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Measuring Conformational Energy Differences using Pulsed-Valve CP-FTMW Spectroscopy

Gordon Brown, Coker College

In the second year of the project, we have focused our attention on the measurement of new molecules that have multiple stable conformers. The results of these experimental tests are reported below. The proposed project was based on the following two-pronged hypothesis referring to using pulsed-valve chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy to measure multiple conformers of the same compound:

Project Hypothesis:

- Relative intensities are proportional to the conformer populations present before the expansion occurs (if helium is used as the carrier gas).
- (Therefore), relative intensities can be used to measure experimental relative energies between conformers.

The above hypothesis was based on the findings of Ruoff et al. described in their seminal paper on the relaxation of conformers in supersonic jets. In this paper, they reported that "When helium was used as the carrier gas all of the conformers showed little if any evidence of conformer relaxation."[1] Therefore, we proposed using relative intensities to measure experimental relative energies.

Initial Findings

In experiments on several systems in our proposal, we have not been able to reproduce Ruoff's finding that conformer relaxation is not observed when using helium as a carrier gas. Furthermore, obtaining reproducible results with a pulsed valve has proved challenging. In the first year of the project, we repeated several measurements from the Ruoff paper. Since these tests proved unsuccessful, we moved toward studying chemicals that had not been previously studied by microwave spectroscopy in the second year of the project.

Recent Findings

In the previous year, we have focused our attention on chemical compounds that have multiple stable conformations that have not been previously studied by microwave spectroscopy. The reason for this is threefold. First, these studies contribute to the literature/database of molecules studies by microwave spectroscopy. If nothing else, we are uncovering new information that was not known before that will likely be useful to other researchers. Second, since we have chosen compounds that have multiple stable conformers, the studies will shed light on the energetics of these compounds (related to our project hypothesis). Third, we can study the same compounds using various carrier gases in order to better understand conformer relaxation in pulsed-jets. Below are listed the compounds we have studied in the past year, including a brief summary of the progress made on them.

- **1-cyclohexene-1-carboxaldehyde (CHCA):** CHCA has two stable conformers, which we labelled *cis* (oxygen atom pointing towards from the double bond) and *trans* (oxygen atom pointing away from the double bond). In this study, we measured the microwave spectrum of the *trans*

CHCA for the first time. Furthermore, we were able to analyze the spectrum and discover the rotational constants and centrifugal distortion constants for the normal species and every ^{13}C isotopologue (measured in natural abundance) of the *trans* species. The *cis* species was not observed in the pulsed jet. The results of this study were presented at the Southeast Regional Conference of the American Chemical Society (SERMACS) in Charlotte, NC, in November 2017.

- **3-chloro-4-fluorobenzaldehyde (3Cl4FBA):** 3Cl4FBA has two stable conformers which we labelled *O-cis* (where the oxygen atom points towards the chlorine atom) and *O-trans* (where the oxygen atom points away from the chlorine atom). In this study, the microwave spectra of both conformers were measured in the pulsed jet for the first time and the rotational parameters of both conformers were successfully discovered. In future work, we aim to vary the carrier gas and measure how the intensity of the two conformers varies (over a wide range of transitions and frequencies). This will provide more information about the energetics of the two conformations.

- **2-chloro-6-fluorobenzaldehyde (2Cl6FBA):** 2Cl6FBA has two stable conformers, which we labelled *O-Cl-cis* (where the oxygen atom points towards the chlorine atom) and *O-Cl-trans* (where the oxygen atom points away from the chlorine atom). Similar to the previous study, the microwave spectra of both conformers were measured in the pulsed jet for the first time and the rotational parameters of both conformers were successfully discovered. We plan to continue working on this system in the future. The results of this study and the study of 3Cl4FBA will be presented at the Southeast Regional Conference of the American Chemical Society (SERMACS) in Augusta, GA, November 2018.

Project Impact:

This project has made a significant impact on the careers of undergraduate students at Coker College and the PI. The undergraduate students have taken part in authentic scientific research, and they have learned analytical thinking skills, presentation skills, and scientific research skills. These skills will serve them well in their careers in STEM fields. The PI was enabled to continue pursuing research in his chosen field of interest and work in the satisfying environment of mentoring students in small, less structured environments. This provides great intellectual satisfaction and certainly stimulates a more effective classroom educator. It is not an exaggeration to state that being involved in undergraduate research (an activity made possible by this grant) is life-changing for both the student and the PI.

[1]R.S. Ruoff, T.D. Klots, T. Emilsson, and H.S. Gutowsky, *J. Chem. Phys*. **93**, (1990) 3142-3150.