MS CHAOS at PSI

Mass spectrometers for the CHemical Analysis of Organic Substances at Paul Scherrer Institute, Switzerland

October 26 – November 11 2005

André Prévôt +

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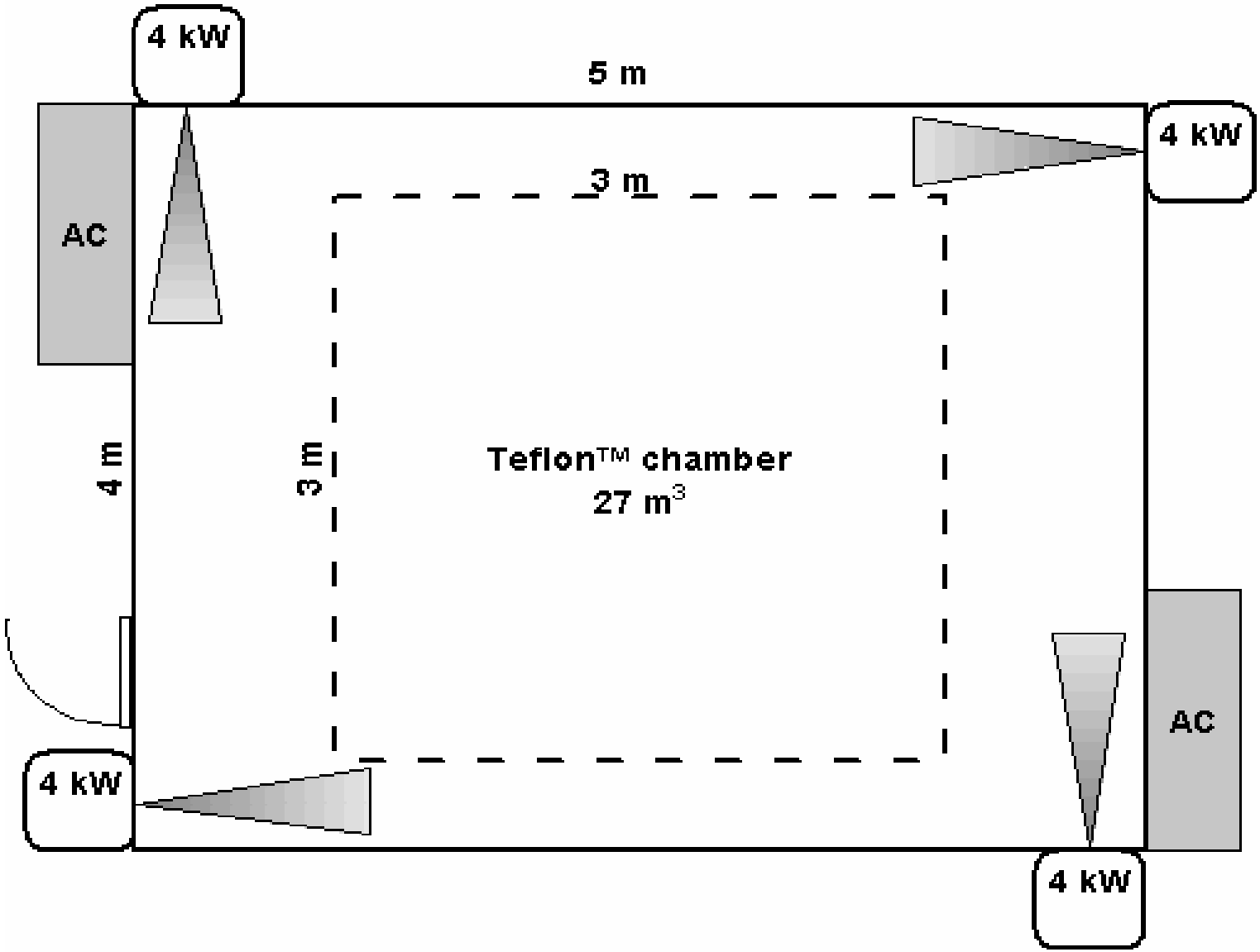
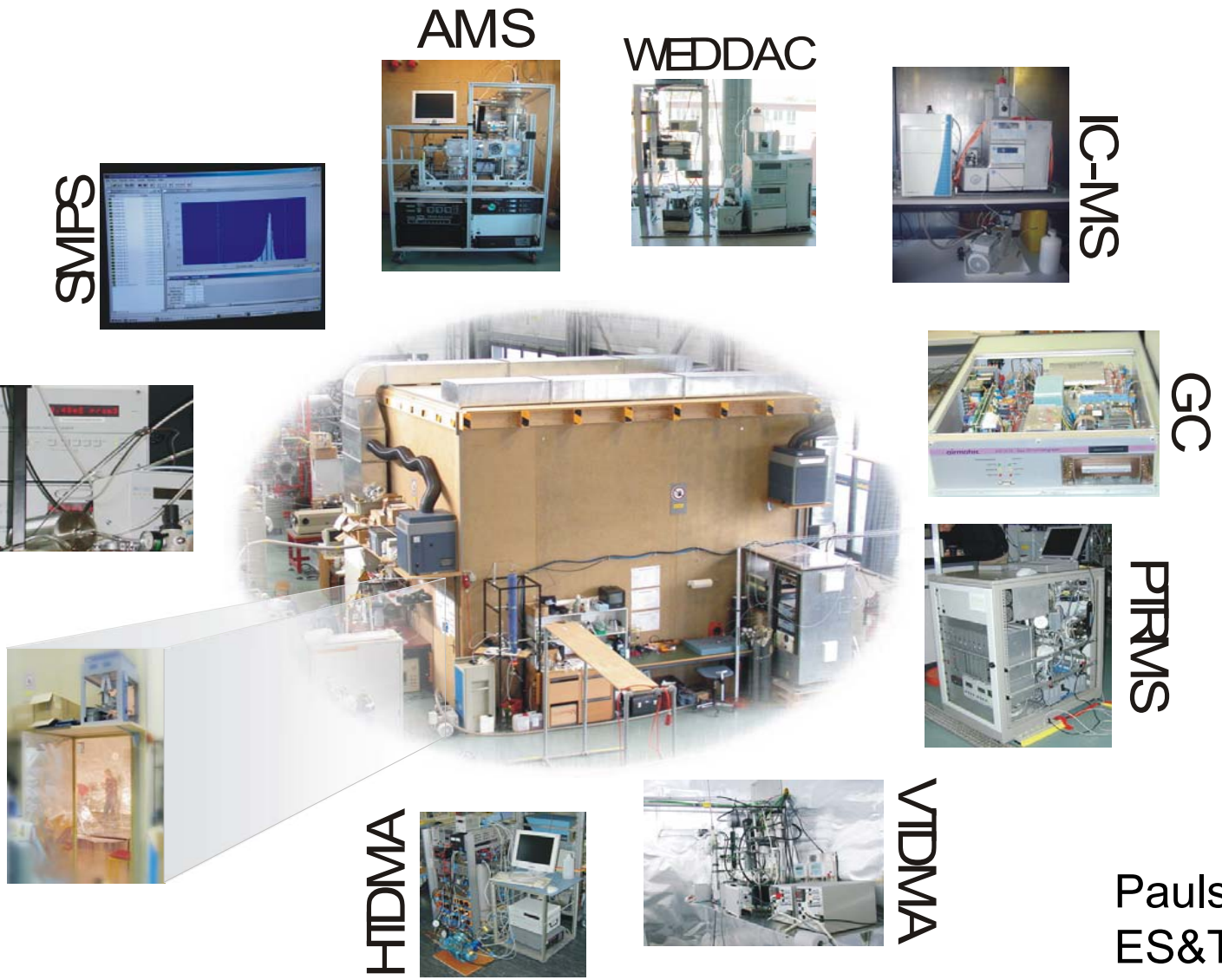
- De Carlo, P., Aiken, A., Kimmel, J., Dunlea, E., Jimenez, J.-L., University of Colorado, Boulder, USA
- Northway, M., Trimborn, A., Worsnop, D., Aerodyne, Billerica, USA
- Hings, S., Drewnick, F. Max Planck Institute of Mainz, Germany
- Parker, A., Wyche, K., Monks, P., University of Leicester, United Kingdom
- Around 10 researchers from PSI, Villigen, Switzerland

FIRST GLANCE AT THE DATA

The PSI smogchamber setup



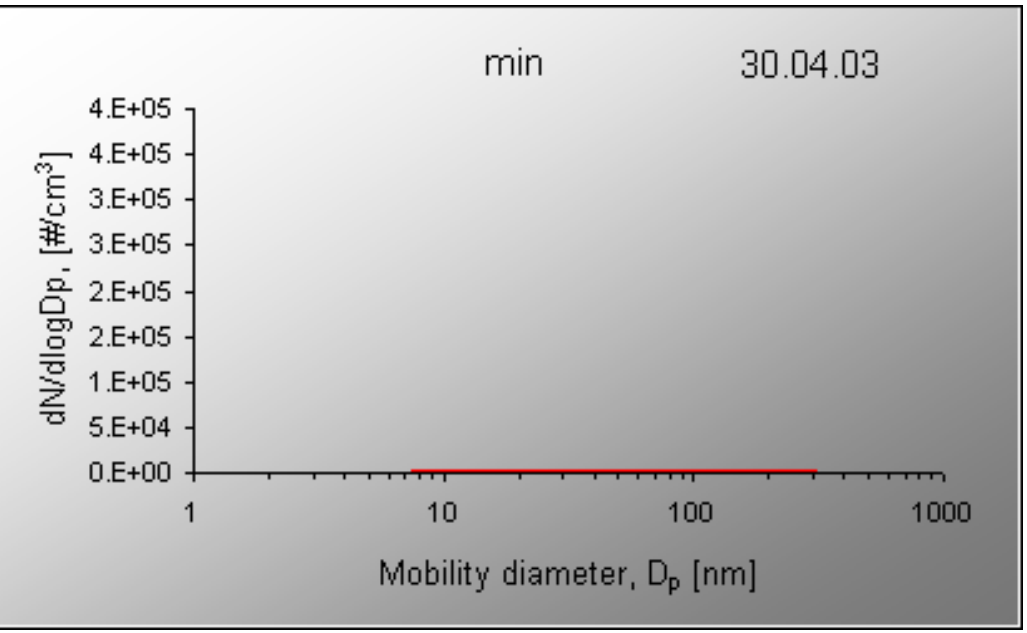
On-line instrumentation at the PSI smog chamber

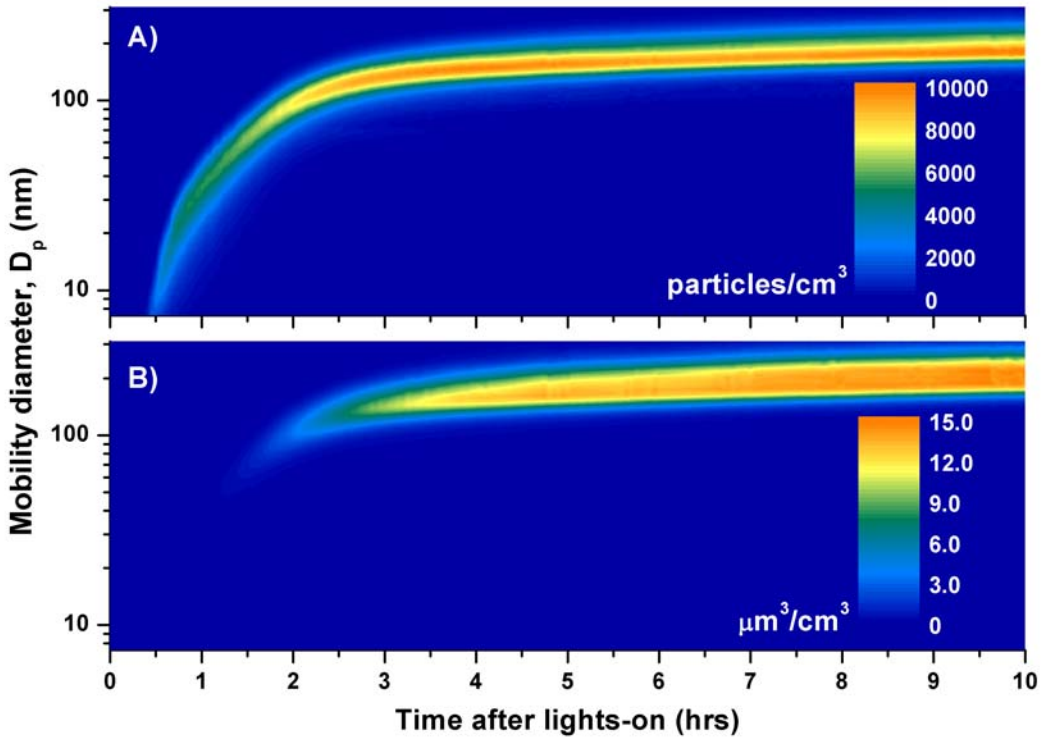


Paulsen et al.,
ES&T (2005)

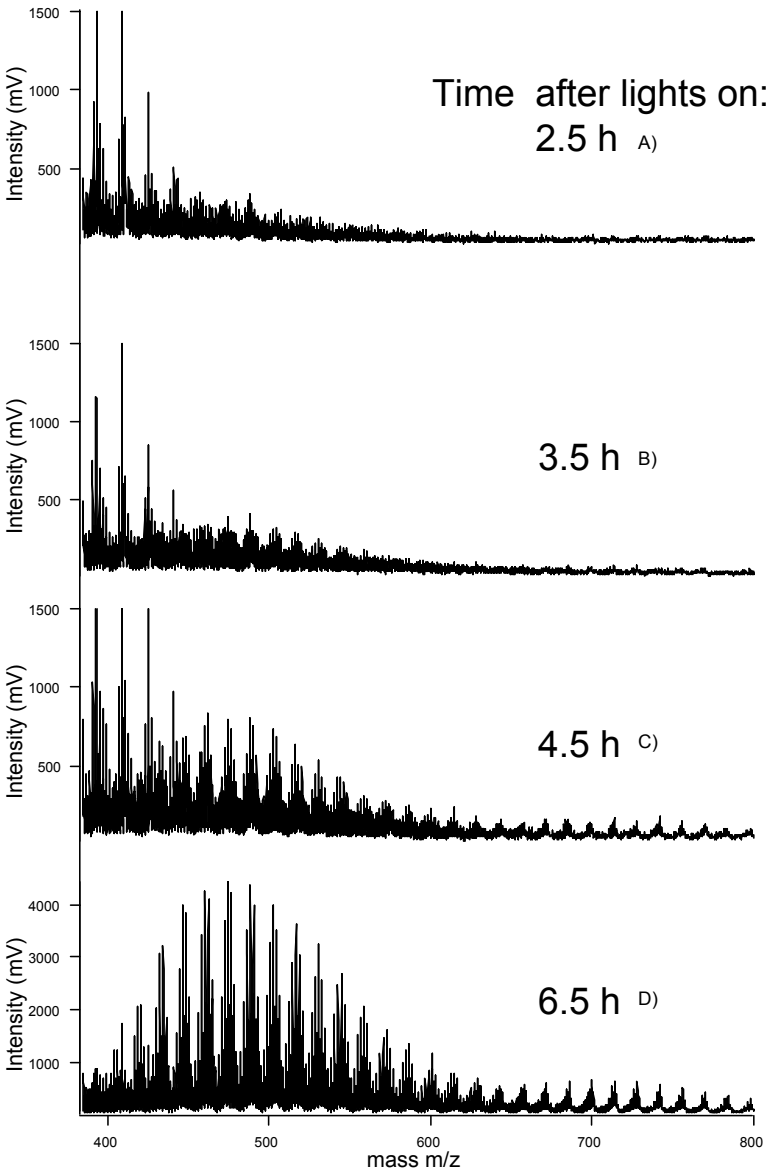
Formation of particles PSI smogchamber

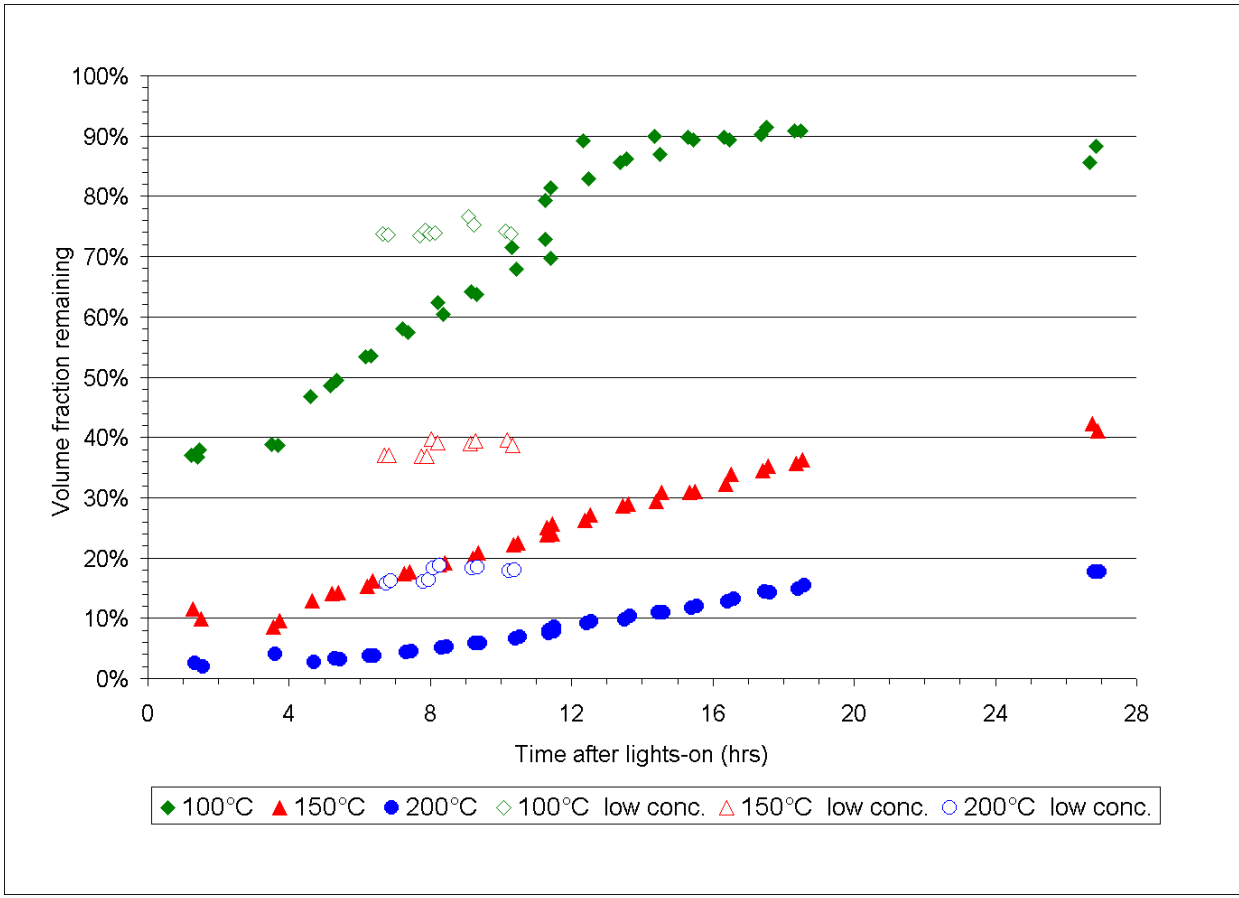
Trimethylbenzene + NOx + light →→ Secondary Organic Aerosol





SOA polymerization, observed by LDI and VTDMA



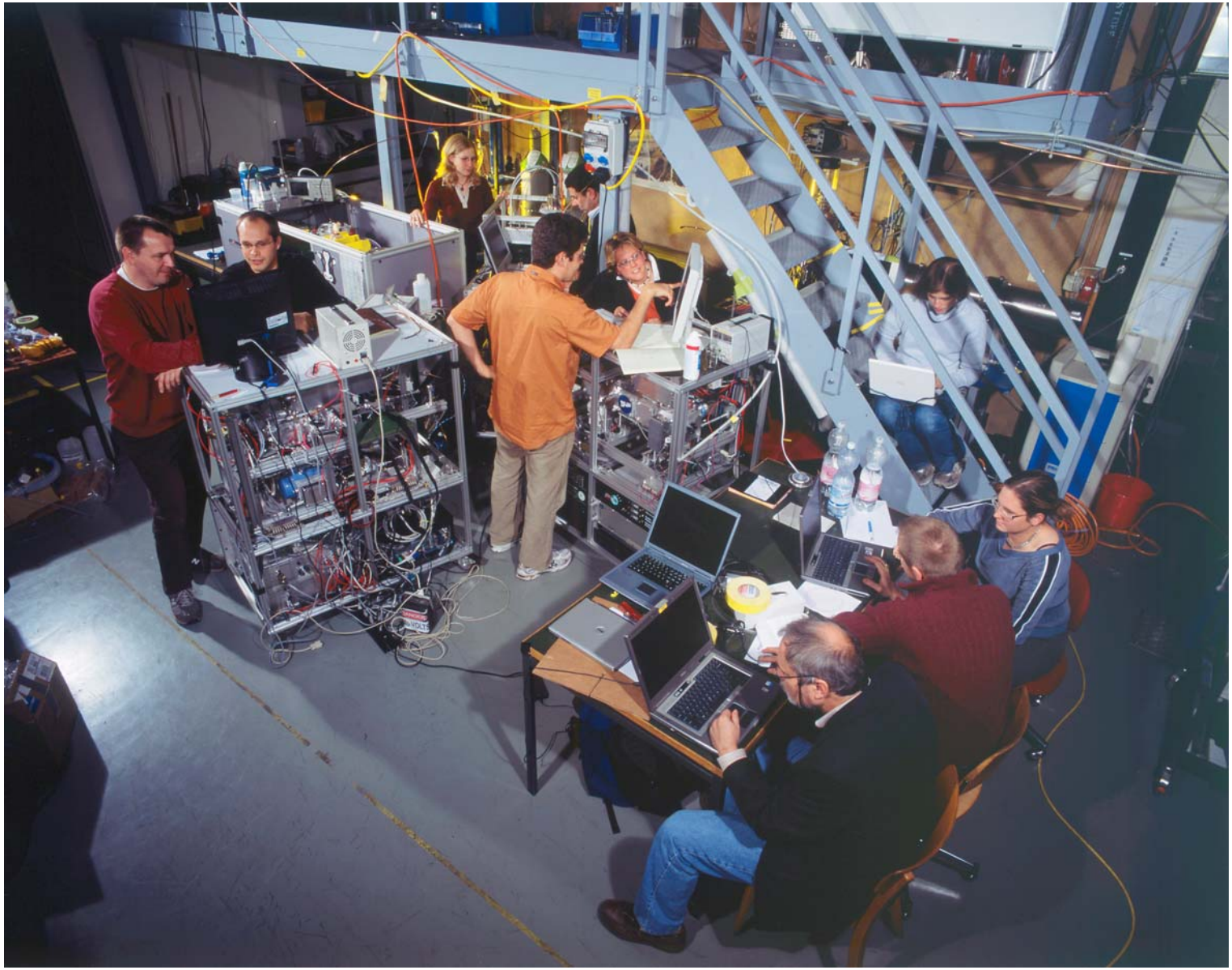


First chemical evidence of polymerization in secondary organic aerosols Kalberer et al., Science, 2004

Mass spectrometers during the MS CHAOS at PSI

- **TSI-ATOFMS** (*Carleton College*)
- **AMS** (C-TOF) with electron impact and VUV ionization (*MPI Mainz and Aerodyne*)
- **AMS** (V-TOF, W-TOF) with electron impact and negative ion mode (*Aerodyne and University of Colorado*)
- **PTR-TOF-MS** and **RO_x-Box** for gas analysis (*University of Leicester*)
- **PTR-MS**, **GC-PTR-MS** for the gasphase, **IC-MS** for organic acids in the gas and aerosol phase, **AMS** (quadrupole) (*Paul Scherrer Institute+FAL*)

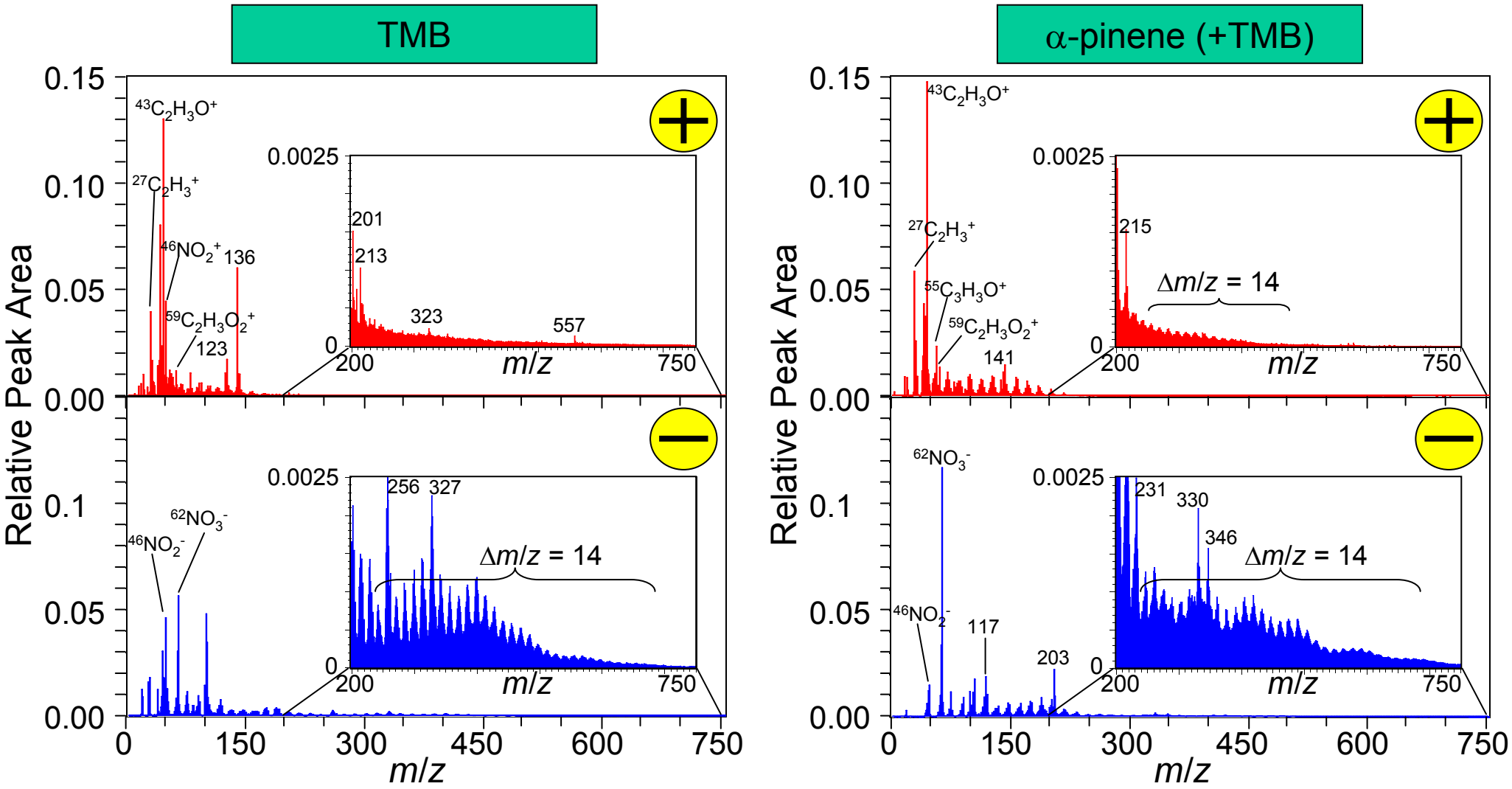
MS CHAOS at PSI



GOALS of the MS CHAOS at PSI

- Investigation if the new available mass spectrometer techniques allow an on-line detection of oligomers (candidates: TSI-ATOFMS, v-TOF-AMS, c-TOF-AMS (electron impact or VUV ionization), PTR-TOF-MS in the gas phase)
- Can we learn something new about the products (with a focus on oligomers) of TMB, isoprene, alpha-pinene in the gas and aerosol phase

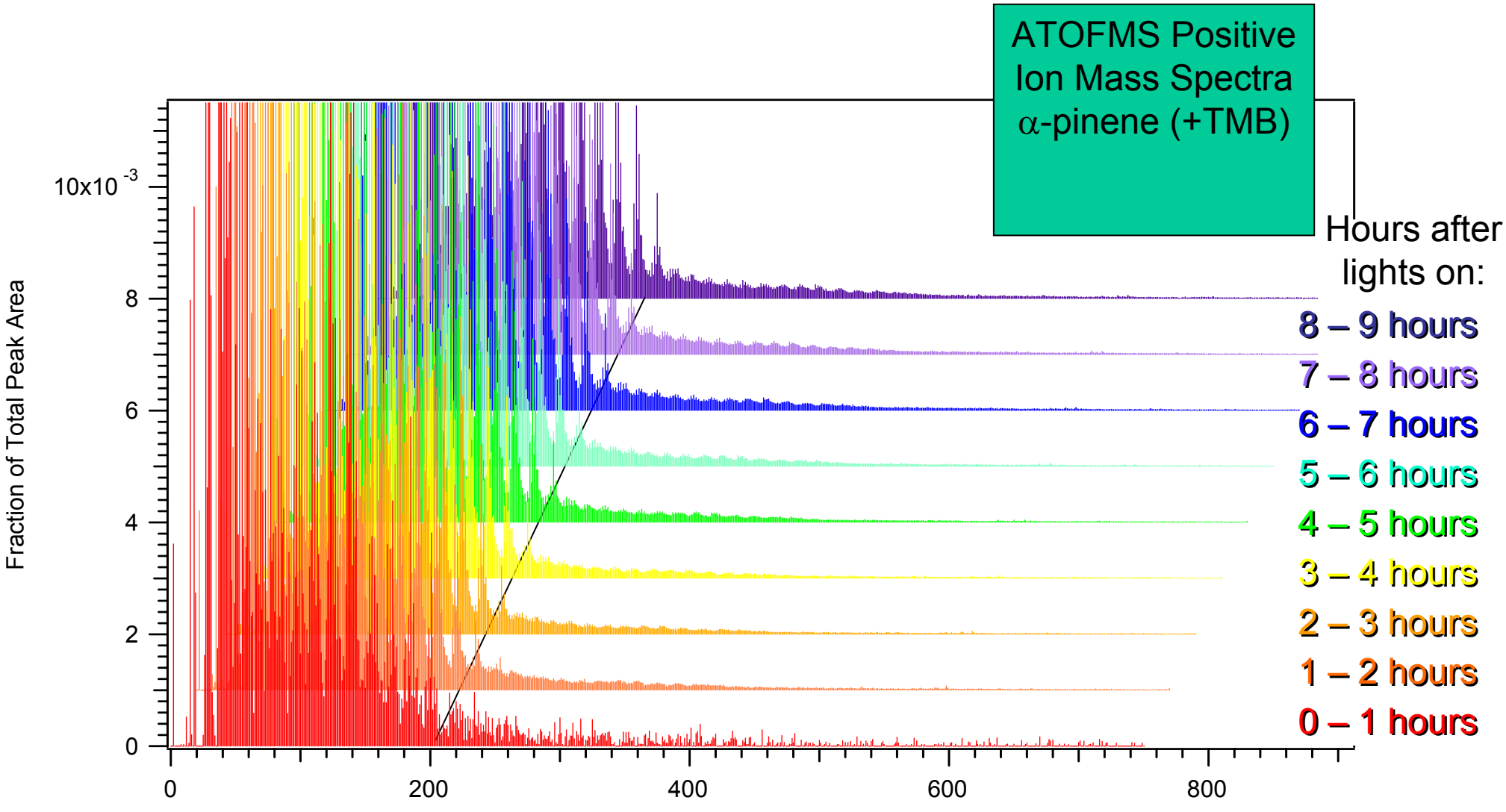
Average Spectra for Entire Smog Chamber Experiments



ATOFMS

D. Gross, Carleton College
Northfield, MN USA

Evolution of High Mass Positive Ions



ATOFMS

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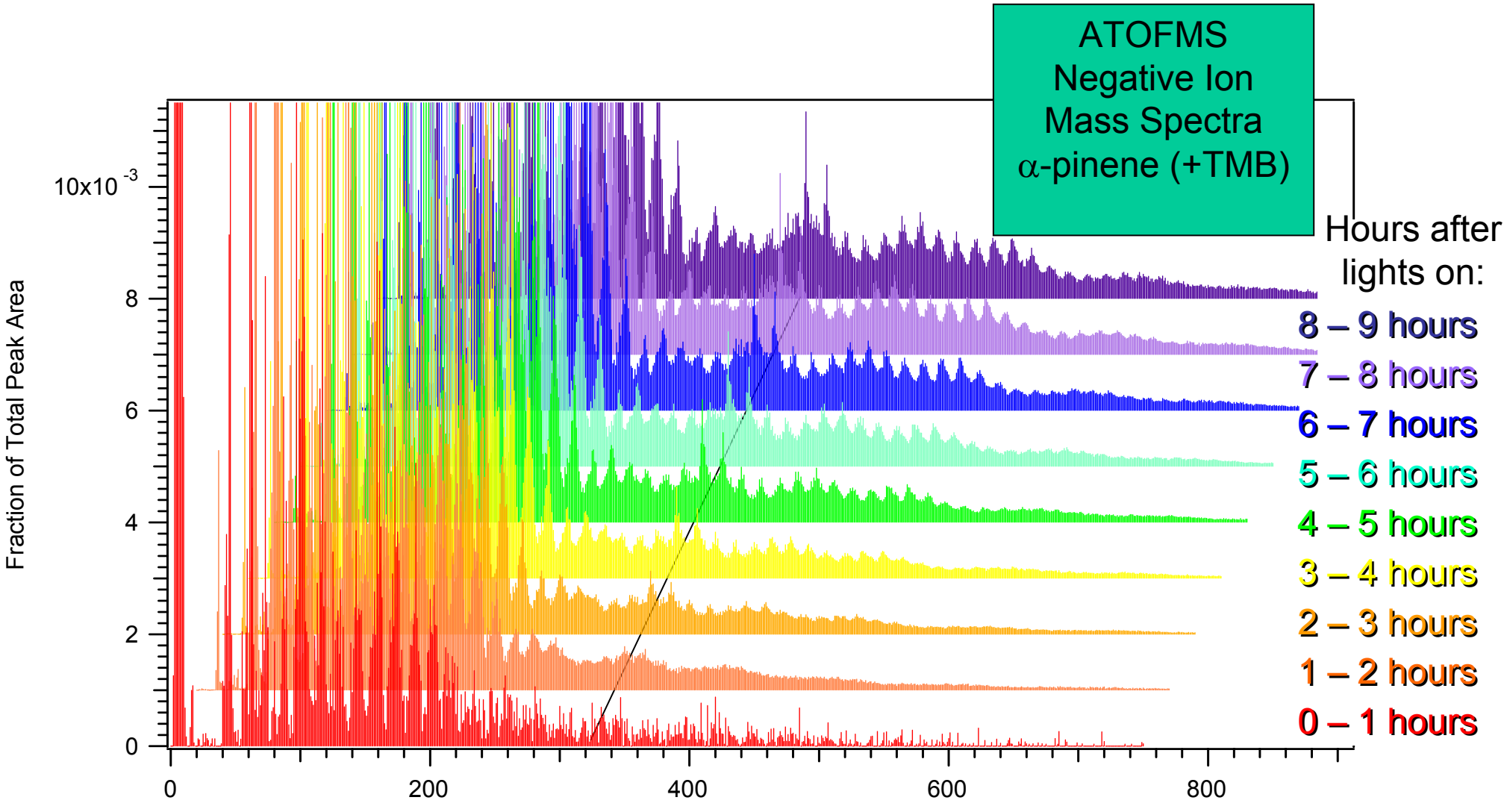
Evolution of High Mass Negative Ions



ATOFMS

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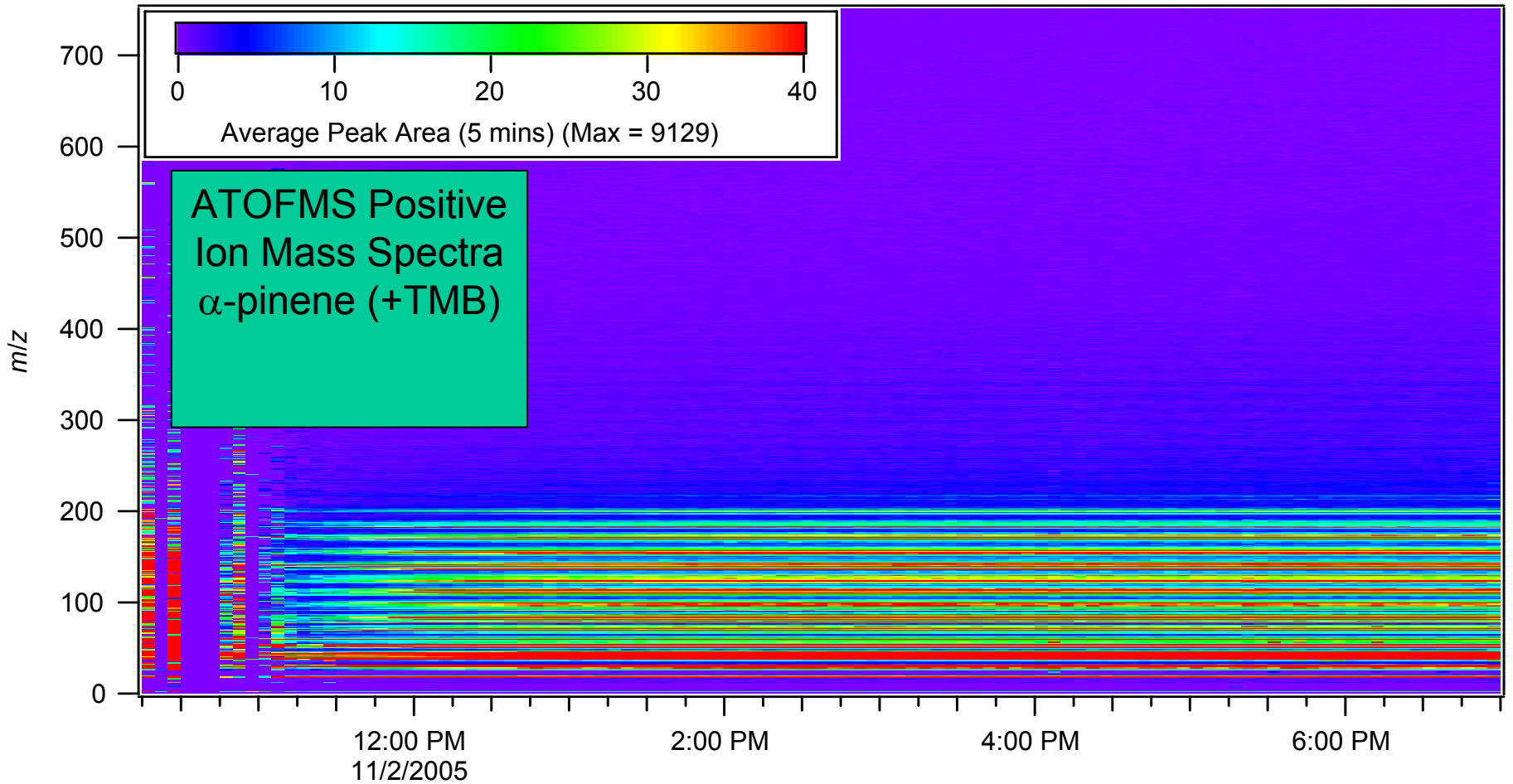
Evolution of Positive Ion Mass spectra, 5 Minute Time Resolution



ATOFMS

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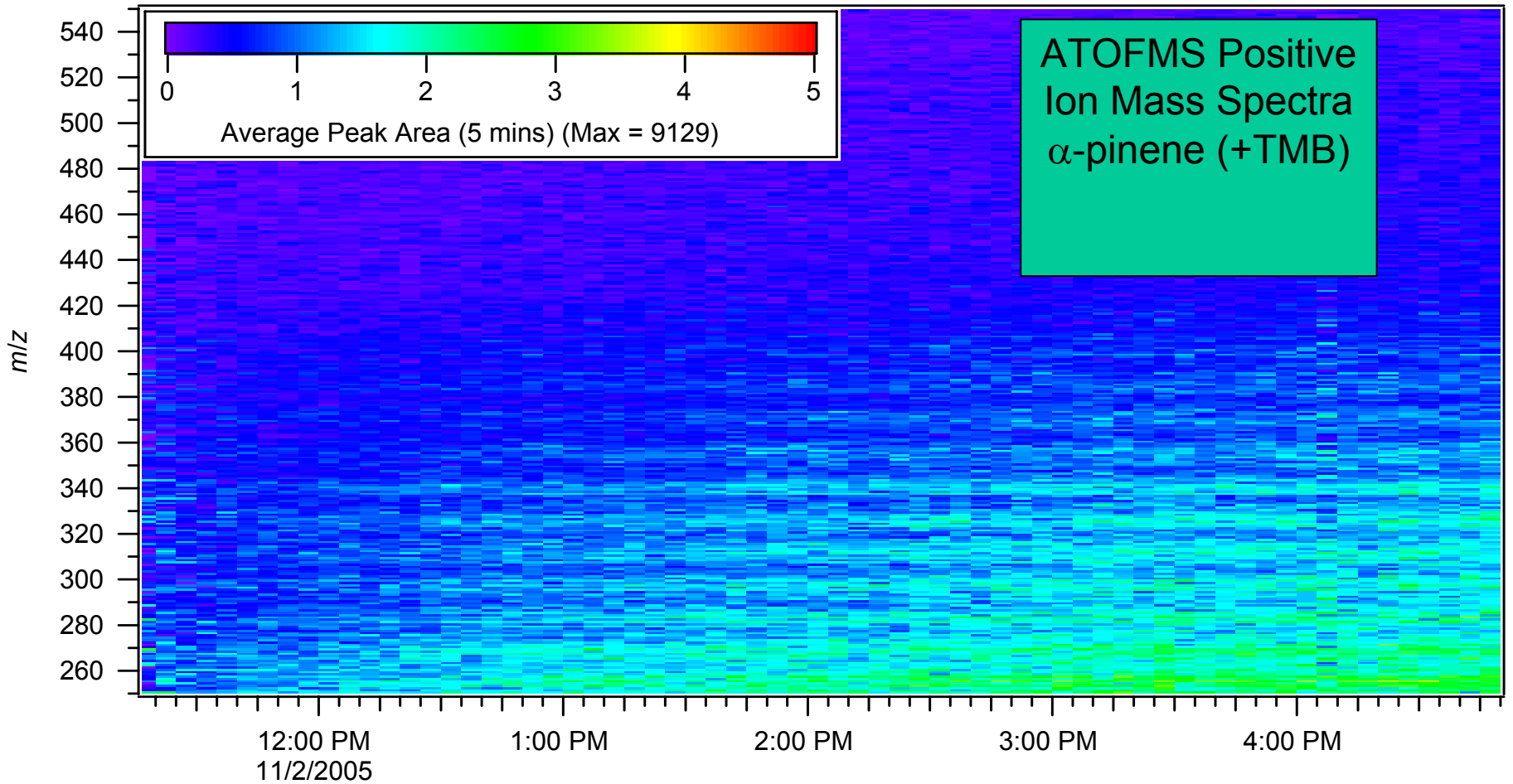
A Closer Look at Time Evolution of High Mass Positive Ions



ATOFMS

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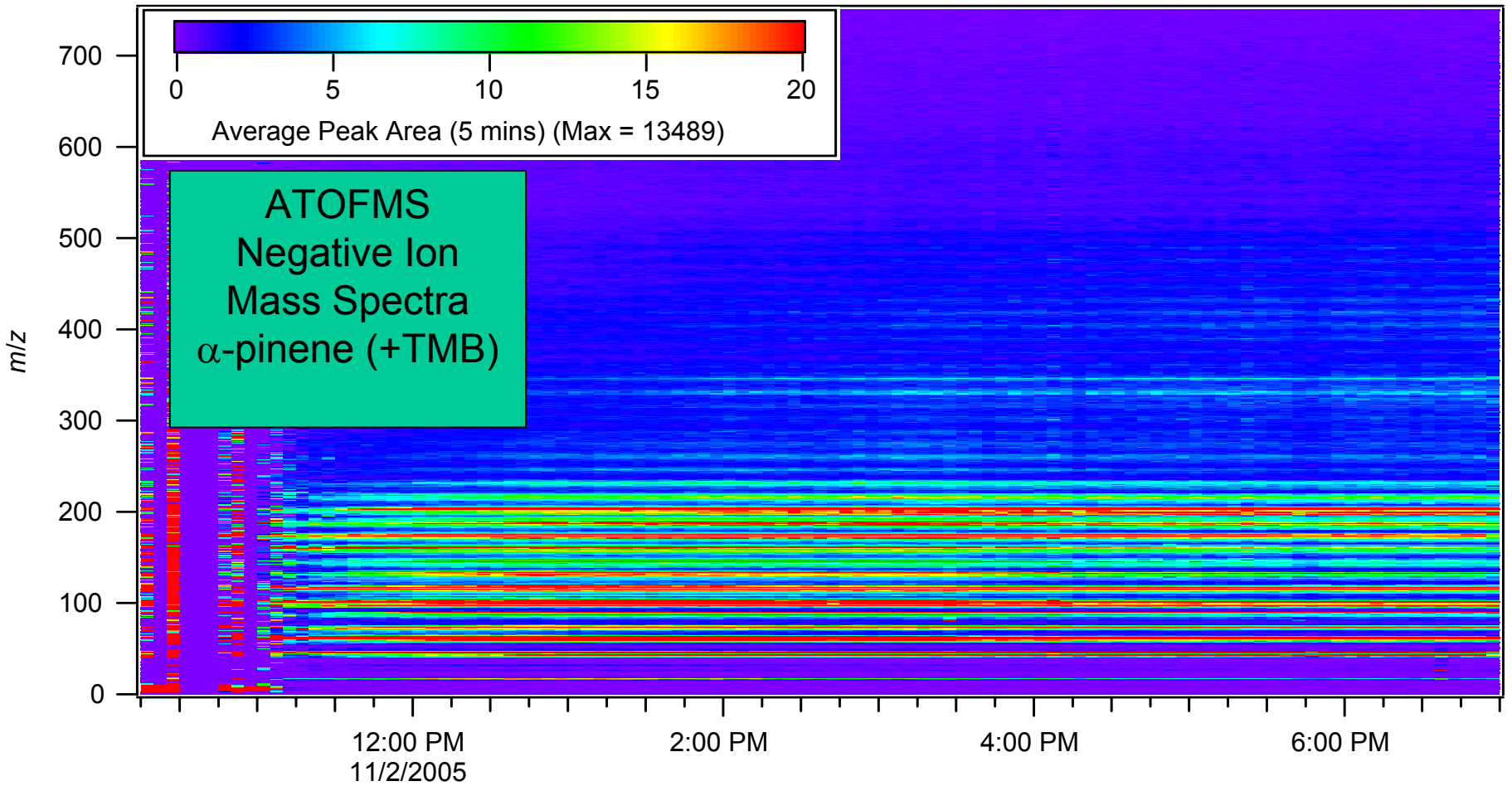
Evolution of Negative Ion Mass Spectra, 5 Minute Time Resolution



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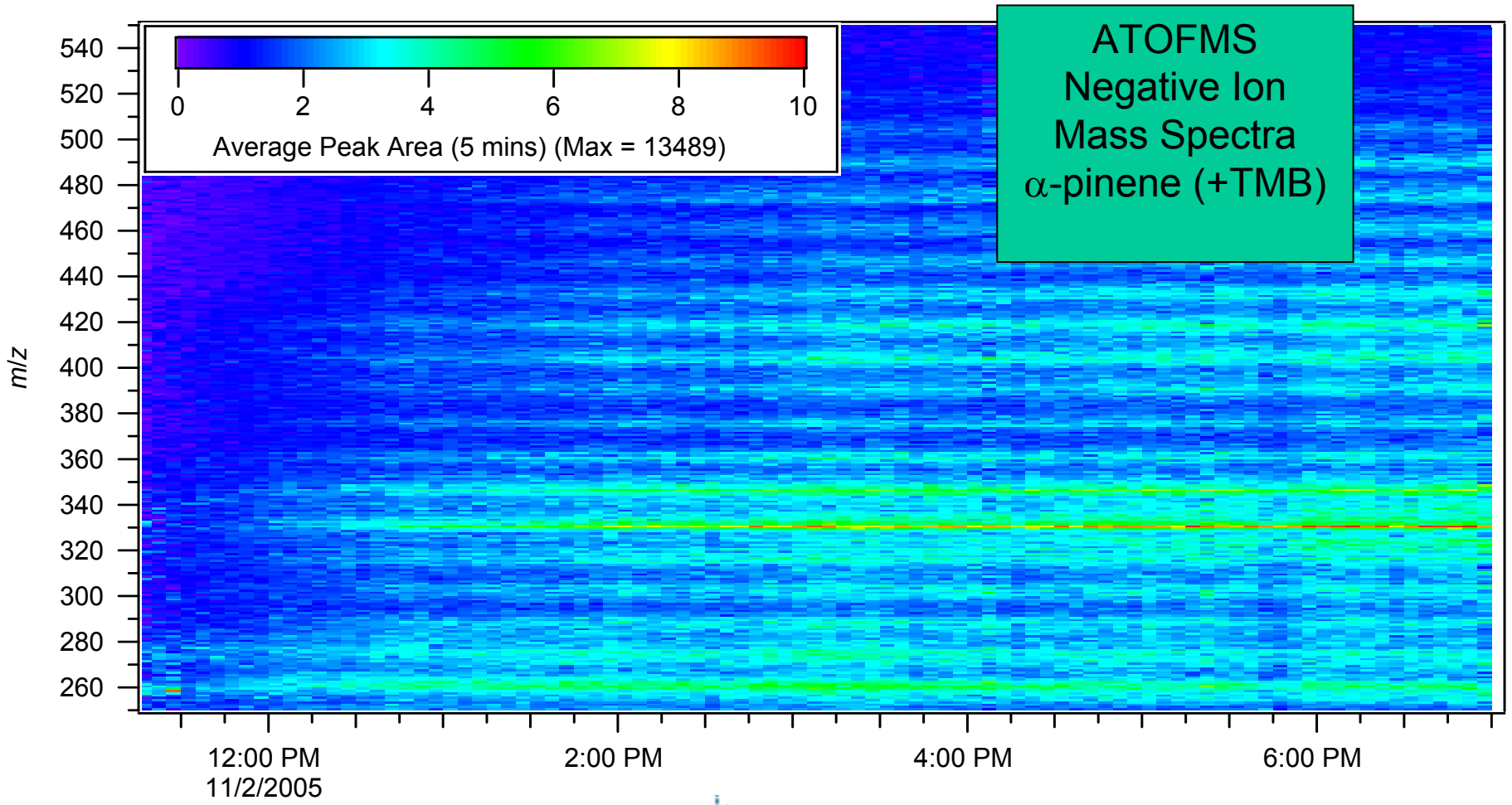
A Closer Look at Time Evolution of High Mass Negative Ions



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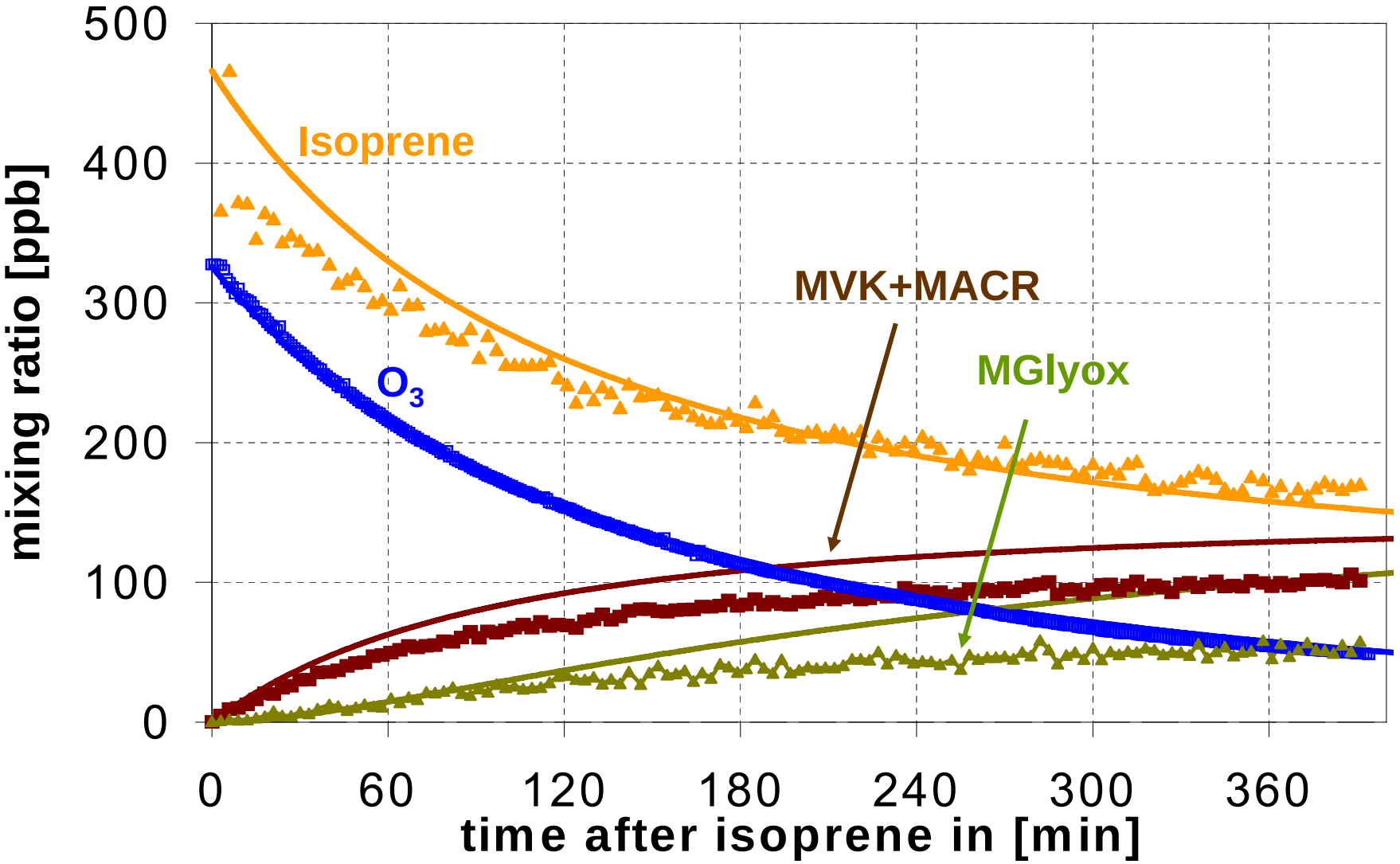
AMS ionization techniques

EI: $R + e^- \rightarrow R_i^+ + 2e^-$

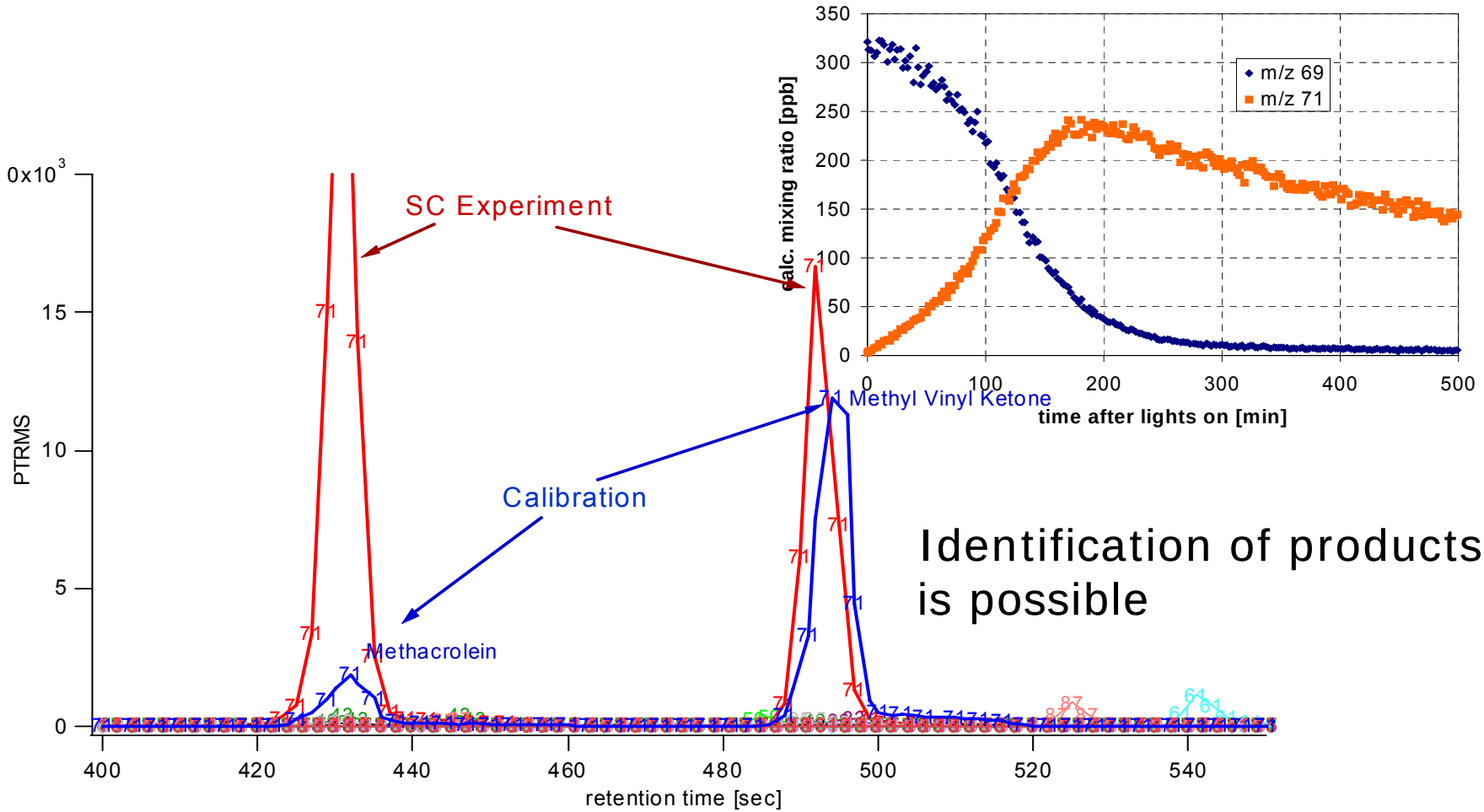
VUV: $R + h\nu \rightarrow R_i^+ + e^-$

Neg. Ions: $RCO_2H + e^- \rightarrow RCO_2^- + H$

PTR-MS in smog chamber experiments, e.g. isoprene

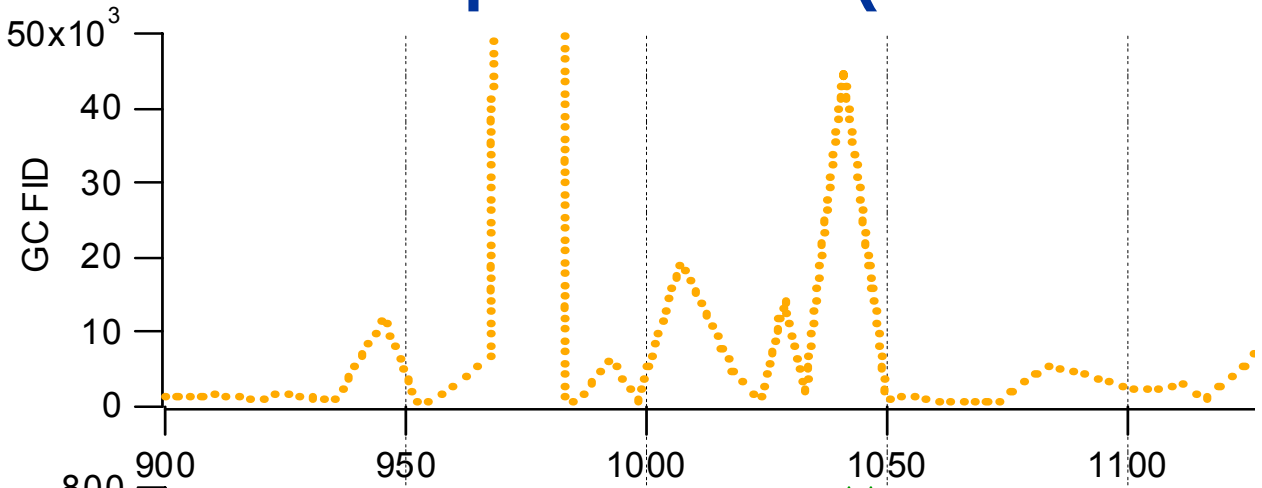


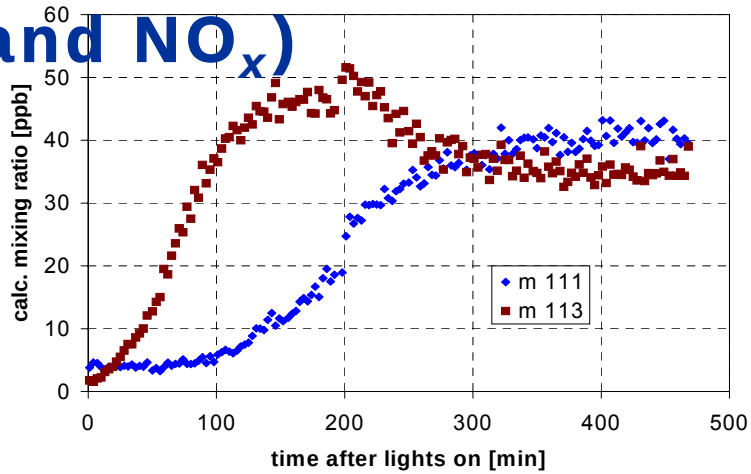
PTR-MS versus GC-PTR-MS in smog chamber experiments (here isoprene and NO_x)

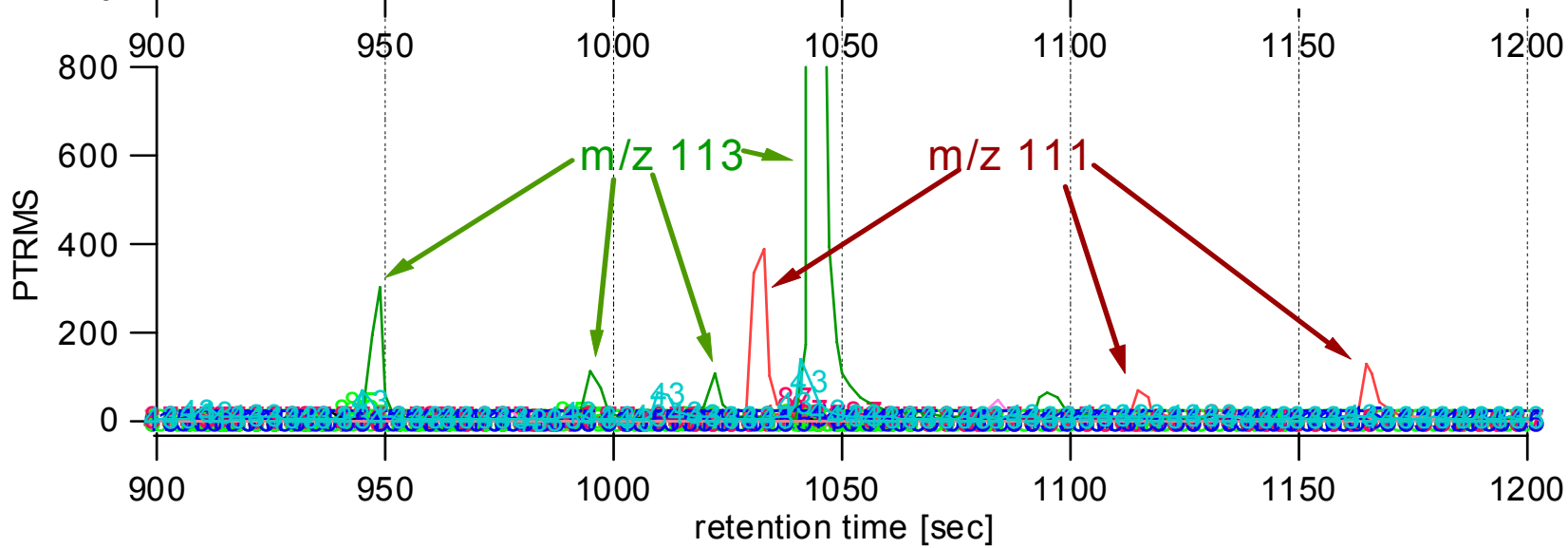


Identification of products is possible

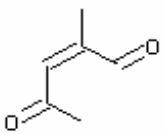
PTR-MS versus GC-PTR-MS in smog chamber experiments (here TMB and NO_x)



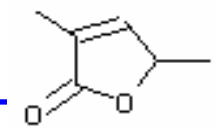




known degradation products of TMB: m/z 113



2-methyl-4-oxo 2 pentenal



3,5 dimethyl-5(2H)-2-furanone

CONCLUSIONS (Oligomerization detection abilility)

- TSI-ATOFMS is capable to measure on-line large molecular masses and has the potential to derive oligomerisation-rates
- V-TOF-AMS (probably also C-TOF-AMS) with electron impact are also able to measure large molecular masses because of much better detection limits compared to the quadrupol-AMS
- TOF-AMS with VUV ionization has the potential to see large molecular ions. Higher intensity lamps could help.
- Lower vaporization temperatures improve the detection ability of oligomers

CONCLUSIONS (new stuff)

- The carbon to oxygen ratio is around 3/1 in the smogchamber experiments. This seems rather high.
- Although we usually observe a single mode in the smogchamber experiments, differences in chemical composition as a function of size can be observed.
- The addition of a GC in front of the PTR-MS provides additional information on the gasphase compounds
- The same higher molecular ions are found for the TSI-ATOFMS and LDI-MS for the TMB system
- The electron attachment negative ion mode of the AMS is very sensitive to acids