Overview of CIMS Applications

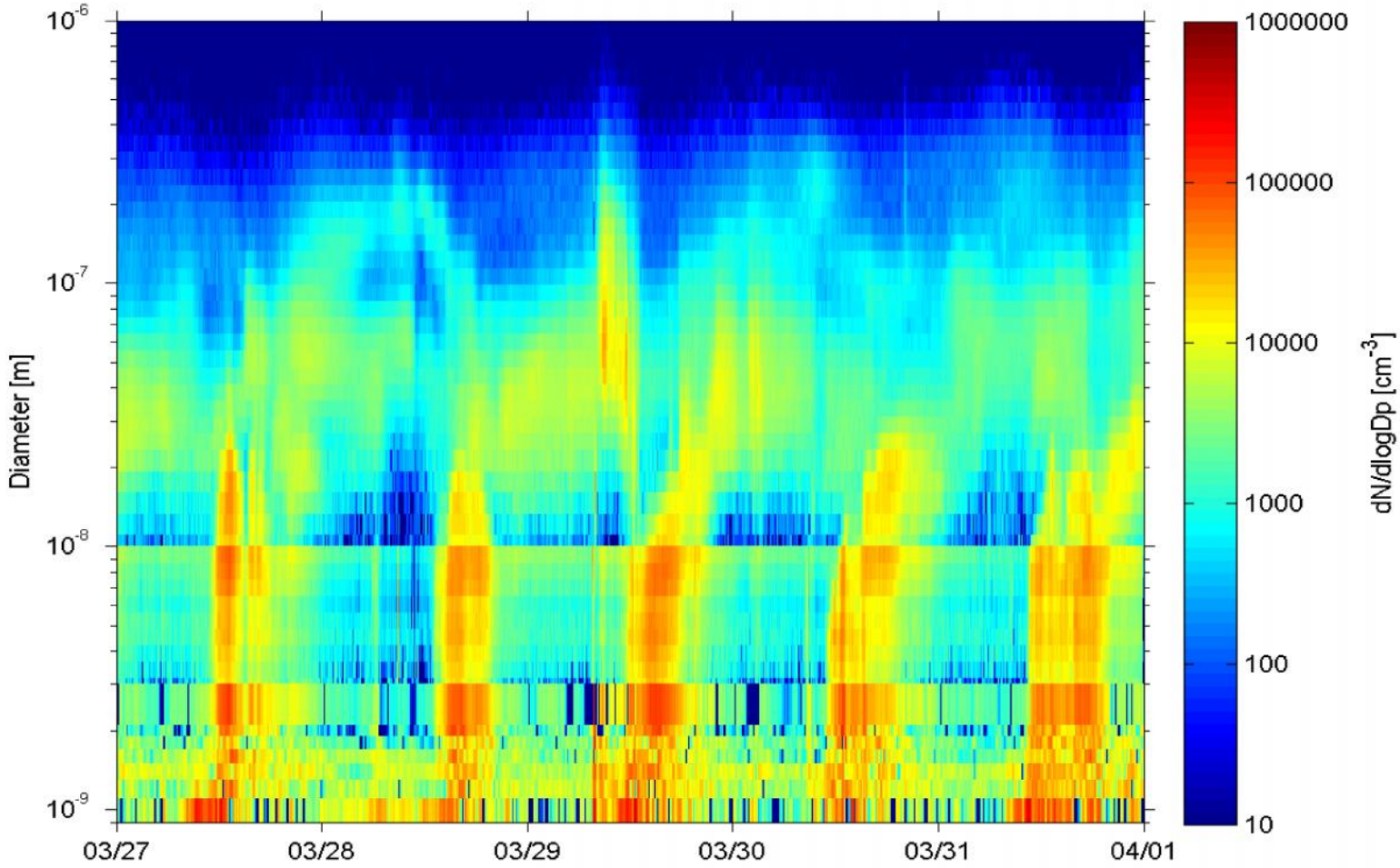
Doug Worsnop

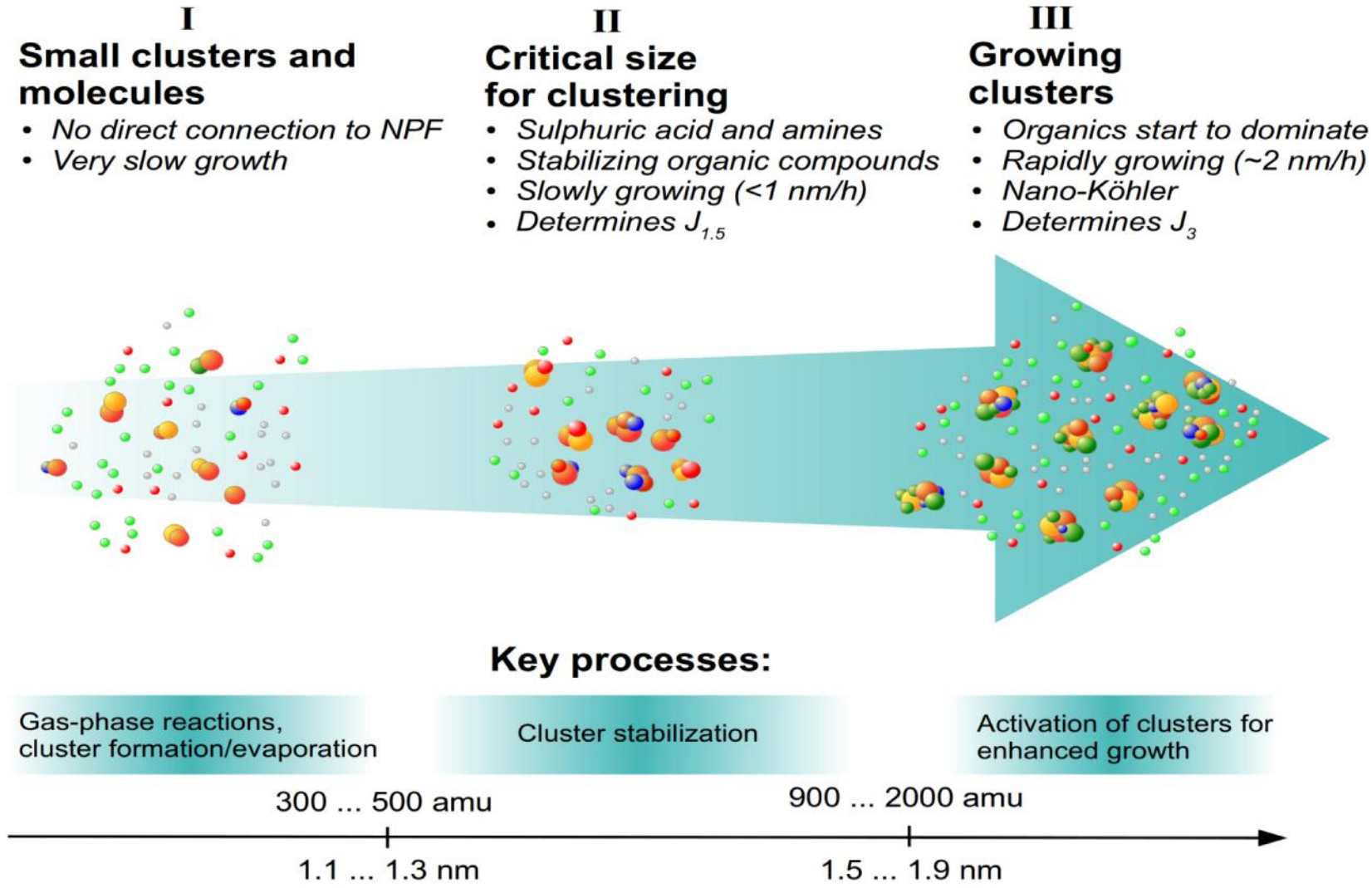
ARI/PKU AMS/CIMS Users Meeting

Tuesday, 9 May

Direct Observations of Atmospheric Aerosol Nucleation

Markku Kulmala,[1]* Jenni Kontkanen,[1] Heikki Junninen,[1] Katrianne Lehtipalo,[1] Hanna E. Manninen,[1] Tuomo Nieminen,[1,14] Tuukka Petäjä,[1] Mikko Sipilä,[1] Siegfried Schobesberger,[1] Pekka Rantala,[1] Alessandro Franchin,[1] Tuija Jokinen,[1] Emma Järvinen,[1] Mikko Äijälä,[1] Juha Kangasluoma,[1] Jani Hakala,[1] Pasi P. Aalto,[1] Pauli Paasonen,[1] Jyri Mikkilä,[2] Joonas Vanhanen,[2] Juho Aalto,[3] Hannele Hakola,[4] Ulla Makkonen,[4] Taina Ruuskanen,[1] Roy L. Mauldin III,[1,5] Jonathan Duplissy,[1] Hanna Vehkamäki,[1] Jaana Bäck,[6] Aki Kortelainen,[7] Ilona Riipinen,[8] Theo Kurtén,[1,9] Murray V. Johnston,[10] James N. Smith,[7,11] Mikael Ehn,[1,12] Thomas F. Mentel,[12] Kari E. J. Lehtinen,[4,7] Ari Laaksonen,[4,7] Veli-Matti Kerminen,[1] Douglas R. Worsnop[1,4,7,13]





Kulmala et al., 2013, Science

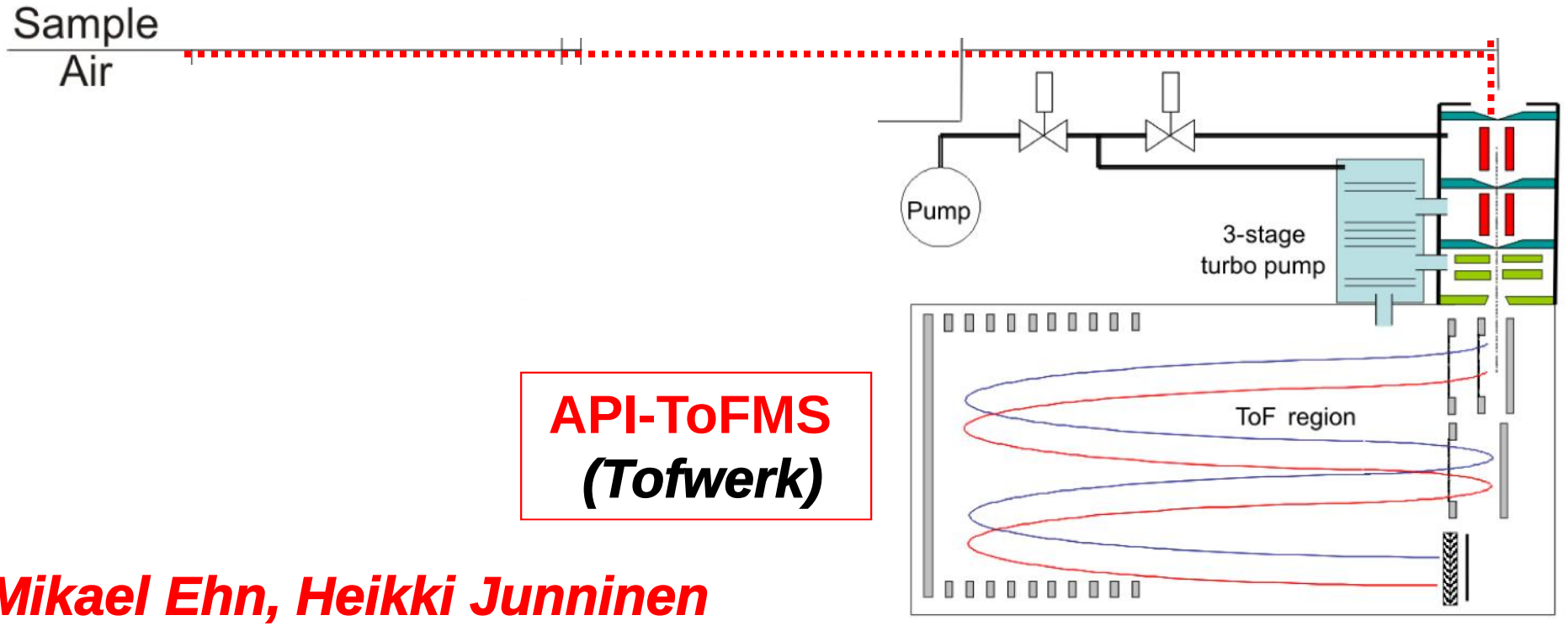
A high-resolution mass spectrometer to measure atmospheric ion composition

H. Junninen[1], M. Ehn[1], T. Petäjä[1], L. Luosujärvi[2], T. Kotiaho[2,3], R. Kostiainen[3], U. Rohner[4], M. Gonin[4], K. Fuhrer[4], M. Kulmala[1], and D. R. Worsnop[1,5]

Atmos. Meas. Tech. Discuss., 3, 599–636, 2010

Atmospheric Measurement Techniques Discussions

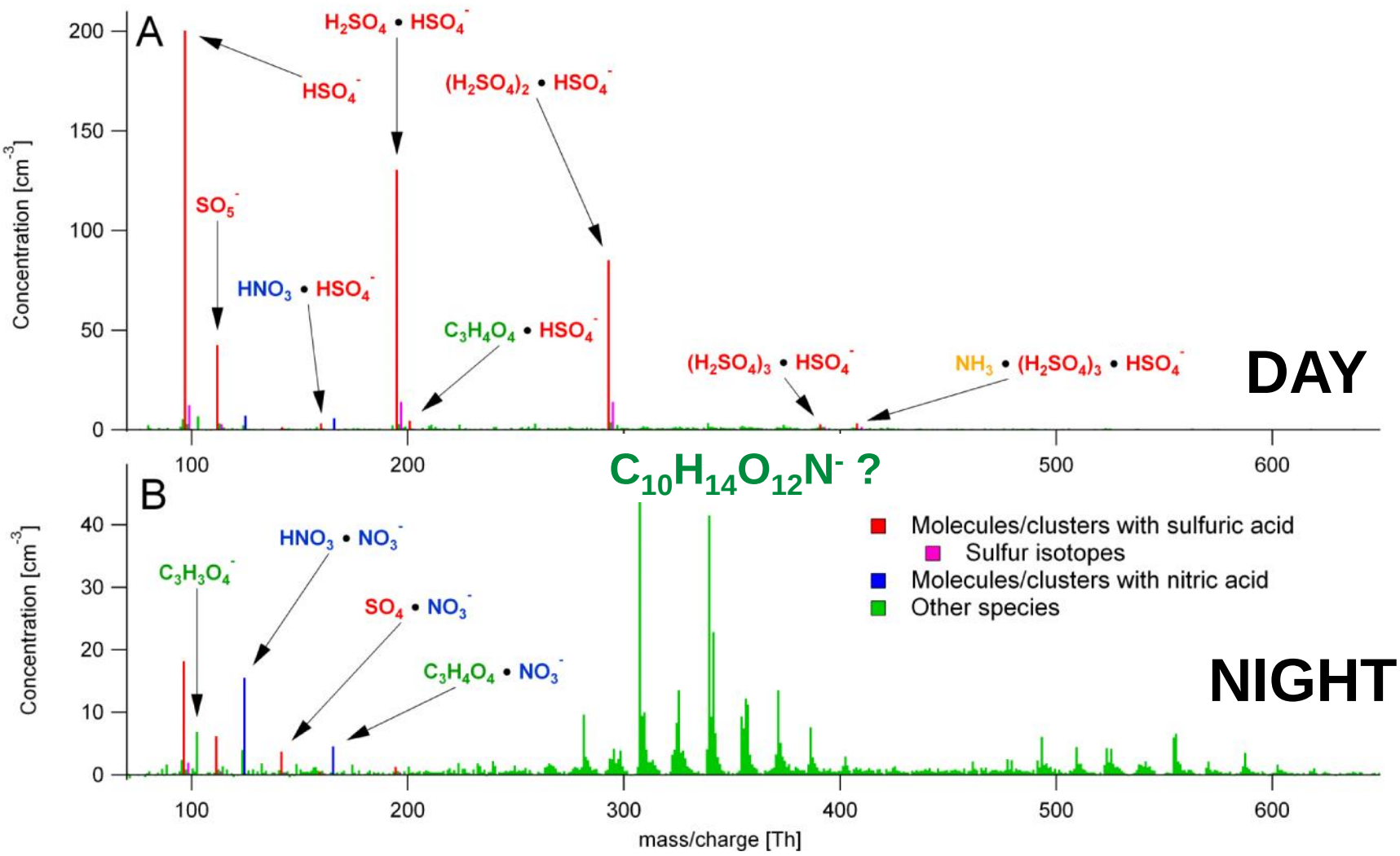
Atmospheric (pressure) Ions



API-ToFMS
(Tofwerk)

Mikael Ehn, Heikki Junninen

Negative ion spectra from Hyytiälä



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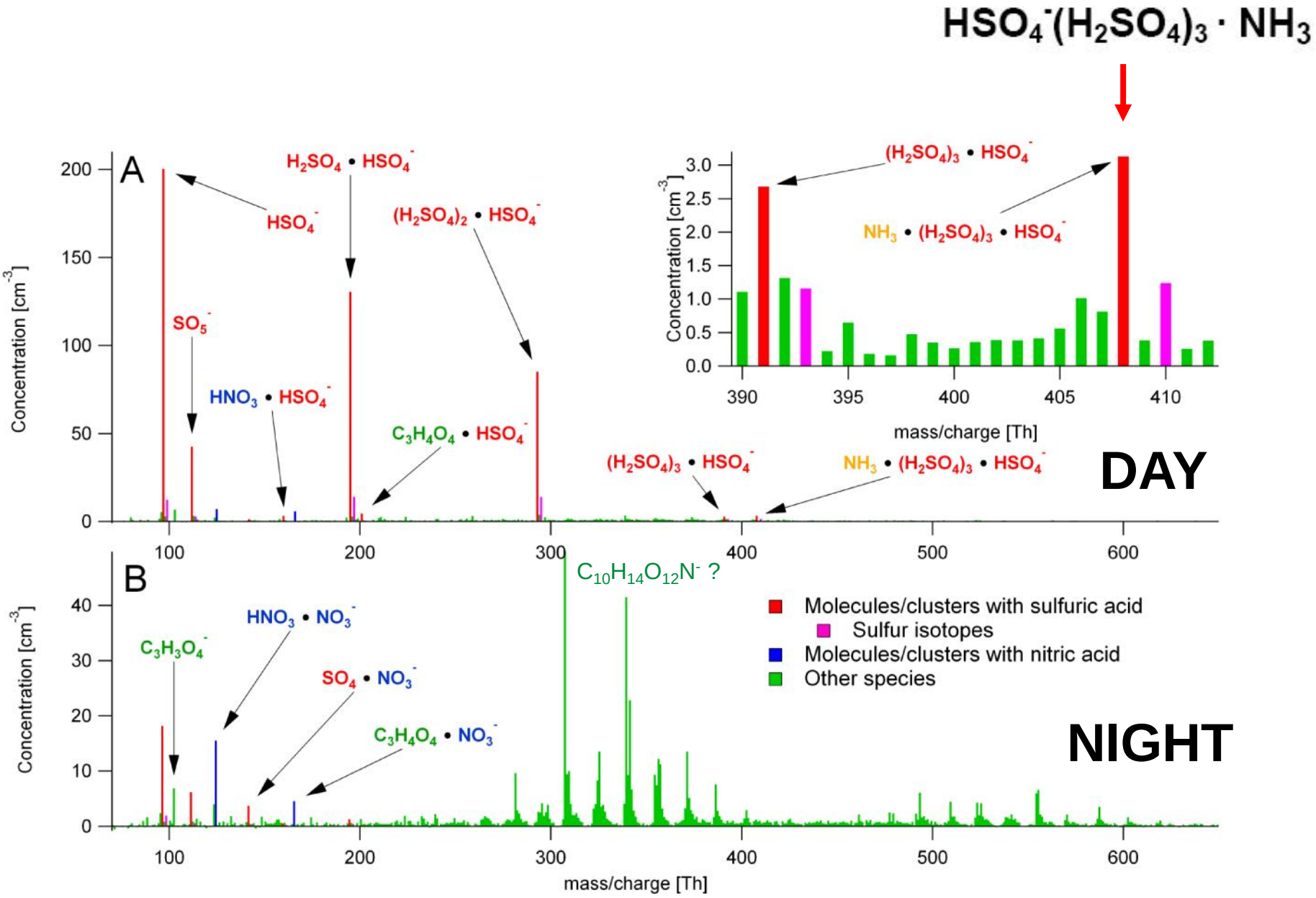
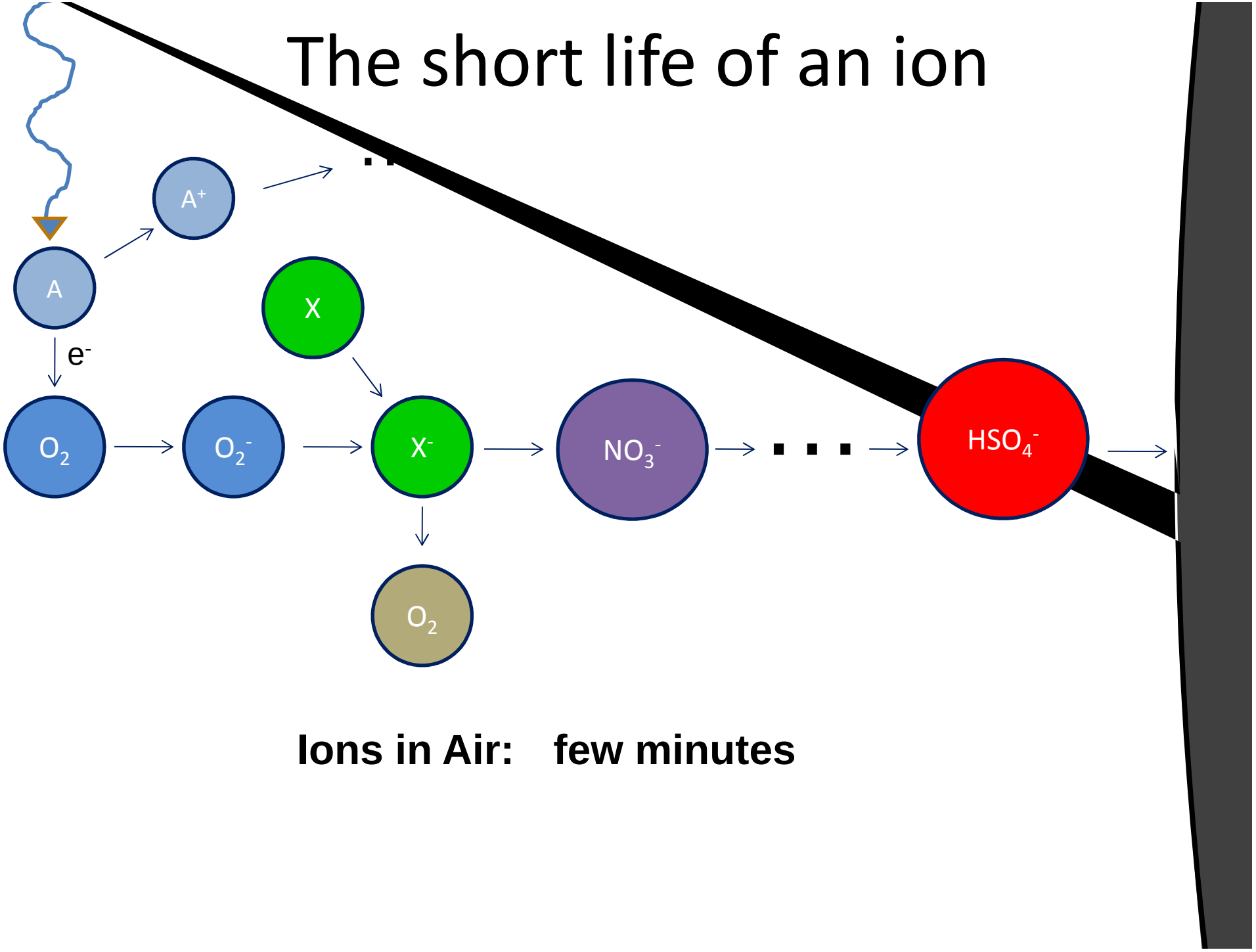
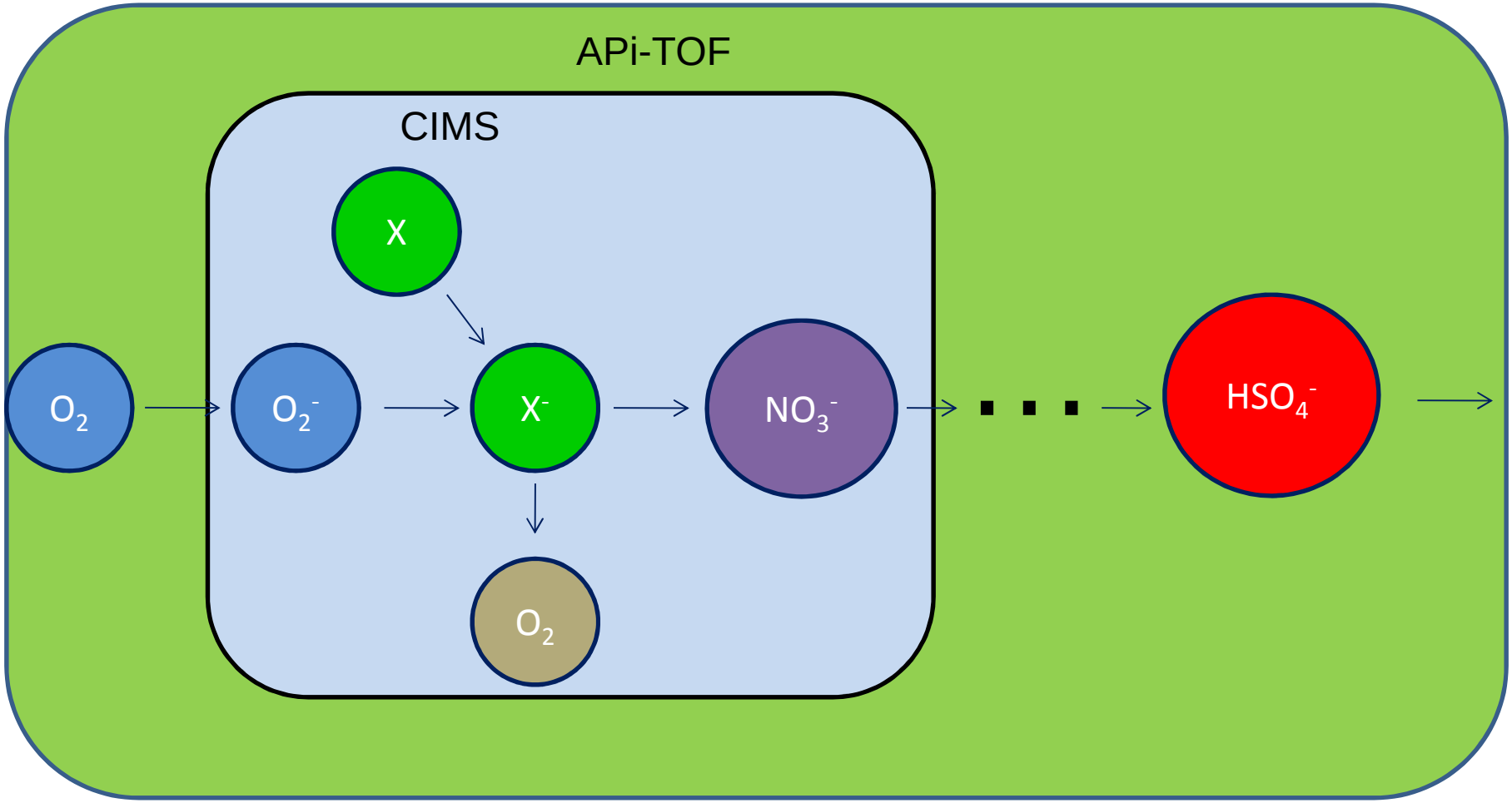


The short life of an ion



Ions in Air: few minutes

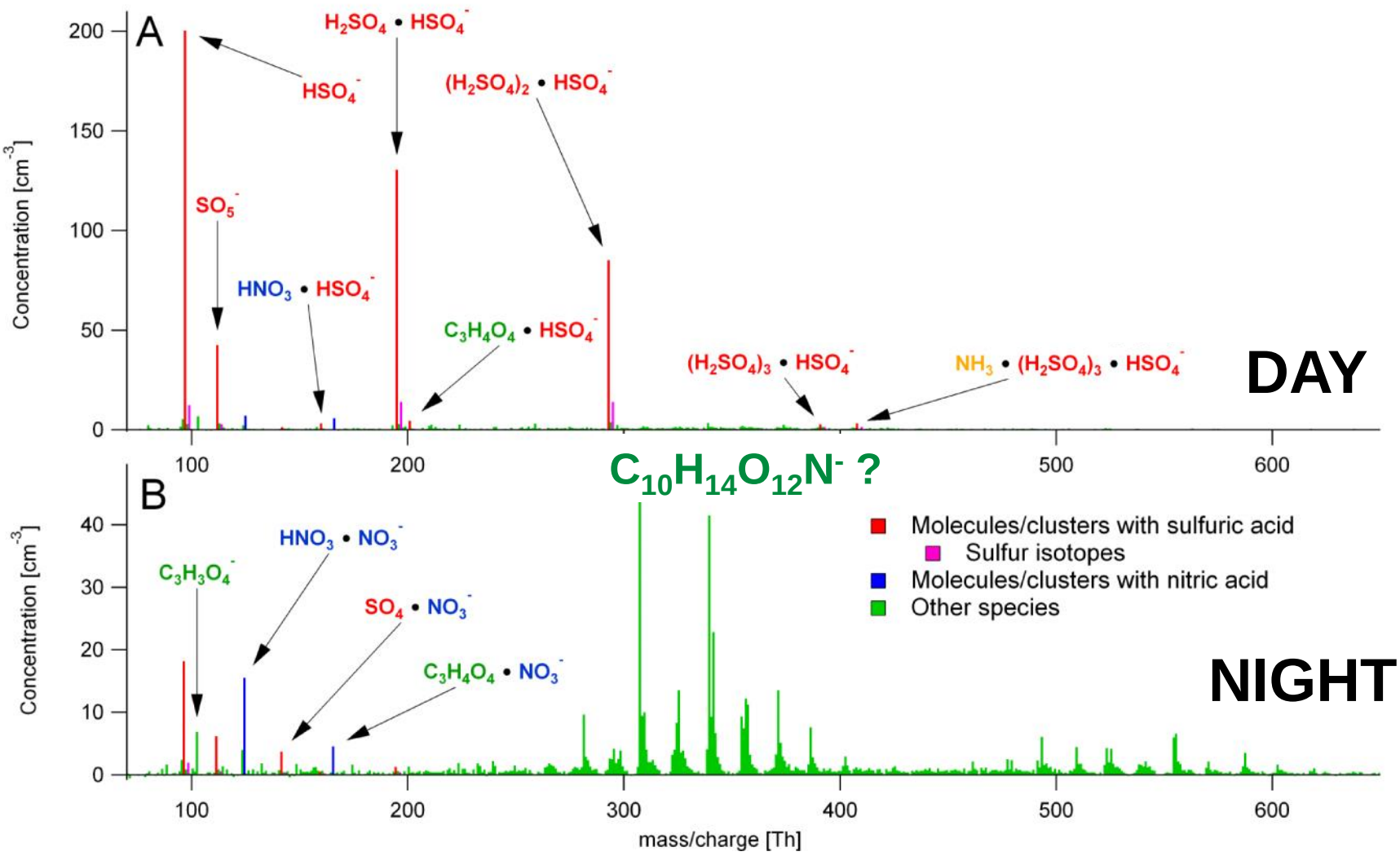
The short life of an ion



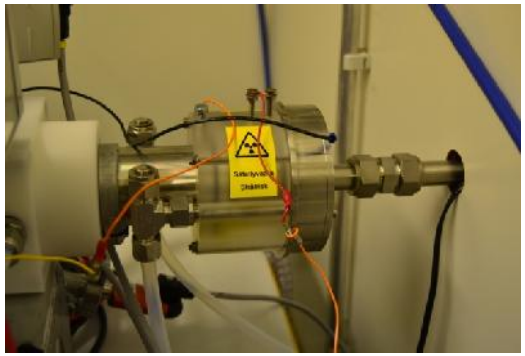
CIMS: **High NO_3^-** **fraction of a second**

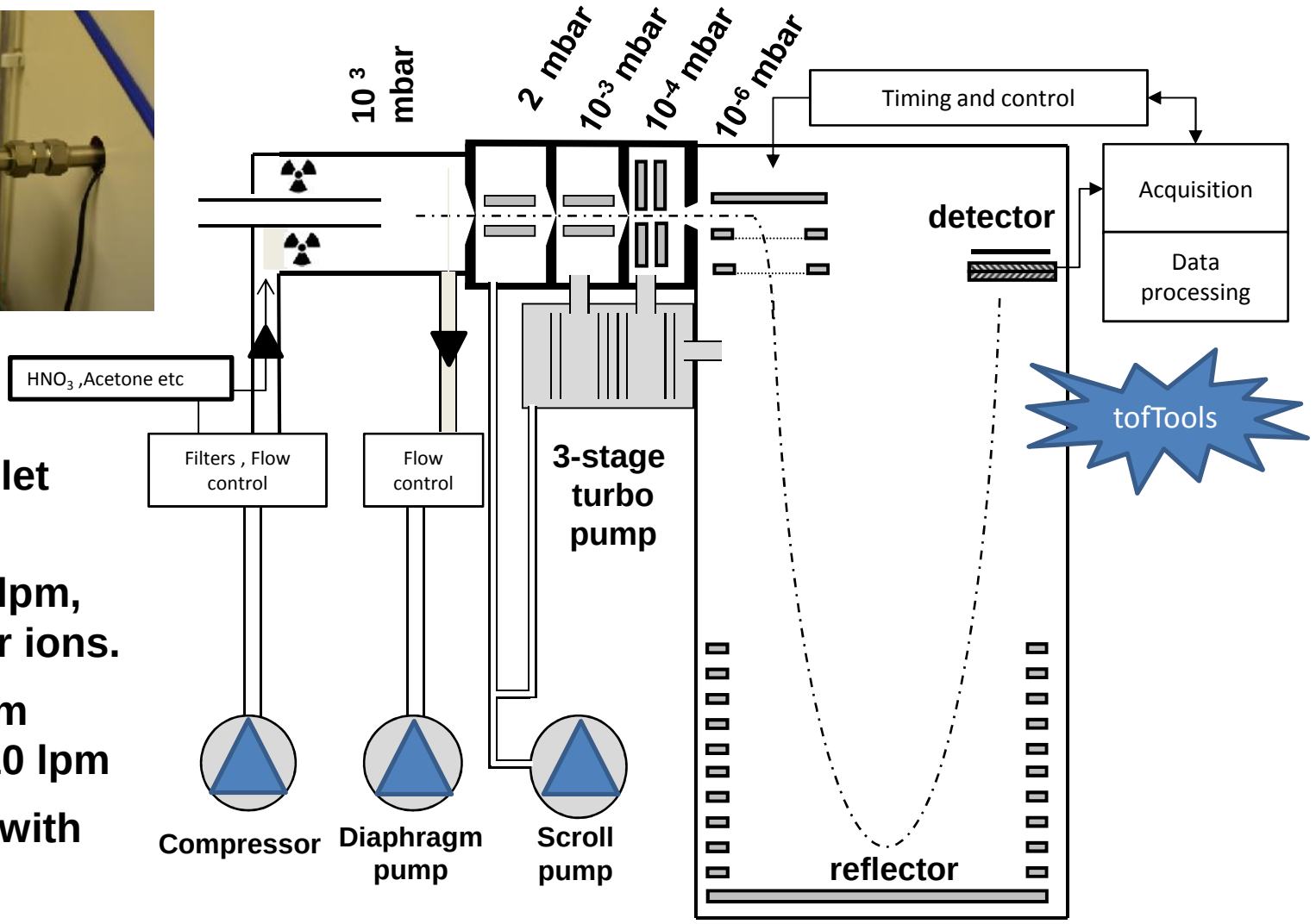
Ions in Air: **Low NO_3^-** **few minutes**

Negative ion spectra from Hyytiälä



CI-APi-TOF for neutral compound measurements





-"Eisele type" inlet design.

-Sheath flow 20 lpm, includes charger ions.

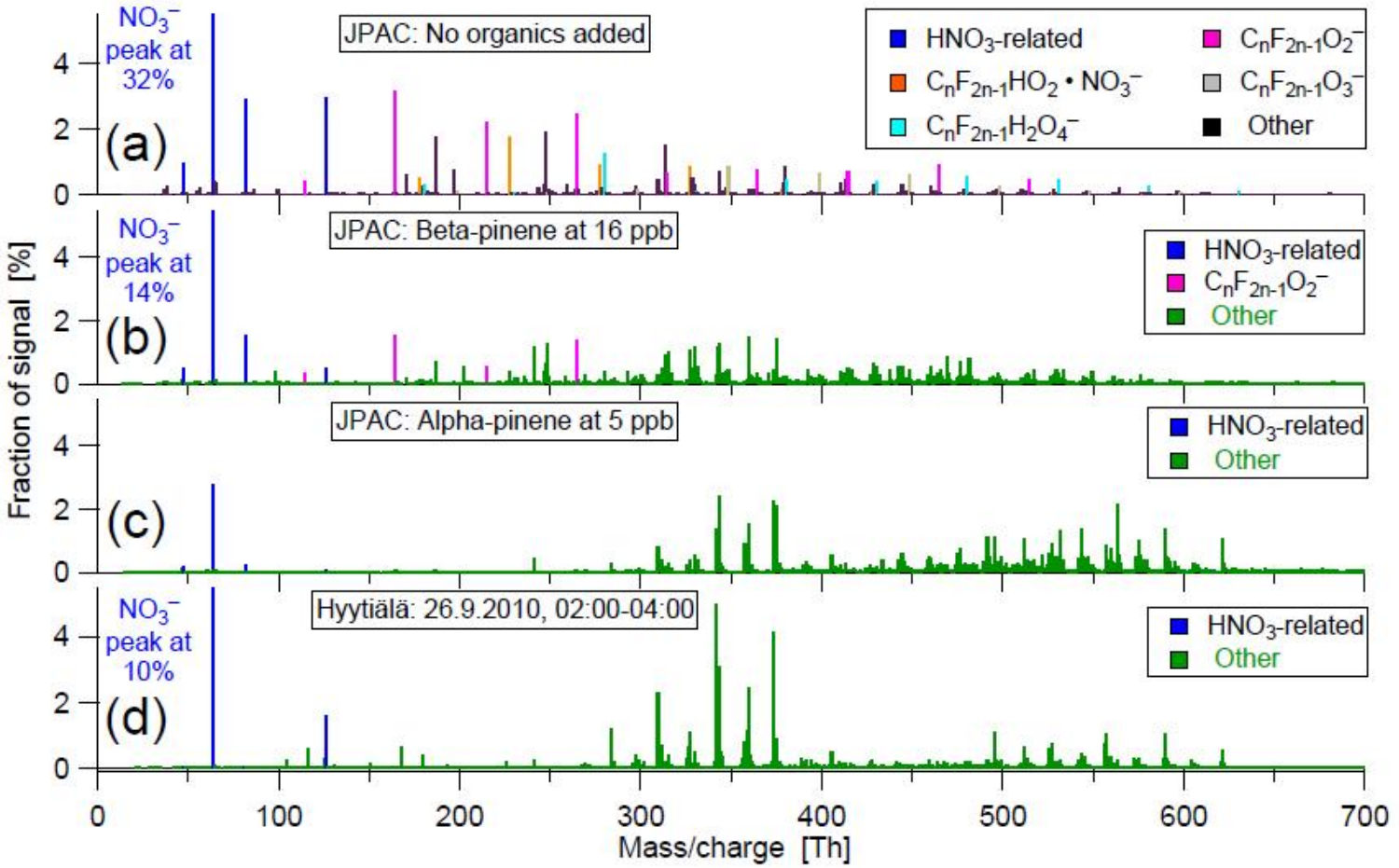
-Total flow 30 lpm -> sample flow 10 lpm

-Sample mixing with electric field

-APi samples 0.8 lpm

Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air

M. Ehn[1], E. Kleist[2], H. Junninen[3], T. Petäjä[3], G. Lönn[3], S. Schobesberger[3], M. Dal Maso[3], A. Trimborn[1,4], M. Kulmala[3], D. R. Worsnop[3,5], A. Wahner[1], J. Wildt[2], and Th. F. Mentel[1]



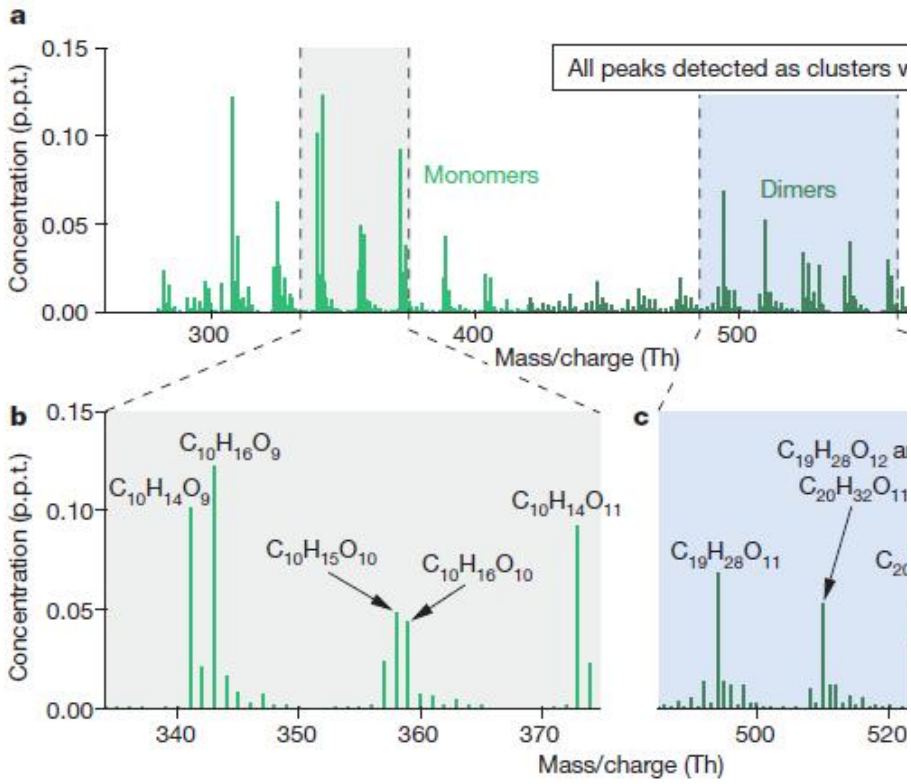
476 | NATURE | VOL 506 | 27 FEBRUARY 2014

LETTER

doi:10.1038/nature13032

A large source of low-volatility secondary organic aerosol

Mikael Ehn[1,2], Joel A. Thornton[2,3], Einhard Kleist[4], Mikko Sipilä[2], Heikki Junninen[2], Iida Pullinen[1], Monika Springer[1], Florian Rubach[1], Ralf Tillmann[1], Ben Lee[3], Felipe Lopez-Hilfiker[3], Stefanie Andres[1], Ismail-Hakki Acir[1], Matti Rissanen[2], Tuija Jokinen[2,5], Siegfried Schobesberger[2], Juha Kangasluoma[2], Jenni Kontkanen[2], Tuomo Nieminen[2,6], Theo Kurtén[7], Lasse B. Nielsen[8], Solvejg Jørgensen[8], Henrik G. Kjaergaard[8], Manjula Canagaratna[9], Miikka Dal Maso[10], Torsten Berndt[5], Tuukka Petäjä[2], Andreas Wahner[1], Veli-Matti Kerminen[2], Markku Kulmala[2], Douglas R. Worsnop[2,9], Jürgen Wildt[4] & Thomas F. Mentel[1]



ELVOC

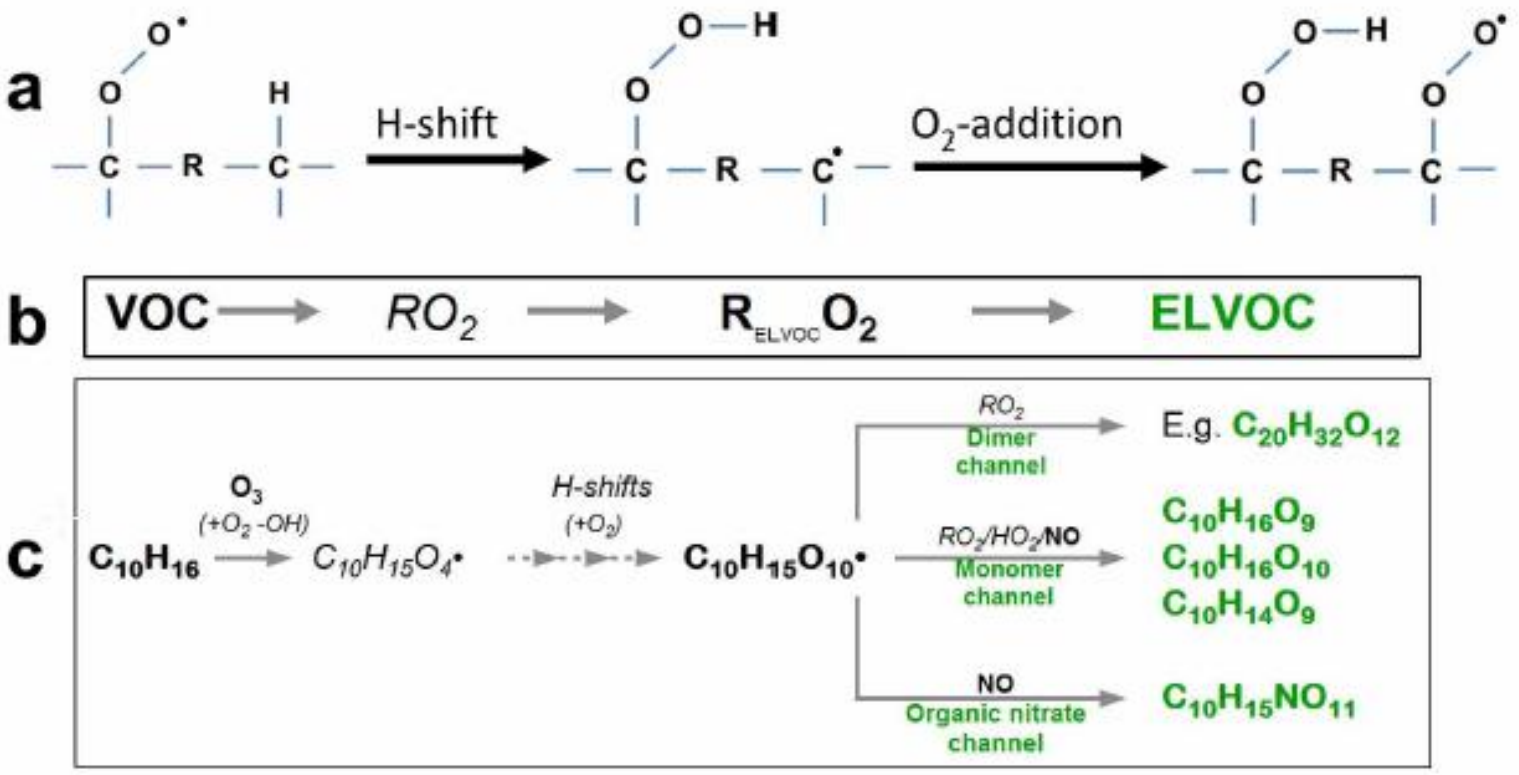
C10,C20 in the gas phase

O/C > 0.7

Nucleation, Clusters

Nanoparticle growth

Auto-oxidation



Ehn et al, Nature, 2014

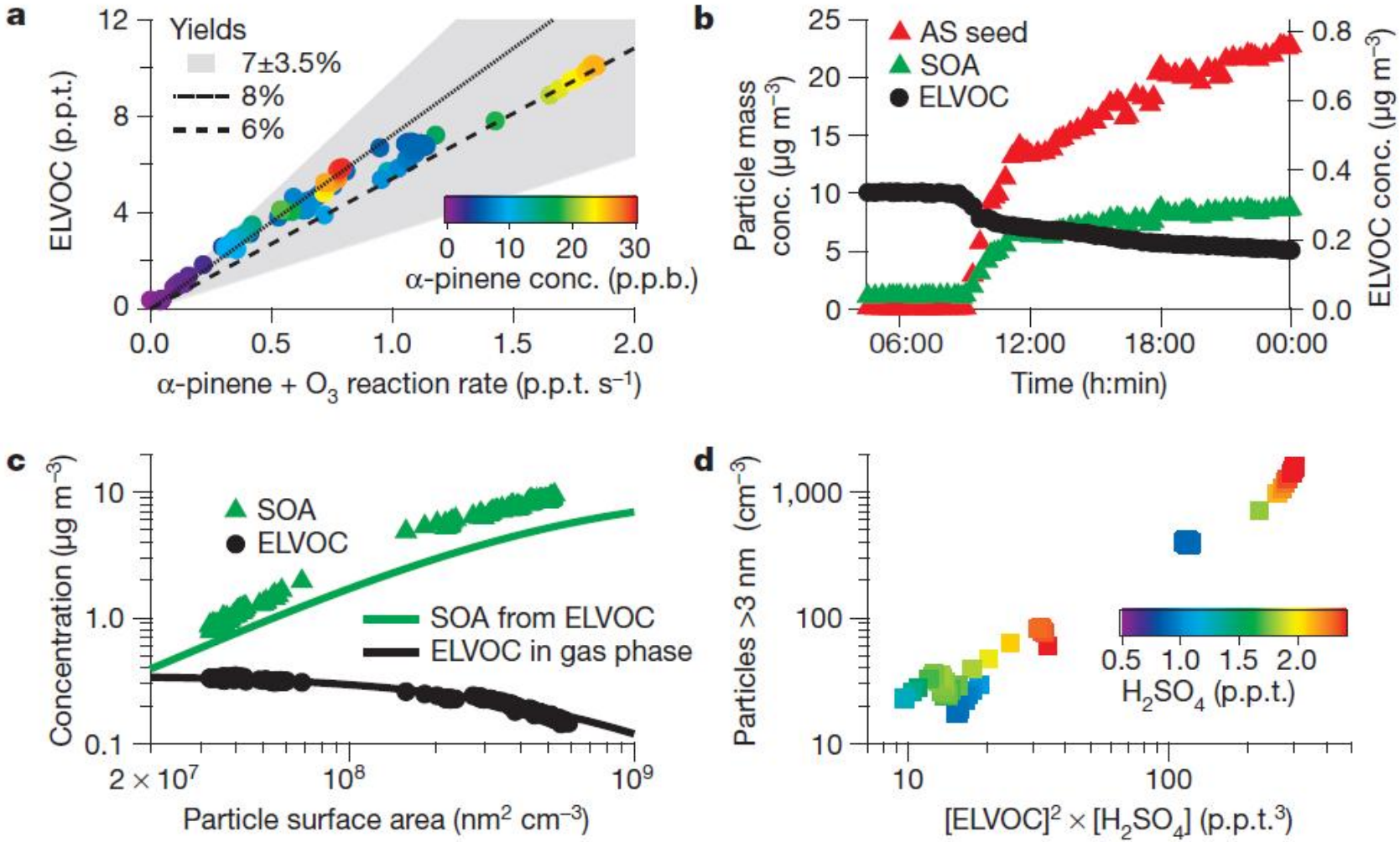
also see Crounse et al, JPC Letters, 2013

A-pinene + O3

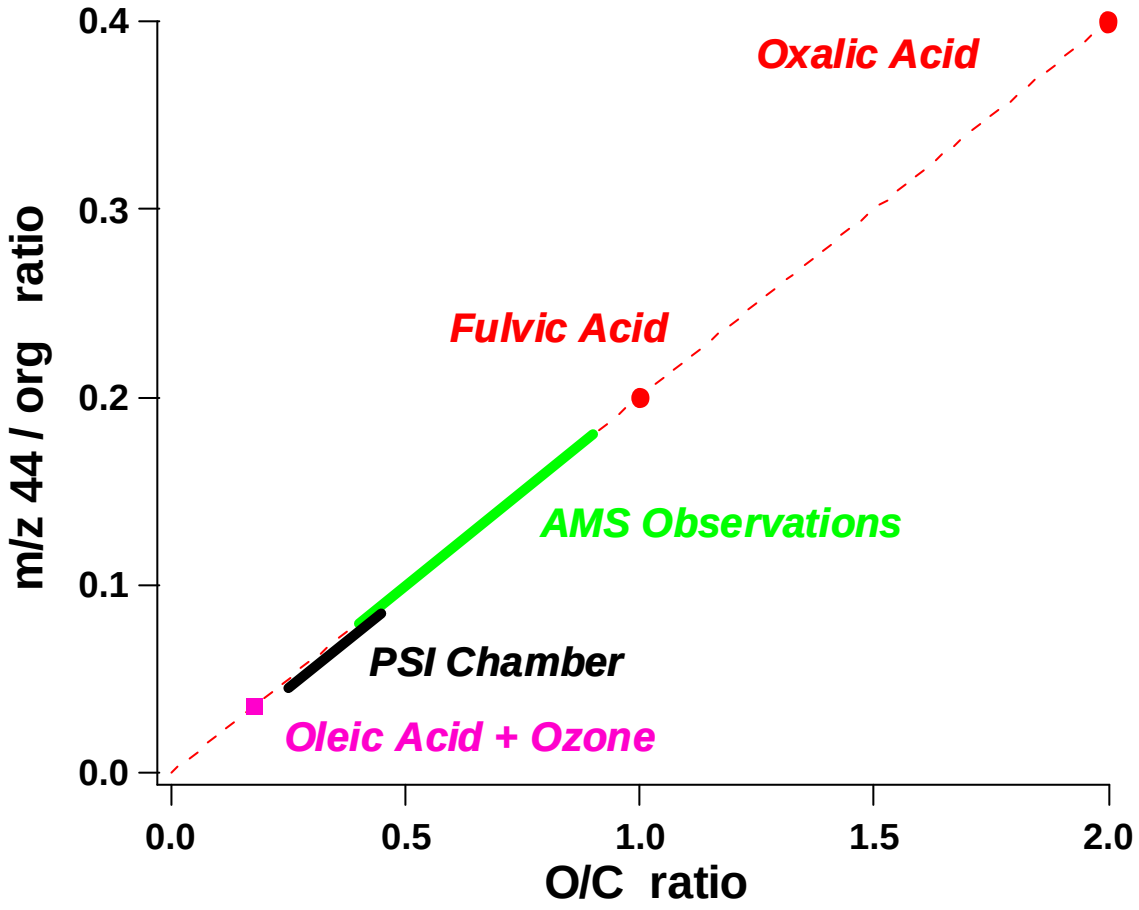
Yield ~ 7+/- 4%

addition of (NH4)2SO4 seed

reduces gas ELVOC **increases condensed SOA**



f44 vs O/C



2004

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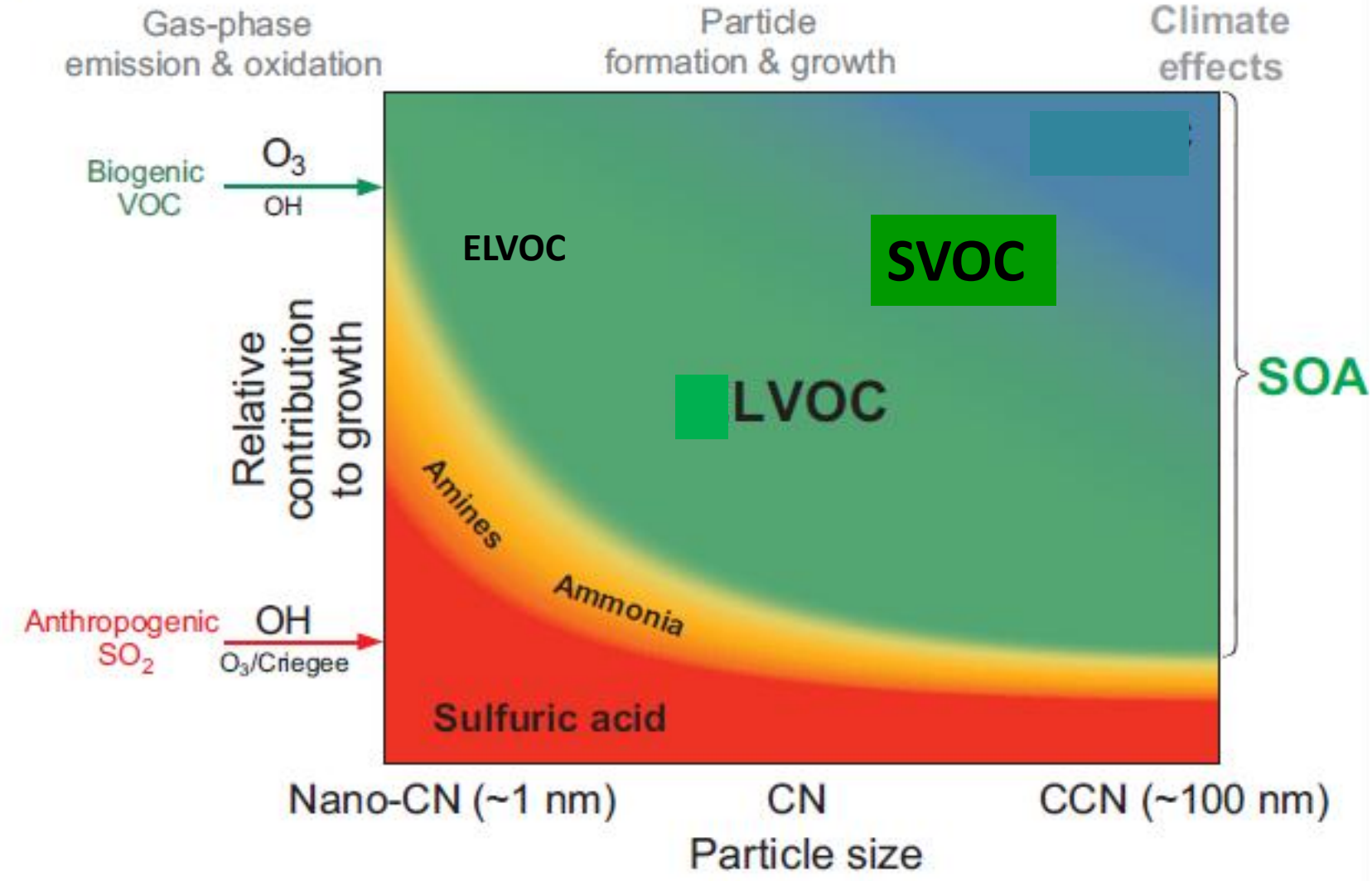
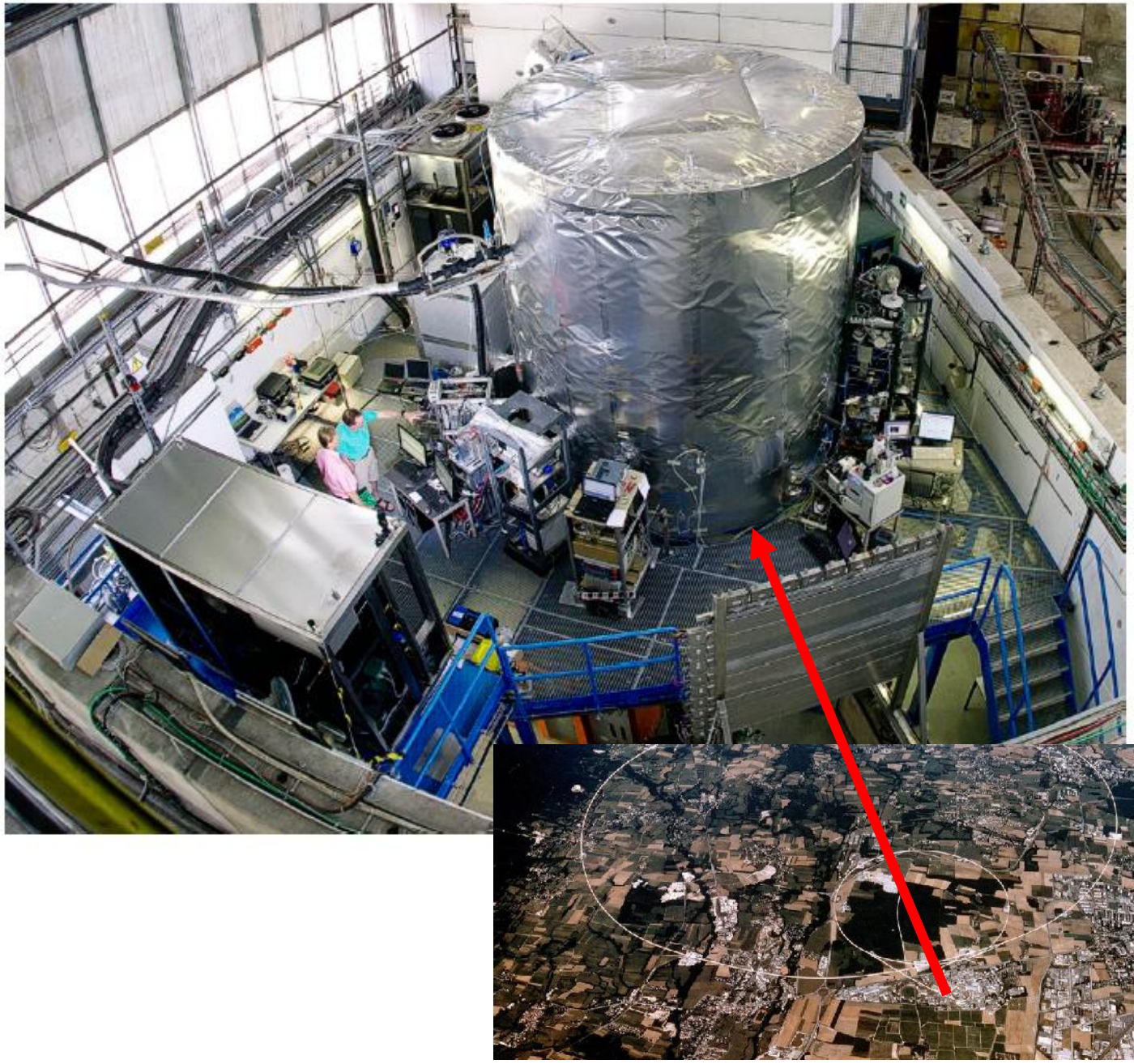


CLOUD at the CERN Proton Synchrotron, July 2011

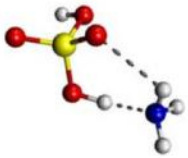


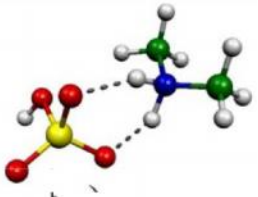
Kirkby,
Curtius,
Carslaw,
Baltensperger,
Kulmala,
(Worsnop,
Donahue)

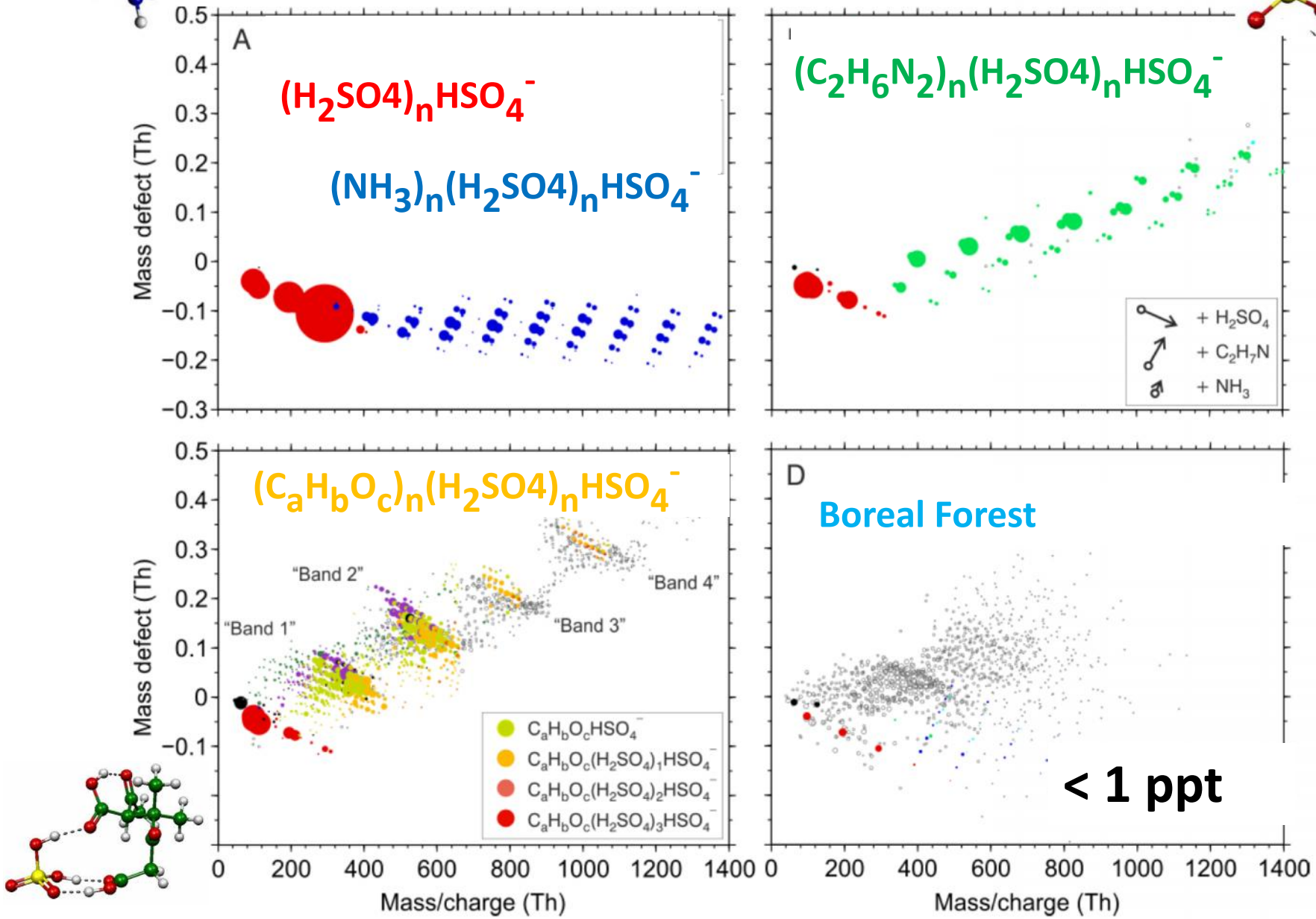
+

the
CLOUD KIDS

Negative Ion Composition

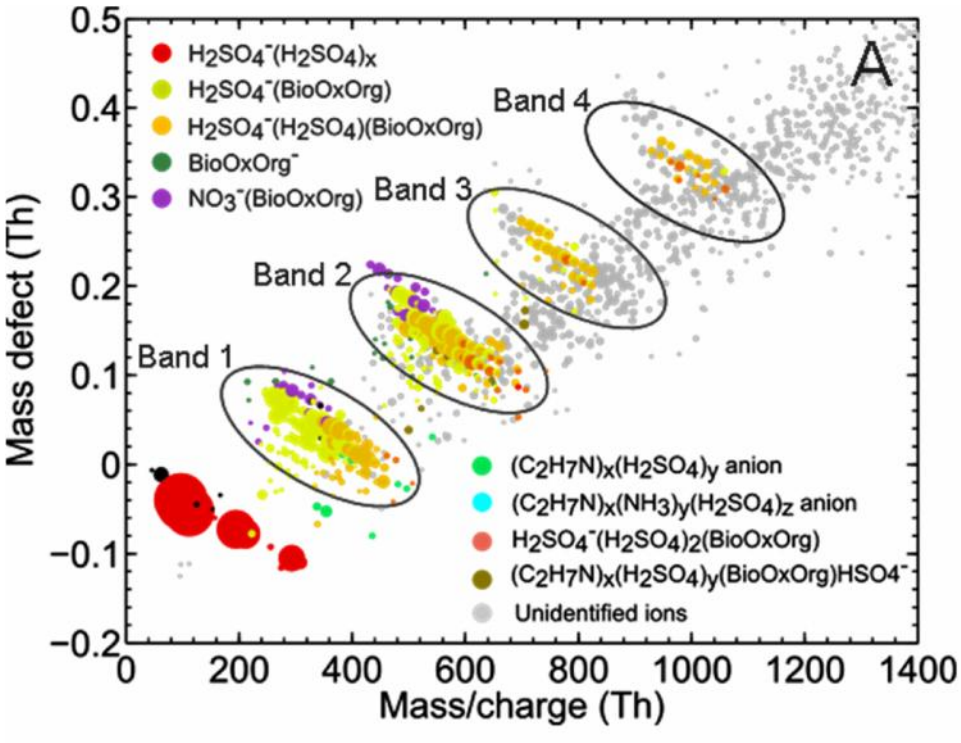


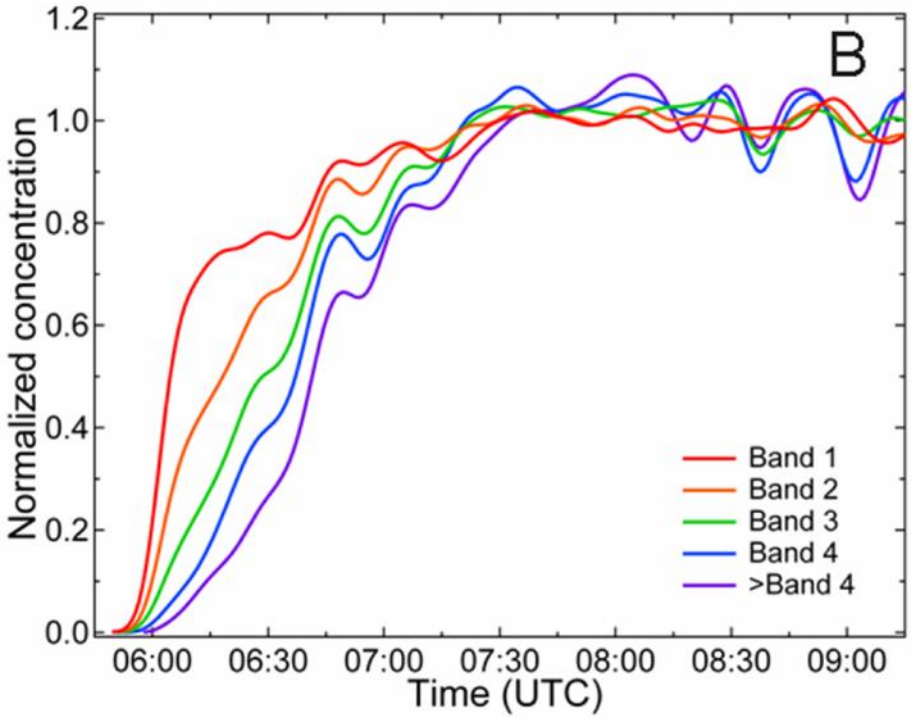




Schobesberger, et al, PNAS

APi-TOF data confirm: Organics participate in cluster formation from the very beginning





Riccobono et al., Sceince, 2014

Ionization Techniques

Electron Impact ***("hard")***

$$R + e^- \rightarrow R^+ + 2\,e^- \rightarrow R_i^+$$ **universal**

Chemical Ionization ***("soft")***

proton transfer

PTRMS $R + H_3O^+ \rightarrow RH^+ + H_2O$ **hydrocarbons**

Acetate $RCOOH + C_2H_4O^- \rightarrow RCOO^- + C_2H_5O_2$ **(carboxylic) acids**

clustering

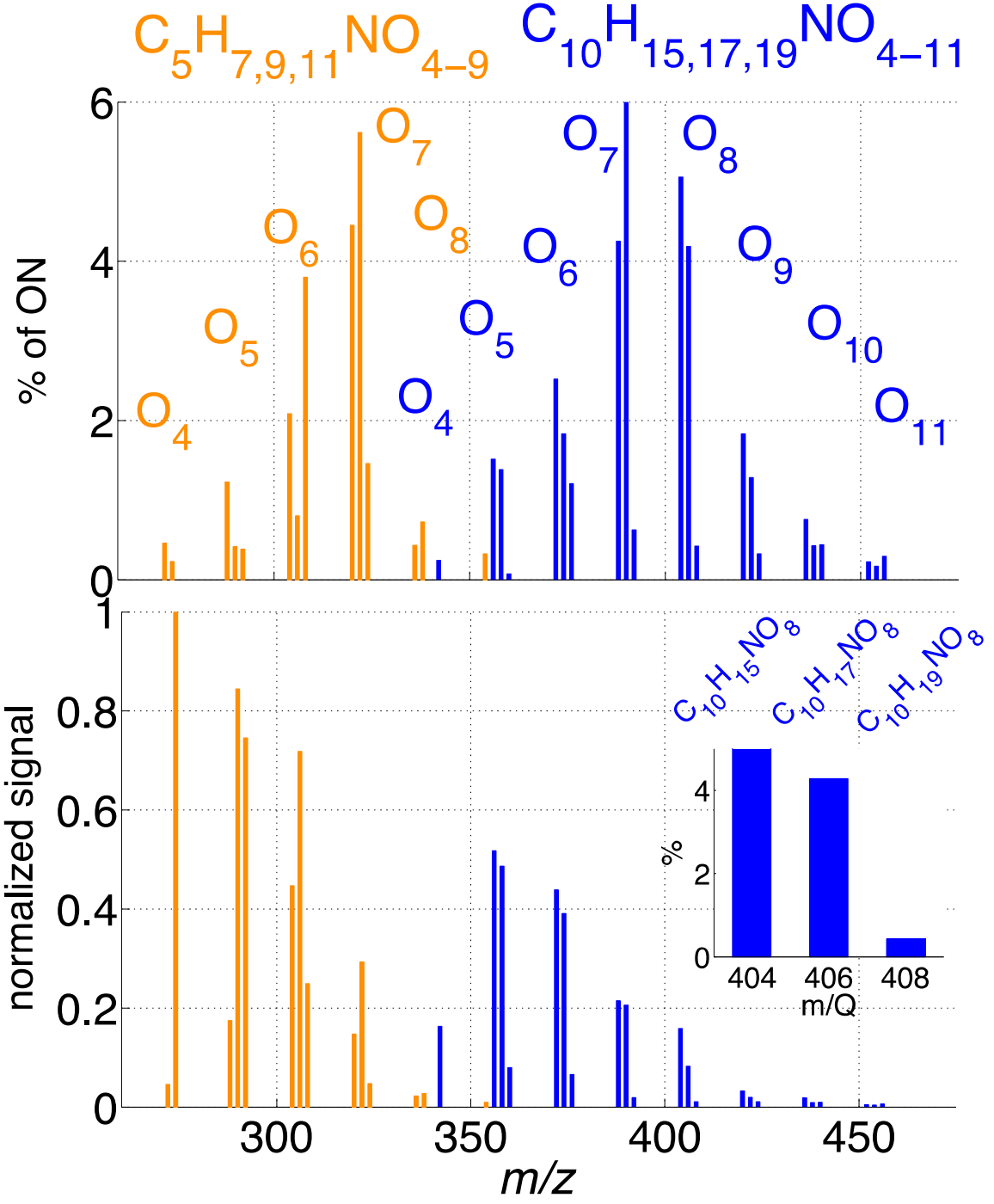
Iodide $R + I^- \rightarrow R.I^-$ **polarized species**

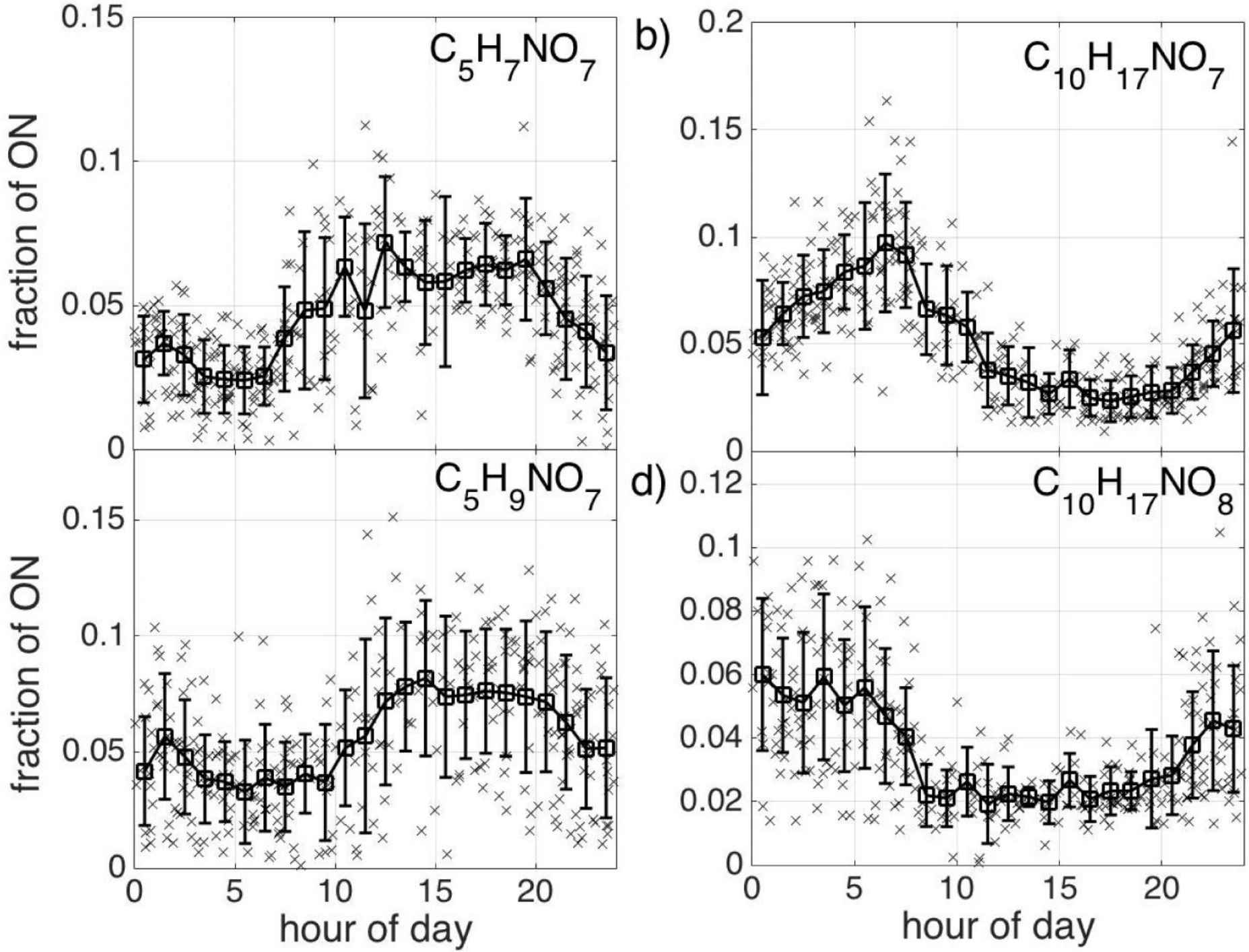
Nitrate $R + NO_3^- \rightarrow R.NO_3^-$ **highly oxidized organics**

$[\ H_2SO_4 + NO_3^- \rightarrow HSO_4^- + HNO_3\ ]$

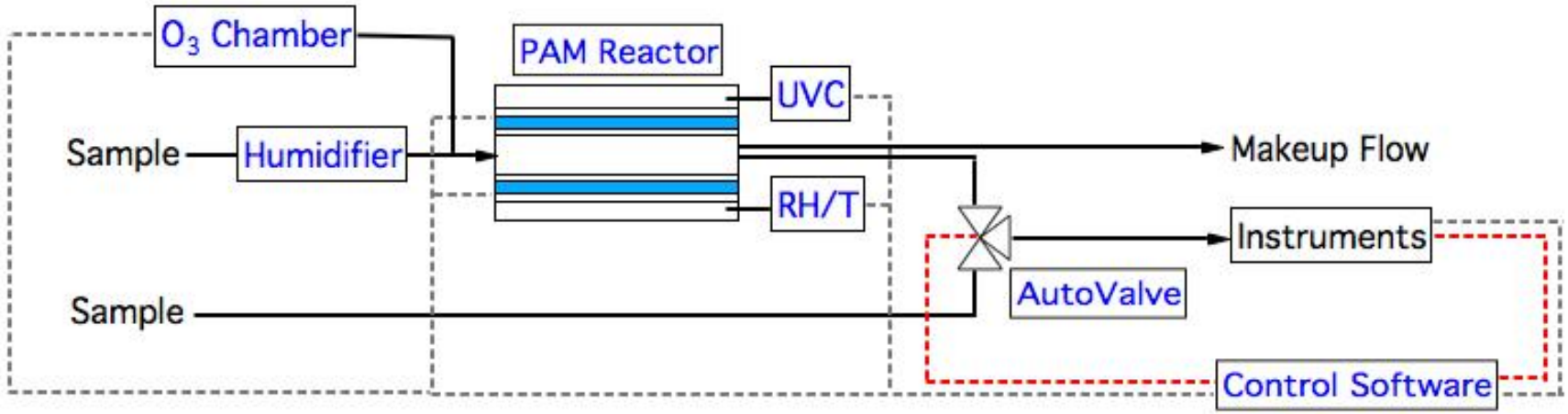
Particle-phase ON

Gas-phase ON



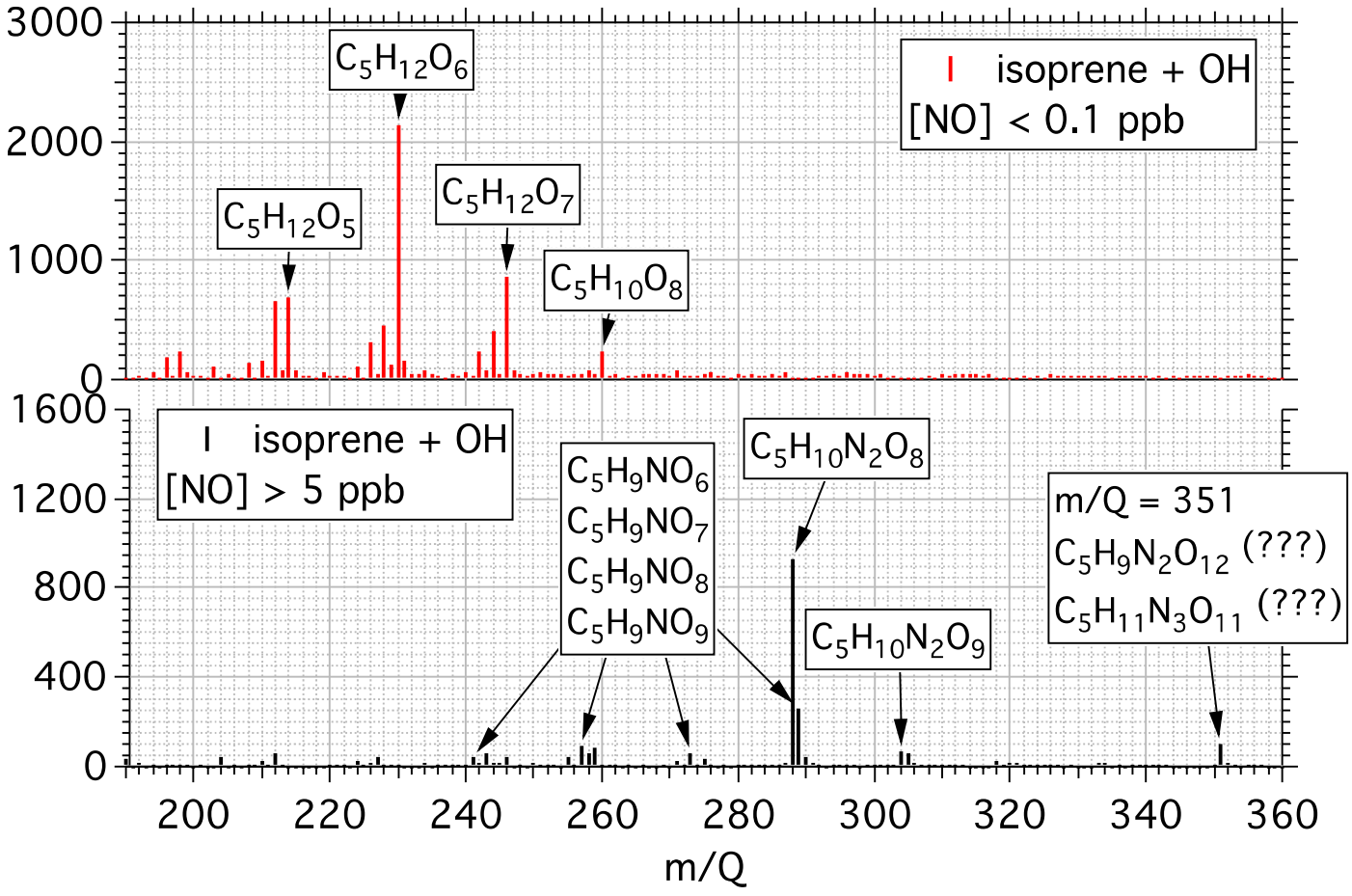

b)
d)
$C_5H_7NO_7$
$C_5H_9NO_7$
$C_{10}H_{17}NO_7$
$C_{10}H_{17}NO_8$
fraction of ON
fraction of ON
hour of day
hour of day
0.15
0.1
0.05
0
0.2
0.12
0.08
0.06
0.04
0.02
0
5
10
15
20

PAM Reactor Components

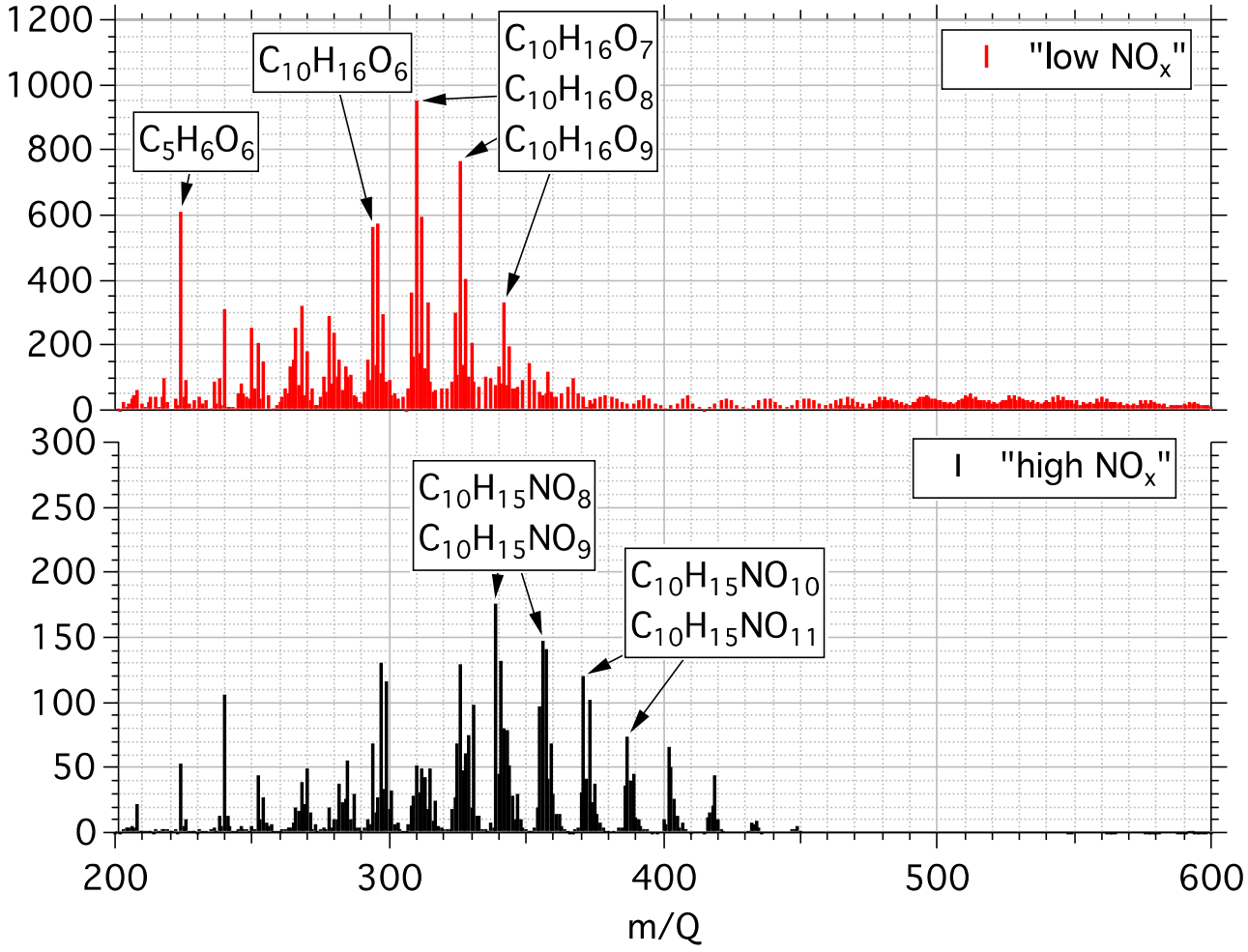


- UV lamps: λ = 185 and 254 nm wavelength
- Humidifier, Autovalve, RH/T, Photodiode
- Electronics box with ballasts and control board
- Control software

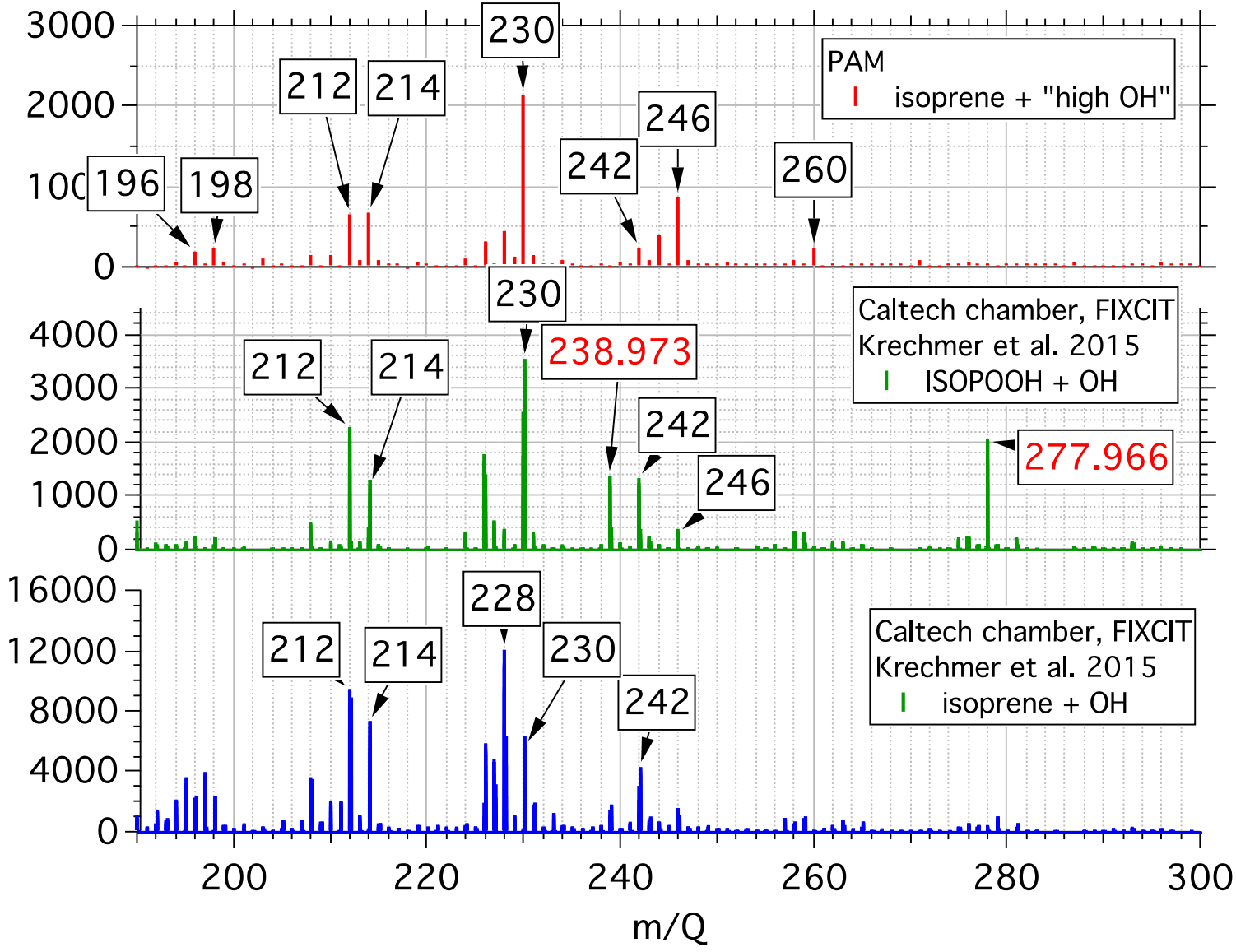
Result 2b – Proof of Concept
isoprene + “high OH”



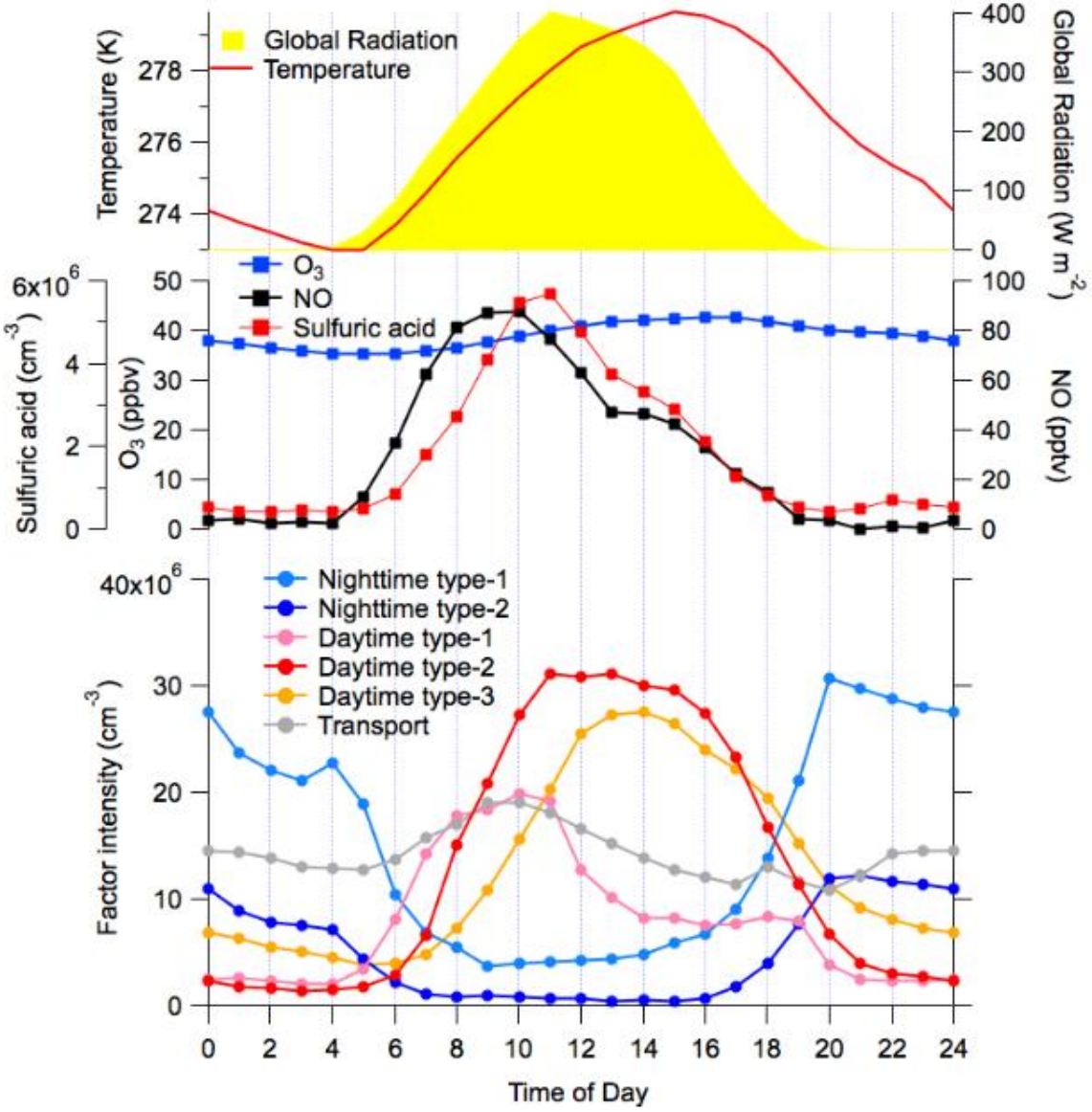
Result 4b
α-pinene + “high OH”



36 ppb isoprene + “high” OH, low NOx comparison with Krechmer et al.



Hyytiälä NO_3- *ToF-CIMS*
PMF Mass Spectral Factors



α-pinene

+

O3, OH, NO (NO3)

→ HOM

"highly oxidized multifunctional organics"

Yan et al, ACPD, 2016