

Experiment 6

VIBRATION-ROTATION SPECTROSCOPY OF DIATOMIC MOLECULES

IMPORTANT: The cell should be stored in the dessicator when not in use to prevent moisture in the atmosphere (Yes, this is Delaware!!!) from injuring the cell windows.

Theory

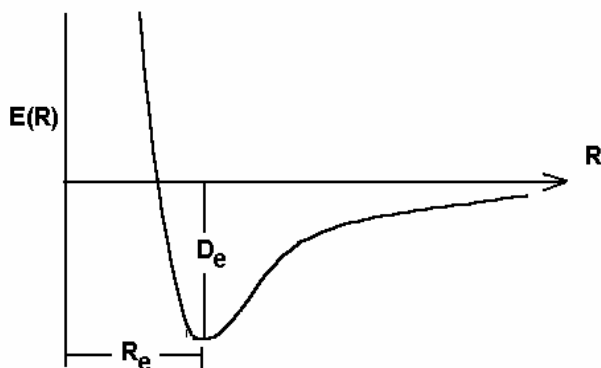


Figure 6.1. The effective internuclear potential as a function of internuclear separation.

For a diatomic molecule, the interaction of the nuclei may be viewed in terms of an effective electron-mediated potential energy that depends on nuclear separation, $E(R)$. [Figure 6.1.] R is the internuclear separation and R_e the equilibrium separation. D_e is the equilibrium electronic energy relative to the vacuum, or the “well depth”. The relative nuclear motion occurs subject to this average potential. In quantum mechanics, one solves Schroedinger’s equation for the nuclear motion to give the eigenstates and their energies as a function of the quantum numbers:

$$E = E_{\text{electronic}} + E_{\text{vib}} + E_{\text{rot}} \quad (6.1)$$

The energy consists of an electronic contribution, D_e , a vibrational contribution, E_{vib} , and a rotational contribution, E_{rot} , each with its own quantum numbers. In the **harmonic approximation**, the vibrational energy depends on a quantum number, n , which can be any non-negative integer:

$$E_{\text{vib},n} = \left(n + \frac{1}{2} \right) hc \omega_e, \quad (6.2)$$

for which c is the speed of light in free space, and ω_e is the fundamental vibrational frequency determined by the force constant, k , and the reduced mass, μ .¹

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}. \quad (6.3)$$

The energy in equation (6.2) is correct only if the molecule is subject to a harmonic potential [i.e. $V = \frac{k}{2}(x - x_{eq})^2$]. One can relax this assumption through inclusion of anharmonic terms to give a more complete description of the vibrational energy. The resulting expression for the vibrational energy is a sum of contributions:

$$E_n = \left(n + \frac{1}{2}\right)\omega_e - \left(n + \frac{1}{2}\right)^2 x_e \omega_e + \left(n + \frac{1}{2}\right)^3 y_e \omega_e + \dots \quad (6.4)$$

The additional terms contain energy parameters $x_e \omega_e$, $y_e \omega_e$, ... that account for the anharmonicity of the potential function. Usually only the first correction term is of significance and the sum is truncated with only the harmonic and first anharmonic terms. Typical data for several diatomic molecules are given in Table 6.1.

Table 6.1. Ground-state Spectroscopic Constants of Selected Diatomic Molecules^a

Molecule	ω_e/cm^{-1}	$x_e \omega_e/\text{cm}^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}
¹ H ₂	4395.2	117.91	60.81	2.993
¹² C ¹⁶ O	2170.21	13.461	1.9314	0.01748
¹ H ⁷⁹ Br	2649.67	45.21	8.473	0.226
¹ H ¹⁹ F	4138.52	90.069	20.939	0.770
² H ¹⁹ F	2998.25	45.71	11.007	0.293

^a J. H. Noggle, *Physical Chemistry*, 3rd Edition, Addison-Wesley-Longmans, New York, 1996.

Vibrational Spectroscopy

When a sample is put in contact with a radiation field, it may take up or emit energy by having molecules change state. The energy exchange only occurs if the energy spacing in the molecule is equal to the quantum of energy of the field, ω .

$$E_{final} - E_{initial} = \omega \quad (6.5)$$

For the moment consider only changes in vibrational energy of a diatomic molecule such as HCl or CO.² For most molecules, $hc\omega_e \ll k_b T$ near room temperatures.³ Therefore, most molecules in a sample are in the lowest-energy (or ground) vibrational state ($n = 0$). Under these conditions, one only considers transitions from this state to explain absorption spectra, i.e. $E_{initial} = E_{vib,0}$. Whether a transition occurs depends not only on the energy-matching, but on quantum mechanical selection rules. There are two important selection rules. For infrared spectroscopy, the molecule must have a dipole moment and transitions are allowed between all states:

$$\Delta n = \pm 1, \pm 2, \pm 3, \dots \quad (6.6)$$

¹ Various units are used to express energy. If h has units of energy×time, then ω_e will have units of length⁻¹. A common unit for infrared spectroscopy is the cm⁻¹ (or wavenumber). The official IUPAC/IUPAP name for this unit is the kayser. From this point forward, the energy will be expressed in cm⁻¹.

² Later we add the possibility of rotational-energy transitions.

³ k_b is Boltzmann's constant, $1.380\ 6503 \times 10^{-23} \text{ J K}^{-1}$.

Since the ground state is so heavily populated under typical conditions, the dominant feature of vibrational spectroscopy is the transition from $n = 0$ to $n = 1$, called the **fundamental**. To within the first anharmonic correction, the energy of the photon necessary to excite this transition is:

$$\Delta E_{\text{vib}} = \omega_e - 2x_e \omega_e. \quad (6.7)$$

Transitions in which the energy changes by more than 1 quantum are allowed. For example, the $n = 0 \rightarrow n = 2$ transition is known as the **first overtone** and occurs at an energy:

$$\Delta E_{\text{overtone}} = 2\omega_e - 6x_e \omega_e \quad (6.8)$$

to the same level of approximation.

Single-quantum ($\Delta n = \pm 1$) transitions from states with $n > 0$ are allowed, but the smaller populations of these states make such transitions less intense and more difficult to observe at room temperature. For example, the transition from the state with $n = 1$ to the state with $n = 2$ occurs at

$$\Delta E_{\text{hot}} = \omega_e - 4x_e \omega_e \quad (6.9)$$

This is close to the fundamental. Such transitions are called **hot bands** because their intensities increase (relative to the fundamental) as one increases the temperature.

Inclusion of Rotational Transitions

In the foregoing discussion, changes in rotational energy were neglected. To analyze infrared spectra properly, one must consider the effects of rotational-energy changes, as well as vibrational-energy changes. In the rigid-rotor approximation, the rotational energy of a diatomic molecule depends on the rotational quantum number, J , as follows.

$$E_{\text{rot},Jm} = \frac{\hbar^2}{2\mu} \left\langle \frac{1}{R^2} \right\rangle J(J+1), \quad (6.10)$$

where the energy, in this equation, is in ergs or joules.

$\langle \dots \rangle$ indicates an average over the vibrational wavefunction. As a first approximation, one treats this as $\frac{1}{R_e^2}$, where R_e is the equilibrium bond distance, given by the minimum in the

potential energy curve of Figure 6.1. The equilibrium moment of inertia $I (= \mu R_e^2)$ and the equilibrium **rotational constant**, B_e , are defined in terms of this quantity.

$$B_e = \frac{\hbar}{4\pi I c} \quad (6.11)$$

and

$$E_{\text{rot},Jm} = B_e J(J+1), \quad (6.12)$$

where the energy and B_e are expressed in cm^{-1} .

Note that the rotational constant of a molecule depends on the moment of inertia, which in turn depends on the reduced mass and the equilibrium bond length. The reduced mass depends on the mass of each isotope. In Table 6.2 are the exact masses of several atoms (expressed on a molar basis).

Table 6.2. Exact Masses of Several Atoms

Atom	Mass (g/mol)	Atom	Mass (g/mol)
^1H	1.0078250	^{16}O	15.9949146
^2H (D)	2.0141018	^{17}O	16.9991312
^{12}C	12 (exactly)	^{35}Cl	34.9688527
^{13}C	13.0033548	^{37}Cl	36.9659026

For a real diatomic molecule, the average over the vibrational state means that the rotation constant is not exactly B_e , but instead depends on vibrational state. The rotational constant including the correction for the vibrational state is given the symbol B_n , where the explicit dependence on the vibrational state is indicated by the subscript. In this way, the rotational energy of a diatomic molecule in a state with quantum numbers, n , J and m is given by:

$$E_{nJm} = B_n J(J+1) \quad (6.13)$$

Perturbation theory gives the vibration-dependent rotation constant, in a first approximation, as:

$$B_n = B_e - \alpha_e \left(n + \frac{1}{2} \right). \quad (6.14)$$

α_e is the vibration-rotation constant that describes how the vibrational state affects the rotational energy. In analyzing spectra, it is treated as a parameter to be determined, just like B_e .

In addition to this correction, there is another purely rotational perturbation that changes the rotational energy of a state - the **centrifugal distortion**. This is taken into account by an additional term in the energy that is determined by the centrifugal distortion coefficient, D_c . With all these definitions, the total internal energy of a diatomic molecule in a state with quantum numbers n , J and m is:

$$\frac{E_{n,Jm}}{hc} = D_e + \left(n + \frac{1}{2} \right) \omega_e - \left(n + \frac{1}{2} \right)^2 x_e \omega_e + B_n J(J+1) - D_c J^2(J+1)^2 \quad (6.15)$$

Because the energy separations of the rotational states (each having a different value of J) may not be much greater than $k_b T$, a sample may contain appreciable numbers of molecules in excited rotational states, even at room temperature. Thus, when rotational energies are considered, transitions from states with various values of J are seen in a spectrum.

Vibration-Rotation Spectroscopy

Infrared spectroscopy concerns changes of vibrational and rotational state, without change of electronic state. Hence, the infrared spectrum is a **vibration-rotation spectrum**. The usual selection rules are:

- $\Delta n = \pm 1$ (Transitions of higher order are known as overtone bands and occur at higher frequencies; we shall not consider them further here, except in the Discussion Questions.)
- $\Delta J = \pm 1$ (for the heteronuclear diatomic molecules examined here)
- The molecule must have a permanent dipole.

Considering only transitions that involve the ground vibration state, the energy change is:

$$\begin{aligned} \Delta E = \omega_e - 2x_e \omega_e + B_e [J'(J'+1) - J(J+1)] - \frac{\alpha_e}{2} [3J'(J'+1) - J(J+1)] \\ - D_c [J'^2 (J'+1)^2 - J^2 (J+1)^2] \end{aligned} \quad (6.16)$$

with the quantum number of the initial rotational state being J and that of the final rotational state being J' . When $J' = J + 1$, there is a net absorption of rotational energy; when $J' = J - 1$, there is a net emission of rotational energy (although overall there is absorption of energy). Transitions of the former kind form the **R branch** and those of the latter form the **P branch** of

the spectrum.⁴ Using equation (6.16), the approximate energies of transition depend on the quantum number J for the initial state. Neglecting the centrifugal distortion terms, this gives:

$$\Delta E = \omega_e(1-2x_e) + 2(B_e - \alpha_e)(J+1) - \alpha_e(J+1)^2 \quad R \text{ branch} \quad (6.17)$$

$$\Delta E = \omega_e(1-2x_e) - 2(B_e + \alpha_e)J - \alpha_e J^2 \quad P \text{ branch}$$

The infrared spectrum consists of a series of transitions due to the different rotational states involved. One apparent quality of such a spectrum is the variation in intensity of these lines. The intensity distribution gives the relative probabilities of occupation of the initial rotational states (those with quantum number J). From these intensities, one can define a **rotational temperature**, T_r , for the distribution, assuming it to be Boltzmann in form. The intensity of a line that arises from the state with quantum number J (compared to that for the line that comes from a state with $J = 0$) is given by the following equation that accounts for the Boltzmann factor and the degeneracy of the rotational level.

$$\frac{I_J}{I_0} = \frac{N_J}{N_0} = \frac{g_J}{g_0} \exp[-(E_J - E_0)/k_b T_r] = (2J+1) \exp[-B_n hc J(J+1)/k_b T_r] \quad (6.18)$$

A comparison of intensities allows one to estimate T_r ; or, knowing T_r , one may estimate B_n . In some experiments in which systems are perturbed by laser excitation, one can change the distribution of molecules in the rotational states (at least for a sufficiently long time to make a measurement) such that the “rotational temperature” is different from the laboratory temperature. The use of the intensity distribution can be used to predict the T_r . Under the conditions of this experiment, the rotational degrees of freedom are in equilibrium with the translational degrees of freedom and the rotational temperature is the same as the laboratory temperature.

Quantum Calculations

The theory above assumes that the potential energy function is known or can be approximated. In actuality, this function is an integral over the electronic wave function of the molecule. Thus, empirical parameters that describe the function like the force constants are related to integrals over the electronic state of the molecule. To calculate these, one must have knowledge of the electronic state of the system. With present-day computers, one may do numerical estimations of the electronic wave functions rather easily and with quite good precision.⁵ Once known, the functions can be numerically integrated to give estimates of the values of parameters such as the force constant, k , or the fundamental frequency, ω_e , based on that estimates of the wavefunctions for that particular electronic state.

Many complex operations involved in such calculations have been collected into “canned” programs such as GAUSSIAN03⁶ or SPARTAN, so that the chemist can use the computer without dealing with problems of computer programming or numerical analysis. However, there is a great deal of chemical knowledge one must still bring to bear on the process to obtain reliable results.

⁴ In spectra of diatomic molecules, the transition for which $\Delta J = 0$ is not allowed. This transition is called the **Q branch** of the spectrum. For more complex molecules, this transition may be allowed, and a Q branch may be part of the spectrum, showing as an intense transition between the R and P branches.

⁵ Only a few years ago, such calculations were only done by a rather small number of experts on rather large computers. Today they may be done with the aid of a personal computer at one's desk.

⁶ John Pople was awarded the 1998 Nobel Prize in Chemistry principally for the development of GAUSSIAN.

The principal problem one must cope with in carrying out *ab initio* quantum calculations is that any procedure uses some approximation to the molecular electronic wave function(s). The quality of the approximation determines how good calculated properties are. A commonly used method is linear combination of atomic orbitals (LCAO), in which one expresses the molecular electronic wave function (or molecular orbital [MO]) in terms of atomic orbitals of the constituent atoms. Since the forms of atomic orbitals are not well known except for hydrogen, even the choice of functional forms of atomic orbitals is an approximation whose quality will affect the results. The set of functions used is called the **basis**. A commonly used basis is the Slater-type orbitals (STO), but other bases are sometimes used, for example Gaussian-type orbitals. These have esoteric acronyms that denote certain features of the set of orbitals, such as 3-21G or 6-31G or 6-311+G(d,p). In principle, an infinitely large basis set allows one to solve the electronic state exactly. However, that would take a great amount of time, so that calculations are always done with a truncated basis; again, the quality of the results depends on how well the truncated set can be used to approximate the real wave function.

Once chosen, the basis is used to determine the “best” electronic wave function by some criterion, such as minimization of energy. A common method is the Hartree-Fock self-consistent field (HF-SCF) method, which emphasizes the average effects of interelectronic interactions, rather than instantaneous interactions. This iterative method finds parameters of the expansion of the molecular orbital that minimize the variational energy integral. Conveniently, computer programs like GAUSSIAN will do all of the work if one describes the desired basis and situation appropriately, returning useable information on the state in the form of parameters.

CAUTION: HCl and DCl are corrosive gases. ALWAYS handle the materials extremely carefully.

Procedure

Obtaining the Infrared Spectra

The instrument for measuring the spectra is a Nicolet Magna IR 550 FTIR spectrometer. If you have not already learned how to use this instrument, your laboratory instructor will help you with the operating parameters for the instrument. If you have taken instrumental analysis, this instrument will be familiar to you. This instrument has a liquid-nitrogen-cooled detector. **Before beginning any spectroscopy, obtain liquid nitrogen and fill the reservoir until liquid nitrogen overflows the fill hole.**

An important part of getting reliable data is positioning the sample. The cell holder must be positioned accurately to allow the full IR intensity to be detected. Make sure the beam passes through the center of the cell. Take great care in inserting the sample into the sample compartment. Do not force the sample to go in, as that may break the sample. Remember that you must wait after closing the sample compartment to allow the system to be purged; wait at least two minutes after closing the compartment lid.

When obtaining the spectrum of the mixture of HCl and DCl, record all pertinent data so you can have them when doing the analysis.

1. You may wish to take a spectrum of the polystyrene standard as the first thing you do to assure yourself that the spectrometer is working properly. Follow the procedure of collecting a background and then taking a spectrum of the sample.
2. For the samples of gases, we have made a cradle into which the cell fits. Install the cradle carefully. If it does not fit properly, **do not force it**. Have the laboratory instructor help you.
3. Before taking the spectrum of the gas, take a spectrum of the empty compartment, using the same parameters as you intend to use in the experimental measurement. This is done with the command **Collect Background**. If you have any problems, you should immediately take a spectrum of the polystyrene standard to confirm proper operation of the spectrometer.
4. Carefully insert the cell into the cradle. Again, if it does not fit easily into the space, see the laboratory instructor before proceeding.
5. Take a spectrum of the HCl/DCl sample using the **Collect Spectrum** command. Unless otherwise specified, accept the default values supplied by the program. When asked a question by the program, reply with "Yes". Unless otherwise specified, all "click" operations are done with the left mouse button. HCl is an impurity in DCl that can be identified because of its lower signals in the spectrum. Be sure this is at a resolution high enough to identify the sharp features of the R and P bands of both materials.
6. Use subtraction of the background to obtain a reasonable high-resolution spectrum if necessary. This is done automatically by the software for the Nicolet spectrometer.
7. Look at the spectrum to be certain you see both the bands of the HCl and DCl. There may be other bands from a bit of water vapor in the compartment, and there are some bands from the epoxy that holds the windows on some cells. The important point to consider is whether you can detect the spectra of HCl and DCl easily.
8. When you have the spectrum recorded, save the data on a 3.5" floppy disk or on a flash drive so that you may analyze the data later. Use the **Save As** command, being sure the file type is CSV. You should be able to import this file into a program like EXCEL on your computer for creating a graph and precisely reading the peak positions.
9. Obtain a spectrum of the CO sample in the same manner.
10. Sign the logbook.

Calculational Chemistry

The calculations are done on PCs in the laboratory. There are two operations: (1) setting up the calculation with GaussView, and (2) running a Gaussian calculation. Subsequently one can view the results with GaussView. Start the PC, using the password provided.

1. Click on the GaussView icon. This should display the main menu of GaussView.
2. To build the HCl molecule. Click of the atom icon of the main display; this gets you to the periodic table. Then click on the "Cl" on this display. Close that display (called the Builder). You should see an HCl molecule in the **Current Fragment** display.
3. Click on the "New" file window and this should put a copy of the HCl molecule into your new file.
4. Click on the bond length icon on the main menu. This will cause the Current Fragment display to become white. Go to the HCl window. Click first on either the H or Cl atom and then on the other. A window should open with a slider to set the length of the bond. Set it at some distance (in Angström units) such as 1.35.

5. Go to the **Calculate** menu and select **Gaussian**. This will bring up the **Calculate** menu in a window with various tabs. Make sure that the Calculation Type is **Energy**. In the Title box, you may type a title such as "HCl, 1.35 Å". Leave everything else at **Default**.
6. Submit the job. The program will ask you to save an input file. Use a name like **HCl135**. Make certain it is saved as a Gaussian job file. The calculation should start at this point. This calculation uses the Hartree-Fock approximation, which gives a reasonably good approximate solution to Schrödinger's equation.
7. When the calculation is done (about a minute for this work), the computer opens a window telling you the job is finished. From the GaussView **File** menu open this file. You must indicate that the output file ends with the extension **.log** or **.out** to get output. You can read the file from GaussView using the **Results** menu. You may simply click on **Summary**, which will cause a box with pertinent results to be shown. You may view the entire file as well.
8. If you are looking at the full file, the output begins with a lot of preliminary stuff. Search the file to find the line that begins with **SCF Done**. The quantity called **E(RHF)** is the calculated energy of the molecule, in atomic units, a. u. or hartrees.⁷ This reported energy is the total energy, that is, the energy required to separate all of the electrons and nuclei to infinity. Record this number along with the internuclear separation in your notebook.
9. Repeat this calculation for a series of different bond lengths. It is easiest to call back in the first file you made, click on the two atoms after clicking on the bond length icon and setting the new length. Save the file with a unique name that will help you to identify which file corresponds to which bond length upon starting the Gaussian calculation. Use a set of bond lengths such as 1.35 Å, 1.45 Å, 1.40 Å, 1.30 Å, 1.25 Å, 1.20 Å, 1.15 Å.
10. With a file having the bond length giving the lowest energy above, set up a new calculation, choosing **Optimization** of the geometry of HCl. After this calculation is finished, use it as starting point to do a frequency calculation; you have to set the job type to **Frequency**. This calculation reports the vibrational frequency of HCl in wavenumbers and the rotational constant. Be sure to record these numbers from the results, as they need to be reported.
11. When you finish, delete all of the files from the Desktop that you created, empty the Recycle Bin and turn off the computer.

Calculations

Data Analysis of the Spectroscopic Results

1. Analysis of HCl Spectra
 - a. Make a table for $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ of the positions of the lines (in cm^{-1}) and the corresponding values of J .⁸ [This can be conveniently done with a computer program such as Excel.]
 - b. On one graph, plot the line positions of transitions in the R branch versus $J + 1$ and the line positions of transitions in the P branch versus J . [Use a dummy index, m , for $J + 1$ and J to make these plots.]
 - c. By multiple-regression analysis of the plots for both species, determine $\omega_e - 2x_e\omega_e$, B_e , and α_e for each material. (You should do the analysis for both the R and P branches and assume D_c is zero.)⁹

⁷ 1 hartree = 627.51 kcal/mol.

⁸ J is the rotational quantum number of the initial rotational state in each case. Be careful.

⁹ Be sure to include estimates of uncertainty in your values for these parameters.

2. There are several other ways to analyze these data. Physical chemists like to find ways to make a linear plot to obtain data. One way to analyze data is via differences between line positions of adjacent lines in a series. This is particularly useful when the equation is of higher order than 1 or 2. Show that the difference between adjacent lines in the R and P branches are given by the following equations, using equation (6.17):

$$\begin{aligned} R \text{ branch: } \omega_{J+1} - \omega_J &= 2B_e - 5\alpha_e - 2\alpha_e J \\ P \text{ branch: } \omega_J - \omega_{J+1} &= 2B_e + 3\alpha_e + 2\alpha_e J \end{aligned} \quad (6.19)$$

Plot the difference in the lines in the two branches for HCl versus J and extract values of B_e and α_e for $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ by this method.

3. Make a table of line positions for each DCl species and analyze these data by either the method of question 1 or question 2. If you use the second method, you must decide how to obtain $\omega_e - 2x_e\omega_e$.
4. Do an analysis of the spectrum of CO by one of these methods.
5. Summarize all derived results on all gases in a single table. In particular, show the values of parameters derived for HCl and DCl by both method 1 and method 2.

Theoretical Chemistry

6. From the results of step 8 of the Gaussian98 calculations, make a table of bond length and energy. In the table indicate whether increasing or decreasing the bond length lowers the energy at each step of your calculation.
7. Make a plot of calculated energy versus bond length.
8. Compare the optimal bond length determined in the optimization calculation (click on the **Inquire** button, then on the two atoms) with the value, R_e , from your analysis of the IR experiment, with the determined value in the single-point calculations and with literature data.
9. Find the dipole moment at the optimal bond length predicted by this calculation. This is part of the output from the calculation. Compare it with a literature value. [Be sure to quote your literature source.]
10. Compare the calculated values of ω_e for HCl to your experimental value and the literature value. The calculated frequency will be larger than the experimental value. There is a systematic error in the Hartree-Fock predictions of the frequency, making the calculated values about 10% too high for all vibrations. A survey of many calculations produces an empirical correction factor of 0.9085. Apply this correction to your calculated results and compare with the literature and your experimental values.

Discussion Questions

1. Derive equations (6.7) and (6.8).
2. What are the spectroscopic effects of ^{35}Cl and ^{37}Cl ? Explain your result by calculating the first five transitions in the R and P branches of H^{35}Cl and H^{37}Cl .
3. Calculate the moments of inertia of each of the four possible species in the HCl/DCl sample from the rotational constants, B_e , you determined.
4. From each moment of inertia, calculate R_e for each of the **four** isotopomers. Within experimental error, are these bond distances different from each other? Explain your answer.

5. The expected position of the Q branch of HCl is different from that of DCl. What are your experimental values for these? Assuming that the anharmonic term is zero, calculate the ratio of the reduced masses of $^1\text{H}^{35}\text{Cl}$ and $^2\text{H}^{35}\text{Cl}$ from your data for the expected positions of the Q branch. How does this agree with literature data for this quantity?
6. Convert your calculated value of the energy (from the GAUSSIAN calculation) to kcal/mol and compare it with the dissociation energy of HCl, $D(\text{HCl})$, from an appropriate reference.
7. Explain why the IR cell is constructed the way it is. In particular, why is it not made completely out of glass?
8. Uncertainty in FTIR depends on the noise at the detector.¹⁰ In many infrared spectrometers, the signal is a ratio of the detected response to a reference response. Explain, with equations if necessary, why it is necessary to consider the noise in the reference channel as well as the noise in the detector channel when calculating signal-to-noise ratios in FTIR experiments. In what kinds of experiments will this be of concern?

¹⁰ H. L. Mark and P. R. Griffiths, "Analysis of Noise in Fourier Transform Infrared Spectra", *Applied Spectroscopy*, 56, 633-639 (2002).