Studying the Formation of HSO_4^- Water Clusters Using High Level Computational Models

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

The clusters $HSO_4^-(H_2O)_n$ where n=1-6 were built using Spartan software and the geometries were minimized. The systems were then run using the MP2/6-31G* and MP2/aug-cc-pVDZ geometry optimizations. We then ran single point calculations 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 $HSO_4^-(H_2O)_6$ cluster were initially built using Spartan software and their geometries was minimized. The systems were run through molecular dynamics simulations at 298° K. After this, we pulled out 100 structures and converted the output files to Gaussian command files. We ran these using MP2/6-31G* geometry optimization, then calculated the single point energy using the aug-cc- pVDZ basis set. The energies of the structures that minimized were obtained and the structures that were within 2.0 Kcal of the low energy structure were then 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 different methods, and discovered that the MP2/aug-cc-pVDZ optimization works best for these systems. Since the thermodynamics of ionic clusters with more than 4 waters are relatively unknown, our goal for the future direction of this project is to keep adding more waters to the system, to see what amount of waters causes the system to become unfavorable. We hope to study the effect that many waters surrounding a system has on the formation of aerosols and ultimately how these aerosols lead to climate changes.

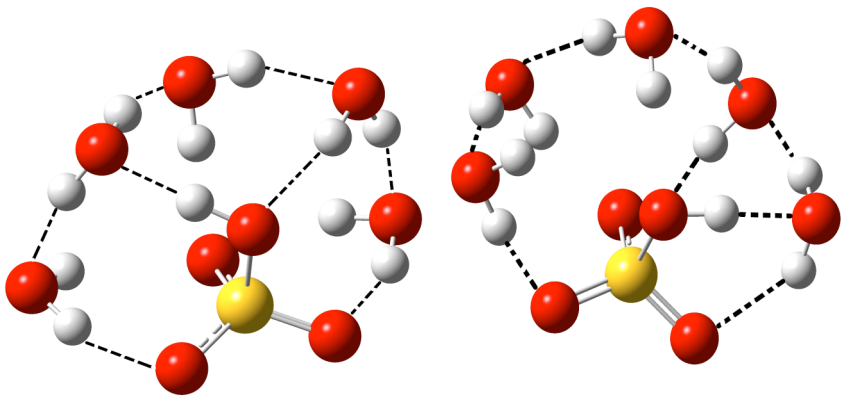

Figure 1. Two low energy structures for $HSO_4^-(H_2O)_5$ at the MP2/aug-cc-pVDZ//MP2/aug-cc-pVDZ level of theory