Experimental studies of the formation of cluster ions formed by corona discharge in an atmosphere containing SO_2, NH_3, and H_2O

Preben Hvelplund[1], Jens Olaf Pepke Pedersen[2], Kristian Støchkel[1], Martin B. Enghoff[2], Theo Kurtén[3]

[1]Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK 8000 Aarhus C, Denmark.
[2]National Space Institute, Technical University of Denmark, Elektrovej, bldg.. 327, DK 2800 Kgs. Lyngby, Denmark
[3]Department of Chemistry, University of Helsinki, P.O. Box 55, FI 00014 Finland,
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Presenting author email: jopp@space.dtu.dk

We report on studies of ion induced nucleation in a corona discharge taking place in an atmosphere containing SO_2, NH_3, and H_2O at standard temperature and pressure. Positive ions such as $H_3O^+(H_2O)_n$, $NH_4^+(H_2O)_n$, and $H^+(H_2SO_4)(H_2O)_n$ and negative ions such as $HSO_5^-(H_2O)_n$, $SO_4^-(H_2O)_n$, $HSO_4^-(H_2O)_n$ and $NO_3^-(H_2O)_n$ have been recorded. Large values of n (> 100) were observed and the experiment indicates the existence of even larger water clusters. In contrast, only clusters with a maximum of 2 sulfuric acid molecules were observed. Fragmentation studies also revealed that the negative ion HSO_5^-, which has been observed in many studies, in our experiments is contaminated by $O_2^-(HNO_3)(H_2O)$ ions, and this may also have been the case in other experiments. Finally an ion with *m/z* = 232 (where *m* is the cluster mass in amu and *z* the charge state), capable of attaching H_2O-molecules was observed and studied by fragmentation.

Experiments

The ions are formed by corona discharge in the laboratory atmosphere, where gases such as SO_2, NH_3, and H_2O could be added to the discharge region. The corona ionizer discharge needle is placed inside a flow reactor, which is attached to the inlet capillary that interface the discharge region to the mass spectrometer. The flow reactor was kept at room temperature and the gas pressure was around 1 atm. The discharge gas was introduced to the flow reactor by flowing synthetic air.

The corona voltage was held between 2 and 3 kV, the tube lens potential was 60 V and the heated capillary temperature was normally held at room temperature. Measurements were done with both positive and negative voltages applied to the discharge needle (relative to the capillary inlet) in order to extract both positive and negative ions. The ions were accelerated by an electrostatic potential of 50 kV. The precursor ions were mass selected with a bending magnet and passed through a 3-cm long gas cell with entrance and exit apertures of 1 and 3 mm diameter containing neon as target gas. The product ions exiting the cell were analyzed according to their *m/z*-value, by scanning the voltage of the electrostatic hemispherical analyzer and fragmentation spectra were obtained in so called mass-analyzed ion kinetic energy spectra (MIKE) spectra.

Mass spectra showing the distribution of ions produced in the ion source were obtained by scanning the magnet with no target gas in the target cell and using a fixed analyzer voltage that was related to the acceleration voltage.

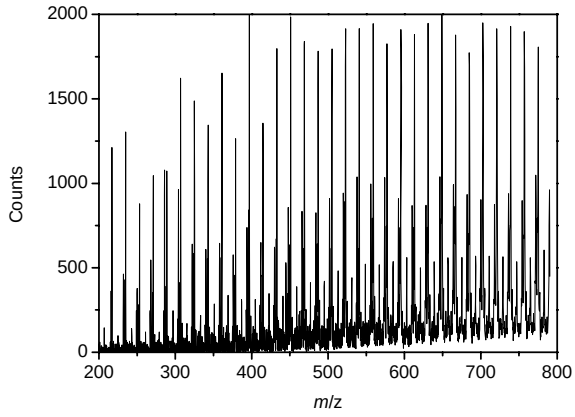

Figure 1. Positive ion *m/z* spectrum.

Figure 1 shows an example of the observed distributions. The largest peaks (around 2000 counts) can be identified as $H_3O^+(H_2O)_n$, with n going from 1 to 38. The largest observed clusters with n=38 is not an upper limit for the cluster size but corresponds to the *m/z*-value, where the scans were stopped, and it is likely that even larger clusters exist at our experimental conditions. The series with peaks at one mass unit less than the previous series (around 1000 counts) can be identified as $NH_4^+(H_2O)_n$. The series with intensities around 500 counts relates to $H^+(H_2SO_4)(H_2O)_n$.

For the negative ions we also observe the existence of clusters with a very large number of water molecules (n>100) and our results also indicate that only experimental limitations constrain us from observing even larger clusters. The large clusters are built around a single core ion containing sulfur or NO_3.

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