Quest for the Neutral Molecular Cluster:

Quantification of Mass Dependent Response Factors in a Novel Chemical Ionization Mass Spectrometer

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Presentation Outline

Aerosols and Climate Change

Reaction Chamber and Cluster Chemical Ionization Mass Spectrometer (CIMS)

Cluster CIMS Mass Dependent Response Factors

Coarse Particles

Fine Particles

- 2.5 μm
- 1 μm
- 0.1 μm
- 0.01 μm
- 1 nm

- 10^{-3}
- 10^{-4}
- 10^{-5}
- 10^{-6}
- 10^{-7}
- 10^{-8}
- 10^{-9}
Particulate Matter: primary and secondary aerosols
Health $(\text{PM}_{2.5}, \text{PM}_{10})$

- Climate relevant: 0.1 to 2.5 $\mu$m
- Direct and Cloud-Albedo/Indirect effects
- Tropospheric lifetime: 1-2 weeks

Growth: condensation and/or coagulation

Nucleation: Molecular Clusters

- Growth: hours to days
- Climate relevant: 0.1 to 2.5 $\mu$m

- 2.5 $\mu$m
- 1 $\mu$m
- 0.1 $\mu$m
- 0.01 $\mu$m
- 1 nm
Aerosol Radiative Forcing

Top of the troposphere

Scattering and absorption

Direct effect

Unpolluted cloud

Polluted cloud

Indirect effects

Adapted from IPCC - AR4
Aerosol Radiative Forcing

Top of the troposphere

Scattering and absorption

Direct effect

Unpolluted cloud

Increased cloud lifetime

Precipitation suppression

Indirect effects

Polluted cloud

Increased cloud height

Adapted from IPCC AR4
Aerosols and Climate Change

Components of radiative forcing for principle emissions

Reference: IPCC AR4
Aerosols and Climate Change

Radiative Forcing Components

- CO₂: 1.66 [1.49 to 1.83] Global High
- N₂O: 0.48 [0.43 to 0.53] Global High
- CH₄: 0.16 [0.14 to 0.18] Global High
- Halocarbons: 0.34 [0.31 to 0.37] Global High
- Ozone: 0.05 [-0.15 to 0.05] Continental to global Med
- Stratospheric water vapour from CH₄: 0.35 [0.25 to 0.65] Continental to global Med
- Surface albedo: 0.07 [0.02 to 0.12] Global Low
- Land use: -0.2 [-0.4 to 0.0] Local to continental Med - Low
- Black carbon on snow: 0.1 [0.0 to 0.2] Local to continental Med - Low
- Total aerosol direct effect: -0.5 [-0.9 to -0.1] Continental to global Med - Low
- Cloud albedo effect: -0.7 [-1.8 to -0.3] Continental to global Med - Low
- Linear contrails: 0.01 [0.003 to 0.03] Continental Low
- Solar irradiance: 0.12 [0.06 to 0.30] Global Low
- Total net anthropogenic: 1.6 [0.6 to 2.4] Global Low

Reference: IPCC AR4
Dominance of Neutrals: Nucleation Event

Kulmala et al., Science 318, 89 (2007)
Nucleation Events: Sulfuric Acid Correlation

- \( \text{SO}_2 + \text{OH} \) (from \( \text{O}_3 \) photolysis) \( \rightarrow \) \( \text{H}_2\text{SO}_4 \)
- Clustering of Hydrated \( \text{H}_2\text{SO}_4 \) occurs under atmospherically relevant conditions
- Observations show similar diurnal patterns for “detectable” particles and

\[
\text{H}_2\text{SO}_4 \frac{dN}{d\log D_p}, \quad \text{cm}^{-3}
\]

Birmili et al., Atmos. Chem. Phys. 361, 3, 2003
**Reaction Chamber**
- 1000 L
- Teflon film reactor
- Temperature controlled casing
- Photochemical production of H$_2$SO$_4$
- Atmospherically relevant precursor gas concentrations
- Sufficient reaction time to reach steady state

**Mass Filter**
- Octopole focusing assembly – transport of intact clusters, gas compression
- Quadrupole mass filter
- Channel electron multiplier

**CIMS Inlet**
- “Soft” chemical ionization, intact cluster
- Transverse ion drift field – neutral cluster detection
- Nitrogen sheath flow to minimize water condensation
Variable Ion Reaction Region

- Ion source: $\text{NO}_3^-$
- Flow Tube
- Charging of clusters
- Ion induced cluster growth

Credit: Fred Eisele
• Nitrogen sheath flow to minimize water condensation
Atmospheric Cluster- CIMS Measurements

Credit: Jeff Rathbone
Atmospheric Cluster- CIMS Measurements

Mass Dependence of:
- Transport
- Inlet Region
- Pinhole / N₂ flow
- Vacuum system
- Octopoles
- Quadrupoles
- Detector

Credit: Jeff Rathbone
Quantifying Cluster CIMS Response vs. Mass

System 1: Electrometer
- Ion counter
- Faraday cage electrometer

System 2: Cluster Chemical Ionization Mass Spectrometer (CIMS)
- Octopole
- Quadrupole
- Turbomolecular Pump
- Turbomolecular Pump

Credit: Mari Titcombe

Rosser & de la Mora (2005) AST, 39:1191-1200
CIMS Calibration

Monomer: 242 amu
First Cluster: 611 amu

Credit: Mari Titcombe, Jhun Zhau
Cluster-CIMS Mass Sensitivity

Electrospray Salts:
- Tetramethyl Ammonium Iodide (TMAI)
- Tetrapropyl Ammonium Iodide (TPAI)
- Tetrabutyl Ammonium Iodide (TBAI)
- Tetraheptyl Ammonium Bromide (THAB)

Credit: Mari Titcombe, Jhun Zhau
Conclusions and future work

- Sulfuric – molecular clusters
- Atmospheric CIMS – correlation analysis
- Laboratory CIMS – ionization source, operating system
- Reaction chamber – chemistry, finally!
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