Influence of carbon monoxide on CO_2 plasma

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Abstract: Herein, the influence of mixture composition in CO_2/CO DC glow discharge is studied by means of Fourier transform infrared spectroscopy. The mixing ratio was varied between 30 and 100 % of CO_2 concentration with total gas flow kept constant at a value of 7.4 sccm. It has been shown that with higher concentration of carbon dioxide the difference between the vibrational temperatures and the rotational temperature decreases.

Keywords: carbon dioxide dissociation, glow discharge, FTIR diagnostics, vibrational temperature.

1. Introduction

Carbon dioxide dissociation is studied in a wide range of applications, starting from CO_2 lasers to oxygen production on Mars. In recent years the emission of carbon dioxide has proven to be one of the main causes of global warming, which increased interest in CO_2 conversion. CO_2 can be dissociated in 3 different main ways, according to thermal, catalytic, and plasma-based processes. Major research efforts in carbon dioxide plasma chemistry have been reviewed by Fridman [1], who discusses the possibility of using non-thermal plasmas for CO_2 utilisation. It is believed that non-equilibrium plasmas are one of the best ways to reach high CO_2 conversion with high energy efficiency. Different types of discharges were used to demonstrate this claim, although CO_2 conversion and energy efficiency depend on the discharge type. For higher energy efficiency a stronger non-equilibrium is required, which can be reached easier at low pressure. In these conditions, a significant fraction of the electron energy is transmitted to the excitation of vibrational states, while the gas temperature remains low.

CO_2 molecule has 3 vibrational modes – symmetric stretch, bending and asymmetric stretch. The latter is believed to have an important role in dissociation process according to the following route. Most of the energy absorbed by electrons is transmitted to the excitation of the vibrational levels of the CO_2 asymmetric mode. Other processes, such as vibrational-vibrational or vibrational-translational energy transfers can depopulate the higher vibrational levels of the asymmetric mode and populate other modes of CO_2 or the internal modes of other species. One of the ways to prevent the loss of CO_2 asymmetric vibration and the quenching process of back reaction is by fast adiabatic cooling, when the composition achieved at higher temperature remains initially the same after quenching.

The products of dissociation of CO_2 are interesting for a variety of reasons. For example, carbon monoxide can be used as one of the ingredients of syngas ($CO + H_2$) production and be a key ingredient in the production of solar fuels. Another dissociation product is oxygen, which can play a very important role in further enhancing dissociation through reaction:

$$CO_2^* + O \rightarrow CO + O_2 \tag{1}$$

On the other hand, recombination of the oxygen atoms with CO molecules leads to a decrease of the conversion degree:

$$CO + O + M \rightarrow CO_2 + M \tag{2}$$

Besides, O_2 can be relevant for oxygen production on Mars. Indeed, the low temperature and low pressure of Martian atmosphere can be an ideal environment for CO_2 plasma dissociation [2].

Although methods to promote high dissociation degrees and high energy efficiencies in CO_2 plasmas are being actively pursued, many fundamental aspects of the plasma are still understudied. One of these is the influence of the CO_2/CO ratio in the discharge. To address this question, low-pressure DC glow discharges are uniform, well-known and reproducible, and form therefore a perfect system for understanding the influence of the mixture composition in the overall discharge behaviour. In this work we report a thorough experimental characterization of these plasmas.

2. Experimental setup

In situ Fourier transform infrared (FTIR) spectroscopy is used in order to detect and accurately determine the vibrational state densities in the plasma. The plasma reactor under study is a cylindrically shaped Pyrex tube, with a 2 cm inner diameter and a length of 23 cm. The electrodes are positioned 17 cm apart, opposite to the gas in- and outlet. The reactor is connected in series with a 40 kΩ resistor to a DC power supply.

The incoming gas consists of the mixture of CO_2 and CO, where the CO_2 concentration is varied between 30 and 100%. The total gas flow is controlled at 7.4 sccm using a mass flow controller (Bronkhorst). The pressure is maintained constant at a value of 2 Torr, using a scroll pump (Edwards), and a pressure gauge (Pfeiffer) with feedback to an automated pressure regulating valve (Pfeiffer).

The reactor is positioned in the sample compartment of a FTIR spectrometer (V70 Bruker). The absorption spectrum is corrected and the emission spectrum is subtracted, as described in [3]. The detected IR spectrum contains several lines of CO and CO_2 vibrational transitions and was fitted according the procedure described in [3]. Only insignificant amounts of O_3 were detected in the spectra.

It is assumed that the rotational and vibrational temperatures are uniform along the length of the reactor and reach a steady state on relatively short distances from the entrance of the reactor. The temperature of the gas on the entrance of the reactor is assumed to be 300 K.

The reduced electric field in the reactor is measured with two metal pins radially pointing inside the positive column of the reactor.

3. Results

Figure 1 depicts dependency of the conversion factor α,

$$\alpha = \frac{[CO]}{[CO]+[CO_2]} \tag{3}$$

for different CO_2/CO mixing ratios without plasma ("plasma off measurements") and for the plasma discharge at a pressure of 2 torr and current of 40 mA. The plasma off measurements are an indication of the amount of the gas injected into the system and can be assumed as a base line for α. After turning the plasma on the amount of CO in the system increases due to dissociation. For low concentrations of CO_2, α for plasma on approaches the plasma off values, which means that the mixture is reaching chemical equilibrium. In other words, most of the produced CO is recombining back into CO_2. On the other end, for the higher concentrations of CO_2, there is a bigger difference between on and off α values, and thus a higher dissociation. Notice that the concept of conversion factor α, as defined in equation (3), is somewhat misleading for a CO_2/CO mixture. For this reason we have introduced a new parameter, α^*, defined in the same way as above but only with the concentration of created CO molecules and not their total value. α^* is represented on the figure 1 as red dashed curve with open symbols.

The behaviour of different temperatures as a function of the CO_2 percentage is presented in figure 2. T_{12} represents the vibrational temperature of the CO_2 symmetric and bending modes, T_3 the vibrational temperature of the CO_2 asymmetric stretching mode, T_{CO} the vibrational temperature of CO and T_{rot} the rotational temperature of CO_2, assumed to be the same as the gas temperature. The vibrational temperatures T_3 and T_{CO} decrease with the CO_2 content. T_{12} deviates from the rotational (or the gas) temperature for the higher concentrations of CO. In this range, the difference between the vibrational temperatures and the rotational temperature increases. At the same conditions, the reduced field, depicted on the figure 2 in dotted line with open symbols, decreases with the CO concentration.

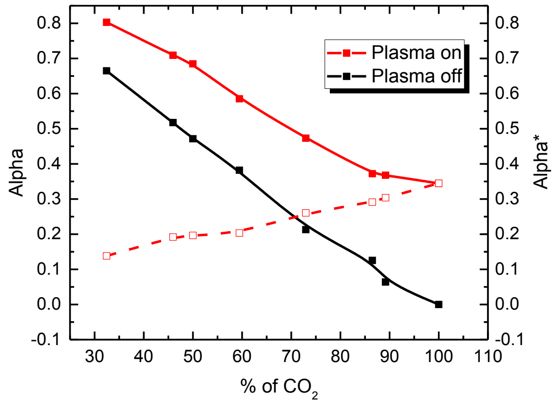

Fig. 1. Variation of the conversion parameters α (full curves) and α^* (dashed curve, see text), as a function of the CO_2 % in the gas mixture, at pressure 2 torr and current 0 (plasma off) and 40 (plasma on) mA

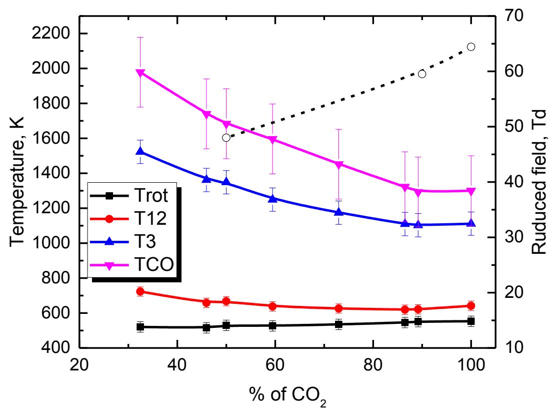

Fig. 2. Variation of the vibrational and rotational temperatures as a function of CO_2 % in the gas mixture (full curves, left axis) and reduced electric field (dashed curve, right axis), for a DC discharge at pressure 2 torr and current 40 mA.

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5. References

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