Optical diagnostics and numerical modeling of nanosecond capillary pulsed discharge in CO_2

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Abstract: Optical and electrical diagnostics of nanosecond discharge ignited in pure CO_2 at gas pressure 15.5 mbar was performed. The reduced electric fields of 250-300 Td and the electric current of 130 A were registered after the front of the fast ionization wave. The numerical modelling of the discharge has shown that the vibrational kinetics is not dominant in the case of high electric fields whereas the excitation of electronic levels of CO_2 with their consequent dissociation onto CO and O plays the leading role as like as the dissociative attachment of electrons to CO_2^+ ions.

Keywords: Nanosecond discharge, carbon dioxide, plasma assisted conversion

1.Introduction

Plasma assisted conversion of carbon dioxide is the object of a strong scientific interest since 1960s. Excitation of vibrational degrees of freedom of molecules of carbon dioxide in discharge plasma at relatively low reduced electric fields of tens (20-50) Td plays the dominant role in plasma assisted conversion of CO_2. It was shown in [1,2]. It was also shown there that the energy efficiency of the dissociation is the most in this case because the minimal electron energy (5.5 eV) is required for dissociation of a CO_2 molecule. However, the dissociation rate remains low when vibrational kinetics is dominant. Excitation of higher (7.2 and 10.5 eV) electronic states with their consequent dissociation onto CO and O becomes the dominant mechanism at the reduced electric fields of hundreds of Td. It requires more electron energy and thus provides less energy efficiency and more dissociation yield than in the case of lower electric fields.

The goal of the study described here is to understand better the case of dominant electronic excitation of molecules of carbon dioxide as well as their consequent dissociation. The nanosecond discharges seem to be a good instrument for the announced purpose since they provide comparatively high electric fields.

2.Experiment

The nanosecond pulses of positive polarity were produced by a high voltage generator. The pulses were delivered to the discharge capillary by a system of high voltage cables. The diameter of the capillary was 1.7 mm and the distance between the electrodes was 75 mm. The discharge was generated by a high voltage pulse with a maximal voltage of 10 kV. The rise time of the pulse was 4 ns and the FWHM was 30 ns. The highest electric current (130 A) was observed at the pressure of 15.5 mbar.

The electric field in plasma was measured by a custom made calibrated capacitive probe. The values of the E/N reached 1200 Td in the front of the fast ionization wave and were around 300 Td behind the front. The synchronized in time waveforms of the reduced electric field and of the electric current are given in Fig.1.

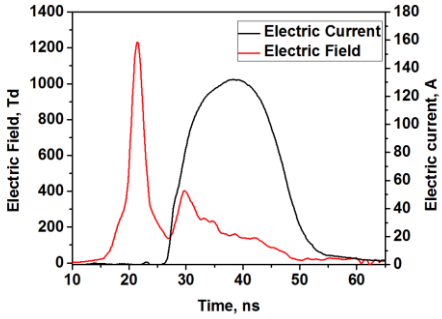

Fig. 1. The profiles of the reduced electric field and electric current

The plasma components were studied by the means of optical emission spectroscopy. A spectrometer Princeton Instruments Acton Series SP-2500i combined with an ICCD-camera Princeton Instruments PI-Max 4 was used for acquisition of emission spectra of the discharge. The second order of diffractional grating was removed by using broad-band filters at the wavelengths higher than 400 nm. The emission was acquired in the spectral range of 200-900 nm (see Fig.2). The correction of sensitivity of ICCD camera and spectrometer wasn't made.

The molecules were represented by CO_2^+ ion's systems: CO_2 flame system (doublet at 288 and 289 nm) and the system of Fox, Duffendack and Barker (FDB, 310-420 nm). The CO molecule was represented by the 4th positive system (200-270 nm). The group of molecular bands in the range of 430-475 nm was not identified. The atomic lines

corresponding to C (248 nm) and O (777 nm, 844 nm) were observed.

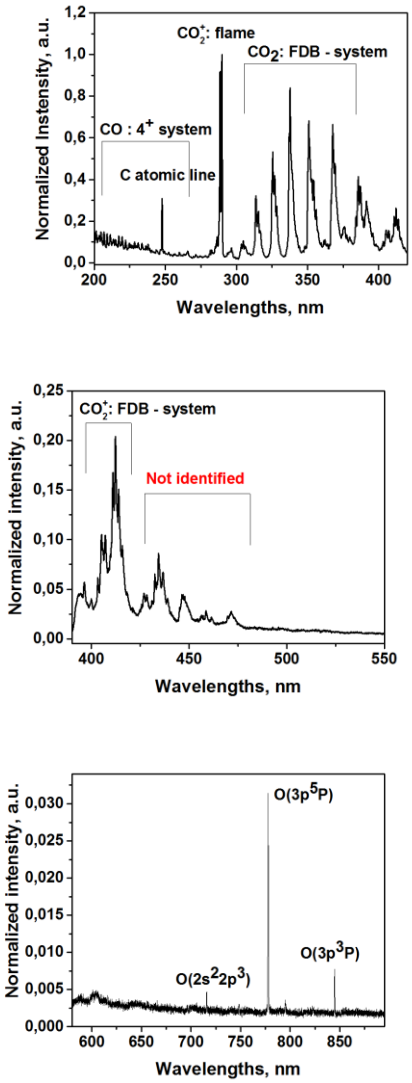

Fig 2. The emission spectrum acquired in the 200-900 range. The main lines bands are marked.

3.Numerical modeling

The zero-dimensional numerical modeling of the discharge was done by the means of non-commercial open source ZDPlasKin code [3]. The code uses the experimental data of the electric field and the initial density of carbon dioxide as the input data. The initial electron density was chosen in such a way that the electric current measured experimentally matches the calculated current.

The kinetic scheme was based on the scheme [4] and included 31 species (electrons, neutral atoms in their ground and excited states, ions and clusters). The cross-sections of the reactions of interaction of electrons with neutral CO_2 with formation of CO, O, CO_2^+ and other ions were taken from [5]. The reactions of formation of electronically excited species [6] as far as their radiative decay [7] were added to the initial scheme in order to describe the emission. The rate and sensitivity analysis have shown that the excitation of electronic levels of CO_2 with their consequent dissociation is the dominant mechanism of conversion of CO_2 onto CO and O; the dissociative attachment of electrons to CO_2^+ plays an important role as well.

4.Conclusion

Stable nanosecond capillary discharge in CO_2 was observed. The maximal value of the electric current (130 A) and the electric field (1200 Td in the front of the fast ionization wave, 300 Td after the front) were recorded at the pressure of 15.5 mbar. The optical emission spectra were acquired in the range of 200-900 nm and the lines of C, O, CO and CO_2^+ had been observed. The numerical modeling of the discharge has shown that the electronic excitation of neutral CO_2 as like as dissociative attachment of electrons to positive ions are the most dominant mechanisms of dissociation of carbon dioxide in the discharge.

5.Acknowledgements

The work was partially supported by French National Research Agency, ANR (ASPEN Project), LabEx Plas@Par and the French-Russian international laboratory LIA KaPPA “Kinetics and physics of pulsed plasmas and their afterglow”. The authors are grateful to Dr. Elena Filimonova (JIHT RAS, Moscow) for helpful advice on CO_2 kinetics.

References

[1] A. Fridman. Plasma Chemistry, Cambridge University Press (2008)

[2] D.Rusanov, A.Fridman, G.Sholin, UFN (1981)

[3] N.D Lepikhin, Thèse de doctorat de l’Univeristé Paris Saclay (2017)

[4] S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, L.C. Pitchford, University of Toulouse (2008)

[5] T. Kozak and A. Bogaerts, PSST (2014)

[6] J. M. Ajello, Journal of Chemical Physics (1971)

[7] O. Zatsarinny and K. Bartschat, J. Phys. B: At. Mol. Opt. Phys. (2004)