# Self-consistent kinetic modeling of CO<sub>2</sub> cold plasmas

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**Abstract:** The complex physical chemistry behaviour of  $CO_2$  reacting plasmas in nonequilibrium conditions is described by means of an advanced 0D State-To-State (STS) Self-Consistent (SC) kinetic model. The model is able to characterize the  $CO_2$  plasma in the most common types of plasma discharges used for  $CO_2$  conversion, focusing on the role of vibrational excitation, of the electronic excited states and of the electron energy distribution function (eedf) of free electrons in the overall kinetics.

**Keywords:** CO<sub>2</sub> conversion/dissociation, vibrational excitation, self-consistent kinetic model, non-equilibrium plasma, electron energy distribution function, Kotov's criterion.

### **1.Introduction**

In the last decades, the increased emission of greenhouse gas (mainly carbon dioxide) and the decreasing reserves of traditional energy sources has renewed the interest in CO<sub>2</sub> conversion by cold non-equilibrium plasmas as a valid alternative to conventional route to increase the energy efficiency of CO<sub>2</sub> conversion. Plasma discharges provide a favourable environment for activating the  $CO_2$  gas by electron impact excitation (vibrational and electronic), increasing CO<sub>2</sub> reactive channels at relatively low gas temperature. Among the complex reactions involved in the conversion chain, the  $CO_2$  dissociation is a key process affecting the overall efficiency. Beside the direct electron impact mechanism, CO<sub>2</sub> dissociation can occur also by selectively pumping energy into the lowest vibrational levels through electron-vibrational (eV) collisions, followed by vibrational-vibrational (VV) processes, which populate the upper vibrational levels inducing dissociation from these levels. This vibrational induced dissociation process has a maximum threshold energy of 5.5 eV, lower than the threshold of 7.0 eV by electron impact, increasing the energy efficiency of the CO<sub>2</sub> dissociation. For this reason, a strong interest in the scientific community has been channelled towards the investigation of the conditions in which vibrational excitation can be maximized in nonequilibrium plasma discharges for a more energy efficient  $CO_2$  dissociation [1].  $CO_2$  plasmas are important also for aerospace applications, such as the study of spacecraft entry in Mars and Venus atmosphere [2] or oxygen production on Mars for in-situ resource utilization in future space exploration missions [3]. The use of nonequilibriun plasma for CO<sub>2</sub> dissociation is also important for biomedical applications. As an example, a helium plasma jet with a 1% CO<sub>2</sub> admixture was used to produce small amounts of CO in safe conditions for the treatment of various human health diseases thanks to its antiinflammatory, vasodilator, anti-apoptotic and antiproliferative effects [4].

The understanding of the chemistry of non-equilibrium reactive plasmas is a challenging problem and needs the implementation of advanced plasma kinetic modelling. Non equilibrium plasma kinetics has many applications in different fields, such as plasma chemistry [5-7], plasma and laser physics [8-10], hypersonic and shock wave flows [11-

13]. The most refined kinetic simulation description is provided by the State-To-State (STS) approach in which the population density of each excited state of atoms and molecules is followed by taking into account the relevant involved collisional processes. This approach becomes essential when the chemistry is dependent on the high lying vibrational or on the electronic excited states. The corresponding time dependent balance equations involve the rate coefficients of each considered reaction. The rate coefficients of heavy particle collisions are in general gastemperature dependent and are often described by using Arrhenius rate taken from the literature. The rate coefficients of electron impact processes are calculated from the energy-dependent cross sections and the electron energy distribution function (eedf), which can be calculated by solving the electron Boltzman equation. The electrons have a key role in CO2 dissociation in nonequilibrium plasma discharges. They can directly dissociate CO<sub>2</sub> molecules and transfer part of the discharge energy to atoms and molecules by means of inelastic collisions, exciting vibrationally and electronically states, and initiate the climbing of the vibrational ladder up to molecular dissociation. Excited states, in turn, give energy back to the electrons by superelastic collisions, affecting the eedf shape and, as a consequence, the electron impact rates [14]. The described scenario confirms the strong coupling between the electron and heavy particle kinetics, showing the importance of using an approach in which the STS master equations describing the vibrational and electronic excited state kinetics of heavy particles are solved simultaneously and self-consistently with the electron Boltzmann equation.

In this contribution, we present the results obtained by using an advanced 0D self-consistent STS kinetic model for the description of CO<sub>2</sub> reactive plasma mixture in nonequilibrium plasma discharge and post-discharge conditions [15-17]. The model provides a complete characterization of the plasma mixture calculating the temporal evolution of chemical species densities, the vibrational distribution function (vdf) of the molecules, the electronic excited state (ees) densities and the eedf. Different discharge configurations can be simulated in a wide range of pressure and gas temperature values, power density and/or applied reduced electric field and residence time, characterizing the most common types of plasma discharges used for CO<sub>2</sub> conversion, i.e. direct current (DC) glow or radio frequency (RF) discharges [18], moderate- and high-pressure MW discharges [19-21], atmospheric-pressure DBDs [22-24], nanosecond repetitively pulsed discharges (NRPD) [25], gliding arc (GA) plasmas [26], glow discharges (GD) [27] etc.

## 2. Details on the kinetic model

The plasma mixture considered is characterized by the following species, i.e.  $CO_2$ , CO,  $O_2$ , C, O,  $CO_2^+$ ,  $CO^+$ ,  $O_2$ ,  $C^+$ ,  $O^+$ ,  $e^-$ . For the CO<sub>2</sub> system, the pure asymmetric mode levels of the kind (0, 0, v) up to the dissociation limit of 5.5 eV (21 levels) and few low lying symmetric and bending levels, i.e. (010) and the first three Fermi levels, are accounted. The corresponding vibrational kinetics is described by including several intramode vibrationalvibrational (VV), intermode vibrational-vibrational (VV'), vibrational-translational (VT)and electron-impact vibrational excitation (eV) processes. The corresponding VV, VV' and VT rate coefficients have been derived following the approach used in [28-29], i.e. by applying Schwartz-Slawsky-Herzfeld (SSH) scaling laws [30], starting from available theoretical and/or experimental rate coefficients involving low lying vibrational levels. One electronic excited state of CO<sub>2</sub> at 10.5 eV is also included (metastable state). A detailed vibrational and electronic excited state kinetics is also considered for the main CO<sub>2</sub> dissociation products, i.e. the CO and O<sub>2</sub> systems, taking into account, respectively, 80 and 34 vibrational levels and several electronic excited states with their related quenching and radiative processes [31-33]. The electron Boltzmann equation calculates the eedf taking into account the effects of the electric field of the discharge and of the relevant collision processes occurring such as elastic electron-molecule and electron-atom, electron-electron, inelastic and superelastic (vibrational and electronic) and electron-induced chemical reactions such as ionization and dissociation with their corresponding reverse processes. The electron impact cross sections entering in the electron Boltzmann equation are taken from available database such as LXCat [34] and PHYS4ENTRY [35], which, unfortunately, do not provide all the needed vibrationalstate resolved cross sections. Scaling laws, such as Fridman's one for eV [6] or simple threshold shifting for ionization and dissociation cross sections, are used to account for missing cross sections. More detailed information about the model and the list of the included kinetic processes can be found in [16].

Some validation of the model results with results already present in literature were performed. In particular, the O<sub>2</sub>-O kinetics was validated by comparison with the modelling and the experimental results of Annusova et al. [36] in low pressure O<sub>2</sub> plasma discharges (P=10 mtorr-80 mtorr,  $T_{gas}$ =620 K -900 K) finding a good agreement for the O<sub>2</sub> vdf, confirming the presence of a declining plateau in the range 3<v<20, generated by the three body O atom recombination, i.e.  $0 + 0 + 0 \rightarrow 0_2(v) + 0$ .

The model was also able to analyse the plasma conditions experimentally investigated by Groen at el. [21] on  $CO_2$  activation in MW discharges at high translational gas temperature (3500 K< Tgas < 5500 K) [17]. By comparing the kinetics results with the corresponding thermodynamics ones, it was showed that the major components of the mixture, i.e. CO and O, could be described by the thermodynamic approach, while the other minor components presented large deviations from equilibrium. A qualitative agreement was found between experimental and theoretical values for the electron density, the E/N values and the electron temperature in both diffuse and contracted plasmas.

Recently, the model was applied to the description of glow discharge conditions at low pressure (P=5 torr), discharge current I=50 mA and residence time  $t_d$ =5 ms [15] and its results compared to the modelling and experimental results by Grofulovic et al. [37] and Klarenaar et al. [27], respectively. A good agreement was found for the low-lying CO<sub>2</sub> vibrational population densities and vibrational temperatures time evolution with comparable electron densities, eedf and reduced electric field values.

#### 3. Vibrational excitation: some results

The model allows to investigate the role of vibrational excitation in CO<sub>2</sub> dissociation. In particular, it can predict conditions in which the vibrational-induced the dissociation process is activated [15]. This is a useful information for driving the experiments towards a more energy efficient CO<sub>2</sub> conversion. As an example, Fig. 1 shows the time evolution during the discharge (t<t\_d=5 ms) of the vibrational-induced dissociation rates (PVM) of the process  $CO_2(00v) + M \rightarrow CO + O + M$  in the following conditions: T<sub>gas</sub>=300 K, pressure P=2-5-10 torr, power density  $P_d=1-5-10-50$  W cm<sup>-3</sup>. The results in Fig. 1 (d)-(e)-(f) show also the corresponding  $CO_2$  vdf at the end of the discharge (t<sub>d</sub>=5 ms) in the same conditions. The activation of vibrational-induced dissociation occurs when the corresponding PVM rate increases of several orders of magnitude. In the present conditions, activation starts at P=2 torr for  $P_d \ge 1 W \ cm^{-3}$ , at P=5 torr, for  $P_d \ge 5 W \ cm^{-3}$  and at P=10 torr for  $P_d \ge 50 W \ cm^{-3}$ . The onset of vibrational-activation process is linked to the presence of an overpopulated CO<sub>2</sub> vdf, characterized by a sufficiently high non-equilibrium plateau in the intermediate and high v range, resulting from the combined effect of e-V and V-V pumping collisions. Our predictions are also in very good agreement with the Kotov's criterion for activation [38]. This criterion is defined in terms of the threshold quantity  $\left(\frac{Q}{N_0^2}\right)^*$ , where Q is the specific power density and N0 the initial number of CO2 molecules, and indicate that vibrational activation occurs when the  $\left(\frac{Q}{N_{0}^{2}}\right)$  >

 $\left(\frac{Q}{N_0^2}\right)^*$ . The  $\left(\frac{Q}{N_0^2}\right)^*$  value was assessed by using a semiempirical balance equation for the vibrational energy with an estimation, by means of numerical simulations, of the conditions in which the rate of producing vibrationally excited states is at least as fast as the rate with which vibrational energy is transferred to translational modes by VT collisions. The corresponding  $T_{vibr}^*$  and  $\left(\frac{Q}{N_0^2}\right)^*$  value ranges were reported as a function of selected  $T_{gas}$  values and are independent from pressure [38].



Fig. 1. (a-b-c) Time evolution during the discharge (t<t\_d=5 ms) of the PVM rates; (d-e-f) CO<sub>2</sub> vdf at t=t\_d=5 ms under the following conditions:  $T_{gas}$ =300 K, P=2-5-10 torr, P\_d=1-5-10-50 W cm<sup>-3</sup>.

#### 4. Future developments

Beside the role of vibrational levels, special attention will be addressed also to the investigation of the role of electronic excited states in the kinetics. The electronic states are, in general, excited by electron impact during the discharge and, especially in the post-discharge, they give energy back to the electrons by means of superelastic processes, creating characteristic peaks in the eedf, as it can be seen in Fig. 2 which shows the eedf time evolution during the post-discharge in the following conditions  $(T_{gas}=300 \text{ K}, P=5 \text{ torr}, t_d=5 \text{ ms}, P_d=5 \text{ W cm}^{-3})$ . The eedf shows a well-evident peak at 10.5 eV, repeated with periodicity  $\Delta \varepsilon = 10.5$  eV due to the superelastic processes involving the electronic excited state  $CO_2(10.5 \text{ eV})$ , i.e.  $e(n\Delta\varepsilon) + CO_2(10.5 \text{ eV}) \rightarrow e((n+1)\Delta\varepsilon) + CO_2$ with n=0, 1, 2..etc. For the CO<sub>2</sub> system, other electronic excited states have been identified by means of electronic structure calculations [39]. For this reason, a more refined electronic excited state scheme for CO2 will be built up, including the

corresponding electron impact excitation cross sections and radiative and quenching rates found in the literature.



Fig. 2 Eedf time evolution in the post-discharge under the following conditions:  $T_{gas}=300$  K, P=5 torr,  $t_d=5$  ms,  $P_d=5$  W cm<sup>-3</sup>.



Fig. 3 CO (vdf) time evolution during the discharge under the following conditions:  $T_{gas}$ =300 K, P=5 torr,  $t_d$ =5 ms,  $P_d$ = 5 W cm<sup>-3</sup>.

The electronic excited states can also affect the vibrational kinetics of the corresponding ground state molecules. This happens, for example for the CO system and the first electronic excited state  $CO(a^3\Pi)$ . This state is involved in quenching processes with a pumping of vibrational levels on CO vdf, i.e.  $CO(a^3\Pi) + CO \rightarrow$ CO(v = 27) + CO [40]. Fig. 3 show the effect of such process in the CO(vdf) time evolution during the discharge in the following conditions:  $T_{gas}$ =300 K, P=5 torr,  $t_d$ =5 ms,  $P_d$ = 5 W cm<sup>-3</sup>. As it can be seen, the quenching of the  $CO(a^3\Pi)$  creates a peak progressively rounded off by VV and VT collisions. As a consequence, it could be important to build up a more refined kinetic model for the CO( $a^3\Pi$ ) state. In particular, new processes involving this state can be inserted into the model, i.e. dissociative excitation of  $CO_2$  by electron impact (e +  $CO_2 \rightarrow$  e +  $CO(a^3\Pi)$  + 0), the dissociative recombination of  $CO_2$  ( $e + CO_2^+ \rightarrow$  $CO(a^3\Pi) + O$ ) and the main quenching and reactive quenching processes of  $CO(a^3\Pi)$  by collisions of the  $CO(a^3\Pi)$  by collisions with  $O_2$ ,  $CO_2$ , O and CO. Another aspect which will be investigated is the effect of the dissociation products in the global kinetics and, in particular, on the CO<sub>2</sub> vibrational kinetics. Actually, as the CO<sub>2</sub> dissociation progresses, the concentration of the dissociation products such as CO, O<sub>2</sub> and O atoms Recent modeling and experimental increases. investigations have highlighted the important role of O atoms in deactivating the CO<sub>2</sub> vdf through VT processes [41-42]. Therefore, an analysis of the main vibrational energy exchange processes between CO<sub>2</sub> and CO/O<sub>2</sub>/O, such as VT CO<sub>2</sub>/CO, VT CO<sub>2</sub>/O<sub>2</sub> and VT CO<sub>2</sub>/O by using the available data taken from literature (see for example [43]) and of their effect on CO<sub>2</sub> vdf time evolution will be performed.

# 5. References

[1] L. D. Pietanza et al., European Physical Journal D, 75, 237 (2021)

[2] V. Marieu et al, Acta Astronautica, **61**, 604 (2007)

[3] V. Guerra et al., Journal of Applied Physics, 132, 070902 (2022)

[4] C. Douat et al., Plasma Processes and Polymers, 18, 2100069 (2021)

[5] M. Capitelli and E. Molinari, Topics in Current Chemistry, **90**, 60-109 (1980)

[6] A. Fridman, Plasma Chemistry (Cambridge University Press) (2008)

[7] K. Hassouni et al., Plasma Sources Science and Technology, **8**, 494 (1999)

[8] L. D. Pietanza et al., Spectrochimica Acta part B: Atomic Spectroscopy, **65**, 616 (2010)

[9] L. D. Pietanza et al., The European Physical Journal D, 45, 369-389 (2007)

[10] R. Celiberto et al., "Physics and Applications of Hydrogen Negative Ion Sources" M. Bacal (ed.), Springer Series on Atomic, Optical, and Plasma Physics 124 Chapter 7 (2023)

[11] G. Colonna et al., Journal of Thermophysics and Heat Transfer, **13**, 372-375 (1999)

[12] G. Colonna et al., Journal of Thermophysics and Heat Transfer, **15**, 308-316 (1999)

[13] G. Colonna et al., Plasma Physics and Controlled Fusion, **57**, 014009 (2015)

[14] L. D. Pietanza et al., Plasma Sources Science and Technology, **24**, 042002 (2015)

[15] L. D. Pietanza et al., Plasma Sources Science and Technology, **31**, 104001 (2022)

[16] L. D. Pietanza et al., Physics of Plasmas, **27**, 023513 (2020)

[17] L. D. Pietanza et al., Plasma Sources Science and Technology, **29**, 035022 (2020)

[18] L. F. Spencer and A. D. Gallimore, Plasma Chemical Processes, **31**, 79 (2011).

[19] T. Da Silva et al., Plasma Sources Science and Technology, **23**, 025009 (2014).

[20] N. de Harden et al., Plasma Processes Polymers, 14, 1600120 (2017).

[21] P. W. C. Groen et al., Plasma Sources Science and Technology, **28**, 075016 (2019).

[22] R. Aerts et al., Plasma Processes Polymers, 11, 985 (2014)

[23] F. Brehmer et al., Journal of Applied Physics, 116, 123303 (2014)

[24] S. Ponduri et al., Journal of Applied Physics, **119**, 093301 (2016)

[25] M. S. Bak et al., IEEE Transactions on Plasma Science, 43, 1002 (2015)

[26] T. Nunnally et al., Journal Physical D: Applied Physics, 44, 274009 (2011)

[27] B. L. M. Klarenaar et al., Plasma Sources Science and Technology, **26**, 1-11 (2017)

[28] T. Kozak and A. Bogaerts, Plasma Sources Science and Technology, **23**, 045004 (2014)

[29] T. Kozak and A. Bogaerts, Plasma Sources Science and Technology, **24**, 015024 (2015)

[30] R. N. Schwartz et al., Journal of Chemical Physics, **20**, 1591 (1954)

[31] L. D. Pietanza et al., Plasma Sources Science and Technology, **26**, 125007 (2017)

[32] L. D. Pietanza et al., Plasma Sources Science and Technology, **27**, 095004 (2018)

[33] L. D. Pietanza et al., Plasma Sources Science and Technology, **27**, 095003 (2018)

[34] LXCat, LXCat database

[35]PHYS4ENTRYDatabase,http://phys4entrydb.ba.imip. cnr.it/Phys4EntryDB/

[36] A. Annusova et al., Plasma Sources Science and Technology, **27**, 045006 (2018)

[37] M. Grofulovic et al., Plasma Sources Science and Technology, **27**, 115009 (2018)

[38] V. Kotov, Plasma Sources Science and Technology, **31**, 094002 (2022)

[39] Y. Itikawa, Journal Physical Chemistry Data, **31**, 3 (2002)

[40] P. I. Porshnev et al., Chemical Physics, **213**, 111-22 (1996)

[41] O. Biondo et al., Plasma Sources Science and Technology, **31**, 074003 (2022)

[42] A. S.Morillo-Candas et al., Journal of Physics D: Applied Physics, **54**, 095208 (2021)

[43] C. Fromentin et al., Plasma Sources Science and Technology, accepted (2023)