Chemical composition of (cluster) ions observed by APi-TOF during nucleation

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New particle formation (NPF) in the atmosphere from the gas phase has been estimated to contribute up to 45% of the global cloud condensation nuclei (CCN) (Merikanto *et al*., 2009). To understand this process, mechanisms of NPF are intensely studied.

The CLOUD experiment at CERN (Geneva, Switzerland) performs chamber studies on nucleation under well-controlled experimental condition to elucidate nucleation mechanisms. Various parameters such as precursor species and concentrations, light condition, trace gas concentrations, relative humidity and temperature are varied to simulate different environmental conditions. By employing an electric field inside the CLOUD chamber or by using the pion beam from the CERN Proton Synchrotron, ion production and removal rates can also be controlled in the experiment.

The Atmospheric Pressure interface Time-of-Flight Mass Spectrometer (APi-TOF, Tofwerk AG) is able to detect atmospheric ions and charged clusters up to 2000 Th with high sensitivity (Junninen *et al.*, 2010). Being able to analyse the chemical composition of gas phase ions and charged clusters below 2 nm, the instrument provides a strong tool to investigate the first steps of NPF (Almeida *et al.*, 2013; Bianchi *et al*., 2014; Schobesberger *et al*., 2013).

The chemical composition of positively and negatively charged clusters was studied using two APi-TOFs: one operating in positive mode and the other one in negative mode to detect (cluster) ions in experiments with galactic cosmic rays (GCRs) or beam present. APi-TOF spectra were obtained under different experimental conditions as summarized in Table 1: different combinations of gas phase precursors which included biogenic and anthropogenic hydrocarbons (HC) as well as the trace gases sulfuric acid and ammonia, different temperature, relative humidity, NOx concentration, and beam intensity.

In the positive spectra, protonated organics or organics charged by a protonated base are observed. In the case of the negative spectra, deprotonated acids or deprotonated acids clustering with organics or ammonia are observed depending on the experimental conditions. Organics clustering with organics were observed both in positive and negative spectra when there were only organic precursors without sulfuric acid or ammonia in the chamber. When sulfuric acid was present, clusters of pure sulfuric acid as well as of sulfuric acid with organic molecules were observed in the negative spectra while the positive spectra only contained organic clusters. The addition of ammonia to the chamber switched the charge on the positive clusters from protons to NH_4^+, and formed ammonia - sulfuric acid clusters carrying a negative charge.

By comparing the spectra under different experimental conditions, it is possible to retrieve information which molecules participate in the formation of small clusters and eventually lead to nucleation.

Table 1. Gas phase precursors

experiment	Biogenic HC	Anthropogenic HC	H_2SO_4	NH_3
1	Yes	No	No	No
2	Yes	No	Yes	No
3	Yes	No	Yes	Yes
4	No	Yes	No	Yes
5	No	Yes	Yes	Yes

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