An *ab initio* Study of the Enhanced Effect of Ammonia on Sulfuric Acid Dimers-Water Formation

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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. However, recent experimental studies[1] have indicated that the ratio of ammonia to SA is more likely to be 1:2 in most condition. In an attempt to understand the enhanced effect of ammonia on SA dimer nucleation with up to three water molecules, we have conducted a computational study using *ab initio* methods. Starting with a neutral isomer, we used molecular dynamics (MD) simulations at various temperatures to sampling all possible structures. We then optimized the geometries and calculated the harmonic vibrational frequencies using B2PLYP/def2-svp. 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 B2PLYP/def2-svp thermodynamic corrections to yield benchmark enthalpies and free energies of formation for $(H_2SO_4)_2NH_3(H_2O)_{n=0-3}$. $(H_2SO_4)_2$-NH_3 is much more tightly bound than SA dimers, H_2SO_4-NH_3, or H_2SO_4-H_2O. Adding water molecules to a $(H_2SO_4)_2NH_3$ shows similar hydration thermodynamics as the $(H_2SO_4)_2(H_2O)_n$ system. A major difference is that the dissociation of the protons of SA dimer hydrates $[(H_2SO_4)_2NH_3(H_2O)_n \rightarrow (H_2SO_4)(HSO_4^-)(NH_4^+)(H_2O)_{n-1}]$ starts without the presence of water while the $(H_2SO_4)_2(H2O)_n$ system needs two waters. The results also show that the most stable structures have the ammonia bridging between the two SA. Finally, the second proton from the SA dimer transfers to the water when there are 3 water molecules.

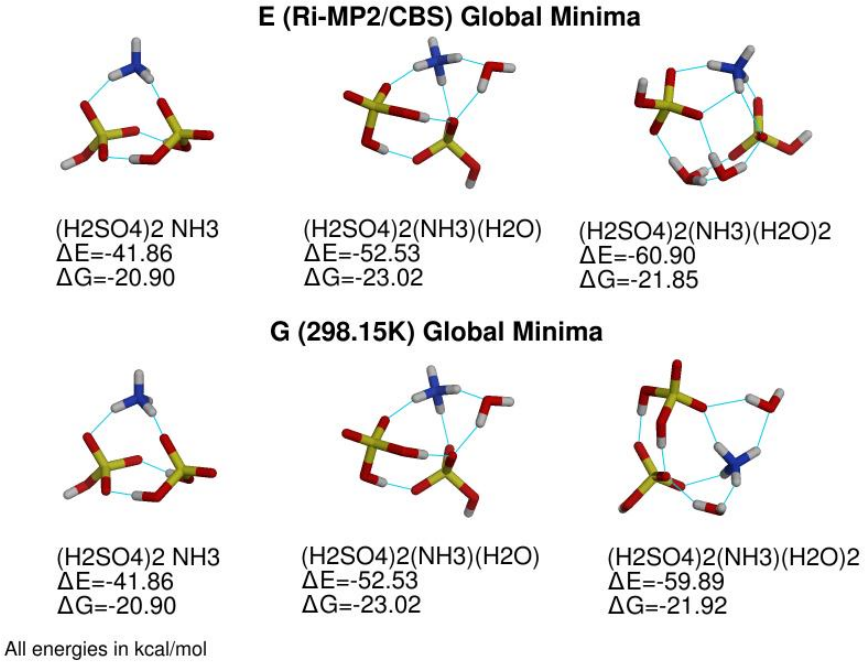

Figure 1: The RI-MP2/CBS electronic and Gibbs free energy global minima for $(H_2SO_4)_2(NH_3)(H_2O)_{n=0-2}$.

[1] Torpo, L., et al. (2007). Significance of Ammonia in Growth of Atmospheric Nanoclusters. *J. Phys. Chem. A, 111*(42), 10671–10674.