INFLUENCE OF ELECTRON ENERGY DISTRIBUTION FUNCTION ON COMPOSITION OF ATMOSPHERIC PRESSURE He/O_2 PLASMAS

Ž. Mladenović[1*], S. Gocić[1], D. Marić[2] and Z. Lj. Petrović[2]

[1]*Department of Physics, Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia*
[2]*Institute of Physics, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*

Abstract. Atmospheric pressure non-equilibrium plasma represent efficient source of reactive species for different kind of applications. Nevertheless, for the purpose of modelling of this non-equilibrium system, Maxwell-Boltzmann distribution is commonly used for calculation of electron rate coefficients. In order to test sensitivity of plasma composition on assumed electron energy distribution function (EEDF), the zero-dimensional global model is applied for helium/oxygen mixture (0.5% of O_2) with humid air impurities. The initial calculation showed that inclusion of non-equilibrium EEDF mainly affects the processes with thresholds considerably higher than the mean electron energy while it does not change much for the processes with the threshold and peak in the region of the mean energy.

1. INTRODUCTION

Having in mind that chemical composition of complex plasmas is often inaccessible by measurements analysis based on numerical models has an important role. In that respect atmospheric pressure plasmas are particularly complex and difficult to describe by models. Results of a global model used for investigation of influence of humid air level on chemistry of reactive species in rf-driven atmospheric-pressure (AP) helium-oxygen mixture (0.5% of O_2) plasmas were presented in a recent paper [1,2]. Model comprises a reaction scheme with 1048 reactions for kinetics of nearly 60 species.

We have created a numerical code for solving the system of time-dependent rate equations with an idea to test sensitivity of plasma composition to selected EEDF. In doing so, we start from the chemical scheme in Appendix of Ref. [1]. Rate coefficients for electron molecule collisions are first calculated with a Maxwell-Boltzmann (MB) EEDF, and then with the non-equilibrium one, obtained by solving the Boltzmann equation BE.

2. MODEL

The time evolution of particle concentration in 0D global model is determined by rate equations, which include rates for processes of creation and destruction of each particle. Two-body rate coefficients for electron impact processes are calculated as [3]:

$$k_{i,exc} = \sqrt{2/m_e} \int_{\varepsilon} Q(\varepsilon)\sqrt{\varepsilon}\, f(\varepsilon) d\varepsilon\,, \qquad (1)$$

where m_e, ε, $Q(\varepsilon)$ and $f(\varepsilon)$ denote electron mass, energy, appropriate total cross section and EEDF, respectively. If MB distribution is assumed, the rate coefficients can be expressed in extended Arrhenius form [1,2]. In non-equilibrium case, rate coefficients for processes in Table 1 are obtained by solving the Boltzmann equation by BOLSIG+ solver [4,5]. MORGAN database [6] with cross sections data for He, O_2 and H_2O is used as input in BOLSIG+. Characteristic cross sections and MB and BE distributions for the same mean energy (electron temperature) are shown in Figure 1. Calculations are shown for the mixture of He 99.5%, O_2 0.5% and H_2O 2.5ppm.

Table 1. List of selected electron-impact processes and rate coefficients [1,2] as a function of T_e [eV].

R.N.	*reaction*	*rate coefficients* [cm^3/s]	*Ref.*
1.	$He + e^- \rightarrow He^* + e^-$	$4.2\cdot10^{-9} T_e^{0.31} \exp(-19.8/T_e)$	[2]
2.	$He + e^- \rightarrow He^+ + 2e^-$	$1.5\cdot10^{-9} T_e^{0.68} \exp(-24.6/T_e)$	[1]
3.	$O_2 + e^- \rightarrow O_2^+ + 2e^-$	$9.0\cdot10^{-10} T_e^{2.0} \exp(-12.6/T_e)$	[1]
4.	$O_2 + e^- \rightarrow O_2(^1\Delta) + e^-$	$1.37\cdot10^{-9} \exp(-2.14/T_e)$	[1]
5.	$O_2 + e^- \rightarrow O_2(^1\sum) + e^-$	$3.24\cdot10^{-10} \exp(-2.218/T_e)$	[1]

The system of rate-equations is solved by MATLAB ODE15s solver with relative and absolute tolerances equal to 10^{-12} and 10^{-6}, respectively. The pulse duration of 5 ms with time-step of 10 ns is chosen as is Ref. [1]. The T_e time dependence for rates calculation is obtained by fitting data from Fig. 2 in Ref. [1], within interval 1.8eV – 3.1eV. Electron concentration is fixed at the value of $10^{11}cm^{-3}$. The initial plasma composition in global model is taken as He + 0.5% O_2 + 250ppm of humid air (78% N_2, 21% O_2, 10^{-2} % CO_2, 10^{-3} % N_2O, 10^{-5} % NO_2, 10^{-6} % NO), with 1% of relative humidity.

3. RESULTS AND DISCUSSION

As shown in Figure 1, BE distribution has a significantly lower high energy tail and minor overlapping with helium cross sections and in particular with ionization cross sections. As a consequence, the rate coefficients for He ionization and excitation are reduced by few orders of magnitude (Figure 2). In

energy region around 1 eV to 3 eV, BE has a similar shape and magnitude as MB distribution. Hence, rate coefficients for $O_2(^1\Delta)$ excitation have similar values (Figure 2). The processes such as ionization or excitation of metastables have rates for MB distribution that are many orders of magnitude larger than those for a non-equilibrium distribution. For the case of Ar plasmas, the influence of EEDF shape on rate coefficients is illustrated in paper [7].

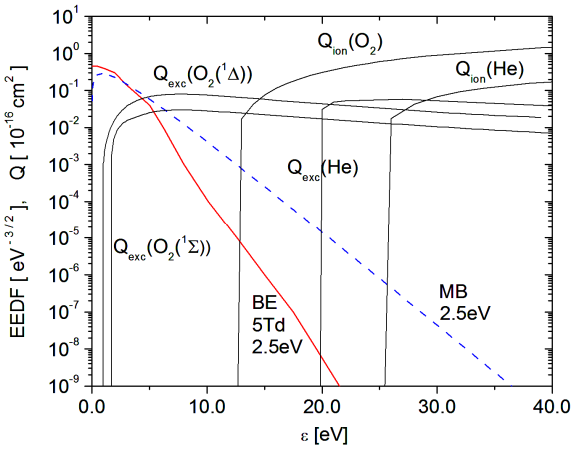

Figure 1. Cross sections for excitation and ionization of He and O_2 and EEDF: Maxwell-Boltzmann (MB) and Boltzmann equation (BE) (2.5eV mean energy).

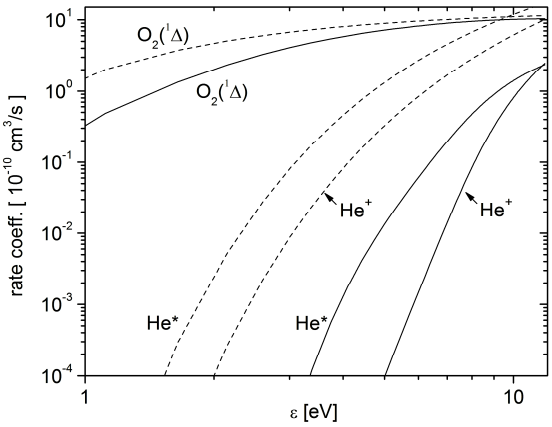

Figure 2. Rate coefficients for O_2 excitation and He excitation and ionization - based on MB (dashed line) and BE (solid line, Morgan set) EEDF.

The comparison of He/O_2 plasma compositions based on the global model calculated with MB and BE distributions is shown in Figure 3. Significantly lower concentrations of He^+, He*, He_2^+, O^+, O_2^+, O_4^+ species are obtained in case with BE rates. The level of He^+ ions is reduced by few orders of magnitude, as a direct consequence of a reduced ionization coefficient (Figure 2). Furthermore, concentrations of He_2^+ and O^+ ions are decreased since the

mean channels of their creations involve He^+ ions. Similarly, the reduction of He* level caused by lower excitation coefficient is followed by O_2^+ decreasing, since Penning ionization of O_2 is an important channel for O_2^+ formation.

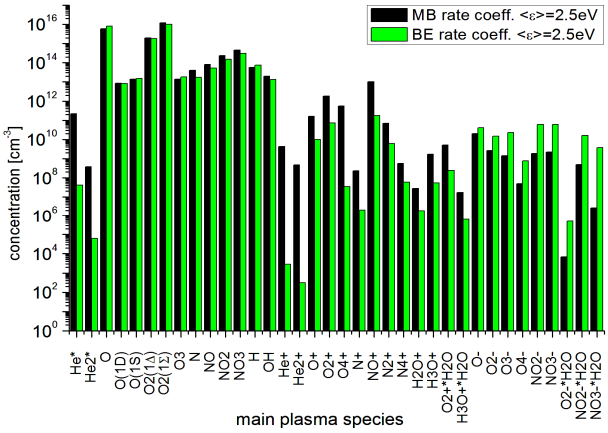

Figure 3. The comparison of plasma composition based on MB (black bars) and BE rate coefficients (green bars).

Concentrations of $O_2(^1\Delta)$ and $O_2(^1\sum)$ are slightly affected by BE distribution, in agreement with rate coefficient behavior in Figure 2. Similar low sensitivity to EEDF can be observed for other reactive species with low thresholds in their dominant channels. On the contrary, concentrations of negative ions are increased for BE rates. In general we may conclude that representation by MB distribution is rather robust if not entirely accurate for processes mainly induced directly by electrons if energy losses are of the same order as the mean energy. This representation fails seriously, as expected [7], for processes with much higher thresholds than the mean energy.

Acknowledgements

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