

# Theoretical study of influence of H<sub>2</sub>O on parameters of low-temperature plasmas in humid mixtures

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Received 30 April 2006

Monte Carlo (MC) electron dynamic simulations in dry and humid N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and air were performed in order to obtain electron energy distribution functions (EEDFs), mean free path ( $\lambda$ ), drift velocity ( $v_d$ ) and collision frequency of electrons ( $\nu$ ), their mean energy ( $\bar{\epsilon}$ ) and rate coefficients of electron impact reactions, as functions of reduced electric field strength ( $E/N$ ) and concentration of H<sub>2</sub>O. The aim was to test the latest compilation of cross-sections for H<sub>2</sub>O, the applicability of the MC method used, and the effect of the H<sub>2</sub>O concentration.

A sensitivity of various parameters to the presence of H<sub>2</sub>O differs, e. g.  $\lambda$  and  $\nu$  are more sensitive than  $\bar{\epsilon}$  and  $v_d$ , and it depends strongly on the  $E/N$ . For  $E/N > 100$  Td the parameters may be approximated as their linear combinations of values in pure gases. The difference is below 10 %. For  $E/N < 100$  Td, the difference increases rapidly and MC simulations in mixtures are necessary. The presence of H<sub>2</sub>O increases the rate coefficients of most studied reactions for  $E/N > 60$  Td. Processes with higher threshold energy imply stronger increase.

*PACS:* 52.65.Pp

*Key words:* MC simulations, plasma, humidity, water

## 1 Introduction

The electrical discharges are widely tested for treatment of various gas mixtures containing water vapors, e. g. flue gas, humid air or N<sub>2</sub> [1, 2, 3]. The presence of water directly influences the plasma chemistry by introducing highly reactive OH radical. However, the influence is also indirect, by changing various plasma parameters and rate coefficients of electron impact reactions. These reactions are crucial, because high energy electrons are the key factor in low-temperature plasma chemistry.

In order to calculate these rate coefficients, the knowledge of electron energy distribution functions (EEDFs) is inevitable. In cold plasma, EEDFs can show strongly non-Maxwellian shape, but they satisfy Boltzmann equation. Thus, one way how to get EEDF is to numerically solve this equation. Another possibility, we also decided for, is to use Monte Carlo (MC) concept. We have therefore developed open source software called “Web-EEDF” [4], based on the algorithm presented by Tas et al. [5].

## 2 Algorithm

The basis of the MC algorithm used by Tas et al. [5] is a re-definition of the EEDF. Usually, it is defined as the energy distribution of an assembly of  $n$  electrons at time  $t$ . Tas and his co-workers state that the same EEDF is found when the energy of a single electron is sampled at  $n$  moments in time. However, they do not sample this electron in regular time intervals, but after it moves a distance  $\Delta s$ , given by the average distance between molecules at a given pressure and temperature.

The electron movement from one molecule to another is straightforward along the electric field vector, and the amount of the energy electron gets from the electric field is given by a parameterization. Then, random numbers decide the type of molecule for possible interaction, whether the electron will in this cycle interact with this molecule or not, and if yes, the type of interaction.

The most important change in our algorithm is that the electron can move in any direction and the amount of the energy it gets from the electric field after it changes its position by the distance  $\Delta s$ , and a new direction of his motion (if the collision does not occur) are calculated. In case of collision, the new direction of the motion of the test electron is chosen randomly.

After each calculation cycle, electron energy, velocity and the time from the last collision ( $\tau$ ) are stored. At the end of the simulation, the EEDF is normalized so that  $\int_0^\infty f(\varepsilon) \cdot \sqrt{\varepsilon} \, d\varepsilon = 1$ . Final results include  $\bar{\varepsilon}$ ,  $v_d$ ,  $\nu$ ,  $\lambda$ , mobility of electrons, rate coefficients of electron impact reactions and the branching of the electron energy towards different processes.

## 3 Cross-sections

For N<sub>2</sub> and O<sub>2</sub>, we use cross-sections obtained from JILA (Joint Institute for Laboratory Astrophysics) available at [ftp://jila.colorado.edu/collision\\_data/](ftp://jila.colorado.edu/collision_data/) [6]. This compilation contains also cross-sections for CO<sub>2</sub> and H<sub>2</sub>O. However, cross-sections for CO<sub>2</sub> were updated according to Itikawa [7], and for H<sub>2</sub>O we also tested sets of Hayashi [8], and the latest compilation of Itikawa and Mason [9].

Our calculations revealed big differences among results obtained by using these three sets of cross-sections. It can be mostly attributed to differences in cross-sections for momentum transfer ( $\sigma_m$ ) and rotational excitations of H<sub>2</sub>O ( $\sigma_r$ ). Itikawa and Mason recommend for rotational excitations theoretical cross-sections calculated by Faure et al. [10] (from 0.001 to 5 eV), which we extended up to 50 eV by cross-sections calculated by Gianturco et al. [11]. We have taken into account only three rotational transitions,  $J = 0 - 0$ ,  $0 - 1$ , and  $0 - 2$ , where  $J$  is the rotational angular momentum. The cross-section for the rotationally elastic process ( $J = 0 - 0$ ) was added to the  $\sigma_m$ . Then, we fitted these rotational cross-sections by calculating  $v_d$  in H<sub>2</sub>O, to obtain good agreement with experimental data of Wilson et al. [12], Lowke and Rees [13], and Ryzko [14, 15].

Figure 1a shows the comparison between experimental (points) and calculated (lines) values of  $v_d$  in H<sub>2</sub>O. For illustration, there are also data obtained using Itikawa and Mason's set without cross-sections for the rotational excitations ('no  $\sigma_r$ '),

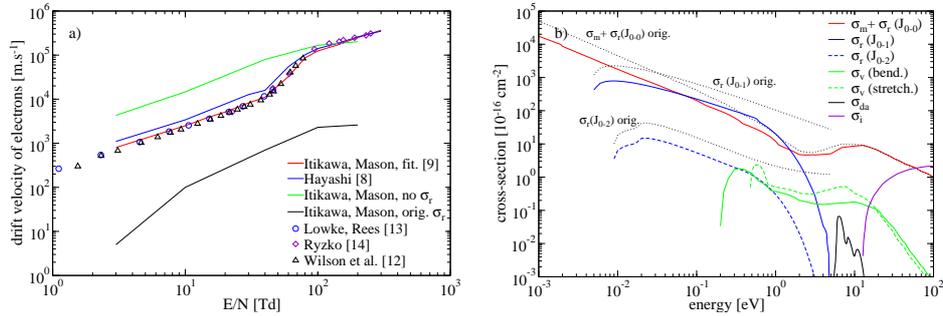


Fig. 1. a) The comparison of calculated and experimental values of  $v_d$  in  $\text{H}_2\text{O}$ ; b) The cross-sections for electron collisions with  $\text{H}_2\text{O}$  used in our calculations.

with original Itikawa and Mason's cross-sections for the rotational excitation before their fitting ('orig.  $\sigma_r$ '), and with Hayashi's cross-sections.

Modified Itikawa's cross-sections approximate the experimental values better for  $E/N < 80$  Td, whereas for higher  $E/N$  Hayashi's cross-sections seem to be slightly better. However, our calculations in humid gases with concentration of  $\text{H}_2\text{O}$  up to 10 vol. % show that the influence of the water is strongest at  $E/N < 80$  Td. In stronger fields, the differences between results obtained by these two sets are minimal. Thus, we decided to use modified set of cross-sections of Itikawa and Mason [9], as shown on Fig. 1b. Besides  $\sigma_m$  and  $\sigma_r$ , final set includes also cross-sections for ionization ( $\sigma_i$ ), dissociative attachment ( $\sigma_{da}$ ), and two vibrational excitations ( $\sigma_v$ , bending and stretching). Fig. 1b also shows original  $\sigma_m$  and  $\sigma_r$  (black dotted lines) published by Itikawa and Mason [9].

#### 4 Results and discussion

We have performed simulations in dry  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , synthetic air ( $\text{N}_2:\text{O}_2 = 4:1$ ), and in their humid mixtures with the concentration of water vapor up to 10 vol. %. The value of  $E/N$  varied from 10 to 400 Td. These calculations were performed at pressure of 1 atm., temperature of 293 K, zero degree of ionization, and with 20 million calculation cycles, i. e. 20 million data samplings. For illustration, one million calculation cycles take approximately 75 s on a computer with processor AthlonXP™ 2000+ with frequency 1667 MHz.

Fig. 2a shows relative values (divided by their final value calculated after 20 million steps) of  $\bar{\epsilon}$ ,  $v_d$ ,  $\nu$ , and rate coefficients for the ionization of  $\text{O}_2$  ( $k_{\text{O}_2^{\text{ion}}}$ ) and  $\text{N}_2$  ( $k_{\text{N}_2^{\text{ion}}}$ ), calculated in dry air at 100 Td and stored after each 250 000 cycles.

As we can see, in order to get reasonable values of  $\bar{\epsilon}$ ,  $v_d$ ,  $\lambda$  and  $\nu$ , much shorter calculations with 5 million cycles are sufficient. Changes of these parameters are below 5 % already after 5 million cycles, and the maximum deviation during the last 5 million cycles is only around 1%. However,  $k_{\text{O}_2^{\text{ion}}}$  and  $k_{\text{N}_2^{\text{ion}}}$  are calculated with lower accuracy. According to Fig. 2a, we can expect that even if we continue in the calculation for another 5 million cycles, their values may vary in the range

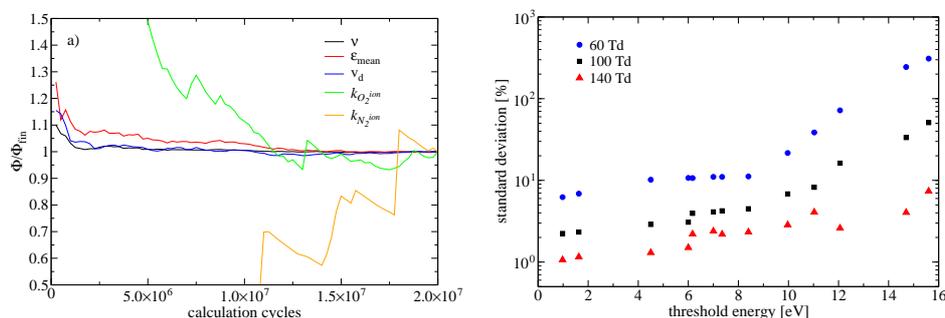


Fig. 2. a) The relative changes of selected quantities during 20 million cycles of simulation; b) The standard deviation of rate coefficients as a function of their  $\varepsilon_{\text{th}}$ .

of  $\pm 5\%$ , and  $\pm 20\%$ , respectively. The reason is in the statistics. Quantities such as  $\bar{\varepsilon}$ ,  $v_d$ ,  $\lambda$  and  $\nu$  are calculated from the whole EEDF, whereas  $k_{\text{O}_2^{\text{ion}}}$  and  $k_{\text{N}_2^{\text{ion}}}$  are calculated only from its ‘tail’, starting from threshold energies ( $\varepsilon_{\text{th}}$ ), 12.06 eV and 15.6 eV, respectively. Generally, we may expect that the rate coefficients of reactions with higher  $\varepsilon_{\text{th}}$  will have higher uncertainties, which will increase with decreasing  $E/N$ . To test this, and also the validity of uncertainties estimated from the Fig. 2a, we repeated simulations with 20 million cycles in air at 60, 100, and 140 Td nine more times.

Fig. 2b shows standard deviations from the mean values of the rate coefficients for electronic excitation and ionization of O<sub>2</sub> and N<sub>2</sub> by electron impact at 60, 100, and 140 Td, as functions of their  $\varepsilon_{\text{th}}$ , as calculated in these ten runs. At 60 Td, the deviation of calculated rate coefficients for processes with  $\varepsilon_{\text{th}} > 12$  eV is more than 50%. At 100 Td, only the rate coefficient for the ionization of N<sub>2</sub>, with  $\varepsilon_{\text{th}} = 15.6$  eV, has the deviation approaching 50%. At 140 Td, all the rate coefficients have already deviations below 10%. The standard deviation of  $k_{\text{O}_2^{\text{ion}}}$  and  $k_{\text{N}_2^{\text{ion}}}$  at 100 Td are 16% and 50%, respectively, which is more than uncertainty derived from Fig. 2a. On contrary, deviations of  $\bar{\varepsilon}$ ,  $v_d$ ,  $\lambda$ ,  $\nu$  are up to 1.5%, which is in good agreement with uncertainty estimated from Fig. 2a.

Due to these deviations, it would be almost useless to perform simulations with concentration of H<sub>2</sub>O < 1 vol.%. The sensitivity of various parameters on the presence of water differs and only some of them, and only at certain  $E/N$ , would be changed enough to exceed statistical deviation. The different sensitivity can be assigned to different processes shaping the EEDF, the vibrational excitations of N<sub>2</sub> or CO<sub>2</sub> on one hand, and the rotational excitation of H<sub>2</sub>O on the other.

These processes influence electrons from different parts of EEDF and they result in different energy losses. The rotational excitations result in the deflection of electrons with minimal change of their energy. The values of  $\nu$  and  $\lambda$  are therefore much more sensitive to the presence of water vapor than  $\bar{\varepsilon}$  and  $v_d$ .

Fig. 3 shows some characteristic results related to the changes of studied parameters due to the presence of water vapor. The values of  $\lambda$  decrease significantly at lower  $E/N$  (Fig. 3a), and they only gradually approach values in dry gases.

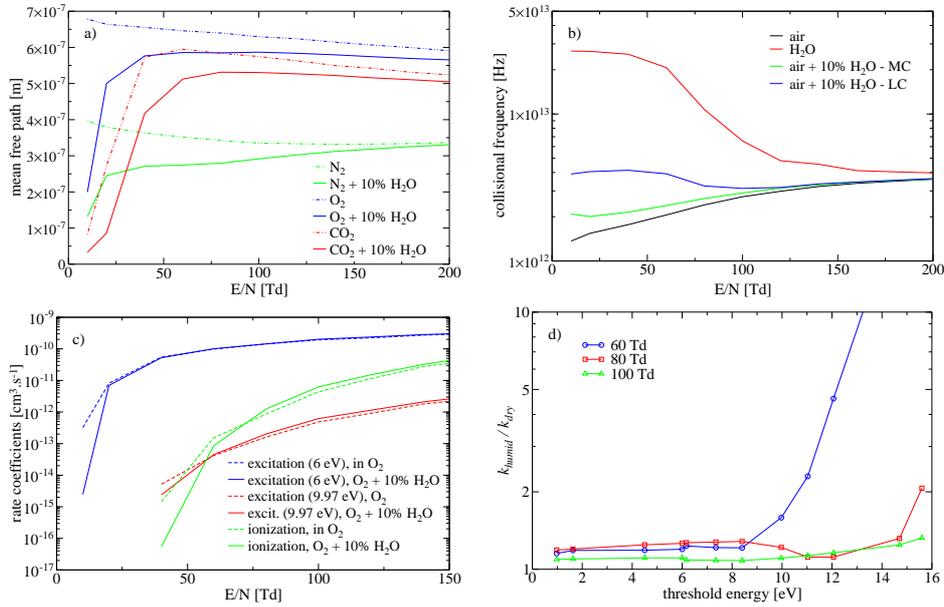


Fig. 3. a) The comparison of  $\lambda$  in dry and humid gases, with 10 % of  $\text{H}_2\text{O}$ ; b) The comparison of  $\nu$  in humid air calculated by MC simulation and LC method; c) Rate coefficients for some electron– $\text{O}_2$  interactions; d) The increase of rate coefficients in mixtures with 10 % of  $\text{H}_2\text{O}$  as a function of  $\varepsilon_{\text{th}}$ .

On contrary,  $\nu$  is significantly higher in humid mixtures at lower  $E/N$  (Fig. 3b). The differences between values of  $\nu$  in humid and dry mixtures decrease with increasing  $E/N$ . In case of humid  $\text{N}_2$  and air the values of  $\nu$  above  $\sim 200$  Td are even lower than in dry  $\text{N}_2$  and air, respectively. The values of  $\bar{\varepsilon}$  and  $v_d$  decreases for  $E/N$  below 50 Td, and increase them afterwards. These changes are relatively small, especially in the case of  $v_d$  for  $E/N > 50$  Td.

The rate coefficients for electronic excitation and ionization are affected by the water in the same way as  $\bar{\varepsilon}$ . They are decreased below  $\sim 50$  Td (due to large  $\sigma_r$ ), and increased in stronger fields (Fig. 3c). The increase is stronger in the region from about 60 to 100 Td. The reason for this can be that above 3 eV is total cross-section of  $\text{H}_2\text{O}$  smaller than in case of  $\text{N}_2$  or  $\text{CO}_2$ . This leads to lower  $\nu$ , electrons can reach higher energies, prolonging thus the ‘tail’ of EEDF. This effect is strongest at lower  $E/N$  (60 ÷ 100 Td). We have also observed that higher  $\varepsilon_{\text{th}}$  implies stronger increase in this region of  $E/N$  (Fig. 3d). However, it is necessary to be careful when interpreting these data due to the high uncertainty of rate coefficients of reactions with high  $\varepsilon_{\text{th}}$  at  $E/N < 100$  Td.

Generally, changes of all parameters are higher at low  $E/N$ . To quantify the influence of  $\text{H}_2\text{O}$ , we compared values of all parameters calculated in humid mixtures by MC simulations, with values calculated by method of linear combination (LC), i. e. from values of these parameters in dry gas and in pure  $\text{H}_2\text{O}$  (Fig. 3b). We have found that the relative differences  $\xi$ , between values calculated by LC method

( $\Phi_{LC}$ ) and MC simulation ( $\Phi_{MC}$ ), defined as  $\xi [\%] = 100(\Phi_{MC} - \Phi_{LC})/\Phi_{LC}$ , are close to zero only at  $E/N > 100$  Td. Below 100 Td, the value of  $\xi$  grows significantly with decreasing  $E/N$  and with increasing concentration of H<sub>2</sub>O. Therefore, to obtain reasonable data for  $E/N < 100$  Td, MC simulations in humid gases are inevitable. For  $E/N > 100$  Td, in case of  $\lambda$ ,  $\bar{\varepsilon}$  and  $v_d$ , and for  $E/N > 150$  Td in case of  $\nu$ , are values of  $\xi$  below 10%. However, changes of these parameters due to the presence of H<sub>2</sub>O are usually smaller than what could be expected according to values obtained by LC method. Thus, values obtained by LC method in humid mixture and by MC simulation in dry gas rather can be used as limits of value which would be obtained by MC simulation in humid mixture.

## 5 Conclusion

The changes of studied parameters due to the presence of water depend on its concentration and  $E/N$ . The influence was strongest below 80 Td, and  $\lambda$  and  $\nu$  had the highest relative changes. However, relatively smaller changes of some rate coefficients may play more important role in plasma chemistry, or in changes of properties of applied discharges, e. g. by increasing the ionization rate coefficients.

Our calculations showed that differences due to uncertainties in cross-sections for water are bigger than statistical uncertainty of applied MC method. However, the calculation of rate coefficients of processes with high  $\varepsilon_{th}$  requires large number of calculation cycles.

We hope that applied program could be useful for a large public and will warmly welcome any suggestions for its further development. Web-EEDF source code can be downloaded from <http://enviro.fmph.uniba.sk/web-eedf/>.

This research has been supported by Science and Technology Assistance Agency under the contract No. APVT-20-032404, and by Slovak Grant Agency VEGA, grant No. 1/3068/06.

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