Kinetic mechanisms in CO_2-N_2 plasmas

C. Fromentin[1,*], T. Silva[1], T. C. Dias[1], E. Baratte[2], A.S. Morillo-Candas[2,5], O. Guaitella[2], A.F. Silva[3], O. Biondo[4] and V. Guerra[1]

Keywords: glow discharge, CO_2 dissociation, vibrational excitation, 0D model.

ABSTRACT

This contribution reports the comparison of simulation results from a 0D self-consistent kinetic model with recent experimental data obtained in low-pressure DC discharges in CO_2-N_2. This comparison allows the development of a new reaction mechanism (i.e., a set of reactions and rate coefficients validated against benchmark experiments) for CO_2-N_2 plasmas. The system of election is a DC glow discharge, operating at pressures in the range p=0.1-10 Torr and discharge currents I=10-50 mA, in a Pyrex tube of radius R=1 cm, which is stable, axially homogenous, and easily accessible to a variety of diagnostics. The set of measurements provides the gas temperature, vibrational temperatures of CO and the various modes of CO_2, reduced field E/N, and densities of $O(^3P)$, $CO(X^1\Sigma^+)$ and $CO_2(X^1\Sigma^+_g)$. The simulation results are obtained with the LoKI (LisbOn Kinetics) [1] simulation tool solving a Boltzmann-chemistry global model.

Investigating the impact of CO and N_2 on the vibrational temperature of the different CO_2 vibrational modes and on the overall conversion is relevant as they can promote CO_2 vibrational excitation. Besides, CO is a product of the dissociation and is therefore always present in the discharge and N_2 can be found as an impurity in industrial CO_2 emissions.
It has been shown that the admixture of N_2 has a beneficial impact on CO_2 decomposition [2,3]. Several reasons can be assigned to it, one of them being the near-resonant transfer of vibration quanta from the first vibrational level of N_2 to the asymmetric mode of CO_2 (v_3) and the fact that vibrationally excited CO_2 can undergo molecular dissociation through the so-called ladder climbing mechanism or by electron impact stepwise processes. Similarly, CO molecules can transfer energy to the v_3 vibration of CO_2 because the energy difference between the first vibrational level of CO and the first asymmetric stretch vibrational level of CO_2 is only 25meV, which is smaller than the average kinetic energy [4]. However, depending on the CO concentration, the presence of CO can either enhance the dissociation of CO_2 or stimulate the reconversion back to CO_2 through the electronic excited state $CO(a^3\Pi)$ which can have an ambivalent role depending on the CO density [5, 6]. These mechanisms will be discussed in the detail at the conference. Understanding the impact of the different processes on the overall kinetics, along with the validation against experimental data, will contribute to further develop the existing models [3, 7, 8] and to better control and enhance CO_2 conversion.

Acknowledgments: This work was partially supported by the European Union's

[1] Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal
[2] Laboratoire de Physique des Plasmas (UMR 7648), CNRS, Univ. Paris Saclay, Sorbonne Université, École Polytechnique, France
[3] Dutch Institute for Fundamental Energy Research, Eindhoven, the Netherlands
[4] Plasma Lab for Applications in Sustainability and Medicine – ANTwerp, Belgium
[5] Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland (current affiliation)

Horizon 2020 research and innovation programme under grant agreement MSCA ITN 813393, and by Portuguese FCT-Fundação para a Ciência e a Tecnologia, under projects UIDB/50010/2020, UIDP/50010/2020, PTDC/FIS-PLA/1616/2021 and EXPL/FIS-PLA/0076/2021.

[1] A. Tejero-del-Caz et al, Plasma Sources Sci. Technol. 28 (2019) 073001
[https://nprime.tecnico.ulisboa.pt/loki]
[2] M. Grofulović et al, Plasma Sources Sci. Technol. 28 (2019) 045014
[3] L. Terraz et al, J. Phys. D: Appl. Phys. 53 (2020) 094002
[4] W. J. Witteman, © Springer-Verlag Berlin Heidelberg 1987
[5] A. Cenian et al, Contrib. to Plasma Phys. 34 (1994) 25–37
[6] A. S. Morillo-Candas et al, Phys. Chem. C 124(2020) 17459−17475
[7] A. F. Silva et al, Plasma Sources Sci. Technol. 29 (2020)125020
[8] S. Heijkers et al, J. Phys. Chem. C 119 (2015) 12815−12828