Searching for Global Minima of Hydrogen Bonded Systems

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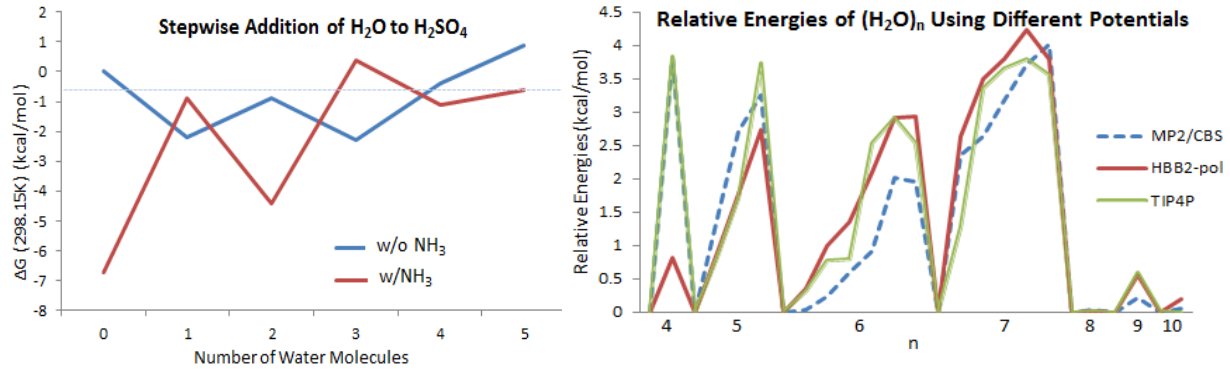
Finding the global minimum of a hydrogen bonded system is never a simple task. Even when the lowest energy isomer is found, there is no guarantee that the structure found is indeed the absolute global minimum. Therefore, our work focuses on not only finding the global minima of hydrogen bonded systems but also thermally accessible low energy isomers at tropospheric temperatures. The systems of interest in our work are atmospheric aerosols containing sulfuric acid, ammonia, and water along with water clusters containing eleven to fifteen water molecules, where we found minima by combining molecular dynamics (MD) or basin-hopping Monte Carlo sampling with RI-MP2 calculations.

Regarding the aerosols system, previous work[1] has shown that binary nucleation with sulfuric acid and water is not sufficient to explain atmospheric observations. Therefore, our search extended to ternary systems containing sulfuric acid, ammonia, and up to five water molecules. Ammonia was chosen as the third species because it is easily available in the atmosphere. Finding minima for $(H_2O)_n$ where n=11-15, proved to be exceedingly difficult. Initially, starting configurations were extracted from MD simulations but there were issues finding low energy structures when we compared our results to reported data. Therefore, we turned to Monte Carlo minimization (basin-hopping) with TIP4P waters to find the starting minima for RI-MP2 calculations, which produced reasonable low energy structures. A comparison of different potentials was also completed for clusters where n=4-15 to test the performance of rigid, non-polarizable TIP4P against the flexible, polarizable HBB2 potential.



(a) (b)

Figure 1. (a) The Gibbs free energy stepwise addition of water to sulfuric acid with and without ammonia. (b) A comparison of the relative energies of low energy isomers of $(H_2O)_n$ calculated at the MP2/CBS, TIP4P and HBB2-pol level.

[1] Kirkby, J., *et al.*: Nature, **2011**, *476*, pp. 429-433