

Experiment 3: The Rovibrational Spectrum of HCl

(was Experiment 4 in the syllabus, but the original Experiment 3 was canceled)

Meet for lab on Thursday, April 10, 10:00 a.m., Olin-Rice 386

Report due on Thursday, April 24 (note change from syllabus)

Logistical Basics for Chemistry 312 Lab Work:

- You are not required to keep a notebook.
- You will follow the five Macalester Chemistry cardinal lab safety rules:
 1. Always wear goggles whenever you are inside a “wet” or “instrumental” lab.
 2. Always wear shoes that cover your feet.
 3. Never consume any food or drink in the lab.
 4. Always wash your hands whenever you leave the lab.
 5. Never work alone in a “wet” or “instrumental” lab, even when “just” using an instrument.
- Each group will turn in one lab report, and all of the members of a group will share the same grade for each lab.

Introduction

In this laboratory, you will record the infrared spectra of two HCl isotopomers, H^{35}Cl and H^{37}Cl . Since the HCl is in its gaseous state, where it can freely rotate, this vibrational spectrum will also contain resolved rotational structure. Such a spectrum is called a *rovibrational spectrum*. You will assign quantum numbers to each transition in your spectra and fit an equation to the measured frequencies to determine values for the principal molecular constants.

The energy levels of a rotating diatomic molecule in its ground and first excited vibrational states are given by the equations

$$v = 1: F'(J) = \tilde{\nu}_0 + B'J(J+1) - D'J^2(J+1)^2 \quad [1]$$

$$v = 0: F''(J) = B''J(J+1) - D''J^2(J+1)^2 \quad [2]$$

The symbols F' and F'' (the “rovibrational terms”) signify the energies of the upper and lower energy levels expressed in cm^{-1} . By convention, spectroscopists use a single prime for quantities relating to the upper state in a transition, and a double prime (or no prime) for quantities relating to the lower state. The symbol B is the rotational constant, and D is the centrifugal distortion constant, which takes into account the effects of the molecule's vibration on the rotational energy levels. Note that each vibrational state has its own rotational constant.

The selection rules for the rovibrational spectrum of HCl are $\Delta v = \pm 1$ and $\Delta J = \pm 1$. (Overtone bands, which are bands with $\Delta v = \pm 2, \pm 3, \dots$, are allowed, but are much weaker than the fundamental band. A general rule of thumb is that each successive higher overtone band is a factor of 10 weaker than the previous one.) With these selection rules, the infrared spectrum of HCl near 2875 cm^{-1} consists of an *R* “branch” (or set of peaks) with $\Delta J = J' - J'' = +1$, and a *P*

branch with $\Delta J = -1$. You will observe absorption only from the ground vibrational level ($v = 0$) to the first excited vibrational level ($v = 1$), because the $v = 0$ level is the only one significantly populated at room temperature. Such a band is called a cold band; hot bands originate from excited vibrational levels of the molecule. You will observe both the H^{35}Cl and H^{37}Cl species in the 2875 cm^{-1} region because our FTIR spectrometer has just high enough resolution to resolve them. The ^{35}Cl : ^{37}Cl natural abundance ratio is 76:24, so the H^{35}Cl will be noticeably stronger. Since the two Cl isotopomers act like distinct molecules (quantum mechanically speaking), you will fit their spectra separately.

If we use Eqns. [1] and [2] to determine the energies of the generic transitions $R(J - 1)$ and $P(J)$, we obtain the general expressions

$$\begin{aligned} R(J - 1) &= F'(J) - F''(J - 1) \\ &= \tilde{\nu}_0 + (B' + B'')J + (B' - B'' - D' + D'')J^2 + (-2D' - 2D'')J^3 + (-D' + D'')J^4 \\ P(J) &= F'(J - 1) - F''(J) \\ &= \tilde{\nu}_0 + (-B' - B'')J + (B' - B'' - D' + D'')J^2 + (2D' + 2D'')J^3 + (-D' + D'')J^4 \end{aligned}$$

From the form of the above two equations, it is possible to fit an identical equation to both branches, namely

$$\tilde{\nu} = \tilde{\nu}_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 + (-2D' - 2D'')m^3 + (-D' + D'')m^4 \quad [3]$$

where m is an integer called the *line number* that takes the values 1, 2, 3, ... for the $R(J)$ branch (that is, $m = J + 1$) and the values $-1, -2, -3, \dots$ for the $P(J)$ branch (that is, $m = -J$).

This is the strategy you should employ. Fit Eqn. [3] to your experimental measurements of the transition frequencies to derive values for the five constants $\tilde{\nu}_0$, B' , B'' , D' , and D'' . Fit each of the two isotopomers *separately* using Excel. Record a minimum of six significant figures for your fitted constants. In Excel, this means that you should select the fitted quartic (or fourth order) equation in x , then choose Selected Data Labels... under the Format menu, and change the Number formatting to Scientific notation with at least six significant figures. Using a little algebra, you will be able to find values for the physically significant constants in Eqn. [3] from the fitted values of the quartic polynomial coefficients. Prof. Varberg and I do *not* recommend doing this by hand with a calculator, which is a boring and error-prone process. Type the values of the polynomial coefficients (carefully!) into separate cells and then let Excel carry out the necessary calculations.

In doing this, you will have determined two values for B_v for each isotopomer of HCl, namely B_0 and B_1 (represented by B'' and B' in the equation above), the rotational constants in $v = 0$ and 1 respectively. From these, you can determine the bond lengths in these two vibrational states using the following formula

$$B_v = \frac{h}{8\pi^2 c \mu R_v^2} \quad [4]$$

where μ is the reduced mass and R_v is the bond length in the vibrational state v . For each isotopomer, you can also determine a value for B_e , the equilibrium value of the rotational constant at the minimum of the potential well, using the expression

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) \quad [5]$$

where α_e is a constant for each isotopomer of HCl. From B_e , you can determine values for R_e , the equilibrium bond length, for each isotopomer. These values should be the same, to within experimental error (assuming the Born-Oppenheimer approximation holds).

For each isotopomer, the rotational constant, the centrifugal distortion constant, and the vibrational frequency are related by a formula derived by Kratzer. The formula holds exactly only for a molecule obeying a Morse potential energy curve, but it should work reasonably for a real diatomic molecule. Note that D_0 in this expression is the centrifugal distortion constant for the $v = 0$ level, not the dissociation energy.

$$D_0 = \frac{4B_0^3}{\tilde{\nu}_0^2} \quad [6]$$

The force constant k of the HCl bond can be determined from the expression

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \quad [7]$$

where the vibrational frequency ν_0 is given in Hz.

Experimental Procedure

Rob Rossi, the James Brown (*i.e.* the hardest working man) in Olin-Rice, will have filled a gas cell with HCl and demonstrated the following instructions for operating the Chemistry Department's Nicolet Fourier 550 Transform Infrared Spectrometer (in Olin-Rice 386):

Collecting Your Data

1. Turn on the monitor and printer. Then launch the program **Omnic E.S.P. 5.1**.
2. Choose **Experiment Setup...** from the **Collect** menu. Set the number of scans you want (typically 16) and the resolution (for HCl, use the highest resolution available: 0.5 cm^{-1}). Select **Collect background before every sample**. Click **OK**. Set the optimum aperture automatically, if it asks you to do so.

- Unlatch and open the central door on the spectrometer and make sure no sample is mounted. Close the door. Then choose **Collect Sample...** from the **Collect** menu. Leave the default spectrum title unchanged and click **OK**. Click **OK** again to acquire the background scan. (You can monitor how many scans have been collected with the status bar at the bottom left of your window.) You should see peaks due to absorption by CO_2 and H_2O .
- Next, open the door, mount the sample cell filled with HCl in the beam path, close the door, and click **OK** to collect the sample spectrum. (The cell is stored in a plastic bucket next to the spectrometer.) Click on **Yes** to add the spectrum to the window. The active spectrum will appear in red. Each peak should be a doublet, with the more intense member of the doublet being due to the more abundant $\text{H-}^{35}\text{Cl}$ isotopomer.
- (You can probably skip this step.) For weak spectra it is useful to perform a baseline correction. Choose **Absorbance** from the **Process** menu, followed by **Automatic Baseline Correction** from the **Process** menu. Click and drag the right boundary marker in the View Finder (that's the skinny spectral window at the bottom of the screen) to eliminate the strong noise peaks at low frequency. Autoscale the spectrum by choosing **Full Scale** from the **View** menu (or setting it on **Automatic Full Scale**). Your window will now contain two spectra: the original (inactive) spectrum in blue, and the corrected (active) spectrum in red. Select the blue spectrum by clicking on it or choosing its title in the title bar. Then delete this spectrum by choosing **Clear** from the **Edit** menu. Doing so will prevent confusion.

Labeling Your Peaks

- You are now ready to characterize your spectrum. Enlarge the window to full screen. Click and drag the blue vertical boundary markers in the View Finder at the bottom of the window to select a wavenumber range of interest. Be sure not to exclude carelessly any weak lines at the edges of your spectrum.
- Choose **Find Peaks...** from the **Analyze** menu. Have some fun with the sensitivity setting (the scroll bar on the left of the window) and the threshold setting (click anywhere on the spectrum to move the threshold up and down) until you are certain that you have found all of the real peaks and none of the noise (the unattainable goal of any spectroscopist!). If you aren't happy with the locations of the boundary markers you chose, click on the **Window** menu and choose Window 1—this is still displaying the original version of your spectrum. Then repeat Step 6.
- When you are satisfied that all of the relevant peaks have been labeled, click the **Print** button (in the upper left of the window) to print a copy of the spectrum and the peak list.
- When you are done, quit the program by selecting **Exit...** from the **File** menu. (You will likely need to click **Yes** twice.)
- Turn off the printer and the monitor. Put the sample cell back in the plastic bucket.

Data Analysis

1. Label the branch assignments for the H^{35}Cl isotopomer on the spectrum you have printed off.
2. Assign the transitions by branch, J , and isotopomer. Note that our FTIR spectrometer plots lower energy (wave number) to the right, which is the standard Herzberg spectroscopic convention.
3. Fit the transition wavenumbers (in cm^{-1}) to Eqn. [3]. Report values for the five directly determinable molecular constants of each isotopomer. Include a copy of your Excel spreadsheet and the graph of $\tilde{\nu}$ vs. m for each isotopomer in your lab report. Please organize your results for the different isotopomers in a combined table in one spreadsheet page.
4. Determine the bond lengths in Å ($1 \text{ Å} = 10^{-10} \text{ m}$) in these vibrational states using Eqn. [4]. Does the bond length shorten or lengthen upon vibrational excitation? Explain this behavior.

Note: To do this calculation properly, you must use precise atomic masses for the various isotopes good to at least six digits as well as similarly precise values for the fundamental constants. Your textbook lists isotopic masses in the Appendix, but unfortunately the values given are not all correct. Please consult the table to the right for the values you need. Furthermore, the value given for the speed of light inside the front cover of your textbook has a typographical error in the seventh digit—the correct value is $c = 2.99792458 \times 10^8 \text{ m s}^{-1}$.

Isotope	Mass (in u)
^1H	1.007825
^2H	2.014102
^{35}Cl	34.968853
^{37}Cl	36.965903

5. Calculate equilibrium values for the rotational constant B_e , the constant α_e , and the bond length R_e from Eqns. [4] and [5]. Compare and comment on the values for the equilibrium bond lengths of the two isotopomers. Also compare your results for H^{35}Cl with the “literature” values given by Atkins/de Paula (Table 13.2 in the Data Section).
6. Test the Kratzer relation, Eqn. [6], for the two isotopomers. Comment on your results.
7. Calculate the force constant in N/m for the two isotopomers from Eqn. [7], again comparing your results with those given in Atkins/de Paula, Data Section Table 13.2. Can you offer a possible explanation for any disagreement between your value and the literature value? Would you expect the force constants of the isotopomers to be equal to each other?

Final Product

You will write a paper with the same sections (Title, Your Names, Abstract, Introduction, Procedure, Results and Discussion, Conclusions, References, Appendix) as your Chemistry 311 written lab reports. However, note that your Procedure should be extremely short (two to three sentences will suffice). The focus of your paper should be addressing the questions posed in the **Data Analysis** section of the instructions.