High Resolution Spectra II: Molecular & Thermodynamic Study of HCl

Introduction

This is your second experiment using the high resolution FTIR. This is a demanding experiment in which there will be no background equations provided by the instructor – at least not at first. All of the necessary relationships may be found in your physical chemistry textbook. In the first semester of pchem, you learned that high resolution spectroscopy may be utilized to calculate fundamental vibration frequencies, force, anharmonicity, and rotational constants as well as bond distances. For this experiment, you will record the spectrum of HCl and then you will decide how best to interpret and model your data. You may decide to take the approach that you took for the CO_2 experiment or consider multivariate analysis.

Experimental:

The synthesis of HCl gas will be performed through the following reaction:

$$SOCl_{2(l)} + 2H_2O_{(l)} \rightarrow 2HCl_{(g)} + SO_{2(g)}$$

which will produce a 2:1 isotopic mixture of $H^{35}Cl$ to $H^{37}Cl$. Likewise, DCl gas will be produced with a similar isotopic mixture through this reaction:

$$SOCl_{2(l)} + 2D_2O_{(l)} \rightarrow 2DCl_{(g)} + SO_{2(g)}$$

The microscale apparatus (see Figure 1) should be assembled and placed in a functional hood.

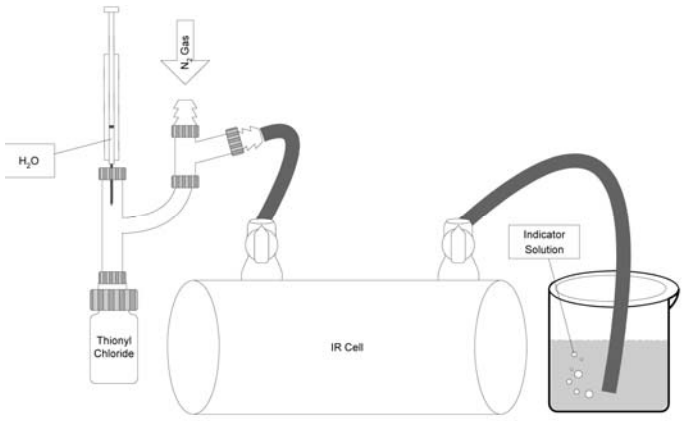

Figure 1: A pictorial representation of the microscale apparatus utilized to produce gas.

Procedure:

- Place 3 drops of thymol blue indicator into a beaker
- Add 1 mL of thionyl chloride to the reaction vessel and purge entire setup with N_2 gas for a few minutes
- Close off cell and collect an FT-IR background spectrum (3100 cm^{-1} to 1600 cm^{-1} – see parameters below).
- Return cell to apparatus
- Use a pinch clamp to close N_2 line
- In a separate vial, place 2 mL of D_2O and 1 mL of dionized H_2O
- Draw 1 mL into your syringe

- Insert syringe into the septum at the top of your apparatus and add the water mixture DROPWISE to the apparatus
- Gas is immediately produced and the reaction proceeds until the indicator changes from yellow to red
- Close inlet and outlet stopcocks on the gas cell simultaneously
- Disconnect the inlet and place into a beaker of water
- Disconnect outlet tube
- Refill the microliter syringe with DI water and add to vessel dropwise until the reaction has gone to completion (no more gas bubbles are generated).
- Use a little NaOH to neutralize the thymol blue solution.

Spectrum Generation:

You will record the high-resolution spectrum of form 3100 cm^{-1} to 1600 cm^{-1}. Prior to running the instrument you should check the measurement parameters to ensure they are set appropriately.

- Open the Spectrum Program on the Desktop
- Hit OK to initialize the instrument
- Under the Instrument Menu - Choose Scan Sample
    - Select single beam
    - Rename the file and write a description
    - Set:
        - "Start" to 3100.0 cm^{-1} and "End" to 2600.0 cm^{-1}
        - "Number of scans" to 16
        - "Resolution" 1.0
    - Choose the Setup button on the right
        - Apodization should be set to weak
        - Interferogram should be selected

After all parameters have been set you are ready to run the scan. It will take several minutes for all 16 scans to be completed and averaged. Save your file as ASCII and email copies to yourselves and me. You will need to include a plot of the spectrum in your report which may be generated in Excel.

Analysis of Results:

You will notice that the P and R branch lines are split due to the ^{35}Cl and ^{37}Cl isotopes in HCl. (There is a similar trend in the DCl spectrum). Determine the identity of the isotope giving rise to these lines. By now you have learned a number of modeling and analysis techniques. Use these techniques and your handy textbook to compute the following for both sets of isotopes:

- fundamental vibration frequency
- force constant
- rotational constant
- equlibrium bond length
- rotational temperature
- vibrational temperature
- rotational partition function
- vibrational partition function
- internal energy

- molar entropy
- molar heat capacity
- chemical potential

You should include a table in your report and compare these values to literature where possible. For each of these values you should propagate error. Also, your spectrum should be labeled to indicate the two sets of branches as well as the transitions (e.g. J = 0 -> J = 1 would be labeled 0 -> 1)

Notebook and Report

Make sure to record all of your data, etc. in your notebook which need to be dated and signed by me before you leave the lab. Your report should be written (as we discussed) in the form of a Communication/Letter publishable by *J. Phys. Chem.*

References

[1]D.A. McQuarrie, "*Quantum Chemistry*" 1983, University Science Books.
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[5]J. M. Hollas, "*High Resolution Spectroscopy*" 1998, John-Wiley & Sons.
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