

1. (4 pts) The force constant of $^{79}\text{Br}-^{79}\text{Br}$ is 240 Nm^{-1} . Calculate the fundamental vibrational frequency and the zero point energy of $^{79}\text{Br}-^{79}\text{Br}$ in cm^{-1} .

The frequency is related to the force constant by: $\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$.

The reduced mass, in units of kg/molecule (**not** g/mol) is:

$$\mu = \frac{m_a m_b}{m_a + m_b} = \frac{(79 \times 10^{-3} \text{ kg} / 6.02 \times 10^{23})^2}{2(79 \times 10^{-3} \text{ kg} / 6.02 \times 10^{23})} = \frac{1}{2} \left(\frac{79 \times 10^{-3} \text{ kg}}{6.02 \times 10^{23}} \right) = 6.56 \times 10^{-26} \text{ kg}$$

Plugging this into the formula for the frequency gives:

$$\omega = \sqrt{\frac{240 \text{ N/m}}{6.56 \times 10^{-26} \text{ kg}}} = \sqrt{36.6 \times 10^{26} \frac{(\text{kg} \cdot \text{m} / \text{s}^2) / \text{m}}{\text{kg}}} = 6.05 \times 10^{13} \text{ s}^{-1}$$

The zero-point energy is just:

$$E_0 = \frac{\hbar\omega}{2} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s} / 2\pi)(6.05 \times 10^{13} \text{ s}^{-1})}{2} = 3.19 \times 10^{-21} \text{ J}$$

Converting to wave numbers:

$$\frac{1}{\lambda} = \frac{E}{hc} = \frac{3.19 \times 10^{-21} \text{ J}}{\frac{1}{2}(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.0 \times 10^{10} \text{ cm/s})} = 231 \text{ cm}^{-1}$$

2. (6 pts) A particular harmonic oscillator has a Hooke's law constant $k = 10,000 \text{ dyne/cm}$, and reduced mass $\mu = 1 \text{ gram}$. Determine the quantum state, ν , of the oscillator if its vibrational energy is equal to the thermal energy ($k_B T$, where k_B is the Boltzmann constant) at $T = 298 \text{ K}$.

Plug+chug=answer!

$$k = \mu\omega^2 \Rightarrow \omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{10^4 \text{ dyne/cm} = \text{g/s}^2}{1 \text{ g}}} = 100 \text{ s}^{-1}$$

$$(v + \frac{1}{2})\hbar\omega = k_B T \Rightarrow (v + \frac{1}{2}) = \frac{k_B T}{\hbar\omega} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{[(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) / 2\pi](100 \text{ s}^{-1})} = 3.9 \times 10^{11}$$

Clearly, this is a nonsensical result! The 390 billionth level does NOT exist! Rather, this problem illustrates that the quantum effects derived for the harmonic oscillator are only meaningful for microscopic "springs", like covalent bonds. The atoms within the macroscopic spring are vibrating due to $k_B T$, but their vibrational frequency is much greater than 100 Hz, and the value of ν , therefore, is very small (usually $\nu = 0$).

3. (6 pts) Find the classical turning point for a harmonic oscillator as a function of the quantum number, ν . (The classical turning point is the value of x , called x_t , where the total energy $(\nu + \frac{1}{2})\hbar\omega_0$ and the potential energy are equal.) Give the result in terms of only the quantum number ν and the constant $\alpha = \frac{\mu\omega}{\hbar}$ used to define the harmonic oscillator wave functions.

Pretty straightforward algebra:

$$(v + \frac{1}{2})\hbar\omega = \frac{1}{2}\mu\omega^2 x_t^2 \Rightarrow x_t = \sqrt{\frac{(v + \frac{1}{2})\hbar\omega}{\frac{1}{2}\mu\omega^2}} = \sqrt{2(v + \frac{1}{2})\frac{\hbar}{\mu\omega}} = \sqrt{\frac{2(v + \frac{1}{2})}{\alpha}}$$

4. (16 pts total) The Simple Harmonic Oscillator wave functions are said to be “orthonormal”, meaning:

$$\int_{-\infty}^{+\infty} \psi_a \psi_b dx = \delta_{ab}$$

a. (8 pts) Show this is true for the first two wave functions

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

$$\psi_1 = N_1 x e^{-x^2/2\alpha^2}$$

In doing so, you will need to also determine the values of the normalization constants, N_0 and N_1 .

b. (8 pts) For an optical transition to occur, the dipole moment of the system has to change as a result of the transition. What this ultimately means is that the expectation value of the transition dipole moment is non-zero, i.e.:

$$\langle \vec{\mu} \rangle = \int_{-\infty}^{+\infty} \psi_f \hat{\mu} \psi_i dx \neq 0$$

where i and f represent the initial and final states, respectively. The dipole moment operator is just a charge, q , acting over a distance, x . Evaluate the integral:

$$\langle x \rangle_{01} = \int_{-\infty}^{+\infty} \psi_1 x \psi_0 dx$$

to see if this would be an allowed transition. Would a transition from $v = 0$ to $v = 2$ be allowed?

a. Normalizing the two functions:

$$\int_{-\infty}^{+\infty} \psi_0 \psi_0 dx = \int_{-\infty}^{+\infty} (N_0 e^{-x^2/2\alpha^2})^2 dx = N_0^2 \int_{-\infty}^{+\infty} e^{-x^2/\alpha^2} dx = N_0^2 \sqrt{\frac{\pi}{1/\alpha^2}} = N_0^2 \alpha \sqrt{\pi} = 1$$

$$\Rightarrow N_0 = \sqrt{\frac{1}{\alpha \sqrt{\pi}}} = \left(\frac{\mu\omega}{\hbar\pi}\right)^{1/4}$$

$$\int_{-\infty}^{+\infty} \psi_1 \psi_1 dx = \int_{-\infty}^{+\infty} (N_1 x e^{-x^2/2\alpha^2})^2 dx = N_1^2 \int_{-\infty}^{+\infty} x^2 e^{-x^2/\alpha^2} dx = N_1^2 \frac{2}{2^2} \frac{\sqrt{\pi}}{(1/\alpha^2)^{3/2}} = N_1^2 \frac{\alpha^3 \sqrt{\pi}}{2} = 1$$

$$\Rightarrow N_1 = \sqrt{\frac{2}{\alpha^3 \sqrt{\pi}}} = \left(\frac{2\mu^3 \omega^3}{\hbar^3 \pi^{1/2}}\right)^{1/2}$$

Showing they are orthogonal:

$\int_{-\infty}^{+\infty} \psi_0 \psi_1 dx = \int_{-\infty}^{+\infty} (N_0 e^{-x^2/2\alpha^2}) (N_1 x e^{-x^2/2\alpha^2}) dx = N_0 N_1 \int_{-\infty}^{+\infty} x e^{-x^2/\alpha^2} dx$. Substitute $y = x^2$ and $dy = 2x dx$ (noting that the limits of integration become $(-\infty)^2 \leq y \leq (+\infty)^2$):

$$\Rightarrow = \frac{N_0 N_1}{2} \int_{+\infty}^{+\infty} e^{-y/\alpha^2} dy = 0$$

b. $\langle x \rangle_{01} = \int_{-\infty}^{+\infty} (N_0 e^{-x^2/2\alpha^2}) x (N_1 x e^{-x^2/2\alpha^2}) dx = N_0 N_1 \int_{-\infty}^{+\infty} x^2 e^{-x^2/\alpha^2} dx = N_0 N_1 \frac{\alpha^3 \sqrt{\pi}}{2}$

Substituting in for the normalization constants gives:

$$\Rightarrow \langle x \rangle_{01} = \frac{1}{\alpha \sqrt{\pi}} \frac{2}{\alpha^3 \sqrt{\pi}} \frac{\alpha^3 \sqrt{\pi}}{2} = \frac{\sqrt{2}}{2} \alpha = \frac{1}{2} \sqrt{\frac{2\hbar}{\mu\omega}} \neq 0$$

If we tried the $v = 0$ to $v = 2$ transition, we would get an integral of the Gaussian multiplied by x^3 . To solve this, we would do the same type of substitution we did when we showed the functions were orthogonal in part a. The end result would be that

$\langle x \rangle_{02} = 0$, so that transition would not be allowed.

5. (6 pts) The "kinetic isotope effect" is an expression used by organic chemists to describe the difference in reactivity between molecules that have deuterium ($^2\text{H} = \text{D}$) compared to those with hydrogen ($^1\text{H} = \text{H}$). The reactivity difference is believed to be due to the difference in bond strength between C-H and C-D. To a first approximation, the bond strength is equal to the Hooke's law constant for the bond.

- Assuming the vibrational frequency of C-H and C-D are equal, which bond is stronger? By what factor is it stronger?
- Why do you suppose the phenomenon is called "kinetic"?

a.
$$\omega = \sqrt{\frac{k_{\text{C-H}}}{\mu_{\text{C-H}}}} = \sqrt{\frac{k_{\text{C-D}}}{\mu_{\text{C-D}}}} \Rightarrow \frac{k_{\text{C-H}}}{\mu_{\text{C-H}}} = \frac{k_{\text{C-D}}}{\mu_{\text{C-D}}} \Rightarrow k_{\text{C-D}} = k_{\text{C-H}} \frac{\mu_{\text{C-D}}}{\mu_{\text{C-H}}}$$

$$k_{\text{C-D}} = k_{\text{C-H}} \left(\frac{m_{\text{C}} m_{\text{D}} / (m_{\text{C}} + m_{\text{D}})}{m_{\text{C}} m_{\text{H}} / (m_{\text{C}} + m_{\text{H}})} \right) = k_{\text{C-H}} \left(\frac{m_{\text{D}} \cdot (m_{\text{C}} + m_{\text{H}})}{m_{\text{H}} \cdot (m_{\text{C}} + m_{\text{D}})} \right) = k_{\text{C-H}} \left(\frac{2 \cdot (12 + 1)}{1 \cdot (12 + 2)} \right) = 1.86 k_{\text{C-H}}$$

In other words, C-D is stronger than C-H by a factor of 1.86.

- Therefore, it is harder to break the C-D, so a reaction that requires this bond to break will occur much more slowly than the same reaction with a C-H bond (hence the term *kinetic isotope effect*).