Study on atmospheric nucleation and the precursor gases in free troposphere

Nucleation2013 campaign at the Jungfraujoch (NUCLEACE)

PI PhD Heikki Junninen
PhD Jonathan Duplissy
PhD Alexey Adamov
PhD Arnaud Praplan

Introduction and motivation

New particle formation and their growth is a major source of cloud condensation nuclei (CCN) in the troposphere (Kerminen et al, 2013). This process contributes significantly to the reported uncertainty in the radiative forcing by aerosols connected to the climate change (Stocker et al. 2013)

Sulphuric acid and extremely low volatile organic compounds (ELVOC) are found to be a critical molecular species that participate in the new particle formation and growth (Ehn et al. 2014). Measurements of sulphuric acid are often conducted by chemical ionization mass spectrometer. There exist a numerous studies measuring sulphuric acid concentrations at the sea level, but in the free troposphere only air born measurements are available and no long-term measurements at all.

In order to understand the new particle formation, measurements from the each step involved are required. Starting with molecular level with the detection of sulphuric acid and other gaseous components to particles up to 40nm in diameter. Array of instruments enables to characterize the formation and growth of atmospheric particles and the role of atmospheric ions at molecular level.

Scientific objectives

Objectives of the study are to calibrate and to measure the concentration sulphuric acid in free troposphere, where this would be the first measurement of its kind. Additionally, in the case of new particle formation event, we are aiming to fully characterize the event. To measure the content of precursor species, air ion concentration and composition, and formed aerosol size distribution.

Reason for choosing station

High altitude station at Jungfaujoch will give unique possibility to study the free tropospheric cluster formation and the role in nucleation observed in the boundary layer.

Method and experimental set-up

Neutral and charged particle size distribution:
NAIS (neutral aerosols and air ion spectrometer) measures air ions (size range of 0.5-40nm) and particles (size range of 2-40nm). In ambient measurements the instruments typically operates in 5min time resolution during which it alternates measurement modes ion-particles-zero measurements, so than in 5min all modes are completed.

Sub-3nm neutral particles concentration and size distribution:

PSM (particle size magnifier) is currently the only commercially available instrument to measure neutral particles in sub-3nm size range. Instrument is based on condensing diethyleneglycol on neutral particles, growing them and detecting by laser beam.

Sub-2nm ion cluster composition and concentration:
APiTOF (Atmospheric Pressure interface Time Of Flight Mass Spectrometer) instrument to measure atmospheric ions with minimal interference. Instrument is a high resolution field deployable mass spectrometer with high enough detection limit, so that atmospheric ions can be detected directly without any pretreatment or collections. Accurate mass delivered by the instrument can be used to determine the chemical identity of atmospheric ions.

Sub-2nm neutral cluster composition and concentration:
CI-APiTOF (Chemical Ionization Atmospheric Pressure interface Time Of Flight Mass Spectrometer) instrument to measure neutral clusters and acidic molecules by charging them with NO3- ion. The instruments mass spectrometer part is identical to previously described APiTOF.

Preliminary results and conclusions

During the project a state-of-art atmospheric aerosol measuring techniques were deployed to Jungfraujoch high alpine station. Aerosol size range covered by deployed instrumentation covered the whole nucleation relevant range. Starting with molecular level with the detection of sulphuric acid and other gaseous components to particles up to 40nm in diameter.

Sulphuric acid is found to be critical molecule that participates in new particle formation, it was measured with atmospheric pressure interface time of flight APiTOF (Junninen et al, 2010) equipped chemical ionization, CI unit (Jokinen et al 2012). The smallest particles in size range of 1-2nm in diameter were measured with particle size magnifier, PSM (Vanhanen et al 2011). Neutral clusters and air ion spectrometer, NAIS was utilized to measure concentration of particles in mobility diameter 2-40 nm and 0.5-40 nm for neutral and charged particles, respectively. Air ion chemical composition was determined with the APiTOF.

Due to high altitude location the ambient pressure at Jungfraujoch station is about 0.6 atm compared to 1 atm at the sea level, where the instruments were originally calibrated. In order to obtain reliable results an additional calibration was performed at the site. Sulphuric acid was calibrated utilizing the method described in Kürten et al 2012. This is the first field H_2SO_4 calibration performed in free tropospheric conditions. Figure 1 shows the results of the calibration performed.

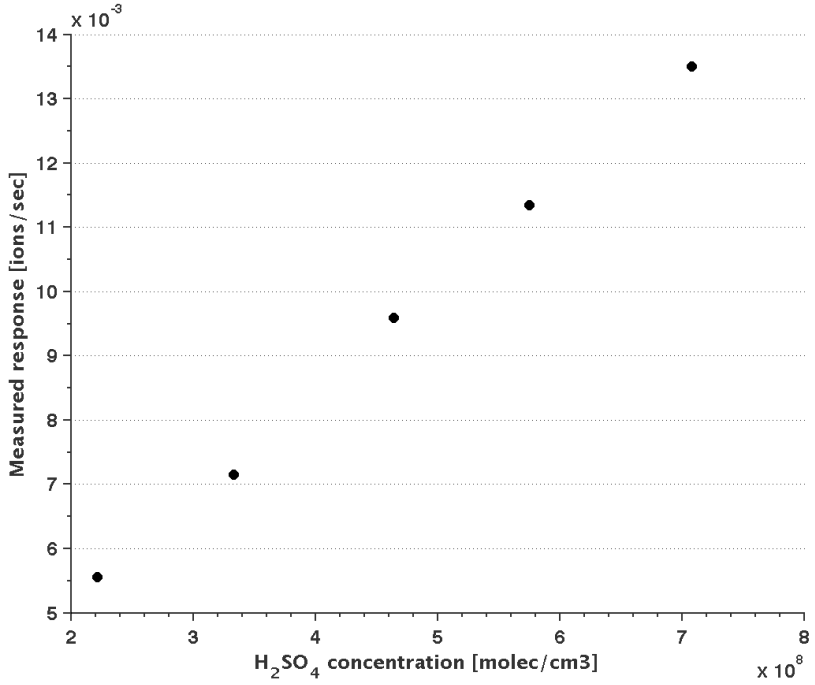

Figure 1. Instrument response to known H_2SO_4 concentration.

Measured sulphuric acid at Jungfraujoch station showed a clear diurnal variation with highest concentrations during the day. Daytime concentrations varied from $7*10^4$ to $6*10^6$ molec/cm^3 and nighttime concentrations varied from $1*10^4$ to $5*10^4$ molec/cm^3 (Figure 2). Clear connection between particle concentration and sulphuric acid concentration was not observed, which means that the particle concentration was controlled by other factors that the new particle formation.

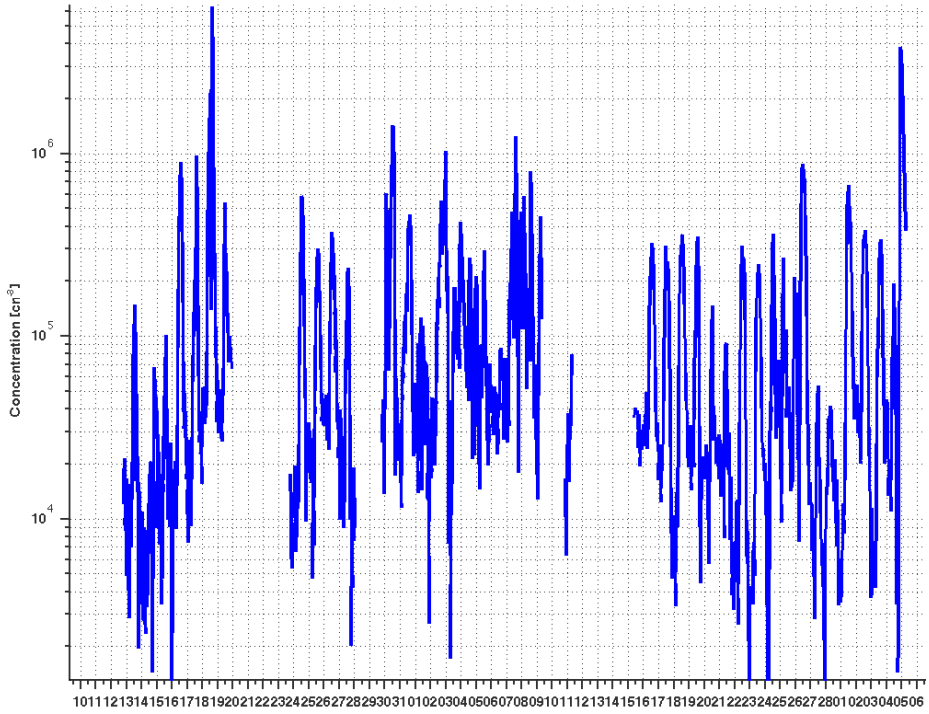

Figure 2. Concentration of sulphuric acid during the whole campaign measured with CI-APiTOF. X-axis are days in February and march 2013.

Measurements of air ion concentration and composition were partly failed during the first half of the campaign due to unexpected sink of ions around the Sphinx building. Off-site measurements showed that the problem indeed was a vicinity of the Sphinx building and that the ion instruments were performing well. The instruments were moved to a new location at the apartment complex of the High Alpine Research Station and ion measurements were conducted there for the rest of the campaign. However, even at the new location the concentrations showed very fast fluctuation that is not observed in other locations. Figure 3 illustrates this behavior. Ion formation through galactic cosmic radiation is a fairly stable process and the only reason for fast ion concentration fluctuation are the sink processes, like preexisting aerosols, cloud droplets, snow and ice crystals. The sampling location was at mountain slope and re-suspended snow and ice crystals occur event at sunny days, causing the fluctuations in air ion concentrations.

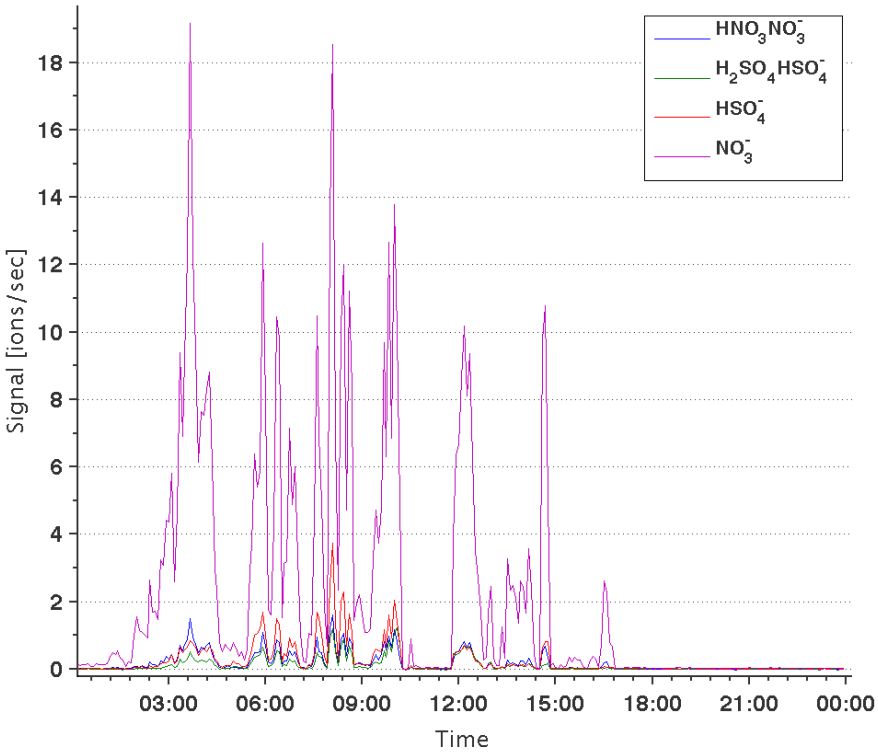

Figure 3. Concentration of air ions on 9th of February 2013 measured with APiTOF. Concentrations show very fast fluctuation that indicates a presence of a fast sink process.

High fluctuation is only visible in smallest ions, the ions measured with APiTOF, Fig3 and the lowest channels of NAIS, Fig 4. For larger ions the fluctuations were not observed.

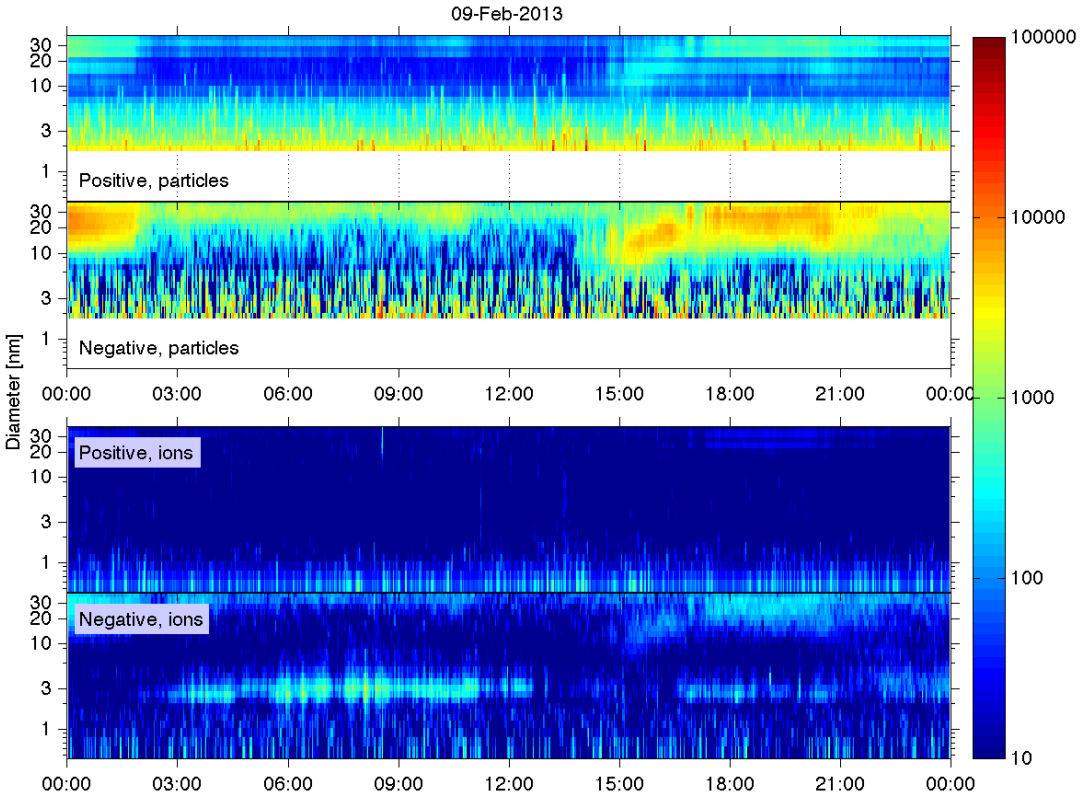

Figure 4. Neutral clusters and air ion spectrometer measurements on 9th of February. Top 2 panels are measurements of neutral particle size distribution which are charged by corona, the lower two panels are naturally charged air ion size distributions.

Outcome and future studies

We conducted successfully the measurements and obtained calibrated time series of concentrations for sulphuric acid at the high altitude station at Jungfaujoch. We had unpredicted problems with ion measurements with all ion instruments and results were only obtained only from the last part of the campaign.

During the 2-month period we had only 5 days during which the new particle formation did happen. Longer campaign is required to capture more events to gain a complete picture of the complex phenomenon.

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Annex

Key words: Mass spectrometry, APiTOF, nucleation, air ions

Collaborating partners/networks: PSI

Address: Department of Physics, University of Helsinki, P.O. Box 64, FI-00014, Helsinki, Finland

Contacts: Heikki Junninen, Tel.: +358 50 4156552, e-mail: Heikki.junninen@helsinki.fi