Supporting information for:

Insight into acid-base nucleation experiments by comparison of the chemical composition of positive, negative and neutral clusters

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The supporting information contains 2 figures and 1 scheme on 9 pages.

The CLOUD chamber

The CLOUD chamber is a 3m-diameter stainless-steel cylinder of 26.1 m^3 volume. Pure air, free of condensable vapors, is obtained from the evaporation of cryogenic liquid nitrogen and liquid oxygen mixed at a ratio of 79:21. Water vapor is added from an ultrapure source to a controlled relative humidity. The chamber can be irradiated by UV light (250-400 nm) to create hydroxyl (OH) radicals by photolysis of ozone in the presence of water vapor.[41] The chamber can be exposed to a 3.5 GeV/c secondary pion beam from the CERN Proton Synchrotron, spanning the galactic cosmic ray intensity range from ground level to the stratosphere. Activating an electric field of 20 kV/m in the chamber sweeps away all the ions produced by cosmic rays, on request, and allows to perform experiments also under neutral conditions.

To avoid contamination from plastic materials (especially organic compounds), all gas pipes are made from stainless steel, and most gas and chamber seals are gold coated. Despite all these measures traces of contaminants, e.g. small volatile organic compounds (VOCs)[42] and NH_3[43], can still be observed. Even though dimethylamine (DMA) was initially absent in the thoroughly cleaned chamber (heated to 373 K), traces of DMA were detected once it had been injected, until the next thorough cleaning was performed (see discussion in the main text).[23]

The nucleation rates ($J_{1.7}$, cm^{-3} s^{-1}) were measured under neutral (J_n), galactic cosmic rays (J_{gcr}) and pion beam (J_π) conditions, corresponding to ion-pair concentrations of about 0, 400 and 3000 ion pairs cm^{-3}, respectively.

APi-TOF and CI-APi-TOF

The chemical composition of the ions was studied using the Atmospheric Pressure interface Time-of-Flight mass spectrometer (APi-TOF).[18,19,30] The instrument is divided in two parts. The first part is the atmospheric pressure interface that efficiently guides ions into the mass spectrometer. It consists of two quadrupoles and an ion lens system. It is equipped with a critical orifice that provides a sample flow of 0.8 l min^{-1}. The second part is the high transmission efficiency time-of-flight mass spectrometer that allows retrieval of mass-to-charge ratio of charged clusters smaller than ~2 nm diameter.

The APi-TOF mass spectrometers, manufactured by Tofwerk AG (Thun, Switzerland) and Aerodyne Research, Inc. (Billerica, MA, USA), have a resolving power close to 5000 (full width at half maximum FWHM at *m/z* >200) and a mass

accuracy better than 10 ppm. The data were analyzed using a Matlab based set of programs (tofTools) developed at the University of Helsinki.[18] When the APi-TOF is not coupled to an ion source, it measures the composition of airborne charged clusters. In the CLOUD chamber, ions are formed by galactic cosmic rays (GCR) or by the pion beam from the Proton Synchrotron. Varying the intensity of the beam thus changes the ion concentration inside the chamber. We can regard the combination of the CLOUD chamber and the APi-TOF as an oversized Chemical Ionization Mass Spectrometer (CIMS) where the CLOUD chamber acts as ion source. However it should be noted here that an important difference between the CLOUD chamber and a CIMS ion source is the extremely long ion reaction time and the poorly defined ion distribution in the chamber. During the experiments described here, two APi-TOF were operated in parallel: the first one in negative mode (APi-TOF(-)) and the other one in positive mode (APi-TOF(+)). This allowed the simultaneous characterization of the negative and positive ions during the nucleation experiments.

In CLOUD the primary positive and negative ions produced in the chamber are mainly N_2^+, O_2^+, N^+ and O^+, and O^- and O_2^-, respectively.[44] These ions undergo rapid ion-molecule reactions; the positive ions react quickly with water vapor to form protonated water clusters.[44] Then the charge is transferred to trace bases such as ammonia and amines that are present in the chamber as impurities. On a similar time scale, the small negative ions react quickly with nitric acid (HNO_3) and H_2SO_4 to form ions such as $(H_2O)_n(acid)_mNO_3^-$ (where acid represents HNO_3 and/or H_2SO_4).[22] The negative ions are dominated by compounds with a high gas-phase acidity, whereas in the positive case the main ions are formed from compounds with a high proton affinity. For example, under clean conditions (beginning of the campaign) pyridinium ($C_5H_6N^+$) was typically found as the main positive ion and nitrate (NO_3^-) as the negative ion.

Charged clusters can be formed by two different mechanisms. Either a precursor of the cluster is ionized and forms stable clusters after collision with other compounds present in the gas phase (ion-induced nucleation, IIN)[45, 46] or a neutral cluster receives a charge by diffusion charging. In the latter case the charge is transferred from another compound to the cluster after its (neutral) formation, e.g. by a proton transfer reaction or by clustering with an ion.

As already mentioned, the chemical composition of the ions was determined only for GCR and pion beam conditions, since the APi-TOF can only measure charged

clusters. However, recently, the APi-TOF was augmented by adding a chemical ionization source in front of it.[21,47] This instrument is called Chemical Ionization APi-TOF (CI-APi-TOF) mass spectrometer. It is able to detect neutral clusters after ionization by a chemical reaction.

The reagent ions used in this study for chemical ionization are $NO_3^-(HNO_3)_{0-2}$.[48] The ionization proceeds either via a proton transfer reaction (i.e., de-protonation of H_2SO_4 to HSO_4^-) or by cluster formation between the neutral compounds and the nitrate ions (Scheme S1):

Scheme S1. Reaction between the primary ion and the clusters in the CI unit.

$$NO_3^-(HNO_3)+(H_2SO_4)_n(C_2H_7N)_n \rightarrow 2HNO_3+(H_2SO_4)_{n-1}(C_2H_7N)_{n-1}HSO_4^-+C_2H_7N$$

$$NO_3^-(HNO_3)+(H_2SO_4)_n(C_2H_7N)_n \rightarrow (H_2SO_4)_n(C_2H_7N)_nNO_3^-+HNO_3$$

With this method, it was possible to identify for the first time in CLOUD the neutral clusters that were participating in the nucleation process.

It is important to note that the chemical composition of the clusters can change when they enter the APi-TOF or even before when they get ionized in the CI-region. At the moment, evaporation and fragmentation of clusters inside the APi-TOF mass spectrometer is not well characterized. For example, it is well known that clusters contain water in the atmosphere, however all the clusters that have been identified in these experiments do not. Water binds only weakly to the clusters in most cases, with evaporation rates of 10^5-10^6 s^{-1}.[16] Thus, the only reason to have it in clusters is the high collision frequency of water with the cluster due to the extremely high concentration of water in the atmosphere. When the cluster enters the APi-TOF the collision rate with water drops substantially and the water is lost from the clusters. Evaporation of sulfuric acid or bases might also occur as was inferred from a comparison of measured and modeled molecular cluster distributions.[32] For more details see the supplement information of Almeida et al. (2013) [ref. 16].

As already mentioned, under the condition of no collisional heating in the MS-inlet we expect water to evaporate but not the base molecules. However, if there is enough collisional heating, this may also happen and there is evidence that this happens for small clusters as observed from some measurements with the ion-mobility-

spectrometer-TOF-MS (IMS-TOF). However, our data base is still too small to draw firm conclusions and therefore these results will be subject of future papers.

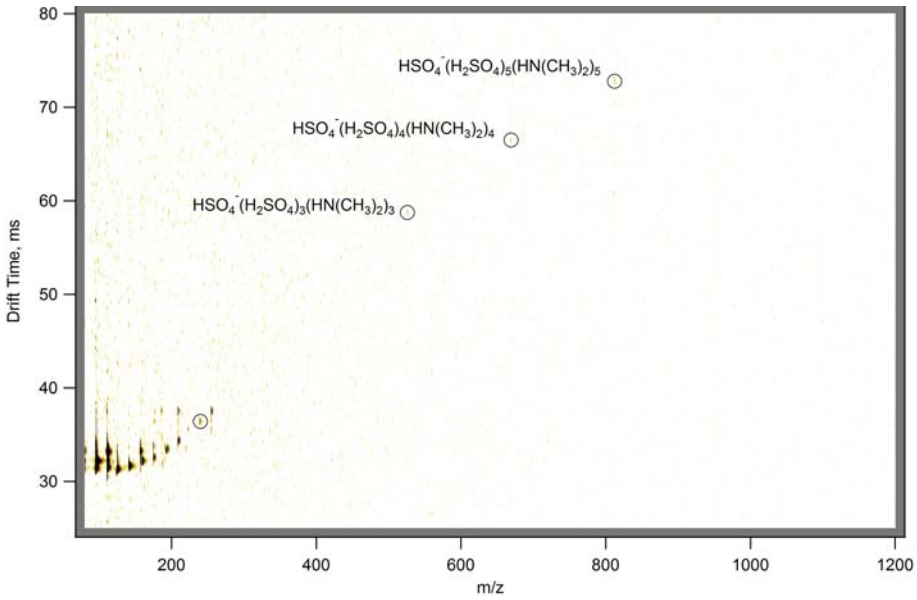

Figure S1. *2D plot of drift time vs mass-to-charge ratio of sulfuric acid-DMA clusters measured during the run 1047.01 with the IMS-TOF. The negative clusters containing 3, 4 and 5 molecules of sulfuric acid are the ones with the best signal-to-noise ratio in both dimensions. Sulfuric acid-DMA clusters are highlighted by open black circles.*

Results as presented in Figure S1 show the drift time and their mass spectrum of the clusters that are present in the CLOUD chamber during a nucleation experiment involving sulfuric acid and DMA (Run 1047.01). The strongest signals arise from small ions (black dots bottom left). These ions show that there are a lot of compounds with the same drift time but different mass, indicative of fragmentation inside the APi-TOF. However this plot also shows that bigger clusters are less prone to fragmentation since there are no other smaller clusters with the same drift time.

Quantum chemical calculations show that the clusters with an excess of sulfuric acid or bases (>2) are much less stable than the clusters we observed here mostly. Therefore, it is likely that these cases do not need to be considered as important.

When we compare the cluster time evolution the three different mass spectrometers do not consider water. These instruments have the same identical issue regarding the impossibility of measuring water in the clusters. However for the purpose of this comparison it is not crucial to see the water molecules in the clusters.

The second source of possible cluster fragmentation could be in the chemical ionization unit. This kind of fragmentation has already been observed during CLOUD experiments and it was discussed in a previous study.[16] The main reason of this fragmentation is that the stabilization of the clusters occurs via proton-transfers or –hydrogen bridges, and ionization adds/removes one of those. Quantum chemical calculations show that the clusters will always loose bases when they get charged negatively and they will loose sulfuric acid when they are charged positively.[31] As the clustering process is driven by acid base chemistry, the key is that for neutral clusters the optimum acid:base ratio is different to the one for positive or negative clusters (mainly because ions are acids or bases and there is some competition with sulfuric acid or ammonia/DMA). Just note that sulfuric acid, once it is deprotonated is a base and therefore if the cluster is small the DMA in excess will “leave” the cluster.

Excluding evaporation inside the mass spectrometer, the APiTOF measures the composition of the ions as they occur in the atmosphere or in the CLOUD chamber. Therefore, this loss of acids or bases due to ionization is not a measurement artifact, but the representation of what happens in the atmosphere when the ions are formed. It is an issue for the measurements of the neutral clusters by CI-APiTOF. Here, chemical ionization of the neutral clusters may change the composition. This is certainly true for small clusters while it is expected to be less severe for larger clusters. Moreover, the neutral clusters will have a certain acid:base ratio and clusters with an excess of base or acid will not be stable, only clusters with the optimum acid:base ratio and maybe +/- 2 acids or bases will be stable and persist much longer. Looking at quantum chemical results published in Almeida et al. (2013) extended data Figure 4 (reproduced as Fig. S2 below) [ref 16], the clusters with the highest concentration fall more or less into the diagonal. For example in the case of clusters with one DMA molecule only those with 1 and 2 sulfuric acid molecules have significant concentrations, the concentration of clusters with 3 SA is rather low, and the one with 4 SA clusters is below 0.01 cm^{-3}. So there is no need to consider the loss of more than 1-2 SA or ammonia/DMA "excess" molecules, because the clusters with more than that will not be stable and probably will have very short lifetimes and their concentration will be extremely low if they are formed at all.

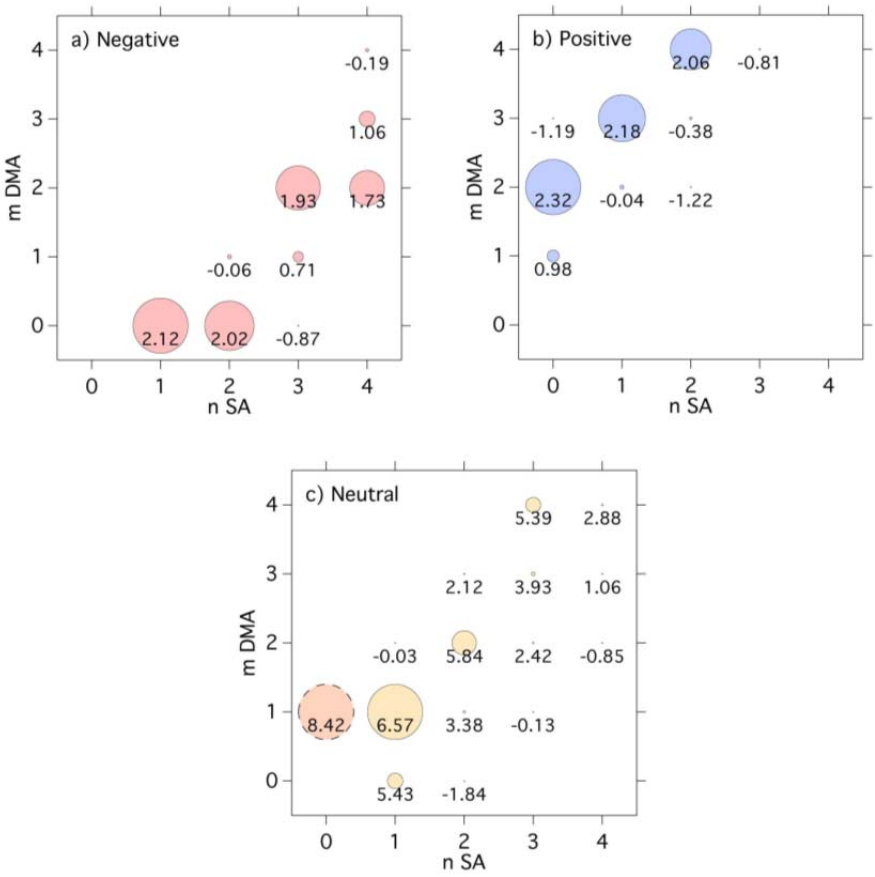

Figure S2. *Theoretical concentrations of negative, positive and neutral clusters during DMA ternary nucleation. Modelled steady-state concentrations (mDMA versus nSA) at* 4.0×10^{6} *cm*$^{-3}$ [H_2SO_4]*, 10 pptv DMA, 4 ion pairs cm*$^{-3}$ *s*$^{-1}$ *and 278 K.* ***a****, negative clusters.* ***b****, positive clusters.* ***c****, neutral clusters. A sticking probability of 0.5 is assumed for all neutral–neutral collisions and 1.0 for all charged–neutral collisions. The numbers below the center of each circle show* $\log_{10}C$*, where C (cm*$^{-3}$*) is the cluster concentration (the threshold is 0.01 cm*$^{-3}$*). The circle areas within each panel are proportional to C (with the exception of the DMA monomer in* ***c****). (Reproduced from Almeida et al., Nature, 2013)*[16]

Moreover, Fig. S2 also shows that the most favorable acid:base ratios are different for neutral, positive and negative clusters. The most abundant neutral clusters fall in the diagonal, the negative clusters are below the diagonal (less bases) and the positive ones above the diagonal (less acids).

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