

Problem Set 4 Solutions

Distributed: February 26, 2016

Due: March 4, 2016

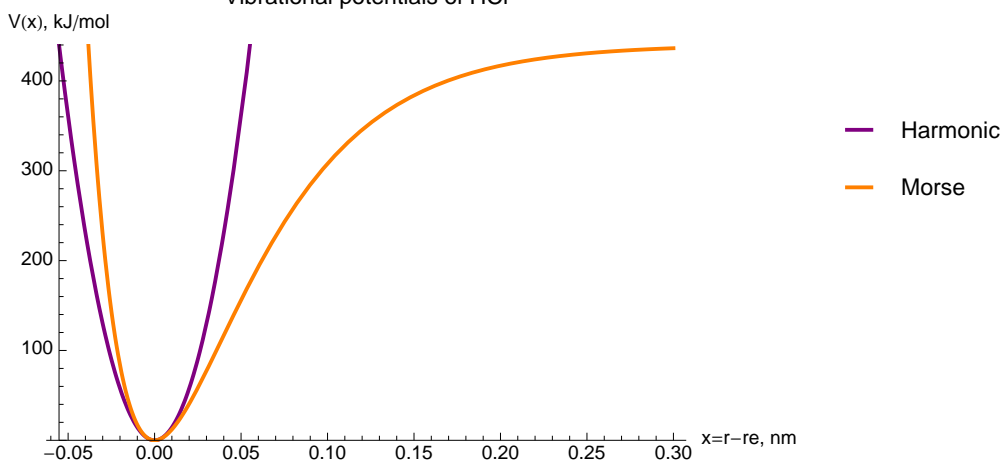
McQuarrie Problems

5-9 Overlay the two plots using Excel or Mathematica. See additional comments below.

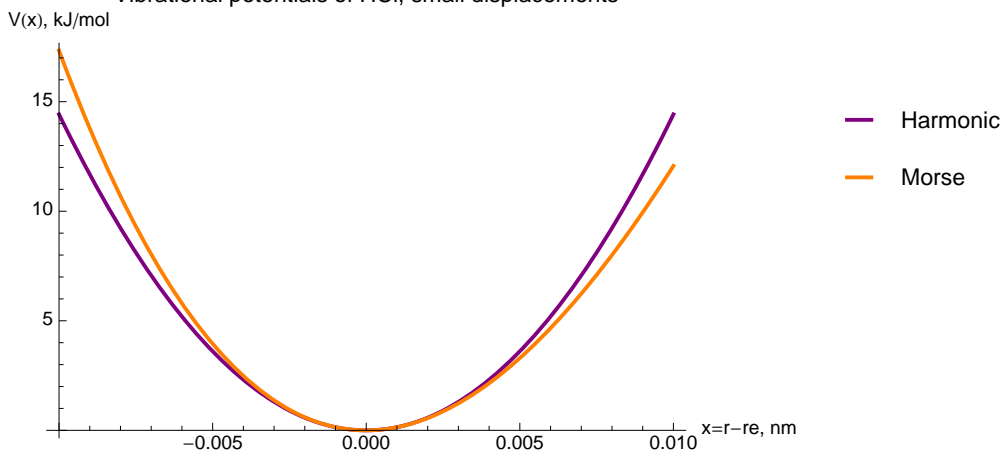
The final result of Example 5-3 defines the force constant in terms of the parameters in the Morse potential: $k = 2D_e\beta^2$. Given $D_e = 7.31 \times 10^{-19}$ J/molecule and $\beta = 1.81 \times 10^{10} \text{ m}^{-1}$ for HCl, k is

$$\begin{aligned} k &= 2D_e\beta^2 = 2 \left(7.31 \times 10^{-19} \text{ J/molecule} \right) \left(1.81 \times 10^{10} \frac{1}{\text{m}} \right)^2 \times \left(\frac{\text{Nm}}{\text{J}} \right) \\ &= \boxed{479 \frac{\text{N}}{\text{molecule} \cdot \text{m}}} \times \left(6.022 \times 10^{23} \frac{\text{molecule}}{\text{mol}} \right) \left(\frac{\text{m}}{10^9 \text{ nm}} \right)^2 \left(\frac{\text{kJ}}{1000 \text{ Nm}} \right) \\ &= \boxed{2.88 \times 10^5 \frac{\text{kJ}}{\text{mol nm}^2}} \end{aligned}$$

Vibrational potentials of HCl



Vibrational potentials of HCl, small displacements



The Morse potential captures the more realistic steep rise as $x \rightarrow 0$ and leveling off to the bond dissociation energy as $x \rightarrow \infty$. For small displacements, the harmonic potential and Morse potential are very similar.

5-13

There's a strong line in the IR spectrum of H^{127}I at 2309 cm^{-1} . Given the intensity of the line, this is probably the fundamental vibrational frequency $\tilde{\omega}$ in wavenumbers.

Using equation 5.39, $\tilde{\omega} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2}$.

The reduced mass μ from the masses of ^{127}I $m_{^{127}\text{I}} = 126.904473 \frac{\text{g}}{\text{mol}}$ and $m_{\text{H}} = 1.00782503207 \frac{\text{g}}{\text{mol}}$ from Wikipedia

$$\mu = \frac{m_{^{127}\text{I}} m_{\text{H}}}{m_{^{127}\text{I}} + m_{\text{H}}} = 0.999884347 \frac{\text{g}}{\text{mol}}$$

which is $1.000 \frac{\text{g}}{\text{mol}}$ with 4 sig figs.

Rearranging equation 5.39, we can solve for k:

$$\begin{aligned} k &= (2\pi c \tilde{\omega})^2 \mu = (2\pi (2.9979 \times 10^8 \frac{\text{m}}{\text{s}}) (2309 \text{ cm}^{-1}))^2 (1.000 \frac{\text{g}}{\text{mol}}) \\ &= 1.891 \times 10^{25} \frac{\text{g m}^2}{\text{cm}^2 \text{ mol s}^2} \times \left(\frac{\text{kg}}{1000 \text{ g}} \right) \left(\frac{100 \text{ cm}}{\text{m}} \right)^2 \left(\frac{\text{mol}}{6.022 \times 10^{23}} \right) \left(\frac{\text{N m}}{\frac{\text{kg m}^2}{\text{s}^2}} \right) \\ k &= \boxed{314.1 \frac{\text{N}}{\text{m}}} \times \left(6.022 \times 10^{23} \frac{\text{molecule}}{\text{mol}} \right) \left(\frac{\text{m}}{10^9 \text{ nm}} \right)^2 \left(\frac{\text{kJ}}{1000 \text{ N m}} \right) \\ k &= \boxed{1.892 \times 10^5 \frac{\text{kJ}}{\text{mol nm}^2}} \end{aligned}$$

The period τ has units of time per cycle, and the frequency has units of cycle per time, so the period of oscillation will be:

$$\begin{aligned} \tau &= \frac{1}{\nu_{\text{obs}}} = \frac{1}{\tilde{\omega} c} = 1.444 \times 10^{-12} \frac{\text{cm s}}{\text{m}} \times \left(\frac{\text{m}}{100 \text{ cm}} \right) \\ \tau &= \boxed{1.444 \times 10^{-14} \text{ s}} \times \left(\frac{10^{15} \text{ fs}}{\text{s}} \right) \\ \tau &= \boxed{14.44 \text{ fs}} \end{aligned}$$

5-14

Given $k = 319 \frac{\text{N}}{\text{m}}$ for $^{35}\text{Cl}^{35}\text{Cl}$, Calculate the fundamental vibrational frequency and

the zero-point energy. Using equation 5.37, $\nu_{\text{obs}} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$ with $m_{^{35}\text{Cl}} = 34.96885268 \frac{\text{g}}{\text{mol}}$

from Wikipedia, so $\mu = 17.48 \frac{\text{g}}{\text{mol}}$

$$\begin{aligned}\nu_{\text{obs}} &= \frac{1}{2\pi} \left(\frac{319 \frac{\text{N}}{\text{m}}}{17.48 \frac{\text{g}}{\text{mol}}} \right)^{1/2} \\ &= 0.680 \left(\frac{\text{mol N}}{\text{g m}} \right)^{1/2} \times \left(\left(6.0221 \times 10^{23} \frac{1}{\text{mol}} \right) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(\frac{\frac{\text{kg m}}{\text{s}^2}}{\text{N}} \right) \right)^{1/2} \\ &= \boxed{1.66 \times 10^{13} \frac{1}{\text{s}}} \\ \tilde{\omega} &= \nu_{\text{obs}}/c \\ &= 55600 \frac{1}{\text{m}} \times \left(\frac{\text{m}}{100 \text{ cm}} \right) \\ &= \boxed{556 \frac{1}{\text{cm}}}.\end{aligned}$$

The zero-point energy for a harmonic oscillator is $E_0 = \frac{1}{2}h\nu$

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2} (6.6261 \times 10^{-34} \text{ J} \cdot \text{s}) \left(1.66 \times 10^{13} \frac{1}{\text{s}} \right) = \boxed{5.53 \times 10^{-21} \text{ J}}$$

5-15

Given that the fundamental (from $v = 0$ to $v = 1$) and first overtone (from $v = 0$ to $v = 2$) for $^{12}\text{C}^{16}\text{O}$ occur at 2143.0 cm^{-1} and 4260.0 cm^{-1} , and using McQuarrie's equation 5.43,

$$\omega_{\text{obs}} = \omega_e v - \omega_e x_e v(v+1)$$

I get two equations:

$$\begin{aligned}2143.0 \text{ cm}^{-1} &= \omega_e - 2\omega_e x_e \\ 4260.0 \text{ cm}^{-1} &= 2\omega_e - 6\omega_e x_e.\end{aligned}$$

Multiplying the first by -2 and adding both, I get

$$-26.0 \text{ cm}^{-1} = -2\omega_e x_e,$$

and $\boxed{\omega_e x_e = 13.0 \text{ cm}^{-1}}$. Plugging this into the first equation,

$$2143.0 \text{ cm}^{-1} = \omega_e - 2(13.0 \text{ cm}^{-1}),$$

and $\boxed{\omega_e = 2169.0 \text{ cm}^{-1}}$. Note that this is about 1% larger than the fundamental frequency.

5-21 Only do $n = 1$. It'll be easier to show this without including any normalization constants in

front of the wavefunction. Justify why it is okay to ignore the constant if you take that approach.

From table 5.4, the unnormalized wavefunction for a harmonic oscillator in the first excited state is $\psi_1(x) = xe^{-\alpha \frac{x^2}{2}}$. To show that this equation satisfies the Schrödinger equation, we have to show that it is an eigenfunction of the Hamiltonian operator.

$$\begin{aligned}\hat{H}\psi_1(x) &= (\hat{T} + \hat{V})\psi_1(x) \\ &= \left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\psi_1(x) \\ &= -\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi_1(x)\end{aligned}\quad (\star)$$

We'll do this in pieces. First, the differential part in the first term, using the product rule:

$$\begin{aligned}\frac{d^2\psi}{dx^2} &= \frac{d}{dx} \frac{d}{dx} \left(xe^{-\alpha \frac{x^2}{2}}\right) \\ &= \frac{d}{dx} \left(e^{-\alpha \frac{x^2}{2}} - \alpha x^2 e^{-\alpha \frac{x^2}{2}}\right) \\ &= -\alpha x e^{-\alpha \frac{x^2}{2}} - \left(2\alpha x e^{-\alpha \frac{x^2}{2}} - \alpha x^3 e^{-\alpha \frac{x^2}{2}}\right) \\ &= -3\alpha x e^{-\alpha \frac{x^2}{2}} + \alpha^2 x^3 e^{-\alpha \frac{x^2}{2}} \quad \text{pulling out } \psi_1(x) = x e^{-\alpha \frac{x^2}{2}} \\ &= (-3\alpha + \alpha^2 x^2) x e^{-\alpha \frac{x^2}{2}} \\ &= (-3\alpha + \alpha^2 x^2) \psi_1(x) \quad \text{using } \alpha = \frac{\sqrt{k\mu}}{\hbar}, \text{ equation 5.45} \\ \frac{d^2\psi}{dx^2} &= \left(-3\frac{\sqrt{k\mu}}{\hbar} + \frac{k\mu}{\hbar^2} x^2\right) \psi_1(x)\end{aligned}$$

Plugging this result in for the kinetic operator term in (\star) ,

$$\begin{aligned}-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} &= -\frac{\hbar^2}{2\mu} \left(-3\frac{\sqrt{k\mu}}{\hbar} + \frac{k\mu}{\hbar^2} x^2\right) \psi_1(x) \\ &= \left(\frac{3\hbar}{2} \sqrt{\frac{k}{\mu}} - \frac{1}{2}kx^2\right) \psi_1(x)\end{aligned}$$

Plugging this result into (\star) ,

$$\begin{aligned}\hat{H}\psi_1(x) &= \left(\frac{3\hbar}{2} \sqrt{\frac{k}{\mu}} - \frac{1}{2}kx^2\right) \psi_1(x) + \frac{1}{2}kx^2\psi_1(x) \\ &= \frac{3\hbar}{2} \sqrt{\frac{k}{\mu}} \psi_1(x).\end{aligned}$$

If we rearrange equation 5.33, $\sqrt{\frac{k}{\mu}} = 2\pi\nu$ and $\hbar = \frac{h}{2\pi}$. Plugging this in, we get,

$$\hat{H}\psi_1(x) = \frac{3}{2}h\nu\psi_1(x) \quad \psi_1(x) \text{ is preserved, and the eigenvalue is } \frac{3}{2}h\nu.$$

We could neglect the normalization constant because for a linear operator like the Hamiltonian, $\hat{H}(a\phi) = a\hat{H}\phi$ for some constant a .

5-26 Summarize how the results of these types of calculations might be used.

Showing that $\langle x^2 \rangle = \int_{-\infty}^{\infty} dx \psi_2(x) x^2 \psi_2(x) = \frac{5}{2} \frac{\hbar}{\sqrt{\mu k}}$, using $\psi_2(x) = N_2 H_2(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}}$, where N_2 and H_2 are the normalization constant and Hermite polynomials for the second excited state given on page 225. To evaluate the integral, I'll start by changing variables using $\sqrt{\alpha}x = \xi$ and $\sqrt{\alpha}dx = d\xi$:

$$\begin{aligned} \left\langle \frac{\xi^2}{\alpha} \right\rangle &= \int_{-\infty}^{\infty} d\xi \frac{1}{\sqrt{\alpha}} N_2 H_2(\xi) e^{-\frac{\xi^2}{2}} \frac{\xi^2}{\alpha} N_2 H_2(\xi) e^{-\frac{\xi^2}{2}} \\ \langle \xi^2 \rangle &= \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} d\xi N_2^2 \xi^2 H_2(\xi) H_2(\xi) e^{-\xi^2} \end{aligned}$$

I want to look only at the Hermite term $\xi^2 H_2(\xi)$, and use the recursion definition of the Hermite polynomials, equation 5.55, $H_n(\xi) = \frac{1}{2}H_{n+1}(\xi) + nH_{n-1}(\xi)$,

$$\begin{aligned} \xi^2 H_2(\xi) &= \xi \left(\frac{1}{2}H_3(\xi) + 2H_1(\xi) \right) \\ &= \frac{1}{2}\xi H_3(\xi) + 2\xi H_1(\xi) \\ &= \frac{1}{2} \left(\frac{1}{2}H_4(\xi) + 3H_2(\xi) \right) + 2\xi \left(\frac{1}{2}H_2(\xi) + 2H_0(\xi) \right) \\ &= \frac{1}{4}H_4(\xi) + \frac{5}{2}H_2(\xi) + 4H_0(\xi) \end{aligned}$$

If I plug this back in, and recognize that the the Hermite polynomials for which $n \neq 2$ will integrate to 0, the average becomes

$$\begin{aligned} \langle \xi^2 \rangle &= \frac{1}{\sqrt{\alpha}} \int_{-\infty}^{\infty} d\xi N_2^2 \left(\frac{5}{2}H_2(\xi) \right) H_2(\xi) e^{-\xi^2} \\ &= \frac{5}{2\sqrt{\alpha}} \int_{-\infty}^{\infty} d\xi N_2^2 H_2^2(\xi) e^{-\xi^2} && \text{Going back to } x \\ \langle x^2 \rangle &= \frac{5}{2\alpha\sqrt{\alpha}} \int_{-\infty}^{\infty} dx \sqrt{\alpha} N_2^2 H_2^2(\sqrt{\alpha}x) e^{-\alpha x^2} \\ &= \frac{5}{2\alpha} \int_{-\infty}^{\infty} dx N_2^2 H_2^2(\sqrt{\alpha}x) e^{-\alpha x^2} && \text{The integral is 1} \\ \langle x^2 \rangle &= \frac{5\hbar}{2\sqrt{k\mu}} && \text{I used } \alpha = \sqrt{k\mu}/\hbar \end{aligned}$$

This is the final result. It can be used to calculate the intrinsic error in a measurement of position for a quantum harmonic oscillator in the second excited state, $\sqrt{\langle x^2 \rangle}$. This limits the precision with which we can know where a quantum object is.

5-27 Summarize how the results of these types of calculations might be used.

To do the same thing as **5-26** for momentum, we want to define another recursion relationship for the Hermite polynomials. We wanna get $\frac{d}{d\xi} H_n(\xi)$ starting with the derivative definition of the Hermite polynomials, $H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$,

$$\begin{aligned}
 \frac{d}{d\xi} H_n(\xi) &= \frac{d}{d\xi} \left[(-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} \right] \\
 &= 2\xi (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} + (-1)^n e^{\xi^2} \frac{d^{n+1}}{d\xi^{n+1}} e^{-\xi^2} \\
 &= 2\xi (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} + \frac{(-1)^{n+1}}{(-1)} e^{\xi^2} \frac{d^{n+1}}{d\xi^{n+1}} e^{-\xi^2} \\
 &= 2\xi (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} - (-1)^{n+1} e^{\xi^2} \frac{d^{n+1}}{d\xi^{n+1}} e^{-\xi^2} \\
 &= 2\xi H_n(\xi) - H_{n+1}(\xi) \\
 &= 2n H_{n-1}(\xi) \qquad \text{From the recursion relationship.}
 \end{aligned}$$

Using this result and $\hat{P}^2 = -\hbar^2 \frac{d^2}{dx^2}$, we can simplify the second derivative of the wavefunction for a general excited state

$$\begin{aligned}
 \frac{d^2}{dx^2} \psi_n(x) &= \frac{d^2}{dx^2} \left[N_n H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right] \\
 &= N_n \frac{d}{dx} \frac{d}{dx} \left[H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right] \\
 &= N_n \frac{d}{dx} \left[2n\sqrt{\alpha} H_{n-1}(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} - \alpha x H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right] \\
 &= N_n \left[4n(n-1)\alpha H_{n-2}(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} - 2n\alpha^{\frac{3}{2}} x H_{n-1}(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right. \\
 &\quad \left. - \alpha H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} - 2n\alpha^{\frac{3}{2}} x H_{n-1}(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right. \\
 &\quad \left. + \alpha^2 x^2 H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right] \\
 &= N_n \left[4n(n-1)\alpha H_{n-2}(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} - 4n\alpha^{\frac{3}{2}} x H_{n-1}(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right. \\
 &\quad \left. - \alpha H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} + \alpha^2 x^2 H_n(\sqrt{\alpha}x) e^{-\alpha \frac{x^2}{2}} \right]
 \end{aligned}$$

I need to work with the second term in the final result to get rid of the x

$$\begin{aligned} 4n\alpha^{\frac{3}{2}}xH_{n-1}(\sqrt{\alpha}x)e^{-\alpha\frac{x^2}{2}} &= 2n\alpha(2\sqrt{\alpha}xH_{n-1}(\sqrt{\alpha}x))e^{-\alpha\frac{x^2}{2}} \\ &= 2n\alpha(2(n-1)H_{n-2}(\sqrt{\alpha}x) + H_n(\sqrt{\alpha}x))e^{-\alpha\frac{x^2}{2}} \\ &= 4n(n-1)\alpha H_{n-2}(\sqrt{\alpha}x)e^{-\alpha\frac{x^2}{2}} + 2n\alpha H_n(\sqrt{\alpha}x)e^{-\alpha\frac{x^2}{2}} \end{aligned}$$

Plugging this back in to the second derivative, the first term cancels, and we get

$$\begin{aligned} \frac{d^2}{dx^2}\psi_n(x) &= N_n \left[-2n\alpha H_n(\sqrt{\alpha}x)e^{-\alpha\frac{x^2}{2}} - \alpha H_n(\sqrt{\alpha}x)e^{-\alpha\frac{x^2}{2}} + \alpha^2 x^2 H_n(\sqrt{\alpha}x)e^{-\alpha\frac{x^2}{2}} \right] \\ &= -2n\alpha\psi_n(x) - \alpha\psi_n(x) + \alpha^2 x^2\psi_n(x) \\ &= (-2n\alpha - \alpha + \alpha^2 x^2)\psi_n(x). \end{aligned}$$

Now I can put this into the integrals for the second excited state, $\langle p^2 \rangle = \int_{-\infty}^{\infty} dx \psi_2(x) \hat{P}^2 \psi_2(x)$, with $\frac{d^2}{dx^2}\psi_2(x) = (-5\alpha + \alpha^2 x^2)\psi_2(x)$

$$\begin{aligned} \langle p^2 \rangle &= \int_{-\infty}^{\infty} dx \psi_2(x) \hat{P}^2 \psi_2(x) \\ &= -\hbar^2 \int_{-\infty}^{\infty} dx \psi_2(x) \frac{d^2}{dx^2} \psi_2(x) \\ &= -\hbar^2 \int_{-\infty}^{\infty} dx \psi_2(x) (-5\alpha + \alpha^2 x^2) \psi_2(x) \\ &= 5\hbar^2\alpha \underbrace{\int_{-\infty}^{\infty} dx \psi_2(x)\psi_2(x)}_1 - \hbar^2\alpha^2 \underbrace{\int_{-\infty}^{\infty} dx \psi_2(x)x^2\psi_2(x)}_{\langle x^2 \rangle = \frac{5}{2\alpha}} \\ &= 5\hbar^2\alpha \underbrace{\int_{-\infty}^{\infty} dx \psi_2(x)\psi_2(x)}_1 - \frac{5}{2\alpha}\hbar^2\alpha^2 \\ &= \frac{5}{2}\hbar^2\alpha = \frac{5}{2}\hbar\sqrt{\mu k} \end{aligned}$$

This is the final result, from which we can calculate the uncertainty in p .

Note that by combining the results from **5-26** and **5-27**, the Uncertainty principle holds, because if we increase mass or the force constant, although we can know x with more certainty, we don't know p .

5-39

$\nu_{\text{obs}} = 2.63 \times 10^3 \text{ cm}^{-1}$ for H^{79}Br , and $\bar{l} = 141 \text{ pm}$. The RMSD bond length in the ground state will be given by $\sqrt{\langle x^2 \rangle}$, where $x = l - \bar{l}$. Using equation 5.60, $\langle x^2 \rangle = \frac{\hbar}{\sqrt{k\mu}} \left(v + \frac{1}{2} \right)$, so in the ground state, $\langle x^2 \rangle = \frac{\hbar}{2\sqrt{k\mu}}$. I can also use equation 5.39,

$k = (2\pi c\tilde{\omega})^2 \mu$. Combining these,

$$\langle x^2 \rangle = \frac{\hbar}{4\pi c\tilde{\omega}\mu},$$

where $\mu = 0.9951 \frac{\text{g}}{\text{mol}}$ to 4 sig figs, using $m_{79\text{Br}} = 78.9183371 \frac{\text{g}}{\text{mol}}$ from Wikipedia. Plugging in values,

$$\begin{aligned} \langle x^2 \rangle &= \frac{\hbar}{4\pi c\tilde{\omega}\mu} \\ &= 1.07 \times 10^{-47} \frac{\text{cm J mol s}^2}{\text{g m}} \times \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(\frac{\text{m}}{100 \text{ cm}} \right) \left(\frac{\text{kg m}^2}{\text{s}^2 \text{ J}} \right) \left(6.0221 \times 10^{23} \frac{1}{\text{mol}} \right) \\ &= 6.44 \times 10^{-23} \text{ m}^2 \times \left(\frac{10^{12} \text{ pm}}{\text{m}} \right) \\ &= 64.4 \text{ pm}^2 \end{aligned}$$

So the RMSD displacement is $\sqrt{\langle x^2 \rangle} = 8.03 \text{ pm}$, or 5.69% of the overall bond length. Interesting.

5-41

Using the expression at the end of problem **5-40**, the fraction of molecules in the ground state is $f_0 = 1 - e^{-h\nu/k_B T}$. Given that $\omega_e = 2650 \text{ cm}^{-1}$ for HBr, we can calculate $\nu = \omega_e c = 7.944 \times 10^{13} \text{ s}^{-1}$.

At 300 K,

$$\begin{aligned} f_0 &= 1 - e^{-h\nu/k_B T} \\ &= 1 - e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(7.944 \times 10^{13} \text{ s}^{-1})}{(1.381 \times 10^{-23} \frac{\text{J}}{\text{K}})(300 \text{ K})}} \\ &= 1 - 3.023 \times 10^{-6} \\ &= \boxed{100\%} \end{aligned}$$

To the precision of the measurement of ω_e , all the molecules are in the ground state at 300 K. At 2000 K,

$$\begin{aligned} f_0 &= 1 - 0.149 \\ &= \boxed{85.1\%} \end{aligned}$$

Fewer of the molecules are in the ground state at 2000 K, but still a surprising majority.