

E. Experiment #5, Vibrational-Rotational Spectra of H^{35}Cl , H^{37}Cl , D^{35}Cl , and D^{37}Cl

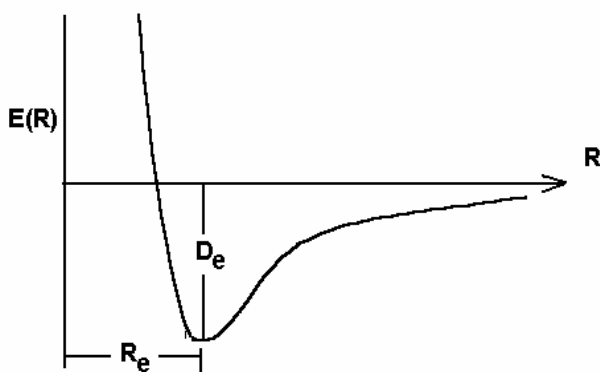
Objectives:

1. Analyze infrared absorption spectra of HCl and DCl gases.
2. Determine the vibration-rotation interaction parameter, vibrational force constants and equilibrium bond lengths for the two isotopomers.
3. Assign the quantum transitions in both the R- and P-branch.
4. Compare/contrast computational predicted values to experimentally obtained values.

Background:

It is recommended that you review the material in Chapter 5 and 13 of McQuarrie and Simon, "Physical Chemistry". These are used as models for vibration and rotation of diatomic molecules, respectively. Pay particular attention to energy levels, how to calculate the vibrational force constant from the vibrational frequency, and the equilibrium bond length from the rotational frequency. Additional information about selection rules for infrared absorption spectra how to extract these frequencies from the measured line positions is given in Chapter 13 of McQuarrie.

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, $E(R)$, Fig. 1. In which R is the internuclear separation, R_e is the equilibrium separation, and 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 Schrödinger's equation for the nuclear motion to give the eigenstates and their energies as a function of the Figure 1. The effective internuclear potential as a function of internuclear separation.

quantum numbers:

$$E = E_{ele} + E_{vib} + E_{rot} \quad (1)$$

The total energy consists of an electronic (E_{ele}), vibrational (E_{vib}), and rotational (E_{rot}) contribution 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.

$$E_{vib} = \hbar\omega \left(v + \frac{1}{2} \right) \quad (2)$$

The simplest model of a rotating diatomic molecule is the rigid rotor model in which the two atoms of mass m_1 and m_2 are considered to be joined by a rigid weightless rod. The allowed energy levels for a rigid rotor may be shown by quantum mechanics to be eq. 3.

$$E_{rot} = B_e J(J+1) \quad (3)$$

In which B_e is the rotational constant (usually given in cm^{-1}). This is a pretty good model for diatomic molecules and it predicts that the spacing between any two adjacent lines in the spectrum is $2B_e$ except for the center gap, which is $4B_e$ (due to the “missing” Q-branch, $\Delta J = 0$).

Real molecules are not really rigid however and are subject to vibration-rotation interactions. When the molecule vibrates its average bond length increases slightly and this decreases the rotational frequency. A more accurate energy level expression (sometimes called the rotational term) is eq. 4.

$$E_{rot} = B_e J(J+1) - \alpha_e \left(v + \frac{1}{2} \right) J(J+1) \quad (4)$$

In which the constant α_e is the vibration-rotation interaction parameter. Notice that the magnitude of this interaction depends on both quantum numbers v and J . The effect of the vibration-rotation interaction is to increase the line spacings in the R branch and decrease the line spacings in the P branch (see below).

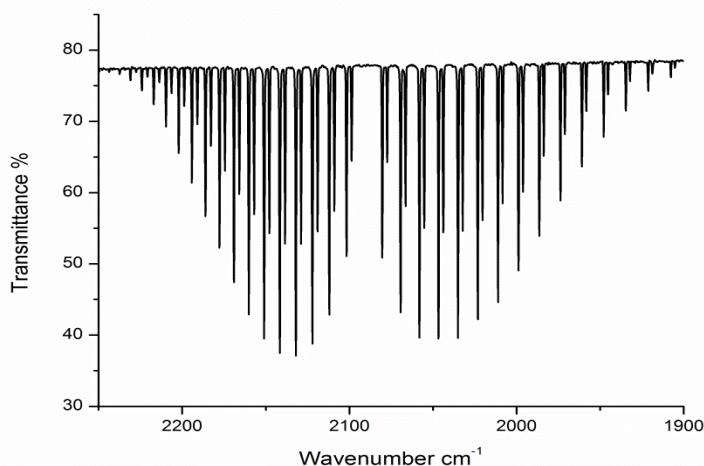


Figure 2. Rovibrational spectra of DCl collected on our IR

vibrational transitions are $\Delta v = \pm 1$, so most of the spectroscopic absorption lines that you will observe in this experiment are associated with the $v = 0 \rightarrow 1$ transition. The different lines that appear in the spectrum are due to different rotational transitions that accompany the vibrational transition. Recall that unlike vibrations, the energy spacings between rotational levels are usually small compared to thermal energies so a large number of rotational states are populated at room temperature.

The spectrum you obtain should appear as two branches (sets of lines about 15-18 lines per set) called the P and R branches (see Fig. 2). Starting from the middle of the spectrum, the first band on the high-frequency side is the R(0) line. These changes in quantum numbers are $v = 0 \rightarrow 1$, $J = 0 \rightarrow 1$. The second line is R(1), which corresponds to $v = 0 \rightarrow 1$, $J = 1 \rightarrow 2$. The third is R(2) and so on. Notice that the R-branch lines are labeled according to the initial value of J . We shall call the initial rotational quantum number J' and the final quantum number J'' . All of the R-branch lines correspond to $\Delta J = 1$ transitions such that $J'' = J' + 1$. The transitions occur at successively higher frequencies because the rotational levels are not evenly spaced. On the low-frequency side of the gap are all of the P-branch lines. These transitions correspond to $\Delta J = -1$ such that $J'' = J' - 1$. The first line is P(1) the second is P(2) and so on. Notice that there is no P(0) line because the final quantum number J'' would be -1 which doesn't exist.

We can express the position of each line in the spectrum as a difference between energy levels. Since all of the lines are associated with the $v = 0 \rightarrow 1$ transition, the line position ν (in cm^{-1}) is given by a

Recall that the energy spacings between vibrational levels are large compared with thermal energies at room temperature. This means that virtually all of the HCl molecules are in the ground vibrational state ($v = 0$). The selection rules for

fundamental vibrational frequency ν_0 and a difference of rotational terms, eq. 5.

$$\nu = \nu_0 + E(v', J') - E(v'', J'') \quad (5)$$

For P- and R-branch lines we make the substitutions $J' = J'' - 1$ and $J' = J'' + 1$, respectively and combine eqs. 4 and 5 to give eq. 6.

$$\begin{aligned} \nu_P &= \nu_0 - (2B_e - 2\alpha_e)J'' - \alpha_e J''^2 \\ \nu_R &= \nu_0 + (2B_e - 2\alpha_e)(J'' + 1) - \alpha_e (J'' + 1)^2 \end{aligned} \quad (6)$$

Notice that these two equations are quite similar and if we define a new variable m , which takes on values of $m = -J''$ for each P-branch line and $m = J'' + 1$ for each R-branch line, all of the line positions can be expressed in a single equation (eq. 7).

$$\nu = \nu_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 \quad (7)$$

The difference in wavenumbers between adjacent lines will be eq. 8.

$$\Delta\nu = \nu(m+1) - \nu(m) = (2B_e - 3\alpha_e) - 2\alpha_e m \quad (8)$$

A graph based on eq. 8 will permit you to calculate both B_e and α_e where the slope is $-2\alpha_e$ and the intercept is $(2B_e - 3\alpha_e)$. The band center ν_0 can be calculated by adjusting the spacing in eq. 8 for a best fit of the linear regression. *It is important to have a graph of the data and the linear regression plus a residuals graph.* The equilibrium vibrational constant can be calculated using eq. 9 and the values given in 10.

$$\nu_e = \nu_0 + 2\nu_e \chi_e \quad (9)$$

$$\nu_e \chi_e(\text{HCl}) = 52.8 \text{ cm}^{-1} \quad (10)$$

$$\nu_e \chi_e(\text{DCl}) = 27.2 \text{ cm}^{-1}$$

The values in eq. 10 can be determined from the overtone spectra of the molecule but doing this is beyond the scope of this class. The force constant, k_e , can be determined using the harmonic oscillator eq. 11 in which $\mu = m_1 m_2 / (m_1 + m_2)$ which is the reduced mass.

$$\nu_e = \frac{1}{2\pi c} \sqrt{\frac{k_e}{\mu}} \quad (11)$$

One of the goals of the experiment is to determine IF the equilibrium bond length R_e and the force constant k_e remain unchanged by isotopic substitution. The bond length is related to B_e by eq. 12.

$$B_e = \frac{h}{8\pi^2 \mu R_e^2 c} \quad (12)$$

Procedure:

1. Record a background spectrum using the evacuated sample cell. The TA will charge the cell first with HCl, and then DCl after the experiment with HCl is finished. Insert the gas cell in the sample compartment and record the sample spectrum.
 - a. Start the IR software by clicking the “Spectrum” icon.
 - b. Navigate to Instrument. Give each sample run a unique name (preferably your initials followed by a number). Scan over the range of 4000 cm^{-1} to 800 cm^{-1} using a resolution of 4 cm^{-1} . Under accessories select “Gas Cell” under sampling, “KBr” under material, and “0.01 M short path...” under Pathlength.
 - c. Take a background using only the evacuated cell, then take a spectra (which should be a straight line).
 - d. Have the TA charge the sample cell (it is important to measure HCl first), and take a spectra. Take note of the frequency region that the interesting peaks show up. Save your spectra in a format compatible with Excel by selecting “Save as” and ascii on each.
 - e. Carefully let the air back into the gas cell, remove the windows (using gloves, being careful to not get them wet with anything), and clean out and dry the inside of the cell. Reassemble and evacuate.
 - f. Start a clean experiment, and under instrument set the sample range to be equal to what you previously recorded [should be around 3200 to 2400] for the HCl, and set the instrument to the highest resolution possible (the smallest number in cm^{-1}) and the number of spectra to 3. Take a new background, and spectra. You should be able to see something similar to figure 2.
 - g. You can save a table of the peak positions by going to process and peak table.
2. Record the spectrum and line positions for DCl following part 1 above.

Processing the Data in Excel

1. In the first column, enter the spectral wavenumbers in decreasing order (for one of the specific isotopomers) leaving an empty cell for the missing Q-branch.
2. In the second column enter the m values as positive above the empty cell and negative below it.
3. In the third column, take the difference between spectral wavenumbers in the first column and place the value in the row next to the lower m value. Now, you will have to guess a value for the Q-branch.

- Next, do a linear regression using m as the **independent variable** and the differences as the **dependent variable**. Use the “=slope”, “=intercept”, and “=rsq” functions in Excel.
- In the fourth column, do the calculation for the differences using the slope and intercept.
- Finally, in the fifth column calculate the residuals.
- Make a graph of spectral wavenumber differences as a function of m (with your calculated values as a line overlaid). Also make a graph of the residuals. The shape of the residuals will help you adjust your guess of the Q-branch, as will the RSQ value. Really, you should fine-tune the Q-branch value to get RSQ as close to 1 as possible.

Computational Study

- Determine R_e (equilibrium bond length) from single point energy (SPE) calculations by changing the bond distance for both HCl and DCl.
 - Determine R_e from optimization calculation.
- Calculate B_e from both 1a and 1b using eq. 12.
 - Calculate B_e based on the energy from the optimized structures obtained from 1b.
- For all calculations use HF/6-31G basis set.

Report:

Using the graphs of peak spacing as a function of m , report the values of B_e , α_e , ν_0 , ν_e , the force constant k_e , and the bond length R_e for all four isotopomers. This information is best done using a table. Clearly show all of your calculations, and declare your constants to 5 significant figures.

What is your conclusion about the effect of isotopic substitution on the above constants from this data? What is the theoretical basis for your conclusion? Compare the predicted value of the isotope shift with the experimentally measured one. Should the force constants and equilibrium bond lengths of the two isotopomers be identical? The questions presented here are not comprehensive, but are meant to be a starting point for your discussion.

For the computational part of the lab you should discuss and compare your results from 1a to 1b as well as 2a to 2b. Make a plot of $E(R)$ from 1a and clearly label R_e and D_e . You should discuss the accuracy of part 1a to part 1b. How close were you able to estimate R_e in terms of % error? Theoretically you should get the same results for B_e from part 2b as you would from using R_e from 1b and eq. 12. Why? Did your results agree?

Discuss. Lastly, compare your computational results for R_e and B_e to experimental results from the first section of the lab. Discuss your results in terms of % error making sure to talk about limitations with both experimental and computational results.