Non equilibrium vibrational and electron energy distribution functions in CO_2/CO cold plasmas

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Introduction

In a series of recent papers [1-4], we have discussed the chemical kinetics of CO reacting mixtures under discharge and post-discharge conditions similar to those occurring in microwave, DBD and nanosecond repetitively pulsed (NRP) discharges. The latter kind of discharges are assuming large importance in plasma assisted combustion, either for reducing the ignition times or for eliminating oscillation instabilities in the combustion process. In the theoretical description of such discharges, the chemical kinetics is usually decoupled from the electron ones, a hypothesis which can be open to questions especially in the post discharge regime. This aspect can become important in NRP discharges and afterglow description, depending on both the duration of the pulse and the corresponding repetition frequency. The latter is of particular importance to establish a sort of memory on the next pulse of what occurring in the previous one. Our studies have underlined the importance of the electronic excited states of CO in affecting the electron energy distribution functions (eedf) of free electrons through superelastic electronic collisions (SEC) expecially in the post discharge, leading the corresponding eedf in the next pulse much pumped than in the previous one. A similar behavior is to be expected by the vibrational distribution function (vdf) as well. In the present contribution, we focus on the description of NRP discharges of CO plasmas by means of a selfconsistent model based on the coupled solution of the electron Boltzmann equation for the eedf and the master equations for the vibrational levels of CO as well as the electronic excited states of CO, O and C atoms. In particular, in the calculation of the electronic excited states, different models have been considered and compared. We take into account optically thin and thick plasma conditions without the inclusion of any quenching model for the electronic excited states and the same thin and thick conditions with the inclusion of a quenching model. The quenching model takes into account the quenching process involving the $a^3\Pi$ state of CO, which pumps energy into the vibrational v=27 level of the CO ground electronic state [5, 6] and some quenching processes involving the low-lying electronic states of O and C atoms [7].

The model

The model is based on the solution of a time dependent Boltzmann equation for the calculation of the eedf, coupled to the non-equilibrium vibrational kinetics of CO molecule for the calculation of the vdf and the electronic excited state kinetics of CO, C and O species, as well as, with a simple dissociation-recombination and ionization-recombination kinetics describing the plasma mixture [1-4].
All the kinetics are self consistently and time dependent solved. Equations and details can be found in refs. [1-4]. The plasma mixture considered is composed by the following species: CO, CO_2, C, O, CO^+, CO_2^+, C^+, O^+ and e^-. The energy level diagrams of CO, C and O are schematically represented in Fig. 1 of [3]. The CO molecule has n_v=80 vibrational levels in the ground electronic state ($X^1\Sigma^+$). Besides the ground state, we consider several

CO electronic excited states: three triplet states, $a^3\Pi$ (6.006 eV), $a'^3\Sigma^+$(6.863), $b^3\Sigma^+$(10.40 eV) and four singlet states, $A^1\Pi$ (8.03 eV), $B^1\Sigma^+$(10.78 eV), $C^1\Sigma^+$(11.40 eV), $E^1\Sigma^+$(11.52 eV).
For C and O atoms, only four and five electronic levels are accounted for, while CO_2, C^+ and O^+ are considered only in their ground states (see Fig. 1(b) of [3]). The electron impact cross sections entering in the electron Boltzmann equation are those corresponding to the processes listed in Table 1 of [1]. The plasma chemistry model includes the processes listed in Table 1 of [4]. Beside CO dissociation by electron impact mechanism (DEM), also CO dissociation by resonant vibrational excitation is included (RES) [8]. Dissociation induced by vibrational excitation is also taken into account by direct dissociation (PVM_1) and the Boudouard process. Electron impact ionization and recombination of CO, C and O are also considered together with C and O recombination into CO and dissociative recombination process of CO^+ into C and O.
The CO vibrational distribution function vdf is obtained from the solution of a coupled system of differential equations, one equation for each vibrational level of the ground electronic state in which electron-vibration (e-V), vibration-vibration (V-V), vibration-translation (V-T), spontaneous emission (SE) and the reactive processes of dissociation-recombination and ionization-recombination involving the CO vibrational ladder are included.
The electronic excited state kinetics of CO, O and C atoms instead is described by a system of differential equations, one equation for each state, in which the terms due to electron impact excitation and de-excitation, spontaneous emission and quenching processes are accounted. The most important quenching channel for CO electronic states is the following one [5, 6]

$$CO\left(a^3\Pi,\ \mathrm{w}=0\right)+CO\rightarrow CO(v=27)+CO \qquad (1)$$

in which the v=27th level of the CO ground electronic state is pumped.

Results

In this section, we report results for a NRP discharge alimented by a sequence of modulated electric field pulses with a pulse duration t_p=20 ns and an interpulse delay times t_{id}=1 μs. The discharge is applied to an atmospheric CO plasma with a constant gas temperature of T_{gas}=1000 K. The electric field is characterized by a time-dependent profile [3, 4, 9] described by an analytical expression (see [3, 4]).
Fig. 1 shows the CO vibrational temperature as a function of time in the four kinetic model assumptions for the first 6 pulses of the NRP discharge with t_{id}=1 μs.
In particular, we consider 1) an optical thick CO plasma, i.e. a plasma where the allowed optical transitions involving the CO electronic states are completely reabsorbed, 2) an optical thin CO plasma, i.e. a plasma allowing the optical decay of the considered CO electronic excited states, 3) a thin plasma with the addition of quenching processes for the $a^3\Pi$ state of CO (see eq. (1)) and for O and C low lying electronic states (see [4]), 4) a thick CO plasma with previous quenching processes. As it can be see, with the sequence of the pulses, a storage of vibrational energy is obtained with a step-up increasing process, more effective in the thick than in the thin case and when the $a^3\Pi$ quenching process is included in the kinetics. This is an indirect effect of a more activated eedf due to superelastic electronic processes, when passing from the thin to the thick case, able to pump more energy in the vibrational ladder through e-V processes. By including the $a^3\Pi$ quenching

process, the vibrational temperature increase is obtained also through the direct pumping of energy in the 27th vibrational level and its subsequent redistribution. Fig. 2 a and b show respectively the eedf and the vdf in the first pulse post-discharge at t=1 μs. As it can be seen in Fig. 2 a, the eedf is dominated by the effect of superelastic electronic collisions which create peak structures in the eedf, whose peaks are proportional to the population of the electronic excited states. The peak structure strongly depends on the model adopted to describe the electronic state kinetics. In the thick case, the electronic excited states are more populated respect to the thin case, as a consequence, the corresponding eedf shape has a structure with higher peaks. In the energy range between 6-12 eV, four well evident super-elastic peaks involving the $a^3\Pi$ (6.006 eV), $A^1\Pi$ (8.03 eV), $b^3\Sigma^+$(10.40-10.78 eV) and $C^1\Sigma^+, E^1\Sigma^+$ (11.40-11.52 eV) are clearly evident in correspondence of their energies.

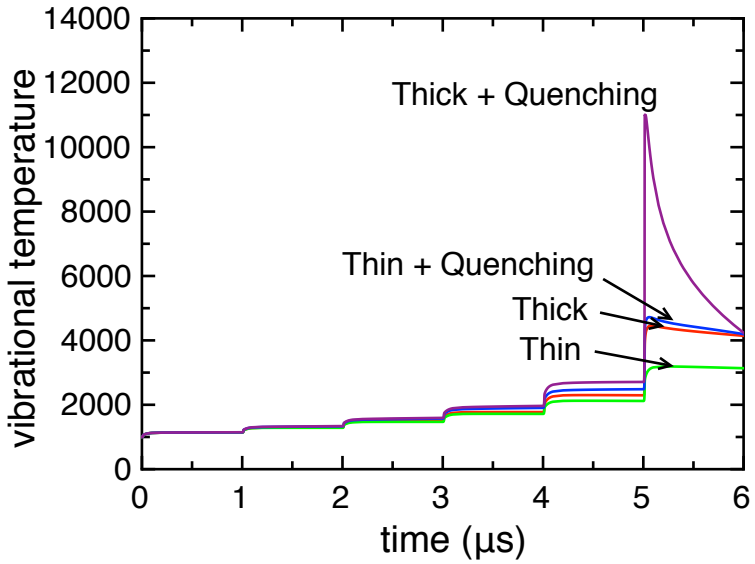

Fig. 1 Vibrational temperature time evolution in the four kinetic model assumptions (Thick, Thin, Thin + Quenching and Thick + Quenching) in the simulation of the NRP discharge with an interpulse delay time t_{id}=1 μs.

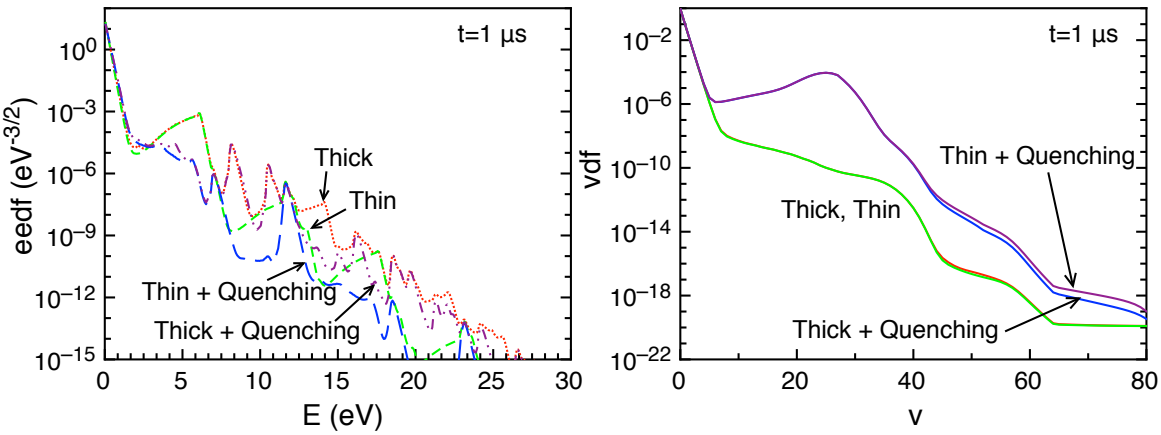

Fig. 2 (a) eedf and (b) vdf in the post discharge of the first pulse at t=1 μs in the four kinetic model assumptions.

By looking to the vdf in Fig. 2 b, the biggest difference occurs when the $a^3\Pi$ quenching process with the vibrational energy pumping in the v^{th}=27 level is included in the model. This process creates a more activated vdf characterized by a peak at v=27, smoothed out in the post-discharge by VV and VT collisions. The resulting vdf, more activated in the

highest part of the vibrational ladder (v>20), strengthens vibrational excitation dissociation channels, in particular the Boudouard ones (PVM_2) which strongly depend on the vdf tail.

Conclusions

The main conclusion of the present contribution is the importance of the kinetics of electronic excited states of CO in affecting the eedf through electronic superelastic collisions. These effects depend on the assumptions made in the construction of different kinetic models for the electronic excited states, differing on the possibility of reabsorption of emitted radiation as well as on the inclusion of quenching processes. In this connection, four models are investigated leading to optically thin and thick plasma conditions and to the inclusion of quenching processes for the electronic excited states of CO, C and O. The most important quenching process in affecting eedf and vdf is that one involving the CO $a^3\Pi$ state, whose effect is either to kill the $a^3\Pi$ state or to produce vibrationally excited states in the CO ground electronic state.
Future work should be devoted to the insertion of the proposed CO kinetics in the corresponding one of the CO_2 for the study of CO_2 activation under cold plasmas. To this end, we should focus on the role of superelastic electronic collisions of CO electronic states in affecting the eedf in the reacting CO_2/CO mixture [10, 11]. This point is extremely important since in our previous works on pure CO_2 discharge the only electronic state of CO_2, which was allowed to participate to super-elastic collisions with cold electrons, was that one at 10.2 eV [10, 11]. The more complete manifold of electronic states of CO becomes essential to understand the structure of eedf in the reacting CO_2/CO mixture.

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