Studying the Formation of HSO_4^- Water Clusters Using Various Basis Sets

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Though their role is not completely understood, sulfur-containing particles are thought to play an active role in the formation of aerosols. In this study, we looked at the ionic $HSO_4^-(H_2O)_n$ clusters, where n=1-6. Studying the thermodynamics of these substances will hopefully help to increase our understanding of the mechanisms involved in aerosol formation in the atmosphere.

The $HSO_4^-(H_2O)_n$ clusters were built using Spartan software and subsequently optimized at the MP2/6-31G* and MP2/aug-cc-pVDZ level. Single point calculations were carried out using the MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ basis sets on each of the optimizations. The $HSO_4^-(H_2O)_5$ and $HSO_4^-(H_2O)_6$ systems were run through molecular dynamics simulations at 298° K. After this, 100 configurations were pulled out and the output files were converted to Gaussian command files. These configurations were run using MP2/6-31G* geometry optimization, then the single point energy was calculated using the aug-cc- pVDZ basis set. The energies of the structures that minimized were obtained, and those within 2.0 Kcal of the lowest energy structure were run using the MP2/aug-cc-pVDZ//MP2/aug-cc-pVDZ and MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ methods.

This method produced 2 low energy structures for the $HSO_4^-(H_2O)_5$ system. We also were able to compare two different optimizations, and discovered that using the MP2/aug-cc-pVDZ optimization gave the lowest energy structures. Since the thermodynamics of ionic clusters with more than 4 waters are relatively unknown, our goal for this project is to determine at which point the addition of water becomes unfavorable. We hope to study the effect that many waters surrounding a system has on the formation of aerosols, particularly those containing ions.

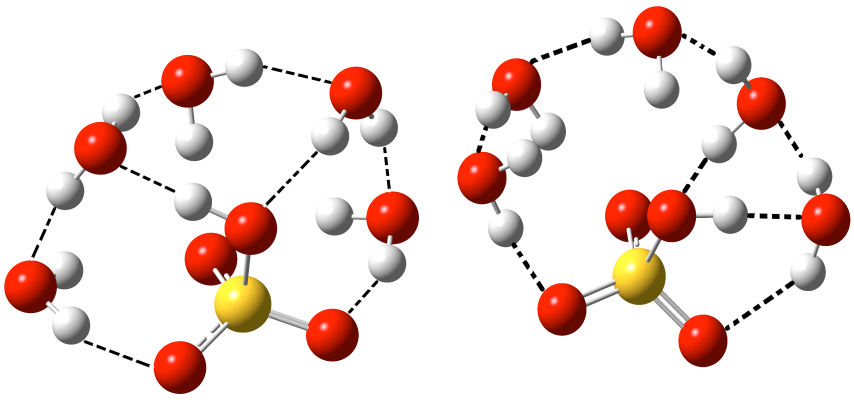

Figure 1. Two low energy structures for $HSO_4^-(H_2O)_5$ at the MP2/aug-cc-pVDZ//MP2/aug-cc-pVDZ level of theory