

Spectroscopy Problem 1 & Computer Assignment 5

Consider a diatomic molecule and suppose the vibration is described by the Morse potential

$$V(x) = D(e^{-2ax} - 2e^{-ax}) + D,$$

where $x = r - r_e$ is the displacement from the equilibrium configuration. The eigenvalues of this model are given by the expression

$$E_n = \hbar\omega_0 \left[\left(n + \frac{1}{2} \right) - \frac{\hbar\omega_0}{4D} \left(n + \frac{1}{2} \right)^2 \right]$$

where

$$\omega_0 = a \sqrt{\frac{2D}{m}}$$

(m is the reduced mass).

- (a) Use a graphics software to sketch the Morse potential for three values of the parameter $D/\hbar\omega_0$ (e.g. set $\hbar\omega_0 = 1$ and choose D values). Show that as $D/\hbar\omega_0 \rightarrow \infty$, the potential becomes effectively quadratic and the eigenvalues approach those of the harmonic oscillator.
- (b) For $D = 5\hbar\omega_0$ calculate the energy eigenvalues for the first four eigenstates and the frequencies of one-, two- and three-photon absorption at zero temperature. How do these compare to the corresponding frequencies for a harmonic potential? Based on what you know about the harmonic oscillator, which of these events should have large intensities for vibrational transitions? Assume the dipole moment operator is linear in x .
- (c) To calculate the correct transition intensities in the Morse potential, you need to know the eigenfunctions and evaluate integrals. This can be done analytically with various approximations and/or a lot of work. However, it is easy to tackle this numerically. Use your symbolic algebra code to calculate the matrix elements of x between the ground eigenstate and each of the three lowest eigenstates. Based on these values, obtain the relative transition intensities for one-photon absorption in a Morse potential and compare to those for a harmonic potential.