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Mass spectrometric analysis of small negative ions ($e/m < 100$) produced by Trichel pulse negative corona discharge fed by ozonised air

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Mass spectrometric analysis of small negative ions ($e/m < 100$) produced by DC negative corona discharge in ozonised wet air both in flow and flow-stopped regimes was conducted at pressure of 30 kPa. The point-to-plane electrode system has been used. The yield of individual ions is strongly affected by trace concentrations of ozone in both regimes. Ozone concentration greater than 25 ppm is sufficient to completely suppress the appearance of O_2^- and a NO_2^- ion as well as their clusters in the mass spectra. The temporal increase in concentration of NO_3^- ions and $NO_3^-(H_2O)_n$ ($n = 1, 2$) hydrated clusters was observed in flow-stopped regime accompanied by reduction in yield of CO_3^- ion and its water clusters $CO_3^-(H_2O)_n$ ($n = 1, 2$), which otherwise are the dominant ions in flowing wet air free of ozone. In contrast the addition of ozone into the flow of wet air resulted in evident increase in abundance of the clusters $CO_3^-(H_2O)_n$ ($n = 1, 2$). This is an evidence of an active role of nitrous oxide produced in flow-stopped regime in sufficient amount. The measured electrical conductivity of drift region confirmed the role of additional dissociative attachment of electrons by ozone molecules as well as a formation of clusters of lower mobility with increasing ozone concentration in the discharge gap.

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Keywords: Corona discharge, Ozone, Mass spectrometry, Mobility, Conductivity, Trichel pulse

1. Introduction

The high sensitivity of negative corona discharge current to the presence of traces of strongly electronegative molecules in discharge gap is well known phenomena. Ozone is an example of such chemical species [1]. The additional dissociative attachment of free electrons by ozone molecules causes the decrease in average mobility of charged particles in the drift region of the discharge gap and consequently accompanied by the decrease of the total discharge current at constant voltage applied on electrodes. The mass spectrometric identification of negatively charged ions extracted from the drift region of the negative corona discharge is an efficient method for the analysis of processes affecting the mentioned effect of the current decrease. The knowledge of the ion composition can contribute towards an understanding of the role of negative ions in devices using corona discharges for example; electrostatic precipitators air cleaners, ionisers and the devices used for corona treatment of polymer surfaces.

Most of mass spectrometric studies of corona discharges have been conducted in air over a wide pressure range (0.2-100 kPa) and with different relative humidity of air [2-21]. A variety of negative ion species have been identified. Including among these are O^- , O_2^- , O_3^- , CO_3^- , CO_4^- , HCO_3^- , NO_2^- , NO_3^- and their clusters with almost H_2O and HNO_3 . There are the great differences in relative abundance of individual detected ions in different

experiments. The relative yield of individual ions is dramatically affected by conditions in experiment especially by air pressure and humidity, flow rate and direction of the flow, volume of discharge reactor and the presence of electronegative impurities in air as example, ozone, carbon dioxide, nitrogen oxides and water.

The pioneering work of Shahin conducted over a wide-pressure range (up to 100 kPa) found NO_2^- and NO_3^- ions were dominant in negative corona discharge fed by dry air at low pressures [2]. These results were subsequently contradicted by of Gardiner and Craggs [3] who at 1 kPa observed predominately CO_3^- ions, whose abundance was more than double that of O_3^- , O^- and CO_4^- . Only traces of O_2^- ions were detected.

The apparent differences between these experimental results might be due to different water concentrations in air. Traces of water can completely change the mass spectra of negative ions [19, 20]. Moreover removal of the water may be accompanied by removal of at least part of the CO_2 component. Hence the composition of air is changed. The removal of CO_2 was shown by Shahin [2] to lead to a dramatic reduction in relative yield of CO_3^- ions. His observation was confirmed by Gravendeel et al. [12, 13] who used synthetic air containing only traces of CO_2 deeply below the usual value of around 300 ppm typical for standard air. The yield of CO_3^- ions was observed to be an order of magnitude below the yield O_3^- ions. Instead of these the NO_3^- ions were observed with intensity comparable to the ozone ions. At pressures close to 40 kPa

the NO_3^- were absolutely dominant. This is evidence that also the CO_2 is trace gas in air dramatically affecting the ion spectra.

As it was mentioned already the water content affects the yields of individual ions, although it must be noted that the effect of water on the ion spectra is less pronounced than in the case of positive corona discharge [2], [17]. Almost all the parent ions found in dry air can form clusters with water.

In this paper the effect of ozone and nitrogen oxide impurities in both dry and humid air is discussed allowing us to interpret these earlier mentioned time relaxation of negative corona discharge current in flow-stopped regime [1] and quantify the importance of controlling trace compounds in any negative ion air discharge.

2. Experimental apparatus

The apparatus used is that of the ELION group at NTH University of Trondheim, Norway and is shown schematically in Fig. 1. It consists of three main parts: (i) a discharge volume, (ii) an intermediate volume containing an electrode system (S, F) to focus the extracted ions into (iii) the mass spectrometer (QM). The discharge chamber contained point-to-plane electrodes for generating the corona discharge. The total volume of the stainless steel discharge chamber was 10 dm^3 . A Pt wire ended by a tip with radius of 0.1 mm was fixed on axis separated from a gold plated brass plane electrode at a distance 10 mm . The electrodes were fed by a stabilised HV power supply. An extraction foil was placed in the central part of the plane electrode. The extracted ions expand through the orifice into an intermediate region where the gas is pumped by diffusion pump away while the ions are focused onto a 2 mm in diameter skimmer opening leading to Balzers OMG 101 quadrupole spectrometer (QM), which was pumped separately. The mass selected ions were finally detected by a photomultiplier. The relative yield Y_r of ions having a mass per charge smaller than 100 was calculated from the measured absolute yield of ions i -type in spectra Y_i by formula

$$Y_r = \frac{Y_i}{\sum Y_i} \times 100[\%]$$

Ambient air of relative humidity of around 50 % was used in experiments. A flow rate $50 \text{ cm}^3/\text{s}$ was maintained by an electronically regulated valve. In order to study the effect of ozone concentrations on the relative ion yields ozone was prepared using a coaxial cylindrical corona discharge ozonizer. The ozonizer was fed by a separate high voltage power supply. It was not possible to measure ozone concentrations directly in the inlet of air into the discharge gap. Therefore the ozone concentration was measured as a function of discharge current in ozonizer in separate experiment by using UV light absorption spectrometry. The Lambert Beer formula was used for calculation of ozone concentration from experimentally detected values of transmittance of UV light in the cell of spectrophotometer. The discharge current of the home made ozonizer was calibrated as a function of ozone concentration at a constant flow rate $50 \text{ cm}^3/\text{s}$. The

calibrated ozonizer was finely used as a source of ozonised ambient air.

The constant air pressure in the discharge gap of 30 kPa was kept in the discharge gap during experiments. To exclude ion-molecule reactions in the intermediate space the pressure in this was stabilised always below the value of 0.2 Pa . At such critical value the mean free length of neutral gas molecules was comparable with the distance between extraction foil and the entrance to the mass spectrometer. Hence in our experiments the effect of ion-molecule reactions in the intermediate space is only marginal. The current voltage characteristics (CV) were measured at different values of the ozone concentration. Moreover the dependence of Trichel pulse frequency as a function of the discharge current was measured at the same conditions. Experiments were carried out at ambient temperature.

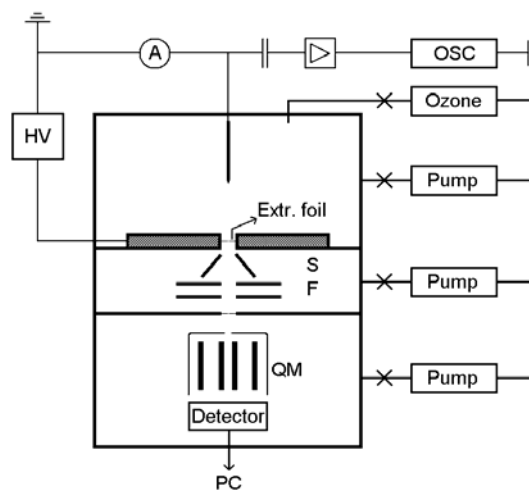


Fig. 1. Schema of used experimental apparatus.

3. Experimental results and discussion

Ambient air having the relative humidity within the range (45-55) % was used in experiment in both flowing and flow-stopped regimes. In the flowing regime in contrast to experiments performed in dry air [18] only the traces of single ion CO_3^- was observed in recorded spectra instead the dominant signals observed were the cluster ions $\text{CO}_3^-(\text{H}_2\text{O})_n$. The yields of minor and major ions in spectrum obtained in flowing wet air containing practically only traces of ozone are shown in Fig. 2 and 3 respectively. These were measured at time $t = 0$ before stopping the flow of air through the discharge tube. All other data shown in both figures were obtained in flow-stopped regime. At such circumstances the neutral chemical products, especially ozone, formed in the discharge was accumulated within the discharge tube. Due to the limited mass range of the mass spectrometer only the ions having the specific mass smaller than 100 were studied, hence only ions $\text{CO}_3^-(\text{H}_2\text{O})$ and $\text{CO}_3^-(\text{H}_2\text{O})_2$ were

analysed. The data shown in Fig. 2 a, b were obtained with an initial discharge current of 50 μ A, detected in flowing regime before the airflow was stopped.

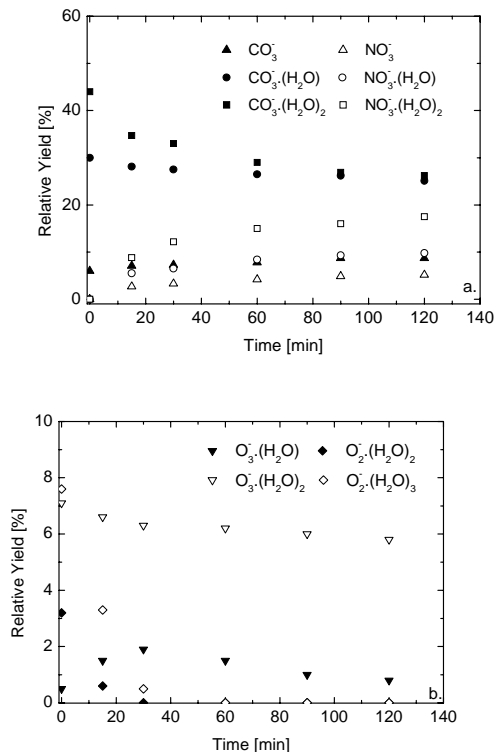
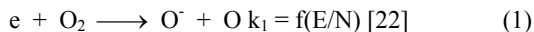


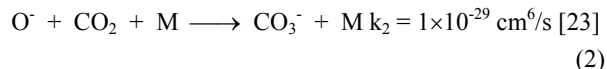
Fig. 2 a., b. Time dependence of relative yield of major (a) and minor (b) ion species detected in spectrum measured in flow-stopped experiment.

The primary ion O⁻ in air is generated at high electric fields, typical for glow region, (reduced electric field $E/N \approx 100$ Td) by dissociative electron attachment reaction

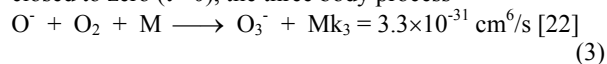


The contribution of O⁻ produced by dissociative electron attachment to carbon dioxide is only marginal due to low concentration of carbon dioxide in ambient air (300 ppm). The same statement is valid for process of dissociative attachment to water molecules.

However, in the presence of carbon dioxide at even so low concentration, the parent ions O⁻ are converted via the fast three body ion-molecule reaction to form CO₃⁻ ions



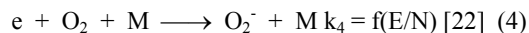
If the concentration of ozone in the discharge gap is closed to zero ($t=0$), the three body process



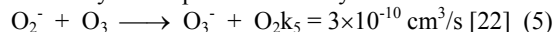
is the only potential source of O₃⁻ ions observed in spectra detected in dry air [18]. The characteristic reaction time

for processes (2) and (3) at the working pressure in our experiment (30 kPa) is $1/k_2[CO_2][M] = 6.2 \mu\text{s}$ and $1/k_3[O_2][M] = 0.3 \mu\text{s}$ respectively. It is therefore evident that the O⁻ ions generated in the glow region should be predominately converted to O₃⁻ ions in this region because the transport time of O⁻ ions through the glow region is of order of microseconds.

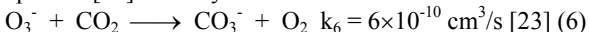
The free electrons, which escape the dissociative attachment (1) in glow region, can be attached via three body process



which becomes to be more important with increasing pressure. If ozone is produced in the discharge gap by processes described elsewhere [1], the O₂⁻ ions formed via (4) can be very fast depleted via binary reaction



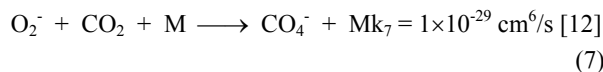
There are several processes that may lead to O₃⁻ depletion [22] but only



is the most important in the current discharge conditions. This is the processes converting the ions O₃⁻ formed in glow region via (3) to CO₃⁻. The process (6) is the second very important source of CO₃⁻ ions besides the process (2) and can explain in combination with (5) a conspicuous decrease in abundance of CO₃⁻ ions with increasing flow rate observed if the flow of air is oriented in opposite direction to ion drift [21]. The ozone molecules, which are formed at the tip of point electrode in glow region, are moved out from the discharge gap, thus ozone absent in the drift region of the discharge gap. Therefore the process (5), which is dominant far from the point electrode, deeply in drift region, starts to be only marginal. Consequently the number of CO₃⁻ ions is decreasing. As an evidence for such statement is the synchronous decrease in abundance both of O₃⁻ and CO₃⁻ in the reverse flow regime studied by Ross and Bell [21]. If the flow is oriented in direction of the ion drift both the abundance of O₃⁻ and CO₃⁻ was found slightly increasing and these were dominant in the ion spectra.

The rate constant for the reaction reverse to (6) is four orders smaller. Therefore in absence of nitrogen oxides CO₃⁻ ion is the most stable ion in dry air as we have shown recently [18].

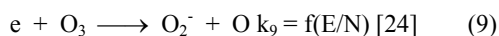
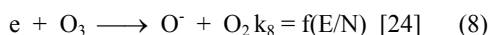
The process (4) can be followed also by fast ion-molecule reaction



The last process explains the relative high abundance of CO₄⁻ ions in spectra in ozone free dry air in our experiments performed at pressures below 30 kPa [18]. The rate of the process (7) is much higher than that of (5). With increasing ozone concentration the process (5) becomes to be dominant. At atmospheric pressure concentration of ozone [O₃] must be comparable with concentration of carbon dioxide [CO₂] to achieve the dominance of the process (5). The considerable increase in abundance of CO₄⁻ ions in reverse flow regime [21] and nearly zero values of that in direct flow is an excellent

evidence for our statement. At low air pressure the rate of the process (5) can be comparable with that of (7) only if $[O_3] \geq [CO_2]$, what was not the case of our present and earlier experiments [18]. Therefore in [18] the relative high yield of CO_4^- was found.

Moreover if the concentration of ozone is not kept at zero level two processes of dissociative electron attachment start to be effective in negative corona discharge, especially in drift region



The processes (8) and (9) are additional to (4), which otherwise determinates the concentration of free electrons in drift region in the case of ozone-free air. The concentration of ozone in the discharge tube in flow-stopped regime increases in time practically exponentially from nearly zero to saturated value. Therefore with increasing ozone concentration in discharge gap the number of free electrons is reduced and the total discharge current decreases to saturated value. This is stabilised when ozone concentration is reached the saturated value. The time dependence of the discharge current in flow-stopped regime is shown in Fig. 3.

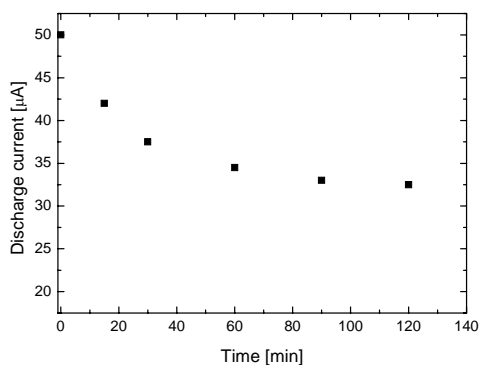
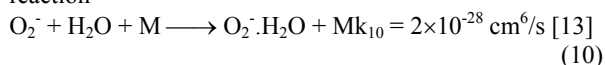


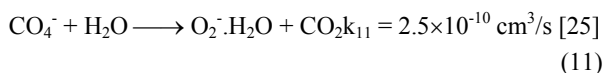
Fig. 3. The time dependence of the discharge current in flow-stopped experiment in wet air.

The decrease of main ionic components, clusters $CO_3^-(H_2O)_n$, $n = (1, 2)$ is accompanied by appearance and a temporal increase of yield of NO_3^- ions and water clusters (Fig. 2 a., b.). Moreover, it is interesting that ions $O_2^-(H_2O)_n$ ($n = 1, 2, 3$) were found in spectra at relatively high concentrations although in dry air the single O_2^- ion was not detected at all [18], most likely because the efficient conversion (7) as it was explained in foregoing. The clusters $O_2^-(H_2O)_n$ may be formed through the reaction

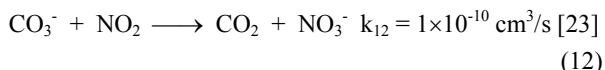


The rate of this reaction in wet air is two orders of magnitude higher than the rate for process (7). The absence of CO_4^- and O_4^- ions in spectra even at low discharge current is an evidence for such statement.

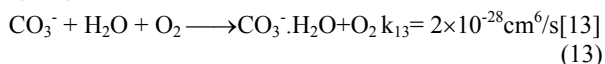
Moreover, if some CO_4^- ions are formed these are efficiently decomposed by the process



If the gas flow is stopped besides the ozone also nitrogen oxides are generated in the discharge gap, hence the concentration of these species increases with time. The mass spectra are changed considerably for wet air in a flow-stopped regime. The relative yields of clusters $CO_3^-(H_2O)$ and $CO_3^-(H_2O)_2$ are found to decrease with time probably due to reaction



which is competitive with that of forming clusters $CO_3^-(H_2O)$

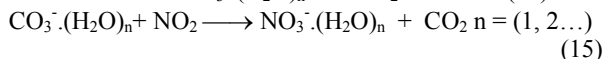


The reaction (12) can be dominant if

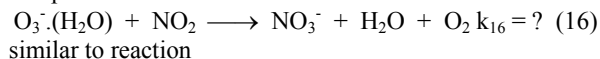
$$[NO_2] \cdot k_{12} \geq [H_2O] \cdot [O_2] \cdot k_{13}$$

what in our experiments means to achieve an equilibrium of $[NO_2] \approx [H_2O]$. At conditions typical for flowing regime in wet such condition can not be fulfilled. This is possible very easily reach in dry air. Therefore in our earlier experiments [6] and recently published paper of Ross and Bell the NO_3^- ions were observed at relatively high amount. The dependence of the abundance on these in our experiment and the direction of flow of in experiments conducted by Ross and Bell [21] is good evidence about the active role of process (12).

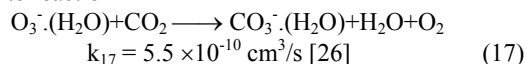
In the presence of sufficient amount of water, typical for ambient air, the process (13) dominates over the process (12). Hence there must be active fast processes between clusters $CO_3^-(H_2O)_n$ and NO_2 similar to (12)



which are most likely active in the production of cluster ions $NO_3^-(H_2O)_n$, $n = (1, 2, \dots)$. The increase in relative yield of such ions is evident from Fig. 2 a.. Unfortunately there are no direct data on such types of reactions [26]. Moreover the presence of small amount of NO_3^- ions in spectra in wet air is surprising because of evident prevalence of process (13) to be compared with (12) at conditions of our experiment. There is most likely active a fast process

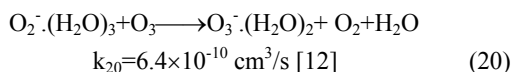
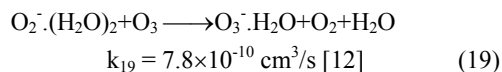
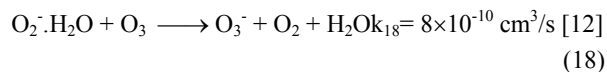


similar to reaction

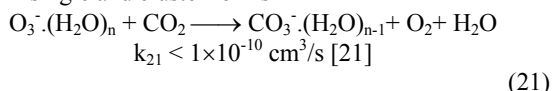


We have to conclude however that there are no experimental data for k_{16} . Taking into account the higher exothermicity of process (16) in comparison with that of (17) one can surmise that k_{16} is close to value of $1 \times 10^{-9} \text{ cm}^3/\text{s}$.

The hydrated forms of O_2^- ion also react very fast with ozone molecules and produce single O_3^- and cluster ions $O_3^-(H_2O)_n$



All hydrated forms are partially converted to CO_3^- ions in single and cluster forms



that are transferred mostly to NO_3^- ion and its clusters (15). Disappearance of water clusters $\text{O}_2^-\cdot(\text{H}_2\text{O})_n$ from mass spectra after accumulation of sufficient amount of ozone confirm our presumption (Fig. 2 b.)

In order to quantify the role of ozone in such flow-stopped discharges a set of experiments was performed in flowing wet and ozonised air (formed in extra ozonizer) in a flowing regime with a flow rate of $50 \text{ cm}^3/\text{s}$. The results are shown in Fig. 4 a,b.

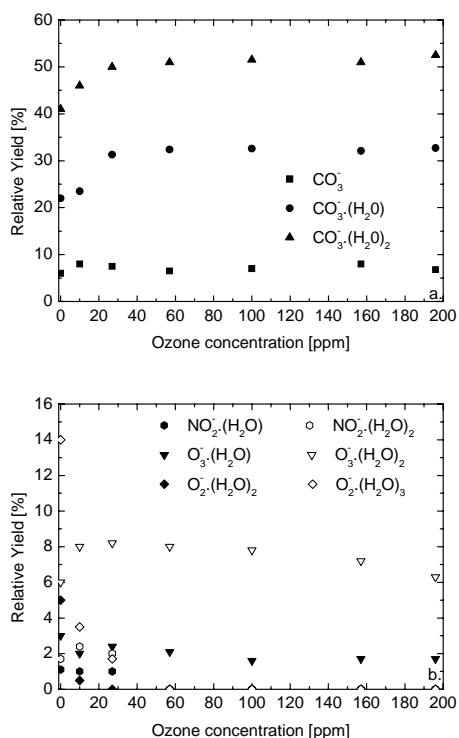
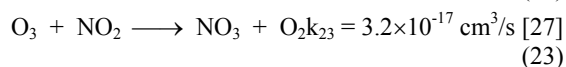
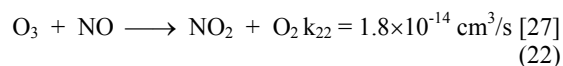


Fig. 4 a., b. The dependence of relative yield of major (a.) and minor ionic species in spectra on ozone concentration in flowing ozonised wet air.

In contrast to experiments performed in the low-stopped regime, in flow regime only traces of NO_3^- were found (concentrations below 1 %, not shown in Fig. 4) There are only $\text{O}_3^-\cdot(\text{H}_2\text{O})_n$ and $\text{CO}_3^-\cdot(\text{H}_2\text{O})_n$ clusters present in spectra of extracted ions. The reasons for disappearance of the minor ions O_2^- and NO_2^- and their clusters are reactions with ozone introduced into wet air. The role of reactions with nitrogen oxides was not confirmed. The absence of NO_3^- ions and its clusters in spectrum is most likely due to low concentration of nitrogen oxides in ozonised air. Nitrogen oxides are generated in ozonizer with ozone but the concentration of these is more than one order smaller than ozone concentration. Moreover during the transport of ozonised air through duct connecting the ozonizer with the discharge tube (approximately 1 m) great part of nitrogen oxides is decomposed via neutral chemical reactions with ozone molecules



If the concentration of ozone is of order 100 ppm the characteristic time for reaction (22) is substantially shorter than the transport time in the duct. Thus the NO is completely decomposed in the duct. The NO_2 concentration is low because of high flow rate through the ozonizer and also is decomposed in the duct connecting the ozonizer and the discharge tube. Hence the existence of NO_3^- ions and its clusters in the static regime is evidence that the concentration of nitrogen oxide in the discharge gap should be considerably higher than it is in the ozonised air introduced into discharge tube.

The observed decrease of relative yield of O_3^- clusters at higher ozone concentrations is caused by reaction of O_3^- clusters with CO_2 molecules (ž). Single O_2^- ions were absent both with and without ozone in air. The O_2^- clusters were found to disappear if ozone concentrations were higher than 25 ppm. The mechanism of depletion is expected to similar to that described in the flow-stopped regime.

As it was shown in foregoing the increase in ozone concentration causes an increase in concentration of ions especially that of $\text{CO}_3^-\cdot(\text{H}_2\text{O})_n$ clusters. The mobility of these is generally to be known smaller than the mobility of single parent ions present in ozone free air. Therefore beside the increase in depletion of free electrons due to additional electron attachment via processes (8) and (9) the average mobility of negatively charged particles in drift region is reduced due to decrease of dominant ion component drifting towards to the plane electrode. Consequently the electrical conductivity I/U (total discharge current I and voltage U applied on electrodes) should be decreasing. The results obtained at different ozone concentration in flowing wet air, shown in Fig. 5 fully confirm such expectation.

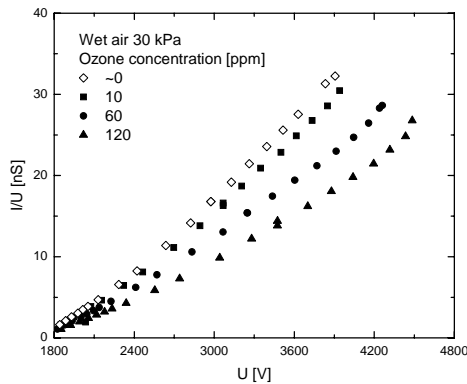


Fig. 5. The dependence of average electrical conductivity of the ionised gas in the drift region on applied voltage at different ozone concentration in flowing wet air.

If we take into account quadratic dependence of the discharge current on applied voltage, experimentally verified by many authors in various electrode system and in various electronegative gasses of constant chemical composition, the electrical conductivity I/U can be expressed in following form

$$\frac{I}{U} = A \cdot \mu \cdot (U - U_0) \quad (24)$$

where A is the constant determined by geometry of used electrode system including also ϵ_0 the vacuum permittivity, μ is the mobility of charged particles in drift region and U_0 is the onset corona discharge voltage. The dependence of electrical conductivity should be linear against voltage U if mobility μ is constant what is valid in our case for voltage values slightly above the onset voltage. With increasing voltage this evidently decline from the linear to higher values. The effect is caused by reduction in number of water molecules in clusters, predominately $\text{CO}_3 \cdot (\text{H}_2\text{O})_n$ with increasing voltage because of increasing electric field in the discharge gap. The reduction has been experimentally observed by several authors [7, 11, 13]. This is an evidence that not only the additional attachment of electrons to ozone via (8) and (9) but also the changes in the spectra of ions in drift region of negative corona discharge is the factor influencing the negative corona discharge current and causing the temporal dependence of this when the concentration of strongly negative impurities in air are temporally changed. The temporal increase in ozone concentration in flow-stopped experiments is a typical example of such situation. The formula (24) does not allow calculating the absolute values of the mobility of charged particle because of unknown value of geometrical factor A . Only the ratio between the mobility at different ozone concentration was estimated from the linear part of individual dependencies shown in Fig. 5. The values are compared to mobility at nearly zero ozone concentration. These can be expressed in the following arrangement 1 : 0.95 : 0.75 : 0.52. From the calculated ratio and the decrease in total current found in flow-stopped experiment shown in Fig. 3 we can surmise that the saturated value of

ozone concentration in mentioned experiments should have been close to value of 120 ± 10 ppm.

The ozone impurity in wet air affected also very efficiently the frequency of Trichel pulses. It is evident from Fig. 6.

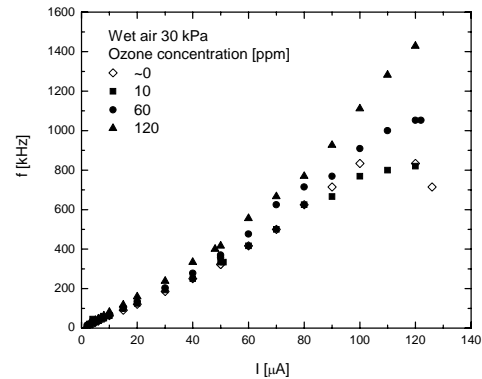


Fig. 6. The dependence of Trichel pulse frequency on the average discharge current I .

The linear dependence of frequency on average discharge current, observed in ambient air at atmospheric pressure and currents below $50 \mu\text{A}$ by Lama and Gallo [28], can be seen in plots shown in Fig. 6 at low current up to $50 \mu\text{A}$. The dependence of the frequency on discharge current can be expressed as

$$f = \frac{1}{Q} \cdot I \quad (25)$$

where Q is charge per one Trichel pulse.

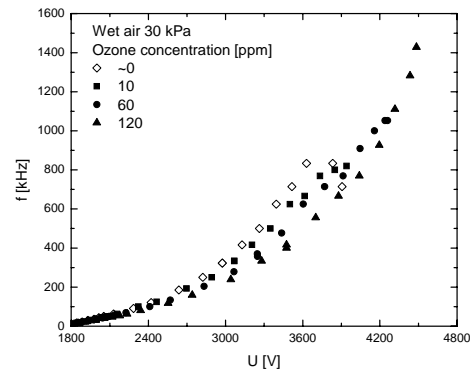


Fig. 7. The dependence of Trichel pulse frequency on the voltage U applied on electrodes.

It is evident that the slope of linear part of dependence (25) in our experiments (Fig. 6) increases hence the charge per one pulse is decreasing with increasing ozone concentration. This can be explained by increase in abundance of less mobile cluster ions in drift region. The total current is reduced as it was discussed in foregoing text. Therefore to reach the same current higher voltage must be applied on electrodes and the electric field is higher what accelerate the removal of negative space charge of ions from the vicinity of the point electrode. The space charge and its movement determine the frequency of

Trichel pulses. At higher voltage the frequency is higher. Hence if the voltage is constant and due to increasing ozone concentration in the gap the ions with lower mobility are appeared, the frequency must decrease with increasing ozone concentration. The effect is evident from Fig. 7. Moreover, the voltage and the frequency of pulses at which the Trichel regime is transferred to glow, pulseless regime are considerably increasing with increasing ozone concentration. In contrast the current of 120 μA at which the transformation of regimes is appeared was practically constant. The deflection of the dependence of frequency and discharge current (25) from the linear at high ozone concentration and high voltages can be explained by the changes in ion composition mentioned in remarks to Fig. 5.

4. Conclusions

The yield of individual ions in wet air is strongly affected by trace concentration of ozone both in flowing and flow-stopped regimes. Ozone concentration greater than 25 ppm is sufficient to completely suppress the appearance of O_2^- and a NO_2^- ion as well as their clusters in the mass spectra. The temporal increase in concentration of NO_3^- ions and $\text{NO}_3^-(\text{H}_2\text{O})_n$ ($n = 1, 2$) hydrated clusters was observed in flow-stopped regime accompanied by reduction in yield of CO_3^- ion and its water clusters $\text{CO}_3^-(\text{H}_2\text{O})_n$ ($n = 1, 2$), which otherwise are the dominant ions in flowing wet air free of ozone. In contrast the addition of ozone into the flow of wet air resulted in evident increase in abundance of the clusters $\text{CO}_3^-(\text{H}_2\text{O})_n$ ($n = 1, 2$). This is an evidence of an active role of nitrous oxide produced in flow-stopped regime in sufficient amount. The low yield of ion O_3^- and its clusters, which otherwise should be dominant in ion spectra in air free of CO_2 [13], is due to effective reaction of such ions with CO_2 molecules. The measured electrical conductivity of drift region confirmed the role both of additional dissociative attachment of electrons by ozone molecules as well as a formation of clusters of lower mobility with increasing ozone concentration in the discharge gap. The changes in the mass spectra have shown a considerable effect on the Trichel pulse frequency. This is increasing with increasing ozone concentration at constant voltage applied on electrodes.

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