The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3420: Physical Chemistry II — Spring 2009

Homework 8

Due in Class: Wednesday, April 15, 2009

As promised, it is time for you to analyze the high-resolution IR spectrum of HCl. A copy of the spectrum is on the attached to this paper. To help you perform the analysis, here is a suggested strategy:

1. Label the P and R- branches of the spectrum. Remember that the x-axis of this particular spectrum is reversed, wave number (and energy) increases toward the left.
2. Label each peak with an initial rotational quantum number (J) and a final rotational quantum number (J_f).

   There are many sets of doublets in the spectrum, which arise from the natural mix of $H^{35}Cl$ and $H^{37}Cl$ in the sample that was analyzed. We will first focus on the larger peaks which are from the more abundant isotope, $H^{35}Cl$.
3. Translate the J value for each peak into the parameter m that we discussed in class. This will enable us to fit both branches of the spectrum. Note: there is no peak for $m = 0$.
4. Prepare an Excel spreadsheet with two columns: m and the wave number of the corresponding $H^{35}Cl$ peak. Fill in the columns using your assigned m values and the wave numbers from the data (of the larger peak in each case).
5. Plot the observed wave numbers of the $H^{35}Cl$ peaks versus m in a scatter plot. Add a polynomial trend line of 3rd order. Be sure to instruct Excel to print the equation on the graph.
6. The equation for the cubic trend line will be displayed on your plot, but will not have the correct amount of significant figures. Double click on the equation and in the "Numbers" tab instruct Excel to use scientific notation and use 6 decimal places.
7. Use the coefficients of the trend line along with the equation developed in class to solve for the parameters $\overline{D}$, $\overline{\alpha}_e$, and $\overline{B}_e$. Using $\overline{B}_e$, calculate the equilibrium bond length (R_e) for $H^{35}Cl$. You will need to lookup the atomic masses of the ^{35}Cl isotope of chlorine and ^{1}H in order to calculate the reduced mass of the molecule. Compare the calculated values to the data in Table 13.2 in the handout "Molecular Spectroscopy"
8. Add a third column to your spreadsheet. This column will be for the observed wave numbers corresponding to the $H^{37}Cl$ peaks. Record these values for the appropriate m. Note: since these peaks are smaller, you will not have values for the peaks with larger m values.
9. Repeat the analysis using the $H^{37}Cl$ peak data.
10. Compare the constant term of each of your polynomial fits, which is equal to ν_o, the fundamental frequency of the anharmonic oscillator ($\overline{\nu}_e - 2\overline{\nu}_e x_e$). Do the values make sense in terms of the two isotopes we are considering?

You will need to turn in the following for this assignment:

- A labeled copy of the IR spectrum with J, J_f, and m for each set of peaks.
- A table with your m values and the corresponding wave numbers for $H^{35}Cl$ and $H^{37}Cl$.
- A plot for each isotope including the cubic (3rd order polynomial) fit and equation.
- The calculations described in (7) above for both isotopes.
- A comparison of your calculated values with literature data for $H^{35}Cl$ and a brief discussion of point (10).