

# Measurement and Interpretation of the HCl Infrared Spectrum

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(modified for SCSU use by N. Winter and M. Dvorak, 1-2-07)

The purpose of this lab is to determine properties of the hydrogen chloride molecule by recording and analyzing the infrared spectrum of gaseous hydrogen chloride. The equilibrium bond length  $R_e$ , vibrational force constant  $k$ , and rotational constant  $B_e$  of HCl are obtained by analyzing the wavenumbers at which peaks appear in its infrared spectrum. Additional constants obtained are the anharmonicity constant  $x_e$ , the centrifugal distortion constant  $D_e$ , and the vibration-rotation interaction constant  $\alpha_e$ .

### Background

The rotation-vibration energy of HCl is approximately the sum of harmonic-oscillator energy and rigid-rotor energy:

$$E \approx h\nu_e(v+1/2) + h^2J(J+1)/(8\pi^2\mu R_e^2); \quad v=0,1,2,\dots; \quad J=0,1,2,\dots$$

$v$  is the vibration quantum number

$J$  is the rotation quantum number

$\nu_e$  is the fundamental vibration frequency =  $(k/\mu)^{1/2} / (2\pi)$ .  $\nu_e$  is in units of  $s^{-1}$ .

$\mu$  is the HCl reduced mass.  $\mu = m_{Cl}m_H/(m_{Cl}+m_H)$

$R_e$  is the equilibrium bond length

In wavenumber units,

$$\tilde{E} \approx \tilde{\nu}_e(v+1/2) + hJ(J+1)/(c8\pi^2\mu R_e^2); \quad v=0,1,2,\dots; \quad J=0,1,2,\dots$$

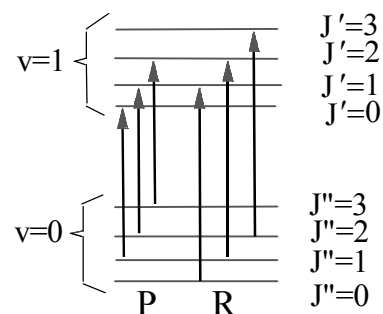
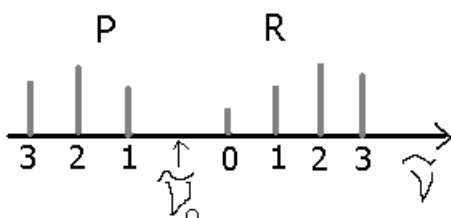
Units of wavenumbers are convenient because infrared spectra are usually recorded in wavenumbers. Notice that  $\tilde{E} = E/(hc)$  and  $\tilde{\nu}_e = 1/\lambda$ . The equilibrium rotation constant  $B_e$  (also in wavenumbers) is defined as

$$B_e \equiv h/(8\pi^2c \mu R_e^2); \quad \text{where } c \text{ is the speed of light.}$$

The infrared absorptions observed in this experiment arise from transitions between  $v=0$  and  $v=1$ , and various  $J'' \rightarrow J'$ , with  $J' = J'' \pm 1$ . The  $J$  for the initial, lower-energy, state is denoted  $J''$ . The

absorption wavenumbers,  $\tilde{\nu} = [\tilde{E}(v=1, J') - \tilde{E}(v=0, J'')]$ . Using equations 2 and 3, we see that absorptions are at the following wavenumbers:

$$\tilde{\nu} \approx \tilde{\nu}_e + B_e [ J'(J'+1) - J''(J''+1) ]$$



Absorptions for which  $J'=J''+1$  are said to belong to the "R" branch; those with  $J'=J''-1$  are on the "P" branch. The spectrum should look qualitatively as sketched at left.

Equation 4 is roughly correct in predicting rotation-vibration transition energies. But quantitative prediction of absorption frequencies requires consideration of three additional factors: centrifugal distortion, vibration-rotation coupling, and vibrational anharmonicity. The effective moment of inertia increases as J increases. This can be understood as the result of centrifugal force increasing the bond length in states having greater angular momentum. The effect is that energy levels do not increase with J as rapidly as equation 1 implies. A correction term  $-J^2(J+1)^2D_e$  is added to the energy  $\tilde{E}(v,J)$ , to account for centrifugal distortion.  $D_e$  is called the centrifugal distortion constant, here in units of  $\text{cm}^{-1}$ . (The same symbol  $D_e$  is used for dissociation energy.)

Energy is also reduced by interaction between vibration and rotation, generally decreasing as both v and J increase. This effect is incorporated with the vibration-rotation interaction constant,  $\alpha_e$ . A correction term  $-\alpha_e(v+1/2)J(J+1)$  is added to the energy  $\tilde{E}(v,J)$ .

Vibrational anharmonicity in HCl causes energy to increase less rapidly with v than equation 1 predicts. This is because diatomic potential energy surfaces are generally less steep on the large-R side than perfect harmonic oscillator potential surfaces. A correction term  $-(v+1/2)^2\tilde{\nu}_e x_e$  is added to the energy to account for anharmonicity. Because this experiment will measure only one vibration-rotation band, with  $v:0 \rightarrow 1$ , the value of  $x_e$  cannot be calculated from the spectrum. You can calculate it from data given in the references.

When these three effects are included, the energy (in wavenumbers) of a (v,J) state is

$$\tilde{E}(v,J) = \tilde{\nu}_e(v+1/2) - \tilde{\nu}_e x_e (v+1/2)^2 + B_e J(J+1) - \alpha_e (v+1/2) J(J+1) - D_e J^2(J+1)^2 \quad (5)$$

Taking the difference of two (v,J) states yields the following equations for the P- and R-branch absorption wavenumbers:

$$\tilde{\nu}_P(J) = \tilde{\nu}_o - 2B_e J'' - \alpha_e J''(J''-2) + 4D_e (J'')^3 \quad ; J''=1,2,3,\dots \quad (6)$$

$$\tilde{\nu}_R(J) = \tilde{\nu}_o + 2B_e J'' - \alpha_e (J''+1)(J''+3) - 4D_e (J''+1)^3 \quad ; J''=0,1,2,\dots \quad (7)$$

where  $\tilde{\nu}_o \equiv \tilde{\nu}_e(1-2x_e)$  (8)

Equations 6 and 7 can be combined into a single equation if one defines the parameter m as follows:

$$m \equiv -J'' \text{ on the P branch} \quad \text{and} \quad m \equiv J''+1 \text{ on the R branch} \quad (9)$$

Then  $\tilde{\nu}_m = \tilde{\nu}_o + 2(B_e - \alpha_e)m - \alpha_e m^2 - 4D_e m^3$  (10)

Equation 10 will be used to analyze the HCl spectrum recorded in this experiment. Equation 10 is simply a cubic equation in m, so after the  $\tilde{\nu}_m$  have been measured, the constants in equation 10 could be obtained by regression analysis. That is a common procedure. We will, however, use the software "Spektri-Sim", which has a nice graphical interface.

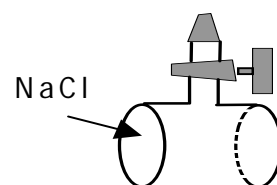
Notice that equation 10 deals only with the wavenumbers at which peaks occur, not with absorption intensities. Intensities of rotation-vibration lines are controlled mainly by temperature, which controls the relative populations of the initial ( $v, J''$ ) states. Absorbance of a particular line ( $m$  value) is approximately proportional to the probability that the HCl molecule is in that initial ( $v, J''$ ) state. All of the molecules originate in the  $v=0$  state, in our experiment, so only the probability of  $J''$  matters. That probability is given by the Boltzmann distribution.

$$\text{Probability}(J'') = (2J''+1) \left[ e^{-J''(J''+1)B_e hc / (k_b T)} \right] / Q_{\text{rot}} \quad (16)$$

In equation 16,  $Q_{\text{rot}}$  is basically a proportionality constant. It is called the "rotational partition function." The *Spektri-Sim* software uses equation 16 to simulate the effect of temperature on peak heights.

### Experimental Procedure

The spectrum of HCl in the gas phase is taken using a gas cell, as sketched at right. The windows of the cell are NaCl, so the cell should be kept dry. When not in use it is stored in a desiccator. You will fill the cell from the head space above concentrated hydrochloric acid, after evacuating the cell.



- Attach the cell to the aspirator/trap setup. Open its stopcock. Let the water run a minute to evacuate the cell.
- Close the cell stopcock.
- Take the cell off the aspirator and record a background spectrum. When removing the cell from the aspirator, pull the hose off the cell before turning off the water. When recording the background spectrum, check that the spectrometer says it is set for  $1 \text{ cm}^{-1}$  resolution and 16 scans.
- If strong HCl peaks appear near  $2900 \text{ cm}^{-1}$ , then flush the cell with air and evacuate it a few times and try again.
- Record the spectrum of HCl. Use absorbance mode rather than transmittance so it will be easier to compare this spectrum with the HCl spectrum you will calculate or perhaps already did calculate in another lab.

You will need to know the wavenumbers and absorbances (peak heights) at absorption maxima. Be careful to choose the taller peak of each pair, which is due to  $\text{H}^{35}\text{Cl}$ . The lower peak of each pair is due to  $\text{H}^{37}\text{Cl}$ . You should locate the peaks and write them down or print them or at least type them into a text file while the data are still on the spectrometer screen.

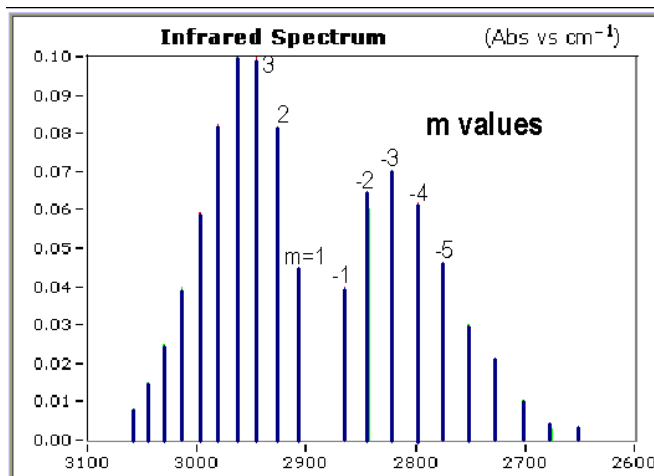
Flush the cell with nitrogen gas a few times. Store the cell in the desiccator, with the stopcock open.

## Calculations

The data for your calculations are absorption wavenumbers, as read from your spectrum, and their associated absorbances and  $m$  values.

Make a table of  $m$ ,  $\tilde{\nu}$  and intensity in a text file so the program *Spektri-Sim* can read them. Under Windows, *Notepad* is convenient for making small text files. The figure at right illustrates  $m$  assignments. Notice that  $m$  is negative for the smaller  $\tilde{\nu}$  and positive for the larger  $\tilde{\nu}$ . The file should contain the data in three columns and numbers on the same line should be separated with tabs, like so:

-2.0	2843.2275	0.1032
-1.0	2864.7034	0.0774
1.0	2905.8420	0.0785
2.0	2925.5205	0.1045



You may want to include some header text such as your name and column titles. Such is easily removed by hand after opening the file in *SpektriSim* and does not affect calculations.

Brief instructions for *Spektri-Sim* are below. If you have trouble running the program, try reading the manual and work through the HBr example. Briefly,

- Start *Spektri-Sim*.
- Click on "experimental spectrum", then "open", and choose your text file. If it won't open, try comparing it to the sample data files that come with *Spektri-Sim*. Once your data appear (in green), choose "Close." Your data (green) should appear in the same window as a theoretical spectrum (red).
- Type your estimates for  $\tilde{\nu}_0$ ,  $B_e$  and  $\alpha_e$  into the respective text boxes below the spectrum.
- Vary the molecular constants until the theoretical spectrum nearly matches your spectrum. As your fit improves the "Standard Deviation of Regression" (SDR) will diminish. The SDR is

$$\text{SDR} = \left[ \frac{1}{N-4} \sum_m (\tilde{\nu}_{m,\text{exptl}} - \tilde{\nu}_{m,\text{theoretical}})^2 \right]^{1/2} \quad (17)$$

- After you get  $\text{SDR} < 3$ , have *Spektri-Sim* refine the constants. Simply click on "Refine."
- If you enter the isotopic masses, *Spektri-Sim* will even calculate the bond length. The isotopic masses of  $^1\text{H}$  and  $^{35}\text{Cl}$  are available in the *CRC Handbook*, or you might pick them up from one of the periodic tables on the web, such as "Web Elements."

After you obtain the value of  $\nu_0$ , use equation 8 to calculate  $\nu_e$ . You need the value of the anharmonicity constant:  $x_e = 1.74 \times 10^{-2}$  (reference 3).

### Lab Report

A short report is adequate for this experiment. Turn in the following:

- Title, names, date, abstract
- Your spectrum
- Your text files of spectral data. Attach printed copies to your report and email the files to me.
- The isotopic masses of  $^1\text{H}$  and  $^{35}\text{Cl}$ .
- A table of your best (*Spektri-Sim* optimized) values, literature values, and percent differences for  $\nu_e$ ,  $B_e$ ,  $\alpha_e$ ,  $D_e$ , the reduced mass, and  $R_e$  for HCl.
- Discussion-In your discussion discuss how altering the value of each constant effects the spectrum and why it does so. Be sure to include the name of each constant with its symbol.
- References

### References

1. Huber K. P. and Herzberg G. (1979) Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, p. 286.
2. McQuarrie D. A. (1984) Quantum Chemistry, University Science, Mill Valley, Table 10.4.
3. Stull V. R. and Plass G. N. (1960) "Spectral Emissivity of Hydrogen Chloride from 1000-3400  $\text{cm}^{-1}$ ," *Journal of the Optical Society of America* **50**, 1279. This article gives  $\alpha_e$ ,  $B_e$ , and  $D_e$ . These authors list constants, and reference G. Herzberg, Spectra of Diatomic Molecules, (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

$$\nu_e = 2989.74 \text{ cm}^{-1} \quad \nu_e x_e = 52.05 \text{ cm}^{-1}$$

4. Eric D. Glendening and Jarno M. Kansanaho, "Spektri-Sim: Interactive Simulation and Analysis of the Infrared Spectra of Diatomic Molecules," *Journal of Chemical Education*, **78**(6), 824, 2001.