Vibration- Rotation Spectroscopy of HCl and DCl

Purpose: To determine the fundamental vibration frequency and bond length for $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$ and to compare the isotope effects to theoretically predicted values.

Introduction

   Vibration spectroscopy is one of the most important tools for the accurate determination of molecular structure. Vibration spectroscopy also plays an important role in environmental chemistry. For example, the albedo of the earth's atmosphere is controlled by the absorption of infra-red light by green house gasses, which include CO_2, H_2O, and CH_4. For normal modes that have a changing dipole moment, the vibrational spectrum of a molecule is observable using infra-red absorption. Such modes are said to be IR active. Raman spectroscopy is used to observe normal modes that are not IR active. The fundamental vibration frequency of a normal mode is dependent on the isotopes of the atoms that are involved. Therefore, vibration spectroscopy is a very useful way to study isotope effects.
   In this exercise we will determine the fundamental vibration frequency and bond length for $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$. The shift in fundamental vibration frequency and rotational constant with isotopic substitution will also be predicted and compared to the experimental values. Because of the natural abundance of ^{35}Cl and ^{37}Cl, the HCl spectrum will contain peaks for both isotopes $H^{35}Cl$ and $H^{37}Cl$. Similarly, the DCl spectrum will contain peaks for both $D^{35}Cl$ and $D^{37}Cl$. The isotopic abundance of ^{37}Cl is 24.22%, so the peaks for the ^{37}Cl containing molecules are one-third the height of the ^{35}Cl containing molecules.

Theory

   The vibrational energy of a diatomic molecule using the harmonic oscillator approximation is:

$$E_\upsilon = h\nu_o (\upsilon + {}^1/_2) \tag{1}$$

where ν_o is the fundamental vibration frequency in s^{-1} and υ is the quantum number for the vibration, Figure 1. The rotational energy for a diatomic molecule using the rigid-rotor approximation is:

$$E_J = \tilde{B}_o \, hc \, J(J+1) \tag{2}$$

where $\tilde{B}_o$ is the rotational constant expressed in cm^{-1}, J is the quantum number for the rotation, and each rotational level has a degeneracy of $g_J = 2J+1$. The crucial connection with molecular structure is through the relationship of ν_o with the force constant for the bond, k:

$$\nu_o = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3}$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ (4)

and the dependence of the rotational constant on bond length, R_o:

$$\tilde{B}_o = \frac{\hbar}{4\pi I c} = \frac{\hbar}{4\pi \mu R_o^2 c} \tag{5}$$

where the moment of inertia $I = \mu R_o^2$ for a diatomic molecule.
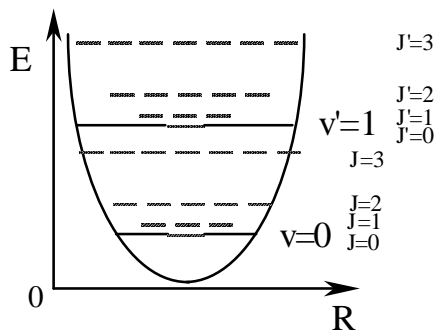

Figure 1. Rotation-vibration levels in a diatomic molecule.

Consider a transition from an initial rotation-vibration state given by the quantum numbers υ, J to a final rotation-vibration state υ', J', Figure 2. This transition is symbolized by $\upsilon',J'\leftarrow\upsilon,J$, where the order is upper←lower. The fundamental vibration transition is from the $\upsilon=0$ to $\upsilon=1$ levels. Most molecules are found in their lowest energy vibration state, $\upsilon=0$. However, the Boltzman distribution of molecules among the rotational levels produces a wide range of initial rotational states. Therefore, the fundamental vibration of a molecule consists of a series of closely spaced lines that correspond to the $\upsilon=0$ to 1 vibrational transition and wide range of rotational transitions, $1,J'\leftarrow0,J$. The selection rule for rotational transitions is that $\Delta J = \pm 1$. For example, $1,1\leftarrow0,0$, $1,2\leftarrow0,1$, $1,3\leftarrow0,2$ have $\Delta J = +1$, and are said to be part of the R-branch. Also, $1,0\leftarrow0,1$, $1,1\leftarrow0,2$, $1,2\leftarrow0,3$ have $\Delta J = -1$, and are part of the P-branch. The $\Delta J = 0$ transition is forbidden and is therefore absent, which would otherwise give the Q branch.
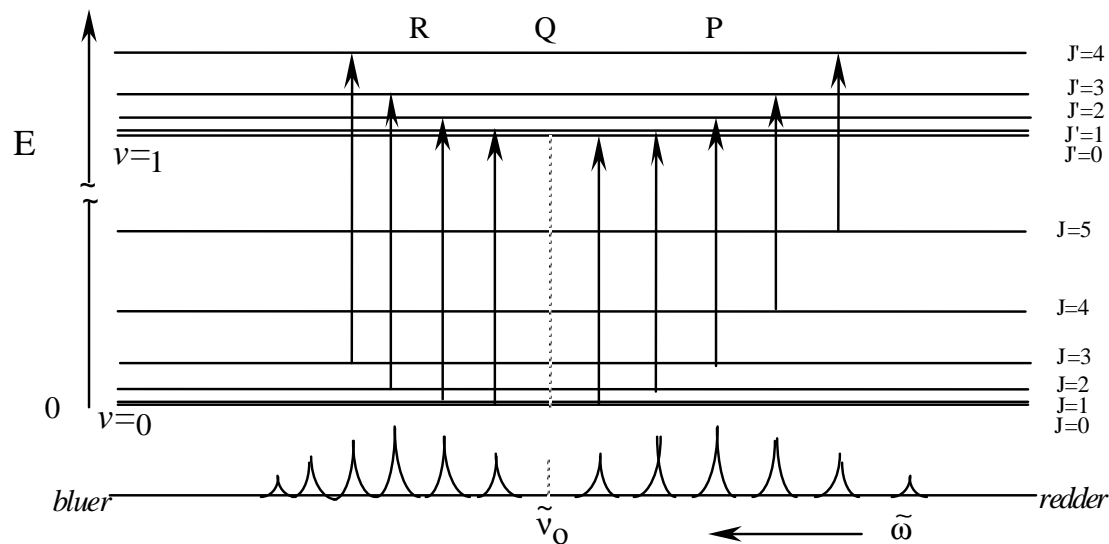

Figure 2. Rotation-vibration transitions for a diatomic molecule.

The energy change for the transitions are:

$$\Delta E_{\upsilon',J'\leftarrow\upsilon,J} = E_{\upsilon',J'} - E_{\upsilon,J} = h\nu_o \, (\upsilon' - \upsilon) + \tilde{B}' \, hc \, J'(J'+1) - \tilde{B} \, hc \, J(J+1) \qquad (6)$$

If the bond length of the molecule doesn't change much on going to the higher vibrational state then $\tilde{B}' = \tilde{B}$ and Eq. 3 simplifies to:

$$\Delta E_{\upsilon',J'\leftarrow\upsilon,J} = h\nu_o \pm 2\tilde{B} \, hc \, J \tag{7}$$

where J is the rotational quantum number for the lower level. This simplification gives the spectrum as a series of equally spaced lines with the spacing between adjacent lines, Figure 3:

$$\Delta E_{\upsilon',J'\leftarrow\upsilon,J+1} - \Delta E_{\upsilon',J'\leftarrow\upsilon,J} = 2\tilde{B} \, hc \, (J+1) - 2\tilde{B} \, hc \, J = 2\tilde{B} \, hc \tag{8}$$
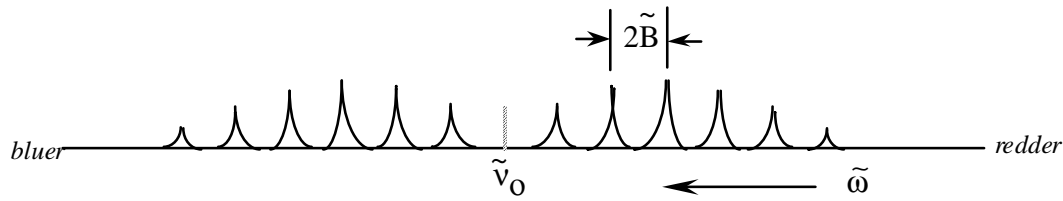

Figure 3. Rotation-vibration spectrum for a transition where the bond length remains constant.

However, for our case, the bond length does change significantly, so that Eq. 6 must be used. The dependence of the rotational constant on the vibration level can be expressed as a Taylor series expansion in $(\upsilon + 1/2)$. Keeping only the linear term gives:

$$\tilde{B}_\upsilon = \tilde{B}_o - \tilde{\alpha}_e (\upsilon + 1/2) \tag{9}$$

where $\tilde{\alpha}_e$ is the vibration-rotation interaction constant in cm^{-1}, which is also called the Coriolis constant. Eq. 6 can be expressed entirely in wavenumbers by dividing by hc:

$$\tilde{\nu} = \Delta E_{\upsilon',J'\leftarrow\upsilon,J}/hc = \tilde{\nu}_O (\upsilon' - \upsilon) + \tilde{B}' J'(J'+1) - \tilde{B} J(J+1) \tag{10}$$

where $\tilde{\nu}$ is the wavenumber of the transition in cm^{-1} and $\tilde{\nu}_O$ is the fundamental vibration frequency also in cm^{-1}. Substituting Eq. 9 into Eq. 10 and taking $\upsilon'-\upsilon=1$ gives:

$$\tilde{\nu} = \tilde{\nu}_o + (\tilde{B}_o - \tilde{\alpha}_e (\upsilon + 1/2)) J'(J'+1) - \tilde{B}_o J(J+1) \tag{11}$$

For the R-branch, where $\Delta J=+1$ giving J'=J+1, Eq. 11 simplifies to:

$$\tilde{\nu}_R = \tilde{\nu}_o + (2\tilde{B}_o - 3\tilde{\alpha}_e) + (2\tilde{B}_o - 4\tilde{\alpha}_e) J - \tilde{\alpha}_e J^2 \tag{12}$$

For the P-branch, where $\Delta J=-1$ giving J'=J-1, Eq. 11 simplifies to:

$$\tilde{\nu}_P = \tilde{\nu}_o - (2\tilde{B}_o - 2\tilde{\alpha}_e) J - \tilde{\alpha}_e J^2 \tag{13}$$

Eqs. 12 and 13 can be combined by defining a new variable m, where m=J+1 for the R-branch and m=-J for the P-branch[1]:

$$\tilde{\nu}_m = \tilde{\nu}_o + (2\tilde{B}_o - 2\tilde{\alpha}_e) m - \tilde{\alpha}_e m^2 \tag{14}$$
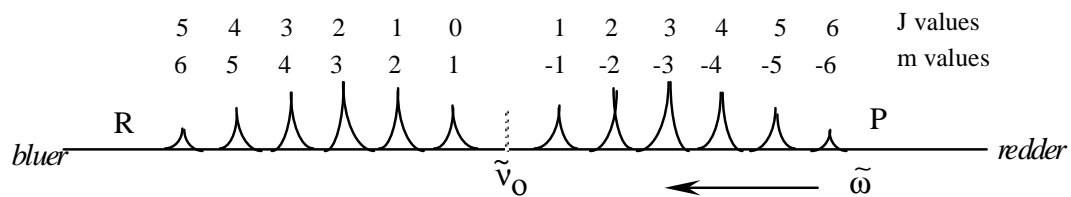
Figure 4. Line indexing for Eq. 14

Eq. 14 is a quadratic equation, that is, it is a second order polynomial. Least squares curve fitting works well for polynomials, just like it does for straight lines. The polynomial coefficients are related to the parameters in Eq.14 as follows:

$$y = c + b\, x + a\, x^2 \tag{15}$$

with the independent variable x = m and where

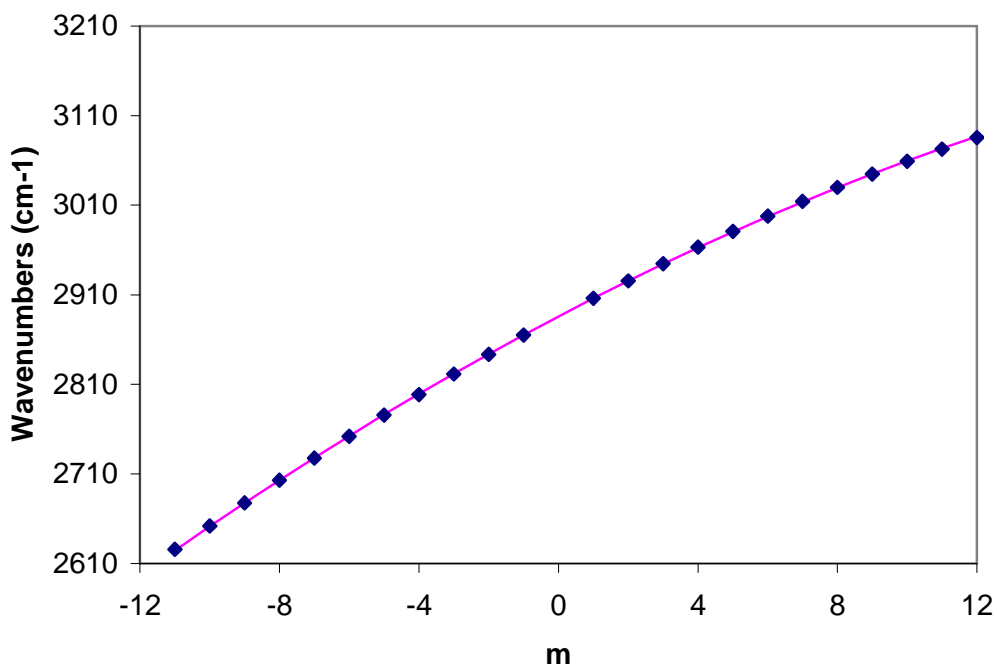$$c = \tilde{\nu}_O \qquad b = (2\tilde{B}_O - 2\tilde{\alpha}_e) \qquad a = -\tilde{\alpha}_e \tag{16}$$

Figure 5. Quadratic curve fitting to the peak positions for $H^{35}Cl$ using m=J+1 for the R-branch and m= -J for the P-branch.

Isotope Effects:

$H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$ each have unique spectra because the substitution of different isotopes changes the reduced mass of the molecule, Eq. 4. H atoms have the largest change in

isotopic mass of all atoms, a factor of ~2 in substituting D (i.e. ^{2}H) for H (i.e. ^{1}H). The study of isotope effects, especially upon deuteration is an important tool in mechanistic organic chemistry. From Eq. 3, theory predicts that the ratio of the fundamental vibration frequency for two different isotopically substituted versions of the same molecule,1 and 2, is:

$$\frac{\tilde{\nu}_o(1)}{\tilde{\nu}_o(2)} = \frac{\sqrt{\frac{k(1)}{\mu(1)}}}{\sqrt{\frac{k(2)}{\mu(2)}}} \tag{17}$$

If the bond strength of the two molecules is the same, the force constants will be the same and Eq. 17 reduces to:

$$\frac{\tilde{\nu}_o(1)}{\tilde{\nu}_o(2)} = \sqrt{\frac{\mu(2)}{\mu(1)}} \tag{18}$$

For example, in going from H^{35}Cl to D^{35}Cl the reduced mass increases by a factor of about 2 (precisely 1.9440) so the fundamental vibration frequency should decrease by a factor of about $\sqrt{2}$. This decrease is good to keep in mind when looking for the spectrum of DCl during your lab. Similarly, from Eq. 5 the ratio of rotational constants for two different isotopically substituted molecules assuming that each molecule has the same bond length is:

$$\frac{\tilde{B}_o(1)}{\tilde{B}_o(2)} = \frac{\mu(2)}{\mu(1)} \tag{19}$$

In using $\tilde{\nu}_o$ and $\tilde{B}_o$ we have not corrected for anharmonicity or centrifugal distortion, respectively, which will case a small deviation between the theoretical and experimental ratios.

Procedure

HCl gas is available in anhydrous form from lecture bottles. The gas cell will be filled from the lecture bottle source using a vacuum line. The gas cell has KBr windows to allow a wide spectral range. Remember that KBr windows are hydroscopic. <u>Water in any form should be carefully excluded</u>. Sources of water include finger prints, your breath, and solvents such as alcohols and acetone. Finger prints are permanent. Methylene chloride is a suitable solvent for cleaning cell windows. Instructions will be supplied in the laboratory for filling the gas cell. The pressure in the cell should be kept as low as possible to avoid collisional line broadening that will decrease the accuracy of the wavenumber determination. At the same time the pressure in the gas cell should be high enough to provide sufficiently good signal-to-noise for accurate determination of the line maxima. A typical target pressure is around 50 torr.

The Generation of DCl

DCl gas is easily generated by the reaction:

$$NaCl\ (s) + D_2SO_4\ (l) \rightarrow DCl\ (g) + NaDSO_4\ (s)$$
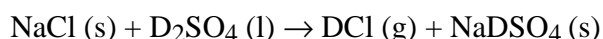
using concentrated D_2SO_4, which is commercially available. Concentrated D_2SO_4, like concentrated sulfuric acid, is very corrosive. So be extremely careful to avoid spills. If any gets

spilled, clean up the spill immediately with lots of water. A convenient apparatus for the reaction is shown below:
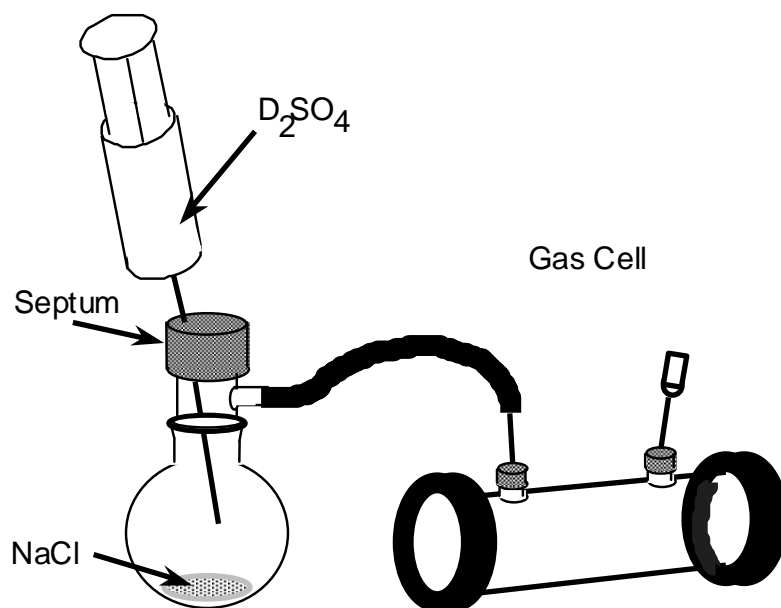
This procedure produces a gas cell filled with a mixture of air, water vapor, and DCl. The background gasses increase collisional line broadening. However, since the spectroscopic constants for DCl produce bigger differences in the rotational spacing, poorer resolution is tolerable, compared to the HCl case. KCl or NaCl windows cannot be used because of the small amount of water vapor and D_2SO_4 vapor produced. Instead, CaF_2 windows are used. The absorption spectrum of CaF_2 does not interfere with the DCl absorption spectrum.

Procedure: Add about 2 g of NaCl to a 25-mL round bottom flask. Use a gas cell with septa on the inlet tubes and CaF_2 cell windows. Some water and D_2O is generated that would fog normal NaCl cell windows, so we use CaF_2 windows instead. Connect the gas cell as shown. Fill a plastic syringe with about 2mL of concentrated D_2SO_4. When you fill the syringe, work quickly to avoid exposure to moisture in the air, which will exchange H^+ for D^+ ions and decrease the purity of your D_2SO_4. Reseal the D_2SO_4 bottle quickly and store in a dessicator. Insert the syringe needle through the septum on the 25-mL flask. Add the D_2SO_4 slowly, drop-by-drop at a rate that keeps the froth that forms from leaving the round bottom flask. Allow the gas cell to fill until the rate of frothing decreases. Then remove the needles from the gas cell.
   Make sure to wash the apparatus well, including the septa and tubing. Draw air through the syringe needles to make sure they are dry before storing.
   Cleaning the gas cell :   After you are finished with the gas cell, simply remove the septa in a fume hood and leave overnight to flush out. You don't need to wash the gas cell.

Spectra:
   Acquire the spectrum of HCl using the Mattson Satellite FT-IR. The data should be acquired at 1.0 cm^{-1} resolution to insure accurate wavenumber determination. The resolution of FT-IR instruments increases with the length of travel of the movable mirror.

Login under your Colby user name. Double click on the EZ Omnic icon to start the intsruemnt operating software. Pull down the Experiment menu and choose "hi_res." Next pull down the Collect menu and choose Experiment Setup… Set the following options:

> No. of Scans: 4
> Final Format: % transmittance
> File Handing: ☑ Save Automatically
> Base name: *type in your initials*
> Background Handing: Collect background before every sample

Close out the Experiment Setup dialog. Then click on the "Col Smp" icon to begin data collection. Start with the IR path clear to take a background spectrum. Follw the on-screen instructions. In the Conformation Window at the end of the data scan, click on Yes to Add the spectrum to Window1. In the spectrum display, you can expand around the area of interest by dragging with the left mouse button and then clicking in the highlighted area.

Data Analysis:
   You need to accurately record the position of each peak using the Find Peaks application. You should make sure peaks for $H^{35}Cl$ and $H^{37}Cl$ or for the second spectrum $D^{35}Cl$ and $D^{37}Cl$ are labeled. You need all four series. It is best to work on half of the spectrum at a time. This choice allows for easier reading of the printouts. First click on the Find Pks icon. A threshold line is added to the spectral display. To label more peaks, the threshold needs to be moved closer to the baseline. Move the cursor close to the baseline and click left. You can move the threshold to label all of the peaks of interest.
   Plot your spectrum with the peak labels. To print, first complete the following printer setup. Pull down the file menu and choose Printer Setup and choose the following options:

> Name: HPLaserJet4050 series PS Instrument Lab
> Size: Letter
> Source: Tray 2

Close the Printer Setup dialog. Click on the Print button in the left-hand side of the spectral display screen.
   You may need to print the spectrum in several sections to obtain peak labels for all the important peaks. When finished labeling peaks, click on the Replace button at the top-right of the Label Peaks screen. When you are ready to take your next spectrum, click on the Clear icon in the top icon bar.

Calculations:

   The <u>calculations and report</u> are individual for the remaining labs this semester. Determine the wavenumbers for each line in your spectra for each molecule, $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$. Determine the index, m, for each line. Use these m values to do the four separate polynomial curve fits. The polynomial curve fitting can be done using the "Nonlinear Least Squares Curve Fitting" Web application or an Excel spreadsheet. The Web application is available from the course Web Home page or
> http://www.colby.edu/chemistry/PChem/scripts/lsfitpl.html

Figure 5 is an example polynomial regression using Excel and the "quadest.xls" spreadsheet. This spreadsheet is on the course Lab Web page. The applet or the spreadsheet are necessary, since most curve fitting programs don't provide an estimate of the fit parameter uncertainties. To do your curve fitting using Excel, paste your peak frequencies into the "quadest.xls" spreadsheet. Nonlinear curve fitting algorithms require an initial guess for the fit parameters. These guesses can often be quite bad and still result in a good solution. The spreadsheet starts with the guesses a=0, b=1, and c=0. If you don't get reasonable fit values, you might need to try guesses that are close to the expected values. Given below are the "quadest.xls" curve fitting results. The guesses are in the first row. The final fit results are in the row labeled "new".

	f(x) =	$a \cdot x^2 +$	$b \cdot x +$	c
guess	coefficient	0	1	0
new	coefficient	-0.305971537	20.39985273	2885.823255
uncertainty	"+-"	0.002983592	0.018157459	0.195385111

The row labeled "uncertainty" lists the standard deviation of the fit results. Propagate the uncertainties through to your final results in terms of force constants and bond lengths. Rather than doing a careful propagation of errors treatment, however, you can just use significant figure rules. For example, from the printout above, we see that the fundamental vibration frequency is 2885.82 ± 0.20 cm^{-1}. Therefore, we know the fundamental vibration frequency to five significant figures. However, upon converting ν_o to the force constant, Eq. 3, ν_o is squared. The relative uncertainty of the square of a number is twice the relative uncertainty of the number. So the force constant will have more like 4.5 significant figures. From the printout above, we see that $(2\tilde{B}_o - 2\tilde{\alpha}_e)$ is $20.39985 \pm 0.\,0.018$ cm^{-1}. Therefore, we know the rotational constant to 0.09% or four significant figures. However, upon converting $\tilde{B}_o$ to the equilibrium bond length, Eq. 5, a square root is taken. The relative uncertainty of the square root of a number is half the relative uncertainty of the number. So the bond length will be known to 0.045%, which is better than four significant figures but not quite five.

Note that the units for the reduced mass, μ, are kg molecule^{-1}. Mono-isotopic masses should be used instead of the isotope-averaged atomic masses that are listed in the periodic table. Mono-isotopic masses are listed in the data section of your text or in standard handbooks (Lange's or the CRC). The units for the bond force constant, k, in Eq. 4 are N m^{-1}. A reasonable range for the force constants for stable diatomic molecules is 100-2000 N m^{-1} (for older units 1-20 mdynes/Å). The units in Eq. 5 for the bond length, R_o, are in m. Note also that $\tilde{B}_o$ should be in units of m^{-1}. The conversion from cm^{-1} can be easily done using 1m = 100 cm, or

$$\tilde{B}_o(m^{-1}) = \tilde{B}_o(cm^{-1}) \frac{100 \text{ cm}}{1m}$$

Report:

1. Report the polynomial fit coefficients and the uncertainties for each of the four molecules. Include the curve fit plots. Report the fundamental vibration frequencies, moments of inertia, reduced masses, and bond lengths for H^{35}Cl, H^{37}Cl, D^{35}Cl, and D^{37}Cl. Report the force constant for H^{35}Cl. Make sure to use the proper number of significant figures, but do adjust for the propagation of errors using squares of numbers or square roots as discussed above. List your

significant figures using the "underlining" convention, for example 123.4̲56. In other words, **give a couple extra insignificant digits**, to make checking your calculations easier and in case you get the number of significant figures incorrectly.

2. Compare your values for the bond length to the literature values for $H^{35}Cl$ (only). Your value is not corrected for centrifugal distortion; even so, a very small deviation from the literature value is expected.

3. Calculate the theoretical ratios $\tilde{\nu}_O(1)/\tilde{\nu}_O(2)$ and $\tilde{B}_O(1)/\tilde{B}_O(2)$ using Eqs. 18 and 19 and compare to the experimental ratios for each pair of ($D^{35}Cl/H^{35}Cl$), ($H^{37}Cl/H^{35}Cl$), ($D^{37}Cl/D^{35}Cl$). How well does theory and experiment compare?

4. Finally, answer the following question: how would an increase in temperature change the spectrum of $H^{35}Cl$?

Note: If you compare your value of the force constant to the literature value, you will find a rather large error (but <5%). This is because we didn't correct for anharmonicity. The observed frequency, $\tilde{\nu}_O$, is related to the corrected fundamental vibration frequency, $\tilde{\nu}_e$, through

$$\tilde{\nu}_O = \tilde{\nu}_e - 2\tilde{\nu}_e\chi_e$$

with all values in wavenumbers. The anharmonicity, $\tilde{\nu}_e\chi_e$, for $H^{35}Cl$ is 52.05 cm^{-1} and for $D^{35}Cl$ is 27.1825 cm^{-1}.[2] To compare to literature values of the force constant, first calculate $\tilde{\nu}_e$ and then use Eq. 3 to calculate the force constant.

References:

1. D. P. Shoemaker, C. W. Garland, J. W. Nibler, *Experiments in Physical Chemistry*, 5th. ed., McGraw Hill, New York, N. Y., 1989. Experiment 38.

2. K.P. Huber and G. Herzberg**,** *Molecular Spectra and Molecular Structure**,** v. 4, Constants of diatomic molecules*, Van Nostrand, Toronto, Canada, 1945**.**