

# A Coupled-Cluster Study of Isomers of H<sub>2</sub>SO<sub>2</sub>

Brian Napolion, Ming-Ju Huang, and John D. Watts

Department of Chemistry, P.O. Box 17910, Jackson State University, Jackson, MS 39217

## Abstract

A theoretical study has been made on six isomers of H<sub>2</sub>SO<sub>2</sub> using coupled-cluster singles and doubles with non-iterative triple excitations (CCSD(T)). The isomers studied are sulfoxylic acid (S(OH)<sub>2</sub>; C<sub>2</sub> and C<sub>s</sub> conformers), sulfinic acid (HS(=O)OH; 2 C<sub>1</sub> conformers), dihydrogen sulfone (H<sub>2</sub>SO<sub>2</sub>; C<sub>2v</sub>), a peroxide (HSOOH; C<sub>1</sub>), thiadioxirane (C<sub>s</sub>), and a superoxide (H<sub>2</sub>SOO; C<sub>s</sub>). Molecular geometries, harmonic vibrational frequencies, and infrared intensities of all species were obtained using the CCSD(T) method and the 6-311++G(2d,2p) basis set. All aforementioned species were found to be local minima, with the exception of thiadioxirane, which has one imaginary frequency. A prior possible infrared observation of sulfinic acid was reassessed based on the present data. In agreement with previous MP2 results, the present CCSD(T) data provide support for at most 4 of the 8 observed frequencies. The CCSD(T) frequencies and intensities should be of assistance in future identification of H<sub>2</sub>SO<sub>2</sub> isomers by vibrational spectroscopy. Relative energies were calculated using the CCSD(T) method and several larger basis sets. As found previously, the lowest energy species is C<sub>2</sub> S(OH)<sub>2</sub>, followed by C<sub>s</sub> S(OH)<sub>2</sub>, HS(=O)OH, H<sub>2</sub>SO<sub>2</sub>, HSOOH, thiadioxirane, and H<sub>2</sub>SOO. Expanding the basis set significantly reduces the relative energies of HS(=O)OH and H<sub>2</sub>SO<sub>2</sub>. The CCSD(T) method was used with extended basis sets and basis set extrapolation in two reaction schemes to calculate the standard enthalpy of formation of C<sub>2</sub> S(OH)<sub>2</sub>.