Towards a reaction mechanism of non-equilibrium CO₂ plasmas

V. Guerra[1], T. Silva[1], M. Grofulović[1], L. Terraz[1], P. Ogloblina[1], C. D. Pintassilgo[1,2],
R. Engeln[3], A. S. Morillo-Candas[4] and O. Guaitella[4]

*[1] Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa,
1049-001 Lisboa, Portugal*
*[2] Departamento de Engenharia Física, Faculdade de Engenharia, Universidade do Porto,
R. Dr. Roberto Frias, 4200-465 Porto, Portugal*
[3] Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
*[4] Laboratoire de Physique des Plasmas (UMR 7648),
CNRS-Univ. Paris Sud-Sorbonne Université-Ecole Polytechnique, 91128 Palaiseau, France*

A joint modelling and experimental investigation is undertaken with the purpose of defining a "reaction mechanism" for non-equilibrium CO₂ plasmas. A step-by-step validation procedure is adopted, by designing experiments focusing on specific phenomena and allowing a meaningful and unambiguous comparison with theoretical predictions. The first stages of this endeavour sanctioned the kinetic scheme describing CO₂ plasmas under a low-excitation regime. Future extensions to describe more general situations are outlined.

1. Introduction

CO₂ plasmas are widely investigated nowadays due to their potential use in several carbon dioxide valorisation strategies, where CO₂ is considered as a viable resource rather than a waste [1]. One of the most prominent is the production of solar fuels, *i.e.*, the conversion of renewable electricity into fuels, which always involves a step of reduction of CO₂ into CO [2]. The interest of CO₂ plasmas for in-situ resource utilisation (ISRU) on Mars has also been recently advocated [3].

In order to tame and tailor the plasma for a specific application, a deep knowledge of the elementary processes and kinetic mechanisms occurring in the processing reactor is required. Modelling and simulation are powerful tools to acquire physical insight into the microscopic mechanisms ruling the global behaviour of the system, providing the interpretation of observed phenomena, describing the measured quantities and allowing to estimate non-measurable ones. Several research teams have been developing models for CO₂ plasmas in recent years, adopting a variety of formulations [4-7]. However, the validation of these models is extremely difficult, due to the scarce experimental data and to the complex operating conditions of plasma reactors, involving the coupling of the different kinetics occurring simultaneously.

Herein we describe the recent modelling effort that is being carried out at IST Lisbon (Portugal) [8-11], aiming at establishing a *reaction mechanism* of non-equilibrium CO₂ plasmas, defined here as "a set of reactions and respective rate coefficients, validated against benchmark experiments." To this

purpose, a detailed self-consistent kinetic model was developed to describe the coupling of the electron, vibrational and chemical kinetics. In parallel, a series of dedicated experiments was performed at LPP (France) and at TU/e (The Netherlands), designed to provide measurements of different quantities in conditions where the influence of many phenomena is eliminated or strongly minimized. In this way, the comparison between model predictions and experimental data offers a step-by-step validation of isolated subsets of the reaction mechanism, ultimately leading to its full determination.

2. Results and discussion

It is well-known that at pressures around 1 Torr, in typical operating conditions there is a very significant fraction of the electron energy that is channelled into vibrational excitation. In addition, in certain conditions vibrational quanta can be up-pumped along the asymmetric stretching mode and enhance dissociation [12]. Accordingly, the main topic of research investigated up to know in the joint effort described here is the input and relaxation of vibrational energy in low-pressure CO₂ plasmas.

The validation of a kinetic mechanism describing the transfer of energy from the electrons to vibrationally excited CO₂ molecules and its subsequent redistribution in vibration-vibration (V-V) and vibration-translation (V-T) energy exchanges can be achieved by finding conditions of low excitation, where only a few vibrational levels are populated and CO₂ dissociation is negligible. In these circumstances, both the influence of species such as O, O₂ and CO in the vibrational kinetics of CO₂ and the role

of chemistry are expected to be vanishingly small. This low-excitation regime can be attained in a ms pulsed DC glow discharge, where it is possible to measure the populations of the lower vibrational levels of CO_2, following their increase during the pulse and their decrease along the afterglow [13].

The kinetic model is based on the LoKI (LisbOn Kinetics) code [14] and accounts for the coupled electron and vibrational kinetics of CO_2 plasmas, by solving the electron Boltzmann equation and a system of rate balance equations describing the time evolution of about 70 individual vibrational levels. It is described in detail in [9-11]. Figure 1 shows the comparison between the calculations and the measurements of the characteristic vibrational temperatures of the bending and asymmetric modes, respectively T_2 and T_3, for a 5 ms pulsed discharge at pressure p=5 Torr and discharge current I=50 mA. In these calculations, the gas temperature is taken from experiment and is given as input to the model. The very good agreement obtained in the afterglow validates the kinetic scheme proposed concerning the CO_2-CO_2 V-T and V-V exchanges. The agreement verified in the active discharge further validates the description of the electron impact (e-V) processes.

The gas thermal balance equation is then added to the model, so that the gas temperature, T_g, is no longer given as an input. Figure 2 depicts the calculated and measured time-evolution of T_g, for the same conditions as in figure 1, assuming as a boundary condition a wall temperature T_w=350 K. The excellent agreement obtained reinforces the validity of the reactions and rate coefficients considered, establishing a reaction mechanism for the low-excitation regime under study.

Work is in progress to extend the reaction mechanism to electron impact dissociation, V-V up-pumping on the asymmetric stretching mode up to high vibration quantum numbers, as well as V-T and V-V exchanges with other species. These generalisations will be done separately, supported by experiments specifically conceived to this purpose, following the step-by-step validation strategy delineated here. They will constitute important milestones in the road towards a complete reaction mechanism for non-equilibrium CO_2 plasmas.

Acknowledgements

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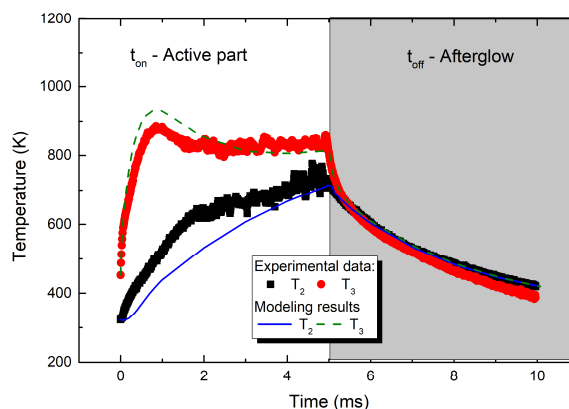[14] A. Tejero-del-caz *et al*, *Plasma Sources Sci. Technol*. (2019), accepted for publication.

Figure 1: Characteristic vibrational temperature of the bending (T_2) and asymmetric stretching (T_3) modes, in a 5 ms DC pulsed discharge at p=5 Torr and I=50 mA.
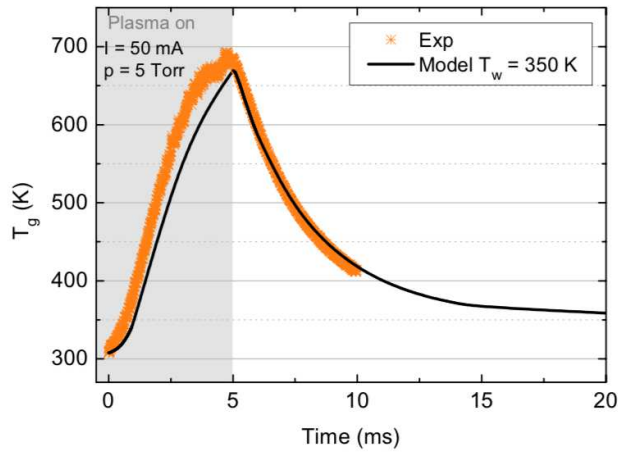
Figure 2: Calculated and measured gas temperature for the same conditions as in Figure 1.