Sulfate Aerosol Formation Rates in the Presence of Different Bases: Ammonia, Methylamine, Dimethylamine, Trimethylamine and Mixed Ammonia-Amines

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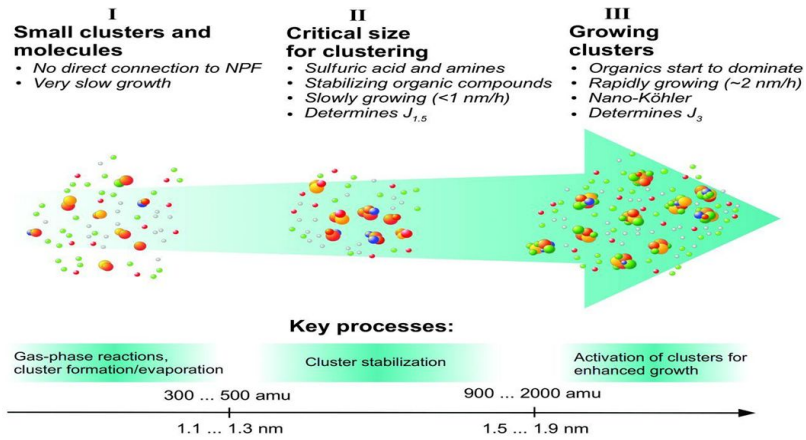
Aerosol particles in the atmosphere reflect back sunlight and regulate the lifecycle of clouds. Our work focused on ternary sulfate aerosols containing methylamine (MA, CH_3NH_2), Dimethylamine (DMA, C_2H_7N), Trimethylamine (TMA, C_3H_9N), ammonia (A, NH_3), the combination of Ammonia and each Amine. Each of these bases and compounds were bonded with a sulfuric acid dimer (S_2) or with one sulfuric acid (S_1). We compared the stability of the clusters formed. These bases were chosen because recent experiments have shown that the presence of heterogeneous bases enhances aerosol structure stability significantly more than homogeneous bases. This work attempts to explain this phenomena using computational tools.

In order to properly sample the possible configurations, we used genetic algorithm (GA) with the PM7 and EFP semiempirical methods. Once we received The unique low energy structures from the final pool of structures for PM7 and EFP they were minimized using the PW91/ 6-31G* density functional method. These structures were then run through PW91, M06-2X and wB97X-D methods with 6-311++G** basis sets. . Although experimental measurements showed that there was a greater strength in the binding for the DMA-A system. The computed binding energy of the clusters yielded a result of DMA_2 (PW91, wB97X-D) or TMA_2 (M06-2X). The differences in results created the need for us to benchmark these 3 functionals against the wave functional, MP2. The benchmarking was done on the S1-base1 systems as well as S1-base2 and S2-base1 systems. All 3 functionals matched the general results of MP2. Overall wB97X-D matched MP2 the best followed by M062X then PW91. The reasons for this difference between experiments and computational predictions will be further explored.



Kulmala, M. et al. Direct observations of atmospheric aerosol nucleation. Science 339, 943–946