Geometries, Thermodynamics, and Concentrations of Hydrated Carbonyl Sulfide Complexes

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Carbonyl sulfide (OCS), with a lifetime of approximately seven years, is one of the most long-lived atmospheric sulfur species and is believed to be responsible for the sulfate aerosol layer in the stratosphere. Morokuma and coworkers have shown computationally that SO_3 bound to the water dimer produces a more energetically favorable reaction for the formation H_2SO_4.[1] McKee and Wine computationally elucidated the mechanism of the reaction of OCS with OH.[2] We calculated geometries, vibrational frequencies, and atmospheric concentrations of $OCS(H_2O)_n$, where n=1-4.

SPARTAN[3] was used to create initial structures for $OCS(H_2O)_n$, where n=1-4, which were optimized at the *ab initio* HF/6-31G* level of theory. Additional structures for n=1-4 were provided by a molecular dynamics simulation using the AMBER8[4] suite of programs. Sensible geometries were chosen from the ensemble of structures, and used as starting structures for calculations in Gaussian 03, version C.02. Gaussian-3 (G3) model chemistry was used to obtain geometries, frequencies, and thermodynamic properties. The resulting structures were then optimized with MP2/aug-cc-pVDZ, which calculated geometries different from those obtained using G3. The MP2/aug-cc-pVDZ structures better correspond with the experimental structure for $OCS(H_2O)$ found by

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[1] Morokuma K.; Muguruma, C. *J. Am. Chem. Soc*. **1994**, 116, 10316.
[2] McKee M. L.; Wine P. H., *J. Am. Chem. Soc.* **2001**, 123, 2348.
[3] SPARTAN. *Spartan*, 5.1.3 ed.; Wavefunction, Inc.: Irvine, CA 92612, 1998.
[4] Case, et al., AMBER 8, University of California, San Francisco. 2004.

Tatamitani and Ogata via Microwave Fourier Transform spectroscopy.[5] These MP2/aug-cc-pVDZ structures will aid our understanding of the role of water in the catalyzed atmospheric oxidation of OCS. Our calculations also show the inadequacy of G3 to model accurately the long-range interactions with sulfur and water, or provide us with thermodynamic properties for the $OCS(H_2O)_n$ complex.

[5] Tatamitani, Y.; Ogata, T. *J. Chem. Phys.* **2004**, 121, 9885.