

Investigation of highly oxidized organic compounds from α -pinene ozonolysis with an Ion-mobility Mass Spectrometer

Ugo Molteni^{1*}, Josef Dommen¹, Federico Bianchi^{1,2}, Heikki Junninen³, Douglas R. Worsnop^{3,4}, Manjula Canagaratna⁴, Urs Baltensperger¹ and the CLOUD collaboration

¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

²Institute for Atmospheric and Climate Science, ETH Zurich, 8092 Zurich, Switzerland

³Department of Physics, University of Helsinki, 00014 Helsinki, Finland

⁴Aerodyne Research Inc., Billerica, Massachusetts 01821, USA

*Corresponding author: ugo.molteni@psi.ch

Keywords: nucleation, cluster, ion mobility, mass spectrometry.

In the troposphere nucleation plays an important role in aerosol production. Even though particles have a significant impact on climate, affecting the Earth's radiation balance by scattering and absorbing solar radiation and by acting as cloud condensation nuclei, nucleation is still poorly understood. Sulfuric acid (H_2SO_4) plays a key role in atmospheric nucleation. A strong correlation between sulfuric acid and nucleation rates has been observed in numerous cases (e.g., Kerminen et al., 2010). Recently it has been shown that ternary cluster species like ammonia and amines can strongly enhance nucleation via acid-base interactions (Kirkby et al. 2011; Almeida et al., 2013). Plants emit large amounts of volatile organic compounds (VOCs), ubiquitously present in the atmosphere, which, through oxidation processes, can lead to secondary organic aerosol (Ehn et al., 2014; Riccobono et al., 2014). The composition and the role of these oxidized organic compounds is still quite unclear.

Chemical ionization atmospheric pressure interface time-of-flight mass spectrometers CI APi-TOF MS with a nitrate ion (NO_3^-)-based ionization system have proved successful to investigate these compounds because they form stable NO_3^- adduct ions. The ion mobility spectrometer (IMS) adds new features to this family of mass spectrometers: it separates the ions at atmospheric pressure according to their mobility before they enter the APi-TOF, where the mass-to-charge is measured. The mobility is governed by the collisional cross section and the mass (chemical composition) of the ions. Thus it is possible to correct potential artifacts like declustering inside the APi, investigate the chemical nature of molecular clusters and separate compounds with the same mass but different structure.

This paper will give an overview of the instrument and demonstrate its capabilities to measure oxygenated volatile organic compounds and their cluster formation. We will illustrate its performance using measurements from the CLOUD (Cosmics Leaving Outdoor Droplets) nucleation experiment at CERN with α -pinene as precursor in ozonolysis experiments. Figure 1 gives an example spectrum using the nitrate ion for chemical ionization. On the y-axis the ions are separated by their mobility while the abscissa gives their corresponding m/z . We observed C_{10} oxidized compounds with 7 to 11 oxygen atoms, which range

from semi-volatile to extremely low volatility organic compounds (SVOCs, ELVOCs). An interesting feature can be seen in Figure 1: Although the drift time (mobility) is related to the reduced mass of the compounds and air, we observe that many ions differing in composition by only two hydrogens are separated by the same difference in drift time as two ions which differ in composition by an oxygen. This is caused by different chemical structure of the C_{10} oxidized compounds, consequent different shapes, and thus different mobilities.

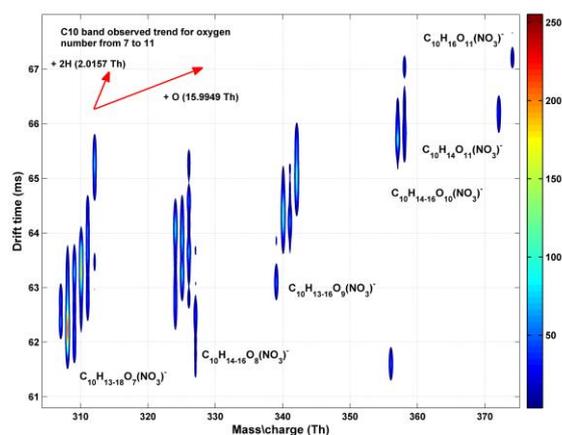


Figure 1 Ion drift time versus m/z from IMS-APi-TOF MS taken in an α -pinene ozonolysis experiment.

Acknowledgements

This work was supported by the Swiss National Science Foundation and the CLOUD collaboration funding.

References

- Almeida et al. (2013). *Nature*, **502**, 359-363.
- Ehn et al. (2014). *Nature*, **506**, 476-479.
- Jokinen et al. (2012). *Atmos. Chem. Phys.*, **12**, 4117-4125.
- Junninen et al. (2010). *Atmos. Meas. Tech.*, **3**, 1039-1053.
- Kerminen et al. (2010). *Atmos. Chem. Phys.*, **10**, 10829-10848.
- Kirkby et al. (2011). *Nature*, **476**, 429-433.
- Riccobono et al. (2014). *Science*, **344**, 717-721.