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MASS SPECTROMETRY OF NEGATIVE IONS FORMED IN A DC CORONA DISCHARGE FED BYA MIXTURE OF O_2 AND N_2

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Corona discharges fed by air are widely used in various types of ionizers, air cleaners, etc. because negative ions have been reported to reduce the levels of airborne microbes, odours and VOCs harmful to human health in indoor air. However the mechanisms of such effects are not yet established [1], [2]. There are several published papers discussing the ions produced in a negative corona discharge fed by air or mixture of nitrogen and oxygen [3], [4], [5]. The authors are more or less united in interpretation of the spectra but there are few masses remaining either unexplained or their interpretation is different in various papers. One of these is the ion with mass to charge ratio of 125 amu. Some authors suggest that it is the water cluster $OH^-(H_2O)_6$ but in our previous paper [6] exploring the ions produced in corona fed by air we suggested that ions with mass of 125 should be NO_3^-• (HNO_3). As the air contained quite high amount of water vapour it was interesting to minimize the influence of water on the processes active in the discharge gap. We have therefore performed another experiment with a mixture of nitrogen and oxygen instead of air. This experiment should reveal the differences in ion mass spectra between corona fed by ambient air and mixture of high purity nitrogen and oxygen.

The experimental apparatus used in these experiments was built in cooperation with Hiden Analytical. A simple point to plane corona discharge was formed by placing a pointed stainless steel needle in close proximity (6 mm) to the wall of a vacuum chamber (the wall acting as a planar electrode). A small orifice (diameter of 0.1 mm) in the wall of the vacuum chamber allowed the products of the discharge to enter a Hiden Molecular Beam Quadrupole MSHPR60. The discharge region was surrounded by a brass chamber forming a volume of approximately 300 cm^3 into which the feed gas for the discharge could be injected. Experiments were performed using the mixture of oxygen (20%) and nitrogen (80%) at atmospheric pressure and ambient temperature of 20 °C. The point electrode was powered by a Glassman HV power supply. The voltage was measured by Fluke HV probe combined with a digital multi-meter. The discharge current was measured using a microampmeter.

The main result of the experiment is the spectrum of negative ions produced in the discharge gap. In comparison with positive corona discharge the spectrum of ions generated by negative corona is much richer in ion types. With an abundance of approximately 45% the most abundant ion was O_3^- and the second most abundant ion was NO_3^-. In an earlier paper [6] we studied the composition of ions formed in negative corona fed by ambient air. We have found the ions were almost exclusively in the form of water clusters containing different numbers of water molecules (even 6 or more) with some of the most highly abundant ions being based on the presence of carbon dioxide in the discharge gap (CO_3^-•$(H_2O)_n$ and HCO_3^-•$(H_2O)_n$). The ions from the present experiment with measured abundances higher than 1% are shown in the Table 1. Apart from the cluster O_3^-•(H_2O) no other ion was found to be in the water cluster form. On the other hand the concentration of water (although less than 45 ppm) was found to be sufficient for formation of considerable amount of HNO_2 and HNO_3. Therefore the abundances of ions NO_x^-•(HNO_y) where x = 2,3; y = 2,3 were higher than 1% as well. The abundance of ions with mass 125 amu was still significant even though the abundances of water clusters OH^-•$(H_2O)_n$ where $1 \leq n < 6$ were below the apparatus sensitivity level. As the generation of cluster OH^-•$(H_2O)_n$ is via a chain of reactions

OH^-•$(H_2O)_n + H_2O + M \rightarrow OH^-$•$(H_2O)_{n+1} + M$

the high abundance of 125 amu ion and low abundance of smaller OH^-•$(H_2O)_n$ clusters suggest that detected signal at 125 amu corresponds not only to OH^-•$(H_2O)_6$ but to NO_3^-•(HNO_3) as well. According to [4] there are two channels of elementary reactions contributing to generation of NO_3^-•(HNO_3) cluster. These channels are dependent on ions O^-, O_2^-, O_3^-, NO_2^- and NO_3^-. The approximate abundances of these ions are shown in the Table l. The presence of CO_3^- can be caused by the residual carbon dioxide in the nitrogen and oxygen cylinder or more probably by possible backstream of air into the reaction chamber through the exhaust. In such case it is possible to suggest that abundances of ions containing hydrogen would be even lower in pure nitrogen and oxygen mixture.

Tab. 1. Abundances of ions in the spectra and ions contributing to generation of NO_3^-•(HNO_3).

Ion	Abundance [%]	Ion	Abundance [%]
O^-	< 1	NO_3^-	≈ 33
O_2^-	≈ 0.6	O_3^-•(H_2O)	≈ 1.2
NO_2^-	≈ 6.5	NO_2^-•(HNO_2)	≈ 1.2
O_3^-	≈ 45	NO_2•$^-(HNO_2)$/NO^-•(HNO_2)	≈ 2
CO_3^-	≈ 1.5	NO_3^-•(HNO_3)	≈ 4

In the end it is possible to say that the lack of carbon dioxide and significant decrease of water vapour in the discharge gap changes the composition of negative ions dramatically. Almost no ions are in the form of water clusters. Due to relatively high abundances of key ions contributing to NO_3^-•(HNO_3) generation and negligible abundances of OH^-•$(H_2O)_n$ clusters ($1 < n < 6$) needed for generation of OH^-•$(H_2O)_6$ it is possible to say that the contribution of water cluster to the signal for mass 125 amu is negligible in comparison with the contribution of NO_3^-•(HNO_3) cluster.

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