Self-consistent electron energy distribution functions in reacting CO_2 discharge and post-discharges conditions

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Introduction

Large attention is nowadays devoted to the understanding of the activation of CO_2 by cold plasmas in different conditions such as microwave (MW), dielectric barrier (DBD) or nano-repetitively pulsed (NRP) discharges. Theoretical efforts are being developed to better understand the electrical conditions necessary for maximizing the CO_2 dissociation process [1-7]. In particular, Bogaerts et al. [1-2] concentrated their efforts on the vibrational plasma kinetics, while Pietanza et al. [3-7] devoted particular attention to the development of the electron energy distribution function (EEDF) in pure CO_2 and CO plasmas. In this contribution, we present new results for MW CO_2 reacting mixture, obtained by applying a self-consistent kinetic model, emphasizing the role of CO_2 and CO electronically excited states (EESs) in affecting the EEDF. EESs play an important role in superposing structures in the EEDF especially in the post-discharge regime due to the action of superelastic collisions.

The model

The self-consistent kinetic model consists in the simultaneous solution of the Boltzmann equation for the electron kinetics and the state-to-state master equations for the vibrational and the electronically excited state kinetics of the molecules and atoms of the mixture [4-7]. The model calculates simultaneously the time evolution of the electron energy distribution function (EEDF), the vibrational distribution function (VDF) of the molecules, the electronically excited states (EESs) of atoms and molecules and the plasma composition in discharge and post-discharge conditions. The model has been applied to a CO_2 reacting plasma characterized by the following neutral molecules (CO_2, CO, O_2), neutral atoms (O, C) and single-charged species (CO_2^+, CO^+, O^+, C^+, e^-). For the molecules, the

vibrational kinetic model has been developed only for the ground EES ($CO_2(\,^1\Sigma_g^+)$, $CO(X^1\Sigma^+)$, $O_2(X^3\Sigma_g^-)$). In particular, for CO_2 we take into account only the pure asymmetric mode levels of the kind (00n) up to the dissociation limit of 5.5 eV (21 levels), the first bending mode (010) and few low-lying Fermi levels which mix symmetric stretching and bending mode levels. For CO and O_2, we take into account 80 and 34 vibrational levels, respectively.

The EESs included into the model are the following: CO_2(10.5 eV), $CO(a^3\Pi, 6\ eV)$, $CO(a'^3\Sigma^+$, 6.863), $CO(A^1\Pi$, 8.03 eV), $CO(b^3\Sigma^+$, 10.4 eV), $CO(B^1\Sigma^+$, 10.78 eV), $CO(C^1\Sigma^+$, 11.40 eV), $CO(E^1\Sigma^+, 11.52\ eV)$, $O_2(a^1\Delta_g, 0.976\ eV)$, $O_2(b^1\Sigma_g^+, 1.627)$, $C(^1D, 1.263\ eV)$, $C(^1S, 2.684\ eV)$, $C(^5S^0$, 4.182 eV), $O(^1D, 1.976\ eV)$, $O(^1S, 4.19\ eV)$, $O(3s^3S^0, 9.146\ eV)$, $O(3s^5S^0, 9.521\ eV)$.

The electron impact cross sections data entering the Boltzmann equation have been taken from available database [3-8] using, for the asymmetric higher vibrational levels cross sections, the scaling law suggested by Fridman [9].

For the plasma chemistry, we take into account several heavy-particle processes which are described by Arrhenius rate coefficients [1-2, 4-7]. To extend these rates also to higher vibrational levels we use the Fridman-Macheret *alfa*-model [9].

The EESs kinetic takes into account electron impact excitation and de-excitation processes, spontaneous emission and heavy-particle quenching processes [7]. It is described by the following differential equation for the density of the i-th EES (n_i) [7]

$$\frac{dn_i}{dt} = K^i_{exc} n_e n_0 - K^i_{de-exc} n_e n_i - \sum_{j<i} \lambda_{ij} A_{ij}\, n_i + Q \qquad (1)$$

where K^i_{exc} and K^i_{de-exc} represents the electron impact excitation and de-excitation rate coefficient, n_e and n_0 the electron density and the ground electronic excited state density, $\lambda_{ij}A_{ij}$ the escape factor and the Einstein coefficient for the radiative transition from the i-th toward the j-th EES, Q the term due to quenching processes.

Results

Fig. 1 shows the EEDF time evolution calculated in a MW test case characterized by the following conditions of constant pressure, gas temperature and power density (P=20 torr, T_{gas}=300 K, P_d=80 Wcm^{-3}) during the (a) discharge (0<t<50 ms) and (b) the post-discharge (50 ms<t<100 ms). In this test case condition, the plasma is assumed totally thick, i.e. $\lambda_{ij} = 0$ in eq. (1) for all the radiative transitions involving the EESs. During the discharge (Fig. 1 a), the EEDF is driven by the electric field reaching soon (t>8 10^{-5} s) a stationary condition. When the discharge pulse is switched off, the EEDF cools down quickly, especially in the low energy range, while the distribution tail is

characterized by the presence of peaks originated from superelastic collisions involving the EESs. One example of superelastic electronic collision is the following one involving the CO_2(10.5 eV) EES, i.e.

$$e(\varepsilon = 0\ eV) + CO_2(10.5\ eV) \rightarrow e(\varepsilon = 10.5\ eV) + CO_2 \qquad (2)$$

This process produces electrons at 10.5 eV thus creating, in the EEDF, the corresponding characteristic peak. By looking to the energies of the peaks, one can go back to the corresponding EES. In particular, by looking to Fig. 1 b, it's clear that the EEDF is characterized not only by the peaks due to the CO_2(10.5 eV) EES but by different peaks due to the CO, O_2 and O EES. At low energy, the peaks due to O_2(0.976 eV) and O(1.976 eV) are evident, while at higher energies one can observe the peaks due to CO(6.863 eV), CO(8.003 eV), O(9.52 eV), CO(10.4 eV), CO(10.78 eV) and finally CO(11.40)-CO(11.52 eV). One important effect of this overpopulated EEDF tail can be observed in the calculation of the electron impact rate coefficients: despite the fast decrease of the electron temperature in the post-discharge, electron impact rate coefficients, such as CO_2 dissociation one, can be still important and give a non-negligible effect to the overall kinetics in the post-discharge.

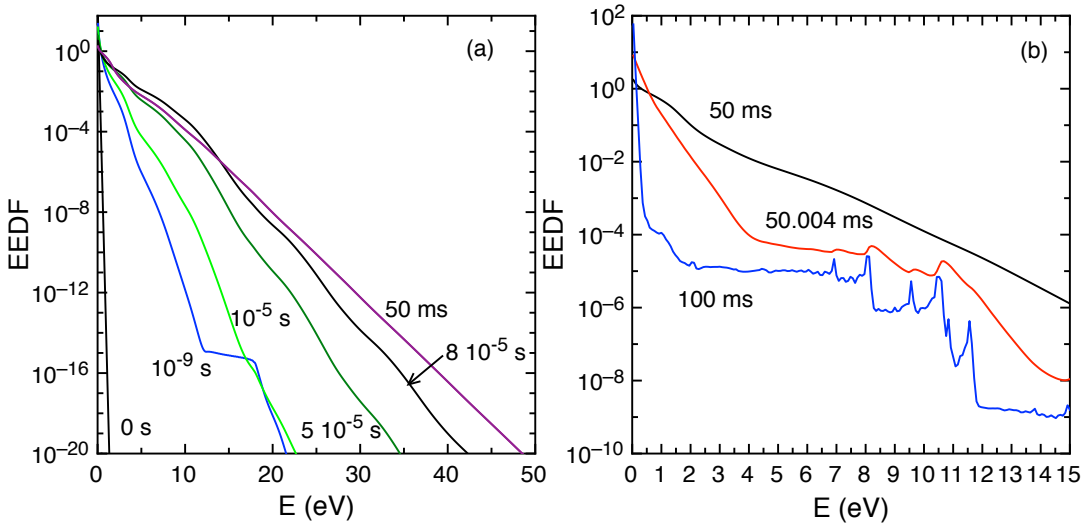

Fig. 1 EEDF time evolution in (a) discharge (0<t<50ms) and (b) post-discharge (50 ms<t<100 ms) conditions for a MW test case characterized by P=20 torr, T_{gas}=300 K, P_d=80 Wcm^{-3}.

The height of the peak is proportional to the corresponding EES density, whose time evolution is described by eq. (1). As a consequence, the non-equilibrium EEDF shape is strongly dependent on the radiative and quenching processes included in the model for the EESs. Next figure (Fig. 2) show the comparison of the EEDF at the end of the post-discharge (t=100 ms) calculated in the optically thick ($\lambda_{ij} = 0$) and thin ($\lambda_{ij} = 1$) condition and by considering the CO_2(10.5 eV) as a dissociative channel. With an optically thin plasma, the resulting EEDF loses all the peaks corresponding to the emitting EESs with the only exception of the CO_2(10.5 eV), CO(11.40 eV) and CO(11.52 eV) ones

for which no radiative transition are accounted. By considering also dissociation from 10.5 eV, the EEDF decreases further by losing also the peak for the CO_2(10.5 eV).

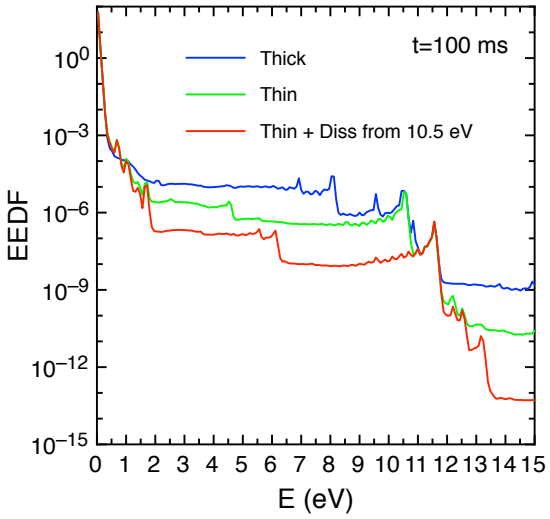

Fig. 2 EEDF at the post-discharge end (t=100 ms) in a MW test case characterized by P=20 torr, T_{gas}=300 K, P_d=80 Wcm^{-3} by considering an optically thick and thin plasma and by considering dissociation from the CO_2(10.5 eV) EES.

Conclusions

The results reported in the present paper clearly show the importance of the EESs in shaping the EEDF, especially in the post-discharge regime. The results depend on the number of excited states considered in the model and on the kinetic model used to describe their time evolution. A more accurate scheme for the EESs of CO_2 is needed since, at this stage, only one state (10.5 eV) has been taken into account. By including the CO, O_2, C and O EESs kinetics to the CO_2 one, the accuracy of the model has been improved. However, a more deeply investigation of all the quenching and radiative processes involving such EESs is necessary.

References

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