36th EPS Conference on Plasma Phys. Sofia, June 29 - July 3, 2009 ECA Vol.**33E**, O-4.036 (2009)

Self-consistent kinetic modeling of Ar-O_2 discharges

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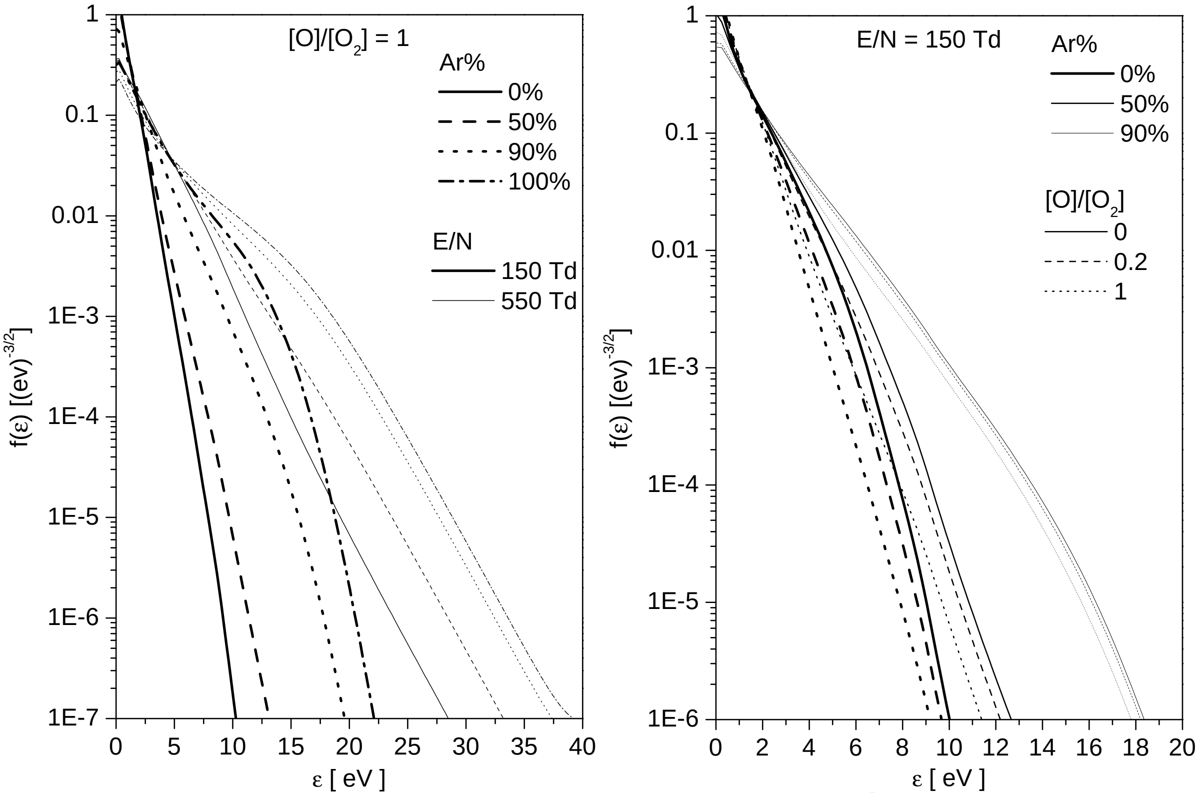
The kinetic modeling of gas discharges has long been recognized as a powerful tool to stimulate and improve the investigation of these systems. Ar – O_2 plasmas are widely used in material processing and biomedical applications, e.g. the post-discharge of Ar – O_2 has been successfully used as oxidizing media in deposition of oxide films [1], and the inactivation of bacterial spores have been achieved in the flowing afterglow of an Ar – O_2 microwave discharge [2]. The aim of this work is to develop a self-consistent model of Ar – O_2 surface-wave discharges, thus contributing to the understanding of the elementary processes occurring in these plasmas.

In this work we develop a self-consistent kinetic model of a surface-wave sustained discharge in Ar – O_2. The system under analysis is a discharge operating at pressure $p = 2$ Torr, field frequency $\omega/2\pi = 2.45$ GHz, in a quartz tube with radius $R = 0.5$ cm. The gas temperature was assumed constant, $T_g = 1000$ K, and all the calculations have been made for an electron density $n_e = 3.74 \times 10^{11}$ cm^{-3}, which is the critical density for surface-wave propagation. These conditions are close to the typical discharge conditions determining the afterglows used in the experimental plasma sterilization studies from [2] and [3].

The present formulation provides the species densities in the discharge, the electric field sustaining the discharge, all the information concerning the electron excitation rate coefficients and transport parameters, as well as all the details concerning the chemical kinetics of each species. This is achieved by solving the homogeneous electron Boltzmann equation, coupled together with the rate balance equations describing the creation and destruction of the most important neutral and charged particles, namely Ar($^1S_0$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$), $O_2(X\ ^3\Sigma_g^-$,v), $O_2(a\ ^1\Delta_g, b\ ^1\Sigma_g^+)$, O($^3P$, ^1D), O_3, Ar^+, $Ar_2{}^+$, $O_2{}^+$, O^+ and O^-, under the assumption of a quasi-neutral discharge. The Boltzmann equation takes into account collisions of electrons with several species, as well as electron-electron collisions. In practice, due to the high dissociation degree found in these discharges, the Boltzmann equation essentially corresponds to the ternary mixture Ar – $O_2(X)$ – O(^3P). The effect of negative ions in the determination of the field is taken into account following the scheme proposed in [4].

Figure 1 a) shows the Electron Energy Distribx on Functions (EEDFs) calculated for two

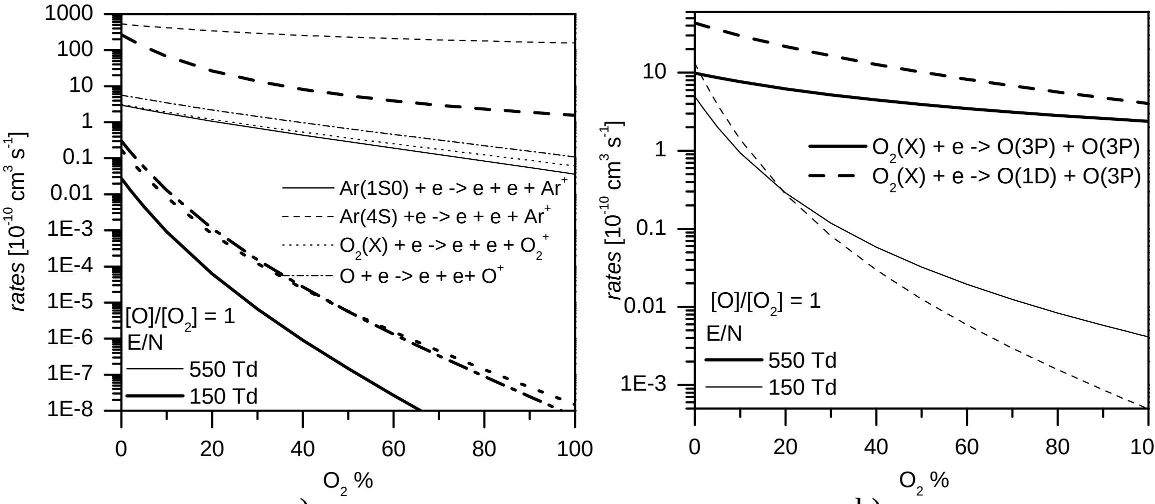


a) b)

Figure 1: a) EEDFs calculated for $E/N = 15 \times 10^{-16}$ Vcm^2 (thick curves) and 55×10^{-16} Vcm^2 (thin curves), for different Ar content in the mixture; b) EEDFs calculated for $E/N = 15 \times 10^{-16}$ Vcm^2 for pure oxygen (thick lines), 50% O_2 – 50% Ar (medium lines) and 10% O_2 – 90% Ar (thin lines), for different dissociation degrees.

values of the reduced electric field $E/N = (E_0/\sqrt{2})/N$, 15×10^{-16} and 55×10^{-16} Vcm^2, the former being representative of pure argon and the latter of pure oxygen, for three different mixture compositions. The dissociation degree was kept constant, [O(^3P)]/[$O_2(X)$]=1, the results corresponding only to Boltzmann calculations, not to the full self-consistent ones. As it can be seen, addition of a relatively small content of oxygen into pure Ar is enough to significantly change the EEDF and, consequently, the electron ionization and excitation rate coefficients. Moreover, the high energy tails of the EEDFs are less populated as oxygen is introduced in the mixture, as a result of a higher global cross section in oxygen. That being so, for constant electron density (and not counting for the magnitude of the electron ionization cross sections), the electric field sustaining the discharge should be higher near pure oxygen than near pure argon.

Since molecular oxygen can be strongly dissociated, the influence of the collisions with atomic oxygen on the EEDF is depicted in figure 1 b), for E/N, 15×10^{-16} Vcm^2. For the present conditions, an higher dissociation leads to less energetic EEDFs. Figure 2 depicts the dissociation (a) and ionization (b) electron impact rate coefficients as a function of the mixture



a) b)

Figure 2: a) Electron impact oxygen dissociation rate coefficients and b) electron impact ionization rate coefficients, as a function of the mixture composition, for E/N, 15×10^{-16} Vcm^2 (thin lines) and 55×10^{-16} Vcm^2 (thick lines).

composition. At constant reduced electric field all the electron impact rate coefficients decrease with the fraction of oxygen in the mixture, in accordance with the changes in the EEDFs revealed in figure 2. Close to pure argon, ionization from the 4s excited states may give a non-negligible contribution to ionization. As a matter of fact, although the concentration of these states is much lower than that of ground-state Ar($^1S_0$) atoms, the corresponding electron impact ionization coefficient is much larger, making electron stepwise ionization to be dominant."

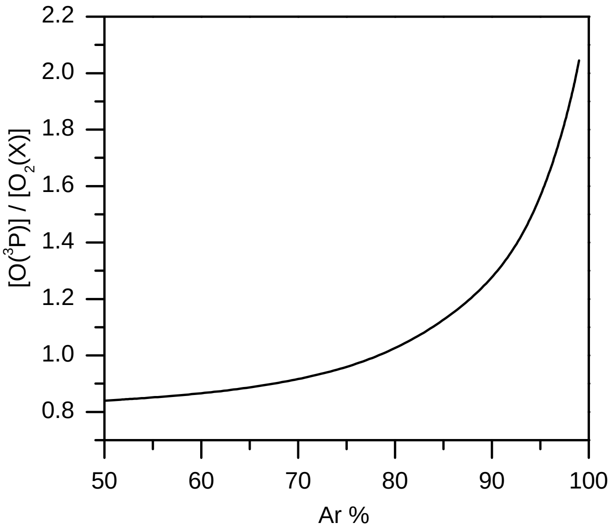


Figure 3: O(^3P)]/[O$_2(X)$] as a function of the Ar content in the mixture.

From the present self-consistent calculation, it turns out that in pure argon electron impact ionization from the 4*s* states contributes about 55% to the total creation of Ar$^+$ ions, whereas ionization from the ground-state provides only 35%. The remaining contribution is given by pooling reactions Ar(4*s*)+Ar(4*s*). As referred above, oxygen can be strongly dissociated. The ratio between the concentrations of ground-state atoms and ground-state molecules, [O(^3P)]/[O$_2(X)$] is represented in figure 3. The dissociation degree is higher for higher Ar percentages in the mixture. This is mostly a consequence of the very

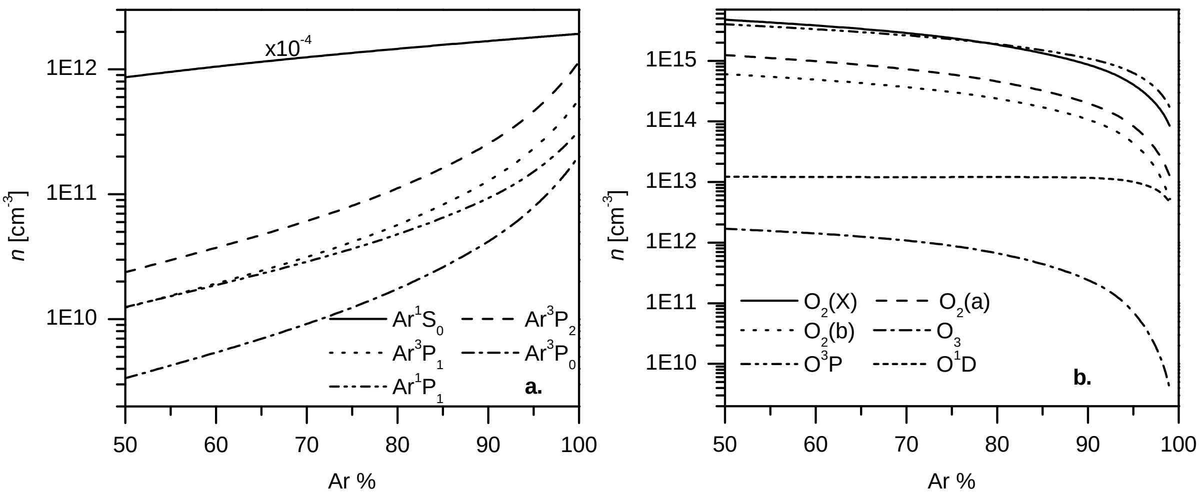


Figure 4: Concentrations of a) Ar species and b) oxygen species as a function of the mixture composition.

efficient dissociation of oxygen molecules in collision with the Ar(4*s*) states, by the reaction $Ar(4s)+O_2(X)\rightarrow Ar(^1S_0)+O(^3P)+O(^3P,^1D)$, which adds up to electron impact dissociation.

The same reaction, together with the quenching by atomic oxygen, $Ar(4s)+O\rightarrow Ar(^1S_0)+O$ is responsible for the fast depletion of the argon excited states upon oxygen addition, as shown in figure 4 a). In turn, figure 4 b) illustrates the dependence of the oxygen species with the mixture composition. It confirms the steep raise of most oxygen species when oxygen is added into an Ar discharge. Furthermore, it corroborates the relevance of oxygen atoms as an important active species, their concentration being comparable to that of ground-state molecules.

The present investigation addresses the kinetics of Ar – O_2 plasmas, for similar conditions as those used in plasma sterilization reactors. Oxygen is strongly dissociated and the Ar(4*s*) states are efficiently quenched by oxygen atoms and molecules. A more complete characterization of the discharge and a study of the early afterglow are currently being developed.

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