Chemistry 362
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Comparison of Harmonic and Morse Oscillators

Potential Energy Curves

The harmonic oscillator potential represents a model for vibrational motion of molecules. The form of the potential energy for the harmonic oscillator is

$$V(x) = \tfrac{1}{2}kx^2,$$

where k is the force constant and x is the bond displacement.

The harmonic oscillator model is particularly useful for low vibrational energies. To model a vibrating molecule at higher energies and to describe bond dissociation, an anharmonic oscillator model, such as the Morse potential, may be employed. The form of the Morse oscillator potential is

$$V(x) = D_e\left[1-e^{-ax}\right]^2 ,$$

where D_e is the dissociation energy and a is related to the force constant k and dissociation energy such that

$$a = \left(\frac{k}{2D_e}\right)^{1/2} ,$$

A comparison of the harmonic and Morse oscillator potentials is given below for a specific example. In this case, the harmonic frequency in wavenumbers was set at 2000 cm^{-1} and the dissociation energy at 40,000 cm^{-1} to represent a model of an O-H bond. The harmonic oscillator and Morse potentials for this example are shown in Figure 1.

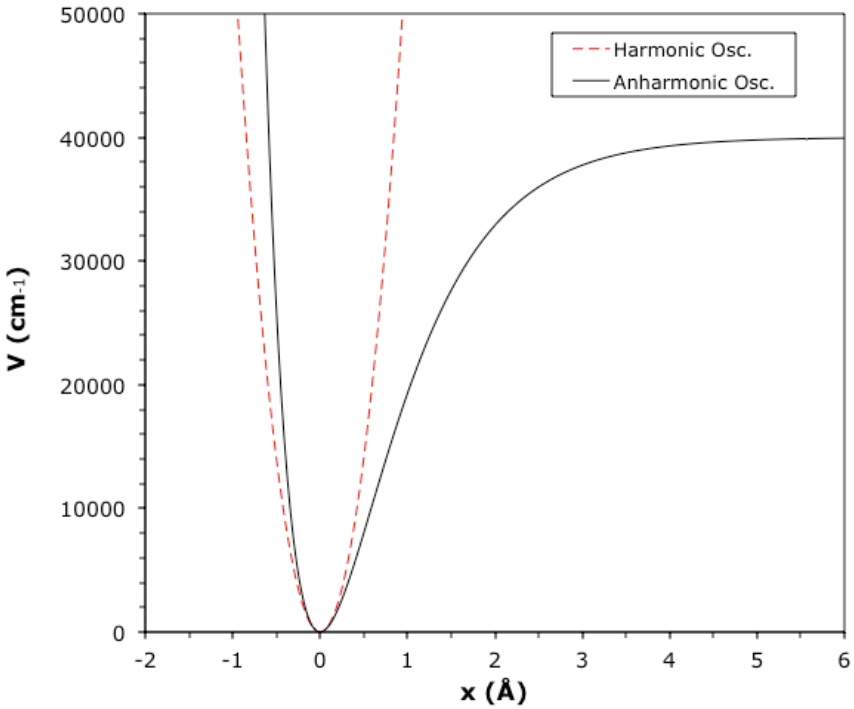

Figure 1. Harmonic and Morse oscillator potential energy functions for model O-H bond.

Energy Levels

The harmonic oscillator energy levels are given by the equation

$$E_{\mathrm{v}} = h\nu_0\left(\mathrm{v}+1/2\right), \quad \mathrm{v}=0,\ 1,\ 2,\ ...$$

where h is Plancks's constant and ν_0 is the harmonic frequency. The energy levels are evenly spaced; that is, the spacing ΔE between adjacent levels is independent of v,

$$\Delta E = E_{\mathrm{v}+1} - E_{\mathrm{v}} = h\nu_0 \ .$$

The anharmonic (Morse) oscillator energy levels are given by the equation

$$E_{\mathrm{v}} = h\nu_0\left(\mathrm{v}+1/2\right) - h\nu_0 x_e\left(\mathrm{v}+1/2\right)^2, \quad \mathrm{v}=0,\ 1,\ 2,\ ...$$

where h is Plancks's constant, ν_0 is the harmonic frequency, and x_e is the anharmonicity constant. In this case, the energy levels are not evenly spaced; the spacing ΔE between adjacent levels decreases linearly as v increases,

$$\Delta E = E_{\mathrm{v}+1} - E_{\mathrm{v}} = h\nu_0 - 2h\nu_0 x_e\left(\mathrm{v}+1\right) \ .$$

The differences in the positions of the quantized energy levels for the harmonic and Morse oscillators are shown in Figure 2. In the figure, the energy levels of the model O-H bond (harmonic frequency 2000 cm^{-1} and dissociation energy 40,000 cm^{-1}) are plotted for both the harmonic oscillator and Morse oscillator models.

The energy levels are shown up to the dissociation limit for the Morse oscillator. Clearly, the harmonic oscillator energy levels exhibit constant spacing, while the energy levels of the Morse oscillator converge as they approach the dissociation limit.

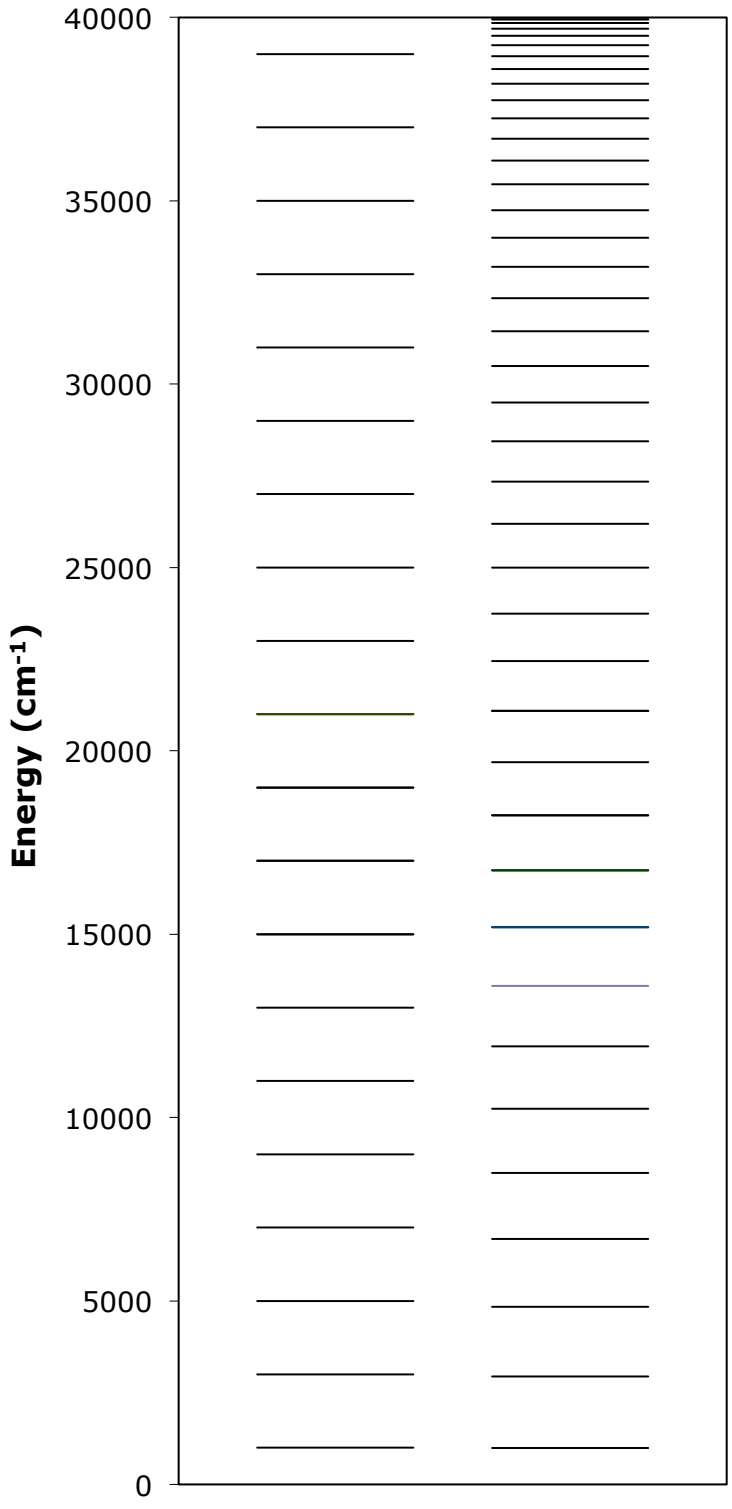

Figure 2. Harmonic and Morse oscillator vibrational energy levels for model O-H bond.