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On the formation of water-containing negatively charged clusters from atmospheric pressure corona discharge in air

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ABSTRACT

In this work we have studied the occurrence of negatively charged clusters in a corona discharge in atmospheric air at standard temperature and pressure. The discharge was operated in the point-to-plane configuration with a needle voltage of −1.2 kV and an electrode gap around 5 mm. The ions formed were accelerated and mass analyzed at an energy of 50 keV. The mass spectra are dominated by hydrated ions such as $O_2^-(H_2O)_n$ and $CO_3^-(H_2O)_n$ in contrast to our earlier studies at lower electrode voltages where mixed clusters such as NO_3^- $(HNO_3)_m(H_2O)_n$ were dominant. In this study we only recorded masses corresponding up to 200 attached water molecules and found that for large n the peaks in the mass spectrum corresponding to $O_2^-(H_2O)_n$ become dominating. We also demonstrate how collision induced dissociation (CID) coupled to charge reversal experiments –CR$^+$ can provide lucid information about cluster composition.

1. Introduction

As demonstrated by Yu and Turco [1,2] and Svensmark et al. [3–5] ion mediated nucleation is an important aerosol formation mechanism and hence may influence cloud formation in the Earth's atmosphere. The tropospheric ion mediated aerosols are a result of ionizing radiation caused by galactic cosmic rays but since (to quote Svensmark et al. [3]) "the role of ions in the production of aerosols is among the least understood, but potentially is an important process in the Earth's atmosphere", ion mediated nucleation studies are of great importance for future climate models. However the role of galactic cosmic rays in aerosol formation in the Earth's atmosphere is still under discussion, see, e.g., Kulmala et al. [6] and Sloan and Wolfendale [7].

A corona discharge ion source coupled to a mass spectrometer has become a standard way to obtain information on production of both positive and negative ions in ambient air or controlled atmospheres [8–16]. Sekimoto and Takayama [12] have studied ion formation as a function of needle voltage from −1.9 to −3.5 kV. They found that at the lowest voltage the mass spectrum was dominated by water cluster ions such as $OH^-(H_2O)_n$ with $n \leq 42$ and at the highest voltage the spectrum was dominated by $NO_3^-(H_2O)_n$ ions. The negative ion evolution was studied as a function of reaction time by Nagato et al. [11] who concluded that the terminal ions NO_3^- and $NO_3^-(HNO_3)$ dominate the spectrum after a reaction time of 10 ms. We have recently studied formation and collision induced dissociation (CID) of mixed clusters $NO_3^-(HNO_3)_m(H_2O)_n$ with $m = 0–3$ and $n = 0–300$ [14]. It was found that the shape of the corona needle plays an important role for the yield of hydrated ions. When a STM needle with a tip radius of around 20 nm was used together with relative high corona voltage, the largest clusters were observed. Water evaporation from $H^+(H_2O)_n$ and $X^-(H_2O)_n$ where X is a small core ion and $n = 5–300$ was studied by Sundén et al. [16]. Loss of water molecules during a free flight of the clusters provided information about size dependent heat capacities of the clusters. Measurements of formation of negative ions produced by corona discharge have recently been conducted in ambient air by Skalny et al. [15]. They found that most ions were in the form of hydrated ions such as $O_2^-H_2O)_n$, $CO_3^-(H_2O)_n$, $O_3^-(H_2O)_n$, $NO_3^-(H_2O)_n$ and $HCO_3^-(H_2O)_n$, with $n \leq 7$ and they discuss how the electrode distance influences the mass spectra.

Skalny et al. [15] also provide an instructive description of the ion molecule reactions governing the cluster formation in the atmospheric pressure discharge region. They argue that the primary ions O^- and O_2^- are formed by dissociative electron attachment and three body electron attachment

$$e^- + O_2 \rightarrow O^- + O \quad (1)$$

and

$$e^- + O_2 + M \rightarrow O_2^- + M \quad (2)$$

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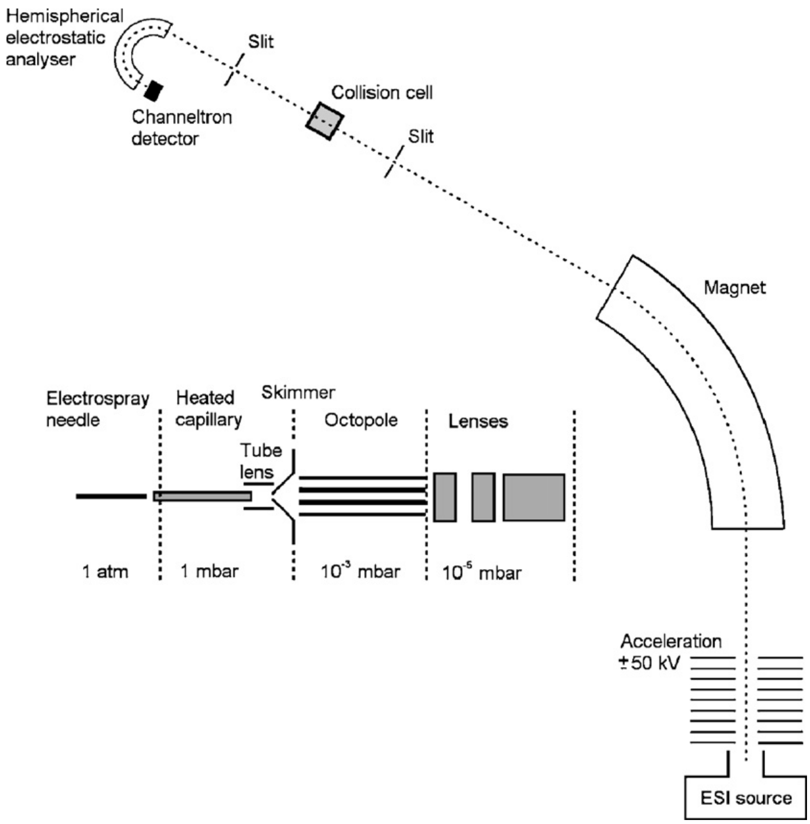

Fig. 1. The experimental setup. Clusters are produced in a point to plane corona discharge in ambient air. The insert shows a schematic diagram of the corona discharge source.

The $CO_3{}^-$ ion and its hydrated cluster ions are then formed in the ion molecule reactions

$$O^- + CO_2 + M \rightarrow CO_3{}^- + M \tag{3}$$

and

$$CO_3{}^-(H_2O)_{n-1} + (H_2O) + M \rightarrow CO_3{}^-(H_2O)_n + M \tag{4}$$

for $n \geq 1$

The hydrated $O_2{}^-$ clusters are growing as a result of interactions between hydrated $O_2{}^-$ and water molecules

$$O_2{}^-(H_2O)_{n-1} + (H_2O) + M \rightarrow O_2{}^-(H_2O)_n + M \tag{5}$$

for $n \geq 1$

Skalny et al. also argue that $CO_3{}^-$ and $O_2{}^-$ and their hydrated cluster ions are lost in the processes

$$CO_3{}^-(H_2O)_n + NO_2 \rightarrow NO_3{}^-(H_2O)_n + CO_2 \tag{6}$$

and

$$O_2{}^-(H_2O)_n + NO_2 \rightarrow NO_2{}^-(H_2O)_{n-1} + O_2 + H_2O \tag{7}$$

These processes are responsible for decrease of $O_2{}^-(H_2O)_n$ and $CO_3{}^-(H_2O)_n$ ions at large electrode distances.

In the present study we report on hydrated ion formation in a negative corona discharge in the point-to-plane configuration in ambient air with a relative humidity around 40%. The electrode distance was around 5 mm and the corona voltage was 1.0–1.2 kV. Under these experimental conditions the spectra were dominated by ions such as $O_2{}^-(H_2O)_n$ and $CO_3{}^-(H_2O)_n$. We terminated the mass scan at $n = 200$ but have shown earlier that we can add many more water molecules to negative and positive core ions. The transmission through the mass spectrometer is, however, reduced for larger clusters because of collisions with residual gas. We also demonstrate how MS–MS (mass spectrometry–mass spectrometry) experiments can give precise information on cluster composition.

2. Experimental

The experimental arrangement is described in detail by Boltalina et al. [17] and shown schematically in Fig. 1. The ions were in the present experiment formed by corona discharge in ambient air. The corona ionizer consists of a discharge needle and a capillary normally used as the interface in our electrospray ion source. The temperature of the capillary can be varied between room temperature and 200 °C. The distance between the needle tip and the entrance end of the capillary was 5 mm. The capillary is made from stainless steel and is 10 cm long with an inner diameter of 0.4 mm. The pressure varies through the capillary from atmospheric pressure at the entrance to around 1 mbar at the exit end. The time it takes the ions to pass the capillary is estimated to be around 1.5 ms. The discharge needle was a special homemade scanning tunnel microscopy (STM) tungsten needle. It is 3 mm long with a diameter of 0.3 mm. The radius of curvature of the tip is measured to be around 20 nm. The corona voltage was between 1.0 and 1.2 kV, the tube lens potential was 60 V and the capillary temperature was varied from 30 to 55 °C. The ions were in the mass spectrometer accelerated by an electrostatic potential of 50 kV. The precursor ions were mass selected with a bending magnet and could be passed through a 3-cm long gas cell with entrance and exit apertures of 1 and 3 mm in diameter containing dioxygen as target gas. The O_2 target gas pressure (around 10^{-3} mbar) was monitored by a cold cathode gauge and the background pressure (around 3×10^{-6} mbar) was measured by an ionization gauge. The product ions exiting the cell were analyzed according to their m/q through scanning the voltage of the electrostatic hemispherical analyzer and fragmentation spectra were obtained. Mass spectra

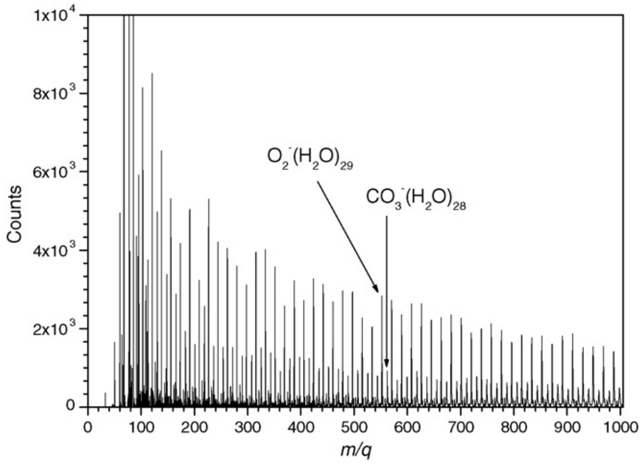

Fig. 2. Negative ion mass spectrum where the corona discharge took place in ambient air at a needle voltage of −1.2 kV.

Table 1
Observed ions with m/q values smaller than 101. The question marks indicate uncertain assignment of ions to the specific m/q value.

amu	Ion
32	O_2^-
45	HCO_2^-
46	NO_2^-
48	O_3^-
50	$O_2^-(H_2O)$
59	$HCNO_2^-$?
60	CO_3^-
61	HCO_3^-
62	NO_3^-
63	HNO_3^-?
64	$NO_2^-(H_2O)$
66	O_3^- (H_2O)
68	$O_2^-(H_2O)_2$
70	O^- $(H_2O)_3$
75	Not assigned
76	$O_2^-(CO_2)$
77	HCO_4^-
78	$CO_3^-(H_2O)$
79	$HCO_3^-(H_2O)$
80	$NO_3^-(H_2O)$
81	$HNO_3^-(H_2O)$?
82	$NO_2^-(H_2O)_2$
84	O_3^- $(H_2O)_2$
86	$O_2^-(H_2O)_3$
87	Not assigned
88	$CO_3^-(N_2)$
89	Not assigned
92	$NO_2^-(H_2O)(N_2)$
93	Not assigned
94	$O_3^-(H_2O)(N_2)$
95	$HCO_4^-(H_2O)$
96	$CO_3^-(H_2O)_3$
97	$HCO_3^-(H_2O)_2$
98	$NO_3^-(H_2O)_2$
99	Not assigned
100	$NO_2^-(H_2O)_3$

showing the distribution of ions produced in the ion source (magnet scans) were obtained by scanning the magnet with no target gas in the target cell and a fixed analyzer voltage related to the acceleration voltage.

3. Experimental results and discussion

A mass spectrum obtained at a corona voltage of 1.2 kV is shown in Fig. 2. It is dominated by ions such as $O_2^-(H_2O)_n$, and $CO_3^-(H_2O)_n$. In Fig. 3 the same spectrum is shown for m/z values between 20 and 100. The most abundant ions in this mass region are also $O_2^-(H_2O)_n$, and $CO_3^-(H_2O)_n$ and it should be noted that also the core ions for these two series are observed albeit at very low intensity for O_2^-. Several peaks are observed in Fig. 3 and their m/q values are all listed in Table 1 together with the most likely molecular assignment.

In principle all the recorded peaks in the mass spectrum can be identified through tandem mass spectrometry applying CID in either the direct or in the charge reversal mode. Examples of the strength of tandem mass spectrometry in the identification of peaks at a specific m/q value are shown in Figs. 4 and 5. Here primary ions believed to be of the forms $O_2^-(H_2O)_n$ and $CO_3^-(H_2O)_n$ are collided with O_2 gas and both spectra with positive and negative fragment ions are recorded in separate experiments. All fragment ion peaks can be assigned to ions likely to originate from the expected parent ion. For cluster ions expected to contain water, loss of 18 or 36 mass units are observed and when the presumed core ion CO_3^- is subjected to fragmentation only ions containing O and C are observed giving rise to an unambiguous identification of the parent ion.

As can be seen from Fig. 6 which displays the spectrum between 100 and 200 amu also core ions besides O_2^- and CO_3^- form hydrated clusters, but the spectrum is still dominated by hydrated ions with O_2^- and CO_3^- as core ions. This pattern continues on Fig. 7 where ions with more than 50 water molecules are recorded. The total spectrum peaks at clusters containing only a few water molecules but as shown earlier [16] and repeated in this investigation this distribution is influenced strongly by the capillary temperature in the way that higher temperature results in a maximum at a lower cluster size. In Fig. 8, a mass spectrum is shown recorded with a capillary temperature of 30 °C. The dominating peaks are again associated with ions such as O_2^- $(H_2O)_n$ but the

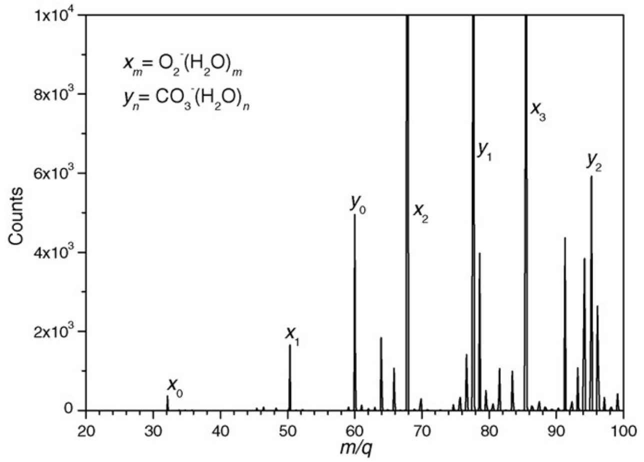

Fig. 3. As Fig. 2 for a mass to charge ratio between 20 and 100 (amu/charge state).

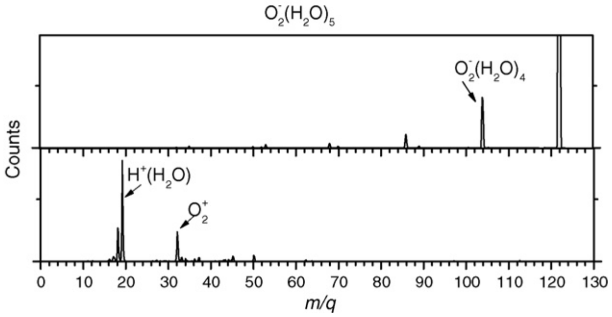

Fig. 4. MIKE spectra obtained after collisions between $O_2^-(H_2O)_5$ and O_2. (a) A fragment spectrum of negative ions and (b) one of positive ions.

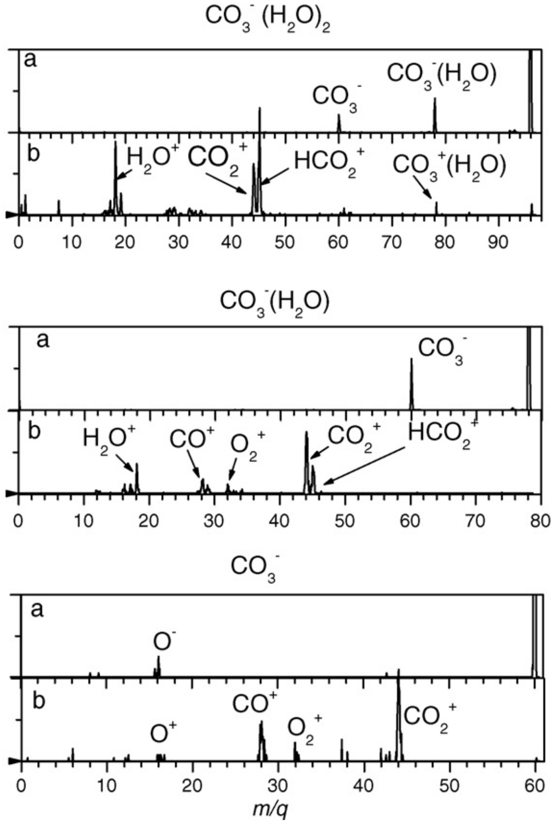

Fig. 5. As Fig. 4 but for the projectile ions $CO_3^-(H_2O)_n$ ($n = 0, 1, 2$).

observed variation in measured peak heights most likely reflects variations in beam intensity during the magnet scan. The measured cluster distribution is also influenced by collisions with residual gas particles and by metastable decay of the cluster ions. The reduction due to these two processes of the $n = 55$ peak amounts to 45% and for $n = 200$ the reduction amounts to 80%. These estimates are based on measurements of total destruction cross sections in atmospheric air and on the assumption that the cross section scales with $n^{2/3}$ (volume scales with n). The evaporation rates due to metastable decay have earlier been measured for water clusters and the reduction of the primary beam due to evaporation alone amounts to 10% and 40% for $n = 55$ and $n = 200$, respectively.

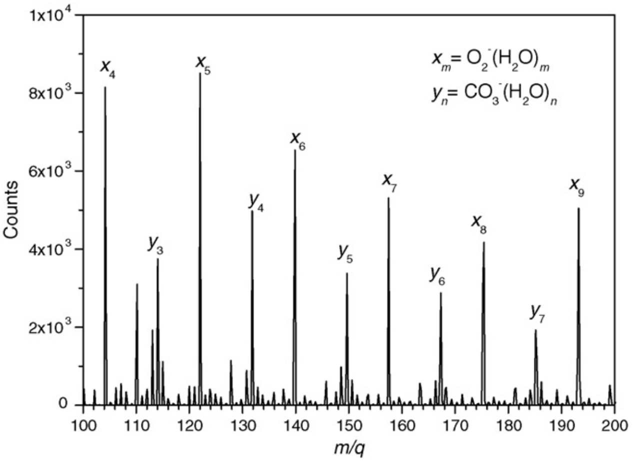

Fig. 6. As Fig. 2 for masses over charge between 100 and 200 (amu/charge state).

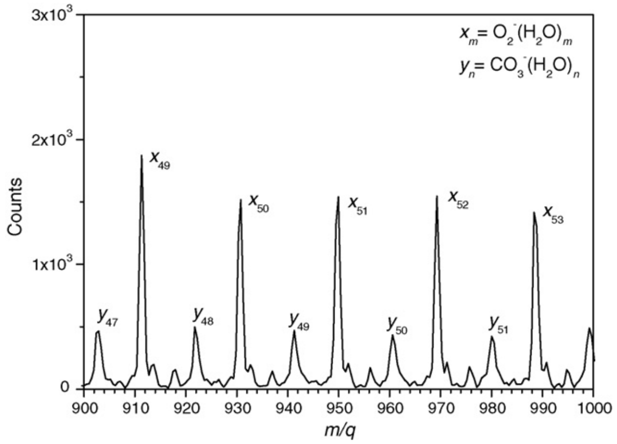

Fig. 7. As Fig. 2 for masses over charge between 900 and 1000 (amu/charge state).

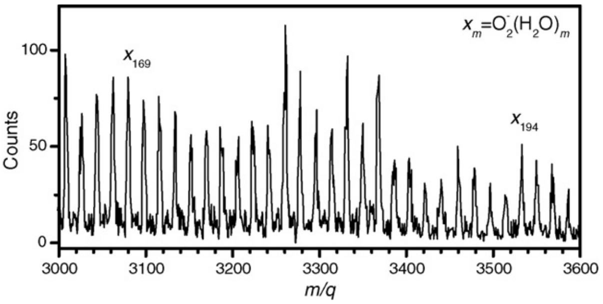

Fig. 8. As Fig. 2 for masses over charge between 3000 and 3600 (amu/charge state).

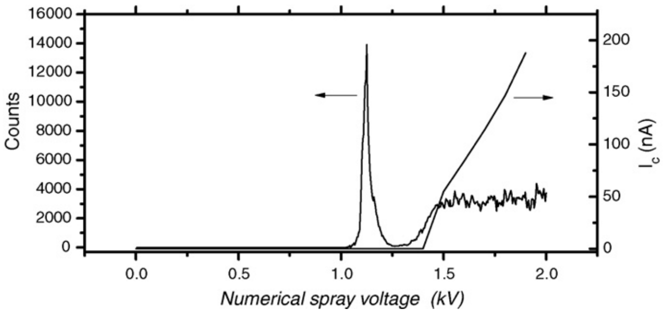

Fig. 9. Corona current and beam intensity for $O_2^-(H_2O)_{10}$ as a function of spray voltage.

In Fig. 9 the count rate of $O_2^-(H_2O)_{10}$ ions is plotted as a function of corona voltage. Also shown is the measured corona current. The count rate peaks around −1.1 kV and is minimum around −1.25 kV before it increases to a steady level at lower corona voltages. The maximum count rate is obtained while the corona current is below 0.01 nA whereas the steady level is obtained in the corona voltage range where the current is increasing to 200 nA. The observed intensity variation with corona voltage can be explained as a result of a competition between formation and destruction of the $O_2^-(H_2O)_{10}$ ions. At around −1 kV formation via reaction (2) starts and then around −1.25 kV reaction (7) leads to a reduction of the signal before formation again increases for even lower corona voltages (larger current).

4. Conclusions

Hydrated ions of O_2^- and CO_3^- with up to 200 water molecules attached have been identified by mass spectrometry. The ions were produced in a corona discharge in ambient laboratory air with a measured relative humidity around 40%. The large water-containing charged clusters are observed at a corona current below

0.01 nA. It is most likely that even larger clusters are produced but for experimental reasons these could not be registered in the present experiment. It is likely that these cluster ions can act as a start for aerosol formation if the cluster growth takes place in the Earth's atmosphere. Quantitative studies of these complex ion molecule reactions in general and the interaction of the cluster ions with water molecules in particular, are of great importance for modeling of ion mediated cloud formation. Compared to neutral clusters, charged clusters have higher growth rates and lower evaporation rates as a result of interaction between ions and polar vapor molecules [1]. Thus charged clusters have an advantage over neutral clusters when it comes to growth rates. We have earlier shown that corona discharge can lead to the formation of mixed clusters as $NO_3^-(HNO_3)_m(H_2O)_n$ when larger corona voltages are applied and work will continue in this laboratory by studies of cluster ion formation in controlled atmospheres.

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