CHARACTERISING CLUSTER FRAGMENTATION IN AN ATMOSPHERIC PRESSURE INTERFACE TIME OF FLIGHT (API-TOF) MASS SPECTROMETER

Monica Passananti, Evgeni Zapadinsky, Juha Kangasluoma, Nanna Myllys, Michel Attoui, Hanna Vehkamäki

INAR
Institute for Atmospheric and Earth System Research

UNIVERSITY OF HELSINKI
FACULTY OF SCIENCE
AIM IS TO UNCOVER MOLECULAR MECHANISMS OF ATMOSPHERIC PARTICLE FORMATION

Sulphuric acid often a key compound
- fossil fuel, volcanoes and plankton

Needs help from other compounds
- base compounds: ammonia and various amines
  - decomposing organisms, animal excreta, industry
- organic compounds

in some environments particles form without \( \text{H}_2\text{SO}_4 \)
MASS SPECTROMETRY CURRENTLY ONLY CHOICE FOR IDENTIFYING ATMOSPHERIC NANOCLUSTER COMPOSITION

- very low concentrations ($1/10^{17}$)
- extremely small clusters (1-2 nm)
  ▶ very challenging

Genuine calibration not possible:
- can not generate known amount of known clusters
- no other method to compare with
Collisions of clusters to background gas inside the instrument could lead to cluster fragmentation. Incorrect cluster concentration and composition.

- Model the changes in clusters
- ‘Calibrate’: change instruments tunings, model the effect of changes
Sulfuric acid clusters:
- \((\text{SA})_1\)
- \((\text{SA})_2\)
- \((\text{SA})_3\)
- \((\text{SA})_4\)
- \((\text{SA})_5\)
- \(\ldots\)

\((\text{H}_2\text{SO}_4)_2\text{HSO}_4^- = (\text{SA})_3\)
\(\text{H}_2\text{SO}_4\text{HSO}_4^- = (\text{SA})_2\)
\(\text{HSO}_4^- = \text{SA}\)
MODEL THE JOURNEY OF THE CLUSTER THROUGH THE INSTRUMENT

**Electrode**

**APiTOF**

**Electrode**

**Carrier Gas**

1. Set random initial conditions on translational, rotational and vibrational energies of the cluster.
2. Generate stochastically time of next collision.
3. Does the cluster get fragmented or reach the end point?
   - **YES**: Update statistics.
   - **NO**: Calculate new energies after the collision.

**A** : $H_2SO_4$  **Sulfuric Acid**

**B** : $H_2SO_4^-$  **Bisulfate Anion**

fragmentation channel

AAB → AB+A
STATISTICAL MODEL FOR COLLISIONS AND FRAGMENTATION

Collision between cluster and carrier gas

Contact between cluster and carrier gas

$10^{-12}$ s

Energy transfer

End of the contact between cluster and carrier gas

Energy redistribution

between vibrational and rotational modes

between vibrational modes

Fragmentation

Reaches the end or experiences another collision ($10^{-5}$ - $10^{-8}$ s)
• Determine energy transfer & fragmentation rate
• Calculated using quantum chemical methods
  • Initial optimization: semi-empirical PM6 method
  • Re-optimization: PW91/6-31+G*, PW91/6-311++G**
  • Optimization & thermochemical parameters: PW91/aug-cc-pVQZ
  • Single point energy: DLPNO-CCSD(T)/aug-cc-pVTZ
MODELED SULPHURIC ACID TRIMER SURVIVAL FRACTION vs CARRIER GAS PRESSURE

Pressure range
2nd chamber

Interface

Pressure range
1st chamber

Voltage between two electrodes

Survival fraction

Pressure, Pa

Travelled distance = 2 mm

Voltage: 2870 V/m, 3690 V/m, 4100 V/m, 4930 V/m, 5750 V/m, 6550 V/m, 7400 V/m, 8300 V/m
EXPERIMENTS AND MODEL AGREE FOR SULPHURIC ACID TRIMER SURVIVAL FRACTION
Dense gas, many collisions, low cluster velocity
Low energy collisions
No fragmentation

Sparse gas, few collisions, high cluster velocity
High energy collisions
Fragmentation

Very sparse gas, no collisions, high cluster speed
No fragmentation

SSQ (Quad1) 2 mbar
BSQ (Quad2) 10^{-3} mbar
PB (Lenses) 10^{-4} mbar

Atmospheric Pressure Interface
The relative transmission was measured for 27 tunings using 4 compounds as standard in the mass range between 103 m/z and 280 m/z (size region of SA₃, SA₂ and SA):

- Malonic Acid: 103 m/z
- Terephthalic acid: 165 m/z
- 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Ionic Liquid): 280 m/z
- 1-Ethyl-3-methylimidazolium dibutyl phosphate (Ionic Liquid): 209 m/z
FRAGMENTATION, NOT TRANSMISSION CHANGE!

Data corrected and not corrected by transmission (by ESI)

Cluster ratio (%) vs. Skimmer Voltage (V)

-19, -14, -12, -10, -9, -8, -7, -4

(SA)3, (SA)2, (SA)1, (SA)3 corrected, (SA)2 corrected, (SA)1 corrected
SIMULATION SEQUENCE

1. Set random initial conditions (on translational, rotational and vibrational energies of the cluster)

2. Time of next collision is defined

3. Does the ion get fragmented due to its energy?
   - Yes: Take into account that the ion is fragmented and start a new realization
   - No: The ion experiences a collision with the carrier gas

4. The ion experiences a collision with the carrier gas

5. Energy transfer between ion and carrier gas molecule

6. Energy redistribution inside the ion

Continue the simulation from point 2
Energy transfer between ions and carrier gas molecules

Tangential component

\[ \sim 10^{-12} \text{ s} \]

Translational energy

\[ \sim 10^{-12} \text{ s} \]

Rotational energy

\[ \sim 10^{-11} \text{ s} \]

Vibrational energy

Normal component

\[ \sim 10^{-12} \text{ s} \]

Translational energy

\[ \sim 10^{-12} \text{ s} \]

Vibrational energy

\[ \sim 10^{-11} \text{ s} \]

Rotational energy