Plasma decay in O_2:CO_2 mixtures after high-voltage nanosecond discharge

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Plasma decay after a high-voltage nanosecond discharge has been studied experimentally and numerically in O_2:CO_2 mixtures for room gas temperature and pressures between 1 and 15 Torr. Time-resolved electron density history was measured by a microwave interferometer for initial electron densities in the range $(1\text{-}3)\times10^{12}$ cm^{-3}. Effective three-body recombination coefficient was determined for O_2^+ ions and thermal electrons.

1. Introduction

In a gas discharge, a non-equilibrium plasma can be generated in which the electron energy distribution differs substantially from a Maxwellian one, the characteristic electron temperature is much higher than the temperature of heavy particles, and the chemical composition and ionization and excitation degrees of the gas are strongly non-equilibrium. Decay of a non-equilibrium plasma after power removal is a complex process when different plasma parameters vary concurrently. Therefore, in the general case, the description of nonequilibrium plasma decay should consider the kinetics of charged and excited particles, as well as the evolution of electron energy distribution.

There is reason to believe that consideration of plasma decay in the afterglow of a high-voltage nanosecond discharge could be simplified because in this discharge it is possible to generate high electron densities under conditions when the density of excited particles is too low to affect the production and loss of charged particles. In this case, the electron energy distribution is Maxwellian due to electron–electron collisions and it is sufficient to consider relaxation of the electron temperature rather than that of the electron energy distribution. In addition, the high-voltage nanosecond discharge produced by a fast ionization wave in a gas is highly uniform and can occur in a large volume. As a result, the loss of electrons due to diffusion is negligible at not-too-low pressures and the discharge afterglow becomes a convenient object to study electron–ion recombination.

Previous studies of nanosecond plasma decay in oxygen and air showed that the rate of three-body electron recombination with O_2^+ ions is an order of magnitude higher than the rate of three-body electron recombination with atomic positive ions [1, 2], the process that has been well studied. This effect can be explained by the dissociative channel of the destruction of highly excited neutral systems formed due to electron capture by a positive molecular ion [3]. The disadvantage of the previous studies [1, 2] was that the plasma lifetime was comparable with the characteristic time of electron temperature relaxation. In this case, the rate of three-body electron-ion recombination was varied in time and its value was difficult to determine because little is known about its dependence on electron temperature.

The purpose of this work was to study plasma decay after a high-voltage nanosecond discharge in O_2:CO_2 mixtures. The mixture composition was selected such that the dominant positive ion was O_2^+, whereas, due to efficient electron-impact vibrational excitation of CO_2 molecules, the time of electron temperature relaxation was much shorter than the time of plasma decay. As a result, it was possible to study recombination of O_2^+ ions with thermal electrons.

2. Experimental setup

The experimental setup and the method to measure electron density in the discharge afterglow have been described in detail elsewhere [1, 4]. The discharge occurred in a quartz tube with inner diameter 47 mm. The metallic electrodes were located at the ends of the tube. The high-voltage and ground electrodes were, respectively, a cone of angle 60° at its vertex and an earthed ring. The distance between the electrodes was 20 cm.

Observations were made in O_2:CO_2 mixtures at room temperature for gas pressures between 1 and 15 Torr. The mole fraction of CO_2 was varied from 5 to 20%. Pulses of amplitude 11 kV in cable, duration 25 ns at half-height and rise time 5 ns were supplied to the electrodes from a high-voltage generator. The amplitude and wave shape of the pulses were measured using a back-current shunt. The energy input did not exceed 0.1 mJ cm^{-3}.

The temporal evolution of electron density in the discharge afterglow was studied with a two-channel microwave interferometer. The frequency of a reference wave was 9.4×10^{10} Hz (a wavelength of 3 mm). A probing signal passed twice through the plasma and returned to the antenna and waveguide to interfere with the reference signal.

For a plane uniform plasma layer, the phase shift of the probing signal, $\Delta\Phi(t)$, is related to the electron density $n_e(t)$ in the following way [5]:

$$n_e(t) = \frac{2\varepsilon_0 mc}{e^2}\frac{\omega\Delta\Phi(t)}{l} \qquad (1)$$

where m is the electron mass, ε_0 is the permittivity of vacuum, c is the light speed in vacuum, e is the elementary charge, ω is the angle frequency and l is the path length of the beam through the plasma. In (1), it was assumed that $\nu_m << \omega$, where ν_m is the frequency of electron momentum relaxation in collisions with other particles. This inequality was satisfied in the pressure range studied. In the case of a non-uniform plasma, such measurements provided electron density averaged over the diameter of the discharge tube. The uncertainty of the electron density measurements was generally around 20–30% and could increase to 70% in the early (<0.3μs) afterglow at low pressures due to imperfect calibration when the phase shift was close to π/2.

3. Kinetic scheme

To simulate the loss of charged particles in the afterglow of the nanosecond pulsed discharge, we numerically solved a system of balance equations for electrons and ions. The kinetic scheme used in this work considered the loss of electrons due to recombination with simple positive ions produced in the discharge and formation of complex positive ions in the discharge afterglow. This effect could be important because the rate of recombination with complex ions is an order of magnitude higher than that of recombination with simple molecular ions. In addition, we considered three-body electron attachment to O_2 molecules, the process that could be important at not-too-high electron energies and sufficiently high gas pressures.

The rates of electron processes depend on the average electron energy that reaches several eV in the discharge phase. In the discharge afterglow, electrons are cooled in elastic and inelastic collisions with cold molecules. In addition, during this phase electrons could be heated due to electron–ion recombination in which low-energy electrons are lost more efficiently. As a result, the average electron energy becomes somewhat higher. To control the effect of electron heating on the rate of plasma decay, we simulated the time evolution of the average electron energy in the discharge afterglow.

In our simulation, it was assumed that the electron energy distribution is a Maxwellian one. This assumption was satisfied because, under the conditions studied, the frequency of electron–electron collisions, ν_{ee}, was much higher than the frequency of electron energy relaxation in collisions with molecules, ν_ε. For instance, we have $\nu_{ee}/\nu_\varepsilon \sim 10^2$ in O_2:CO_2 mixtures studied for 3 Torr, mean electron energy of 0.1 eV and $n_e = 10^{12}$ cm^{-3}. In this case, to study electron thermalization, we numerically solved the equation for the evolution of the electron temperature, T_e, in the discharge afterglow. This equation took into account the loss of electron energy in elastic and inelastic electron-molecule collisions and "recombination heating" due to the loss of low-energy electrons in recombination with positive ions.

The initial value of T_e was assumed to be 1 eV, an estimated value of the effective electron temperature in the discharge. The calculated results are not sensitive to this magnitude because the rate of electron thermalization decreases sharply with decreasing electron energy. In fact, hot electrons quickly lose their energy in the inelastic collisions with excitation of electronic states of O_2 and CO_2 molecules; however, when the electron energy decreases below the energy threshold of these processes, electrons relatively slowly become cold in the elastic and inelastic collisions with excitation of vibrational and rotational levels of molecules.

4. Results and discussion

Most studies were made in an O_2:CO_2=9:1 mixture. Such a mixture composition ensures that positive ion composition is dominated by oxygen ions, whereas a 10% addition of CO_2 leads to electron temperature relaxation prior to plasma decay (see figure 1). Therefore, the plasma decays at constant electron temperature which is equal to T = 300 K.

Variation of CO_2 mole fraction in the mixtures studied from 5 to 20%, the gas pressure being the same, did not affect noticeably the measured data of electron density history. The experiments were made for gas pressures from 2 to 15 Torr.

Figure 2 shows the measured evolution in time of the electron density during the plasma decay in a O_2:CO_2=9:1 mixture at 10 Torr. Calculated electron history is also presented in this figure. Little is known about the rate of three-body electron

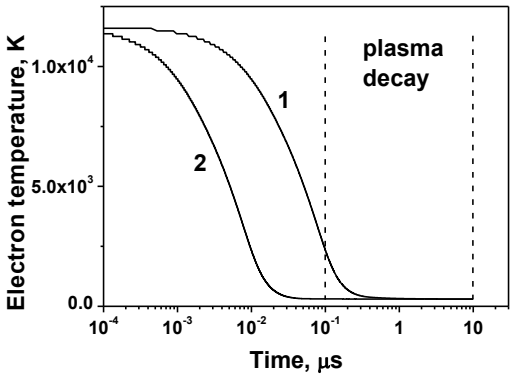

Figure 1. Evolution in time of the electron temperature in an O_2:CO_2=9:1 mixture for 1 (curve 1) and 10 Torr (curve 2).

recombination with molecular ions. Its value is usually taken by analogy with the similar rate for atomic ions, although the difference between the three-body recombination rates can be an order of magnitude and higher [3]. We made calculations changing the rate of the process

$$2e + O_2^+ \rightarrow \text{neutral products} \qquad (2)$$

from k_3(300 K) = 10^{-19} cm^6/s, a typical value for atomic ions (see [1, 2]), to 10^{-18} cm^6/s, the value suggested in [1, 2]. Agreement between measurements and calculations is much better for k_3(300 K) = 10^{-18} cm^6/s.

We also made an attempt to analytically derive the value of the three-body electron-ion recombination coefficient from measured electron density history. The recombination coefficient was obtained taking into account this process, dissociative electron-ion recombination and three-body electron attachment to O_2 molecules. It was assumed that positive ion composition is dominated by O_2^+ ions and that the density of negative ions is much lower than the electron density. This model does not take into account electron recombination with complex ions that can be important in the final phase of plasma decay, especially for high gas pressures. In this simplified model, the three-body recombination coefficient is obtained from an analytical solution of the system of three differential equations using the measured electron density history.

Figure 3 shows the obtained values of the recombination coefficient for the electron density data shown in figure 2. The value of k_3 varies slightly in time because the model used is oversimplified. However, the obtained results can be used to estimate the rate of three-body recombination. Its value is much higher than k_3(300 K) = 10^{-19} cm^6/s, the rate coefficient for recombination of atomic ions, and is close to k_3(300 K) = 10^{-18} cm^6/s, the rate suggested in [1, 2].

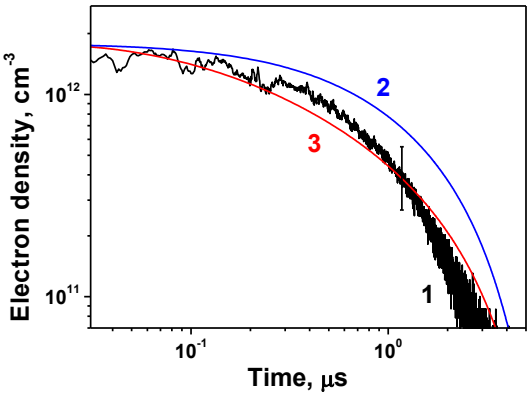

Figure 2. Evolution in time of the electron density in an O_2:CO_2=9:1 mixture for 10 Torr. Curve 1 corresponds to measurements. Calculations were made for k_3(300 K) = 10^{-19} (curve 2) and 10^{-18} cm^6/s (curve 3).

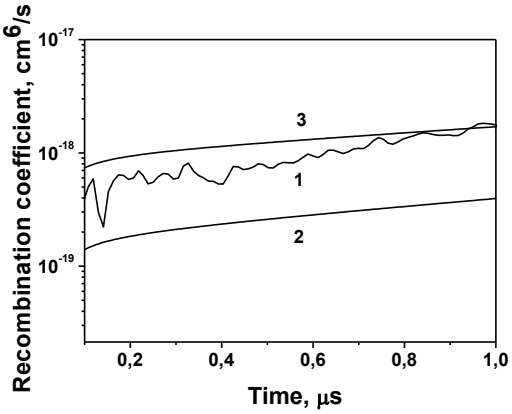

Figure 3. Effective three-body electron-ion recombination rate coefficient in an O_2:CO_2=9:1 mixture for 10 Torr. Curve 1 is obtained from measurements. Curves 2 and 3 correspond to calculations for k_3(300 K) = 10^{-19} and 10^{-18} cm^6/s, respectively.

In the studied pressure range, the estimated value of k_3 increases with gas pressure. This could be explained in the following way. Three-body electron recombination is a multi-step process in which highly excited Rydberg molecules are formed when a free electron is captured by a molecular ion. Rydberg molecules can be re-ionized or "stabilized" in collisions with other particles. However, these molecules have some states that are capable of dissociating into products that cannot be re-ionized

[3]. Transitions to these states can be due to collisions with neutral particles and this favors electron-ion recombination. Therefore, the effective recombination rate may increase with gas pressure.

Figures 4 and 5 show, respectively, the calculated evolution in time of ion composition and frequencies of electron loss in an O_2:CO_2=9:1 mixture for 10 Torr assuming k_3(300 K) = 10^{-18} cm^6/s. It follows from the curves in these figures that, between 0.1 and 1 μs, the period of time when most experimental observations were made, the dominant positive ion is O_2^+ and the dominant process of electron loss is three-body electron recombination with O_2^+ ions.

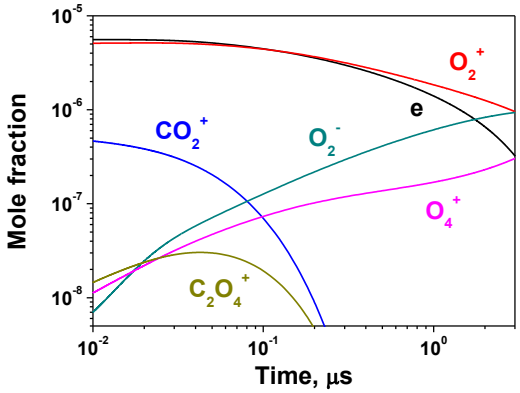

Figure 4. Evolution in time of electron and ion mole fractions in an O_2:CO_2=9:1 mixture for 10 Torr.

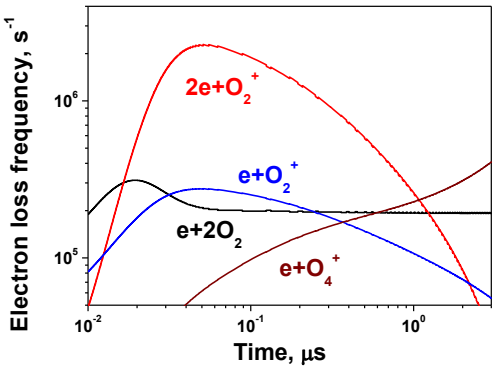

Figure 5. Evolution in time of the rates of electron loss in an O_2:CO_2=9:1 mixture for 10 Torr.

5. Conclusions

We have studied experimentally and numerically plasma decay after a high-voltage nanosecond discharge in O_2:CO_2 mixtures under conditions when the dominant positive ion is O_2^+ and electrons are thermalized. From the analysis of measured time-resolved electron density histories, the rate of three-body recombination for thermal electrons with O_2^+ ions was obtained. The value of the recombination coefficient is much higher than that for atomic ions and is close to that suggested in [1, 2]. The mechanism of an increased value of three-body recombination rate for molecular ions can be associated with an additional dissociation channel of stabilization of highly excited Rydberg molecules that are formed when a free electron is captured by a molecular ion [3].

6. Acknowledgements

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7. References

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