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Session 1

Kinetic mechanisms in CO2-O2 plasmas: Development of a reaction mechanism

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This contribution reports the development of a reaction mechanism for CO_2-O_2 plasmas. To this purpose, simulations from a 0D self-consistent kinetic model are compared with recent experimental data from measurements performed in low-pressure DC discharges. The comparison allows a refinement of the available kinetic schemes and the development of a new *reaction mechanism* (*i.e.*, a set of reactions and rate coefficients validated against benchmark experiments) for CO_2-O_2 plasmas.

Investigating the impact of O_2 on CO_2 conversion is relevant because O_2 is a product of CO_2 dissociation and can be present as an impurity in industrial CO_2 emissions. Besides, by enlarging the range of operating conditions, kinetic schemes validated for pure O_2 and pure CO_2 can be put to further tests and refined. Therefore, to unveil the coupling mechanisms occurring in CO_2-O_2 plasmas it is desirable to study different mixtures, from pure CO_2 to pure O_2. The research teams at Instituto Superior Técnico (IST) from Universidade de Lisboa, Laboratoire de Physique des Plasmas (LPP) from École Polytechnique, and Lomonosov Moscow State University (MSU) currently carryout a joint effort to investigate pure oxygen plasmas, that has recently lead to measurements of the gas temperature, T_g, reduced electric field, E/N, densities of $O(^3P)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, O_3 and O^-, and $O(^3P)$ loss frequencies (MSU/LPP), used for preliminary validation of numerical simulations (IST/MSU). Concerning CO_2-O_2 and CO_2, a set of measurements of T_g, E/N, $O(^3P)$, $CO(X^1\Sigma^+)$ and $CO_2(X^1\Sigma^+_g)$ densities and $O(^3P)$ loss frequencies was recently provided by LPP. In both cases the chosen system 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 simulation results were obtained with the LoKI (LisbOn Kinetics) [1] simulation tool solving a Boltzmann-chemistry global model.

The admixture of O_2 has a detrimental impact on CO_2 decomposition [2], as it leads to a decrease of the dissociation fraction. Several reasons can be assigned for it, one of them being the quenching of vibrationally excited CO_2, which may lead to molecular dissociation through the so-called ladder climbing mechanism [3]. Another possible explanation is the enhancement of various reverse reaction mechanisms producing back CO_2 from vibrationally or electronically excited CO in collisions with O or O_2 [4]. The addition of O_2 can also modify the ion conversion pathways and induce changes in the plasma parameters. Therefore, molecular oxygen plays an important role in CO_2 plasma kinetics and on the efficiency of CO_2 conversion. Understanding the impact of the different elementary processes on the overall kinetics, along with the validation against experimental data, will contribute to further develop the existing models and thus to better control and enhance CO_2 conversion. For this purpose, a proper description of the CO_2 and CO vibrational population is fundamental along with a detailed kinetic scheme for O_2, as partially done in [5,6] and further developed in the framework of the present collaboration between LPP, MSU and IST.

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[1] A. Tejero-del-Caz *et al, Plasma Sources Sci. Technol.* **28** (2019) 043001
[2] M. Grofulović *et al*, *Plasma Sources Sci. Technol.* **28** (2019) 045014
[3] A. Fridman *Plasma Chemistry* (2008) (Cambridge: Cambridge University Press)
[4] A.S. Morillo-Candas *et al*, submitted to *J. Phys. Chem. C* (2020)
[5] A. Annušová *et al*, *Plasma Sources Sci. Technol.* **27** (2018) 045006
[6] T. Silva *et al*, *J. Phys. D: Appl. Phys.* **51** (2018) 464001