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Typical measurement sequence

The nucleation rates (J cm^{-3}s^{-1}) are measured under neutral (J_n), galactic cosmic ray (J_{gcr}) or charged pion beam (J_{ch}) conditions. For J_{gcr} a beam stopper blocks the pions and the chamber is irradiated by GCRs together with a small parasitic component of penetrating beam muons, whereas, for J_{ch}, the beam stopper is opened and the pion beam is normally set to a time-averaged rate of $(5-6)\cdot 10^4$ s^{-1}. Neutral nucleation rates are measured without any beam and with the high voltage (HV) of the clearing field electrodes set to $\pm$30 kV. Ion-induced nucleation is therefore completely excluded as a background to the measured neutral nucleation rates since, under these conditions, small ions are swept from the chamber in about one second. Both J_{gcr} and J_{ch} comprise the sum of ion-induced and neutral nucleation rates, whereas J_n measures the neutral rate alone.

The ion pair concentration is around 400 cm^{-3} for J_{gcr}, representative of the boundary layer, and around 3000 cm^{-3} for J_{ch}, corresponding to high latitudes and altitudes [1, 2]. Over the continental boundary layer at mid- and low-latitudes, ionisation from radon decay exceeds that from cosmic rays [3]. Radon decay does not contribute significantly over oceans or above the boundary layer. Radon decay is also absent from the CLOUD chamber since the air is prepared from cryogenic liquid nitrogen and oxygen.

Figure S2 shows a typical sequence of measurements of the nucleation rates, J_n, J_{gcr} and J_{ch}. The experimental conditions are first established (gas concentrations, temperature, etc.) and the chamber largely cleared of pre-existing aerosols so that the initial loss of freshly nucleated particles is well characterised and determined by the chamber walls. High voltage is applied to the clearing field electrodes to sweep ions from the chamber. The run is started by opening the shutter of the UV system at a selected aperture (Fig. S2a, 03:45 UTC), which rapidly establishes a chosen [H_2SO_4] in the chamber by photolytic oxidation of SO_2 in the presence of O_3 and H_2O (Fig. S2b).

Particles begin to appear in each aerosol counter after a time delay that depends on the particle growth rate and the detection size threshold (Fig. S2c). The nucleation rates are derived from the formation rates measured in the particle counters, dN/dt (i.e. the gradients of the curves in Fig. S2c), according to the procedure described in Methods. When the neutral nucleation rate, J_n, has been measured, the clearing field is turned off (04:33 UTC). This allows GCRs to generate ion pairs that remain in the chamber, as shown by the appearance of small ion clusters ($n H_2SO_4$, $n \leq 3$) in the Atmospheric Pressure Interface Time Of Flight (APi-TOF) mass spectrometer

(Fig. S2b). Larger cluster ions appear and build up at progressively later times, reaching a steady state distribution just as the particle counters show an acceleration of the counting rate. The ions give rise to a distinct increase in the nucleation rate, J_{gcr}, due to ion-induced nucleation at ground-level GCR intensity (Fig. S2c). In the next step, the CERN pion beam is turned on (04:58 UTC) and a further sharp increase is observed in the nucleation rate, corresponding to J_{ch}. At low NH_3 concentrations, the ion-induced nucleation exclusively involves negatively-charged clusters (an example nucleation event is shown in Fig. S4). Finally, the run is ended by closing the UV shutter, turning on the clearing field HV and starting to clear the chamber of aerosols in preparation for the next run (05:19 UTC).

Supplementary references

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[3] Zhang, K., *et al.* Radon activity in the lower troposphere and its impact on ionization rate: a global estimate using different radon emissions. Atmos. Chem. Phys. Discuss. **11**, 3251–3300 (2011).

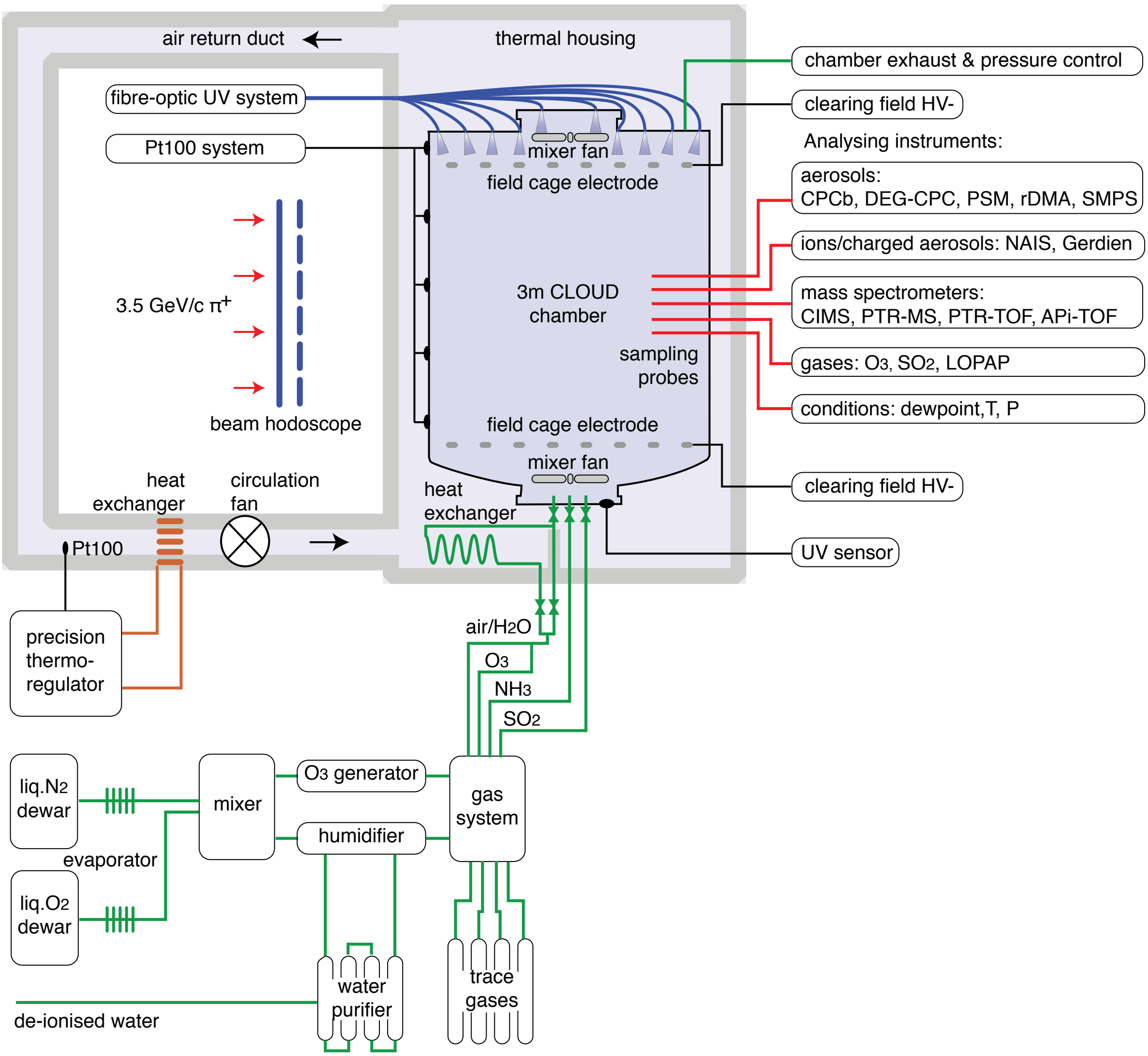

Fig. S 1. CLOUD schematic. Schematic diagram of the CLOUD experiment at the CERN Proton Synchrotron.

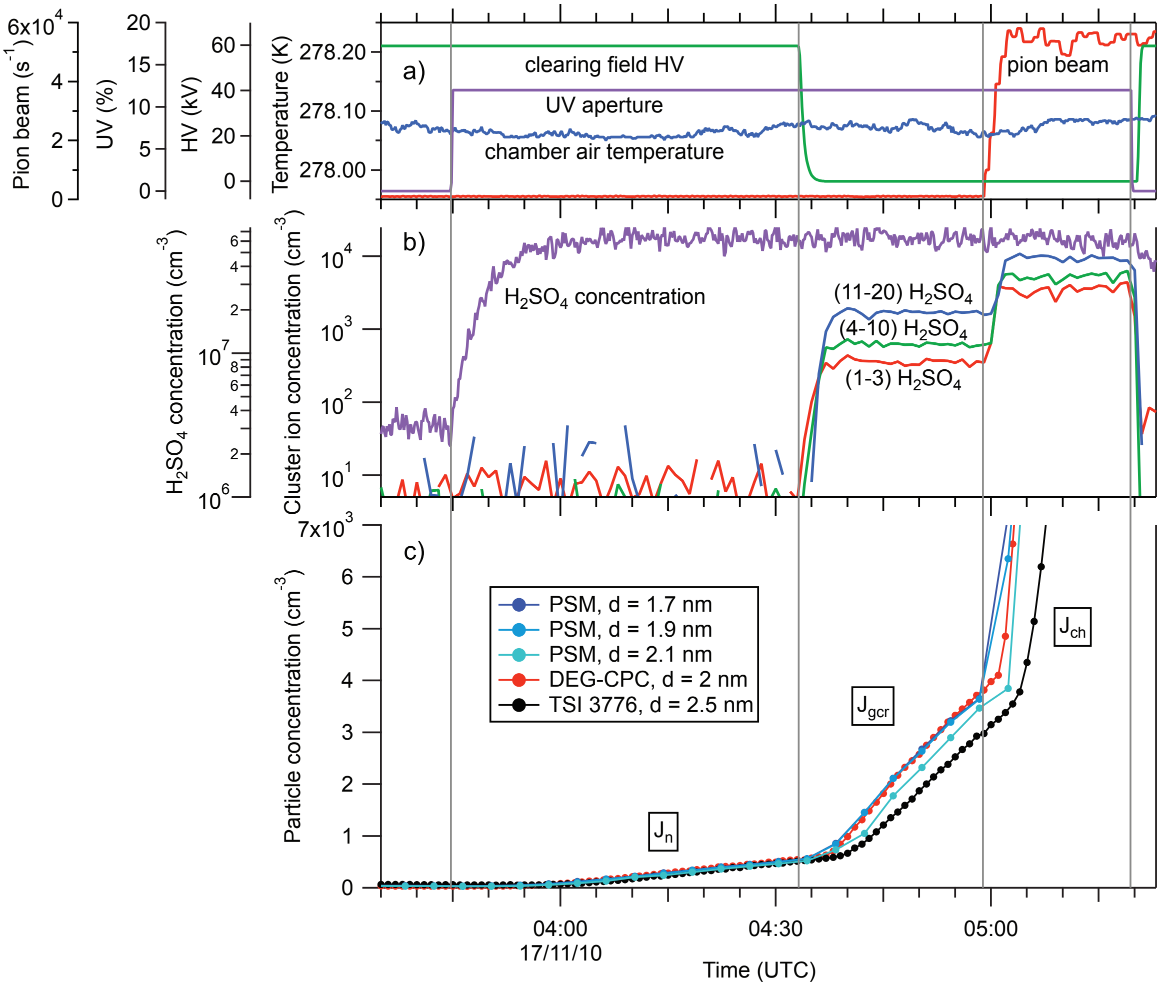

Fig. S 2. Typical measurement sequence. Example of a typical run sequence, as a function of Coordinated Universal Time (UTC), to measure a set of neutral, GCR and charged pion beam nucleation rates, J_n, J_{gcr} and J_{ch}, respectively: a) control parameters and chamber air temperature, b) [H_2SO_4] and cluster ion concentrations, and c) aerosol particle number concentrations. The run conditions are NH_3 = 200 pptv and RH = 38%. The production of ions from GCRs and then, at higher rate, from the pion beam causes sharp increases in the cluster ion concentrations (b) and particle formation rates (c). The onset times are progressively delayed according to the number of H_2SO_4 molecules in the cluster (b) or the 50% detection size threshold, d, of the particle counter (c).

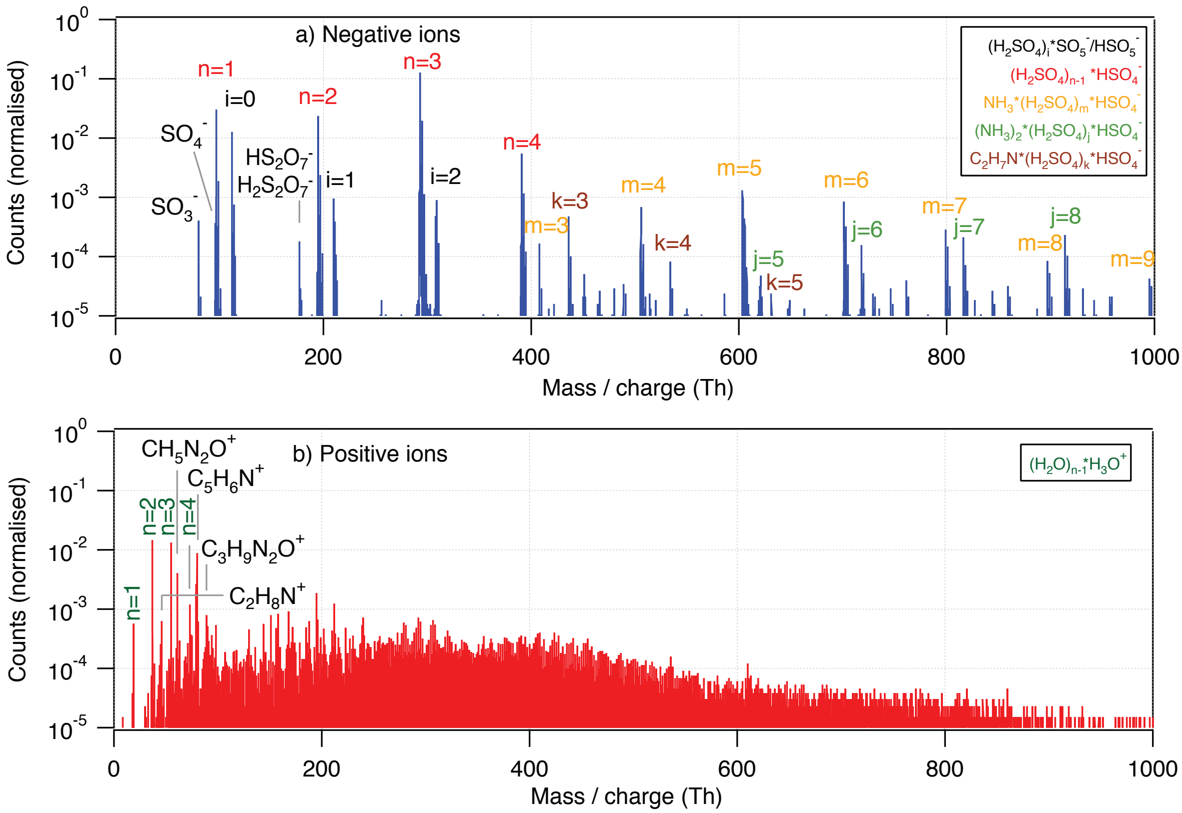

Fig. S 3. Cluster spectra examples. Examples of raw APi-TOF spectra at 292K: a) negative and b) positive ions. The run conditions are $[H_2SO_4] = 10^9$ cm^{-3}, NH_3 = 35 pptv, RH = 38%, and $J_{ch} \sim 10$ cm^{-3}s^{-1}.

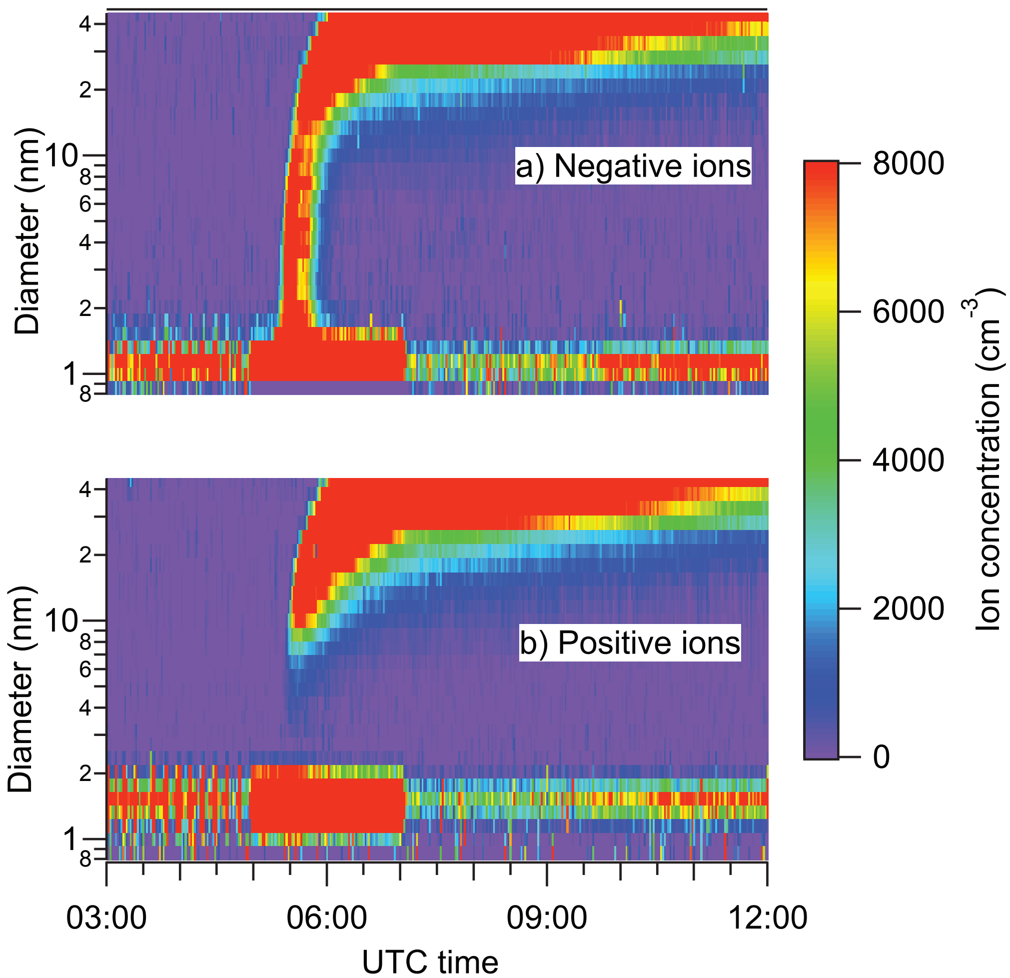

Fig. S 4. Nucleation event example. Example of a nucleation event (without additional NH_3) showing the growth versus time of a) negatively and b) positively charged particles, measured with the NAIS. The chronology is: 05h00 pion beam on, 05h15 UV on, and 07h00 pion beam and UV off (the nucleation of new particles is quenched by depletion of H_2SO_4 on the large aerosol population). Charged nucleation is observed only for negative particles; diffusion charging of both signs is observed for particles larger than about 10 nm.