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.

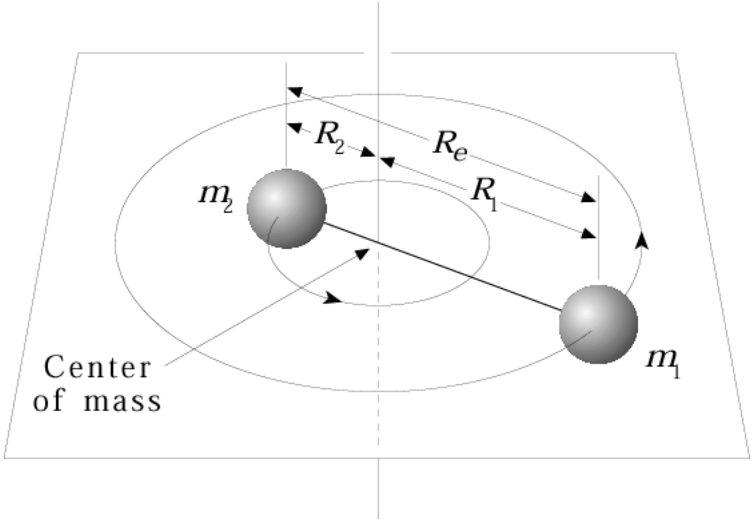
Kinetic Energy:

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



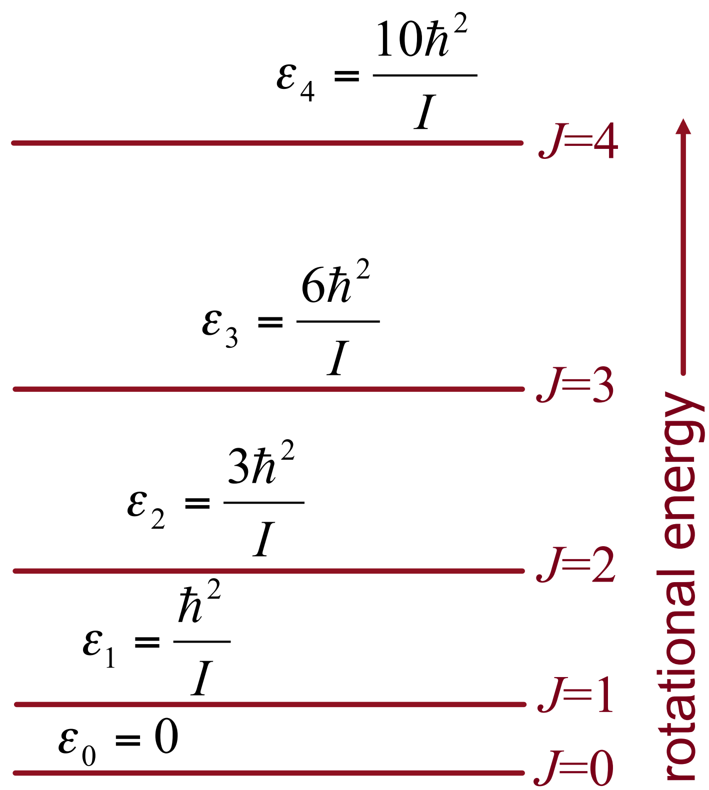
moment of inertia: $I = m_1 R_1^2 + m_2 R_2^2$

The Schrödinger equation for the rigid rotator provides energy levels:

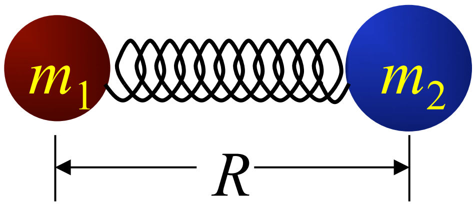
$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0,1,2,\ldots$$

The degeneracy of a given level, g_J, is:

$$g_J = 2J + 1$$



Vibrational Energy Levels



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

careful, "nu" and "vee"

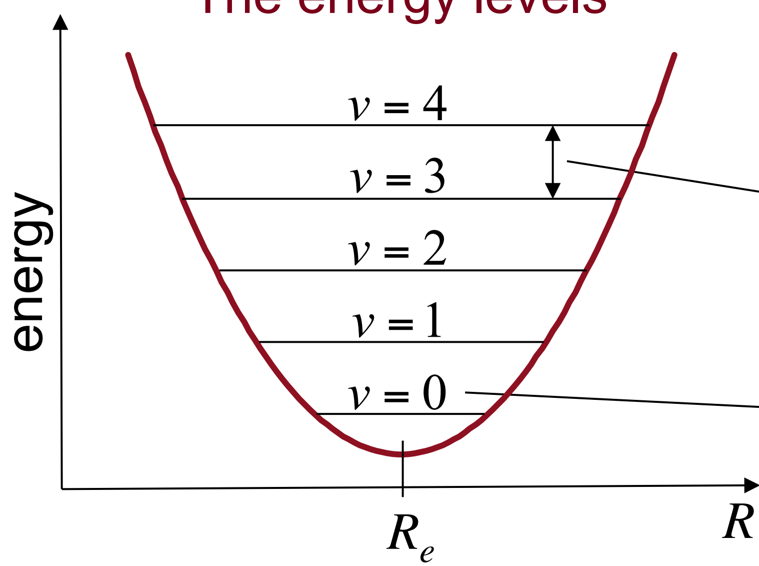
Solving the Schrödinger equation for the QM harmonic oscillator yields the energy levels:

$$\varepsilon_v = h\nu\left(v + \frac{1}{2}\right)$$

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

The levels are non-degenerate, that is $g_v = 1$ for all values of v.

The energy levels

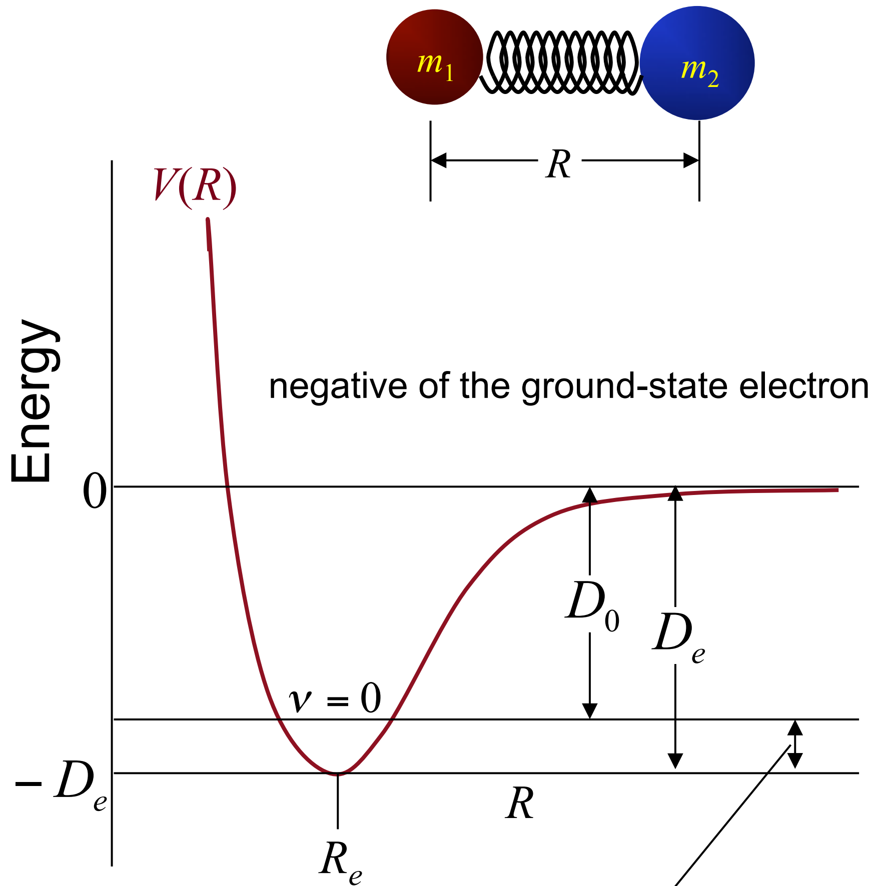


The energy levels are equally spaced by $h\nu$.

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

$$\varepsilon_0 = \frac{1}{2}h\nu$$

Bond Dissociation energy



The *dissociation energy* and the *electronic energy* of a diatomic molecule are related by the zero point energy,

negative of the ground-state electronic energy

$$D_e = D_0 + \frac{h\nu}{2}$$

dissociation energy

The zero-point vibrational energy: $h\nu/2$

For example, for $H_2(g)$:

$$D_e = 458\ \text{kJ} \bullet \text{mol}^{-1}$$

$$D_0 = 432\ \text{kJ} \bullet \text{mol}^{-1}$$

$$\tilde{\nu} = 4401\ \text{cm}^{-1}\left(= 52\ \text{kJ} \bullet \text{mol}^{-1}\right)$$