An *ab initio* Study of the Hydration of Sulfuric Acid Dimers

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A presence of sulfuric acid (SA) has been known to play an important role in the formation of atmospheric aerosol particles. Recent experimental studies[1] have determined that the critical nucleus of sulfuric acid aerosols under atmospheric conditions is 0.7-1.4 nm in diameter and likely contains two sulfuric acids in its core. That implies once a two sulfuric acid cluster forms, its growth into a large aerosol (1 - 10000 nm) is thermodynamically favorable. In an attempt to understand the thermodynamics of forming a bigger system of 2 SA molecules with up to eight water molecules, we have conducted a computational study using *ab initio* methods. Starting with a large set of stable isomers determined by Ding et al.[2], we optimized the geometries and calculated the harmonic vibrational frequencies using MP2/6-31+G* with analytic gradients and hessians. Then, the single point energies were calculated at the RI-MP2/aug-cc-pVXZ, X = D, T, Q and the binding energy was extrapolated to the complete basis set (CBS) limit. The RI-MP2/CBS binding energies were combined with the MP2/6-31+G* thermodynamic corrections to yield benchmark enthalpies and free energies of formation for $(H_2SO_4)_2(H_2O)_{n=0-8}$. Sulfuric acid dimers are much more tightly bound than water dimer or H_2SO_4-H_2O. Adding water molecules to a sulfuric acid dimer shows similar hydration thermodynamics as the H_2SO_4 $(H_2O)_n$ system. A major difference is that the dissociation of the protons of SA dimer hydrates $[(H_2SO_4)_2(H_2O)_n \rightarrow (H_2SO_4)(HSO_4^-)(H_3O^+)(H_2O)_{n-1}]$ starts in the presence of two waters while the single SA system needs at least four waters. The results also show that starting with $(H_2SO_4)_2(H_2O)_3$, ionic structures are more favorable than neutral ones. Finally, most stable structures have at least one bridging water between the two SA.

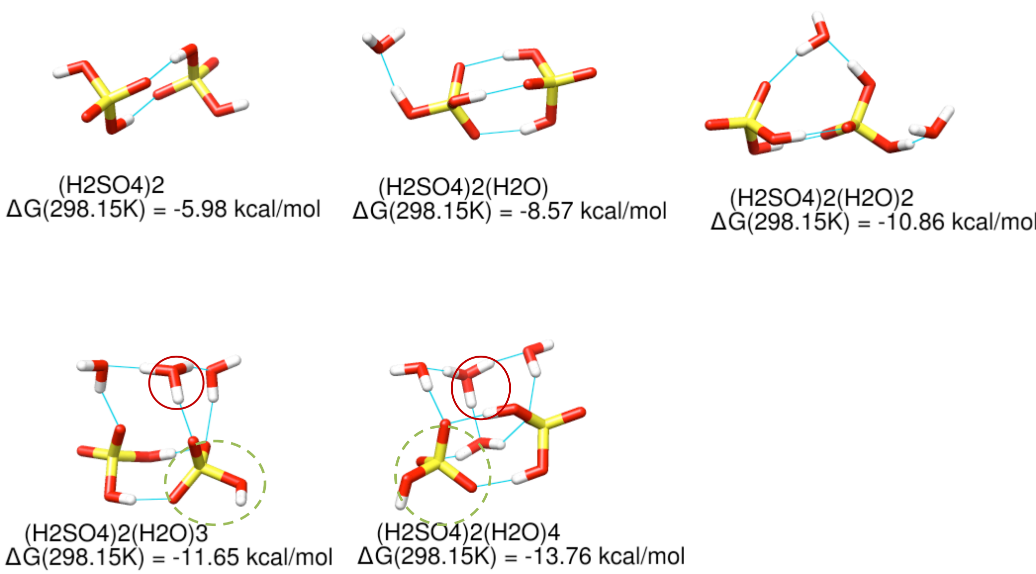

Figure 1: The RI-MP2/CBS Gibbs free energy global minima for $(H_2SO_4)_2(H_2O)_{n=0-4}$.

[1] Sipila, M., et al. (2010). The Role of Sulfuric Acid in Atmospheric Nucleation. *Science*, *327*(5970), 1243–1246.

[2] Ding, C. G., et al. (2003). Two sulfuric acids in small water clusters. *J. Phys. Chem. A*, *107*(41), 8648–8658.