

## Chem 3322 homework #9 solutions

### Problem 1

Calculate the percentage difference in the fundamental vibrational wavenumber of

(a)  $^1\text{H}^{35}\text{Cl}$  and  $^2\text{H}^{35}\text{Cl}$  using the assumption that their force constants are the same.

(b)  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$  using the assumption that their force constants are the same.

Solution:

The wavenumber times the speed of light is the frequency  $\nu$ , (and for percentage different multiplying by a constant (speed of light) doesn't change anything) and  $2\pi\nu = \sqrt{k/\mu}$ , so

$$\frac{\nu_1}{\nu_2} = \sqrt{\frac{\mu_2}{\mu_1}} \quad (1)$$

If we define the percentage difference to be the difference divided by the average of the two frequencies, we get

For part (a) 33% and for part (b) 0.075%

### Problem 2

The spacing between vibrational energy levels is substantially larger than the spacing between (low-lying) rotational energy levels, which itself is substantially larger than the spacing between translational energy levels. Consider  $\text{N}_2$ , for which  $\hbar\omega = 2360 \text{ cm}^{-1}$  (note: you need to convert this wavenumber value to an energy) and the bond length is 109.76 picometers.

a) For a given vibrational state, how many rotational states have energy less than the energy gap to the next vibrational state? That is, find  $\ell$  such that the energy of the state  $(n, \ell)$  is greater than or equal to the energy of the state  $(n + 1, 0)$ . Note that since the vibrational energy level spacing is constant (from the harmonic oscillator approximation), this will be the same for any vibrational level  $n$ . Include a sketch to illustrate your answer.

Solution:

Here you will need to convert the  $\text{cm}^{-1}$  (given for  $\hbar\omega$ ) into an actual energy to do the problem (this conversion involves the speed of light).  $E_{n\ell} = \hbar\omega(n + 1/2) + \hbar^2\ell(\ell + 1)/(2\mu r_0^2)$  and  $E_{n+1,\ell=0} = \hbar\omega(n+3/2)$ . We are asked to find  $\ell$  such that  $E_{n\ell} > E_{n+1,\ell=0}$ , or, equivalently,  $E_{n\ell} - E_{n+1,\ell=0} > 0$ . Let us solve the equation  $E_{n\ell} - E_{n+1,\ell=0} = 0$ , and then we should take  $\ell$  bigger than this value:

$$E_{n\ell} - E_{n+1,\ell=0} = 0 \Rightarrow E_{n\ell} = E_{n+1,\ell=0} \Rightarrow -\hbar\omega + \hbar^2\ell(\ell + 1)/(2\mu r_0^2) = 0 \quad (2)$$

$$\Rightarrow \omega = \hbar\ell(\ell + 1)/(2\mu r_0^2) \quad (3)$$

Manipulating a bit, we can use the quadratic equation, which gives solutions for  $\ell$  of

$$\ell = \frac{-1 \pm \sqrt{1 + 8\mu\omega r_0^2/\hbar}}{2} \quad (4)$$

This equation gives  $\ell = 33.887$ , implying that  $\ell = 34$  will make  $E_{n\ell} - E_{n+1,\ell=0} > 0$ .

**b)** After what rotational level does the rotational spacing become larger than the vibrational spacing? Include a sketch to illustrate your answer.

Solution:  $E_{n+1,\ell} - E_{n,\ell} = \hbar\omega$  and  $E_{n,\ell+1} - E_{n,\ell} = (\ell + 1)\hbar^2/(\mu r_0^2)$ . So we should find  $\ell$  such that

$$\ell > \frac{\mu r_0^2 \hbar \omega}{\hbar^2} - 1 \quad (5)$$

This gives  $\ell > 590.12$ , so we should take  $\ell = 591$ .

**c)** Calculate the translational energy level spacing assuming a particle in a three dimensional box model with a box size of  $L = 10$  cm. You can assume the transition is from the lowest energy state to the next lowest energy state. What part of the electromagnetic spectrum does this frequency belong to?

Solution:

The three dimensional particle in a box energy levels are

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2} \quad (6)$$

The lowest transition is from  $n_x = 1, n_y = 1, n_z = 1$  to  $n_x = 2, n_y = 1, n_z = 1$ . The mass is the total mass of the molecule (not the reduced mass). This works out to  $\Delta E = 3.54 \times 10^{-40}$  J. This is a wavelength of  $5.61 \times 10^{14}$  m and a frequency of  $5.34 \times 10^{-7}$  Hz. This is below the radio wave frequencies.

### **Problem 3**

The fundamental vibrational frequencies for  $^1\text{H}^{19}\text{F}$  and  $^2\text{H}^{19}\text{F}$  are  $4138.52 \text{ cm}^{-1}$  and  $2998.25 \text{ cm}^{-1}$ , respectively.  $D_e = 5.86 \text{ eV}$  for both molecules (Morse model). Work out the difference in bond energy for these two molecules in kJ/mol.

Solution:

$$D_0^{DF} - D_0^{HF} = \left( (D_e - \frac{1}{2}2998.25 \text{ cm}^{-1}) - (D_e - \frac{1}{2}4138.52 \text{ cm}^{-1}) \right) hc \quad (7)$$

$$= 1.14 \times 10^{-20} \text{ J} = 6.86 \text{ kJ/mol} \quad (8)$$

#### Problem 4

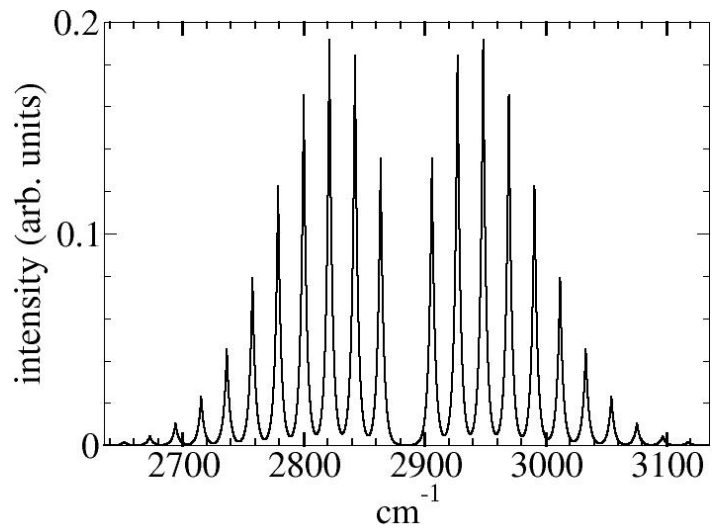


FIG. 1: Rotationally resolved vibrational spectrum of HCl.

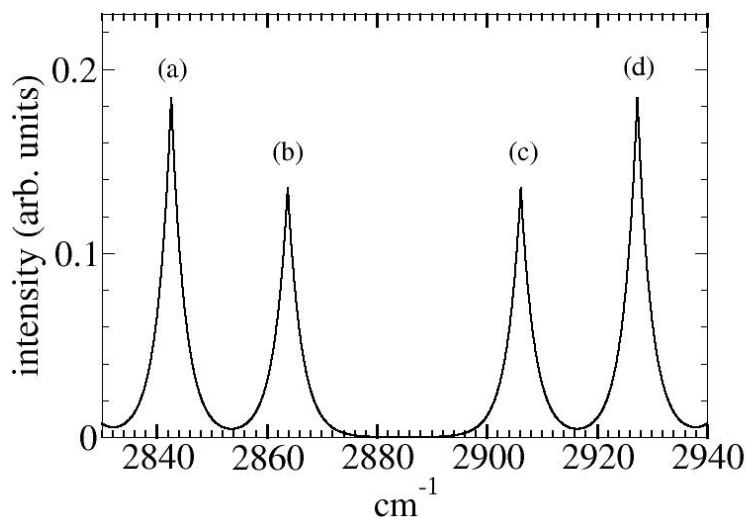


FIG. 2: Detail from Fig. 1. The peak marked (a) is at  $2842.63 \text{ cm}^{-1}$ , (b) is at  $2863.81 \text{ cm}^{-1}$ , (c) is at  $2906.19 \text{ cm}^{-1}$ , and (d) is at  $2927.37 \text{ cm}^{-1}$ .

For this problem, use  $^1\text{H} = 1.0078 \text{ amu}$  and  $^{35}\text{Cl} = 34.969 \text{ amu}$ .

a) From Figures 1 and 2 estimate the equilibrium bond length of  $^1\text{H}^{35}\text{Cl}$ .

Solution:

The peak (c) to peak (d) spacing is  $21.18 \text{ cm}^{-1}$  which is the pure rotational peak spacing since both peaks include  $n : 0 \rightarrow 1$  so when subtracted the vibrational transition is absent. From question 6 on homework 7, this gives us

$$21.18 \text{ cm}^{-1} = \frac{\hbar^2}{\mu r^2} \quad (9)$$

which yields  $r = 1.27 \text{ \AA}$ .

b) From Figures 1 and 2 estimate the force constant of the  $^1\text{H}^{35}\text{Cl}$  bond.

Solution:

Averaging peaks (b) and (c) gives the pure vibrational transition at  $2885 \text{ cm}^{-1}$  which gives

$$2885 \text{ cm}^{-1} = \hbar\omega = \hbar\sqrt{k/\mu} \quad (10)$$

which yields  $k = 480.9 \text{ N/m} = 480.9 \text{ J/m}^2$ .

c) For each of the peaks marked in Figure 2, which are for the  $^1\text{H}^{35}\text{Cl}$  molecule, predict the corresponding peak locations for the  $^2\text{H}^{37}\text{Cl}$  molecule. Use  $^2\text{H} = 2.0141 \text{ amu}$  and  $^{37}\text{Cl} =$

36.9659 amu. Assume the force constant is unchanged upon isotopic substitution. Assume the equilibrium bond length is unchanged upon isotopic substitution.

Solution:

For  ${}^1\text{H}^{35}\text{Cl}$  the reduced mass is  $\mu = 0.979569$  amu and for  ${}^2\text{H}^{37}\text{Cl}$  reduced mass is  $\mu = 1.910031$  amu. This gives the ratio of reduced masses as 1.9499 and the square root of the ratio as 1.3964.

Thus the pure vibrational transition  $\Delta n = 1$  is at  $2885/1.3964 = 2066.06 \text{ cm}^{-1}$  and the pure rotational spacing is  $21.18/1.9499 = 10.862 \text{ cm}^{-1}$ .

Thus the peaks are at:

- (a)  $2066.06 - 2(10.862) = 2044.34 \text{ cm}^{-1}$ .
- (b)  $2066.06 - 1(10.862) = 2055.20 \text{ cm}^{-1}$ .
- (c)  $2066.06 + 1(10.862) = 2076.92 \text{ cm}^{-1}$ .
- (d)  $2066.06 + 2(10.862) = 2087.78 \text{ cm}^{-1}$ .