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A mass spectrometric study of ions extracted from point to plane DC corona discharge fed by carbon dioxide at atmospheric pressure

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ABSTRACT

Mass spectra of the negative ions formed in both positive and negative corona discharges using carbon dioxide as the feed gas containing traces of water (around 50 ppm) operating at atmospheric pressure were analysed. Most of the ions detected were in the form of clusters containing large numbers of water molecules. Discharges operated with a positive polarity contain $H_3O^+\cdot(H_2O)_n$ clusters. In contrast an analysis of a negative corona discharge operating at atmospheric pressure and room temperature shows much more complex anionic spectra with five groups of ions and theirs clusters, having the relative yields close to 10% and higher, being observed (CO_3^-, CO_4^-, O_2^-, HCO_3^-, and HCO_4^-). The relative yield of each type of ions is found to be strongly affected by the discharge current. Mechanisms for the formation of such ionic species are discussed in detail.

1. Introduction

Studies of the physical and chemical characteristics of discharges fed by carbon dioxide are necessary for the study of many disparate areas of modern science and technology. For example the need to understand the decomposition of CO_2 in closed-cycle TEA CO_2 lasers has led to extensive study of the kinetics of CO_2 chemistry in electrical discharges [1–3]. The role of electron collisions has been found to be particularly important in limiting the operational lifetime of closed-cycle TEA CO_2 lasers [4,5]. Such discharges are also good experimental devices to explore chemical processes in planetary atmospheres (with electrical energy being used as a mimic of solar UV flux) [6–8]. Carbon dioxide is a key constituent of many planetary atmospheres (most notably Mars where it is the dominant (>98%) chemical species). Recent results from the Mars Express mission have revealed the presence of significant amounts both molecular oxygen and ozone in the Martian atmosphere, which may influence the solar UV flux reaching the Martian surface. Since the chemical formation of molecular oxygen and ozone is independent of the method by which initial oxygen atoms are created in the atmosphere (by solar UV photolysis in the Martian atmosphere) an electrical discharge in pure carbon dioxide (allowing electron induced dissociation of CO_2) provides an excellent laboratory system for probing both oxygen and ozone production in the Martian atmosphere [10]. In addition to such electron stimulated processes ion-molecule reactions can also play an active role especially in processes of re-association of carbon dioxide molecules and the formation of ozone. To evaluate the role of ion-molecule reactions knowledge of their role in the drift region of the discharge is required. Knowledge of the composition of ions formed in the discharge is also necessary if we are to develop more detailed models of physical and chemical properties of corona discharges in carbon dioxide. For example knowledge of the spectrum of ions produced is an important guide to understanding heterogeneous processes occurring on the surface of the outer electrode of the corona discharge.

However to date there is relatively little direct information on the mass spectra of ions produced by corona discharges and there are, to date, no data on the ionic spectra produced in corona discharges fed by carbon dioxide at atmospheric pressure. However, one mass spectrometric study has been performed by Gardiner et al. in negative corona discharge initiated in carbon dioxide at low pressures 10–30 Torr [9] which might be expected to provide an indication of the species to be found in higher pressure systems. They observed only CO_3^-, O_2^- and O^- ions with CO_3^- being dominant at 10 Torr, however increasing the pressure led to an increase in the relative abundance of oxygen anions. Unfortunately such measurements probably can not be extrapolated to atmospheric pressure because, according Rokushika et al. [10], the character of the ions formed in CO_2 at atmospheric pressure changes so drastically that the comparison to low-pressure experiments is meaningless. Rokushika et al. studied the mobility of positive and

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negative ions formed in CO_2 using an ion mobility spectrometer (IMS). The ions were produced by radioactive source of particles. They concluded that a large numbers of cluster ions were formed both in positive and the negative corona operated at high pressure. Surprisingly the mobility of all negative clusters was the same and the only the difference in the mobility they could observe was between hydrated and non-hydrated positive ions.

In present paper a study of the ionic spectra produced by positive and negative corona discharges in carbon dioxide is presented. Mass spectrometric analysis of spectra has been performed at atmospheric pressure at a constant distance between point and plane electrodes at various voltages (hence various discharge currents) applied to the electrodes.

2. Experimental apparatus

The apparatus used in these experiments is shown schematically in Fig. 1. A simple point to plane corona discharge was formed by placing a pointed stainless steel needle in front of the wall of a vacuum chamber (the wall acting as a planar electrode). A small orifice with a diameter of 100 μm in the wall of the vacuum chamber allowed the products of the discharge to enter a Hiden Molecular Beam Quadrupole MS HPR60. The discharge region was surrounded by a plastic chamber forming a volume of approximately 300 cm^3 through which the CO_2 feed gas for the discharge was flowed at a flow rate of 1000 cm^3/min. Experiments were performed using carbon dioxide of 99.995% purity at atmospheric pressure and at an ambient temperature 20 °C. The point electrode was powered by a Glasmann HV source whose output was controlled by using a HV probe combined with digital multi-meter. The discharge current was detected by a microammeter.

3. Results and discussion

All the present experiments were performed in a flowing regime with low flow rate to ensure sufficient production of ozone for maintaining a stable discharge with negative polarity of corona. At higher volume flow rates the discharge became unstable with a tendency to spark at the corona onset. The effect of the flow rate on the stability of negative corona discharge in CO_2 has been discussed recently [11]. The relative yield Y_r of ions having a mass per charge smaller than 160 was calculated from the measured absolute yields of ions (Y_i) by

$$Y_r(\%) = \frac{Y_i}{\sum Y_i} \times 100$$

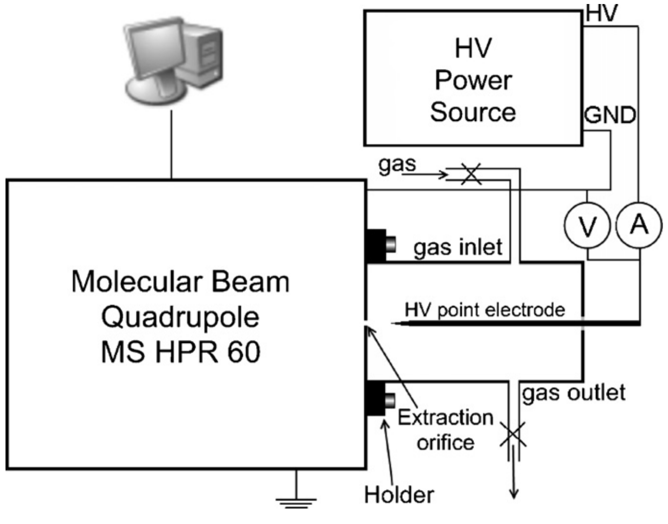

Fig. 1. A schematic diagram of the experimental apparatus used in the present experiments.

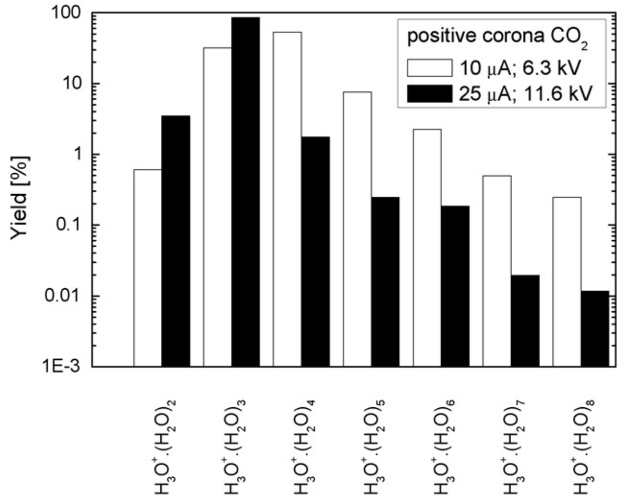

Fig. 2. Relative yield of clusters $H_3O^+ \cdot (H_2O)_n$ at two selected discharge currents.

The abundances of ions at $Z < 60$ and $Z > 160$ were negligible and are therefore not displayed. Practically all the ions detected were in the form of clusters, mostly containing water, although some clusters containing CO_2 were also observed. No corrections for mass discrimination effects due to the extraction of the ions was made, the data is, therefore, as directly recorded.

3.1. Positive corona discharge

Only water hydrated clusters $H_3O^+ \cdot (H_2O)_n$, $n = 2–8$ were observed in the mass spectra (Fig. 2). The relative yields of all other ions were found below 1%. Hence such ions were not analysed. Due to relative high purity of basic gas (99.995%) the production of other ions can be neglected.

Surprisingly neither CO_2^+ primary ions nor their clusters were observed in the measured spectrum. The primary ions are predominately formed by electron impact ionisation [12]:

$$e + CO_2 \rightarrow 2e + CO_2^+ \quad k_1 = f(E/N) \tag{1}$$

The primary ions CO_2^+ predominately react with water molecules (content of water vapour of 50 ppm) [5]:

$$CO_2^+ + H_2O \rightarrow HCO_2^+ + OH \quad k_2 = 3 \times 10^{-9}\ \mathrm{cm^3/s} \tag{2}$$

This process is relatively fast, $\tau = (1/k_2) \cdot [H_2O] \approx 0.1$ μs, hence practically all primary ions CO_2^+ are converted via (2) to HCO_2^+ in glow region of the discharge gap. The next process [5]:

$$HCO_2^+ + H_2O \rightarrow H_3O^+ + CO_2 \quad k_3 = 3 \times 10^{-9}\ \mathrm{cm^3/s} \tag{3}$$

is also fast $\tau = (1/k_3) \cdot [H_2O] \approx 0.1$ μs. This is the source of H_3O^+ ions which is the basis of all the $H_3O^+ \cdot (H_2O)_n$ clusters.

3.2. Negative corona discharge

Anion mass spectra have been measured at three selected discharge currents. Five dominant anions (and their solvated clusters) were observed in our spectra and in addition several unidentified negative ions (masses 80, 98, 108, 110, 111, 127, and 144) albeit with typical abundances 1–2%. Identification of such unidentified negative ions will require some additional experiments so will not

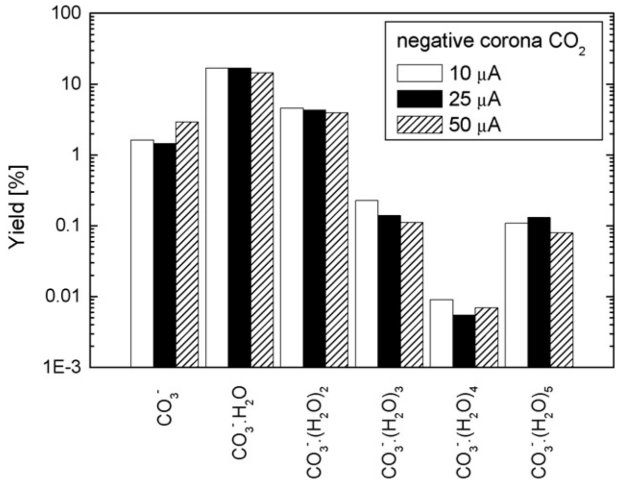

Fig. 3. The relative yields of CO_3^- ions and its solvated clusters $CO_3^-{\cdot}(H_2O)_n$.

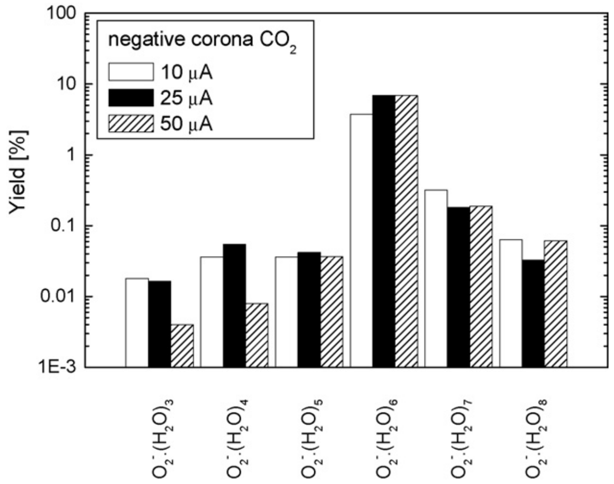

Fig. 4. The relative yields of solvated clusters $O_2^-{\cdot}(H_2O)_n$.

be discussed further. Most of dominant ions were found both in monomer state and in the form of water clusters.

3.2.1. CO_3^- and its solvated clusters $CO_3^-{\cdot}(H_2O)_n$

The origin of these anions, the most dominant in our spectra (Fig. 3) is well known and has been described by several authors [3–5,9,11,12]. The primary process [5]:

$$e + CO_2 \rightarrow O^- + CO \quad k_4 = f(E/N) \tag{4}$$

is active only in the vicinity of the central wire electrode due to the high energy threshold for the process. The primary O^- ions are immediately converted to CO_3^- ions in pure CO_2 via the fast process [5]:

$$O^- + CO_2 + CO_2 \rightarrow CO_3^- + CO_2 \quad k_5 = 1 \times 10^{-29}\,\mathrm{cm^6/s} \tag{5}$$

At atmospheric pressure the corresponding reaction time of process (5) is of 0.14 ns. Hence all primary negative atomic ions O^- are removed from the spectra.

The second process, typical for glow region of negative corona discharge in pure carbon dioxide, which substantially affects the properties of the discharge, is the dissociation of CO_2 by electron impact [5]:

$$e + CO_2 \rightarrow O + CO + e \quad k_6 = f(E/N) \tag{6}$$

This is followed either by the homogenous process of molecular oxygen formation [13]:

$$O + O + CO_2 \rightarrow O_2 + CO_2 \quad k_7 = 1 \times 10^{-29}\,\mathrm{cm^6/s} \tag{7}$$

or a heterogeneous process of molecular oxygen formation on the walls of the outer electrode.

$$O + O + \mathrm{wall} \rightarrow O_2 + \mathrm{wall} \quad k_8 = \text{discussed in Ref. [13]} \tag{8}$$

Molecular and atomic oxygen may then combine to form ozone, indeed the concentration of molecular oxygen we have measured in a static regime may approach a value of 10%. This finding is in good agreement with Rubcov and Eremin [2]. The high efficiency of O_3 formation is supported by relatively high concentrations of ozone produced in the discharge via the classic three-body process [11,13]:

$$O + O_2 + CO_2 \rightarrow O_3 + CO_2 \quad k_9 = 1.7 \times 10^{-33}\,\mathrm{cm^6/s} \tag{9}$$

The rate constant k_9 decreases with gas temperature. The value of k_9 is quoted at $T = 300$ K, hence the reaction time $\tau_9 = 80\,\mu s$ ($[O_2] \approx 1\%$), is substantially longer than the transport time of oxygen atoms from the glow region. This can explain the relative high concentrations of ozone measured in a negative corona discharge fed by carbon dioxide. Hence the carbon dioxide in equilibrium regime contains molecular oxygen ozone and non-negligible amounts of oxygen atoms. This chemical mixture can explain some peculiarities of the observed anionic observed spectra.

Ion-molecule reactions of CO_3^- ions with molecular oxygen and ozone have low reaction rates and hence can be neglected in the plasma. However the reaction with oxygen atom is efficient and produces O_2^- [5]:

$$CO_3^- + O \rightarrow O_2^- + CO_2 \quad k_{10} = 8 \times 10^{-11}\,\mathrm{cm^3/s} \tag{10}$$

As it will be shown in Section 3.2.2 solvated clusters of O_2^- anions were detected in the measured spectra with relatively high abundances.

Solvated clusters $CO_3^-{\cdot}(H_2O)_n$ are formed by sequential reactions:

$$CO_3^-{\cdot}(H_2O)_n + H_2O + CO_2 \rightarrow CO_3^-{\cdot}(H_2O)_{n+1} + CO_2 \tag{11}$$

The rate constants of individual steps of hydration are not known, but from our results we can estimate that these should be of order $1 \times 10^{-28}\,\mathrm{cm^6/s}$ which is a realistic value for hydration [5].

3.2.2. $O_2^-{\cdot}(H_2O)_n$ clusters

The relative yields of such clusters are shown in Fig. 4 for different discharge currents.

$O_2^-{\cdot}(H_2O)_n$ clusters are formed from O_2^- anions which are most likely produced by the ion-molecule reaction (10), via the sequential process [14]:

$$\begin{aligned} &O_2^-{\cdot}(H_2O)_n + H_2O + M \\ &\quad \rightarrow O_2^-{\cdot}(H_2O)_{n+1} + M \quad k_{12} = 2 \times 10^{-28}\,\mathrm{cm^6/s} \end{aligned} \tag{12}$$

A second source of O_2^- ions may be relevant if ozone is formed in sufficient amounts. Low energy electrons (around 1 eV) can be effectively attached in the drift region via electron attachment [15]:

$$e + O_2 \rightarrow O_2^- + O \quad k_{13} = f(E/N) \tag{13}$$

The third, and most likely to be the most effective process producing ions O_2^-, is the three-body electron attachment process [13]:

$$e + O_2 + CO_2 \rightarrow O_2^- + CO_2 \quad k_{14} = f(E/N) \tag{14}$$

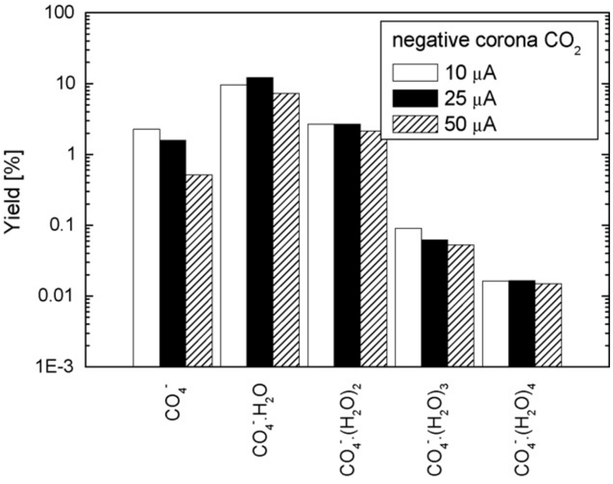

Fig. 5. The relative yields of CO_4^- ions and its solvated clusters $CO_4^-{\cdot}(H_2O)_n$.

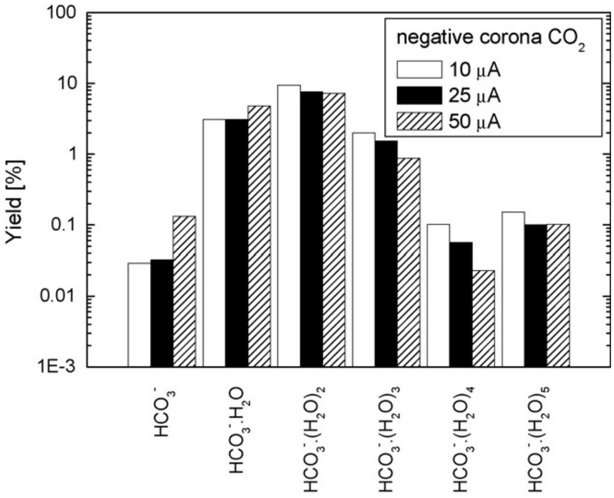

Fig. 6. The relative yields of HCO_3^- ions and its solvated clusters $HCO_3^-{\cdot}(H_2O)_n$.

which will be important if sufficiently high concentrations of molecular oxygen are formed via processes (7) and (8). This hypothesis is supported by earlier measurements of Gardiner et al. [9]. These authors observed an increase in the abundance of O_2^- ions with increasing pressure of carbon dioxide what suggests an active three-body process. To verify our hypothesis further measurements in mixtures of carbon dioxide with molecular oxygen are necessary.

3.2.3. CO_4^- and its solvated clusters $CO_4^-{\cdot}(H_2O)_n$

CO_4^- and its solvated clusters $CO_4^-{\cdot}(H_2O)_n$ were the second most abundant class of anions in the measured spectra, comparable with the abundance of CO_3^- and its solvated clusters $CO_3^-{\cdot}(H_2O)_n$. The relative yields of individual clusters are shown in Fig. 5 at three selected discharge currents.

The origin of the CO_4^- ions is a three-body process [13]:

$$O_2^- + CO_2 + CO_2 \rightarrow CO_4^- + CO_2 \quad k_{15} = 1 \times 10^{-29}\ \mathrm{cm^6/s} \tag{15}$$

Solvated clusters $CO_4^-{\cdot}(H_2O)_n$ are formed by sequential reactions:

$$CO_4^-{\cdot}(H_2O)_n + H_2O + CO_2 \rightarrow CO_4^-{\cdot}(H_2O)_{n+1} + CO_2.$$

There are no data on formation of water clusters with CO_4^-, but we can presume that the rate of such processes is comparable with those for CO_3^- (10). An interesting ion molecule reaction involving CO_4^- leading to ozone anions is then possible [13]:

$$CO_4^- + O \rightarrow O_3^- + CO_2 + O_2 \quad k_{16} = 1.3 \times 10^{-10}\ \mathrm{cm^3/s} \tag{16}$$

This may be an important process once sufficiently high concentrations of ozone are reached in the discharge.

3.2.4. HCO_3^- and its solvated clusters $HCO_3^-{\cdot}(H_2O)_n$

The HCO_3^- ion was observed recently by Nagato et al. in the mass spectra of ions extracted from negative corona discharge initiated in air [16]. In our experiments clusters of $HCO_3^-{\cdot}(H_2O)_n$ were found with high abundances, see Fig. 6. According Nagato et al. [16] HCO_3^- anions are produced by the very fast reaction of OH^- ions with carbon dioxide molecules [16]:

$$OH^- + CO_2 + M \rightarrow M + HCO_3^- \quad k_{17} = 7.6 \times 10^{-28}\ \mathrm{cm^6/s} \tag{17}$$

The reaction time is very short, only 1.8 psec, hence each OH^- is immediately converted to HCO_3^- ion. A similar situation is found in the case of water clusters [14]:

$$OH^-{\cdot}(H_2O)_n + CO_2 \rightarrow HCO_3^-{\cdot}(H_2O)_{n-1} + H_2O \quad k_{18} \approx 1.5 \times 10^{-11}\ \mathrm{cm^3/s} \tag{18}$$

where $HCO_3^-{\cdot}(H_2O)_n$ clusters are formed directly. The characteristic reaction time is around 2.5 ns.

Nevertheless there is a basic question about the origin of OH^- and its clusters $OH^-{\cdot}(H_2O)_n$. Neither the basic ion OH^- nor its clusters were observed in the spectrum. This is in accord with the short reaction times of processes (17) and (18). However in contrast to our observations OH^- ions were observed by Gravendeel and de Hoog [14] and Nagato et al. [16]. According Gravendeel the relative yield of these was increasing with increasing air pressure within the range 500–1000 mbar. This suggests that three-body processes might be the origin of OH^-.

The situation in corona discharge in air has been discussed recently [17]. We suggest that the primary ion O^-, formed by process (4), reacts via three-body process with water molecule [18]:

$$O^- + H_2O + O_2 \rightarrow O^-{\cdot}H_2O + O_2 \quad k_{19} = 1.3 \times 10^{-28}\ \mathrm{cm^6/s} \tag{19}$$

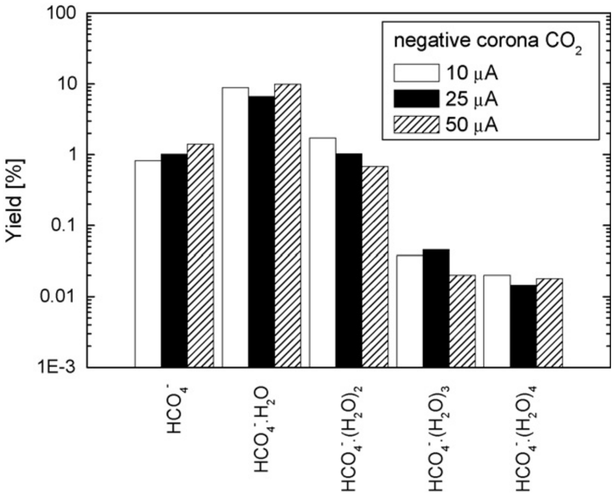

Fig. 7. The relative yields of HCO_4^- ions and its solvated clusters $HCO_4^-{\cdot}(H_2O)_n$.

In the second step the $O^-{\cdot}H_2O$ clusters are converted in bimolecular process [18]:

$$O^-{\cdot}H_2O + H_2O \rightarrow OH^-{\cdot}H_2O + OH \quad k_{20} > 1 \times 10^{-11}\,\text{cm}^3/\text{s} \qquad (20)$$

and the $OH^-{\cdot}H_2O$ cluster is formed, which is necessary for process (18) to develop. Further experiments performed at various CO_2 humidity are required for verification of such a hypothesis.

3.2.5. HCO_4^- and its solvated clusters $HCO_4^-{\cdot}(H_2O)_n$

The last group of dominant ions observed in our mass spectra are HCO_4^- and its solvated clusters $HCO_4^-{\cdot}(H_2O)_n$. The relative yields of these ions are shown in Fig. 7. The existence of HCO_4^- ions in spectra measured in an air fed negative corona discharge was also reported recently by Nagato et al. [16]. The yield of these ions was however low in their experiment. There is no information known to the authors on the process of formation of such ions. We can only presume that the process is similar to (17):

$$OH + CO_3^- + M \rightarrow M + HCO_4^- \quad k_{21} \qquad (21)$$

Experiments with humid carbon dioxide could confirm this hypothesis.

4. Conclusions

We have observed major differences in the mass spectra of ions extracted from positive and negative corona discharges in carbon dioxide. Discharges operating with a positive polarity show only $H_3O^+{\cdot}(H_2O)_n$ clusters. In contrast an analysis of a negative corona discharge operating at atmospheric pressure and room temperature shows very complex anionic spectra. Five groups of ions and theirs clusters, having the relative yields close to 10% and higher were observed in spectra (CO_3^-, CO_4^-, O_2^-, HCO_3^-, and HCO_4^-). Possible mechanisms for the formation of these anions were discussed. For a better understanding of processes of ion formation in corona discharge fed by carbon dioxide experiments at various relative humidities of CO_2 are required.

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