MOLECULAR ENERGY STATES:

Molecular energy states arise from:

(A) The rotational energy levels.
(B) The vibrational energy levels.
(C) The electrical energy levels.

$$E=E_r+E_v+E_e$$

Rotational states are separated by quite small energy intervals (10^{-3} eV is typical), and the spectra that arise from transitions between these states are in the microwave region with wavelengths of 0.1 mm to 1 cm. Vibrational states are separated by somewhat larger energy intervals (0.1 eV is typical), and vibrational spectra are in the infrared region with wavelengths of 10,000 A to 0.1 mm. Molecular electronic states have higher energies, with typical separations between the energy levels of valence electrons of several electron volts and spectra in the visible and ultraviolet regions. A detailed picture of a particular molecule can often be obtained from its spectra, including bond lengths, force constants, and bond angles.

A) ROTATIONAL ENERGY LEVELS:

The lowest energy levels of a diatomic molecule arise from rotation about its center of mass. We may picture such a molecule as consisting of atoms of masses m_1 and m_2 a distance R apart, as in Fig. (14). Where

$$R=r_1+r_2 \text{...........}(6)$$

where r_1 and r_2 are the distances of atoms 1 and 2 respectively from the center of mass. Since

$$m_1r_1=m_2r_2 \text{............}(7)$$

or $$r_1=\frac{m^1}{m_2}r_2$$

from eq.(6)

$$r_1=\frac{m^2}{m_1+m_2}R \quad , \quad r_2=\frac{m^1}{m_1+m_2}R \text{ ....}(8)$$

The moment of inertia of this molecule about an axis passing through its center of mass and perpendicular to a line joining the atoms is

$$I=m_1r_1^2+m_2r_2^2 \quad \text{.......}(9)$$

by definition, the moment of inertia may be written

$$I = \left(\frac{m_1 m_2}{m_1+m_2}\right)(r_1+r_2)^2 = m'R^2 \quad \text{……..(10)}$$

where

$$m' = \frac{m_1 m_2}{m_1+m_2} \quad \text{……...(11)} \quad \textbf{Reduced mass}$$

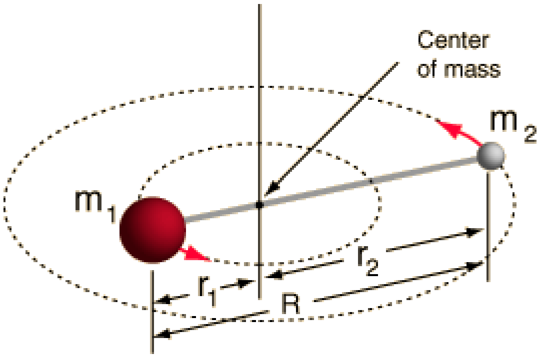

FIG. (14), A diatomic molecule can rotate about Its center of mass.

is the reduced mass of the molecule. Eq. (10) states that the rotation of a diatomic molecule is equivalent to the rotation of a single particle of mass m' about an axis located a distance of R away.

Using the laws of classical physics, the rotational kinetic energy of the diatomic molecule is equal to:

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \text{……..(12)}$$

Using the angular velocity:

$$\omega = \frac{v}{r} \text{ or } v = \omega r$$

Then

$$T = \frac{1}{2}\omega^2 m' R^2 = \frac{1}{2}\omega^2 I \text{ …….(13)}$$

The angular momentum L of the molecule has the magnitude

$$L = I\omega \text{ ....(14)}$$

where ω is its angular velocity. Angular momentum is always quantized in nature, as we know. If we denote the rotational quantum number by J we have here

$$L = \sqrt{J(J+1)}\,\hbar \qquad J = 0,1,2,3,\ldots\ldots \qquad (15)$$

.

The energy of a rotating molecule is 1/2 $\omega^2 I$, and so its energy levels are specified by

$$E_J = \frac{1}{2} I\omega^2 = \frac{L^2}{2I} = \frac{J(J+1)\hbar^2}{2I} \quad \text{.........} (16)$$ **Rotational energy levels**

Comparing equations (13) and (16), we find that the difference between classical mechanics, which gives values continuous non-specific energy and between quantum mechanics, which gives values specific energy

Rotational spectra arise from transitions between rotational energy states. Only molecules that have electric dipole moments can absorb or emit electromagnetic photons in such transitions, which means that nonpolar diatomic molecules such as H_2 and symmetric polyatomic molecules such as CO_2 (O=C=O), do not exhibit rotational spectra. (Transitions between rotational states in molecules like H_2, CO_2 can take place during collisions, however.) Furthermore, even in molecules that possess permanent dipole moments, not all transitions between rotational states involve radiation. Certain selection rules summarize the conditions for a radiative transition between rotational states to be possible. For a rigid diatomic molecule the selection rule for rotational transitions is

$$\Delta J = \pm 1 \quad \text{.......}(17)$$

In practice, rotational spectra are always obtained in absorption, so that each transition that is found involves a change from some initial state of quantum number J in the next higher state of quantum number $J+1$. In the case of a rigid molecule, the frequency of the photon absorbed is

$$\upsilon_{J-J+1} = \frac{\Delta E}{h} = \frac{E_{J+1}-E_J}{h} = \frac{\hbar}{2\pi I}(J+1) \quad \text{.......}(18)$$ **Rotational spectra**

where I is the moment of inertia for rotations. The spectrum of a rigid molecule therefore consists of equally spaced lines, as in Fig. (18), The frequency of each line can be measured, and the transition it corresponds to can often be ascertained from the sequence of lines; from these data the moment of inertia of the molecule can be readily calculated, (Alternatively, the frequencies of any two successive lines may be used to determine I if the spectrometer used does not record the lowest-frequency lines in a particular, spectral sequence).