Growth of Neutral $H_2SO_4•(H_2O)_{n=1-6}$ Aerosols in the Troposphere

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The H_2SO_4/H_2O system is the most important binary nucleation system in the atmosphere: significant concentrations of SO_4^{2-} exist in the troposphere and the stratosphere is predominantly comprised of hydrated sulfuric acid. H_2SO_4 is hygroscopic and therefore important to cloud condensation nucleation (CCN). In an attempt to better understand the process by which primary aerosols become secondary aerosols, we study neutral $H_2SO_4•(H_2O)_n$, n = 1 – 6 clusters.

For n =1 – 4, we optimize Kurten *et al.*'s[1] structures and generate thermodynamic data at the RI-MP2/aug-cc-pVDZ level of theory. Configurational snapshots from constant temperature molecular dynamics (MD) simulations were used to generate candidate structures for n = 5,6. Subsequent RI-MP2/aug-cc-pVDZ geometry optimizations provided accurate structures and energy extrapolations using RI-MP2/aug-cc-pVXZ, X = D, T, Q yielded benchmark quality RIMP2/CBS thermodynamic quantities. The populations of these clusters under atmospherically relevant conditions were calculated using the RIMP2/CBS free energies of formation. The interesting hydrogen bonding formations, interplay between energy and entropy as well as the favorability of di-ionic structures with increasing cluster sizes is noted.

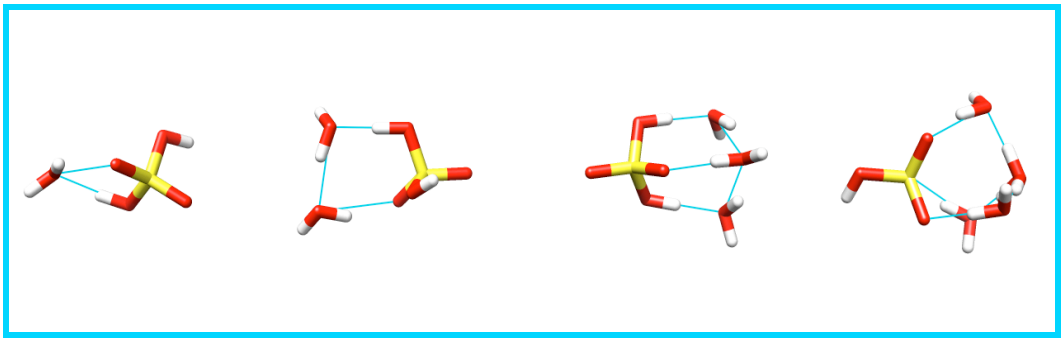

Fig 1. Most stable structures of $H_2SO_4•(H_2O)_n$, n = 1–4 clusters with respect to their Gibbs free energy at 298.15K [G(298.15)]

[1] Kurten, T. *et al.* (2007). *Boreal Env. Res.*, *12*(3), 431–453.