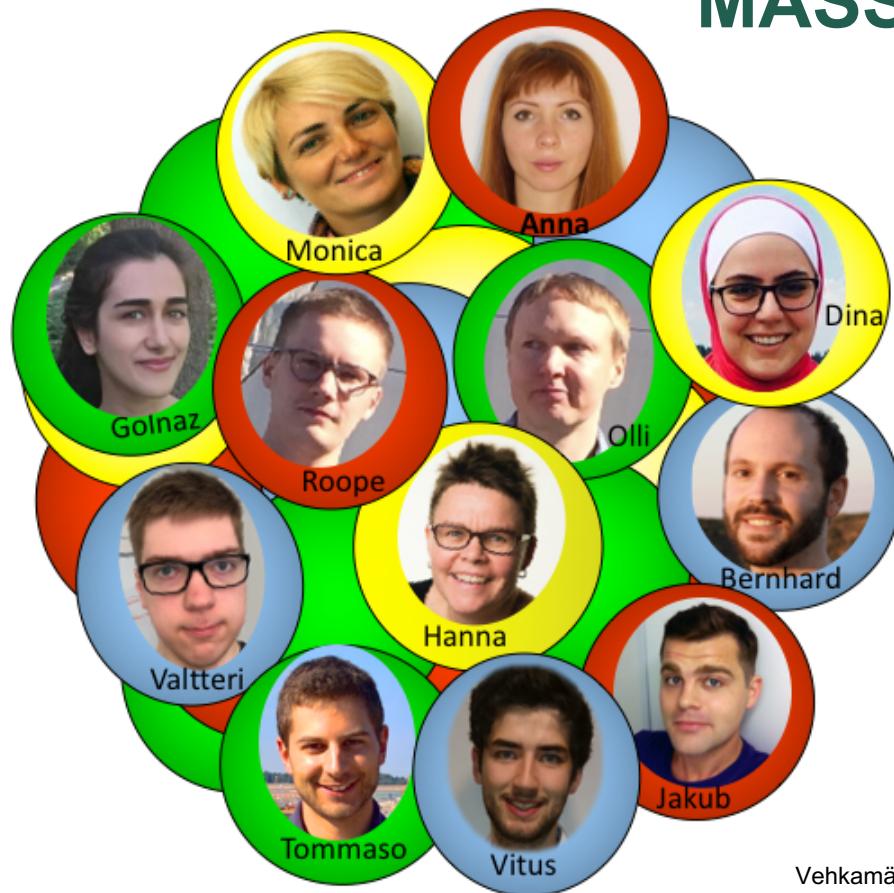


CHARACTERISING CLUSTER FRAGMENTATION IN AN ATMOSPHERIC PRESSURE INTERFACE TIME OF FLIGHT (API-TOF) MASS SPECTROMETER



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Zapadinsky, Juha Kangasluoma,
Nanna Myllys, Michel Attoui,
Hanna Vehkämäki



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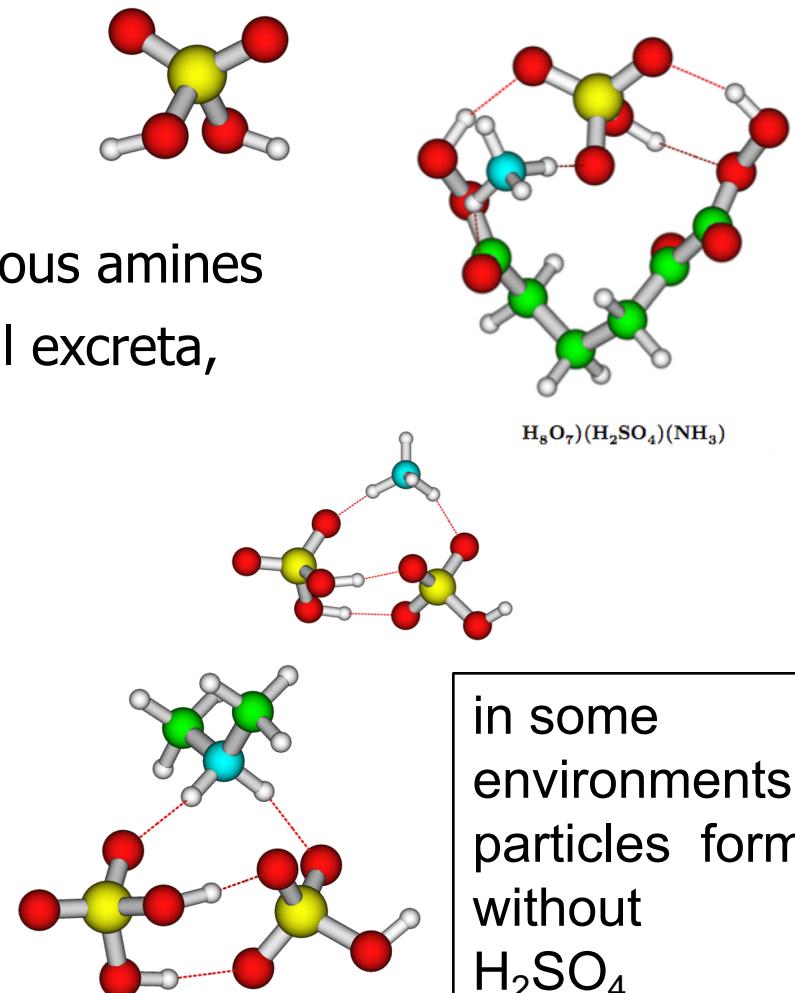
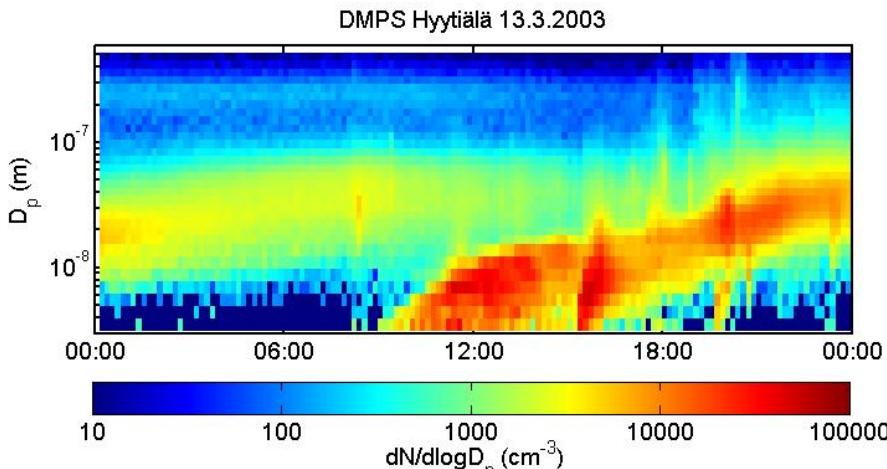
AIM IS TO UNCOVER MOLECULAR MECHANISMS OF ATMOSPHERIC PARTICLE FORMATION

Sulphuric acid often a key compound

- fossil fuel, volcanoes and plankton

Needs help from often compounds

- base compounds: ammonia and various amines
 - decomposing organisms, animal excreta, industry
- organic compounds



MASS SPECTROMETRY CURRENTLY ONLY CHOICE FOR IDENTIFYING ATMOSPHERIC NANOCLUSTER COMPOSITION

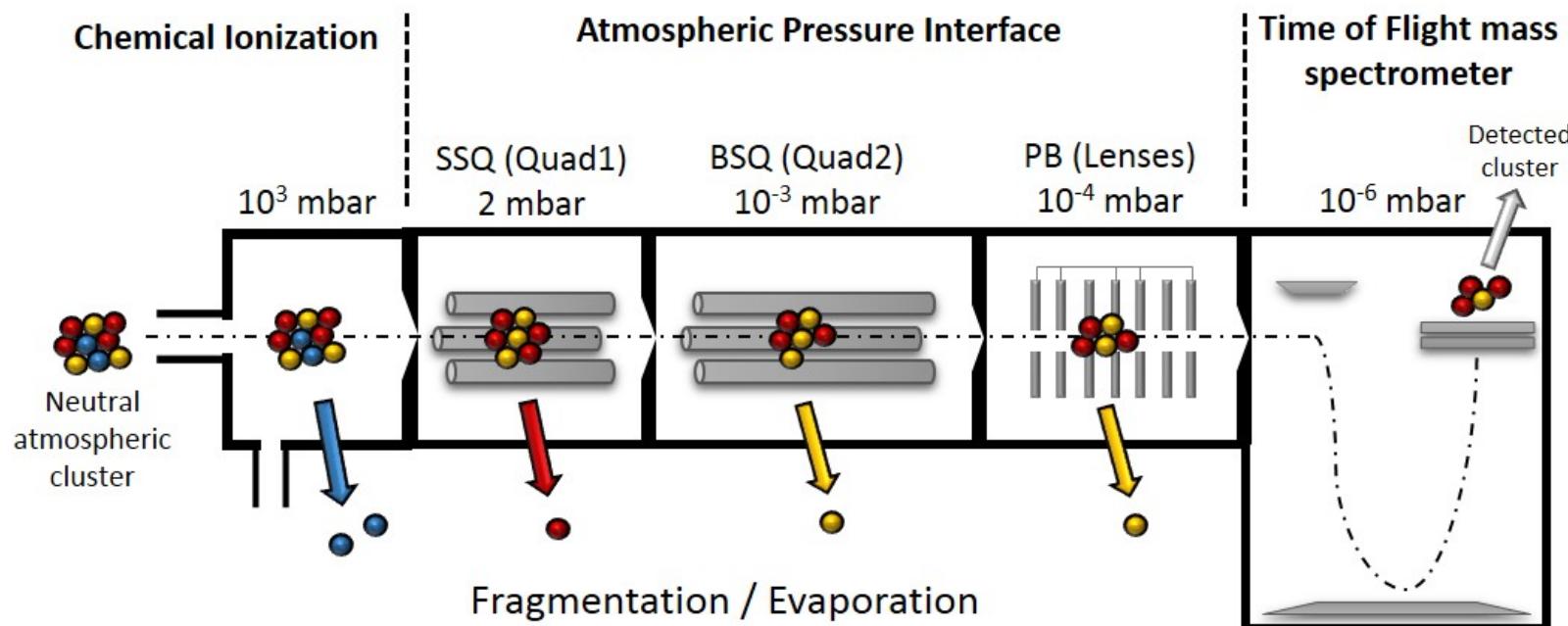


- very low concentrations ($1/10^{17}$)
- extremely small clusters (1-2 nm)
 - very challenging

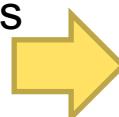
Genuine calibration not possible:

- can not generate known amount of known clusters
- no other method to compare with

CHEMICAL IONIZATION ATMOSPHERIC PRESSURE INTERFACE TIME OF FLIGHT MASS SPEC



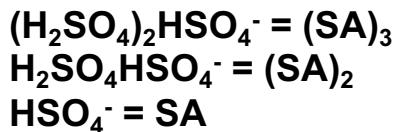
Collisions of clusters to background gas inside the instrument could lead to **cluster fragmentation**



Incorrect cluster concentration and composition

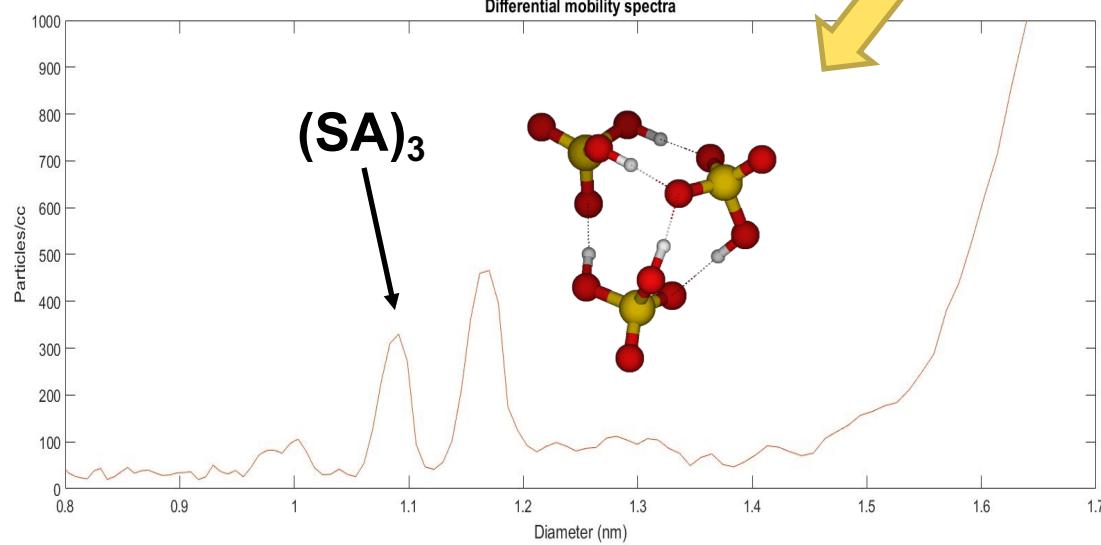


- Model the changes in clusters
- ‘Calibrate’: change instruments tunings, model the effect of changes

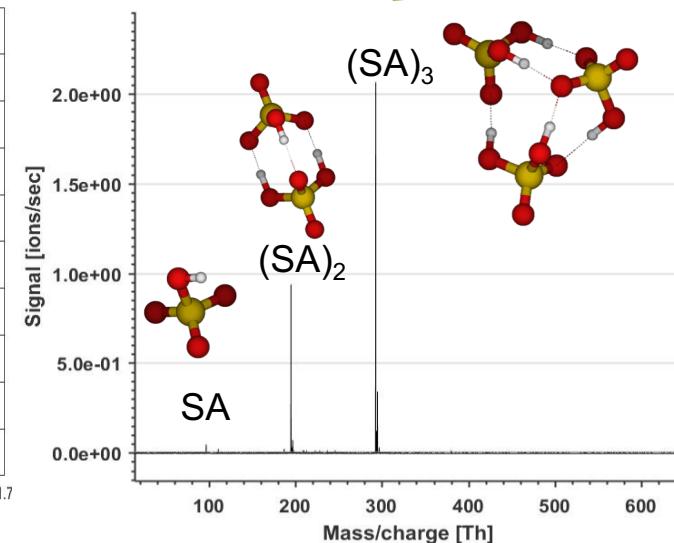
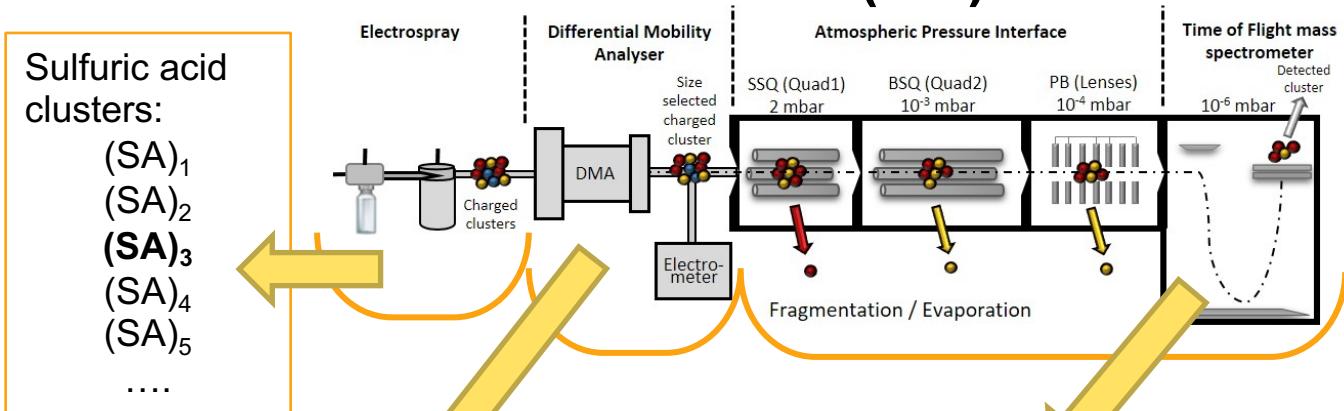


Sulfuric acid clusters:

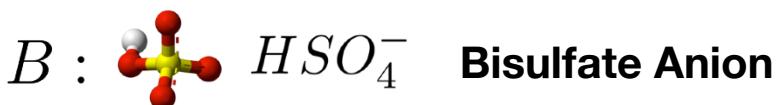
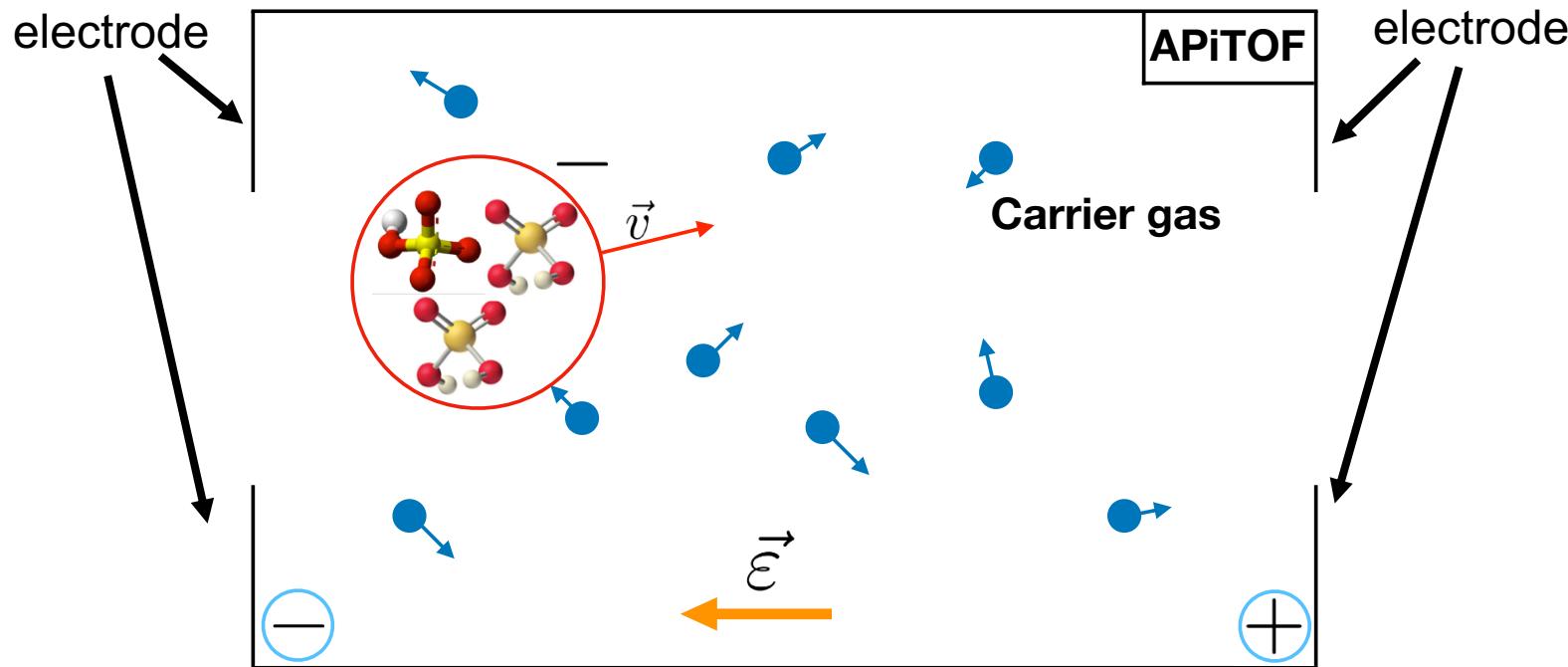
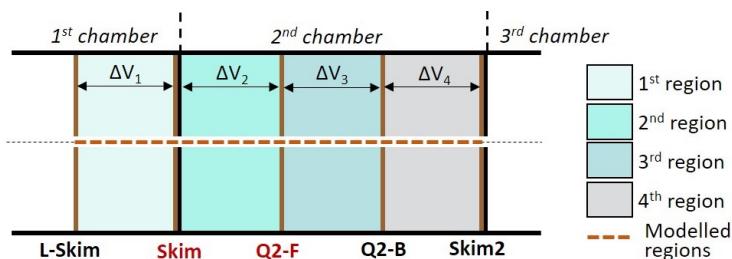
- (SA)₁
- (SA)₂
- (SA)₃**
- (SA)₄
- (SA)₅
-



EXPERIMENTAL TEST SYSTEM: ELECTROSPRAY-GENERATED NEGATIVELY CHARGED SULPHURIC ACID (SA) CLUSTERS

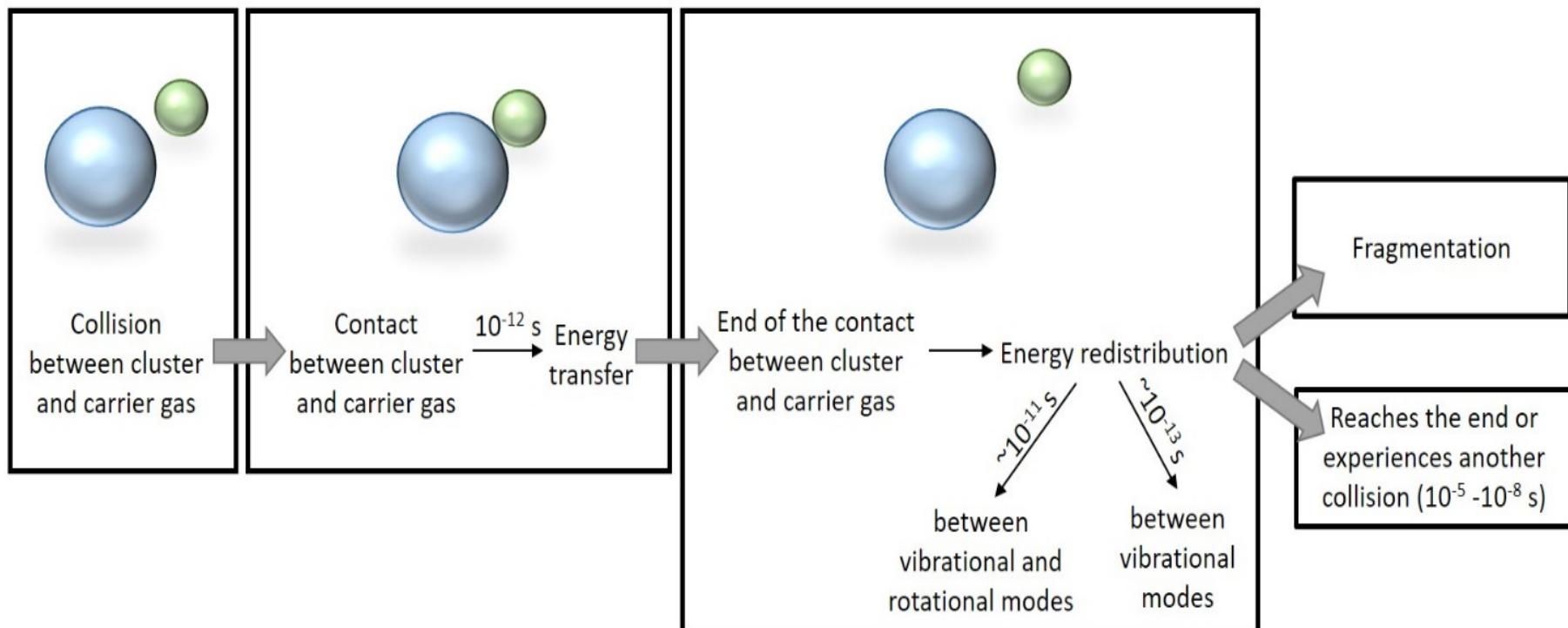


MODEL THE JOURNEY OF THE CLUSTER THROUGH THE INSTRUMENT

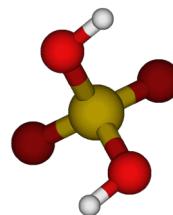


fragmentation channel
 $AAB \rightarrow AB+A$

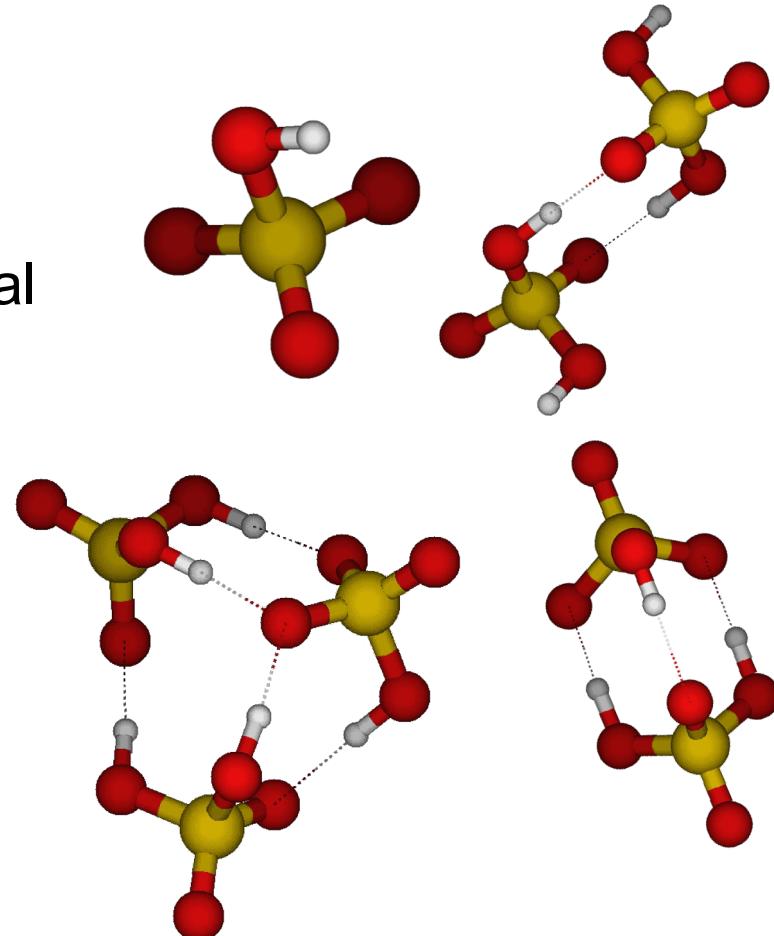
STATISTICAL MODEL FOR COLLISIONS AND FRAGMENTATION



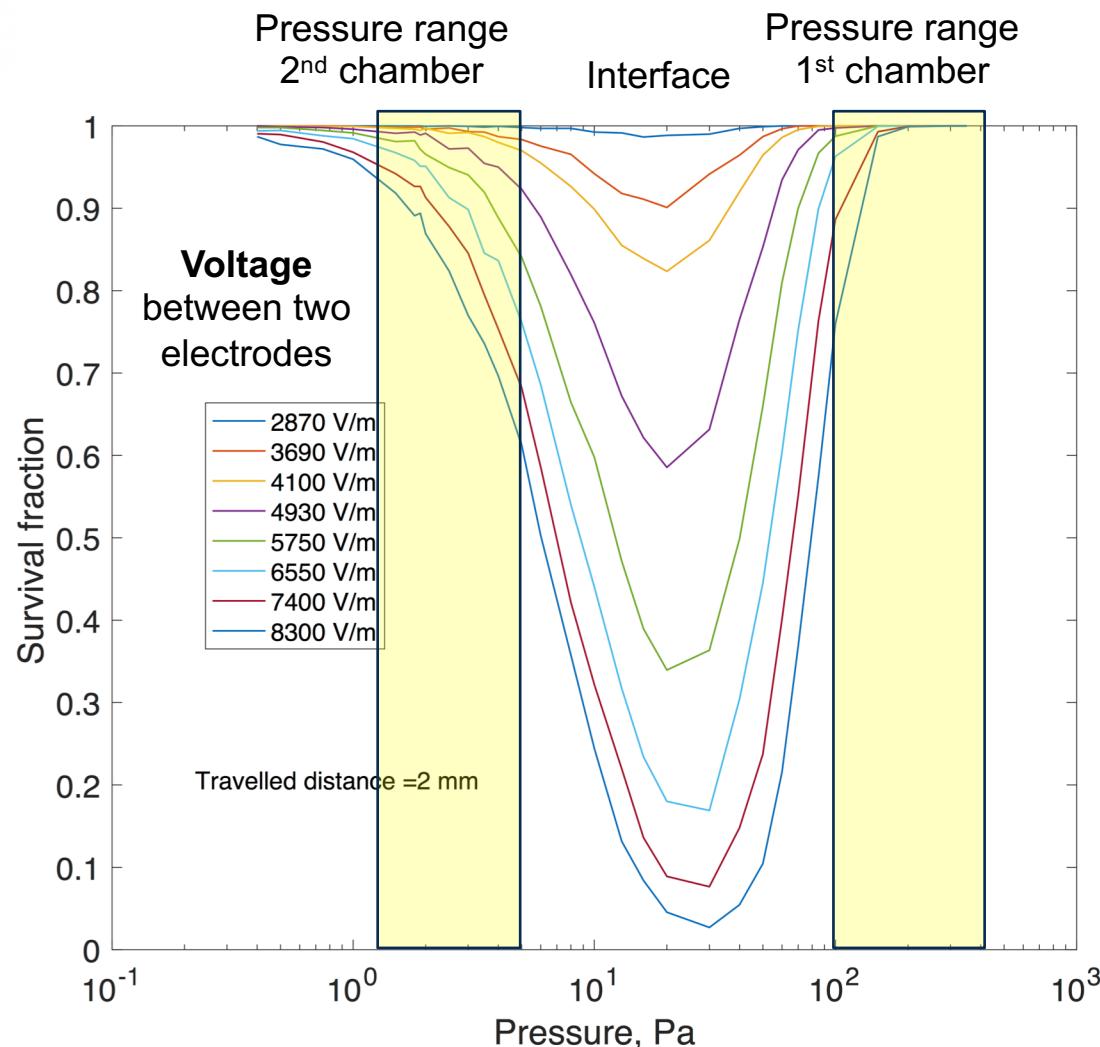
ROTATION AND VIBRATION ENERGY STATES OF CLUSTERS



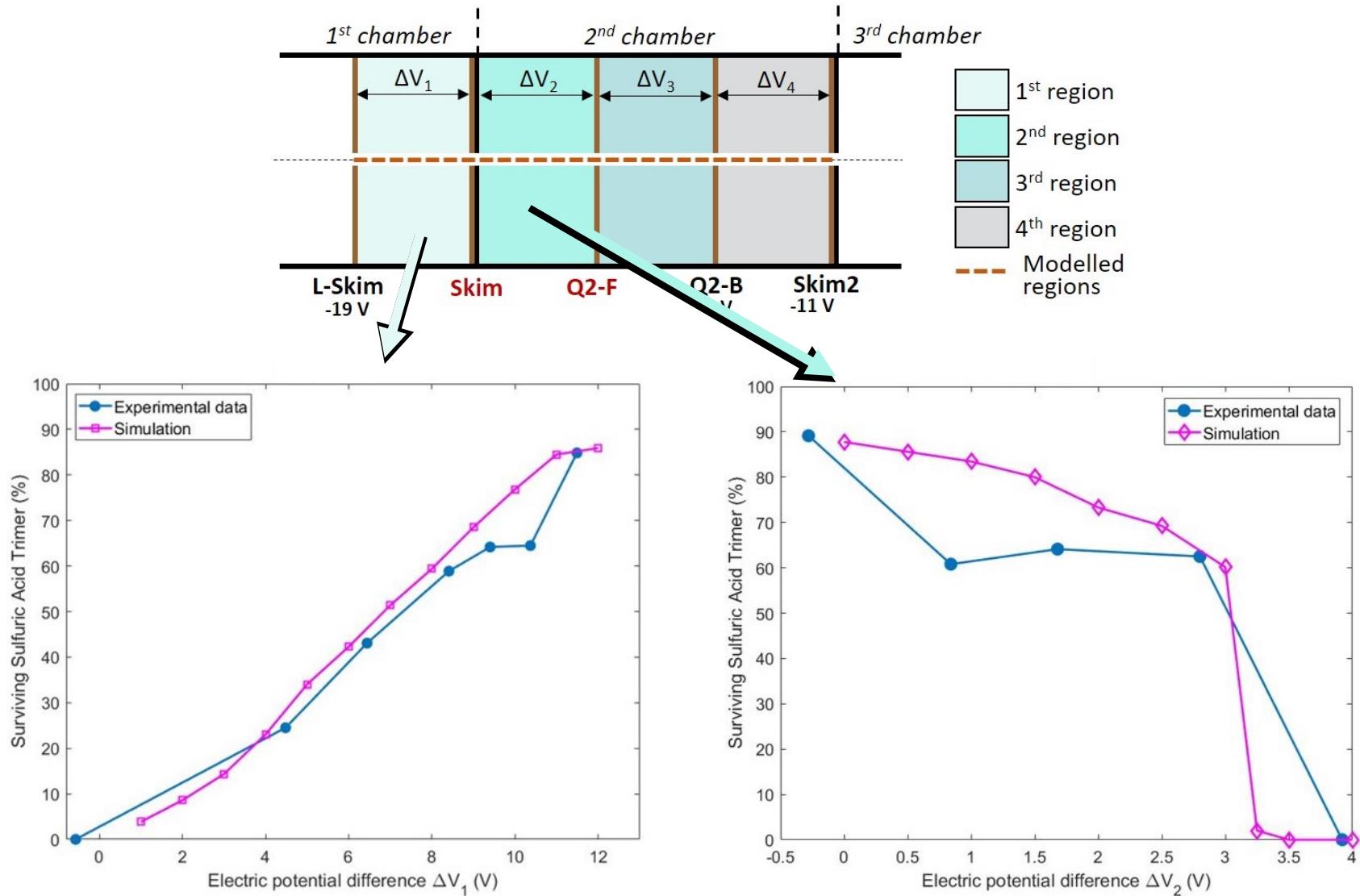
- Determine energy transfer & fragmentation rate
- Calculated using quantum chemical methods
 - Initial optimization: semi-empirical PM6 method
 - Re-optimization: PW91/6-31+G*, PW91/6-311++G**
 - Optimization & thermochemical parameters: PW91/aug-cc-pVQZ
 - Single point energy: DLPNO-CCSD(T)/aug-cc-pVTZ



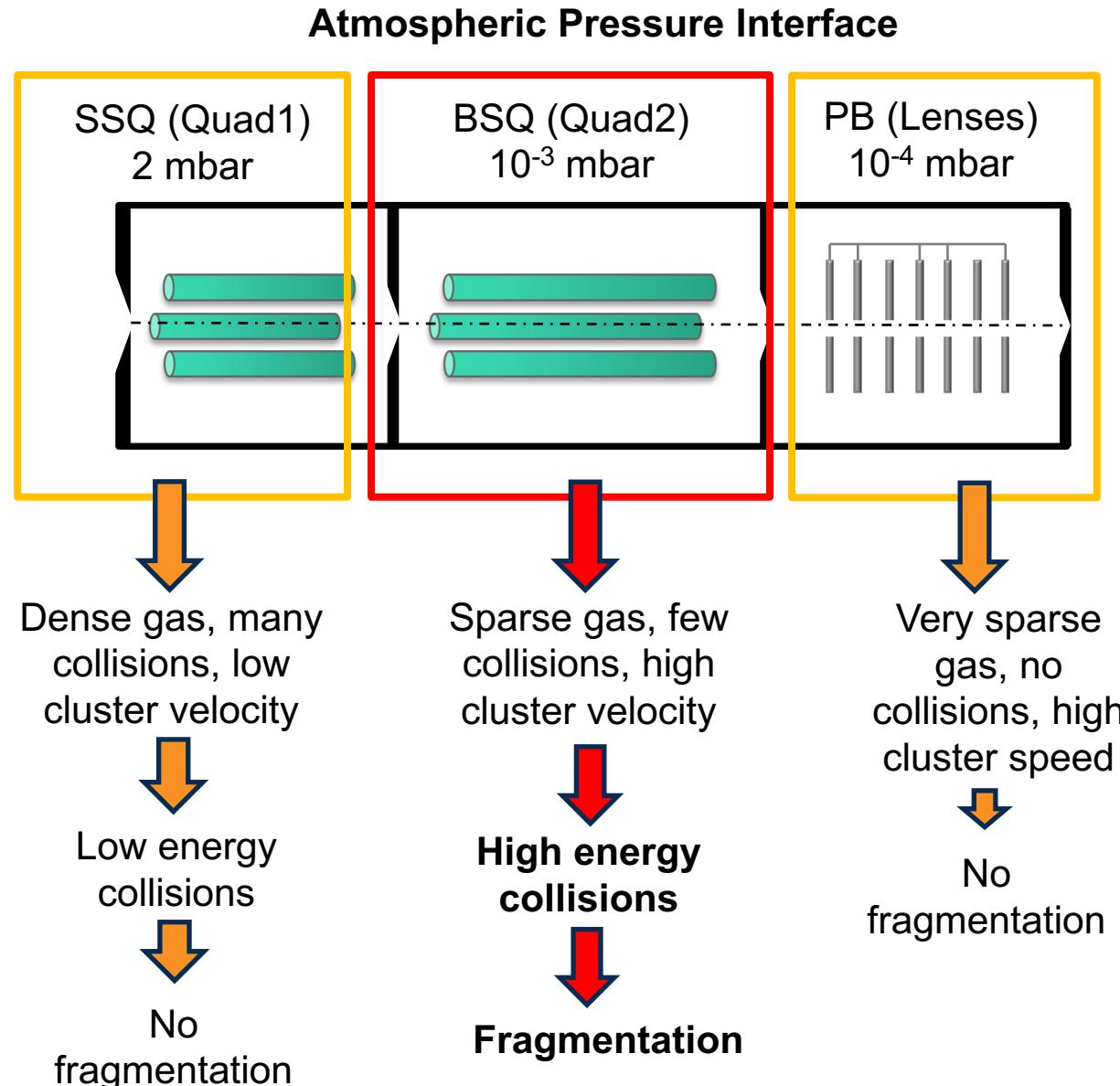
MODELED SULPHURIC ACID TRIMER SURVIVAL FRACTION vs CARRIER GAS PRESSURE



EXPERIMENTS AND MODEL AGREE FOR SULPHURIC ACID TRIMER SURVIVAL FRACTION



FRAGMENTATION: WHERE AND WHY?

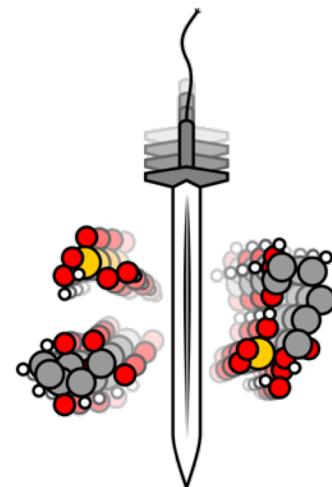
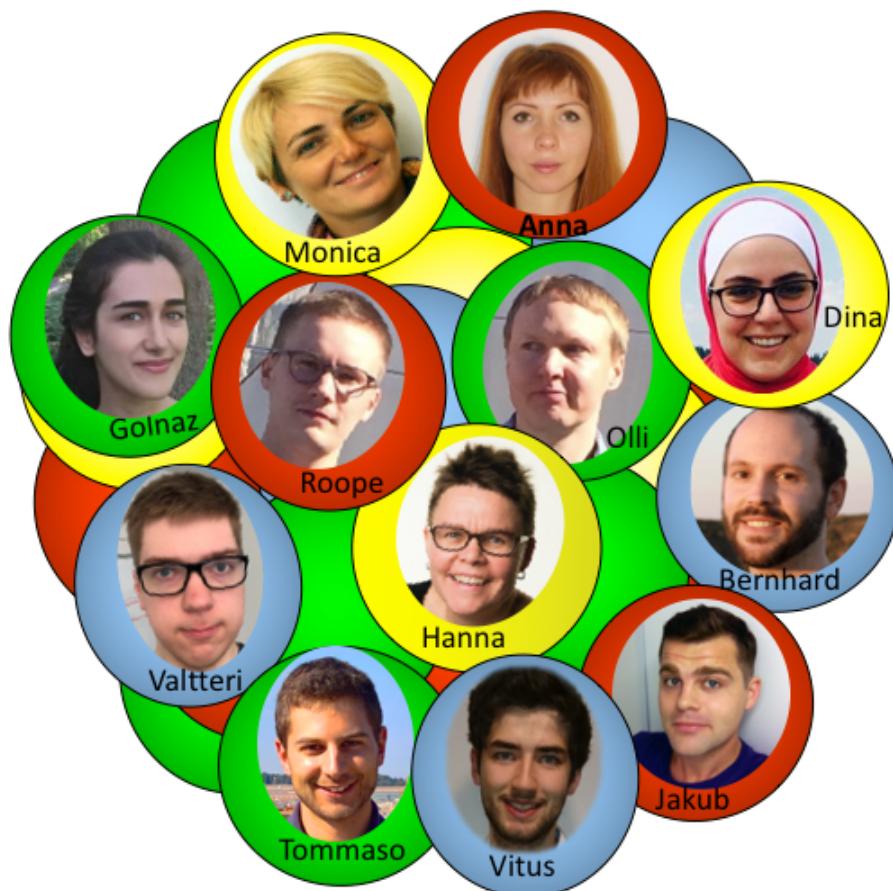




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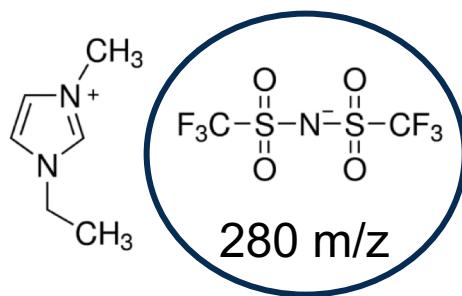
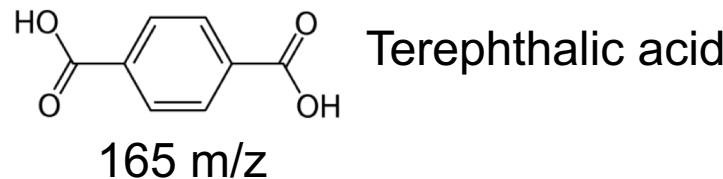
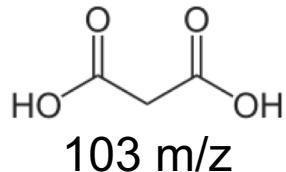
**ERC AdG
DAMOCLES
2016-2021**



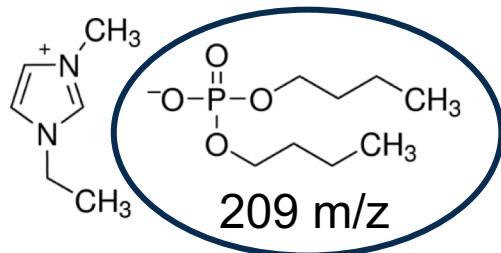


FRAGMENTATION OR TRANSMISSION CHANGE?

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)

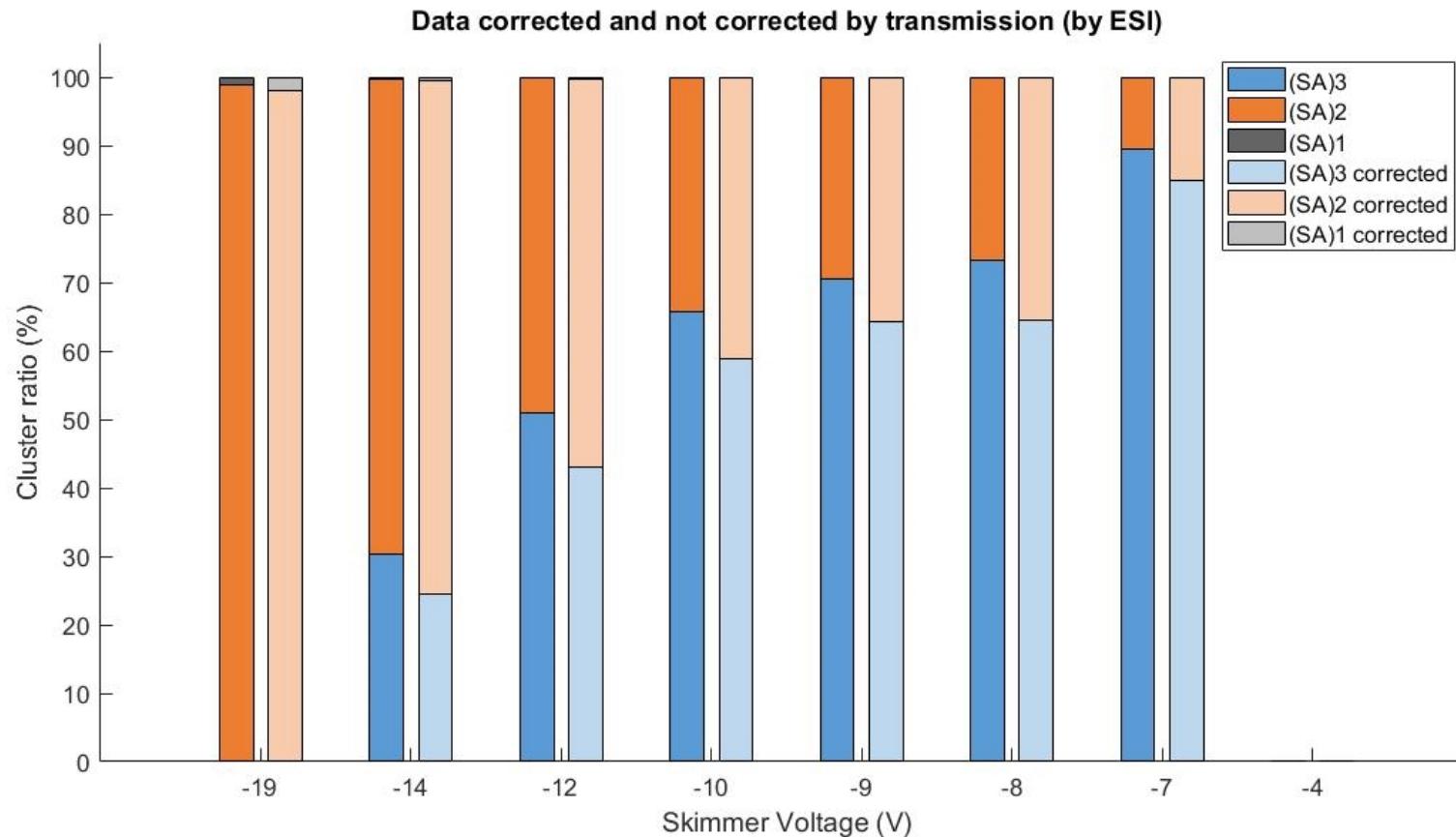


1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
(Ionic Liquid)

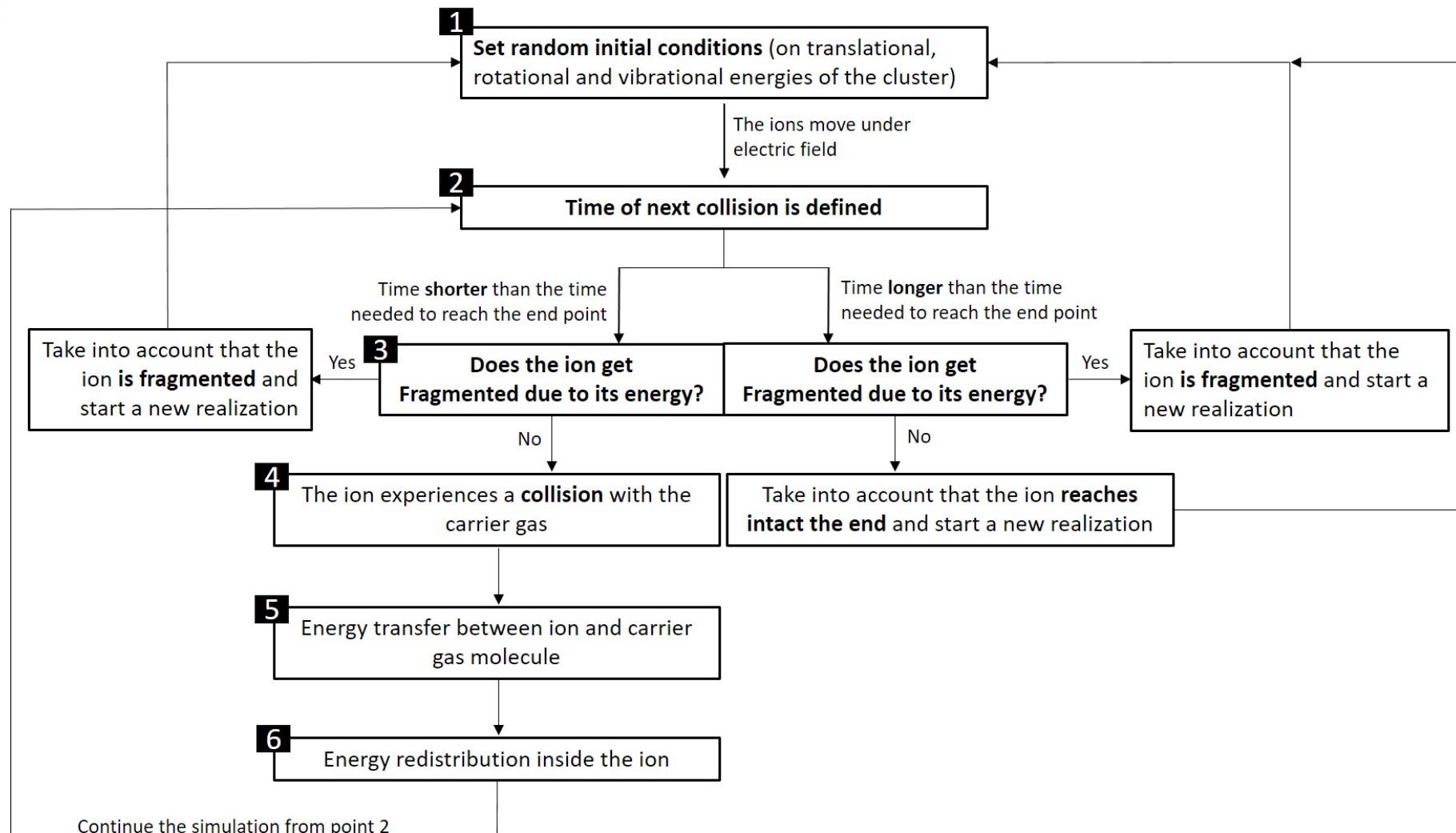


1-Ethyl-3-methylimidazolium dibutyl phosphate
(Ionic Liquid)

FRAGMENTATION, NOT TRANSMISSION CHANGE!



SIMULATION SEQUENCE



ENERGY TRANSFER

Energy transfer between ions and carrier gas molecules

