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The DC corona discharges in flowing dry and humid carbon dioxide

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We report the results of an experimental study of the role of humidity in a DC corona discharge fed by carbon dioxide. The discharge is studied as a function of both positive and negative polarity. The formation of water clusters is suggested as playing a key role in the electrical characteristics in the discharge and the mobility of the measure ions. The formation of ozone is also shown to be important in characterising the properties of the corona discharges.

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1. Introduction

The need to understand the decomposition of CO_2 in closed-cycle TEA CO_2 lasers has led to the 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 since previous research has shown that a considerable proportion of the CO_2 molecules within the laser system will be decomposed by electron impact to form atomic oxygen and carbon monoxide during the excitation discharge. The rate of such irreversible CO_2 decomposition therefore limits the operational lifetime of closed-cycle TEA CO_2 lasers [4, 5]. The study of plasma initiated chemical process in discharges fed by gases may also be used as a mimic of planetary atmospheres, including Mars – which is essentially a carbon dioxide atmosphere with only traces of other gases [6-8]. Dissociation of CO_2 could be a source for oxygen production in Martian atmosphere [9] and is expected to be responsible for the observation of ozone in the Martian atmosphere. In this paper we report the results of a detailed study of the chemical processes engendered in a DC corona discharges fed by carbon dioxide and explore the role of humidity in controlling that chemistry.

Several studies of CO_2 decomposition in corona discharges have been published over the last two decades both in pure carbon oxide and/or its mixtures with other gases, predominately air. Using a system of point-to-plane electrodes Boukalfa et al. [10] concluded that the relatively large CO yields [approaching 200 ppm] measured in an air + 3% CO_2 mixture indicated the importance of CO_2 dissociation by excited N_2^* molecules. However in this study no ozone measurements were made and the authors noted that ozone could be an important source of error in the determination of CO concentrations since ozone may have reacted with the chemical detectors used for CO detection.

The effect of CO_2 concentrations on ozone concentrations in positive and negative corona discharges using a wire-to-plate configuration of electrodes has been investigated in mixtures of air + CO_2 (up to concentrations of 2 %) [11]. Significant concentrations of ozone (up to 2 ppm) were only observed in a narrow region downstream of the corona wire in the case of negative corona. In positive corona the ozone concentrations were found to be an order of magnitude below those found in corona with a negative polarity. However, it should be noted that flow velocity (1 $m.s^{-1}$) used in these experiments is relatively high and this may explain the extremely low values of ozone concentration reported.

Recently we reported the chemical products contained in pure CO_2 and mixtures CO_2 + O_2 treated by negative corona discharge with particular emphasis on the production of ozone [12]. The discharge current in pure CO_2 was found to be highly sensitive to the presence of trace concentrations of molecular oxygen and to changes in the flow speed through the discharge gap. The ozone concentration increased monotonically with increasing content of oxygen whereas the CO concentration exhibited a flat maximum for oxygen concentrations around of 4%. The remarkable sensitivity of the discharge current on the flow rate was ascribed to changes in concentration of ozone produced in the discharge.

In none of these experiments was the effect of humidity explored. Since humidity often changes daily in the experimental laboratory it is possible that many of the changes reported in the previous work could be due to different amounts of water vapour in the feed gas. The goal of the present project is to study the effect of water content on ozone production in a CO_2 fed DC discharge and to determine whether the presence of water vapour affects the electrical properties of the corona discharges having both positive and negative polarities.

2. Experimental apparatus

A schematic diagram of the apparatus used in these experiments is shown in Fig. 1. Two reactors containing identical coaxial cylindrical electrodes systems (a stainless steel inner electrode of diameter 125 μm and stainless steel outer electrode of 16 mm in diameter) were used in these experiments. The active part length of each discharge tube was 10 cm. A Spellman SL 150 high voltage power supply unit was used to drive the discharge electrodes. The voltage supplied to the electrodes was measured by using the high voltage probe (HVP) Fluke 80K-40 combined with digital voltmeter FLUKE 189. The discharge current was monitored by digital ampmeter FLUKE 189. Both the current and voltage data were acquisited by PC.

A corona discharge was generated in one of the reactors while the second reactor was used as a reference reactor. Both reactors were placed in the analysis compartment of a Shimadzu UV spectrometer. The UV transmittance through the cell was recorded on-line with the discharge voltage and currents simultaneously monitored by a PC. The ozone concentration in the discharge gap was monitored using the Lambert-Beer formula.

The gas flow of dry CO_2 from a gas cylinder was divided into two independent flows regulated by flow controllers. One of them was kept at the minimum humidity of gas in cylinder (45 ppm) and the other was enriched in water vapour by passing the flow of dry CO_2 through water contained in a bubbler kept at constant temperature. These two flows were then mixed together to achieve the required water concentration in CO_2. The humidity was measured using a humidity meter (HM) Michell Instruments at the inlet of gas into the discharge reactor. The humid carbon dioxide was flowed through the discharge cell at a constant flow rate, Q = 15 ccm per minute, while the reference cell was filled with untreated gas and then sealed. Experiments were performed using two different values of humidity, dry CO_2 45 ppm and wet CO_2 7000 ppm, which correspond to relative humidity of 0.2 % and 30 %, respectively. All the experiments have been carried out at ambient temperature and atmospheric pressure.

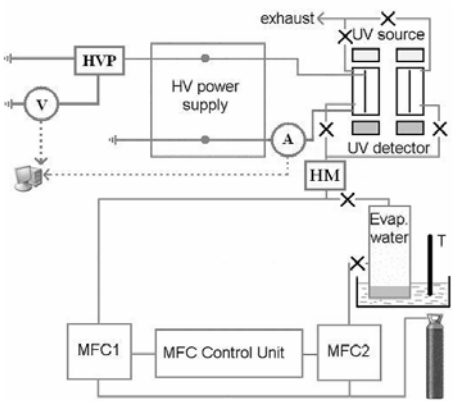

Fig. 1. Schematic diagram of the experimental apparatus used in the present experiments.

3. Experimental results

The corona discharge current J (μA/cm) per unit length of the outer electrode collecting the current is shown in Figures 2 and 3 as a function of voltage U on electrodes. The average values of the measured onset voltages are shown, together with selected the typical current voltage characteristics. The onset voltage in a positive corona discharge of dry CO is much higher than that in the corresponding negative corona discharge (under the same flow conditions etc). Furthermore in the negative corona discharge the current increases with voltage above the onset in accordance with the Townsend formula [13]. In contrast in the positive corona discharge about 1 kV above the onset the discharge current was seen to fall to zero after a few seconds with the discharge entering into an unstable oscillatory mode. There was little effect from humidity on the onset voltage in either positive or negative corona discharges.

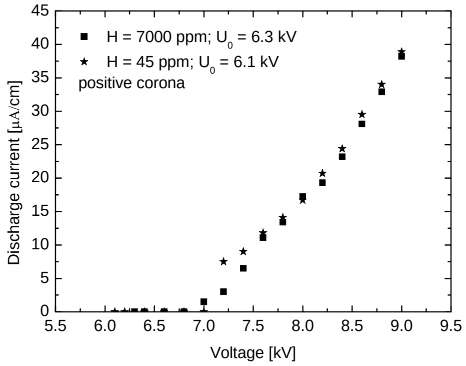

Fig. 2. Current-voltage characteristics of a positive corona discharge in dry and wet carbon dioxide. H is the relative humidity.

The current at the same voltage on electrodes in the negative corona discharge is approximately five times higher than that of the positive corona. However the current in the negative corona was found to decrease with increasing humidity. The higher currents in the negative corona discharge correspond with higher values of the average mobility of charged particles drifting down the drift region of such discharge, calculated from current-voltage data. The mobility μ of positive and negative charged particles was calculated using the Townsend formula [13] where the experimentally measured data of onset voltage is U_0, the voltage on electrodes U and the average current density J per unit length of the outer electrode.

$$\mu = \frac{J.R^2 \ln(R/r_0)}{8\pi\varepsilon_0 U.(U - U_0)} \qquad (1)$$

and ε_0 is the vacuum permittivity and R and r_0 radius of the outer and inner electrode respectively.

The calculated mobility as a function of voltage on the discharge electrodes is shown in Figs. 4 and 5.

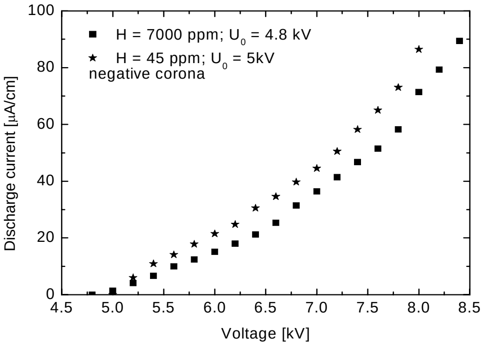

Fig. 3. Current-voltage characteristics of negative corona discharge in dry and wet carbon dioxide.

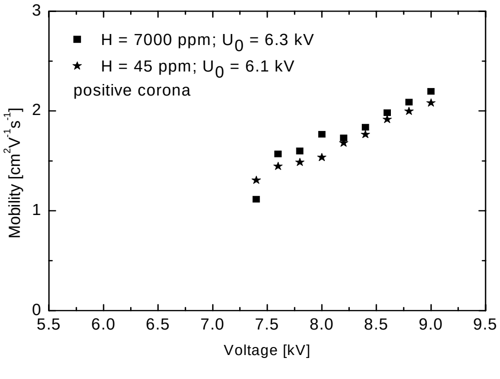

Fig. 4. Mobility of particles drifting in the drift region of the positive corona discharge.

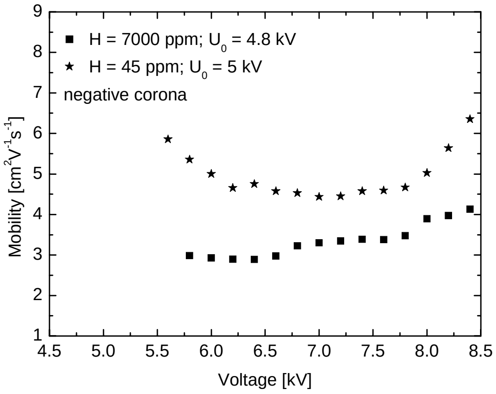

Fig. 5. Mobility of particles drifting in the drift region of the negative corona discharge.

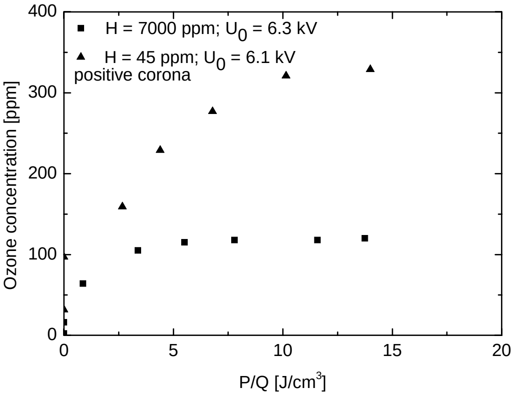

Fig. 6. Dependence of ozone concentration on Becker parameter P/Q measured in positive corona discharge.

The ozone concentrations in the discharge are plotted as a function of so called Becker parameter η in Figures 6 and 7. The Becker parameter is an average energy input into unit volume of the discharge gap. If the flow rate is Q and the total discharge current at voltage U is I, the Becker parameter can be expressed as [14]

$$\eta = \frac{I.U}{Q} = \frac{P}{Q} \qquad (2)$$

where P is the discharge power. The concentration of ozone at the same Becker parameter is evidently higher in the negative corona discharge. The ozone concentration is considerably reduced in humid carbon dioxide in both positive and negative corona.

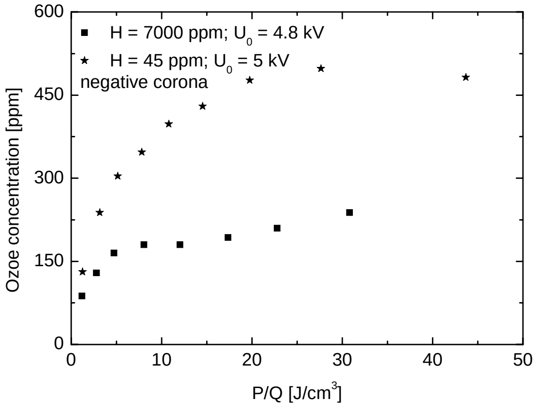

Fig. 7. Dependence of ozone concentration on Becker parameter P/Q measured in negative corona discharge.

4. Discussion of the experimental results

Before we discuss the observed differences in the macroscopic properties of positive and negative corona discharges in carbon dioxide, it is necessary to recall the different mechanisms for the generation of secondary electrons in these two types of discharges. In discharges with positive polarity the secondary electrons are generated by photoionisation in both the ionising and the drift regions, while secondary electrons in a negative corona discharge are released from the inner electrode by the impact of positive ions. Therefore while the maximum concentration of free electrons in a positive corona discharge is at the inner electrode, the concentration of electrons increases across the ionising region of the negative corona discharge reaching a maximum at the boundary between the ionising region and the drift region.

4.1. Electrical parameters of the discharges

Secondary electrons formed beyond the ionising region of the positive corona discharge by photoionization are either recombined with positive ions drifting from ionizing region towards the outer electrode or are attached to CO_2 molecules at the boundary between ionising and drift region by dissociative attachment (DA)

$$e + CO_2 \rightarrow O^- + CO \quad k_1 = 3.6 \times 10^{-13}\ \mathrm{cm^3/s}\ [15] \quad (3)$$

This process (1) is maximised at electron energies close to 4.2 eV i.e. at relatively high mean electron energy. However the rate constant is low. Hence outside the ionising region electron attachment is negligible. If the ozone is formed at voltages slightly above the onset voltage, (100-200) V, some secondary electrons can be removed from the discharge by dissociative attachment to ozone. There are two DA channels for ozone, one yielding O^- the other O_2^- both of them having a maximum production cross section for electrons with energies around 1 eV. The maximum rate constant for process

$$e + O_3 \rightarrow \text{products } (O^-, \text{ or } O_2^-) \quad (4)$$

is $k_2 = 2 \times 10^{-9}$ cm^3/s and will be dominant in the drift region where the reduced electric field E/N is low [16]. Hence some of the secondary electrons, which otherwise could contribute to sustaining a discharge may be converted to s less mobile negative ions. Thus the onset voltage in a mixture of $CO_2 + O_3$ is shifted to a higher value and the discharge will be extinguished after few seconds of discharge operation once sufficient amounts of ozone molecules are formed in the gap removing free electrons . When the ozonated mixture is removed from the discharge gap by the flow of the gas the discharge can start again at the previous onset value. This is the most likely an explanation for the observed oscillatory nature of the discharge in the negative corona discharge at voltages slightly above the onset value observed in experiments (see Fig. 2).

The formation of negative ions via (2) has no or only a marginal effect on the generation of secondary electrons in a negative corona discharge. Therefore the current of negative corona discharge increases at voltages above the onset and no disruption is observed in the self sustaining discharge.

The current in a positive corona discharge is limited by the mobility of charged particles in the drift region. Comparing the rate constants of all ionization processes at E/N close to 120 Td, typical for conditions in ionizing region in this case, the generation of CO_2^+ ions is clearly the dominant process

$$e + CO_2 \rightarrow 2e + CO_2^+ \quad k_3 = 2.6 \times 10^{-12}\ \mathrm{cm^3/s}\ [15] \quad (5)$$

A few of the CO_2^+ ions can then undergo charge exchange process

$$CO_2^+ + O \rightarrow O_2^+ + CO \quad k_4 = 2.6 \times 10^{-10}\ \mathrm{cm^3/s}\ [5] \ (6)$$

where the atomic oxygen required for the last process is formed via electron impact dissociation

$$e + CO_2 \rightarrow e + O + CO \quad k_5 = 8.7 \times 10^{-11}\ \mathrm{cm^3/s}\ [15] \ (7)$$

Hence the CO_2^+ ion should be dominant in any spectra of positive ions formed in the positive corona discharge fed by dry CO_2. Currently there are no direct mass spectrometric data to confirm such a statement but the mobility data corresponding to positively charged particles, shown in Fig. 4., are close to the expected mobility values of CO_2^+ ion (1.13 cm^{2}V^{-1}s$^{-1)}$ especially at low voltage U, and hence at low values of electric field in drift region [17]. The observed increase in the ion mobility at higher values of U suggests that the CO_2^+ ions are replaced by O_2^+ ions produced by charge exchange (6). The concentration of oxygen atoms increases with increasing U hence reaction (18) becomes increasingly significant at higher U and the ratio of $[O_2^+]/[CO_2^+]$ increases. Since the mobility of O_2^+ ions (2.24 $cm^2/V.s$ at E/N = 30 Td [18], typical value in drift region) is higher than the mobility of CO_2^+ ions the average mobility of a mixture CO_2^+ and O_2^+ increases as more O_2^+ are formed.

There is little effect of humidity on the mobility of particles or on CV characteristics (Fig. 2.). In presence of water the following binary ion-molecule reaction is dominant

$$CO_2^+ + H_2O \rightarrow HCO_2^+ + OH \quad k_6 = 3.0 \times 10^{-9}\ cm^3/s\ [5], \quad (8)$$

which is followed by formation of H_3O^+ ion

$$HCO_2^+ + H_2O \rightarrow H_3O^+ + CO \quad k_7 = 3.0 \times 10^{-9}\ cm^3/s\ [5] \quad (9)$$

Contributions from the ionization process

$$e + H_2O \rightarrow 2e + H_2O^+ \quad k_8 = 1.1 \times 10^{-12}\ cm^3/s\ [15] \quad (10)$$

is likely to be marginal because of low concentrations of water (7000 ppm) and similarity of rate constants in processes (5) and (10).

In contrast the characteristics of a negative corona discharge are completely different. There is a strong effect of humidity on both the CV characteristics (Fig. 3.) and the mobility of charged particles drifting toward the outer electrode is much higher in dry CO_2 than in humid CO_2 (Fig. 5.). The primary ion formed in the ionizing region of negative corona discharge in dry carbon dioxide is O^- produced via dissociative electron attachment to CO_2 molecule (1). These primary ions are converted to stable ions CO_3^- via the fast ion-molecule reaction

$$O^- + CO_2 + CO_2 \rightarrow CO_3^- + CO_2 \quad k_9 = 9.0 \times 10^{-29}\ cm^6/s\ [5] \quad (11)$$

The dominance of CO_3^- ions in drift region of negative corona discharge had been confirmed by mass spectrometric analysis of ions extracted from negative corona discharge fed by carbon dioxide [19]. Reaction (3) is confined only to the ionizing region which has a radius comparable with the radius of the inner electrode (and hence is very small). Since the threshold for DA to CO_2 is high (close to 4 eV) only a small proportion of the electrons in the discharge will be able to form O^- ions. The high value of calculated mobility (Fig. 5) supports this argument as does the observed dependence of the slope of the CV characteristics of negative corona discharge on the flow rate of dry CO_2 [12].

The electron component in the discharge current is strongly affected by presence of any additional electron attachment reactions in the drift region of the discharge. Such additional DA process can be initiated by presence of electronegative impurity gases in the drift region. These can be either added into the stream of CO_2 (oxygen in experiments described in [12]) or can be produced directly in the discharge gap via plasma-chemical reactions. Ozone is one of the major species generated by processes in discharge. If ozone is present in the drift region then the concentration of free electrons is diminished via dissociative electron attachment (4) and the total discharge current is decreased. This leads to the observed decrease in average mobility of negatively charged particles in the drift region. The values of the calculated mobility are observed to be above the known value of the mobility of the dominant ion CO_3^- being of 1.35 $cm^2V^{-1}s^{-1}$ [19]. An increase in the calculated mobility above 7.5 kV observed in experiments suggests that a portion of negative ions exists in cluster form. The form of such clusters must be verified by IMS or mass spectrometric studies but they are most likely $CO_3^-.(CO_2)_n$ and $CO_4^-.(CO_2)_n$ clusters formed especially at low voltages. These clusters are decomposed in higher electric fields thus the average mobility increases at high U values. Unfortunately there is a lack of data on rate constants of processes of cluster formation in CO_2. Hence the quantitative analysis of experimental data is not possible at present time.

Any increase in the humidity of carbon dioxide caused a remarkable reduction of the negative corona discharge current since the mobility of charged particles was changed. The strong dependence of the mobility on voltage U was also found to reduce in a humid gas. If we also take into account the observed reduction of ozone in humid CO_2, (see Fig. 7.) we can postulate two potential reasons for the observed current depression:

- electron attachment to water molecules
- formation of less mobile water clusters

Unfortunately the data for the dissociative attachment

$$e + H_2O \rightarrow H^- + OH \quad (12)$$

$$\rightarrow O^- + H_2 \quad (13)$$

remains scared and contradictory. It is evident that the rate constant for these processes is strongly influenced by the buffer gas in which the process is active [20]. No data for the rate constant of attachment processes (12 and 13) in wet carbon dioxide are known. However according the total rate constant for DA to water (both processes 12 and 13) reaches its maximum 1.0×10^{-10} cm^3/s at electron energy 4 eV hence at nearly the same electron energy as the maximum cross section for DA to CO_2. The rate constant (12+13) decreases at low electron energies and is 3.0×10^{-11} cm^3/sec at electron energy of 2 eV [20] but the rate constant for DA to CO_2 is zero. Hence electron attachment to water molecule is still active for 2 eV electrons while attachment to carbon dioxide is inactive. Accordingly in humid CO_2 discharge water may replace ozone as the source of DA and remove electrons from the discharge, explaining the lower currents.

The second process that may play a key role in humid CO_2 is a formation of very stable water clusters

$$CO_3^- + H_2O + X \rightarrow CO_3^-.(H_2O) + X \quad k_{12} = 1.0 \times 10^{-28}\ cm^6/s\ [21] \quad (14)$$

This is followed by consecutive reactions through which $CO_3^-.(H_2O)_n$ are formed. The lower the reduced electric field the higher the number of water molecules within the cluster. The formation of $O^-.(H_2O)$ is only marginal because the rate constant for this process is of the same order as that for process (11) but the concentration of O^- is considerably lower in comparison of CO_3^- ions due to very effective ion conversion (11). The mobility of clusters $CO_3^-.(H_2O)_n$ is apparently below that of CO_3^-. Therefore the discharge current in wet CO_2 is most likely suppressed also by formation of clusters containing water molecules.

4.2. Ozone formation

The mechanism of ozone generation in corona discharges fed by dry carbon dioxide has been discussed in detail recently [12] therefore only briefly we remind the basic principles. The primary process is the electron impact dissociation of CO_2 to neutral products (7). Data on the rate constant for reaction (7) are scattered and depend on the buffer gas as well as the energy of electrons. The value k_5 corresponds to energy of electrons at the boundary between ionizing and drift region. Process (7) is confined to the ionizing region and is folowed by formation of oxygen molecules

$$O + O + CO_2 \rightarrow O_2 + CO_2 \quad k_{13} = 1.0 \times 10^{-32}\ \text{cm}^6/\text{s}\ [5] \qquad (15)$$

Finally ozone molecules are formed via third body process

$$O + O_2 + CO_2 \rightarrow O_3 + CO_2 \quad k_{14} = 1.8 \times 10^{-33}\ \text{cm}^6/\text{s}\ [5] \qquad (16)$$

The re-association of O + CO is very low because the corresponding rate constant is three orders of magnitude below that corresponding to process (15) [5]. As it is evident from Fig. 6 and 7 the ozone concentration is strongly reduced in the discharge gap in both positive and negative corona discharges fed by humid carbon dioxide. A similar effect of humidity has been observed in air and oxygen [22, 23]. There are two processes leading to reduction of ozone concentration due to addition of water molecules into CO_2:

- processes competitive with (15) and (16), which are reducing the concentration of atomic oxygen
- processes of ozone decomposition via plasma chemical reactions initiated by water molecules.

Two dominant processes in the first group of processes are reactions of excited oxygen atoms

$$O(^1D) + H_2O \rightarrow OH + OH \quad k_{15} = 2.2 \times 10^{-10}\ \text{cm}^3/\text{s}\ [24] \qquad (17)$$

$$O(^1S) + H_2O \rightarrow OH + OH \quad k_{16} = 5.0 \times 10^{-10}\ \text{cm}^3/\text{s}\ [24] \qquad (18)$$

Excited oxygen atoms $O(^1D)$ and $O(^1S)$ are produced together with atoms in the ground state $O(^3P)$ via reaction (7) but since the yield of atoms in higher excited states is low and the rate constant corresponding to reaction of atoms in ground state is also low reactions (17), and (18) could be competitive with reactions (19), and (20)

$$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2 \quad k_{17} = 1 \times 10^{-10}\ \text{cm}^3/\text{s}\ [5] \qquad (19)$$

$$O(^1S) + CO_2 \rightarrow O(^1D) + CO_2 \quad k_{18} = 3.6. \times 10^{-13}\ \text{cm}^3/\text{s}\ [5] \qquad (20)$$

However if we evaluate the concentrations of water $[H_2O]$ in the discharge needed for either of these reactions to be dominant in the plasma the following conditions should be fulfilled

$$[H_2O] \geq \frac{k_{17}[CO_2]}{k_{15}} \qquad (21)$$

$$[H_2O] \geq \frac{k_{18}[CO_2]}{k_{16}} \qquad (22)$$

It can be easily find that the water concentration at pressure 760 Torr (from (5) for reaction (19) to be important would have to be ~45 % and a value of 720 ppm would be necessary for reaction (20) from (6) to be important. It is then evident that in the present experiments with humidity 7000 ppm reaction (20) may be important but the amount of $O(^1S)$ is still small compared with $O(^3P)$.

The second mechanism that can lead to reductions in the ozone concentration is chemical decomposition initiated by addition of water. The direct reaction of ozone with water molecule can be neglected because the rate constant is of order 1.0 × 10^{-22} cm^3/s [25] but ozone decomposition may be induced through catalytic kinetics (19), and (20)

$$O_3 + OH \rightarrow HO_2 + O_2 \quad k_{19} = 6.5 \times 10^{-14}\ \text{cm}^3/\text{s}\ [15] \qquad (23)$$

followed by

$$O_3 + HO_2 \rightarrow 2O_2 + OH \quad k_{20} = 2.0 \times 10^{-15}\ \text{cm}^3/\text{s}\ [15] \qquad (24)$$

producing once again the highly active radical OH. The initial radical OH is either produced via (18) or (25)

$$e + H_2O \rightarrow H + OH + e \quad k_{21} = 2.6 \times 10^{-12}\ \text{cm}^3/\text{s}\ [15] \qquad (25)$$

Hydrogen atoms produced by (25) also contribute to ozone destruction

$$O_3 + H \rightarrow O_2 + OH \quad k_{22} = 2.8 \times 10^{-11}\ \text{cm}^3/\text{s}\ [15] \qquad (26)$$

Moreover the process (26) contributes to the catalytical cycle (23 and 24).

5. Conclusions

The experiments presented have confirmed that the formation of ozone is important in characterising the properties of the corona discharges in carbon dioxide. The effect is more pronounced in negative corona discharge and depends strongly on the humidity of CO_2. Below 1500 ppm the effect is marginal but at higher values (up to 7000 ppm) the presence of water leads to a strong decrease in ozone concentrations. Using the literature we have attempted to explain these phenomena but a mass spectrometric study of ions extracted from discharge gap is necessary for further conclusions. Furthermore, in order to quantify these arguments we now need to develop a physico-chemical simulation of the discharge.

Acknowledgements

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