**Integrated Experimental And Computational Approach To Molecular Based Characterization Of Aerosol Particle Formation**

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***Highlight summary of the proposed research:*** Aerosols play an important role in Earth's climate by influencing the radiative energy balance directly through interaction with solar radiation and indirectly through cloud condensation.[1,2] A fundamental understanding of aerosol formation processes is essential towards the development of reliable and predictive climate models.

The creation of new aerosol particles from gaseous precursors in the atmosphere, as opposed to direct emission from Earth's surface, has been particularly difficult to characterize. The nucleation phase of this process occurs at small length scales (~1nm or less), which presents significant challenges for conventional characterization methods. As a result there is much uncertainty regarding the actual nucleation pathways and species involved. One of the important open questions is the impact ammonia/amines,[2-8] and organic acids on the typical nucleation process involving sulfuric acid and water.

This problem is addressed in our proposal through the application and development of molecular based description of aerosol nucleation. The unique feature of our approach is the integration of experimental photoelectron spectroscopy measurements and theoretical description based on quantum and statistical mechanical calculations. We will provide extensive structural and chemical analysis of nucleating clusters involving atmospherically important species. The subsequent thermodynamical analysis of the corresponding nucleation pathways will be used to establish connection with classical nucleation theory through quantum-mechanically derived surface tension parameters.

***Project Description:***
Knowledge of cluster chemical composition and structure along nucleation pathways is a basic prerequisite towards building a mechanistic understanding of aerosol formation pathways. The small size of critical clusters (less than 1nm) involved in the nucleation process is just outside the resolution of modern aerosol field measurement techniques,[12-14] and different characterization methods are required. IR action spectroscopy [15,16] and mass spectrometry[17-19], and have been used provide useful information about small atmospherically relevant cluster complexes. In our project we propose to utilize negative ion photoelectron spectroscopy (PES) - a technique that has not yet been widely used for cluster/aerosol characterization. The unique feature of PES is that it directly probes the energetic properties of the clusters. The primary experimental quantity in PES is the electron binding energy (EBE) – the difference in cluster energies before and after the electron detachment process. Given its sensitivity to the details of local environment, the EBE provides an ideal probe to study clusters of different size and composition. In our experimental setup, the clusters will be produced from solutions containing the corresponding chemical components using an electrospray ionization (ESI) source, and analyzed and separated using time-of-flight (TOF) mass spectrometry.[20] Then selected clusters of interest will be probed and photo-detached using negative ion photoelectron spectroscopy at various photon energies ranging from 266 nm to 157 nm.

*Ab-initio* modeling has been used successfully in the past to characterize clusters relevant to aerosol formation.[21-25] In our project such calculations are directly integrated with experimental PES characterization, which would significantly improve reliability of theoretical results for large size clusters. Calculations will be performed using NWChem[26], a high performance computational chemistry package developed at EMSL. Following our previous work in this area,[27,28] calculations will involve the generation of an ensemble of lowest energy isomers and EBE calculations. The latter step will link calculations with the experimental data and identify the actual cluster observed experimentally. The generation of isomer structures would be facilitated using recently developed genetic optimization algorithm, which combines fragments of previously optimized clusters to generate diverse and unbiased population of candidate structures. Actual optimizations will be performed using density functional theory (DFT) using B3LYP approximation for the exchange-correlation functional. Various levels of theory will be used for EBE calculations, including higher levels of theory such as coupled cluster with perturbative triples (CCSD(T))[29]. In additional to conventional *ab-initio* techniques, fragment-based calculations[30] will also be utilized. The accuracy of these calculations will be benchmarked by direct comparison to experimental data for small cluster sizes.

The second component of our project is focused on the molecular description of thermodynamic parameters of nucleation process. Specifically, our objective is to provide surface tensions parameters used in classical nucleation theory (CNT) directly from the *ab-initio* cluster free energies. This can be accomplished by extrapolating CNT model, valid at the macroscopic bulk limit, down to the molecular scale where *ab-initio* effects play a dominant role. By fitting the two models together, we can access bulk values of surface tensions parameters over the wide range of external conditions and also examine size dependent variations at the molecular level.[31-34] At the simplest level cluster-free energies will be obtained using the rigid-rotor harmonic oscillator approximation utilized in nearly all quantum chemistry calculations. More accurate values can be calculated through the integration of vibrational power spectrum generated from *ab initio* molecular dynamics of the clusters at relevant atmospheric conditions. This approach is more accurate because at atmospheric conditions the clusters sample many configurations –not just a single minimum. Finally, for small clusters, direct calculation of cluster-free energies will be investigated in conjunction with thermodynamic-free energy cycles and fragment based approximation to molecular interactions and compared to those calculated harmonically and from the vibrational spectra for consistency.

As a first step the methodology described would be applied to binary bisulfate ion water complexes. Initial measurements for small clusters (up to two water molecules) have already been performed[35], and will be extended to larger clusters. In tandem with this work, theoretical characterization of related neutral sulfuric acid will be performed. In our investigation of the ternary complexes, we will focus on two major classes of species – ammonia/amines[2-8] and organic acids.[8-11] Previous studies suggested that ammonia or amines can stabilize the embryonic clusters and decrease the evaporation through the base-stabilization mechanism,[28,36] while the organic compounds can stabilize and reduce the nucleation free energy barriers by forming strong hydrogen bonds with nucleation precursors.[28,37] As a first step the methodology described would be applied to binary bisulfate ion water complexes. Initial measurements for small clusters (up to two water molecules) have already been performed[35], and will be extended to larger clusters. In tandem with this work, theoretical characterization of related neutral sulfuric acid will be performed. In our investigation of the ternary complexes, we will focus on two major classes of species – ammonia/amines[2-8] and organic acids.[8-11] Previous studies suggested that ammonia or amines can stabilize the embryonic clusters and decrease the evaporation through the base-stabilization

mechanism,[28,36] while the organic compounds can stabilize and reduce the nucleation free energy barriers by forming strong hydrogen bonds with nucleation precursors.[28,37]

**Impact on EMSL user program and science theme**: The proposed project is aimed to provide molecular level understanding of aerosol formation directly relating to EMSL science theme for Atmospheric Aerosol Systems.

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