

Physical Chemistry II Laboratory

The Rovibrational Spectra of H³⁵Cl and H³⁷Cl Using FTIR

Write-Up Due Date: Thursday, April 17

(You may record spectra and write your reports in teams or as individuals)

In this laboratory, you will record rovibrational transitions of two HCl isotopomers, H³⁵Cl and H³⁷Cl, using Fourier transform infrared (FTIR) spectroscopy. You will then fit equations to your peak locations to determine values for the principal molecular constants.

Introduction

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

$$v = 1: S'(J) = \bar{\nu}_o + B'J(J+1) - D'J^2(J+1)^2$$

$$v = 0: S''(J) = B''J(J+1) - D''J^2(J+1)^2$$

The variables S' and S'' signify the rovibrational terms of the upper and lower vibrational states in units of 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.) 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. (More on this later.)

The selection rules for the rovibrational spectrum of HCl are $\Delta v = \pm 1$ and $\Delta J = \pm 1$. Therefore, the infrared spectrum of HCl near 2900 cm^{-1} consists of an **R branch** ($\Delta J = J' - J'' = +1$) and a **P branch** ($\Delta J = -1$). You will observe absorption only from the ground vibrational state ($v = 0$) to the first excited vibrational state ($v = 1$), because the $v = 0$ state is the only one significantly populated at room temperature. (Note that unlike for rotations, diatomic vibrational states have no degeneracies to facilitate the population of excited states.)

If we evaluate the above expressions for the wavenumbers of the transitions $R(J-1)$ and $P(J)$, we obtain the general expressions

$$\begin{aligned} R(J-1) &= S'(J) - S''(J-1) \\ &= \bar{\nu}_o + (B' + B'')J + (B' - B'' - D' + D'')J^2 + (-2D' - 2D'')J^3 + (-D' + D'')J^4 \end{aligned}$$

$$\begin{aligned} P(J) &= S'(J-1) - S''(J) \\ &= \bar{\nu}_o + (-B' - B'')J + (B' - B'' - D' + D'')J^2 + (2D' + 2D'')J^3 + (-D' + D'')J^4 \end{aligned}$$

Now, from the form of the above two equations, it should be clear *that we can fit the same equation to both branches*, namely

$$\bar{\nu} = \bar{\nu}_o + (B' + B'')m + (B' - B'' - D' + D'')m^2 + (-2D' - 2D'')m^3 + (-D' + D'')m^4$$

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

This is the strategy you should employ: Fit the above equation to your experimental measurements of the transition frequencies to derive values for the five constants. Fit the data for each isotopomers *separately* using Excel. Be sure to display each constant to a minimum of five significant figures. In Excel, this involves selecting the fitted quartic equation in x , choosing Selected Data Labels... under the Format menu, and changing the Number formatting to Scientific notation with at least five significant figures.

By fitting a line to your data, 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. From these, you can determine the bond lengths in these two vibrational states using the following formula

$$B_v = \frac{h}{8\pi^2 c \mu R_v^2}$$

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

$$B_v = B_e - \alpha_e(v + \frac{1}{2})$$

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, within experimental error.

We can also determine the ($v = 0$) force constant k for the H-Cl bond from the equation

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

where the vibrational frequency ν_o is given in Hz.

Finally, we can test the accuracy of the Morse oscillator approximation for a diatomic molecule. Kratzer derived (*Z. Phys.* **1920**, 3, 289) the following relationship for a diatomic molecule perfectly described by a Morse potential:

$$D_0 = \frac{4B_0^3}{\bar{\nu}_0^2}$$

Note that D_0 in this expression is the centrifugal distortion constant for the $v = 0$ level, not the dissociation energy.

Experimental Procedure

The following are instructions for operating the Chemistry Department's Nicolet Fourier 550 Transform Infrared Spectrometer:

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.
3. Unlatch and open the central door on the spectrometer and make sure no sample is mounted. Then choose **Collect Sample...** from the **Collect** menu. Please name your spectrum file in the form *56<yourname>.spa* (with a maximum filename of eight letters) and click **OK**. Click **OK** again to acquire the background scan. (You can monitor how many scans have been collected at the left side of the status bar towards the bottom of your window.) You should see peaks due to absorption by CO_2 and H_2O .
4. Next, mount the sample cell filled with HCl in the beam path 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.
5. (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

6. You are now ready to characterize your spectrum. Start by creating a log file to record the peak locations. Choose **Open Log...** from the **File** menu. Please name your file *56<yourname>.log*. Click in the spectral window to show your spectrum again. Enlarge the window to full screen.

7. 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.
8. Choose **Find Peaks...** from the **Analyze** menu.
9. 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) until you are certain that you have found all of the real peaks and none of the noise (the unattainable goal of any spectroscopist!). When you are satisfied, click the **Print** button (in the upper left of the window) to print a copy of the spectrum and the peak list. This action will also save the peaks to your log file.
10. When you are done, quit the program by selecting **Exit...** from the **File** menu. (You will likely need to click **Yes** twice.) Save the spectrum file in the **Chem 56-2003** folder, so that you can go back to it later if necessary.
11. Turn off the printer and the monitor. Put the sample cell back in the plastic bucket.

Report Guidelines

Instead of writing a full-blown report (the kind you loved writing for P-Chem I), your report for this lab need only address the following:

1. Include a copy of your spectrum and table of line positions. On your spectrum, identify the P and R branches. Label each transition in your table by branch, J , and isotopomer. Note that our FTIR plots lower energy (wave number) to the right.
2. Fit the transition wavenumbers (in cm^{-1}) to the equation shown on pp. 1-2. Report values for the five directly determinable molecular constants of each isotopomer. Include a copy of your Excel data file and the graph of $\bar{\nu}$ vs. m for each isotopomer.

For all of your subsequent calculations, be sure to use accurate values for isotope masses (as found on p. 1074 of Atkins and de Paula) as well as for any fundamental constants required.

3. Determine the bond length in Å ($1 \text{ Å} = 10^{-10} \text{ m}$) for each vibrational state of each isotopomer. Does the bond length shorten or lengthen upon vibrational excitation?
4. Calculate equilibrium values for the rotational constant B_e , the constant α_e , and the bond length R_e . 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 value given by Atkins and de Paula (Table 16.2, p. 1097).
5. Calculate the force constant in N/m for the two isotopomers, again comparing your results with those given in Atkins and de Paula Table 16.2. Would you expect the force constants of the isotopomers to be equal (within experimental error) to each other? (Note: You are not expected to quantify the experimental error in your measurements.)

6. Use the Kratzer relation to compute a value of D_0 for each isotopomer. Compare these values to the values of D'' you obtained from your fit, and comment on your results