Colorado State University

CHEM 372
Physical Chemistry Laboratory

Notes for
Rotational-Vibrational Spectroscopy
of ^{1}HCl and ^{2}HCl

The following is a set of short notes to outline the experiment in question and to provide helpful guidance to those executing the experiment.

A. Heteronuclear atomic molecules provide excellent "test beds" for proofing models of the mechanics of atoms in molecules and their interaction with electromagnetic radiation.

B. In another experiment in this laboratory, the absorption spectra of diatomic molecules was analyzed and predicted by use of the "harmonic oscillator" that models the interatomic distance between two atoms - behavior that gives rise to a varying molecular electric dipole that ultimately gives rise to an absorption, typically in the IR region.

C. The harmonic oscillator can be improved upon by inclusion of the "rigid rotor" model that together will predict more detailed spectroscopic features.

D. The gas cell used in this experiment is constructed with IR transparent ends (made from disks of NaCl, which is transparent to IR radiation) and is several centimeters long to provide sufficient optical density (absorbance) from the low-density gas. It must be stored in a desiccator when not in use to prevent "fogging" of the water-sensitive NaCl end plates. It must also be cleaned (flushed out) by gently (!) flowing nitrogen gas through it while it is in the hood. Collect a background spectrum (use "absorbance" mode not "percent transmittance") using the nitrogen-cleaned cell.

E. Collect a high-quality IR spectrum of ^{1}HCl gas obtained from a "lecture bottle" (use "absorbance" mode not "percent transmittance"). Convert the spectrum file to ASCII format, transfer it to a suitable computer and analyze it with Igor Pro. Repeat this process until a suitable spectrum is obtained.

F. In order to collect a corresponding spectrum of ^{2}HCl this isotopically substituted molecule must be prepared in the laboratory. A convenient procedure (with significant modifications!) for this purpose can be found in the textbook "Experiments in Physical Chemistry" authored by Shoemaker and Garland. Flowing 2HCl gas through it rather than the vacuum based procedure described in the textbook fills the two-valve cell used in this laboratory.

G. Estimate the volume of the cell filling apparatus (to the ±20% level - do not overestimate) from the round-bottom generating flask to and including the cell itself (apparatus "down wind" from the cell is inconsequential). Use a convenient volume

between two and three times this estimate to ensure that a sufficient quantity of ^{2}HCl is generated to flush the cell adequately.

H. Calculate the amount of benzoyl chloride and deuterated water needed to generate the needed amount of ^{2}HCl.

I. Collect a high-quality IR spectrum of ^{2}HCl gas obtained (use "absorbance" mode not "percent transmittance"). Convert the spectrum file to ASCII format, transfer it to a suitable computer and analyze it with Igor Pro. Repeat this process until a suitable spectrum is obtained.

J. Analyze both spectra using Igor roughly according to the Shoemaker and Garland procedure. Since the procedure was written prior to the widespread availability of high performance computers and software it used certain outdated conventions. For example, identify the absorption maxima wavelengths and plot them (rather than the nearest-neighbor wavelength differences). Fit these spectra, separately to both second and third order polynomials to extract the experimental values of parameters to use in the model. Perform a suitable F-Test on the extracted values to determine if the third order polynomial fit is statistically more significant than the second order one. Complete the analysis as described in the procedure.