Simulated absorption spectra of atmospherically-relevant sulfur molecules

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Small sulfur-containing molecules are thought to play important roles in the atmospheric chemistry of Earth and other planets. However, because of inherent physiochemical challenges, there are gaps in what is currently experimentally known about some of these molecules, including some electronic absorption spectra.

We have simulated electronic absorption spectra of several sulfur-containing molecules using a nuclear ensemble approach. The ensembles are based on Wigner sampling of vibrational frequencies calculated at the CCSD(T) level of theory, with electronic excited state transitions for each geometry in the ensemble calculated at the EOM-CCSD level of theory.

We have benchmarked the accuracy of our simulated electronic absorption spectra by comparing them to experimentally measured spectra, where available. In general, we find very good agreement between theory and experiment, and that the ideal calculation parameters are similar for the different molecules. This suggests that the theoretical approach that has been developed is reasonably robust, and can be expected to yield similar accuracy for molecules where the experimental electronic absorption spectra are unknown.

We have applied our theoretical approach to simulate the electronic absorption spectra of sulfuric acid (H_2SO_4) and OSSO, molecules which have yet to be successfully experimentally measured, despite considerable experimental efforts to do so. For H_2SO_4, our simulated cross-sections in the actinic region are greater than previous estimates, suggesting that further experimental investigation is warranted. For OSSO, we find that our simulated cross-sections are consistent with an unknown absorber in the atmosphere of Venus, suggesting that OSSO may be responsible.