

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 24: Harmonic and anharmonic oscillator modeling of vibrations

References

1. Levine, *Physical Chemistry*, Chapter 17.12

Key Concepts

- The harmonic oscillator can be used to understand the origin of IR spectra. Absorption of IR radiation occurs when the energy of vibrational transition equals the energy of the radiation: $\Delta E_{transition} = h\nu_{obs}$, where ν_{obs} is the observed frequency of absorption.
- Vibrational transitions are limited by selection rules, which for the QMHO says that $\Delta v = \pm 1$, where v is the vibrational quantum number. Therefore, only transitions to adjacent vibrational states are observed. Also, to absorb IR radiation a molecule must have a dipole moment (permanent or transient).
- So since $\Delta v = +1$ for IR absorption, we can write the following relation:

$$\nu_{obs} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \bar{\nu}_{obs} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

- The wave functions of the QMHO have the form:

$$\psi_v = N_v H_v(\alpha^{1/2} x) e^{-\alpha x^2/2}$$

where N_v is a normalization factor, $H_v(z)$ are Hermite polynomials and $\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$. For example, $H_0(z) = 1$ and the wave function for the ground vibrational state ($v = 0$) is:

$$\psi_0 = N_0 e^{-\alpha x^2/2}$$

- It is interesting to note that if you look at the probability (ψ^2) you notice that there is a finite probability of existing in a state outside the permitted range of the harmonic oscillator. This is an example of tunneling, a quantum mechanical effect of transmission of a wave (ex: electron) through a barrier of higher energy.
- A more sophisticated model of the potential energy well of the bonding curve involves using an anharmonic oscillator. This accounts for the asymmetry of the bonding curve around the minimum (R_e). This can be accomplished by including more terms in the Taylor expansion around the minimum, i.e. higher order terms, for example a cubic term.
- The anharmonic oscillator results in a slightly different expression for the quantized vibrational energy levels:

$$E_v = h\nu_e \left(v + \frac{1}{2} \right) - h\nu_e x_e \left(v + \frac{1}{2} \right)^2$$

where x_e is the anharmonicity constant and accounts for the asymmetry of the bonding curve.

- Some interesting results of this model:

1. The vibrational energy levels are no longer equally spaced. As v increases the anharmonic correction term increases in magnitude resulting in levels that are more closely spaced.
2. The selection rules become relaxed resulting in observable transitions for $\Delta v = \pm 1, \pm 2, \pm 3, \dots$. The fundamental transition, $\Delta v = \pm 1$ is still the strongest, while the overtones ($\Delta v = \pm 2, \pm 3, \dots$) are much weaker. The overtones allow for the characterization of the anharmonicity of the bonding curve.