Kinetic mechanisms in oxygen plasmas. I. A comparative analysis of two reaction schemes

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This is the first of two contributions reporting a joint effort involving 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. A thorough comparison between the kinetic schemes used to model oxygen discharges at IST and MSU is carried out, supported by recent and new measurements performed in low-pressure DC discharges. The influence of different reactions, rate coefficients and species considered, in the model predictions, is studied in detail. The present results lay the foundations for the development of a new reaction mechanism for O_2 plasmas.

The research teams at Instituto Superior Técnico (IST), Laboratoire de Physique des Plasmas (LPP) and Lomonosov Moscow State University (MSU) have produced an ample literature describing their studies on the non-equilibrium kinetics of O_2 plasmas. Herein we report a collective effort from the three laboratories to coordinate their investigation, initiated recently in [1]. The system of election is a DC glow discharge, operating at pressures in the range p=0.1-10 Torr and discharge currents I=10-40 mA, in a Pyrex tube of radius R=1 cm, which is stable, axially homogenous, and accessible to a variety of diagnostics. The present communication aims at a systematic comparison between the kinetic schemes developed independently at IST [3,4] and MSU [5]. The purpose of this work is not to focus on a comparison with experimental data, which is presented in a companion paper to this conference [2], but rather to understand in detail how different mechanisms and the corresponding rate coefficients influence quantities like the concentrations of different species. Together with the experimental work developed between LPP and MSU, this comparison will lead to a refinement of the available kinetic schemes and will allow the development of a new *reaction mechanism* (*i.e.*, a set of reactions and rate coefficients validated against benchmark experiments) for O_2 plasmas.

The IST kinetic scheme is described in detail in Annušová *et al* [3] and is used here with no modifications, except for the detachment reaction $O^- + O \rightarrow O_2 + e$, which is considered with the rate coefficient k_1=1.9×10^{-16} m^{3}s^{-1} [6]. The gas temperature, T_g, and the atomic oxygen recombination probabilities $O(^3P)$ + wall → 1/2O_2 were obtained experimentally in [1], while the deactivation probabilities of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ (hereinafter O_2(a) and O_2(b)) at the wall are taken as γ_a=1.5×10^{-4} and γ_b=0.135, respectively. Other values of $\gamma_{a,b}$ from [4] were also examined. Apart from differences in the rate coefficients and the electron-impact cross sections of several individual processes, the MSU kinetic scheme further includes the kinetics of the Herzberg states ($A^3\Sigma_u^+$, $A'^3\Delta_u$=$C^3\Delta_u$, $c^1\Sigma_u^-$) and $O(^1S)$ metastables, but excludes the kinetics of vibrationally excited ozone, O_3^*. For the purpose of the present investigation, the electron impact cross sections are kept as in the IST kinetic scheme. All the calculations are made using a 0D formulation as in [3], and the corresponding Boltzmann-Chemistry global model is solved using the LoKI (LisbOn Kinetics) simulation tool [7].

Figure 1 shows the calculated number densities of $O_2(a)$ and $O_2(b)$ metastable states for different assumptions in the model. The differences between the predicted concentrations from the two kinetic schemes are relatively small. One major effect concerns the formation of ozone at the walls, as proposed by Lopaev *et al* [8,9]. The description adopted here for this mechanism is similar to that used in [10], with a recombination probability of atomic oxygen into ozone increasing from 1.3×10^{-4} at p=1 Torr to 1×10^{-3} at p=7.5 Torr. This process affects significantly the concentration of ozone (not shown here) along with other species. This study also reveals the importance of the quenching of $O_2(b)$ by oxygen atoms $O_2(b) + O(^3P) \rightarrow O_2(a,X) + O(^3P)$. Indeed, the addition of a reactive quenching process as proposed by MSU, considered here with a rate coefficient $k_2=15.6\times10^{-17}\exp(-3700/T_g)$ m^3/s, results in the predicted $O_2(b)$ concentration following the experimentally-observed trend with pressure, but with an absolute density lower by about a factor of 3. Moreover, the branching ratio of the products of collisional quenching of $O_2(b)$ between $O_2(X,v)$ and $O_2(a)$ also affects the absolute values of $O_2(a,b)$ concentrations.

Our study further reveals some sensitivity of the simulations to the kinetics of $O(^1D)$ (in particular to the excitation from $O(^3P)$ by electron impact), wall losses of $O_2(b)$ and electron impact dissociation from $O_2(a,b)$ states. A comparison of reference simulations with experimental data is presented in [2].

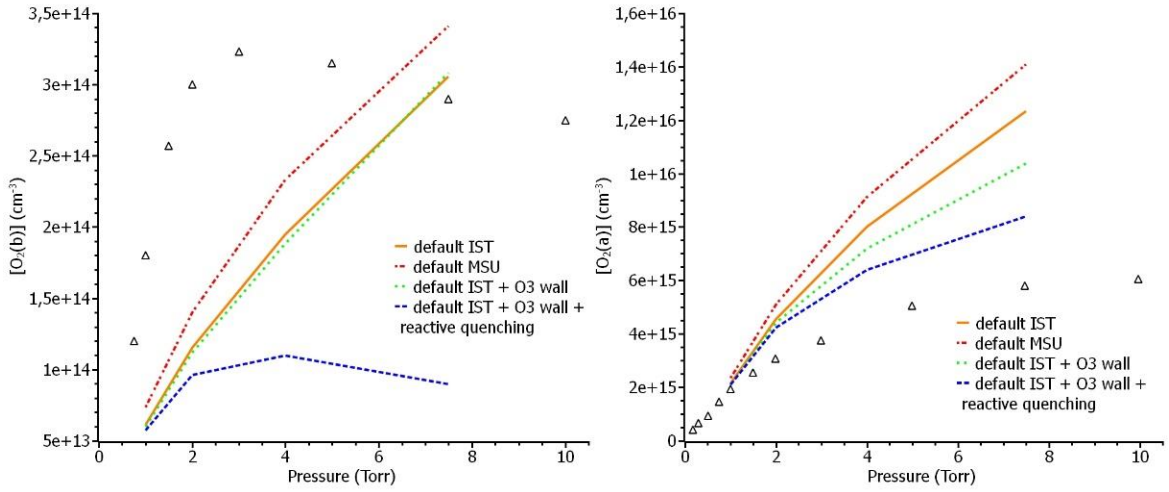

Fig 1. Experimental (△) and calculated concentrations of $O_2(a)$ and $O_2(b)$ metastable states for: the IST scheme (–); the MSU scheme for heavy-particles (-·-); IST + formation of O_3 at the wall (···); IST + formation of O_3 at the wall + reactive quenching of $O_2(b)$ molecules by $O(^3P)$ atoms (--).

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