

Studying the Formation of Ionic $\text{HSO}_4^- \cdot (\text{H}_2\text{O})_{n=1-6}$ Aerosols

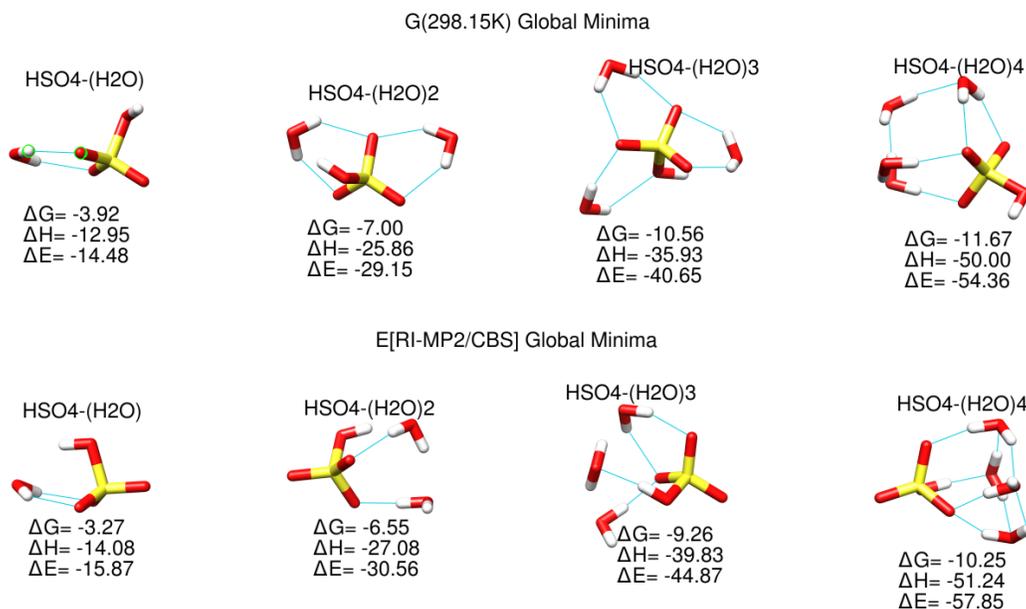
Devon Husar, Berhane Temelso, George, C. Shields

Department of Chemistry, College of Arts & Sciences, Bucknell University, Lewisburg, PA 17837

The $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ system is known to be one of the most important binary nucleation systems in the atmosphere. Being a strong acid, H_2SO_4 quickly dissociates into HSO_4^- and H_3O^+ in the presence of four or more waters. In this study, we concentrated on the hydration of HSO_4^- with up to 6 waters in order to increase our understanding of aerosol formation from these small clusters which are smaller than the detection limit of current experimental techniques.

For $n=1,2$, we calculated RI-MP2 complete basis set limit (CBS) binding electronic and Gibbs free energies starting with initial structures provided by Kurten *et al.*¹ For $n=3-6$ we extracted 100-200 configurational snapshots from molecular dynamics simulations and optimized them using with RI-MP2/aug-cc-pVDZ before extrapolating their binding energies to the complete basis set (CBS) limit using RI-MP2/aug-cc-pVXZ (X=D, T, Q) single point energies. RI-MP2/aug-cc-pVDZ harmonic vibrational frequencies were used to calculate thermodynamic corrections to the RI-MP2/CBS electronic binding energy. This method produced 12 isomers for $\text{HSO}_4^-(\text{H}_2\text{O})_3$ and 10 isomers of $\text{HSO}_4^-(\text{H}_2\text{O})_4$ that were within 2 kcal/mol of the electronic or Gibbs free energy global minimum isomer.

We have found that for the smallest systems the waters prefer to form hydrogen bonds with the oxygens of HSO_4^- , whereas for $n=3, 4$ they form hydrogen bonds with one another as well. By comparing this system to the neutral H_2SO_4 water cluster, it can be seen that the larger ionic clusters have more and stronger hydrogen bonds because the hydrogen are more attracted to the negatively charged core ion than to the neutral molecule. For every $\text{HSO}_4^-(\text{H}_2\text{O})_{n=1-4}$, the electronic energy and Gibbs free energy global minimum isomers are different and they differ by at least 1 kcal/mol due to the entropic effects. The thermodynamics for the formation of $\text{HSO}_4^-(\text{H}_2\text{O})_{n=1-4}$ is favorable at 298.15K and we are currently working on studying the $\text{HSO}_4^-(\text{H}_2\text{O})_5$ and $\text{HSO}_4^-(\text{H}_2\text{O})_6$ systems.



At 298K
Units in Kcal/mol

Figure 1. The lowest RI-MP2/CBS Gibbs free energy (top) and electronic energy isomers of $\text{HSO}_4^-(\text{H}_2\text{O})_n$, $n=1-4$

¹ Kurten, T., et al.(2007). *Boreal Environ. Res.*, 12(3), 431-453.