3.6: The Rigid Rotor and Harmonic Oscillator

Treatment of the rotational motion at the zeroth-order level described above introduces the so-called 'rigid rotor' energy levels and wavefunctions: $E_J = \hbar^2 \frac{J(J+1)}{2\mu R_e^2}$ and $Y_{J,M}(\theta,\phi)$; these same quantities arise when the diatomic molecule is treated as a rigid rod of length R_e. The spacings between successive rotational levels within this approximation are

$$\Delta E_{J+1,J} = 2hcB(J+1),$$

where the so-called rotational constant B is given in cm^{-1} as

$$B = \frac{h}{8\pi^2 c\mu R_e^2}.$$

The rotational level J is (2J+1)-fold degenerate because the energy E_J is independent of the M quantum number of which there are (2J+1) values for each J: M= -J, -J+1, -J+2, ... J-2, J-1, J.

The explicit form of the zeroth-order vibrational wavefunctions and energy levels, $F_{j,v}^0$ and $E_{j,v}^0$, depends on the description used for the electronic potential energy surface $E_j(R)$. In the crudest useful approximation, $E_j(R)$ is taken to be a so-called harmonic potential

$$E_j(R) \approx \frac{1}{2} k_j (R - R_e)^2;$$

as a consequence, the wavefunctions and energy levels reduce to

$$E_{j,v}^0 = E_j(R_e) + \hbar \frac{\sqrt{k}}{\mu} \left(v + \frac{1}{2} \right), \text{ and}$$

$$F_{j,v}^0(R) = \frac{1}{\sqrt{2^v v!}} \sqrt[4]{\frac{\alpha}{\pi}} e^{\frac{-\alpha(R-R_e)^2}{2}} H_v \sqrt{\alpha}(R - R_e),$$

where $\alpha = \frac{\sqrt{k_j \mu}}{\hbar}$ and $H_v(y)$ denotes the Hermite polynomial defined by:

$$H_v(y) = (-1)^v e^{y^2} \frac{d^v}{dy^v} e^{-y^2}.$$

The solution of the vibrational differential equation

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right] F_{j,v}(R) + E_j(R) F_{j,v}(R) = E_{j,v} F_{j,v}$$

is treated in EWK, Atkins, and McQuarrie.

These harmonic-oscillator solutions predict evenly spaced energy levels (i.e., no anharmonicity) that persist for all v. It is, of course, known that molecular vibrations display anharmonicity (i.e., the energy levels move closer together as one moves to higher v) and that quantized vibrational motion ceases once the bond dissociation energy is reached.