Chem 3322 homework #10 solutions

Problem 1

A portion of the pure rotational spectrum of carbon monoxide was recorded on a far infrared spectrophotometer, as shown. The instrument cannot obtain data below 15 cm^{-1}.

a) From the given spectrum, estimate the bond length of CO as accurately as you can (in other words, use all the data).

Solution:

From question 4 of homework 8, we know that the spacing between the lines is given by

$$\frac{\hbar^2}{\mu r_0^2} \tag{1}$$

Since μ appears in this formula, we need to know the atom masses. The isotopic information is not specified. However, for oxygen, ^{16}O is 99.8% abundant with a mass of 15.994914 amu and ^{12}C is 98.9% abundant with a mass of 12 amu (this is an exact value) so there isn't really any ambiguity here since both isotopes are almost 100% adundant. This gives $\mu = 1.138 \times 10^{-26}$ kg. Since we have 6 spacings, we should average them to get the most accurate value. The average spacing is 3.85 cm^{-1}. This yields $r = 1.13$ Å.

b) For the seven observed peaks, assign each of them to their corresponding carbon monoxide rotational transition in terms of the rotational quantum numbers by carefully analyzing the given data.
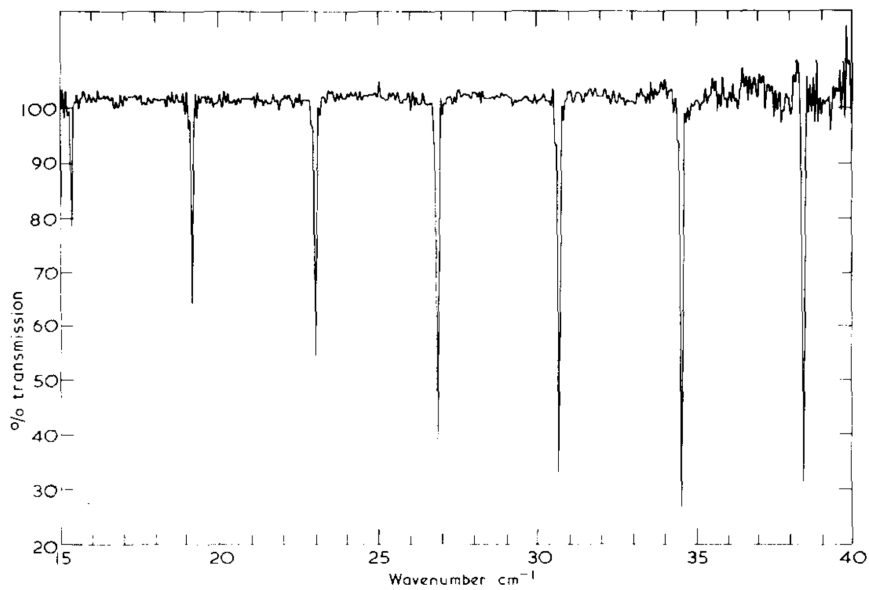
Solution: Again from question 4 of homework 8, we know that the peaks correspond to

$$\Delta E_{\ell \to \ell+1} = \frac{(\ell+1)\hbar^2}{\mu r_0^2} \tag{2}$$

So we can compute these transitions from our r_0 value from part (a) as follows

ℓ	$\ell+1$	$\Delta E_{\ell \to \ell+1}$
1	2	7.700
2	3	11.55
3	4	15.40
4	5	19.25
5	6	23.10
6	7	26.95
7	8	30.80
8	9	34.65
9	10	38.50
10	11	42.35

Therefore we can clearly see that the seven observed peaks correspond to lines 3-9 of the table.

Transmission spectrum of carbon monoxide. Pressure 200 torr, path length 203 mm.

FIG. 1:

Problem 2

Do problem 5-13 from your textbook.

$$\tilde{x} = \frac{(6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(2.998 \times 10^8\ \text{m} \cdot \text{s}^{-1})(2886\ \text{cm}^{-1})(100\ \text{cm} \cdot \text{m}^{-1})}{4\left(\dfrac{440.2 \times 10^3\ \text{J} \cdot \text{mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}}\right)}$$

$$= 0.01961$$

$$\tilde{\nu}\tilde{x} = (2886\ \text{cm}^{-1})(0.01961) = 56.59\ \text{cm}^{-1}$$

5–13. In the infrared spectrum of H^{79}Br, there is an intense line at 2559 cm^{-1}. Calculate the force constant of H^{79}Br and the period of vibration of H^{79}Br.

$$\tilde{\nu}_{obs} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{5.34}$$

$$k = (2\pi c \tilde{\nu}_{obs})^2 \mu$$
$$= \left[2\pi(2.998 \times 10^{10}\ \text{cm} \cdot \text{s}^{-1})(2559\ \text{cm}^{-1})\right]^2$$
$$\times \left[\frac{(1.008\ \text{amu})(78.92\ \text{amu})}{79.93\ \text{amu}}\right](1.661 \times 10^{-27}\ \text{kg} \cdot \text{amu}^{-1})$$
$$= 384\ \text{N} \cdot \text{m}^{-1}$$

The period of vibration is

$$T = \frac{1}{\nu} = \frac{1}{c\tilde{\nu}} = 1.30 \times 10^{-14}\ \text{s}$$

5–14. The force constant of ^{79}Br^{79}Br is 240 N·m^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of ^{79}Br^{79}Br.

$$\tilde{\nu}_{obs} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \tag{5.34}$$

$$\tilde{\nu}_{obs} = \frac{1}{2\pi(2.998 \times 10^{10}\ \text{cm} \cdot \text{s}^{-1})}\left\{\frac{240\ \text{N} \cdot \text{m}^{-1}}{\left[\dfrac{(78.92\ \text{amu})^2}{78.92\ \text{amu} + 78.92\ \text{amu}}\right](1.66 \times 10^{-27}\ \text{kg} \cdot \text{amu}^{-1})}\right\}^{1/2}$$

$$= 321\ \text{cm}^{-1}$$

We use Equation 5.27 to find the zero point energy:

$$E_0 = \tfrac{1}{2}h\nu = \tfrac{1}{2}hc\tilde{\nu} = 3.19 \times 10^{-21}\ \text{J}$$

5–15. Verify that $\psi_1(x)$ and $\psi_2(x)$ given in Table 5.3 satisfy the Schrödinger equation for a harmonic oscillator.

The Schrödinger equation for a harmonic oscillator is

$$\frac{d^2\psi_v}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_v - \frac{1}{2}kx^2\right)\psi_v = 0 \tag{5.26}$$

where $E_v = h\nu(v + \frac{1}{2})$. From Table 5.3,

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

where $\alpha = (k\mu)^{1/2}/\hbar$. Substituting ψ_1 into the Schrödinger equation with $v = 1$ gives

$$\frac{d^2\psi_1}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_1 - \frac{1}{2}kx^2\right)\psi_1 = 0$$

$$\frac{d}{dx}\left[\left(\frac{4\alpha^3}{\pi}\right)^{1/4}\left(e^{-\alpha x^2/2} - \alpha x^2 e^{-\alpha x^2/2}\right)\right] + \frac{2\mu}{\hbar^2}\left(\frac{3h\nu}{2} - \frac{1}{2}kx^2\right)\left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2} = 0$$

$$-3\alpha x e^{-\alpha x^2/2} + \alpha^2 x^3 e^{-\alpha x^2/2} + \left(\frac{3h\mu\nu}{\hbar^2} - \frac{k\mu x^2}{\hbar^2}\right)xe^{-\alpha x^2/2} = 0$$

$$-3\alpha x + \alpha^2 x^3 + \frac{3}{\hbar}(2\pi\nu)\mu x - \alpha^2 x^3 = 0$$

$$-3\alpha x + 3\alpha x = 0$$

where $k = (2\pi\nu)^2\mu$. Substituting ψ_2 into the Schrödinger equation with $v = 2$ gives

$$\frac{d^2\psi_2}{dx^2} + \frac{2\mu}{\hbar^2}\left(E_2 - \frac{1}{2}kx^2\right)\psi_2 = 0$$

$$\left(\frac{\alpha}{4\pi}\right)^{1/4}\frac{d}{dx}\left[4\alpha xe^{-\alpha x^2/2} - \alpha x(2\alpha x^2 - 1)e^{-\alpha x^2/2}\right]$$
$$+ \frac{2\mu}{\hbar^2}\left(\frac{5h\nu}{2} - \frac{1}{2}kx^2\right)\left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2} = 0$$

$$(5\alpha - 11\alpha^2 x^2 + 2\alpha^3 x^4)e^{-\alpha x^2/2} + \left(\frac{5h\mu\nu}{\hbar^2} - \frac{k\mu}{\hbar^2}x^2\right)(2\alpha x^2 - 1)e^{-\alpha x^2/2} = 0$$

$$5\alpha - 11\alpha^2 x^2 + 2\alpha^3 x^4 - \frac{5}{\hbar}(2\pi\nu)\mu + \alpha^2 x^2 + \frac{10}{\hbar}(2\pi\nu)\mu\alpha x^2 - 2\alpha^3 x^4 = 0$$

$$5\alpha - 11\alpha^2 x^2 - 5\alpha + 11\alpha^2 x^2 = 0$$

Both ψ_1 and ψ_2 are solutions to the Schrödinger equation.

5–16. Show explicitly for a harmonic oscillator that $\psi_0(x)$ is orthogonal to $\psi_1(x)$, $\psi_2(x)$, and $\psi_3(x)$ and that $\psi_1(x)$ is orthogonal to $\psi_2(x)$ and $\psi_3(x)$ (see Table 5.3).

From Table 5.3, we have

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4}(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

$$\psi_3(x) = \left(\frac{\alpha^3}{9\pi}\right)^{1/4}(2\alpha x^3 - 3x)e^{-\alpha x^2/2}$$

Problem 3

Do problem 5-22 from your textbook.

5–19. Prove that the derivative of an even (odd) function is odd (even).

If $f(x)$ is even, it can be represented by a power series of the form

$$f(x) = f_0 + f_2 x^2 + f_4 x^4 + O(x^6)$$

where the only allowed values of n in x^n are even. The derivative of this function is

$$f'(x) = 2f_2 x + 4f_4 x^3 + O(x^5)$$

which is an odd function expressed in a power series. Similarly, if $g(x)$ is odd, it can be represented by

$$g(x) = f_1 x + f_3 x^3 + f_5 x^5 + O(x^7)$$

where the only allowed values of n in x^n are odd, and its derivative is

$$g'(x) = f_1 + 3f_3 x^2 + 5f_5 x^4 + O(x^6)$$

which is an even function.

5–20. Show that

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_2(x) x^2 \psi_2(x) dx = \frac{5}{2} \frac{\hbar}{(\mu k)^{1/2}}$$

for a harmonic oscillator. Note that $\langle x^2 \rangle^{1/2}$ is the square root of the mean of the square of the displacement (the *root-mean-square displacement*) of the oscillator.

From Table 5.3, $\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2}$. So

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_2(x) x^2 \psi_2(x) dx$$

$$= 2\left(\frac{\alpha}{4\pi}\right)^{1/2} \int_0^{\infty} dx (2\alpha x^2 - 1)^2 x^2 e^{-\alpha x^2}$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} dx (4\alpha^2 x^6 - 4\alpha x^4 + x^2) e^{-\alpha x^2}$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \left[4\alpha^2 \left(\frac{15}{16\alpha^3}\right) - 4\alpha \left(\frac{3}{8\alpha^2}\right) + \left(\frac{1}{4\alpha}\right)\right] \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$= \frac{5}{2\alpha} = \frac{5}{2} \frac{\hbar}{(\mu k)^{1/2}}$$

5–21. Show that

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi_2(x) \hat{P}^2 \psi_2(x) dx = \frac{5}{2} \hbar(\mu k)^{1/2}$$

for a harmonic oscillator.

From Table 5.3 and Table 4.1, $\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2}$ and $\hat{P} = -i\hbar d/dx$. So

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi_2(x) \hat{P}^2 \psi_2(x) dx$$

$$= 2\left(\frac{\alpha}{4\pi}\right)^{1/2} \int_0^{\infty} dx (2\alpha x^2 - 1)e^{-\alpha x^2/2} \left\{-\hbar^2 \frac{d^2}{dx^2}\left[(2\alpha x^2 - 1)e^{-\alpha x^2/2}\right]\right\}$$

$$= -\hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} dx (2\alpha x^2 - 1)e^{-\alpha x^2} \left(5\alpha - 11\alpha^2 x^2 + 2\alpha^3 x^4\right)$$

$$= -\hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} dx \left(4\alpha^4 x^6 - 24\alpha^3 x^4 + 21\alpha^2 x^2 - 5\alpha\right) e^{-\alpha x^2}$$

$$= -\hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \left[4\alpha^4 \left(\frac{15}{16\alpha^3}\right) - 24\alpha^3 \left(\frac{3}{8\alpha^2}\right) + 21\alpha^2 \left(\frac{1}{4\alpha}\right) - 5\alpha \left(\frac{1}{4}\right)\right] \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$= \hbar^2 \frac{5}{2} \alpha = \frac{5}{2} \hbar(\mu k)^{1/2}$$

5–22. Using the fundamental vibrational frequencies of some diatomic molecules given below, calculate the root-mean-square displacement (see Problem 5–20) in the $v = 0$ state and compare it with the equilibrium bond length (also given below).

Molecule	$\tilde{v}/\text{cm}^{-1}$	l_0/pm
H_2	4401	74.1
$^{35}Cl^{35}Cl$	554	198.8
$^{14}N^{14}N$	2330	109.4

We will use Equation 5.34 to find k. Solving for k gives

$$k = (2\pi c \tilde{v})^2 \mu$$

The root-mean-square displacement is given by $\langle x^2 \rangle^{1/2}$. For the ground state,

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_0(x) x^2 \psi_0(x) dx$$

$$= 2\left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} x^2 e^{-\alpha x^2} dx$$

$$= 2\left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{\pi}{\alpha}\right)^{1/2} \left(\frac{1}{4\alpha}\right) = \frac{1}{2\alpha} = \frac{\hbar}{2(\mu k)^{1/2}}$$

$$= \frac{\hbar}{4\pi c \tilde{v} \mu}$$

and so the root-mean-square displacement of the molecule is

$$\langle x^2 \rangle^{1/2} = \left(\frac{\hbar}{4\pi c \tilde{v} \mu}\right)^{1/2}$$

For H_2,

$$\langle x^2 \rangle^{1/2} = \left\{\frac{1.055 \times 10^{-34} \text{ J·s}}{4\pi (2.998 \times 10^{10} \text{ cm·s}^{-1})(4401 \text{ cm}^{-1})\left[\left(\frac{1.008}{2}\right)(1.661 \times 10^{-27} \text{ kg})\right]}\right\}^{1/2}$$

$$= 8.718 \times 10^{-12} \text{ m} = 8.718 \text{ pm}$$

For $^{35}Cl^{35}Cl$,

$$\langle x^2 \rangle^{1/2} = \left\{ \frac{1.055 \times 10^{-34} \, \text{J} \cdot \text{s}}{4\pi(2.998 \times 10^{10} \, \text{cm} \cdot \text{s}^{-1})(554 \, \text{cm}^{-1})\left[\left(\frac{34.97}{2}\right)(1.661 \times 10^{-27} \, \text{kg})\right]} \right\}^{1/2}$$

$$= 4.172 \times 10^{-12} \, \text{m} = 4.172 \, \text{pm}$$

and finally, for $^{14}N^{14}N$,

$$\langle x^2 \rangle^{1/2} = \left\{ \frac{1.055 \times 10^{-34} \, \text{J} \cdot \text{s}}{4\pi(2.998 \times 10^{10} \, \text{cm} \cdot \text{s}^{-1})(2330 \, \text{cm}^{-1})\left[\frac{14.003}{2}(1.661 \times 10^{-27} \, \text{kg})\right]} \right\}^{1/2}$$

$$= 3.215 \times 10^{-12} \, \text{m} = 3.215 \, \text{pm}$$

These values are all much smaller than the equilibrium bond lengths.

5–23. Prove that

$$\langle K \rangle = \langle V(x) \rangle = \frac{E_v}{2}$$

for a one-dimensional harmonic oscillator for $v = 0$ and $v = 1$.

The operators for $V(x)$ and $K(x)$ given in Table 4.1, the expressions for $\psi_v(x)$ given in Table 5.3, and Equation 5.30 for the vibrational energy levels are

$$\hat{V}(x) = \frac{kx^2}{2}$$

$$\hat{K}(x) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$$

$$E_v = \hbar \left(\frac{k}{\mu}\right)^{1/2} \left(v + \frac{1}{2}\right)$$

For $v = 0$,

$$\langle K \rangle = \int_{-\infty}^{\infty} dx \, \psi_0(x) \left(\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2}\right) \psi_0(x)$$

$$= -\frac{\hbar^2}{\mu}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} dx \, e^{-\alpha x^2}\left[\alpha^2 x^2 - \alpha\right]$$

$$= -\frac{\hbar^2}{\mu}\left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left[\alpha^2\left(\frac{1}{4\alpha}\right) - \alpha\left(\frac{1}{2}\right)\right] = \frac{\hbar^2\alpha}{4\mu}$$

$$= \frac{\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_0}{2}$$

and

$$\langle V \rangle = \int_{-\infty}^{\infty} dx \, \psi_0(x) \left(\frac{kx^2}{2}\right) \psi_0(x)$$

$$= k \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} dx \, x^2 e^{-\alpha x^2}$$

$$= k \left(\frac{\alpha}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\frac{1}{4\alpha} = \frac{k}{4\alpha} = \frac{\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_0}{2}$$

For $v = 1$,

$$\langle K \rangle = \int_{-\infty}^{\infty} dx \, \psi_1(x) \left(\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2}\right) \psi_1(x)$$

$$= -\frac{\hbar^2}{\mu}\left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_0^{\infty} dx \, e^{-\alpha x^2}\left(\alpha^2 x^4 - 3\alpha x^2\right)$$

$$= -\frac{\hbar^2}{\mu}\left(\frac{4\alpha^3}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left[\alpha^2\left(\frac{3}{8\alpha^2}\right) - 3\alpha\left(\frac{1}{4\alpha}\right)\right]$$

$$= \frac{3\hbar^2\alpha}{4\mu} = \frac{3\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_1}{2}$$

and

$$\langle V \rangle = \int_{-\infty}^{\infty} dx \, \psi_1(x) \left(\frac{kx^2}{2}\right) \psi_1(x)$$

$$= k \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_0^{\infty} dx \, x^4 e^{-\alpha x^2}$$

$$= k \left(\frac{4\alpha^3}{\pi}\right)^{1/2}\left(\frac{\pi}{\alpha}\right)^{1/2}\left(\frac{3}{8\alpha^2}\right) = \frac{3k}{4\alpha}$$

$$= \frac{3\hbar}{4}\left(\frac{k}{\mu}\right)^{1/2} = \frac{E_1}{2}$$

5–24. There are a number of general relations between the Hermite polynomials and their derivatives (which we will not derive). Some of these are

$$\frac{dH_v(\xi)}{d\xi} = 2\xi H_v(\xi) - H_{v+1}(\xi)$$

$$H_{v+1}(\xi) - 2\xi H_v(\xi) + 2v H_{v-1}(\xi) = 0$$

and

$$\frac{dH_v(\xi)}{d\xi} = 2v H_{v-1}(\xi)$$

Such connecting relations are called *recursion formulas*. Verify these formulas explicitly using the first few Hermite polynomials given in Table 5.2.

We will verify these formulas for $v = 0, 1,$ and 2. The Hermite polynomials for these values of v are

$$H_0(\xi) = 1 \qquad H_1(\xi) = 2\xi \qquad H_2(\xi) = 4\xi^2 - 2$$

Problem 4

For HCl (isotopic information not known), you measure the following vibrational transitions:

$n = 0 \to 1$ 2885.64 cm^{-1}

$n = 1 \to 2$ 2781.54 cm^{-1}

$n = 2 \to 3$ 2677.44 cm^{-1}

$n = 3 \to 4$ 2573.32 cm^{-1}

What tells you that this molecule is not a harmonic oscillator?

Estimate its dissociation energy in kJ/mol.

Solution:

The spacing between energy levels is not constant, which tells us this molecule is not a harmonic oscillator.
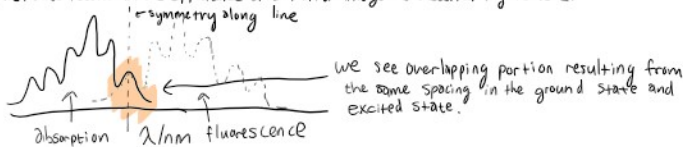
We will estimate its dissociation energy using the Morse oscillator model. The formula for the Morse energy levels in given in Eq. (3) below.

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) - \frac{(\hbar\omega)^2}{4D_e} \left(n + \frac{1}{2} \right)^2 \tag{3}$$

There are two unknowns in this equation: ω and D_e. We are given four pieces of data in the problem, so we should be able to solve for the two unknowns. After that the final answer is given by $D_0 = D_e - \hbar\omega/2$ because the D_e energy is measured from the potential minimum but the molecule retains its zero point energy and this must be accounted for. There are several ways to carry out the solution, you can look at page "An3" of my lecture notes (last page of the Old Lecture Notes, part 6) for one method. You should get around (very roughly) 496 kJ/mol.

From Figures 15.1 and 15.2 of the textbook, and the discussion in the notes/videos, explain the "mirror image" statement on page 595 of the textbook in your own words (and sketches). You are to provide as much detail as you can. The book's description is terse – you need to fill in the details.
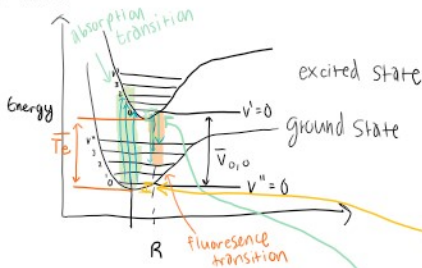
When we assume that the spacing between the ground state vibrational levels are the same as the spacing between the excited state vibrational levels, we will see an overlap in the spectra of fluorescence and absorption when the vibrational frequencies are the same. This results in the appearance of a mirror image as shown in Figure 15.2.

← symmetry along line

we see overlapping portion resulting from the same spacing in the ground state and excited state.

absorption λ/nm fluorescence

To further understand why this mirror image occurs, we first need to see how the peak positions are symmetric. In order to do this, we can first look at the equation that predicts frequencies of an electronic transitions in the absorption spectrum:

Eq. 13.24 $\bar{v}_{obs} = \overline{T}_e + (\frac{1}{2}\overline{v}'_e - \frac{1}{4}\overline{x}'_e\overline{v}'_e) - (\frac{1}{2}\overline{v}''_e - \frac{1}{4}\overline{x}''_e\overline{v}''_e) + \overline{v}'_e v' - \overline{x}'_e\overline{v}'_e v'(v'+1)$ where $\overline{T}_e$ is the difference from the lowest point of the ground state electronic potential energy curve and the excited electronic state.

We also can look at figure 13.7:

absorption transition

excited state

Energy

$v'=0$ ground state

$\overline{T}_e$

$\overline{v}_{0,0}$

$v''=0$

R   fluorescence transition

The zero-point energies of the upper and lower state are the first two terms of eq. 13.24, so we know that we can rewrite it to eq. 13.25:

Absorption : $\bar{v}_{obs} = \bar{v}_{0,0} + \overline{v}'_e v' - \overline{x}'_e \overline{v}'_e v'(v'+1)$ where $\bar{v}_{0,0} = \overline{T}_e + (\frac{1}{2}\overline{v}'_e - \frac{1}{4}\overline{x}'_e\overline{v}'_e) - (\frac{1}{2}\overline{v}''_e - \frac{1}{4}\overline{x}''_e\overline{v}''_e)$
$v'=0,1,2,3\ldots$

these will cancel

Since the term in green represent the excited state vibrational transition while the term in yellow represents the ground state vibrational transition in the zero point energies, and we assume that these transitions are equal from the explanation of the "mirror image" idea, then these two will cancel out leaving $\bar{v}_{0,0} = \overline{T}_e$.

Since the fluorescence transition (represented in orange) is a transition from the excited state to ground state, opposite to the absorption transition (represented in green), we can rearrange the absorption transition equation above in terms of fluorescence to get.

Fluorescence : $\bar{v}_{obs} = \bar{v}_{0,0} + \overline{x}''_e\overline{v}''_e v''(v''+1) - \overline{v}''_e v''$
$v''=0,1,2,3\ldots$

If we make the assumption that $\overline{x}''_e = \overline{x}'_e$ and $\overline{v}''_e = \overline{v}'_e$ then we can reorganize the above equations:

Absorption: $\bar{v}_{obs} = \bar{v}_{0,0} + \overline{v}'_e v' - \overline{x}'_e\overline{v}'_e v'(v'+1)$ $\xrightarrow{\text{plug } \overline{x}''_e = \overline{x}'_e \& \overline{v}''_e = \overline{v}'_e}$ $\bar{v}_{obs} = \bar{v}_{0,0} + \overline{v}'_e v' + \overline{x}'_e\overline{v}'_e v'(v'+1)$
$v'=0,1,2,3\ldots$

Fluorescence: $\bar{v}_{obs} = \bar{v}_{0,0} + \overline{x}''_e\overline{v}''_e v''(v''+1) - \overline{v}''_e v''$ $\longrightarrow$ $\bar{v}_{obs} = \bar{v}_{0,0} + \overline{x}'_e\overline{v}'_e v''(v''+1) - \overline{v}'_e v''$
$v''=0,1,2,3\ldots$

Now we can assume that $v'=v''=0$:

Absorption: $\bar{v}_{obs} = \bar{v}_{0,0} + 0 + 0$ } $\bar{v}_{0,0} = \bar{v}_{obs}$ (Absorption) = $\bar{v}_{obs}$ (fluorescence)   & $\dfrac{\bar{v}_{obs}(Abs) + \bar{v}_{obs}(fluor)}{2} = \bar{v}_{0,0}$ when $v'=v''$

Fluorescence: $\bar{v}_{obs} = \bar{v}_{0,0} + 0 + 0$ when they both equal zero

This demonstrates an overlap in the peaks and that they must be symmetric at all positions when looking at the 0→0 vibronic transition. This would result in the mirror image.

Now that we have described how the positioning of the peaks are the same, we must also look at how the intensity of the peaks are symmetric. Before we can look at the probability density for the vibrational levels we must understand how the vertical transition works from the ground state to excited state. The Frank-Condon Principle states that when we cause an electronic transition, the electrons become excited instantaneously because of their light weight, but because of the heavier weight of the nuclei, the nuclei do not change their geometry on the small time scale. This allows for the vertical transition to be represented by a straight upward arrow shown in the figure below.
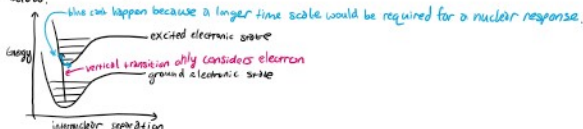
this can happen because a larger time scale would be required for a nuclear response.

excited electronic state

Energy

vertical transition only considers electron

ground electronic state

internuclear separation

From this principle, we can look at the probability density curves for the different vibrational levels and compare them in order to understand the intensities. As the excited electronic state's equilibrium position is slightly shifted to the right for the value of the internuclear separation, the probability densities look like what is shown below:

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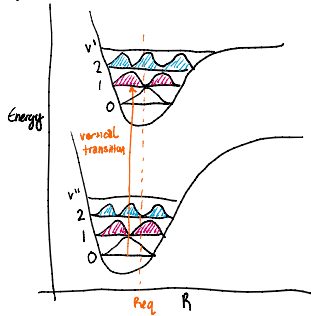
Because of this, we can see that there is a slight overlap in the probability density between the ground state and corresponding excited state. For example, if we were to look at the transition from $0 \rightarrow 0$:

Where the orange would demonstrate the overlap
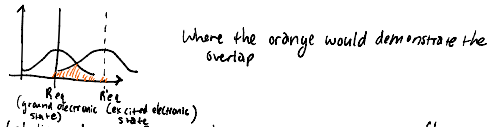
Now we can compare the probability density for an absorption transition vs. a fluorescence transition as shown below:

Absorption: $v''=0 \rightarrow v'=1$ Fluorescence: $v'=0 \rightarrow v''=1$
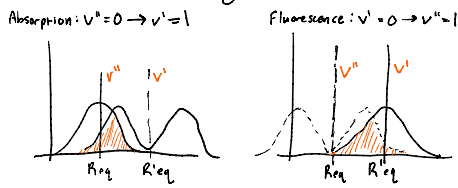
If we make the same assumption we did when comparing position and say that $v'=v''$, then we can conclude that in both of these transitions, the area in the probability densities that are overlapping have to be equal to each other. Because the areas are the same, then the intensities must also be equal to one another making them symmetric and supporting the mirror image. Because we have now proven that both the position and intensity of the peaks are symmetric in the fluorescence and absorption spectra, we have proven the mirror image statement.