Understanding of CO_2 decomposition in microwave plasma by optical plasma diagnostics methods

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Abstract: This work is related to different optical plasma diagnostics methods which have been used for integrated characterization of CO_2 decomposition in pulsed surfaguide microwave discharges operating in CO_2, CO_2-Ar and CO_2–N_2 gas mixtures. The results obtained by a combination of optical emission spectroscopy, optical actinometry, absorption spectroscopy with gas chromatography technique are presented and analyzed.

Keywords: plasma diagnostics, microwave discharge, OES, CO_2 conversion, OAS, gas chromatography

1. Introduction

Carbon dioxide (CO_2) is one of the main greenhouse gases emitted as a result of human activities, which makes the study of CO_2 dissociation highly demanding issue nowadays, requiring a special attention and efficient solutions. Considerable research is currently being carried out on the dissociation of CO_2 for a wide range of industrial applications, including treatment at the power plants and production of valuable chemicals, e.g., for the fuel synthesis (syngas) [1-3]. Among the different approaches proposed for CO_2 dissociation, the cold plasmas have a great potential for molecular decomposition [1], namely due to the high degree of non-equilibrium and high selectivity achieved for plasma chemistry. During the last decade the numerous studies have been undertaken concerning the CO_2 molecular dissociation in cold plasmas, both in scientific and industrial domains [4-6]. In spite of these works, the kinetic mechanisms of CO_2 dissociation are not yet well-understood. In fact, CO_2 dissociation in plasma keeps attracting the attention of many researchers who study the chemistry of this molecule with accurate models for a particular plasma reactor [7-9]. In order to validate these theoretical results is crucial to have a good experimental approach that provides a way of studying many important plasma parameters. Therefore, the aim of this work is to develop different plasma diagnostics methods for the understanding of the discharge chemistry in CO_2-containing discharges with focus on the decomposion process.

2. Experimental set-up

In this study a pulsed microwave plasma surfaguide discharge (MSGD) operating at moderate pressures (~ 10 Torr) is used. These types of discharges are already proven to be efficient sources of atomic species produced as a result of dissociation in the discharge volume [10]. The discharge was sustained inside a quartz tube with 14 mm of inner diameter, and 24 cm length surrounded by another (polycarbonate) tube for the cooling purpose. The inner tube was cooled down by 10 ◦C oil flow during the measurements. The gas mixture injected from the top of the system was regulated by electronic mass flow controllers. At the bottom of the quartz tube, an additional diaphragm was installed to maintain the pressure difference between the discharge and the post-discharge regions. A more detailed description of this system can be found in [10].

3. Plasma diagnostics results

3.1 – Discharge region

The plasma discharge region is analysed by Optical Emission Spectroscopy (OES). This diagnostic is an easy-to-implement non-intrusive technique, which is particularly useful to study a large variety of chemical processes in plasma. In our case, OES measurements were made along the discharge tube where the light from the plasma itself is recorded through an optical fiber as shown in Fig.1.

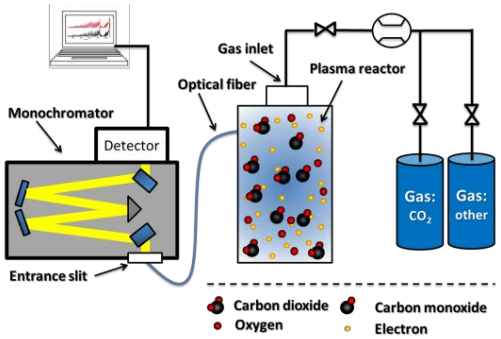

Fig.1. Schematic representation of a CO2-containing low temperature discharge.

In pure CO_2 discharges the main products which are observed by optical emission are atomic oxygen (O) and carbon monoxide (CO). Because of this, for diagnostic purposes, the plasma has also been generated in CO_2+N_2 and CO_2+Ar gas mixtures. A considerable amount of plasma physics knowledge has been extracted from the plasma emission spectra. For instance, the characteristic plasma temperatures, such as gas temperature (T_{gas}) (via CO rotational bands), vibrational temperature (T_{vib}) (via N_2 vibrational bands), and electron temperature (T_e) (via Ar excited states) can be determined as a function of time at different axial positions along the gas flow in the discharge tube. In Fig.2 the gas temperature is obtained for a pure CO_2 discharge during a single plasma pulse using the experimental CO Angstrom ($B^1\Sigma^+ \rightarrow A^1\Pi$) band spectra. The time-resolved temperature measurements were analyzed using three different approaches (see Fig. 2). These results show that, at a fixed energy delivered per plasma pulse (E_p), the gas temperature grows at the beginning of the pulse followed by saturation after about 0.4 ms. These effects were observed previously for other gas mixtures in the same type of discharges [11]. More details can be found in [12] where a peak-ratio method is proposed for the evaluation of gas temperature.

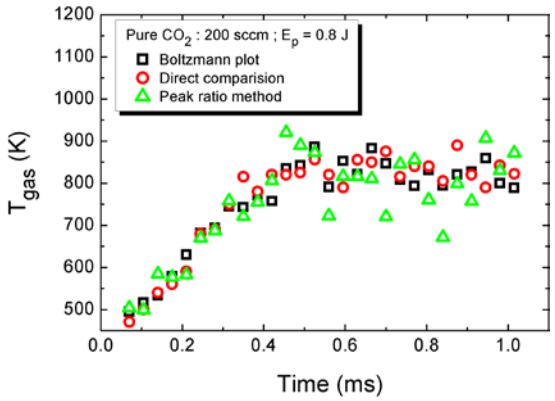

Fig. 2. Time evolution of gas temperature determined based on the CO rotational band using the Boltzmann method (black squares), direct spectral comparison with simulated spectra (red circles), line ratio method (green triangles).

The conversion rate of CO_2 has been measured by optical actinometry in CO_2+N_2 gas mixtures. N_2 molecule is chosen as an actinometer due to the proximity of the N_2(C) (11.05 eV) and CO(B) (10.78 eV) excited states. Under the assumption of the corona model, it becomes possible to relate the concentration of the excited states to the ground states ones. A linear proportionality between the dissociation degree and the energy per molecule (E_m) is obtained, as shown in Fig.3. At the same time the plasma energy efficiency was found to be constant for different E_m. A detailed description of the actinometry method can be found in [13].

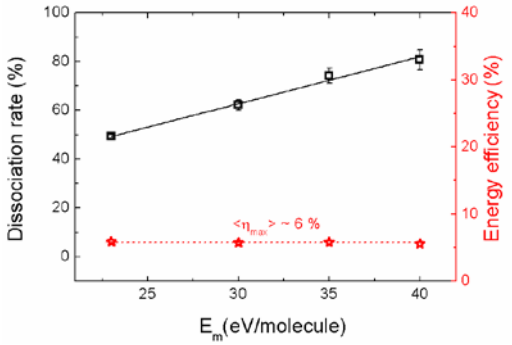

Fig. 3. CO2 dissociation rate (left scale) along with its energetic efficiency (right scale) as a function of the energy supplied per molecule.

Electronic parameters are obtained in Ar and CO_2-Ar gas mixtures. It's worth noting that in most of plasmas involving argon, the four levels from the first excited configuration ($1s_5$, $1s_4$, $1s_3$, $1s_2$) can have high population densities and serve as energy reservoirs in chemical reactions. The densities of these states are determined in this work by self-absorption employing the radiation escape factor (self-absorption) concept [14-15]. As an example of this method, Fig.4(a) shows a decrease of densities for the 1s Ar states with an increase of power in a pure Argon discharge. This trend is likely to be linked with an increase in the ionization rate due to pooling reactions and ionization collisions of electrons with the $1s_j$ levels [16]. Finally, the electron temperature can be estimated using an extended corona model associated to different experimental line ratios from different radiative states [17], while the electron density (n_e) is estimated from the balance between different creation and loss mechanims of metastable states. Fig. 4(b) shows a linear increase of electron density with the power, while the electron temperature remains approximately constant.

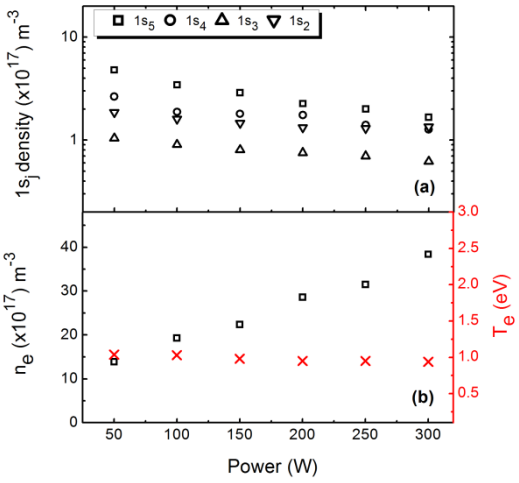

Fig. 4. (a) Densities of Ar 1s states measured by self-absorption. (b) Electron density (left scale) measured from the balance between creation and loss mechanims of metastable states. Electron temperature (right scale) measured from the balance between creation and loss mechanims of radiative states.

3.2 – Post-discharge region

In order to get a complete picture of the decomposition process, measurements on the post-discharge region have been performed by two different techniques: (i) Resonant Optical Absorption Spectroscopy (ROAS) and (ii) Gas Chromatography (GC). The ROAS diagnostic is described in [18] and used here to measure oxygen metastable species in CO_2 gas mixtures. Fig.5 shows an increase of oxygen metastable density (possibly related to an increase of CO_2 conversion rate with the applied power, as observed previously in the discharge region).

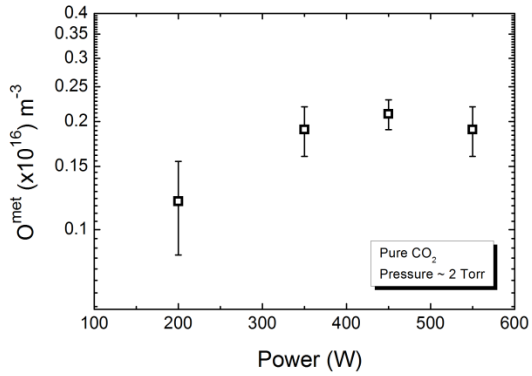

Fig.5. Density of oxygen metastables as function of the applied power.

The composition of the post-discharge has been also analyzed by a gas chromatograph (Bruker) equipped with a carbon molecular sieve column and a Molecular sieve 5A column in series and connected to a thermal conductivity detector. Argon was used as a carrier gas (see Fig.6). The low pressure sample is diluted with neutral gas prior to its injection in the chromatograph. For pure CO_2 discharges the following products were detected by gas chromatography: CO_2, CO, and O_2.

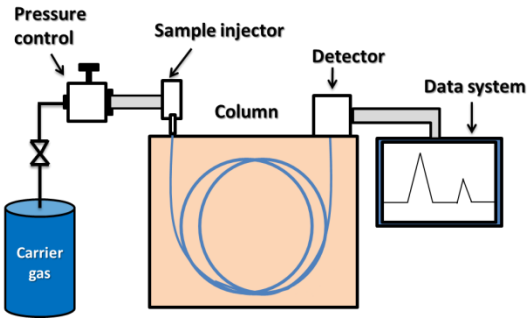

Fig.6. Schematic representation of the gas chromatograph used in CO_2 low temperature discharges.

The molecular percentage of the decomposition products (χ) is studied as a function of different experimental parameters. Fig.7 shows the evolution of CO_2 conversion as a function of the pressure in the discharge for different values of energy per molecule of CO_2. In general statement, the conversion of CO_2 increases with the pressure in the plasma. An increase of

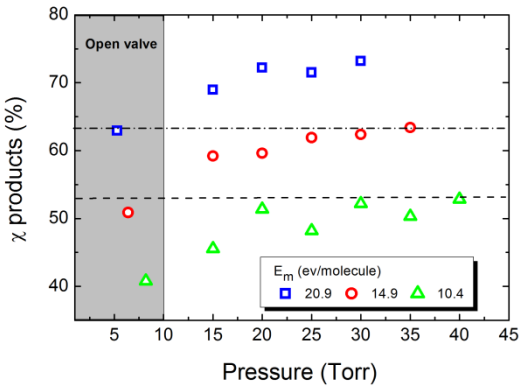

Fig.7. Comparision of the percentage of decomposition products as a function of pressure for different specific energy inputs.

about 10% in the percentage of decomposition products is obtained for the range (5-40 Torr) of pressures used. This effect should be associated to an increase of the electron density and electron-neutral collision rate which leads to an increase of conversion rate. In Fig.8 is shown the evolution of the decomposition process as a function of the duty cycle in plasma pulse for different values of energy per molecule of CO_2. In this case, the mean power is kept constant and the conversion rate increases about 10% when the duty cycle changes from 5 to 50%. This trend might be linked to a decrease of gas heating (already observed in [19] for N_2 discharges in the same kind of reactor) with an increase of duty cycle.

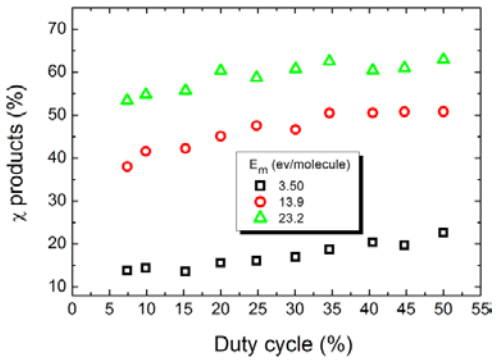

Fig.8. Comparision of the percentage of decomposition products as function of duty cycle for different specific energy inputs.

4. Summary

Pulsed microwave surfaguide discharges operating in CO_2-containing gas mixtures are characterized by several non-intrusive plasma characterization methods based on optical emission spectroscopy. Important plasma parameters such as the gas and electron temperature are measured from different plasma diagnostics. The plasma composition is also analysed by resonant absorption spectroscopy and gas chromatography. Based on these measurements it has been shown that the dissociation degree can be substantially modified by varying different experimental parameters such as the power balance and the plasma duty cycle. The combined set of the obtained data provides a deeper understanding and control of the CO_2 dissociation processes in the microwave frequency-based low temperature discharges.

5. Acknowledgments

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