# Structure and Growth Thermodynamics of Sulfuric Acid Trimer Hydrates

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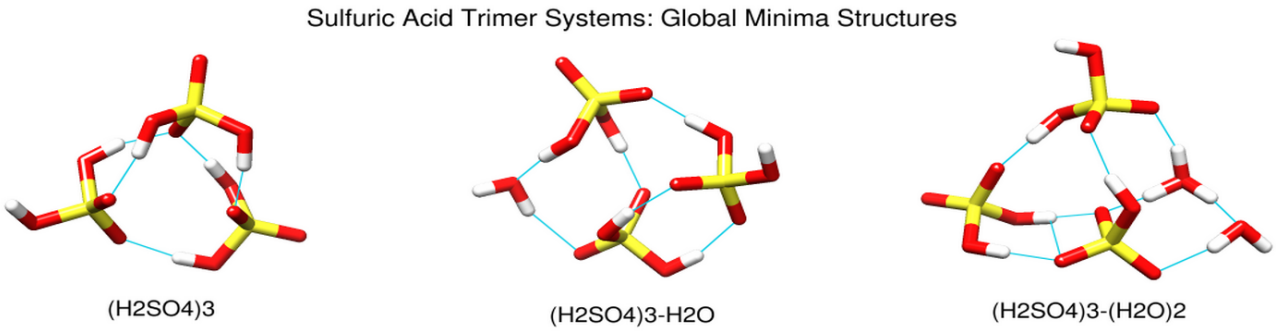
The $H_2SO_4$-$H_2O$ binary system plays an important role in the formation of atmospheric aerosols. Although many articles have investigated the formation of sulfuric acid monomer and dimer hydrates -- $(H_2SO_4)_{n=1-2}(H_2O)_m$, few have included larger systems containing 3 sulfuric acids bound to multiple waters. The purpose of our research is to determine if a sulfuric acid trimer hydrate is stable enough to form a critical cluster.

Starting with initial coordinates from Torpo *et al.*[1], we ran molecular dynamics simulations and extracted up to 300 configurations which were subsequently clustered and optimized using PBE0/def2-svp optimizations and B2PLYP/def2-svp. The final electronic and free energies for the low energy structures were determined by extrapolating RI-MP2/aug-cc-pVXZ (X=D,T,Q) single points and combining them with B2PLYP/def2-svp thermodynamic corrections to obtain the binding electronic and Gibbs free energies for each of the cluster size.

Our previous studies[2] have shown that the addition of sulfuric acid to the $H_2SO_4$-$H_2O$ cluster leads to increasingly lower electronic and Gibbs free energy. Our results lead us to affirm the previous results and show that the thermodynamics of adding water to a sulfuric acid monomer, dimer or trimer hydrates does not greatly change as the difference in electronic or Gibbs free energy are found to be about 1 kcal/mol. It is also noted that the first acid dissociation of sulfuric acid [ $H_2SO_4$-$H_2O \rightarrow HSO_4^-$-$H_3O^+$] occurs in the presence of two waters in the case of the sulfuric acid trimer whereas four waters are needed for the sulfuric acid monomer. Our next step is determining whether a sulfuric acid trimer hydrate bound to three waters leads to a greater tendency towards the formation of bisulfate ions.




[1] L. Torpo et al. *J. Phy. Chem. A.* (**2007.**) 111.10671-10674.
[2] Temelso, B., *et al.*: J. Phys. Chem. A, **2012,** *116 (9),* 2209–2224