Role of Organosulfates in Atmospheric New Particle Formation: Theoretical Investigation

Background:

Organosulfates ($ROSO_3^-$) have emerged as major components of secondary organic aerosol (SOA) in both marine and continental atmospheres. These compounds form through reactions of biogenic volatile organic compounds (VOC's) such as isoprene and monoterpenes with sulfate-containing species. Although organosulfates are widely detected in field measurements, their potential involvement in the earliest stages of atmospheric new particle formation (NPF) remains almost completely unexplored.

Current nucleation models dominated by sulfuric acid, ammonia, amines, and water do not account for the dual chemical functionality of organosulfates, which contain both an organic backbone and a strongly acidic sulfate ester group. Their ability to hydrogen-bond, coordinate with acids/bases, and stabilize multi-component clusters makes them promising, yet poorly understood, candidates in cluster growth. Understanding their role is essential for improving predictions of aerosol formation, cloud formation, and climate forcing under future emission scenarios.

Objectives:

1. Identify representative organosulfates (isoprene-derived, monoterpene-derived, aromatic) relevant to diverse atmospheric environments.
2. Determine the thermodynamic stability of binary and ternary clusters containing organosulfates with sulfuric acid, ammonia, dimethylamine, and water.
3. Evaluate hydration effects on cluster stability (n = 0-5 H_2O).
4. Predict nucleation rates using the Atmospheric Cluster Dynamics Code (ACDC) under marine, biogenic and polluted urban conditions.
5. Compare nucleation pathways against classical H_2SO_4-DMA systems to reveal whether organosulfates enhance, inhibit, or do not influence early-stage particle formation.

Methodology:

- Cluster Generation: Use ABCluster to globally search low-energy configurations of OS- H_2SO_4 ,OS-amine, OS- H_2SO_4-amine, and hydrated clusters.
- Quantum Chemistry: Optimize structures using relevant basis set , compute Gibbs free energies at 298 K and analyze intermolecular interactions.
- Cluster Dynamics: Supply computed energies to ACDC to calculate growth rates under varied atmospheric concentrations.
- Comparison: Benchmark organosulfate cluster energetics and nucleation efficiencies against established sulfuric-acid-based systems.

Expected Outcomes:

- Thermodynamic data for organosulfate-containing clusters.
- Identification of specific organosulfates capable of stabilizing pre-nucleation clusters.
- Nucleation rate predictions revealing organosulfates as potential promoters/inhibitors of NPF.
- New mechanistic insights into organic–inorganic interactions during particle formation.

Significance:

This work will deliver the systematic investigation of organosulfates in early-stage atmospheric nucleation. By integrating quantum chemistry with dynamic nucleation modeling, the project addresses a knowledge gap in modern atmospheric aerosol science. Results will help refine climate models and deepen understanding of how evolving VOC and sulfate emissions influence global aerosol formation.