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Formation rates, stability and reactivity of sulfuric acid – amine clusters predicted by computational chemistry

Theo Kurtén (1), Ismael Ortega (2), Oona Kupiainen (2), Tinja Olenius (2), Ville Loukonen (2), Heidi Reiman (1), Matthew McGrath (2), and Hanna Vehkamäki (2)

(1) University of Helsinki, Department of Chemistry, Finland (theo.kurten@helsinki.fi), (2) University of Helsinki, Department of Physics, Finland

Despite the importance of atmospheric particle formation for both climate and air quality, both experiments and non-empirical models using e.g. sulfuric acid, ammonia and water as condensing vapors have so far been unable to reproduce atmospheric observations using realistic trace gas concentrations. Recent experimental and theoretical evidence has shown that this mystery is likely resolved by amines. Combining first-principles evaporation rates for sulfuric acid – dimethylamine clusters with cluster kinetic modeling, we show that even sub-ppt concentrations of amines, together with atmospherically realistic concentrations of sulfuric acid, result in formation rates close to those observed in the atmosphere. Our simulated cluster formation rates are also close to, though somewhat larger than, those measured at the CLOUD experiment in CERN for both sulfuric acid – ammonia and sulfuric acid – dimethylamine systems. A sensitivity analysis indicates that the remaining discrepancy for the sulfuric acid – amine particle formation rates is likely caused by steric hindrances to cluster formation (due to alkyl groups of the amine molecules) rather than by significant errors in the evaporation rates.

First-principles molecular dynamic and reaction kinetic modeling shed further light on the microscopic physics and chemistry of sulfuric acid – amine clusters. For example, while the number and type of hydrogen bonds in the clusters typically reach their equilibrium values on a picosecond timescale, and the overall bonding patterns predicted by traditional "static" quantum chemical calculations seem to be stable, the individual atoms participating in the hydrogen bonds continuously change at atmospherically realistic temperatures.

From a chemical reactivity perspective, we have also discovered a surprising phenomenon: clustering with sulfuric acid molecules slightly increases the activation energy required for the abstraction of alkyl hydrogens from amine molecules. This implies that the oxidation rate of amines by OH and possibly other oxidants may be decreased by clustering, thus prolonging the chemical lifetime of amines in the air.