Modeling the Enhancement of Aerosol Formation Due to Amines

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The binary H_2SO_4-H_2O system is the most important pathways by which aerosols form in the atmosphere and the presence of ternary species like amines has been shown to increase aerosol formation rates. In this study, we concentrated on the hydration of system of sulfuric acid (H_2SO_4) and methylamine (NH_2CH_3) with up to 3 waters in order to improve our understanding of aerosol formation from this ternary system. Being a strong acid-base system, H_2SO_4-NH_2CH_3 quickly forms a tightly bound HSO_4-NH_3CH_3 complex on which water condenses more readily than it would on H_2SO_4 itself. For the H_2SO_4-$NH_2CH_3(H_2O)_{n=0-3}$, we ran molecular dynamics (MD) simulations and randomly sampled up to 300 structures which were subsequently clustered by similarity. The sufficiently different structures were first optimized using PBE0/def2-svp and finally with RI-MP2/aug-cc-pVDZ. The low energy structures were subject to energy extrapolation to the complete basis set limit (CBS) using RI-MP2/aug-cc-pVXZ (X=D, T, Q) and thermodynamics corrections using RI-MP2/aug-cc-pVDZ harmonic vibrational frequencies.

We found that there is proton transfer between sulfuric acid and methylamine even in the absence of water and that it is strongly bound. The RI-MP2/CBS electronic binding energy of H_2SO_4-NH_2CH_3 was -21.8 kcal/mol compared to -16.8 kcal/mol for H_2SO_4-NH_3 and -12.8 kcal/mol for H_2SO_4-H_2O. Looking at the standard Gibbs free energy of adding water, it is more favorable in the case of H_2SO_4-NH_2CH_3 than in H_2SO_4-NH_3 or H_2SO_4-H_2O. To further understand the role of other bases in aerosol formation, we are also investigating the binding thermodynamics of dimethylamine, $NH(CH_3)_2$ and trimethylamine, $N(CH_3)_3$ to sulfuric acid.

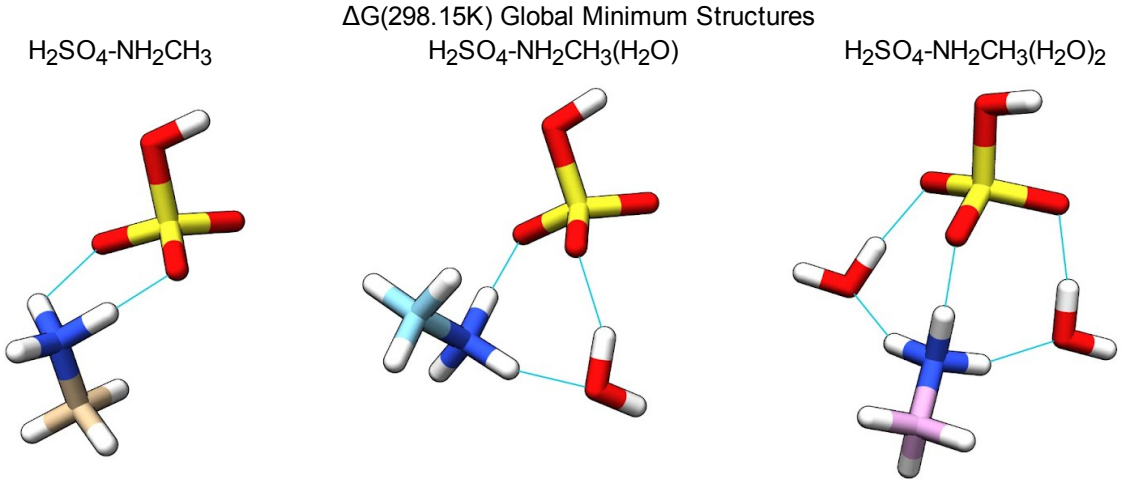

Figure 1. The lowest RI-MP2/CBS Gibbs free energy (at 298.15K) of H_2SO_4-$NH_2CH_3(H_2O)_{n=0-2}$.