

Time-evolution of the CO₂ conversion studied by *in situ* FTIR absorption and isotopic exchange

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Abstract: The evolution of the building up of the equilibrium conversion in CO₂ plasmas is studied by means of infrared absorption in both DC glow and radio-frequency pulsed discharges. Varying different parameters, such as the pulse duration, and comparing with a OD kinetic model allow an estimation of the electron impact dissociation cross section. The use of isotopic oxygen in CO₂-O₂ gas mixtures makes possible a deep study of the impact of the back reaction (CO+O) in the steady-state CO₂ dissociation fraction.

Keywords: CO₂ plasma, electron impact dissociation, isotopic exchange, CO oxidation

1. Introduction

CO₂ plasmas are attracting a lot of interest nowadays due the current context of global warming and the increase of anthropogenic greenhouse gas emissions, along with the necessity of finding new sources of fuels and chemicals. Instead of considering CO₂ as a waste, it can be used as a raw material from which it is possible to generate more complex organic compounds, such as energy-dense hydrocarbon fuels, ideally creating a closed carbon cycle. The use of plasmas presents many advantages compared with traditional thermal dissociation methods, in particular with regard to the efficiency but also to the possibility to be integrated into the electrical network and take advantage of the available energy from intermittent renewable sources.

Many different types of discharges have been studied in the last years focused on trying to increase both the energy efficiency and the conversion. However some mechanisms, essential for describing the CO₂ plasma kinetics, are not yet well understood. This results in some discrepancies remaining between experimental data and model predictions, which makes difficult to conceive more efficient conversion processes. Among the processes that are still surrounded by large uncertainties, three of them are:

- The electron impact dissociation cross section which is critical since electron impact dissociation is one of the main dissociation mechanisms in certain types of discharges (glow, DBD, etc.) and is undoubtedly one of the most relevant processes involved in CO₂ plasmas. However, the cross section for this process is given in literature with very different values [1].
- The back reaction between CO and O under plasma conditions and its influence in the steady-state concentrations, which remains uncertain due to the difficulties to differentiate between the direct CO₂

dissociation and dissociation followed by recombination between CO + O.

- The role of the vibrationally excited molecules in equilibrium conversion of CO₂ since very few rates are available in the literature for many of the possible reactions involved, e.g. for CO_v*+O.

In order to gain insight about these processes we have designed an experiment so-called “building up”, which is performed in static conditions (closed reactor) in order to follow step by step the evolution of a fixed amount of CO₂ molecules. A defined number of plasma pulses are ignited while consecutive measurements of the CO and CO₂ concentrations by infrared absorption provide the time evolution of the equilibrium conversion up to the steady-state value. Knowing the characteristic time of the vibrational excitation in similar conditions (see example in figure 1) and varying the pulse duration and delay between pulses we can first give constraints to the value of the direct electron impact dissociation cross section. We can also discriminate between electron impact dissociation and the possible contribution of the vibrational up pumping mechanism to the CO₂ dissociation.

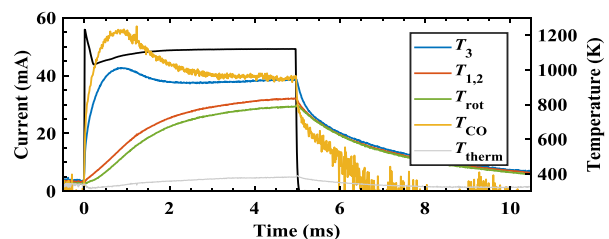


Figure 1: Evolution of the vibrational temperatures ($T_{1,2}$ and T_3) and the rotational temperature (T_{rot}) of CO₂ and the vibrational temperature of CO (T_{CO}) in a pulsed 5-10 ms On-Off CO₂ DC glow discharge at 4 Torr 50 mA [2].

The exchange of oxygen atoms between different molecules, and therefore the back reaction, is studied by adding a controlled amount of isotopic oxygen (O^{18}) to the initial gas mixture. The experimental results are compared with the results obtained with a OD kinetic describing the chemistry in the discharge.

2. Experimental setup, measurement procedure and fitting of the data

The plasma has been ignited in a cylindrical Pyrex (2 cm inner diameter and 23 cm length) plasma reactor positioned in the sample compartment of an FTIR spectrometer (Bruker, Vertex 70) with a spectral resolution 0.2 cm^{-1} . The FTIR is operated in Rapid Scan mode and the reactor is closed, therefore the experiments are performed in static conditions. Two types of discharges are studied and compared: glow discharge, powered by pulsed DC voltage, and pulsed radio frequency discharge.

Starting either from CO_2 or from a mixture of CO_2/O_2 , a train of plasma pulses (with a defined total plasma On time per train of 50 ms) is sent to the reactor. Subsequently a spectrum is acquired with the plasma Off. This procedure, schematically presented in figure 2, is repeated 500 times i.e. the total plasma On time is around 25s, long enough to reach the steady-state equilibrium. Several parameters are varied including the pulse duration (keeping constant the total plasma On time per train), the delay between pulses, pressure (in the range of 0.5 to 8 Torr), discharge power or gas mixture.

The FTIR spectra is fitted with an MATLAB script developed by Klarenaar *et al.* [3]. This script has been adapted to account for a set of 12 isotopes of CO_2 and 6 isotopes of CO recently included in HITRAN database.

The contribution of these different isotopes to the experimental spectra of CO_2 and CO can be clearly distinguished and fitted. An example of the fitting of a spectrum in thermal equilibrium including all the isotopes accounted for in the fitting script is shown in figure 3.

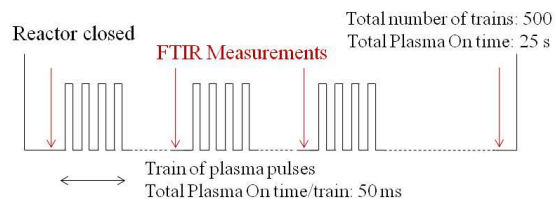


Figure 2: Scheme of the measurement procedure.

3. Results

An example of the time evolution of the dissociation fraction represented by the ratio between CO over ($CO_2 + CO$) as a function of the total plasma On time is shown in figure 4 for two pressures and two gas mixtures (100% CO_2 and 25% CO_2 -75% O_2^{16}). The initial slope (qualitatively pointed out in the graph), representing the dissociation from a mixture close to pure CO_2 , is dependent on the initial gas density and the power. Through the analysis of the data for different pulse duration and the comparison with the model, an estimation of the electron impact dissociation cross section is given, and it is found to be close to the theoretical values estimated by Polak and Slovetsky [4]. The comparison with other theoretical predictions is discussed. The steady state value of the dissociation fraction is strongly dependent on the power, pulse duration, the delay between pulses and the amount of

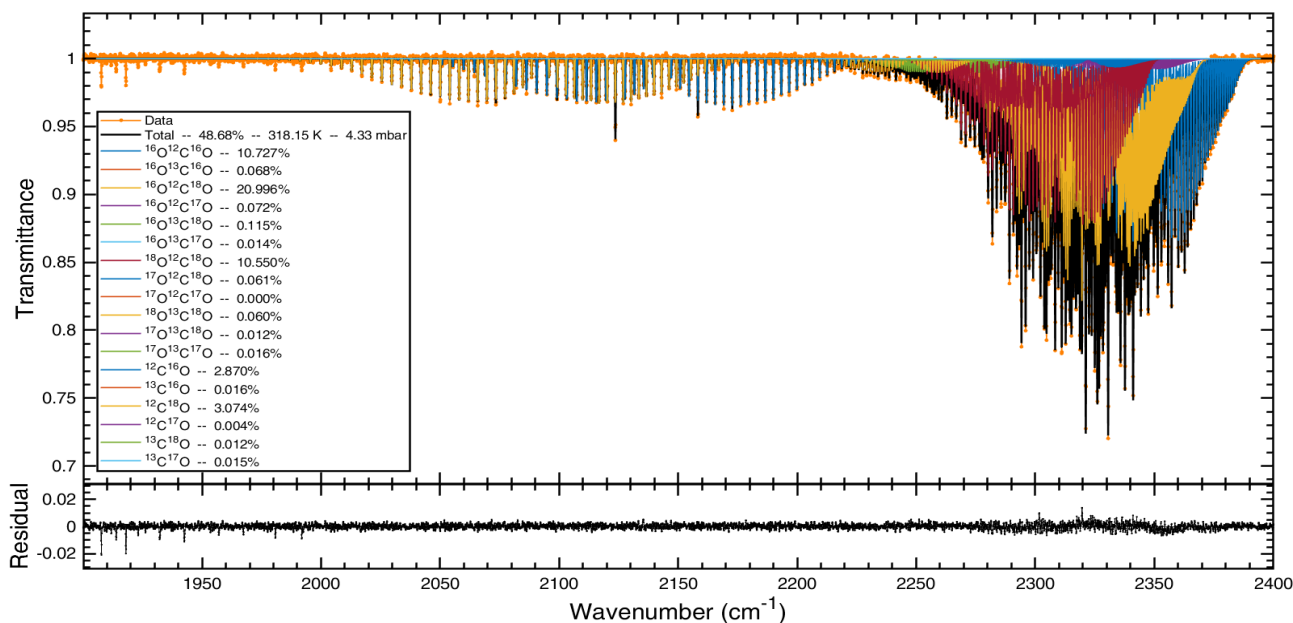


Figure 3: FTIR spectra obtained in a mixture of CO_2 - O_2 showing the bands corresponding to CO_2 and CO with the corresponding fitting accounting for the contribution of all the isotopes included in the fitting script.

oxygen content, showing the impact of both the back reaction and the vibrational excitation level of the involved molecules.

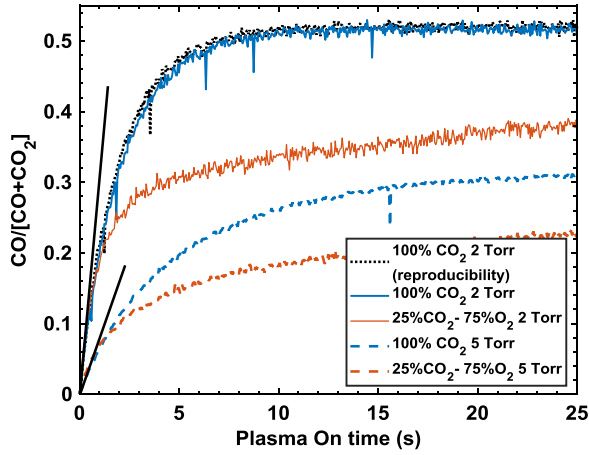


Figure 4: Evolution of $\text{CO}/[\text{CO}+\text{CO}_2]$ as a function of the total plasma On time for two pressures (2 and 5 Torr) and two different gas mixtures obtained with a pulsed RF plasma at 40 W. A reproducibility example is also shown and the initial slope is pointed out qualitatively indicated.

Similar experiments, for different CO_2/O_2 proportions, but using $\text{CO}_2^{16}-\text{O}_2^{18}$ mixture allow us to trace the exchange of oxygen atoms and follow the time evolution of the back reaction, showing a fast exchange of O atoms, faster than expected from literature. The isotopic tracing, made possible by the inclusion of new information in HITRAN

database, provides therefore a valuable insight in the chemistry of the plasma, and helps in decoupling the back reaction from the dissociation rate. This approach can be further applied in other CO_2/CO -contained plasmas.

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