Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 1.6

Diatomic Molecular Energy Levels
How is energy stored in a Molecule?

Electronic energy. Changes in the kinetic and potential energy of one or more electrons associated with the molecule. Same as many-electron atoms.

Kinetic Energy:

Translational energy. The molecule can move (translate) in space. Same particle-in-a-box solutions as for atoms.

Rotational energy. The entire molecule can rotate in space. Schrödinger equation: Rigid-rotator.

Vibrational energy. The nuclei can move relative to one another in space. Schrödinger equation: Quantum-mechanical harmonic oscillator.
Rotational Energy Levels—Diatomics

The Schrödinger equation for the rigid rotator provides energy levels:

\[ \varepsilon_J = \frac{\hbar^2}{2I}J(J+1) \quad J = 0,1,2,\ldots \]

The degeneracy of a given level, \( g_J \), is:

\[ g_J = 2J + 1 \]

Moment of inertia:

\[ I = m_1R_1^2 + m_2R_2^2 \]

\[ \varepsilon_0 = 0 \quad J = 0 \]

\[ \varepsilon_1 = \frac{\hbar^2}{I} \quad J = 1 \]

\[ \varepsilon_2 = \frac{3\hbar^2}{I} \quad J = 2 \]

\[ \varepsilon_3 = \frac{6\hbar^2}{I} \quad J = 3 \]

\[ \varepsilon_4 = \frac{10\hbar^2}{I} \quad J = 4 \]
Vibrational Energy Levels

Vibrational motion is modeled as a harmonic oscillator, with two masses attached by a spring.

The energy levels are equally spaced by $\hbar \nu$.

The energy of the lowest state is NOT zero. The difference is called zero-point energy.

The levels are non-degenerate, that is $g_\nu = 1$ for all values of $\nu$.

Solving the Schrödinger equation for the QM harmonic oscillator yields the energy levels:

$$\varepsilon_\nu = \hbar \nu \left( \nu + \frac{1}{2} \right)$$

$\nu = 0, 1, 2, \ldots$

The energy levels are equally spaced by $\hbar \nu$.

The energy of the lowest state is NOT zero. The difference is called zero-point energy.

$$\varepsilon_0 = \frac{1}{2} \hbar \nu$$
The dissociation energy and the electronic energy of a diatomic molecule are related by the zero point energy,

\[ D_e = D_0 + \frac{h\nu}{2} \]

For example, for \( \text{H}_2(\text{g}) \):

\[ D_e = 458 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ D_0 = 432 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ \tilde{\nu} = 4401 \text{ cm}^{-1} \left( = 52 \text{ kJ} \cdot \text{mol}^{-1} \right) \]