**Vibration-Rotation Spectrum of HCl and DCl**

**Physical Chemistry II Lab**

**CHM4111L**

**Dr. Clark**

**1. Objective and Relation to Lecture**

Provide a brief description of the purpose of the experiment. What are you trying to achieve or learn?

**2. Introduction / Theory**

n this experiment, the vibration-rotation spectrum of hydrogen chloride (HCl) and deuterium chloride (DCl) will be analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The spectra will allow the determination of the rotational constants ​, vibrational frequencies , anharmonic vibrational corrections , and vibrational-rotational coupling constants for each molecule. These parameters reveal molecular characteristics such as bond lengths and vibrational energies. The centrifugal distortion constants and the plots of vs. are excluded from this analysis. The experiment involves fitting the positions of rotational lines in the spectra of HCl and DCl to derive the aforementioned molecular constants.

**3. Materials and Equipment**

* Fourier Transform Infrared Spectrometer (FTIR)
* Gas cell
* Vacuum system with gauge
* Liquid nitrogen
* HCl and DCl gas mixture (generated in situ)
* Water

**4. Safety Precautions**

* Handling DCl: DCl is highly toxic and corrosive. Ensure proper ventilation, wear gloves, lab coat, and safety goggles, and handle the DCl canister with extreme care. Always consult your TA or instructor before proceeding with DCl handling.
* Vacuum System: Ensure the vacuum system is properly set up before using it to avoid damage to equipment or injury. Never exceed the recommended pressure readings.
* Liquid Nitrogen: Use caution when handling liquid nitrogen as it can cause severe cold burns. Always wear insulated gloves.

**5. Experimental Procedure**

**Procedure:**

Preparation of the Vacuum System

1. Retrieve the FTIR gas cell from the desiccator.
2. Set up the vacuum system with the FTIR cell in place and exposed to vacuum.
3. Turn on the vacuum pump and evacuate the system until the pressure gauge reads ~30 mmHg.
4. Fill the trap with liquid nitrogen.
5. Close the system from the pump and the cell from the vacuum apparatus.
6. Remove the evacuated cell, which will serve as the blank, and take it to the FTIR instrument.

FTIR Setup and Background Scan

1. Log in to the FTIR instrument using the provided credentials (User: pchemlab, Password: CHM4411L).
2. Create a personal folder in My Documents\CHM4411L with your initials as the folder name.
3. Open the Spectrum Express software (User: CHM4411L, Password: CHM4411L).
4. Set up the software for sample absorption with a resolution of 1.0 cm⁻¹ and 8 scans.
5. In the instrument auto-name tab, enter "HCl-DCl" for both the auto-description template and sample ID.
6. Place the blank cell into the sample holder, replace the cover, and click the background button to collect background data.
7. Once the background scan is complete, remove the cell from the FTIR instrument.

Gas Cell Preparation and Data Collection

1. Return the gas cell to the vacuum apparatus, open the udder and cell to expose the system to the vacuum, and then close it off again.
2. Open the DCl canister slightly to adjust the pressure gauge to ~20-25 mmHg. Verify the system setup with your TA or instructor.
3. If needed, add a small amount of water to the system to generate the required HCl.
4. Return the cell to the FTIR and perform a scan by clicking the "Scan" tab.
5. Save the file in both ASCII or CSV formats for further analysis.
6. Label the peaks using the peak-labeling tool in the software.
7. Create a text version of your peak table for plotting the P & R branches of the spectra.

**7. Calculations and Analysis**

1. What is the rotational constant ​, for HCl and DCl?

* Fit the rotational lines in the spectra to determine the rotational constant ​. How does this value compare to the literature values?

2. What are the vibrational frequencies for HCl and DCl?

* From the peak positions, calculate the vibrational frequencies for both HCl and DCl. How do these experimental frequencies compare to known values?

3. How do you determine the anharmonic vibrational correction ?

* Using the spectral data, derive the anharmonic vibrational correction . What is the physical significance of this correction?

4. What are the vibrational-rotational coupling constants for HCl and DCl?

* Fit the spectra to determine the vibrational-rotational coupling constants . How do these constants influence the rotational-vibrational energy levels?

5. How can you plot the vs. curve?

* Based on the data, plot the vs. (quantum number) for both HCl and DCl. What does the shape of the plot indicate about the molecular behavior?

6. What is the role of the anharmonicity in the vibration-rotation spectrum?

* Analyze how the anharmonicity affects the spacing between the rotational lines in the spectra of HCl and DCl. How does this manifest in your data?

7. How do you apply a quadratic fit using Excel’s trend line function?

* Explain how you would apply a quadratic fit to the spectral data using Excel’s trend line function. What equation from the text do you use, and how do the results from Excel compare to manual calculations?

8. What are the P and R branches in the spectra, and how do you plot them?

* Label the peaks corresponding to the P and R branches in your spectra and create a plot. How do these branches reflect the transitions occurring in the molecule?

9. How do the experimental rotational constants ​, compare to theoretical predictions?

* After calculating the rotational constants, compare them to theoretical predictions or literature values. What factors could explain any discrepancies?

10. What conclusions can be drawn about the molecular structure from the vibration-rotation spectrum?

* Based on your calculated values of ​, , and , what conclusions can you draw about the bond lengths and force constants of HCl and DCl? How does the substitution of hydrogen with deuterium affect these properties?