Rigid rotator model

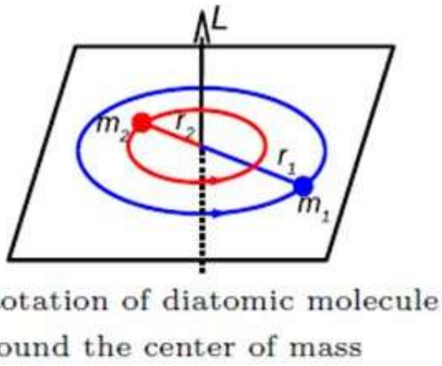

Figure 5.1: Rotation of diatomic molecule about the center of mass

$$KE = \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 = \frac{1}{2}(m_1 r_1^2 + m_2 r_2^2)\omega^2 = \frac{1}{2}I\omega^2$$

Moment of inertia: $I = m_1 r_1^2 + m_2 r_2^2 = \mu r^2 \;\; where \; \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad and \;\; r = r_1 + r_2$

(Use $r_1 = \frac{m_2}{m_1+m_2} r \; and \; r_2 = \frac{m_1}{m_1+m_2} r$ which comes from the lever rule)

This can be thought of as a single body of mass μ rotating about the COM at the distance r. Need to solve only one equation now.

Angular momentum, $L = I\omega$; Kinetic energy $KE = L^2/2I$, no potential energy

$$\hat{H} = \widehat{KE} = -\frac{\hbar^2}{2\mu}\nabla^2$$

In spherical polar coordinates,

$$\nabla^2 = \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \quad constant\ r$$

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right] = \hat{L}^2/2I$$

Square of the angular momentum is a naturally occurring operator in QM!

$$\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$$

Solving,

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0,1,2 \ldots$$

Selection rule $\Delta J = \pm 1$ and molecule must possess a permanent dipole moment

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I}[(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{I}(J+1) = \frac{h^2}{4\pi^2 I}(J+1)$$

$$\nu = \frac{h}{4\pi^2 I}(J+1) = 2B(J+1); \quad B = \frac{h}{8\pi^2 I} \; in\, Hz$$

B is called the rotational constant of the molecule.

$$\bar{\nu} = 2\bar{B}(J+1); \quad \bar{B} = \frac{h}{8\pi^2 cI} \quad in\, cm^{-1}$$

Typical values: μ for a diatomic molecule $10^{-25} - 10^{-26}$ kg, bond distance ~ 10^{-10} m (100 pm), $I {\sim} 10^{-45} - 10^{-46}$ kg.m^2

Gives absorption frequency ~ $10^{10} - 10^{11}$ Hz (microwave region)

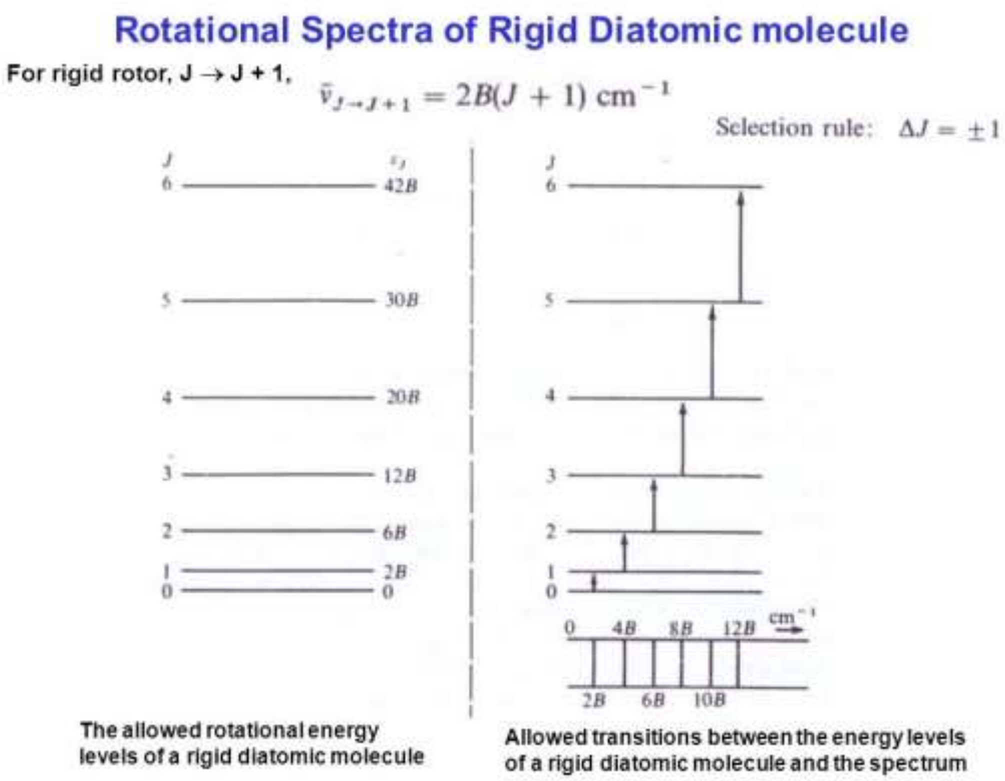

Figure 5.2: Energy levels and spectra of a rigid diatomic molecule