Kinetic mechanisms in oxygen plasmas. II. Development of a reaction mechanism

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This is the second of two contributions reporting a joint effort of Instituto Superior Técnico (IST) from Universidade de Lisboa, Laboratoire de Physique des Plasmas (LPP) from École Polytechnique, and Lomonosov Moscow State University (MSU), devoted to fundamental studies in oxygen plasmas. Recent measurements of $O(^3P)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, O_3, O^- and E/N, performed in low-pressure DC discharges, are used to in a preliminary validation of numerical simulations from a 0D self-consistent kinetic model. The dominant elementary processes with impact on the overall coupled kinetics are highlighted. Together with the validation against experimental data, they provide clues for further developments of the model.

This contribution addresses the common effort from the research teams at Instituto Superior Técnico (IST), Laboratoire de Physique des Plasmas (LPP) and Lomonosov Moscow State University (MSU) to develop a new *reaction mechanism* for O_2 plasmas, defined here as a set of reactions and rate coefficients validated against benchmark experiments. An extensive experimental characterization of oxygen DC discharges, operating at pressures in the range p=0.1-10 Torr and currents I=10-40 mA, generated in a Pyrex tube of radius R=1 cm, was done recently by LPP and MSU. In particular, the measurements comprise the concentrations of ground-state atoms, $O(^3P)$, molecular metastable states, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ (hereafter denoted as $O_2(a)$ and $O_2(b)$), vibrationally excited molecules of the electronic ground state, $O_2(X\ ^3\Sigma_g^-,v)$, ozone, O_3, and negative ions, O^-, the gas temperature, T_g, the reduced electric field, E/N, and the atomic oxygen loss frequency. In parallel, a comparison between the kinetic models developed at IST and MSU is presented in a companion paper to the conference [1] and establishes the bases for refinement of the models. The self-consistent 0D calculations presented here correspond to an early first step in this process.

The current simulations are made with the LoKI simulation tool [3] and are based on the kinetic scheme from [2], with a several modifications: *i*) the detachment reaction $O^-+O\rightarrow O_2+e$ is considered with the rate coefficient from [1,4]; *ii*) the O-atom wall recombination probability and the wall deactivation probability of $O_2(a)$ are taken from [1,5]; *iii*) ozone formation at the wall is included following [1,6]; *iv*) reactive quenching of $O_2(b)$ by oxygen atoms is considered as in [1,7,8]; *v*) the kinetics of the Herzberg states according to MSU is added to the model. This scheme is denoted here as "reference case". Another set of simulations, based in [1] + *i*) + *ii*) is designated as IST*.

Fig. 1 shows the comparison of the calculated concentrations of the heavy particles at I=30 mA, for the two sets of simulations, together with experimental data. Despite some differences of detail and the too low density predicted for the $O_2(b)$ state, there is an overall good agreement with experiment.

The behaviour of the different concentrations can be explained by the predominance of various mechanisms occurring within the discharge. Focusing on the major species of interest, $O(^3P)$ atoms are mainly created by electron impact dissociation from $O_2(X,0)$, producing either two $O(^3P)$ atoms or one $O(^3P)$ and one $O(^1D)$ atom. Concerning the $O(^3P)$ destruction channels, only wall recombination and

electron excitation to the ^1D state play a significant role, with contributions of around 64%–75% and 25%–8%, respectively, at 1 and 7.5 Torr. Nevertheless, most of the O(^1D) produced is converted back to O(*3P*) by wall deactivation and quenching by O(^3P) and $O_2(X)$, and thus this channel does not constitute a true destruction mechanism of ground-state atoms.

The metastable state $O_2(a)$ is mainly populated by electron impact upon $O_2(X)$, especially at higher pressure (7.5 Torr) for which its contribution reaches 67%. Another important process for the creation of $O_2(a)$ is the quenching of $O_2(b)$ by O atoms (53% at 1 Torr). The relative importance of each mechanism depends strongly on the pressure. The contribution of Herzberg states becomes relevant at higher pressure, exceeding 10% at 7.5 Torr. $O_2(a)$ molecules are also destroyed by electron impact collisions leading to the formation of $O_2(b)$ and to dissociation.

The second molecular electronically excited state, $O_2(b)$, is partially formed by electron impact on $O_2(X)$ and on $O_2(a)$, but is primarily created as a result of energy transfer from O(^1D) to $O_2(X)$, which accounts for 67% at 1 Torr and 43% at 7.5 Torr of its total creation. $O_2(b)$ is lost through three principal mechanisms, namely the quenching by O(^3P) atoms leading to $O_2(X)$ and $O_2(a)$, and deactivation at the wall. These processes have a similar contribution to the destruction of $O_2(b)$ at low pressure, whereas the $O_2(X)$ formation represents 80% of the total destruction at 7.5 Torr. Note, however, that the product branching ratios resulting from quenching by O atoms are still subject to debate [1,7,8].

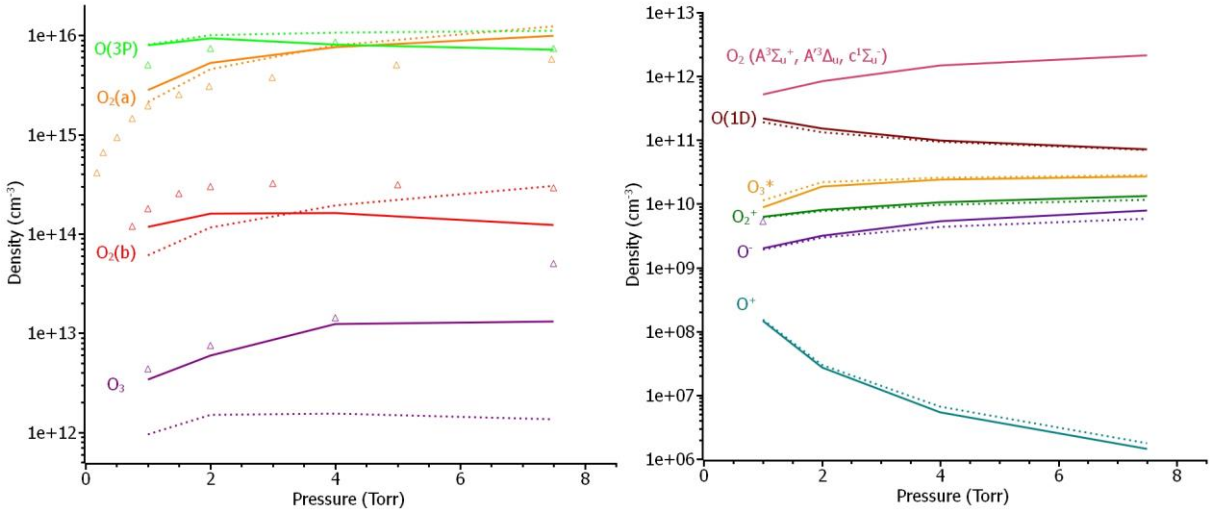

Fig 1. Comparison of the experimental values (△) and calculated concentrations of several species accounted for in the simulations, for the reference case (−) and IST* (···) (see text).

The present results confirm the strong coupling between the kinetics of O(^3P), $O_2(a)$, $O_2(b)$ and O(^1D). Wall processes play a significant role in the overall kinetics and electron-impact cross sections (*e.g.*, for excitation of O(^1D) and dissociation from ground and excited states) and the temperature dependence of some rate coefficients may affect the results and require further investigation. The identification of the main energy transfer pathways, associated with the vast experimental characterization under way, will allow the development of a new reaction mechanism for O_2 plasmas.

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