Nucleation of Tropospheric Aerosols:
A Joint Laboratory and Theoretical Study of Multicomponent Systems

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Nucleation of Tropospheric Aerosols:
A Joint Laboratory and Theoretical Study of Multicomponent Systems

Molecular-Scale Simulations

- develop models of molecular interactions controlling cluster formation
- develop methods for calculating the rates of cluster formation and decomposition (condensation & evaporation)
- model kinetics of nucleation as function of temperature and component concentration

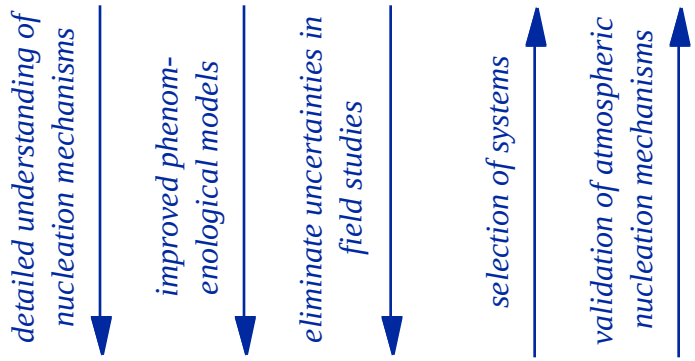
model validation and refinement ←

→ *interpretation*

Laboratory Experiments

- use laminar flow tube reactor to measure nucleation rates as a function of temperature and component concentration
- use ion cyclotron resonance and mass spectrometric techniques to measure composition of nucleated particles

EMSL/PNNL Project



Atmospheric Chemistry Modeling and Field Studies

develop an understanding of aerosol dynamics, including the role of nucleation on aerosol formation and composition

Nucleation of Tropospheric Aerosols:

Molecular simulations of cluster formation in sulfuric acid- water systems

BC Garrett, SM Kathmann, LX Dang, KA Peterson, GK Schenter, SS Xantheas

Molecular Interactions

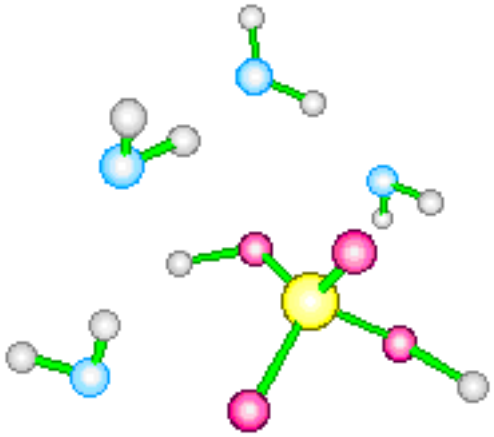
- Intermolecular interactions characterized by high-level ab initio electronic structure calculations
- Interaction energies fitted to many-body analytic functions

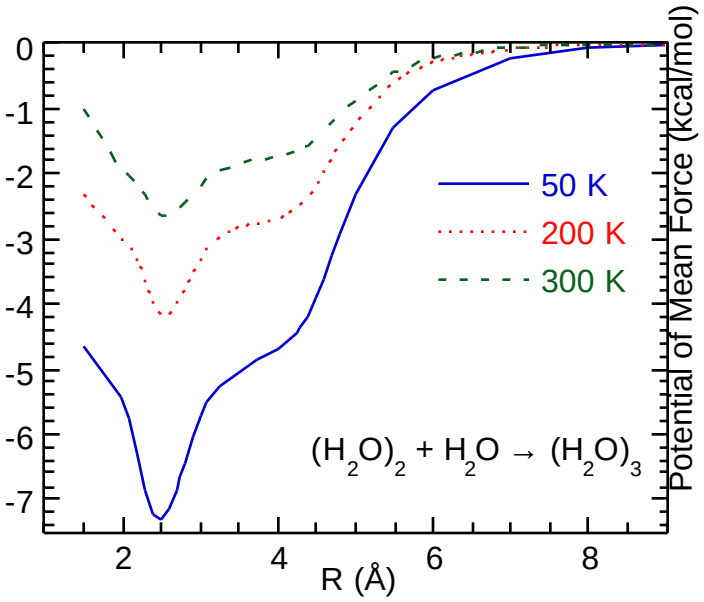
Cluster Formation and Decomposition Rates

- Condensation rates approximated by collision rate of monomers with clusters
- Evaporation rates approximated from detailed balance: requires equilibrium distribution of clusters (or equivalently the free energies of cluster formation)
- Cluster free energies calculated by statistical mechanical techniques (potential of mean force or Bennett's method)

Nucleation Kinetics

- Ordinary differential equations for cluster concentra-tions solved numerically



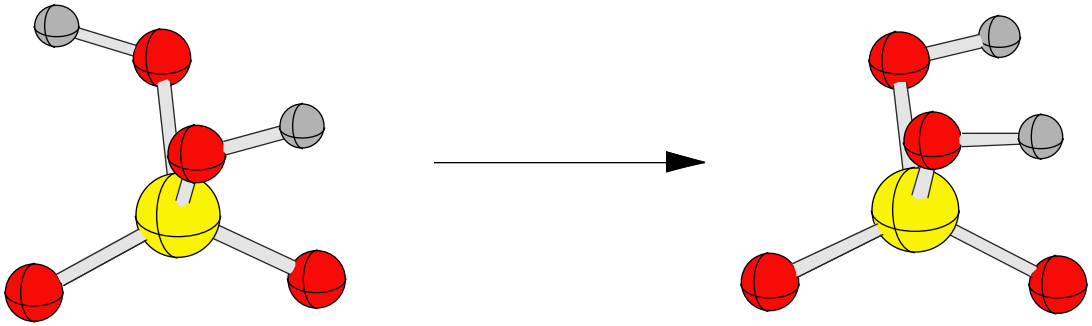


Ab initio Electronic Structure Calculations of Molecular Interactions:

MP2/aug-ccpVDZ+d calculations for sulfuric acid and water

KA Peterson

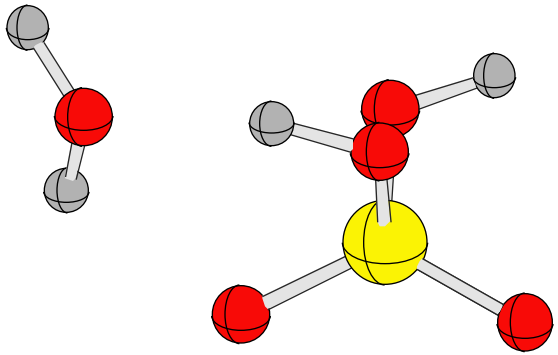
H_2SO_4 isomerization energy



ΔE_{isom} = 1.3 kcal/mol

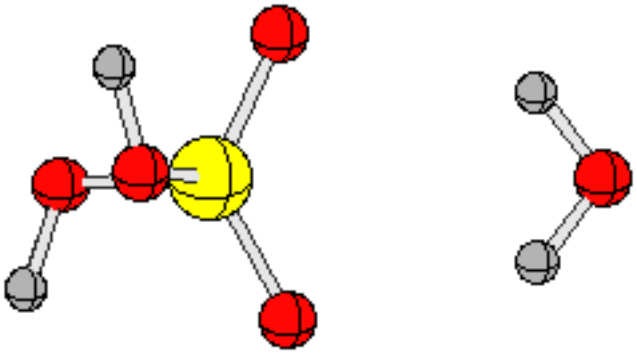
ΔH_{isom}(0 K) = 1.0 kcal/mol

H_2SO_4 - H_2O binding energies



ΔE_b = 12.7 kcal/mol

ΔH_b(0 K) = 10.4 kcal/mol



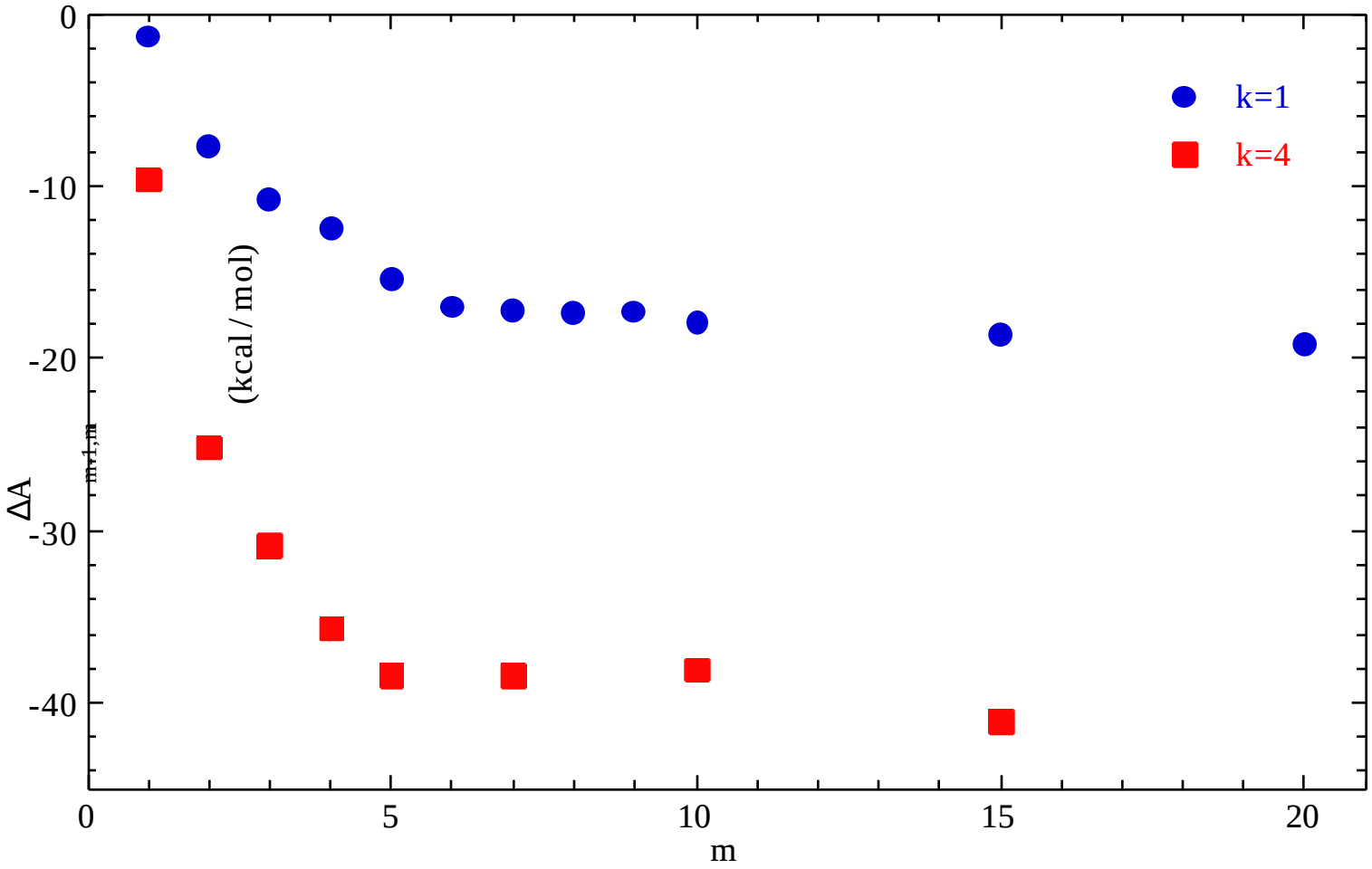
ΔE_b = 3.8 kcal/mol

ΔH_b(0 K) ≈ 1.5 kcal/mol

Helmholtz Free Energies for Sulfuric Acid-Water Cluster Formation

SM Kathmann

Incremental Free Energies, ΔA, for $(H_2SO_4)_{m-1}(H_2O)_{k(m-1)} + H_2SO_4(H2O)_k \rightarrow (H_2SO_4)_m(H_2O)_{k(m)}$
computed by Bennett's method using the interaction potential of Kathmann and Hale

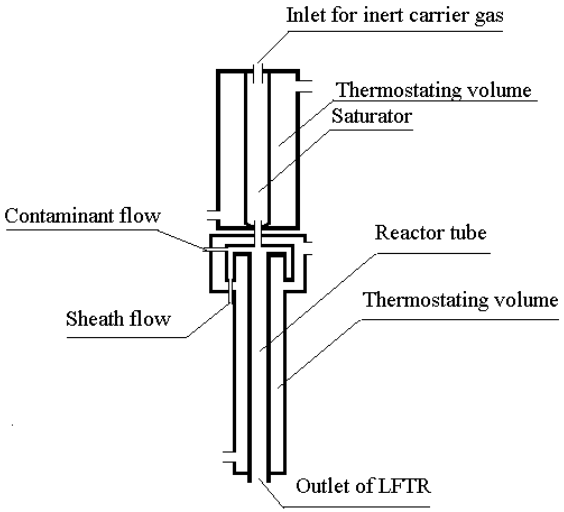


Nucleation of Tropospheric Aerosols:
Experimental Studies of Multicomponent Systems

NS Laulainen, SE Barlow, and VB Mikheev

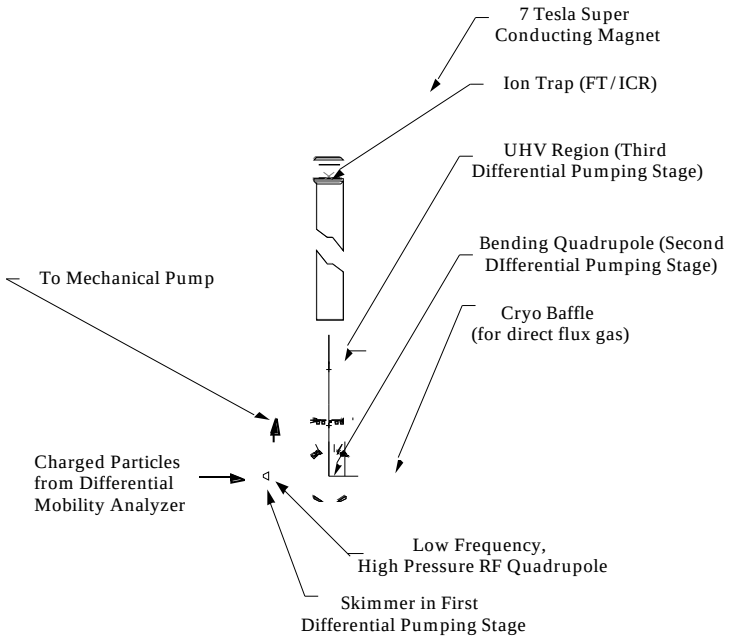
Laminar Flow Tube Reactor

- Application of the Laminar Flow Tube Reactor technique to quantify aerosol nucleation rates under controlled conditions of temperature, supersaturation, and contaminant concentrations
- Contaminant species introduced coaxially into host flow near location of maximum supersaturation
- Contaminant species may be exposed to UV or other ionizing radiation
- Each contaminant molecule can serve as a nucleation center
- Characteristics of LFTR determined through detailed computer calculations

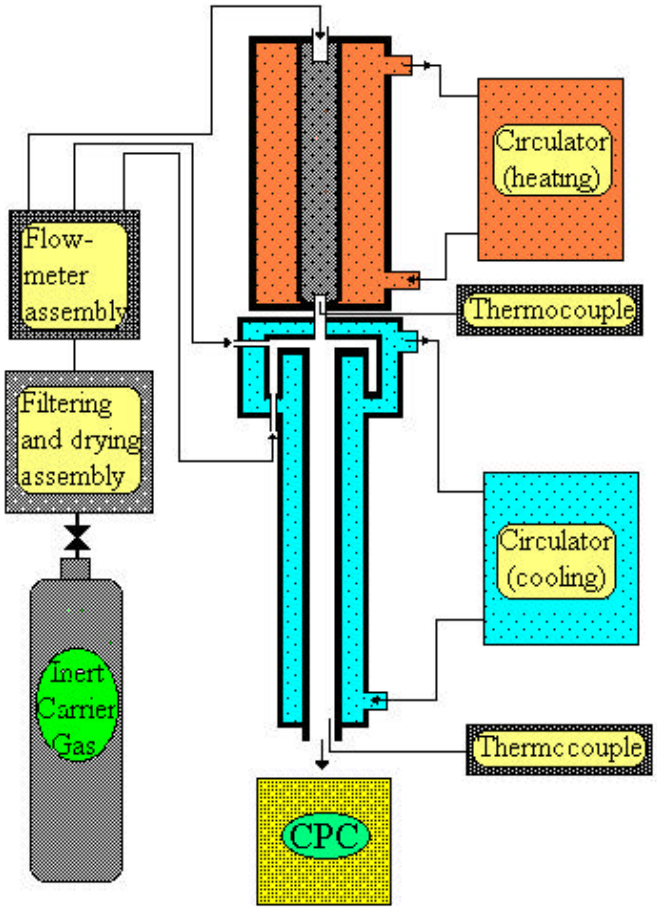


Ion Cyclotron Resonance/Mass Spectrometer

- Nucleated particles sampled and detected by sensitive particle counter and mass spectroscopy; differential mobility analyzer provides size discrimination



Laminar Flow Tube Reactor Schematic



Interface of Laminar Flow Tube Reactor with Ion Cyclotron Resonance/Mass Spectrometer