

CHEM 3420: Physical Chemistry II — Spring 2009

Homework 7 — Solutions

1. To determine the force constant we need to use the expression that relates the fundamental frequency to the force constant and reduced mass:

$$\bar{\nu}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where k is in N/m, μ is in kg, and c is the speed of light in cm/s.

Rearranging to solve for k :

$$k = \mu(2\pi c\bar{\nu}_e)^2$$

The reduced mass of this diatomic molecule is:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_1^2}{2m_1} = \frac{m_1}{2} = \frac{34.9688 \text{ amu}}{2} \times \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 2.9024 \times 10^{-26} \text{ kg}$$

Solving for k :

$$k = 2.9024 \times 10^{-26} \text{ kg} (2 * \pi * 3 \times 10^{10} \text{ cm/s} * 564.9 \text{ cm}^{-1})^2$$

$$\boxed{k = 329.1 \frac{\text{kg}}{\text{s}^2} = 329.1 \text{ N/m}}$$

2. The zero point energy of a harmonic oscillator is the energy when $v = 0$.

$$E_v = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right)$$

where E_v is the energy (in Joules) of the v -th vibrational level, k is the force constant in N/m, h is Planck's constant in Js, and μ is the reduced mass in kg.

The reduced mass of this molecule (using rough values of the mass of each atom in amu) is:

$$\mu = \frac{35 \times 1}{35 + 1} \text{ amu} \times \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.614 \times 10^{-27} \text{ kg}$$

Solving for E_0 :

$$E_0 = \frac{6.626 \times 10^{-34} \text{ Js}}{2\pi} \sqrt{\frac{516 \text{ N/m}}{1.614 \times 10^{-27} \text{ kg}}} \left(0 + \frac{1}{2} \right) = 2.982 \times 10^{-20} \text{ J}$$

$$\boxed{E_0 = 2.982 \times 10^{-20} \text{ J}}$$

Translational energy, aka kinetic energy can be found using the familiar relationship:

$$KE = \frac{1}{2}mv^2$$

which leads to the question what to use for m , the reduced mass or real mass. My argument would be for the real mass since we are now considering translational motion as opposed to rotational motion. Either approach was acceptable.

$$v = \sqrt{\frac{2E_0}{m}} = \sqrt{\frac{2 * 2.982 \times 10^{-20} \text{ J}}{36 \text{ amu} * 1.66 \times 10^{-27} \text{ kg/amu}}} = 998 \text{ m/s}$$

where v is velocity in this case, NOT a quantum number!

$$\boxed{\text{translational velocity} = 998 \text{ m/s}}$$

At 300 K, the root mean square speed is:

$$v_{rms} = \sqrt{\frac{3k_bT}{m}} = \sqrt{\frac{3 * 1.381 \times 10^{-23} \text{ JK} * 300 \text{ K}}{36 \text{ amu} * 1.66 \times 10^{-27} \text{ kg/amu}}}$$

$$\boxed{v_{rms} = 456 \text{ m/s}}$$

3. As the temperature increases, a solid is able to access higher energy vibrational states. In order to observe thermal expansion, the displacements in the elongated direction must be larger than those in the compressed direction.

For a harmonic oscillator, the potential is symmetric. When a higher energy state is attained, the vibrational displacements do get larger, but they are of equal magnitude for both the positive and negative displacement from the equilibrium separation. Therefore, there is no net increase in length and no thermal expansion.

For an anharmonic potential, like the Morse potential, the shape of the potential is not symmetric. As you reach higher vibrational states the displacement in the stretched direction is larger than in the compressed direction. Therefore there is a net displacement towards a longer bond and you will observe the material getting larger. To have thermal expansion an anharmonic bonding curve is necessary.

4. (a) From the data given, we can use the anharmonic oscillator model to predict the frequency of transition from the $v = 1$ to $v = 0$ state.

$$E_v \text{ (cm}^{-1}\text{)} = \bar{\nu}_e \left(v + \frac{1}{2} \right) - \bar{\nu}_e x_e \left(v + \frac{1}{2} \right)^2$$

$$\bar{\nu}_{obs} = \Delta E_v = |E_0 - E_1| = \bar{\nu}_e \left(1 + \frac{1}{2} \right) - \bar{\nu}_e x_e \left(1 + \frac{1}{2} \right)^2 - \left[\bar{\nu}_e \left(0 + \frac{1}{2} \right) - \bar{\nu}_e x_e \left(0 + \frac{1}{2} \right)^2 \right]$$

$$\bar{\nu}_{obs} = \bar{\nu}_e - 2\bar{\nu}_e x_e = 2169.8 \text{ cm}^{-1} - 2(13.3 \text{ cm}^{-1})$$

$$\boxed{\text{The absorption occurs at } \bar{\nu} = 2143.2 \text{ cm}^{-1} \text{ or } \nu = 6.43 \times 10^{13} \text{ s}^{-1}}$$

- (b) D_o is the spectroscopic dissociation energy which includes the zero-point energy of the lowest vibrational state:

$$D_o = D_e - E_0 = D_e - \frac{1}{2}\bar{\nu}_e - \frac{1}{4}\bar{\nu}_e x_e$$

or in words, the spectroscopic dissociation energy equals the electronic dissociation energy minus the extra energy you get when you consider you are really in the $v = 0$ vibrational state and not at the minimum of the bonding curve. In the above expression, all of the terms are in units of cm^{-1} .

$$D_o = 90542 \text{ cm}^{-1} - \frac{1}{2}(2169.8 \text{ cm}^{-1}) - \frac{1}{4}(13.3 \text{ cm}^{-1})$$

$$\boxed{D_o = 89454 \text{ cm}^{-1} \text{ or } 1.778 \times 10^{-18} \text{ J}}$$