Molecular Geometry and the Chlorine Nuclear Quadrupole Coupling Constant of Chlorosulfonic Acid

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INTRODUCTION

Chlorosulfonic acid is a super acid with an approximate pKa of -6.49. This acid is used as a catalyst in the production of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) which are substances known as surfactants. Surfactants are used in materials such as frying pans which prevent other substances from sticking onto the surface. PFOS and PFOA are chemicals that have bioaccumulated around the world because of their stability and strong interaction with water. This strong interaction with water is due to the polar ends of PFOS and PFOA.

This study of chlorosulfonic acid is part of a systematic study on a series of sulfonic acids to understand the properties of PFOS in order to advance the removal of these substances from the environment.

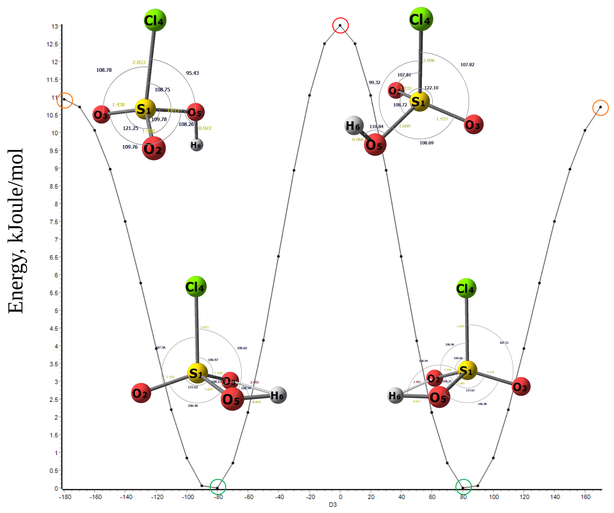
MATERIALS AND METHODS

Quantum chemical calculations were performed using the Lonestar 5 supercomputer of the Texas Advanced Computing Center. Initially, a potential energy scan was conducted along the Cl_4, S_1, O_5, and H_6 dihedral angle. This allowed us to see the most stable conformers of chlorosulfonic acid. From here, we were able to optimize the molecular structure of the acid with great precision. The results reported were obtained using Density Functional Theory (DFT) and Møller-Plesset perturbation theory (MP2) with an aug-cc-pVTZ basis set. This was also done for chlorosulfonic acid interaction with one water molecule.

The reported results include values such as rotational constants, dipole moments, and nuclear quadrupole coupling constants. These values were used to simulate microwave spectra which predict the frequencies in which chlorosulfonic acid undergoes rotational motions.

RESULTS

Figure 1: Potential Energy Scan along the Cl_4, S_1, O_5, and H_6 dihedral angle



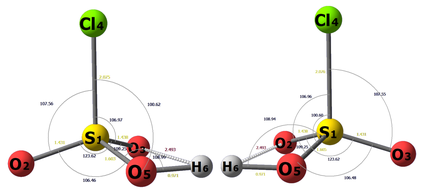
RESULTS

Figure 1 shows the potential energy scan of chlorosulfonic acid. The bottom two structures are the most stable structures while the top two are structures corresponding to the energy barriers, meaning they are not as stable. Geometry optimization was done on the most stable structure of this project to obtain the spectroscopic parameters.

Table 1: Monomer Rotational Constants

	Values	DFT (aug-cc-pVTZ)	MP2 (aug-cc-pVTZ)
Rotational Constants (MHz)	***A***	4905.55	4928.69
	B	2746.01	2824.43
	C	2727.71	2795.87
Dipole Moments (Debye)	μ_a	0.58	0.69
	μ_b	2.2	1.9
	μ_c	1.6	2.0
Hyperfine Constants	χ_{aa}	-72.84	-67.22
	χ_{bb}-χ_{cc}	0.998	2.15

Figure 2: Optimized Monomer Structure



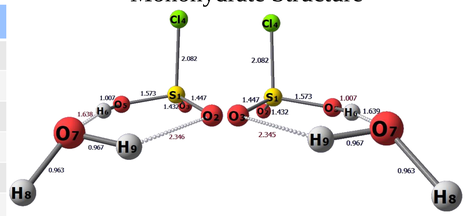
Note: Hyperfine constants refer to nuclear quadrupole coupling induced by chlorine with spin state of 3/2.

Table 1 contains the rotational constants, dipole moments, and nuclear quadrupole coupling constants of our observed molecule. The nuclear quadrupole coupling constants are a form of measurement of the electric field gradient produced by the chlorine atom. This is unique to atoms with a nuclear spin greater than ½. **Figure 2** shows the optimized structures of chlorosulfonic acid. Both structures shown in **Figure 2** have the same energies and are both represented by the values in **Table 1.**

Table 2: Monohydrate Rotational Constants

	Values	DFT (aug-cc-pVTZ)	MP2 (aug-cc-pVTZ)
Rotational Constants (MHz)	***A***	2989.28	2990.72
	B	1673.23	1770.59
	C	1368.36	1431.05
Dipole Moments (Debye)	μ_a	4.3	4.1
	μ_b	1.1	1.0
	μ_c	0.04	0.03
Hyperfine Constants	χ_{aa}	8.75	14.31
	χ_{bb}-χ_{cc}	-78.68	-81.05

Figure 3: Optimized Monohydrate Structure



Note: Hyperfine constants refer to nuclear quadrupole coupling induced by chlorine with spin state of 3/2.

Table 2 shows the rotational constants, dipole moments, and nuclear quadrupole coupling constants of the chlorosulfonic acid monohydrate (its interaction with one water molecule). The acid interacts with the water molecule and is stabilized by the hydrogen bonds represented by the dotted lines (shown by **Figure 3**). Again, both structures in **Figure 3** have equal energies and are both represented by **Table 2** values**.** Additionally, both structures show the hydrogen bonds are about 2.34Å for O_3-H_9 and O_2-H_9 interactions and 1.64Å between the H_6-O_7 interaction (Å is Armstrong or $1x10^{-10}$m).

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- The authors acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin for providing {HPC, visualization, database, or grid} resources that have contributed to the research results reported within this paper. URL: http://www.tacc.utexas.edu

SIMULATED SPECTRA

Figure 4: Simulated Spectrum of Chlorosulfonic Acid

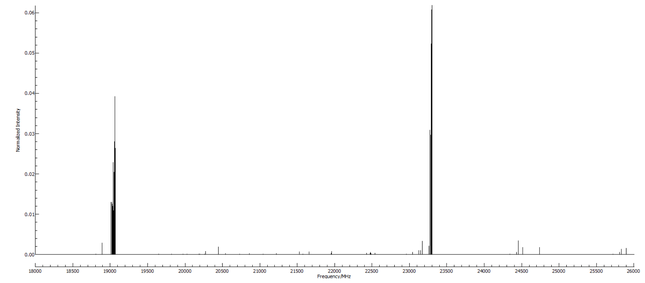
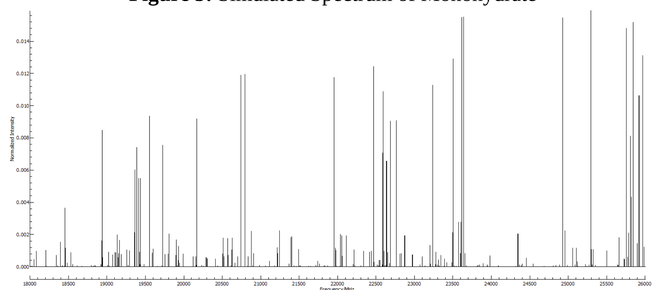


Figure 5: Simulated Spectrum of Monohydrate



The simulated spectra are shown above, represented by **Figure 4** and **Figure 5**. **Figure 4** shows the simulated microwave spectrum for chlorosulfonic acid. **Figure 5** shows the predicted microwave spectrum for the acid and its interaction with one water molecule (the monohydrate). These simulated spectra where built using the theoretical rotational values reported in **Table 1** and **Table 2**, respectively. In the future, the rotational spectra for these molecules will be analyzed based on the simulated spectra.

CONCLUSION

In conclusion, this project has consisted of running theoretical calculations on chlorosulfonic acid and its monohydrate. The potential energy scan allowed us to observe the most stable structures and to geometrically optimize them. With this, we were able to simulate the microwave spectra which gives information on where rotational transitions occur.

The future of this project is underway to obtain the observed values for the dihydrate and trihydrate structures. Additionally, the goal is to obtain the rotational spectra through microwave spectroscopy and assign the spectra with the guidance of this work.

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