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.[5] Gaussian-3 (G3) model chemistry was used to obtain geometries, frequencies, and thermodynamic properties. The resulting unique structures were then optimized with MP2/aug-cc-pVDZ. We then performed single-point energy calculations using the MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVTZ methods. We have also extrapolated a complete basis set limit of each global minimum for n=1-4. The low energy dimer at 0 K corresponds with the experimental structure for $OCS(H_2O)$ observed by Tatamitani and Ogata via Microwave Fourier Transform spectroscopy.[6] We have also calculated atmospheric concentrations of the $OCS(H_2O)$ dimer of 6.78×10^6 molec•cm^3 at 298.15 K.

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