PROCEEDINGS OF SCIENCE

Influence of air and water vapor on OH radical's production in atmospheric pressure low temperature helium plasmas: investigation by global model

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A numerical 0D global model is developed with an aim to study the influence of air and water vapor impurities on electron energy distribution function and chemical composition of atmospheric pressure helium plasma, focusing on the main reactive oxygen and nitrogen species. Model includes 1488 reactions among 74 species, taken from the literature. Rate coefficients for electron impact processes are calculated using two-term Boltzmann solver BOLSIG+, with cross section data mainly taken from Quantemol-DB database. The main channels for production and consumption of reactive species are examined for a constant electron concentration 10^{10} cm^{-3} and electron temperature 2 eV. We have performed parametric study where mole fraction of air and water vapor were varied in the wide range, using data from the literature. The calculations are done for 100 ppm and 10000 ppm of air in plasma, and for each of these values the content of water vapor was 100 ppm, 1000 ppm, 2000 ppm etc. to 8000 ppm. Through the influence of these contents on electron energy distribution function (EEDF) and appropriate rate coefficients, the variations of the most important production and consumption processes for O, OH, N and NO are analysed in detail. Results show that increasing of air and water vapor contents require higher E/N values to achieve given mean electron energy, rising the energy tail of EEDF and the values of rate coefficients for the electron impact processes with high energy thresholds, such as dissociation of O_2, N_2 and H_2O, important for initial production of O, OH, N and NO. Thus, for the same amount of water vapor, increasing of air content in plasma leads to higher concentration of OH radical and consequently higher level of H_2O_2. For the same amount of air, higher content of water vapor generally leads to decrease of O and N concentrations through chemical reaction with OH radicals.

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1. Introduction

Atmospheric pressure low-temperature plasma (LTP), usually formed in mixing of plasma with humid air after discharge ignition in helium or argon, represents an efficient source of various reactive oxygen and nitrogen species (RONS) very important for applications in biomedicine and agriculture. Complex chemical composition of this kind of plasmas is often inaccessible by measurements and thus analysis based on numerical models has an important role. In that respect, global models (spatially averaged, 0-dimensional) are particularly developed with aim to study the complex chemical composition with large number of included processes. We have created a numerical code for solving the system of time-dependent rate equations, in order to study the influence of air and water vapor on electron energy distribution function (EEDF) and some reactive species. Model comprises 1488 reactions among 74 species, taken from the literature [1,2]. Rate coefficients for electron impact processes are calculated by numerical solving of Boltzmann equation (BE), using the two-term electron Boltzmann-solver BOLSIG+ [3] with cross section data mainly taken from Quantemol-DB database [4].

2. Model

The time evolution of particle concentration in 0D global model is calculated by numerical solving of system of particle balance equations:

$$\begin{aligned}\frac{dn_i}{dt} = \sum_j\sum_m k_{jm}^{(S)} n_j n_m + \sum_l\sum_p\sum_q k_{lpq}^{(S)} n_l n_p n_q + \frac{F_i^{fgc}}{V} n_i^{fgc}(t=0) - \\ - n_i \sum_r k_{ir}^{(L)} n_r - n_i \sum_s\sum_f k_{isf}^{(L)} n_s n_f - \frac{F_i}{V} n_i(t), \qquad (1)\end{aligned}$$

where t, n_i, n_j ... n_f denote time and number density of i-th, j-th and f-th species, respectively. $k_{jm}^{(S)}$ and $k_{lpq}^{(S)}$ denote rate coefficients for two-body and three-body “source” reactions for i-th species, while $k_{ir}^{(L)}$ and $k_{isf}^{(L)}$ denote rate coefficients for two-body and three-body “loss” reactions for i-th species. F_i represents the flow of i-th species and superscript “fgc” stands for the “feed gas component”, for which an additional source term is included in Eq. (1) that describes the flow from inlet of the system. Model includes only gas phase processes, due to the lack of data concerning particle-surface reaction probabilities in atmospheric pressure plasmas. The content of air was 100 ppm and 10000 ppm, and for each of these values the content of water vapor was varied in wide interval from 100 ppm, 1000 ppm, 2000 ppm to 8000 ppm, according to the data presented in literature [5,6]. Global model calculation was done for a constant value of electron concentration 10^{10} cm^{-3} and electron temperature 2 eV. The calculated values of electron temperature for atmospheric pressure LTP in literature vary in interval 2 - 4 eV [2,6,7]. Measured values by spectroscopic methods are 1 - 1.5 eV but authors clearly state that mainly bulk electrons behind the ionization front contribute to the Thomson scattering signal [8]. As presented in [6], the growth in plasma electronegativity due to higher amount of water vapor in self-consistent calculation leads to higher values of electron temperature, necessary for sustain of discharge. In this paper, we analyze the influence of air and water vapor on reactive species based on swarm analysis only at lower value of electron temperature 2 eV, i. e. through pronounced differences between EEDFs and rate coefficients which strongly determine the results of global model calculation. We have taken the constant values of absorbed power density 14 W/cm^3 and flow rate 5 slm in calculation, from results presented in a recent paper [2]. The gas temperature during calculation was taken at value 296 K. The system of particle balance equations is solved by MATLAB ODE15s solver with relative and absolute tolerances equal to 10^{-12} and 10^{-6}, respectively. We have chosen the time step 50 ns and the total time of calculation to be 15 ms because calculated concentrations in our model reach steady-state after this time interval.

3. Results and discussion

Figure 1 presents BE electron energy distribution functions (EEDF) calculated in BOLSIG+ for helium plasma and different amount of air and water vapor. It can be concluded that higher amount of air requires higher reduced electric field in order to achieve the same mean electron energy, and as a consequence, rises the high energy tail of EEDF for mean electron energy energy 2 eV. Water vapor has analogous influence on EEDF for each amount of air but the effect is more pronounced at 100 ppm of air than 10000 ppm. As a direct consequence of higher energy tail of EEDF, rate coefficients for the electron impact dissociation processes, which initially produce O, OH, N and other reactive species such as NO, are increased at higher content of air and water vapor, as presented in Figure 2.

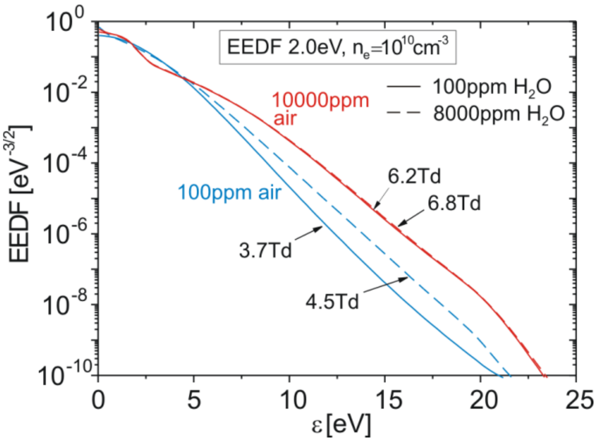

Fig. 1. EEDF calculated by BOLSIG+ for mean electron energy 2 eV with 100 ppm (blue lines) and 10000 ppm air (red lines).

In Figure 3 we present the concentrations of selected reactive oxygen and nitrogen species (RONS), calculated by global model for different amount of air and water vapor, while in Figure 4 we present the most important processes in our model which produce OH radical. For each process we also present the percent of contribution in total production of OH. We have made such analysis for each of the species presented in Figure 3. Differences in concentration of selected species and chemical pathways can be explained based on different plasma composition due to different amount of air and water vapor, but also having in mind the influence of these parameters on rate coefficients for electron impact processes which lead to production of RONS, as presented in Figure 2.

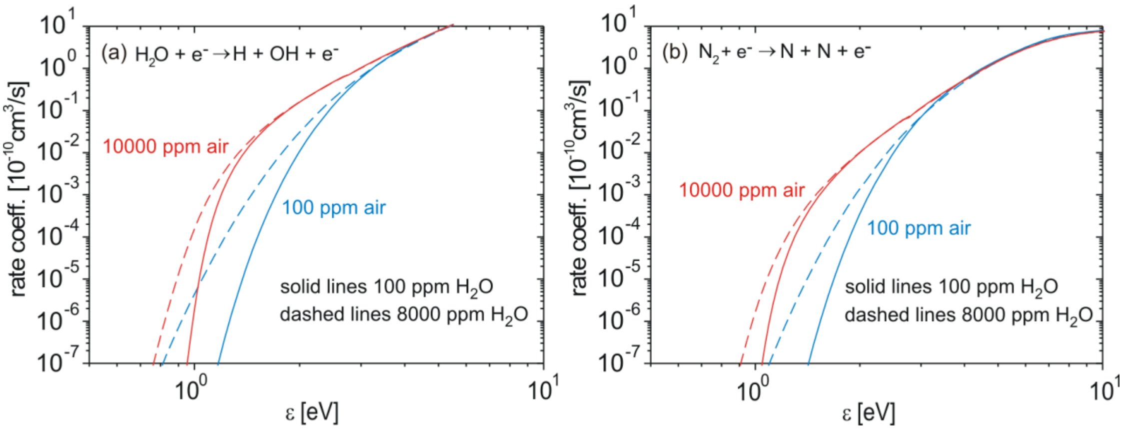

Fig. 2. Rate coefficients calculated by BOLSIG+ for (a) dissociation of H_2O and (b) dissociation of N_2 for 100 ppm air (blue lines) and 10000 ppm air (red lines).

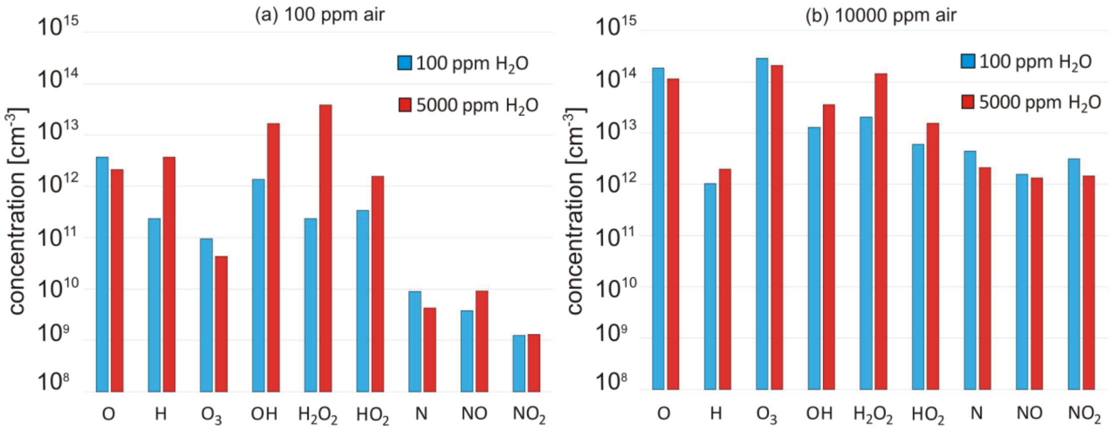

Fig. 3. Concentration of RONS in plasma as a function of water vapour content for (a) 100 ppm of air and (b) 10000 ppm of air.

As presented in Figure 3, for the same amount of water vapor, increasing of air content in plasma leads to higher concentration of OH radical, mainly through reinforced electron impact dissociation of H_2O molecules, resembling the influence of air on EEDF and rate coefficients. Concentrations of other species presented in Figure 3 are changed mainly due to different plasma composition at higher amount of air. On the other hand, for the same amount of air, higher content of water vapor leads to decrease of O and N concentration, mainly through destruction pathways with OH radical, $O + OH \rightarrow H + O_2$ and $N + OH \rightarrow H + NO$ which are also important production channels for H and even NO as a precursor for NO_2 through NO + O + He → NO_2 + He.

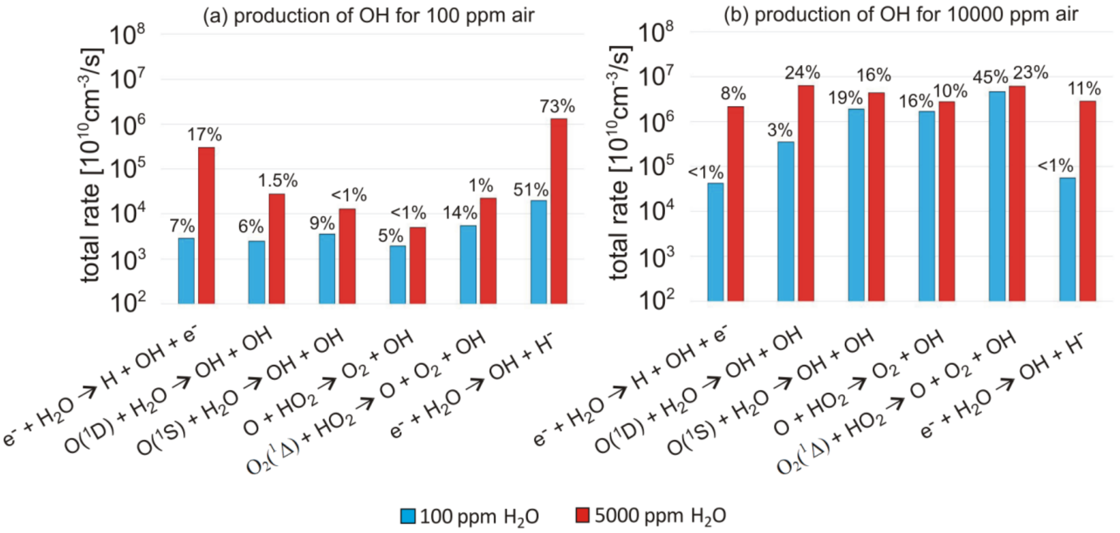

Fig. 4. The main production processes of OH radical as a function of water vapour content for (a) 100 ppm of air and (b) 10000 ppm of air.

As presented in Figure 4, at low amount of air the main OH production channels are electron impact dissociation and dissociative electron attachment involving H_2O molecules. Attachment has higher total production rate than dissociation due to lower energy threshold. At higher amount of air, chemical kinetics of OH radical becomes more complex, involving reactive species O, $O(^1D)$, $O(^1S)$ and $O_2(^1\Delta)$ which have reinforced production in electron impact dissociation and excitation of O_2 molecules. These effects resemble both the influence of air on plasma composition and on EEDF.

As presented in [6], differences between EEDFs for a different amount of air and water vapor depend also on mean electron energy (electron temperature) as a parameter of distribution function, and are much more pronounced at lower mean energies. The growth in plasma electronegativity at higher amount of water vapor in self-consistent calculation leads to higher values of electron temperature, which further determine the total rates of production and consumption processes for important reactive species. Our goal in this paper was to analyze the influence of air and water vapor on reactive species based on swarm analysis only, i. e. through EEDF and rate coefficients which strongly determine the results of global model calculation, without taking in account the changes in plasma electronegativity, electron concentration and electron temperature. As presented in our previous work [6], et 2 eV rate coefficients for electron impact dissociation of N_2, O_2 and H_2O molecules are several orders of magnitude higher than for production of He^*(19.8 eV). As a consequence, according to results presented in this paper, Penning ionization of H_2O molecules and further ion conversion $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ has a negligible contribution to production of OH radicals in comparison to electron impact dissociation of H_2O (7.6 eV) or even dissociative electron attachment to H_2O (5.5 eV). The second important remark is that processes H + NO_2 → OH + NO and H + HO_2 → 2OH become unimportant in production of OH when comparing to results presented in [6] due to lower production of H and NO at 2 eV. The consumption pathway OH + NO_2 + He → HNO_3 + He becomes less pronounced even at 10000 ppm of air and negligible at 100 ppm of air, since NO is the precursor in production of NO_2.

We have made analogous analysis for production and consumption for each of the 74 species included in our global model during calculation. We have chosen to present the results only for production of OH radical at lower mean electron energy due to its importance for biomedical application of atmospheric pressure LTP. Primary chemical pathways which determine the chemical kinetics of hydrogen peroxide, atomic oxygen and ozone, and their connection with OH radical at 2 eV are schematically presented in Figure 5. Hydrogen peroxide is mainly produced in the three-body association process OH + OH + He → H_2O_2 + He and its chemical kinetics is determined by OH radicals as a precursors. Analogous conclusion stands for ozone due to pronounced process O + O_2 + He → O_3 + He, where O atoms are produced in electron impact dissociation and dissociative attachment to O_2 molecules, analogously like OH radicals involving H_2O molecules.

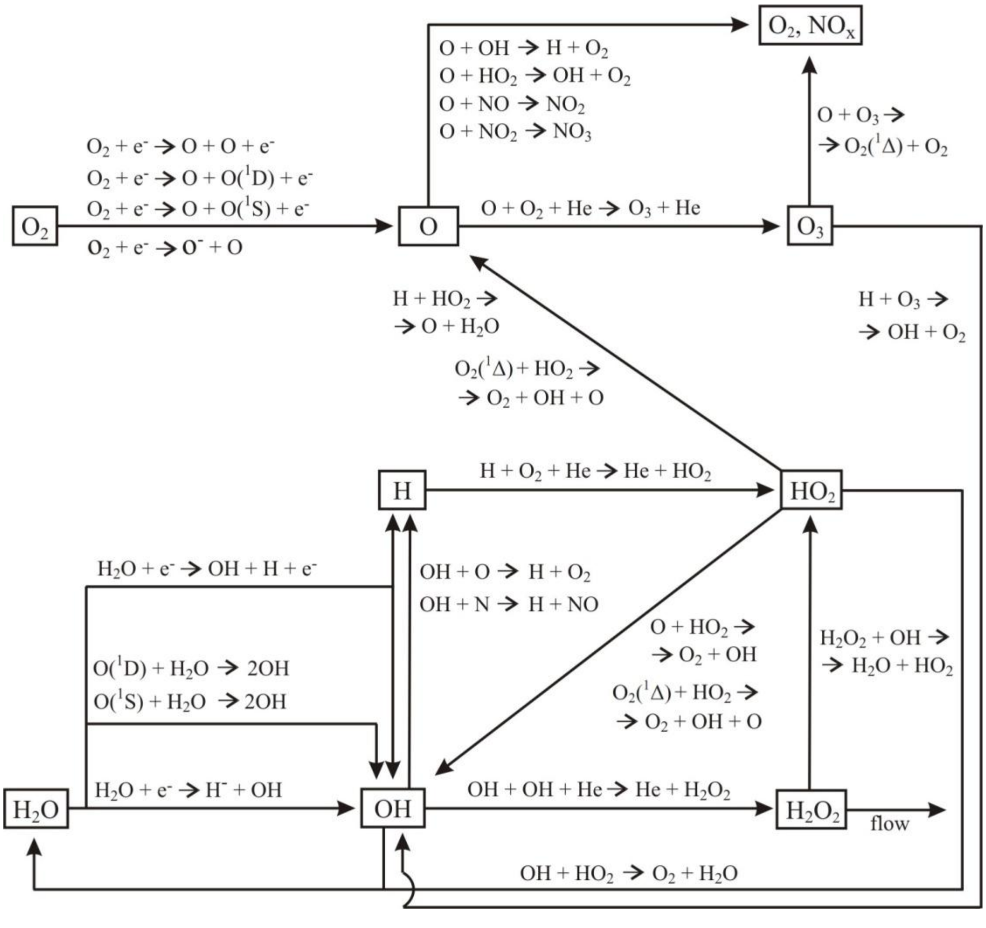

Fig. 5. Primary chemical pathways for production and consumption of species OH, H, O, O_3, HO_2 and H_2O_2 for a wide range of conditions (100 - 10000 ppm air and 100 - 8000 ppm H_2O).

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