

A Study on the Hydration Thermodynamics of SO_4^{2-} and H_3O^+ Aerosol clusters

Edgardo Parrilla, Berhane Temelso, George C. Shields

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

Elevated concentrations of sulfates in the atmosphere lead to an increased albedo effect, which helps by offsetting the negative effects of greenhouse gases. Sulfur particles (aerosols) in the atmosphere interact with water molecules in order to form aerosol clusters commonly referred to cloud condensation nuclei (CCN). Our aim for this study is to better understand the formation of CCN whose size ($\sim 3\text{nm}$ or less) is below the detection limit of current experimental apparatus. Reliable computational studies have shown that it takes only four water molecules to cause H_2SO_4 , a strong acid, to dissociate to HSO_4^- and H_3O^+ . Further addition of water leads to the dissociation of HSO_4^- to SO_4^{2-} and more H_3O^+ , which both form very strong hydrogen bonds with water due to their charge. It is thus important that one investigates the hydration of SO_4^{2-} and H_3O^+ to understand the role of sulfuric acid as a CCN.

For $n=1-6$ of the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ cluster, we optimized structures obtained from Jieli *et al.*ⁱ at the RI-MP2/aug-cc-pVDZ level and extrapolated to the binding energy to complete basis set (CBS) limit using RI-MP2/aug-cc-pVXZ (X=D, T, Q) single point energies. From these results we obtained thermodynamic properties (enthalpy, electronic energy and Gibbs free energy). For the sulfate ion, we employ the same approach, except that the structures for $\text{SO}_4^{2-}(\text{H}_2\text{O})_{n=3-5}$ are taken from 200 configurational snapshots of molecular dynamics simulations for each cluster. After systematically screening out unstable structures using low level methods, 60-40 lowest energy isomers are optimized using RI-MP2/aug-cc-pVDZ and single point calculations were done with RI-MP2/aug-cc-pVXZ (X=D, T, Q) levels of theory to find thermodynamic properties (enthalpy, electronic energy and Gibbs free energy). This scheme yielded between 10 and 16 low energy structures for the SO_4^{2-} hydrates. The observed hydrogen bonds on the sulfate system are much stronger than those of H_2SO_4 and HSO_4^- hydrates due to the negative charge on the SO_4^{2-} core. The hydration thermodynamics of both the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ are substantially more favorable than those of water clusters as well as H_2SO_4 and HSO_4^- hydrates.

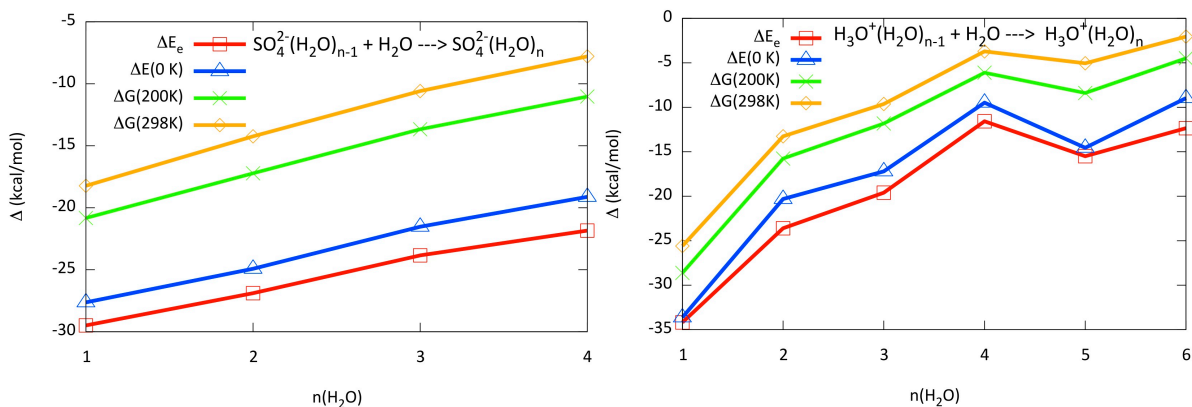


Figure 1: The RI-MP2/CBS stepwise hydration energies of the sulfate and hydronium ions.

ⁱ Jieli, M., & Aida, M. (2009). *J. Phys. Chem. A*, 113(8), 1586-1594.