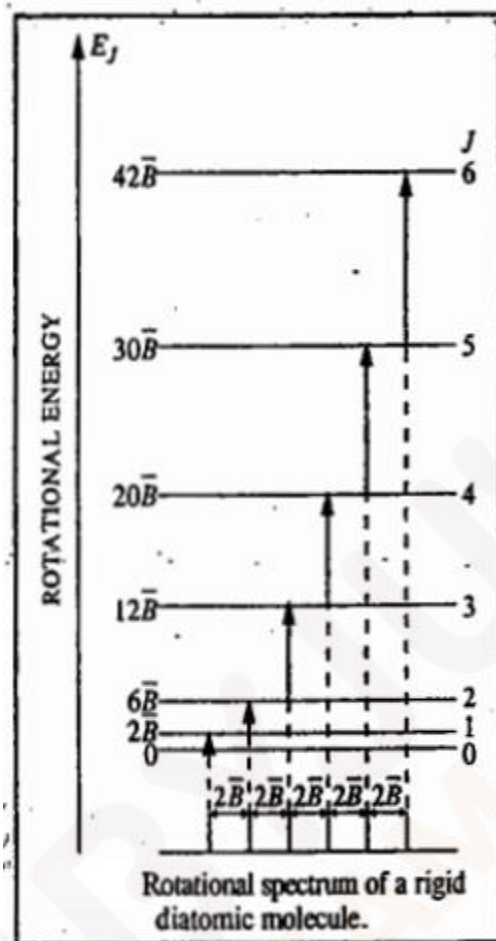
Where, D_J is the centrifugal distortion constant given by $D_J = 4B^3 / \bar{v}^2$, where $\bar{v}$ is the vibrational frequency of the molecule.

Next, a selection rule is needed to determine the radiative transition between the rotational energy levels.

$$\Delta J = \pm 1 \qquad\qquad\qquad ..... (15)$$

i.e., only those transitions are allowed in which the rotational quantum number changes by unity. The + sign refers to absorption and' the - sign to emission of radiation. Microwave-spectra are usually observed as absorption spectra so that the operative part of the selection-rule is $\Delta J = +1$. For a transition taking place from J to J + 1, the rotational frequency i is given by:

$$V_{(J\to J+1)} = B(J+1)(J+2) - BJ(J+1) \qquad\qquad .... (16)$$

$$= B(J^2 + 3J + 2) - B(J^2 + 1) \qquad\qquad ..... (17)$$

$$= 2B(J+1)\,cm^{-1} \qquad\qquad ..... (18)$$

Thus, $\qquad\qquad v_{(0\to1)} = 2B; v_{(1\to2)} = 4B;$

$$v_{(2\to3)} = 6B; v_{(3\to4)} = 8B, \text{ etc,}$$

The rotational spectrum of a rigid diatomic molecule consists of a series of lines at 2B, 4B, 6B, 8B, etc. Evidently, these lines are equally, spaced by an amount of 2B called frequency separation.

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