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Electron energy distribution functions, vibrational and electronic kinetics of reacting CO and CO₂ microwave plasmas: a state to state approach

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Abstract – The coupling between the different quantities in pure reacting CO plasmas and pure CO₂ plasmas in microwave discharge conditions are presented and discussed. The results show very similar qualitative behavior for both the mixtures, particularly for the vibrational distributions of molecular species and for the electron energy distribution function. Both the distributions show non-equilibrium trend justifying the use of state to state approach for the kinetic description of CO₂ plasma mixture in microwave discharges. In particular, the electron energy distribution functions show characteristic peak structures in the post discharge, linked to the electronic excited states population.

Keywords: state to state kinetic models; CO₂ conversion; vibrational kinetics; electron Boltzmann equation; CO; non-equilibrium vibrational and electron distributions

Riassunto – Viene presentato e discusso l'accoppiamento tra le diverse quantità che caratterizzano plasma puri di CO e CO₂ in condizioni di scarica a microonde. I risultati mostrano un comportamento qualitativo molto simile in entrambe le miscele, in particolare, sia per le distribuzioni vibrazionali delle specie molecolari che per la funzione di distribuzione dell'energia elettronica. Entrambe le distribuzioni mostrano andamenti di non-equilibrio che giustificano l'uso dell'approccio stato a stato per la descrizione cinetica della miscela di plasma di CO₂ nelle scariche a microonde. In particolare, le funzioni di distribuzione dell'energia elettronica mostrano caratteristiche strutture a picchi nella fase successiva alla scarica, legate alla popolazione degli stati elettronici eccitati.

Parole chiave: modelli cinetici stato a stato, conversione CO₂; cinetica vibrazionale; equazione di Boltzmann per gli elettroni; CO; distribuzioni vibrazionali ed elettroniche di non-equilibrio

INTRODUCTION

A state to state approach for understanding the plasma kinetics in atomic and molecular plasmas is currently used to get information about the microscopic and macroscopic properties of the relevant systems [1-3]. The approach is based on the coupling of vibrationally and electronically excited state kinetics

of heavy particles with the Boltzmann equation for the calculation of the electron energy distribution function (eedf). The method was initiated many years ago for understanding the properties of infrared CO laser with and without the presence of Helium [4-5]. The vibrational kinetics was used to understand the theoretical and experimental plateaux of the vibrational distribution function (vdf) of CO with a simple kinetics including the pumping of vibrational energy by free electrons on the first vibrational levels of CO (e-V), the redistribution of the introduced quanta by vibrational-vibrational energy exchange processes (V-V) and their destruction by vibrational translational energy exchange processes (V-T).

In these last years, a more accurate treatment of CO plasma kinetics [6-8] has been performed in order to improve the kinetics models describing the CO₂ activation by cold plasmas [9-10]. The CO₂ plasmas, depending on the experimental conditions, can be characterized by high concentration of CO₂ dissociation products such as CO, O₂, O atoms with their corresponding positive and negative ions with the consequence that their kinetics cannot be neglected and should be treated as much as accurate as that one of the CO₂ system. Moreover, the CO molecule, characterized by several electronic excited states, some of them metastable, strongly affect the eedf, shaping it with characteristic structures due to superelastic electronic collisions, especially in post-discharge conditions.

The use of state to state approach is of fundamental importance for the description of CO₂ microwave discharge, since recent results have shown that such discharges can be characterized by strong vibrational non equilibrium conditions which strongly enhanced the CO₂ conversion.

Another important key point for the description of the CO₂ activation in cold plasma is the use of the selfconsistent solution of the heavy particle and the electron kinetics due to the strict correlation between the vdfs of molecules, the electronic excited state concentrations and the eedf both in discharge and post-discharge conditions.

For the description of the applied discharge, contrary to our previous works in which the reduced electric field was used as an input parameter [9-10], more recently, we are using as electrical parameter the power density as reported also by Bogaerts et al [11-12]. In this way, our model is more stable and simulations can be performed in conditions closer to the experimental ones.

In this paper, we present results obtained by using a selfconsistent state to state kinetic model for the description of CO and CO₂ plasma mixtures under microwave discharge conditions showing similarities and differences of the two systems in the same discharge conditions.

The model

The model used has been discussed in several papers [6-10]. Basically, it consists of the coupling between the Boltzmann equation for the eedf and the vibrational and electronic kinetics for the excited states. In the model, we take into account several kinetic processes, among these a very crucial role is performed by superelastic vibrational and electronic collision processes, which create characteristic structures in the eedf depending on the vibrational and electronic level concentrations. Moreover, also state to state dissociation/recombination processes for both neutral and ionized species are inserted in the model and coupled to the electron kinetics. The list of all the state to state electron impact cross sections and heavy particle rate coefficients for the CO₂ and CO systems used in the model can be found in our previous works [6-10].

The most important input data of the model which characterized the global behavior of the plasma mixture are the gas temperature, the pressure, the discharge power density and the corresponding residence time, which are fixed to the following values for all the reported results: $T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/cm³, $t_d=50$ ms.

The model results show the time evolution of microscopic properties such as CO₂, CO and O₂ vdfs and eedf and macroscopic quantities such as molar composition and vibrational temperatures. The two plasma mixtures considered, i.e. the pure CO and pure CO₂ ones, differs on the initial molar composition: the initial molar fractions are 1 for CO in the pure CO and 1 for CO₂ in the pure CO₂ mixtures, while the initial molar fractions of the other species are negligible, i.e. 10^{-10} . In this way, we select two different plasma mixtures in which the kinetics is dominated, respectively, by the CO and the CO₂ systems. In both cases, the initial electron molar fraction is 10^{-6} .

CO reacting plasma

The application of the power density to an initial CO pure plasma is such to initiate the plasma chemistry in the medium. In particular, figure 1 reports the time evolution of (a) the reduced electric field (E/N) calculated from the imposed power density, (b) the electron molar fraction and (c) the CO and CO₂ vibrational temperature. Since the power density is kept constant during the residence time, the time evolution of the E/N and the electron molar fraction are strong coupled and complementary ($P_d \propto N_e (E/N)^2$).

Figure 2 report the molar fractions time evolution in (a) discharge and (b) post-discharge conditions. The

CO specie remains the main component of the mixture in both conditions. The molar fractions of CO_2 and C coincide because the main dissociation channel for CO in the reported case study is the Boudouard reaction [13] involving vibrationally excited CO molecules, i.e. the reaction



O and O_2 species are instead minority species.

The CO, CO_2 and O_2 vdf time evolution is reported in figure 3. As it can be observed, the three vibrational distributions present large deviations from the corresponding Boltzmann ones at $T_g=300$ K. In particular, the vdf of CO (figure 3 a, b) is largely dependent on the reaction



where $a^3 \Pi$ is the first CO electronic excited state at 6 eV. This reaction forms a peak at $v=27$ which is then re-

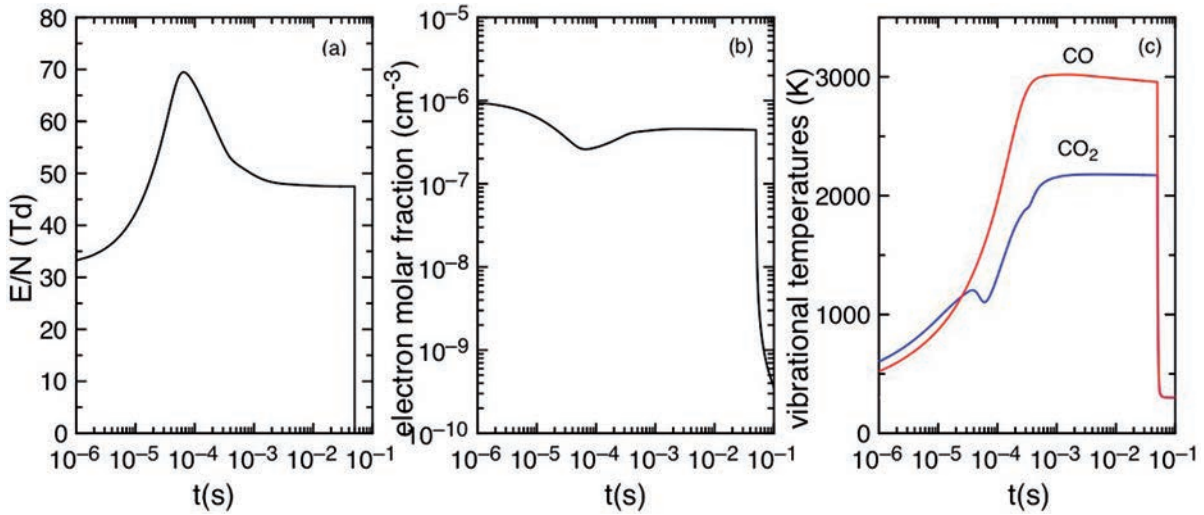


Fig. 1. Time evolution of (a) the reduced electric field (E/N), (b) the electron molar fraction and (c) the CO and CO_2 vibrational temperatures in an initially pure CO reacting plasma under discharge and post-discharge conditions ($T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/ cm^3 , $t_d=50$ ms).

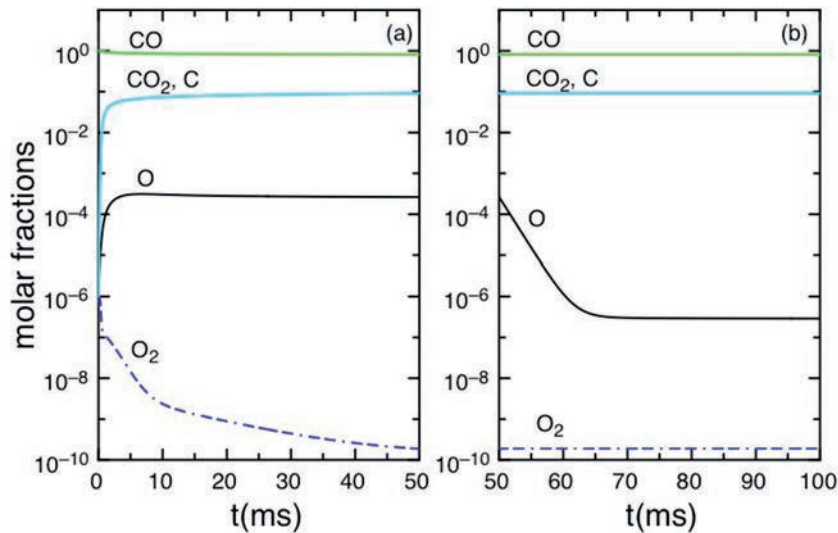
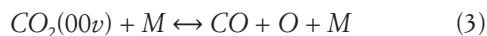


Fig. 2 Molar fraction time evolution in pure CO reacting plasma under (a) discharge and (b) post-discharge conditions ($T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/ cm^3 , $t_d=50$ ms).

distributed by V-V and V-T processes forming a non-equilibrium distribution at the end of pulse. In the corresponding post discharge conditions, the vdf is controlled by V-V processes forming a plateau up to $v=30$, while V-T rates dominate the V-V processes for $v>30$.

The vdf of the asymmetric mode levels of CO_2 (see figure 3 c, d) is also dominated by V-V and V-T processes. The dissociation process



becomes important for $v>16$, depopulating the vdf tail. In the post discharge regime, the vibrational distribution of CO_2 keeps the form of the last vibrational distribution of the discharge at the early times, while at longer times the vibrational temperature decreases forming however extended plateaux governed by V-V and V-T processes.

Also the vdf of O_2 (see figure 3 e, f) shows long plateaux at the end of discharge as well as in the post discharge. These plateaux are essentially generated by the recombination of atomic oxygen, i.e.

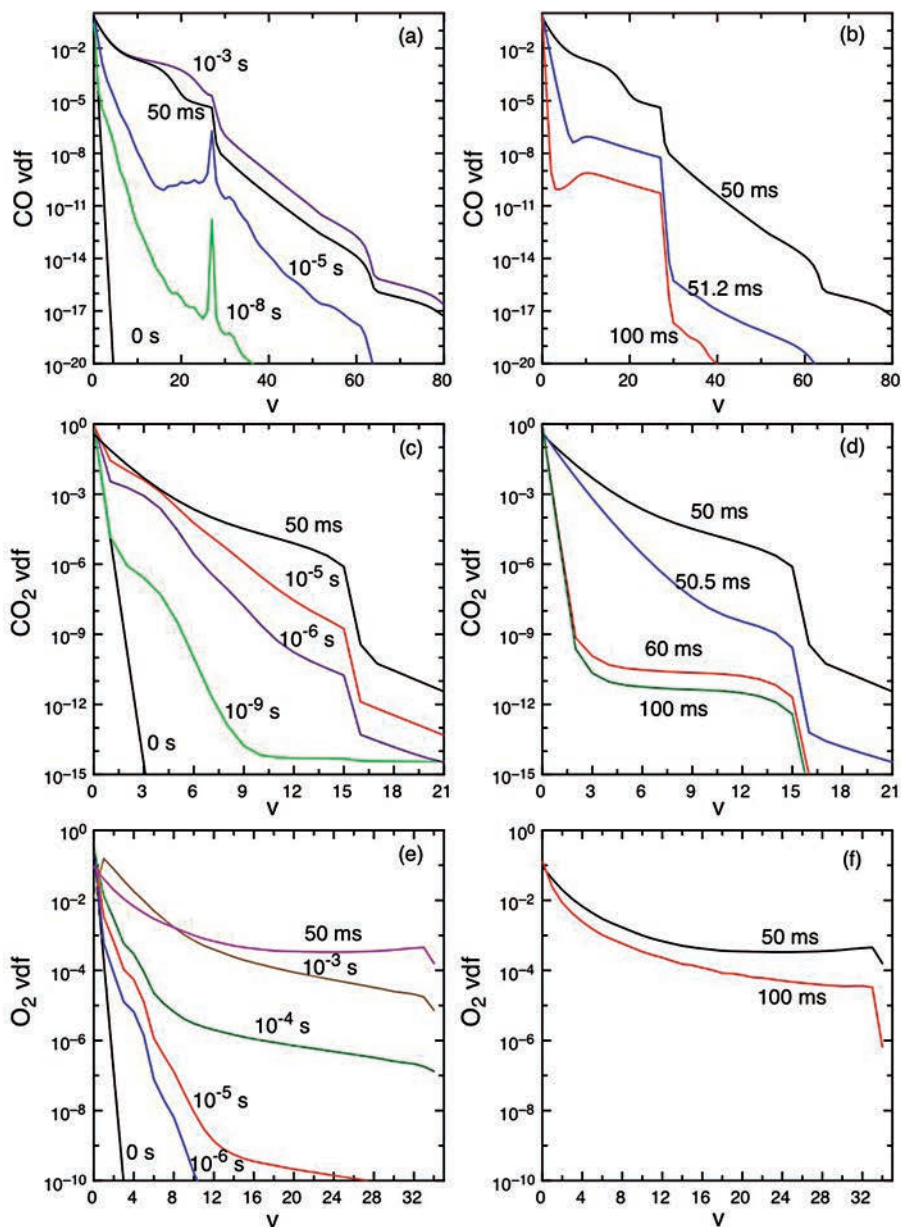


Fig. 3. Vdf time evolution of CO (a, b), CO₂ (c, d) and O₂ (e, f) molecules in pure CO reacting plasma under discharge (a, c, e) and post-discharge (b, d, f) conditions ($T_{\text{gas}}=300\text{ K}$, $P=20\text{ torr}$, $P_d=80\text{ W/cm}^2$, $t_d=50\text{ ms}$).

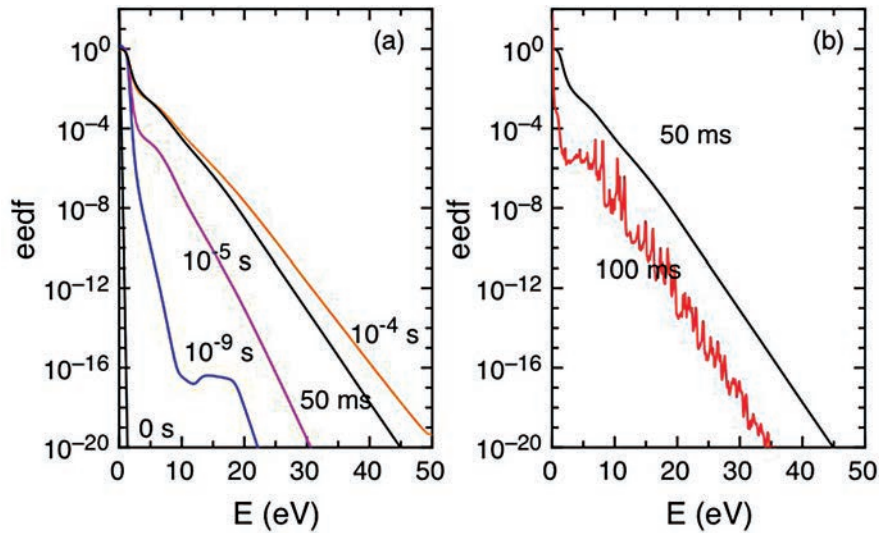
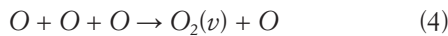


Fig. 4. Eedf time evolution in pure CO reacting plasma under (a) discharge and (b) post-discharge conditions ($T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/cm³, $t_d=50$ ms).



the atomic oxygen formed by O_2 electron impact dissociation processes.

The eedf time evolution of the pure CO reacting mixture is reported in figure 4 in (a) discharge and (b) post-discharge conditions. In the first case, the eedf behavior is governed by the action of the self-consistent reduced electric field E/N with a non-negligible role of superelastic vibrational collisions with the global effect of heating up the electron gas. In the post discharge, the eedf cools

down quickly presenting a well-structured shape due to the superelastic electronic collisions coming from the electronically excited states of CO, CO_2 , C and O.

CO₂ reacting plasma

Next figures show the behavior of the pure CO_2 plasma mixture. In particular, figure 5 reports the time evolution of (a) the reduced electric field (E/N), (b) the electron molar fraction and (c) the CO_2 and CO vibrational

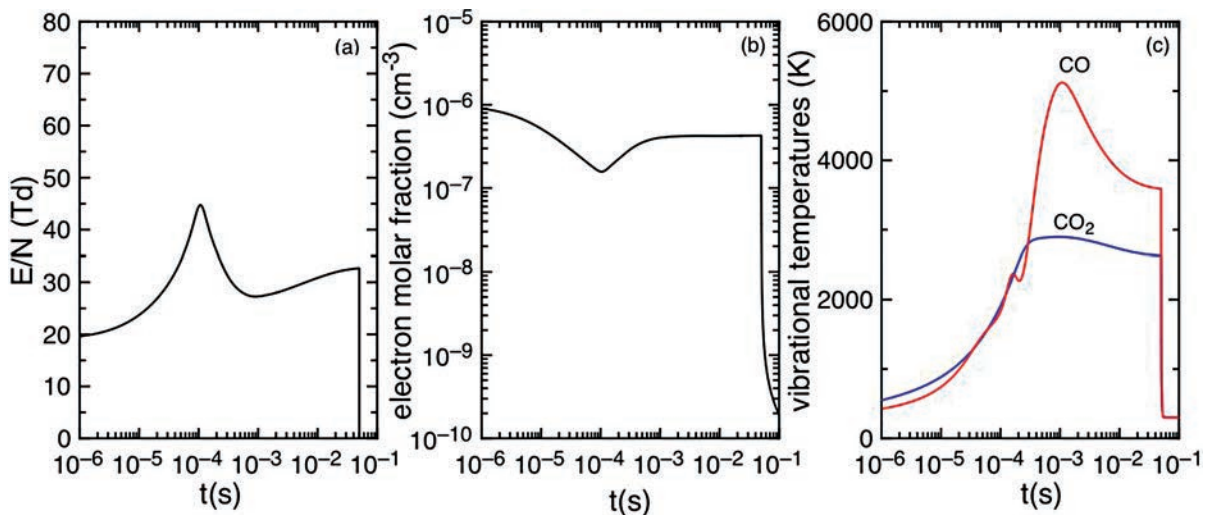


Fig. 5. Time evolution of (a) the reduced electric field (E/N), (b) the electron molar fraction and (c) the CO_2 and CO vibrational temperatures in an initially pure CO_2 reacting plasma under discharge and post-discharge conditions ($T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/cm³, $t_d=50$ ms).

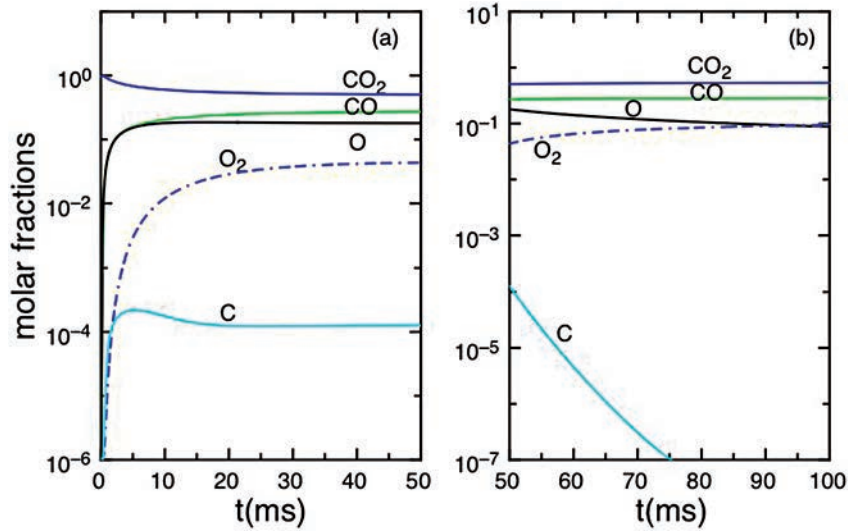


Fig. 6 Molar fraction time evolution in a pure CO_2 reacting plasma under (a) discharge and (b) post-discharge conditions ($T_{\text{gas}} = 300$ K, $P = 20$ torr, $P_d = 80$ W/cm 3 , $t_d = 50$ ms).

temperatures in the case of a pure CO_2 reacting plasma in the same conditions previously investigated for the pure CO plasma. Comparison these results with those obtained for the pure CO plasma (figure 1) shows a similar time evolution of previous macroscopic quantities with differences in the absolute values.

By looking to the molar fraction time evolution (see figure 6), it is clear that the kinetic is dominated by the CO_2 dissociation which occurs both by electron impact collisions and by the following two heavy-particle dissociation processes:

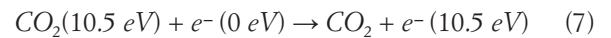


which form CO, O and O_2 as products. In this case, the CO dissociation via the Boudouard process is less important and this time the C atom is a minority specie in the mixture. During the post-discharge, O atom recombination into O_2 keep on increasing the O_2 molar fraction.

The time evolution of the CO_2 , CO and O_2 vdf for the pure CO_2 case is reported in figure 7 in (a) discharge and (b) post-discharge conditions. The behavior is very similar to the pure CO case showing non-equilibrium plateau characterizing the vdf's highest part both in discharge and in post-discharge conditions.

Finally, figure 8 reports the eedf time evolution for pure reacting CO_2 plasma which behaves like the corresponding eedf reported in figure 4 for pure reacting CO plasma. The main differences can be observed in the shape of the eedf in the post-discharge regime. The peak

structure is due to superelastic electronic collisions and depends on the population of the electronic excited states present in the mixture. The most important superelastic electronic collisions occurring are those involving the electronic excited states of the two main components of the mixture, i.e. CO_2 and CO. In particular, in our model, the CO_2 system is characterized only by one metastable electronic excited state at 10.5 eV, while the CO system is characterized by seven electronic excited states at different energies. The corresponding superelastic collisions are the following:



where X and E_X represent the CO electronic excited states and their energies, in particular ($a^3\Pi$, 6 eV), ($a'^3\Sigma^+$, 6.863 eV), ($A^1\Pi$, 8.03 eV), ($b^3\Sigma^+$, 10.4 eV), ($B^1\Sigma^+$, 10.78 eV), ($C^1\Sigma^+$, 11.40 eV) and ($E^1\Sigma^+$, 11.52 eV).

Conclusions and perspectives

The main conclusions of the present work are the similarity of the behavior of reacting CO and CO_2 pure plasmas in microwave discharge conditions for all the reported quantities, i.e. the electron and molar fractions, the vibrational distribution of molecular species (CO_2 , CO and O_2) and the electron energy distribution function (eedf). Quantitatively, however, the absolute values differ for both discharge and post discharge conditions. In both cases, non-equilibrium vibrational and electron

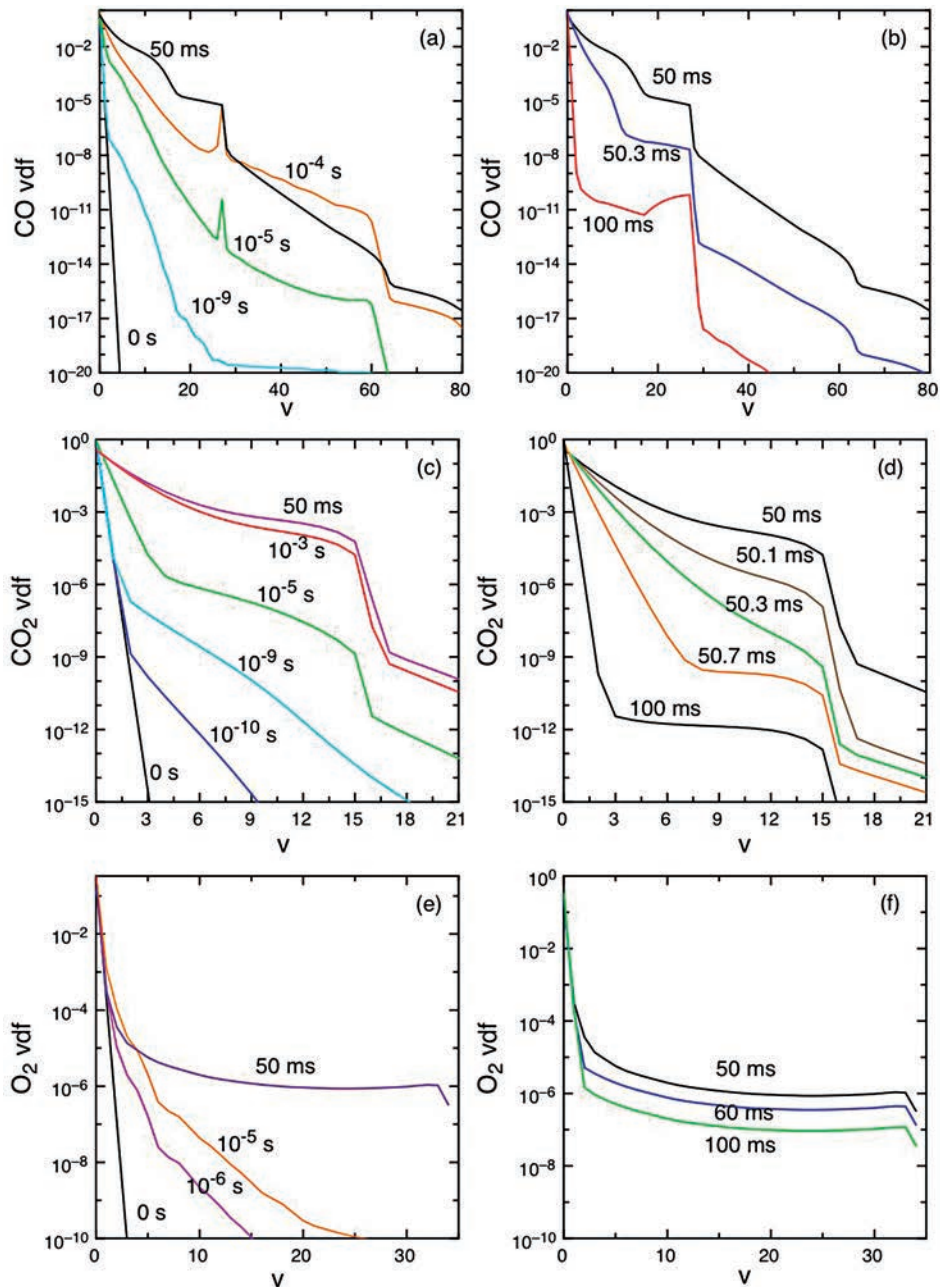


Fig. 7. Vdf time evolution of CO (a, b), CO₂ (c, d) and O₂ (e, f) molecules in a initially pure CO₂ reacting plasma under discharge (a, c, e) and post-discharge (b, d, f) conditions ($T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/cm³, $t_d=50$ ms).

distributions are observed, confirming the importance of the state-to-state approach for the description of CO₂ and CO mixtures in microwave discharges. The eedf, in particular, is strongly dependent on the electronic excited state levels of the dominant species of the mixtures due to the corresponding superelastic electronic collisions, which enrich the eedf shape with characteristic peaks. The kinetic description of the CO₂ plasma mix-

ture cannot disregard the important role of the CO system especially for the calculation of the eedf due to the high number of electronic excited states characterizing the CO molecule. Moreover, it is of great importance also the development of accurate electronic excited state kinetics models for all the mixture species which take in account the main radiative and quenching processes involving such states. As an example, the introduction of

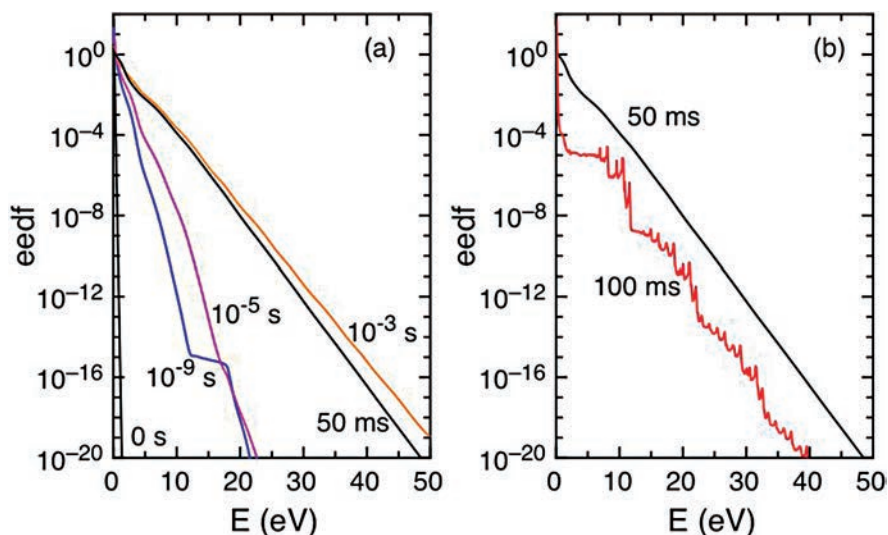


Fig. 8 Eedf time evolution in pure CO_2 reacting plasma under (a) discharge and (b) post-discharge conditions ($T_{\text{gas}}=300$ K, $P=20$ torr, $P_d=80$ W/cm 3 , $t_d=50$ ms).

the quenching process involving the first electronic excited state of CO ($a^3\Pi$, 6 eV) pumping energy into the $v=27$ vibrational level greatly affects both the CO vdf and the eedf.

The improvement of the model is strongly linked also to the accuracy of the reaction rates of the processes included. A lot of work is being made in this direction, in particular, by the papers of Bogaerts *et al.* [11-12], with the inclusion of the Boudouard reaction [13] and with the discussion of the most suitable electron impact dissociation cross section for CO_2 [14].

Another crucial aspect of the model is the definition of the vibrational energy level diagram of the CO_2 molecule. The more used description of the CO_2 vibrational ladder is that one used in our approach and presented for the first time by Bogaerts *et al.* [9-10], which takes into account only the pure asymmetric mode levels up to the dissociation limit and few low-lying Fermi levels. However, a more complete vibrational level scheme can be found in Armenise and Kustova [15-16] which takes into account all the symmetric, bending and asymmetric mode vibrational levels of CO_2 and their coupling, reaching a number of levels two orders of magnitude higher than that one considered by Bogaerts *et al.* This approach is particularly important for the vibrational kinetic description of conditions characterized by very low electron density, as those obtained during hypersonic flow in Mars atmosphere, as well as for situation of weak vibrational pumping when only the first coupled levels are used [17-18], as those characterizing CO_2 lasers.

Moreover, it is important to underline that the self-consistent model applied in this work is the best method to be used to understand the physics of CO_2 activation in cold plasmas. The parametric method used in our first works [19], i.e. the analysis of the results by parametrizing the CO_2 vibrational temperatures, the electron density and the reduced electric field values, helped only in the understanding of the eedf dependence on such parameters. However, the strict correlation between the vibrational, chemical and electron kinetics both in discharge and post-discharge conditions requires the simultaneous solutions of all the kinetic equations as performed in the self-consistent approach.

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