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Abstract. Using Monte Carlo simulation, the translational relaxation of energetic O^- ions produced by dissociative electron attachment to molecules was studied in water vapor plasmas in a strong electric field. Initial O^- ions are energetic and are more reactive than the ions being in equilibrium with the electric field. Because of this, the energetic O^- ions have a chance to be involved in endothermic reactions prior to energy relaxation of these ions. The probabilities of charge exchange and electron detachment in ion-molecule interactions were calculated versus the reduced electric field. It was shown that several percent of energetic O^- ions produced in water vapor plasma by dissociative electron attachment to H_2O molecules are rapidly transformed to OH^- ions due to charge exchange collisions or are decomposed to release free electrons. The total probability of charge exchange and electron detachment from energetic O^- ions increases up to around 90% when these ions are produced by dissociative electron attachment to O_2 molecules if oxygen is added to water vapour. This means that, in this case, most of energetic ions formed from O_2 molecules are involved in charge exchange and electron detachment reactions prior to their thermalization.

1. Introduction

Non-equilibrium discharge plasmas generated in water vapor, humid air and other H_2O-containing mixtures are important for atmospheric electricity, discharges in the presence of liquid water (discharges with a liquid water electrode, in bubbles and foam) and widely used in technology, with applications ranging from air purification to plasma medicine [1-3]. Therefore, a large body of research is devoted to numerical simulation of the properties of discharge H_2O-containing plasmas taking into account ionization and ion conversion.

Water vapor is an electronegative gas and the formation of negative ions greatly affects the properties of H_2O-containing plasmas. These properties depend not only on the ratio between the density of negative ions and electron density, but on the negative ion composition as well. The density and composition of negative ions in non-equilibrium discharge plasmas are governed by the rates of ion-molecule reactions including ion formation, conversion and destruction. The rates of these reactions in weakly-ionized gases and plasmas in a strong electric field are usually calculated using the non-Maxwellian ion energy distribution and the corresponding reaction cross sections. This distribution is assumed to be in equilibrium with the applied electric field and is controlled by the reduced electric field E/N (N is the gas number density) and by the elastic and inelastic cross sections for ion-molecule interaction.

Translational energy distributions of particles produced in chemical reactions also are non-Maxwellian ones. In many collisional processes, translationally energetic (superthermal) neutral and

charged particles are formed. Energetic particles are usually thermalized in collisions with neutral particles. However, the high-energy particles can participate in inelastic collisions that do not occur when the particles are thermalized. As a result, the effective reaction rates change and additional products are formed. This effect has been well studied for energetic atoms formed in chemical reactions (see [4] and references therein). The effect of superthermal particles was also studied for O^- ions produced by dissociative electron attachment to O_2 molecules in oxygen discharge plasmas [5]. It was shown that up to 6% of energetic O^- ions are rapidly converted to O_2^- ions in charge exchange collisions.

The objective of this work was to extend the calculations made in [5] to reactions in water vapor plasmas and in H_2O-containing plasmas. We used the Monte Carlo technique to simulate the translational energy relaxation of energetic O^- ions formed by dissociative electron attachment to molecules. The effect of high-energy O^- ions on charge transfer and electron detachment was numerically studied.

2. The method of simulation

The Monte Carlo technique was used to simulate the energy relaxation of high-energy O^- ions in water vapor in a stationary uniform electric field. We assumed that O^- ions with excessive translational energy were produced by dissociative electron attachment to H_2O and to O_2 when some amount of oxygen was added to the gas.

We used the Monte Carlo technique that is the same as in our previous work [5, 6]. An ion was assumed to be originated with a given initial translational energy. To simulate the motion of O^- ions in water vapor, we used the set of cross sections taken from [7]. This set includes elastic scattering, electron detachment

$$O^- + H_2O \rightarrow e + H_2O_2 \quad (1)$$

and charge exchange

$$O^- + H_2O \rightarrow OH^- + OH. \quad (2)$$

This set of the cross sections was validated in [7] by comparing the calculated ion transport coefficients with measured data.

The initial distribution for O^- ions produced by dissociative electron attachment to H_2O and O_2 molecules was calculated by analogy with the approach used in [5] and averaged over the electron energy distribution. The electron distribution was calculated with the Bolsig+ code and a self-consistent set of electron cross sections for H_2O [8].

3. Calculated results

The kinetic energy of O^- ions produced by electron attachment is in the range 0 – 0.8 eV for the attachment to H_2O molecules and in the range 0.5 – 3 eV for the attachment to O_2 molecules. The initial ion energy distribution changes with time and tends to the ion energy distribution when the ions are in equilibrium with the electric field. In a similar way, the mean ion energy decreases with time and tends to the equilibrium mean value corresponding to a given value of E/N.

The initial ions are energetic and are more reactive in comparison with thermalized ions. The probabilities of endothermic ion-molecule reactions (charge exchange and electron detachment) are elevated when the ions are energetic and tend to equilibrium values with increasing number of collisions. The equilibrium probabilities for endothermic ion-molecule reactions increase with E/N because these processes have energy thresholds and their equilibrium rate coefficients also increase with E/N.

Firstly, let us consider the kinetics of O^- ions formed by electron attachment to H_2O molecules. Figure 1 shows the total charge exchange probability, P_{ce}, for O^- ions in all collisions before their thermalization in water vapor versus E/N. For comparison purposes figure 1 presents the charge exchange probability, $P_{ce\ th}$, for the thermalized ions (in equilibrium with the electric field) after the same number of collisions. The excess charge exchange probability $P_{ce\ ex} = P_{ce} - P_{ce\ th}$ that characterizes the effect of energetic O^- ions on charge exchange collisions is also shown in figure 1.

The probability P_{ce} can reach 11% (for 300 Td), whereas the excess probability for energetic O^- ions reaches a peak value of ≈ 4% for E/N = 200 Td. It may be concluded that, for such values of E/N, the end negative ion products formed by dissociative electron attachment to H_2O molecules are 96% of O^- ions and 4% of OH^- ions. The OH^- ions are generated by charge exchange in collisions of energetic O^- ions with H_2O molecules.

The effect of the energetic O^- ions on charge exchange is much more profound when these ions are formed by electron attachment to O_2 molecules (see figure 2) that can be present in water vapor plasma due to small admixtures. In this case, the excess probability for energetic O^- ions reaches a peak value of ≈ 37% for E/N = 100 Td. These values of E/N are practically important because they are close to the breakdown reduced electric field in water vapor and air.

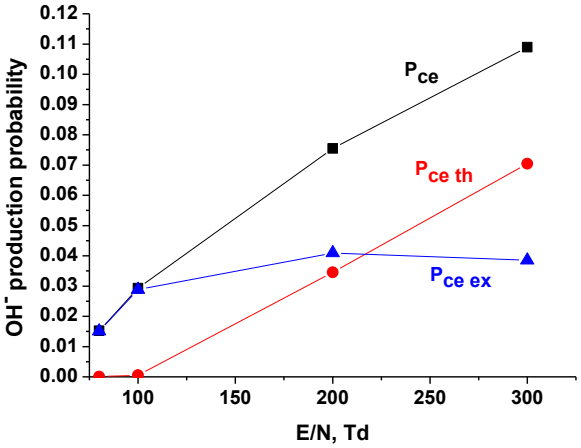

Figure 1. Charge exchange probability during O^- ion energy relaxation in water vapor as a function of E/N: (P_{ce}) the total probability, ($P_{ce\ th}$) the probability for thermalized ions and ($P_{ce\ ex}$) the excess probability of energetic ions. The ions are formed by electron attachment to H_2O molecules.

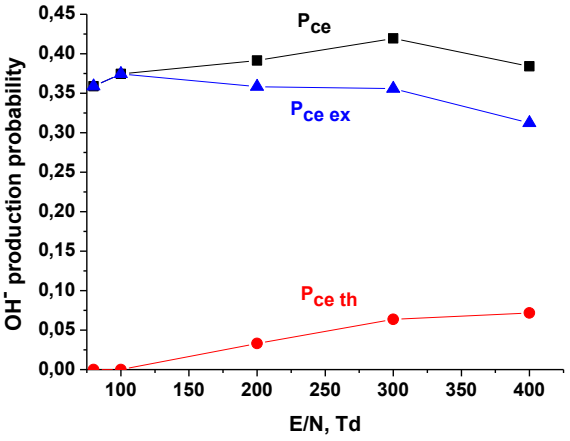

Figure 2. Charge exchange probability during O^- ion energy relaxation in water vapor as a function of E/N: (P_{ce}) the total probability, ($P_{ce\ th}$) the probability for thermalized ions and ($P_{ce\ ex}$) the excess probability of energetic ions. The ions are formed by electron attachment to O_2 molecules.

Figures 3 and 4 show, respectively, the calculated probabilities for electron detachment in collisions between O^- ions and H_2O molecules in water vapor when these ions are produced in electron attachment to H_2O and O_2, respectively. For this reaction, by analogy with the charge exchange reaction, we introduced the total probability (P_d), the probability for thermalized ions ($P_{d\ th}$) and the excess probability for energetic ions ($P_{d\ ex} = P_d - P_{d\ th}$). In the case of electron attachment to H_2O molecules, the probability P_{ce} reaches 8.5% (for 300 Td), whereas the excess probability for energetic O^- ions reaches a peak value of ≈ 2% for E/N = 200 Td. In the case of attachment to O_2 molecules, the effect of the energetic O^- ions on electron detachment is also much more profound. Here, the excess probability for energetic O^- ions reaches a peak value of ≈ 30% for E/N in the range 100 - 400 Td.

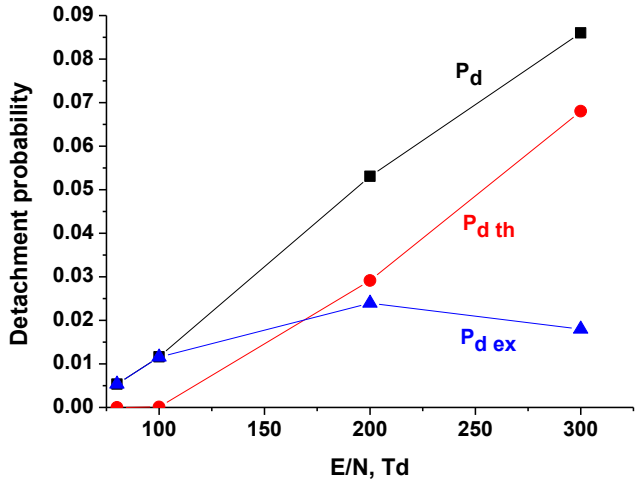

Figure 3. Electron detachment probability during O^- ion energy relaxation in water vapor as a function of E/N: (P_d) the total probability, ($P_{d\ th}$) the probability for thermalized ions and ($P_{d\ ex}$) the excess probability of energetic ions. The ions are formed by electron attachment to H_2O molecules.

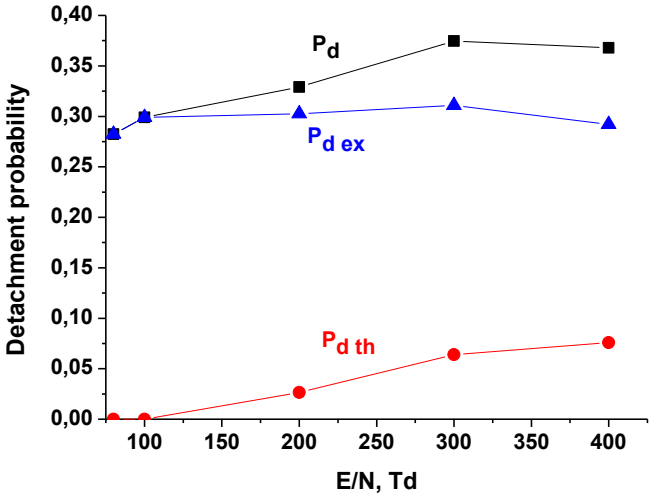

Figure 4. Electron detachment probability during O^- ion energy relaxation in water vapor as a function of E/N: (P_d) the total probability, ($P_{d\ th}$) the probability for thermalized ions and ($P_{d\ ex}$) the excess probability of energetic ions. The ions are formed by electron attachment to O_2 molecules.

4. Conclusions

Using Monte Carlo technique we studied the energy relaxation of energetic O^- ions generated by dissociative electron attachment to H_2O and O_2 molecules in water vapor in a strong electric field. The initial energy of the O^- ions is higher than the mean ion energy. Therefore, these ions can efficiently participate in endothermic reactions. Our calculations showed that the effect of the energetic ions formed by electron attachment to H_2O leads to a 4% increase in the probability of charge exchange and to a 2% increase in the probability of electron detachment prior to ion thermalization. The effect is much more profound for O^- ions formed by electron attachment to O_2 molecules. In this case, up to 37% of the energetic O^- ions are converted to OH^- ions in the charge exchange reaction and 30% of these ions are decomposed in the electron detachment reaction prior to ion thermalization. It may be concluded that only one third of the energetic O^- ions formed by electron attachment to O_2 are thermalized in water vapor plasmas. Other two thirds of these ions are converted to OH^- ions or are decomposed to release free electrons. The effect of energetic O^- ions should be taken into account when simulating the properties of water vapor plasmas.

Acknowledgements

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