The Effect of Amines on the Enhancement Aerosol Formation

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The binary H_2SO_4-H_2O nucleation is the most important pathway by which aerosols form in the atmosphere and the presence of ternary species like amines increases 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 5 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_2SO4 itself. For the H_2SO_4-$NH_2CH_3(H_2O)_{n=0-4}$, we ran molecular dynamics (MD) simulations and randomly sampled up to 200 structures. The sufficiently different structures were first optimized using MP2/6-31G* 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 RIMP2/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.

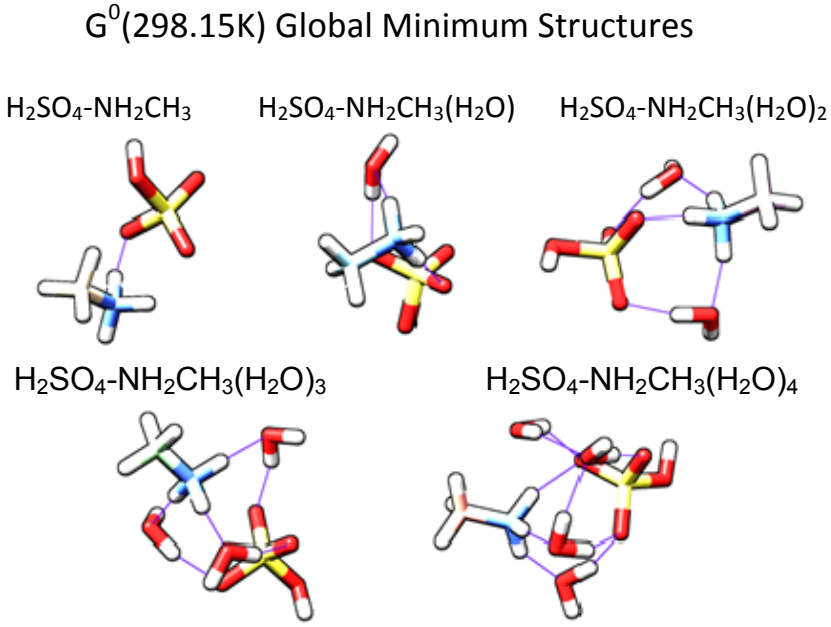

Figure 1. The lowest standard Gibbs free energy minima of H_2SO_4-$NH_2CH_3(H_2O)_{n=0-4}$.