



Beyond electron impact: Dissociation driven by molecular collisions in CO₂ nanosecond pulsed plasmas

Tiago C. Dias^{a,b,*}, Luca Matteo Martini^c, Paolo Tosi^c, Vasco Guerra^d

^a Department of Applied Physics and Science Education, Eindhoven University of Technology, Eindhoven, The Netherlands

^b Electrical Engineering and Computer Science Department, University of Michigan, Ann Arbor, USA

^c Department of Physics, Università di Trento, Italy

^d Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal

ARTICLE INFO

Keywords:

CO₂ conversion

Delayed dissociation

High-temperature molecular chemistry

0.5D radial model

Atmospheric pressure nanosecond plasmas

ABSTRACT

The efficient conversion of CO₂ into value-added chemicals is a central challenge in green chemistry and sustainable process engineering. Non-thermal plasmas attract increasing interest as they enable chemical activation under mild conditions and offer direct compatibility with electrified, renewable-energy-driven processes. Recent experiments have shown that CO₂ conversion in atmospheric pressure nanosecond pulsed discharges peaks on the microsecond timescale, when the electron density is already negligibly small. Elucidating the origin of this delayed conversion is essential for the development of energy-efficient plasma reactors for CO₂ processing. In this work, we develop a 0.5D kinetic model, where the species' concentrations and the plasma properties are spatially averaged over a volume of varying radius, that expands/contracts as the pressure in the discharge channel is higher/lower than the background gas pressure. We show that electronic and vibrational excitation by electron impact during the discharge initiate a cascade of energy-transfer processes that ultimately increase the gas temperature, allowing high-temperature chemistry to occur microseconds after discharge. Moreover, an explicit treatment of channel dynamics is essential, as it strongly influences the recombination kinetics during the afterglow. Our results challenge the conventional picture of electron-impact dissociation as the dominant mechanism in atmospheric pressures CO₂ nanosecond discharges. These findings open new perspectives to attain operating regimes with high CO₂ yield and competitive energy efficiency, for example by optimizing the pulsing patterns, specially in the context of future devices integrating plasma decomposition with product separation.

1. Introduction

The interest in plasma-activated CO₂ conversion was revived about a decade ago, when Soviet-era reports claiming energy efficiencies above 80% [1,2] were rediscovered by the Western scientific community [3–6]. Such high values of energy efficiency were attributed to vibrational non-equilibrium, where the vibrational “temperatures” would exceed the translational and rotational ones and promote dissociation at low energy cost. This hypothesis congregated a large effort by the scientific community aimed at exploring non-thermal plasma technologies for CO₂ utilization as a potential route toward carbon circularity [7–10]. However, despite appreciable progress [9, 10] and the development of the first prototypes [9], experimental evidence for vibrationally-induced dissociation remains elusive to date and there are still significant gaps in the fundamental understanding of the CO₂ dissociation pathways in non-thermal plasmas [7,8], which currently hinder the attainment of competitive dissociation and energy

efficiency performance parameters and the path towards industrial implementation [10].

The electron impact cross sections for CO₂ dissociation are nowadays relatively well established [11] and dissociation by direct electron impact, both from the vibrational ground-state 00⁰0 and from the vibrationally excited 01¹0, 02²0 and 10⁰0+02⁰0 states, was identified as the dominant dissociation channel in low-pressure DC discharges [12–14]. Similarly, dissociation in atmospheric pressure DBD discharges is well explained by direct electron impact [5,15–17]. In turn, thermal chemistry justifies the CO₂ conversion observed in intermediate pressure MW discharges, where the relatively high pressures (~ 30 – 300 mbar) and gas temperatures (~ 2000–5000 K) promote a local equilibrium between the vibrational and gas temperatures [18–20].

To the best of our knowledge, the only experimental demonstration of vibrational dissociation due to non-equilibrium vibration-vibration

* Corresponding author at: Department of Applied Physics and Science Education, Eindhoven University of Technology, Eindhoven, The Netherlands.
E-mail address: t.cunha.dias@tue.nl (T.C. Dias).

(V-V) ladder-climbing mechanism [21] in CO₂ is provided by the optical pumping experiments by Q. Ong [22]. In these experiments, a narrow-band laser with a linewidth of FWHF of 0.2 cm⁻¹ is tuned to excite a single ro-vibrational transition of CO₂ ($v_3=0$, $J=22 \rightarrow v_3=1$, $J=23$) and CO, formed by ladder-climbing up to dissociation limit, is accumulated over 10000 laser pulses and is detected and quantified by Fourier transform infrared (FTIR) spectroscopy. However, these results revealed a rather difficult V-V ladder-climbing process, with energy efficiency below 0.1% at $p = 1$ bar, and were obtained under conditions far from those found in a plasma. Therefore, they are not readily translatable to realistic gas discharge conditions, where experimental confirmation of vibrational dissociation is still lacking and efficient non-equilibrium V-V ladder climbing appears unlikely.

In a recent study of pulsed nanosecond discharges at atmospheric pressure in a pin-to-pin configuration, Montesano et al. have shown that while most of the energy is deposited in the breakdown phase, CO₂ dissociation occurs only after a delay of the order microseconds, leaving the system in a quasi-metastable condition in the intervening time [23]. This delayed dissociation is the signature of mechanisms mediated by CO₂ excited states rather than by direct electron impact. These findings challenge the established view of dominant electron-impact dissociation in these discharges [24–26], rooted in the presence of reduced electric fields well above 150 Td [27,28], where 60%–80% of the electron energy is predicted to be channeled into dissociation [7,24]. They therefore call for an investigation of dissociation in atmospheric pressure nanosecond discharges.

The aim of this work is to identify the physical principles and mechanisms underlying the delayed CO₂ dissociation experimentally observed in atmospheric pressure nanosecond discharges [23], and to provide a clear interpretation of the phenomenon. To this purpose, we develop a 0.5D radial model by considering an axisymmetric discharge with a time-varying radius, where any pressure increase/decrease in the discharge channel leads to its radial expansion/contraction into the surrounding medium at the sound speed, while all physical quantities in the governing equations are volume-averaged. The model is based on the 0D LibOn KInetics tool suite (LoKI-B+C) [29,30], that is here modified to account for the discharge expansion/contraction. In particular, the particle continuity and the gas energy equations are modified according to the Reynolds transport theorem, to account for a control volume with a deforming boundary. These equations are coupled with the electron kinetics, described by the electron energy equation under the local-energy approximation [31], and the system of equations is closed with the ideal gas law.

The structure of this paper is as follows. In the next section we detail the formulation of the model and derive the system of equations to be solved. In Section 3, we present and discuss the results, including an assessment of how the model assumptions influence the outcomes. Finally, Section 4 summarizes the main conclusions and outlines directions for future research.

2. Model formulation

Volume-averaged models, often denoted as global models or 0D models, are powerful tools to investigate the kinetics and plasma chemistry in gas discharges. These models can easily handle dozens of species and hundreds of reactions at low computational cost. Moreover, despite lacking the rigor of 1D or 2D simulations, 0D models were successfully used to study inhomogeneous systems such as plasma jets, dielectric barrier discharges (DBD), microwave plasmas and high-power impulse magnetron sputtering discharges [32].

A vast literature on 0D models to study the detailed kinetics of CO₂ plasmas is currently available, covering different operating pressures and gas temperatures, and focusing on different aspects of the kinetics, so that the references given here are merely indicative [5,6,11, 25,26,33–35]. In this work, we capitalize on the existing knowledge of the CO₂ kinetics to analyze the results of Montesano et al. [23]

for nanosecond pulsed discharges at atmospheric pressure. However, these discharges involve currents that can reach several tenths of A in short time intervals, leading to the propagation of a pressure wave and discharge expansion into the surrounding medium, and cannot be adequately described with a 0D model. Therefore, we formulate a 0.5D radial model by representing an axisymmetric discharge with a temporally varying radius, where pressure changes within the discharge channel induce radial expansion or contraction into the ambient medium at the acoustic speed. These assumptions align well with the fluid model calculations by Castela et al. [36] and Tholin and Bourdon [37]. On the other hand, all other variables in the governing equations are expressed as volume-averaged quantities.

In the remainder of this section, we revisit how the particle continuity and gas energy equations can be written for a control volume that is not fixed in time, how to write the corresponding volume-averaged equations in our 0.5D formulation, and how to couple these balance equations with the electron kinetics.

2.1. Particle continuity

The continuity equation for the gas density of a neutral species i , $n_i(\mathbf{r}, t)$, can be written as

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (n_i \mathbf{v}) + \nabla \cdot (D_i \nabla n_i) + S_i, \quad (1)$$

where $\mathbf{v}$ is the fluid averaged advective velocity, D_i is the mixture-dependent diffusion coefficient of species i , and S_i is the net production (sources - sinks) of species i [38,39]. By using Reynolds transport theorem for a control volume $V = \pi R^2 L$, where L is the length of the discharge and $R = R(t)$ is its time-varying radius, and further assuming that (i) the averaged source terms S_i are approximately given by products of volume-averaged species densities and reaction rate coefficients calculated at the average gas temperature, (ii) the diffusion coefficients can be calculated using a volume-averaged gas mixture, (iii) the radial diffusion can be estimated assuming a Bessel radial density profile with $n_i(R) = n_{0,i}$, where $n_{0,i}$ is the density of species i in the surrounding medium, the continuity equations (1) take the form

$$\frac{d\bar{n}_i}{dt} = -\frac{D_i}{\Lambda^2} (\bar{n}_i - n_{0,i}) + \bar{S}_i - \frac{2v}{R} \bar{n}_i. \quad (2)$$

In this expression, $\Lambda = R/2.405$ is the diffusion length, and v is the velocity of the radial expansion/contraction of the control volume, related to the advective velocity, $\mathbf{v}$, and to the absolute value of the sound speed of the surrounding medium, c_s , by

$$\mathbf{v} = v \mathbf{e}_r = \begin{cases} -c_s \mathbf{e}_r & , \bar{p} < p_0 \\ 0 \mathbf{e}_r & , \bar{p} = p_0 \\ c_s \mathbf{e}_r & , \bar{p} > p_0 \end{cases}, \quad (3)$$

where p_0 is the pressure of the surrounding medium. The detailed derivation of expression (2) is given in Appendix A.

The rate-balance equations for the different ions have the same form as (2), with D_i replaced by an appropriate diffusion coefficient of species i , taken here as the ambipolar diffusion coefficient. Note that the volume processes dominate the losses of the ionic species, so that the choice of the charged-particle transport model [40] has a negligible impact in the results.

2.2. Gas energy conservation

The gas temperature is calculated from the gas energy conservation equation,

$$\frac{\partial (N C_V T)}{\partial t} = -\nabla \cdot (-\lambda \nabla T + N C_V T \mathbf{v}) - p \nabla \cdot \mathbf{v} + \sum_m R_m \Delta H_m + \bar{\tau} \cdot \nabla \mathbf{v}, \quad (4)$$

where we have neglected the ionic contribution to Joule heating, N is the total gas density, λ is the thermal conductivity, C_V is the heat

capacity at constant volume, T is the gas temperature (assumed to be the same for all the heavy-particles), R_m is the rate of reaction m , ΔH_m is the enthalpy release into gas heating due to reaction m (including electron elastic collisions), and $\bar{\tau}$ is the viscosity tensor [38,41]. Under the assumptions considered in this work, the latter term is null since the fluid velocity is uniform [38]. Moreover, by performing additional calculations with an imposed heat transfer coefficient of $100 \text{ W m}^{-2} \text{ K}^{-1}$ which likely represents an upper-bound estimate, we have verified that convective heat losses can be safely neglected in the present conditions.

Similarly to the continuity equation, we consider a control volume whose surface is expanding with the fluid advective velocity. Under the assumptions that (i) the thermal conductivity is close to the value calculated with the average gas temperature $\bar{T}$, (ii) the temperature profile is parabolic, (iii) the heat capacity is close to the value calculated with the average gas temperature, and (iv) the averaged pressure is approximately $\bar{p} = k_B \bar{N} \bar{T} \simeq k_B \bar{N} \bar{T}$, the gas energy equation can be written as

$$C_V \bar{N} \frac{d\bar{T}}{dt} = -\frac{8\lambda}{R^2} (\bar{T} - T_0) + \sum_m \bar{R}_m \Delta H_m - \frac{2v\bar{p}}{R} - C_V \bar{T} \left(\frac{d\bar{N}}{dt} + \frac{2v\bar{N}}{R} \right), \quad (5)$$

where T_0 is the temperature of the surrounding medium. The terms on the r.h.s represent, in order, the thermal conduction, the enthalpy release, the work done by the discharge while expanding against the surrounding medium, and a term due to changes in the number of particles in the control volume. Note that the second part of the latter annihilates the decrease of density that is only due to volume expansion. The detailed derivation of Eq. (5) is given in Appendix B.

2.3. Electron energy equation

The electron kinetics is coupled to the heavy-particle kinetics by solving an equation for the mean electron energy, $\langle \epsilon \rangle$, which can be expressed as follows [31]:

$$\frac{d(n_e \langle \epsilon \rangle)}{dt} = n_e (P_{\text{in}} + P_{\text{coll}}), \quad (6)$$

where n_e is the electron density, P_{in} is the input power per electron, and P_{coll} is the net power transferred by collisions per electron, with both powers expressed in eV s^{-1} . P_{in} is deduced from the total input power, P_{tot} , as follows: $P_{\text{in}} = P_{\text{tot}}/(n_e V)$. The reduced electric field, E/N , is obtained from the electron mobility, μ_e , and P_{in} : $E/N = \sqrt{P_{\text{in}}/(\mu_e N^2)}$.

The electron-impact rate coefficients, transport parameters, and the power transfer to the different channels depend on the instantaneous value of $\langle \epsilon \rangle$, corresponding to the local energy approximation (LEA) [31,42,43]. The electron energy distribution function (EEDF) is obtained from Monte Carlo simulations using the open-source numerical code LoKI-MC [44], with electron impact cross sections taken from [11]. The validity of the LEA for atmospheric pressure nanosecond discharges was established in [31]. The current Monte Carlo simulations and cross sections set ensure a correct description of the EEDF at least for E/N values as high as 1000 Td , well above the maximum value considered in this work ($\sim 220 \text{ Td}$, see Fig. 3). Notice that, for the purposes of the present work, the lower-accuracy local-field approximation together with a two-term Boltzmann solver such as LoKI-B [29] could, in principle, also provide sufficiently accurate results [31].

2.4. Plasma chemistry

The chemical kinetics considered in this work builds on the high temperature scheme from [45] and the low temperature one used in [46]. The reaction scheme from [45] is a thermal chemistry set based on the GRI-Mech 3.0 database [47]. Accordingly, the reaction rate coefficients of the heavy-particle reactions are temperature activated and the intervening species are considered in their electronic ground-state, with no internal structure (*cf.* Table 3 in [45]). The ion-ion, ion-neutral and associative ionization processes are the same as in

Tables 5 and 6 from [45]. Additionally, we consider a detailed kinetics of the electronically excited states of CO_2 , CO , O_2 and O , following [46, 48]. The detailed list of species and the complete kinetic scheme used in this work are given in Tables C.1–C.3 in Appendix C.

We do not account for a detailed state-to-state vibrational kinetics, as a simpler formulation already captures the main qualitative features of CO_2 dissociation in nanosecond discharges (see Figs. 1 and 2 in Section 3). Furthermore, it is not clear if a more detailed formulation of the vibrational kinetics would lead to better quantitative predictions, due to the uncertainties in the reaction rate coefficients of vibrational energy exchanges for high vibrational quantum numbers and at high temperatures [14,49]. Nevertheless, vibrational excitation mediates the transfer of energy from the electrons into the translational degrees of freedom. Therefore, we assume that the electron energy input into the excitation of vibrational levels, Q_V , leads to gas heating due to vibration-vibration (V-V) and vibration-translation (V-T) energy exchanges. Following Losev et al. [50], the corresponding characteristic relaxation time, τ_{VT} , is approximated as the V-V relaxation of the asymmetric stretching mode to the bending and symmetric stretching modes, $\tau_{VV_{32}}$, followed by the V-T relaxation of these modes, $\tau_{VT_{12}}$, *i.e.*, $\tau_{VT} = \tau_{VV_{32}} + \tau_{VT_{12}}$. Q_V is obtained directly from the EEDF, while $\tau_{VV_{32}}$ and $\tau_{VT_{12}}$ are taken from [50]. In practice, the delayed contribution of gas heating from vibrations is implemented by solving an additional equation for the total vibrational energy reservoir, E_V , with the source term Q_V and the loss term $-E_V/\tau_{VT}$, and by adding the corresponding source term $E_V/(V\tau_{VT})$ to the gas energy Eq. (5).

3. Results and discussion

The system under study is the pin-to-pin atmospheric pressure CO_2 discharge described in [23]. In their experiment, an influence of the pulse sequence on the discharge behavior is reported, with pulses 2–5 within a burst differing depending on whether the interpulse time is $33 \mu\text{s}$ or $100 \mu\text{s}$. In contrast, the first pulse remains identical in both cases [23]. Herein we compare our simulation results exclusively with the first pulse, ensuring that the comparison is independent of the interpulse time. Our analysis considers a single power pulse (P_{tot}), with a deposited energy of $\sim 5 \text{ mJ}$ [23]. We define a *reference model* that assumes a triangular power pulse of 40 ns , an initial radius of the plasma channel of $R(t=0) = 0.16 \text{ mm}$, an initial ionization degree of 10^{-6} , and collisional data as specified in Section 2. Note that (i) the choice of the initial radius is aligned with the results of 3D simulations in pin-to-pin configurations [36], and (ii) the results of the heavy-species kinetics are weakly dependent on the initial ionization degree (the calculated heavy-particle concentrations obtained by varying the initial ionization degree by an order of magnitude in either direction are indistinguishable in a figure, for times above 1 ns).

Considering the simplifications in the model and the complexity of the system, our model should be regarded primarily as a framework for describing and interpreting the underlying phenomena, with emphasis on the qualitative behavior of the discharge rather than on quantitative agreement with the specific experimental dataset. Accordingly, its value lies in predicting universal trends, elucidating the hierarchy of dominant mechanisms as a function of operating parameters, and consolidating the results into general, transferable guidelines rather than providing case-specific numerical predictions. These are the purposes of this Section. The results obtained from this reference model are presented and analyzed in Section 3.1, while Section 3.2 examines how the key assumptions influence the model's predictions.

3.1. Reference model

The model predictions are compared with the time-resolved measurements of the dissociation fraction and gas temperature reported in [23]. The former was obtained by collisional-energy-transfer laser-induced-fluorescence (CET-LIF) using OH as sensor of the background

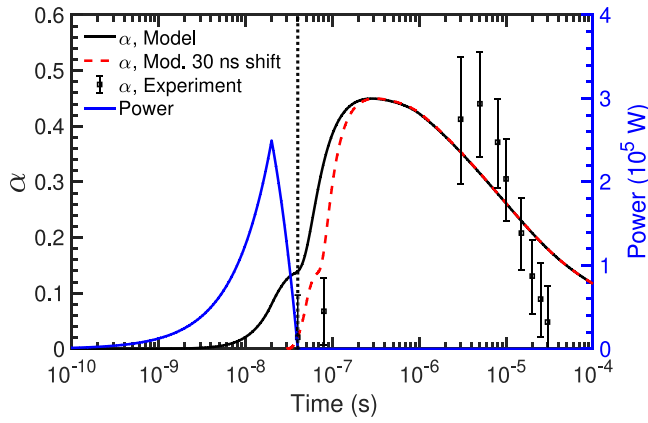


Fig. 1. CO₂ conversion α as a function of time (left axis) calculated from the reference model (—), with a 30 ns shift in $t = 0$ (---) (see text), and experimental data from [23] (■). To guide the eye the power pulse is also represented (—, right axis) and a dashed vertical line indicates the end of the discharge.

gas [51], while the latter was obtained from the emission of nitrogen's second positive system $N_2(C^3\Pi_u, v' = 0) \rightarrow N_2(B^3\Pi_g, v = 0)$ [52]. Fig. 1 shows the comparison of the calculated and measured CO₂ dissociation fraction, $\alpha = \frac{[CO]}{[CO_2] + [CO] + [C]}$, as a function of time, together with the power pulse used as input to the simulation. Our predictions (full curve) exhibit remarkable qualitative and quantitative agreement with the experimental data from [23] and capture the phenomena of delayed dissociation, α peaking after the end of the discharge pulse. There is a minor disagreement on the onset of dissociation, which seems too fast as compared with experiment. This difference may stem from both the simplifications made in the model to describe a very complex system and to the experimental challenges in diagnosing it. For instance, there might be a time delay between the measurements of the dissociation and of the power, and the power input curve used in this work has an idealized shape. As an illustration of the possible impact of these uncertainties, Fig. 1 also depicts the comparison between model and experiment when a shift of 30 ns on the experimental identification of $t = 0$ is considered (dashed curve). It is clear that the predictions in this case are much closer to the measurements for the early instants of the afterglow than before, while both sets of predictions remain very similar at longer afterglow times.

An initial insight into the mechanisms associated with delayed CO₂ dissociation is given by Fig. 2, which shows the evolution of the gas temperature, T_g , as a function of time. Similarly to the dissociation fraction (Fig. 1), there is a good agreement between our simulations and the experimental data from [23]. The initial rise in the gas temperature appears with a short delay in relation to the power pulse (the peak in T_g occurs $\sim 4 \times 10^{-8}$ s after the peak of the power pulse), and T_g reaches values as high as 4000 K. In this high temperature range, CO₂ dissociation is thermally driven and can in principle be described by thermal chemistry [19,20]. The CO₂ dissociation comes with a further delay of ~ 0.1 μ s. It is worth noting that our results are well aligned with the analysis from [53], where it is shown that even for high temperatures and when CO₂ molecules have enough vibrational energy to support dissociation, the reaction rates are limited by kinetics and at $T_g = 3000$ K dissociation takes place only after 0.01–0.1 μ s.

The calculated reduced electric field, E/N , and electron temperature, T_e , are represented as a function of time in Fig. 3. E/N rises sharply during the power pulse, in sub-nanosecond time-scales, reaching a maximum value of ~ 220 Td. It then stabilizes in a plateau during most of the 40 ns discharge, at about 150 Td, and decreases quickly in the afterglow. The electron temperature has a similar behavior, with a plateau value close to 3 eV. These results anticipate that electron

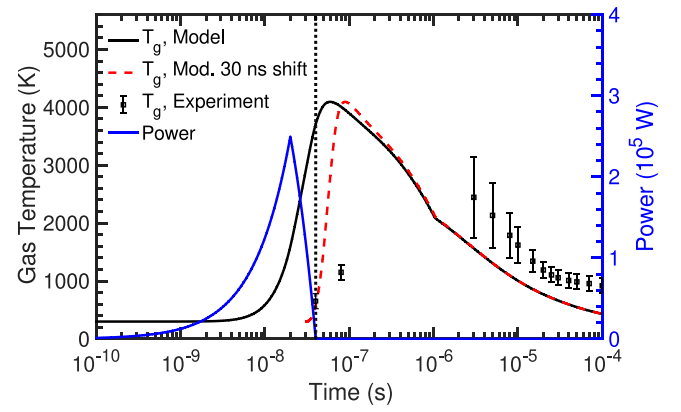


Fig. 2. Gas temperature as a function of time, with the same notation as in Fig. 1.

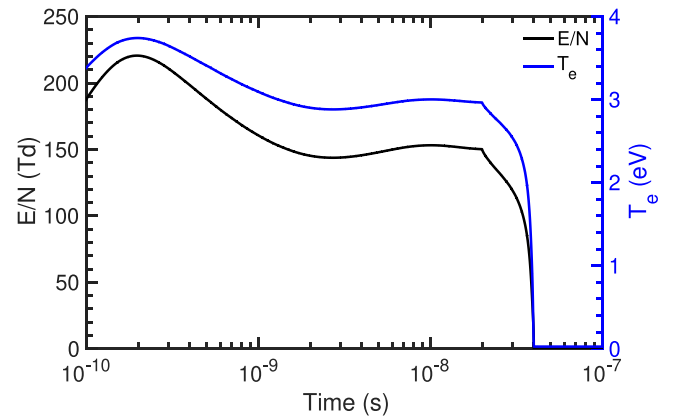


Fig. 3. Calculated reduced electric field E/N (—) and electron temperature T_e (—) as a function of time.

impact processes, including dissociation, are only effective during the short duration of the power pulse, as it is further discussed below. Note that the calculated values of the electron temperature are in good agreement with experimental measurements obtained under similar conditions (see Figure 9 of Ceppeli et al. [52]).

Figs. 4–6 show the time-evolution of the volume densities of the main ground-state neutral species (CO₂, CO and O₂ molecules, and O and C atoms), electronically-excited neutral species (CO₂(e_1) - see [46] -, CO($a^3\Pi_r$), O₂($a^1\Delta_g$), O₂($b^1\Sigma_g^+$), and O₂($A'^3\Delta_u$, $A'^3\Sigma_u^+$, $c^1\Sigma_u^-$), the latter denoted here as O₂(Hz)) and charged species (electrons, positive ions CO₂⁺ and O₂⁺, and negative O⁻ ions), respectively. Inspection of these figures reveals that the various electronically excited states are strongly populated in the discharge pulse (by electron impact), CO₂(e_1) and CO(a) reaching gas fractions as high as ~ 1 %, while they are quickly quenched as soon as the discharge is over. The only exception is the O₂(a) metastable state, which is long-lived and survives up to times above ~ 0.1 ms. Similarly, the charged particles do not remain in the afterglow. Nevertheless, the plasma exhibits a significant ionization degree, n_e/N , where n_e and N denote the electron and gas densities respectively, above 10^{-4} . These data are consistent with the Stark broadening measurements from [52]. It is further noted that oxygen is strongly dissociated for times up to tenths of μ s. This reflects the creation of O-atoms due to CO₂ dissociation and the O₂ formation taking place only afterwards, when the gas temperature is sufficiently low to allow for 3-body atomic recombination.

The instantaneous gas heating rates and the cumulative energy spent on heating (represented as fraction of the total input energy) of the main heating processes are represented in Fig. 7, as a function of

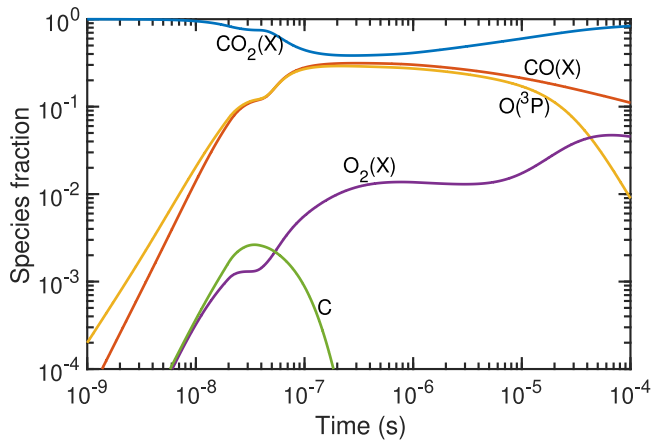


Fig. 4. Volume densities of the main ground-state neutral species as a function of time.

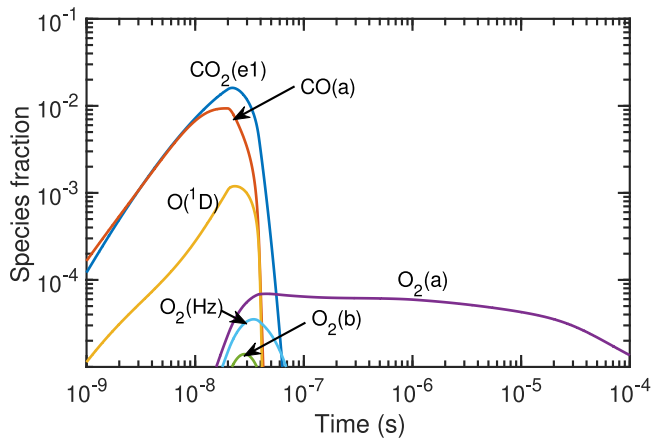


Fig. 5. Volume densities of the main electronically-excited neutral species as a function of time. The reader is referred to [46] for more details on the identification of these species.

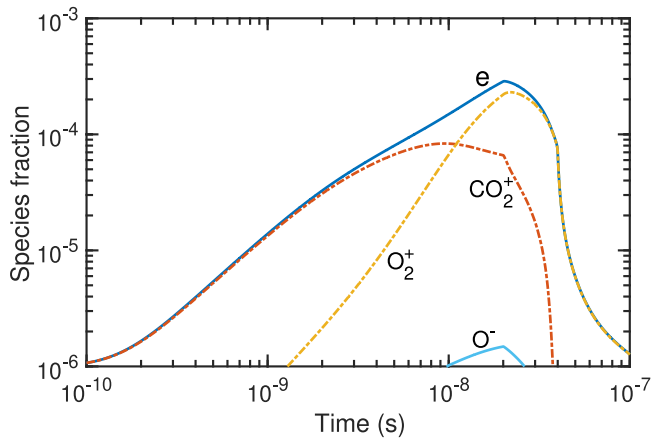
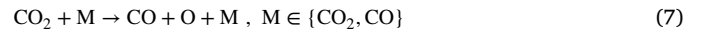


Fig. 6. Volume densities of the main charged species as a function of time.

time. We can verify that fast gas heating associated with the quenching of electronically excited states occurs during the plasma pulse, with CO₂ excited states, generically denoted as CO₂(e₁), and CO(a) metastable states giving the larger contributions. Such fast gas heating has also been identified, e.g., in nanosecond discharges at atmospheric pressure in air [54,55], at intermediate pressures in N₂, air and N₂-O₂

mixtures [56,57], and at low-pressure discharges in CO₂ [58]. At the end of the discharge pulse the electronically excited states are almost completely quenched back to the ground state (cf. Fig. 5) and do not contribute anymore to the gas heating. In turn, vibrationally excited states release their energy with a delay governed by the vibrational-translation time, τ_{VT} (see Section 2.4), which is represented in Fig. 8. As a result, although vibrational relaxation accounts for less than 20% of the gas heating during the discharge phase, it continues to supply energy to the gas up to about 100 ns, and during the afterglow its contribution to the total gas heating approximately doubles relative to its role during the discharge.

We can now analyze the main mechanisms for production of CO molecules in the discharge and its afterglow. The instantaneous CO creation rates associated with the main CO₂ dissociation mechanisms, as well as their relative contribution to the total CO dissociation rate, are represented in Fig. 9. During the discharge, CO₂ is dissociated by direct electron impact and by dissociation involving the CO(a) metastable state. This state is formed by direct electron impact (see Fig. 5) and subsequently contributes to CO₂ dissociation via CO(a)+CO₂ → 2CO(X)+O(3P). The importance of CO(a) in enhancing CO₂ dissociation was also pointed out in [59,60]. However, as the discharge pulse ends, the electron and metastable densities are quickly depleted and the instantaneous contribution of these mechanisms to promote further CO₂ dissociation becomes vanishingly small. As a consequence, the contribution of electron impact dissociation to the total CO formation amounts only to ~25%, while the dissociation induced by CO(a) contributes with ~10%. In turn, as the gas temperature raises in the afterglow (Fig. 2), the thermally activated reactions

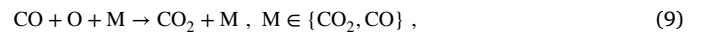


become very effective and bring additional CO₂ dissociation, with a total contribution to dissociation reaching ~60%. These reactions are thus at the origin of the observed delayed CO₂ dissociation. An additional contribution of 5% is given by reaction



Further insight can be obtained from Figs. 10 and 11, which show the evolution of the gas pressure, and the discharge radius and gas density, respectively. A rapid increase in gas pressure is observed (Fig. 10), reaching values above 10 atm at around 100 ns. This pressure rise induces a radial expansion of the discharge channel up to ~1 μs, after which it begins to contract. The discharge expansion is an important gas-cooling mechanism during the afterglow and thus significantly influences the recombination kinetics (cf. Figs. 15 and 12). Additional cooling mechanisms include changes in the total number of particles (see Eq. (5)) and, to a lesser extent, thermal conduction.

To finalize the discussion of our reference model for atmospheric pressure ns CO₂ pulsed discharges, Fig. 12 shows the main mechanisms of CO recombination into CO₂ in the discharge and in the post-discharge. It can be confirmed that the decay of the CO density in the afterglow is due to three-body recombination, following the gas cooling,



which is the reverse of the dissociation processes (7), together with losses by diffusion. This conclusion is in agreement with the findings from [26]. The picture of the kinetics of CO is now clear and reveals the key role of the gas temperature, both in promoting thermally activated dissociation reactions and the delayed dissociation mechanism, and in controlling the dynamics of the recombination.

3.2. Modifications to the reference model

In this section, we evaluate how the main underlying assumptions affect the model's results and the robustness of its predictions. These

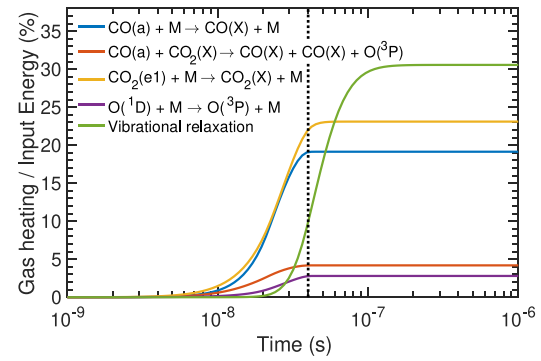
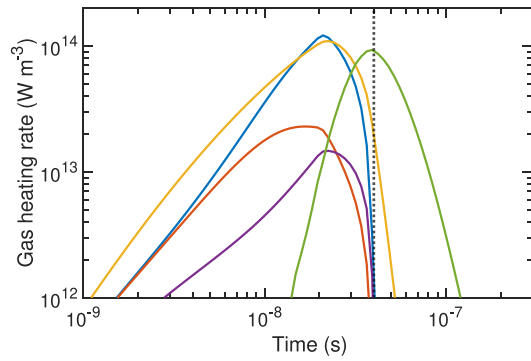


Fig. 7. Instantaneous power transfer (left) and cumulative fractional energy spent (right) into gas heating, as a function of time. The dashed vertical line indicates the end of the discharge.

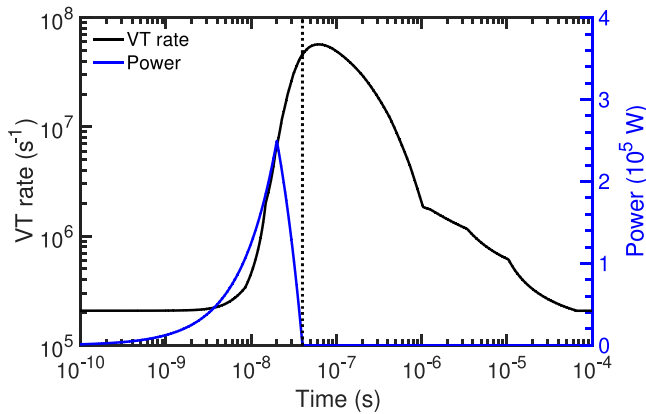


Fig. 8. Vibrational relaxation rate, τ_{VT}^{-1} , as a function of time (—). To guide the eye the power pulse is also represented (—, right axis) and a dashed vertical line indicates the end of the discharge.

assumptions include the length of pulse, the initial discharge radius, the velocity of expansion/contraction of the discharge channel, the plasma chemistry set, the rate of quenching of electronically excited states, the vibrational energy relaxation time, and the rate of diffusion of the heavy-particles.

Fig. 13 illustrates the influence of the assumed discharge pulse duration on the CO₂ conversion and the gas heating. It can be seen that the pulse length mainly affects the initial growth of the CO fraction, with longer pulses delaying the onset of dissociation, as expected since the energy per pulse is kept constant in the simulations. Accordingly, a longer pulse brings the simulations closer to the experimental data for times below ~ 100 ns, although the uncertainties in both the model and the experiment (cf. Fig. 1 and its discussion) do not allow to draw any definitive conclusions in this regard. The pulse length has also some influence in the peak value of the dissociation, with shorter pulses leading to slightly lower values. Nevertheless, despite some relatively minor quantitative differences, the qualitative picture of the discharge and its afterglow detailed in Section 3.1 remain the same.

The impact of the initial radius of the discharge channel, $R(t = 0)$, on the simulations is shown in Fig. 14. A smaller discharge radius implies a higher power density in the discharge, resulting in faster gas heating and stronger CO₂ dissociation. The dissociation fraction can increase from $\sim 20\%$ for $R(t = 0) = 0.18$ mm to $\sim 80\%$ for $R(t = 0) = 0.14$ mm. While our interpretation of the delayed CO₂ dissociation phenomenon is not modified by variations of $R(t = 0)$, the figure reveals that quantitative predictions of CO₂ dissociation in nanosecond discharges are strongly dependent on an accurate description of the initial discharge channel. In particular, our results demonstrate that dissociation driven by molecular collisions is highly sensitive to the

peak value of the gas temperature. For instance, if the power density is such that $T_g \lesssim 2500$ K (not shown), then electron impact dominates dissociation, as the gas is not hot enough to effectively activate the molecular pathway.

Fig. 15 demonstrates the need of using (at least) a 0.5D description of the system, accounting for the expansion and contraction of the discharge channel, by comparing the results from our base model with those of a pure 0D model, where no radius variation of the channel is considered. The latter case corresponds to a sound speed $c_s = 0$ in the present formulation. An intermediate situation with $c_s = 170$ m/s is also depicted in the figure. It is clear that a 0D model cannot describe the main trends and time-scales observed experimentally. As a matter of fact, the channel expansion is essential to adequately capture the time-scales associated with the cooling of the gas and the trend of CO+O recombination. Interestingly enough, within reasonable values the actual value of the sound speed used in the simulations has a relatively small influence in the results.

The data in Fig. 15 warrant an additional remark. Previous studies have suggested that rapid quenching (i.e., gas cooling) enhances the CO yield [61–64]. At first glance, this appears to contradict our results, in which the faster cooling associated with channel expansion leads to a more rapid decay of CO than in the lower-cooling case, where expansion is neglected ($c_s = 0$). Note, however, that in the simulations made without channel expansion, the gas temperature remains above 3000 K for much longer than when expansion is included. Consequently, the higher CO concentrations observed at longer afterglow times are not the result of beneficial quenching, but rather of continued thermally driven dissociation that persists after the pulse. Furthermore, our simulations for $c_s = 0$ do not represent a physically realistic scenario and, therefore, comparisons with the 0.5D expanding-channel calculations and the results of [61–64] should be interpreted with caution. The role of fast quenching is subtle and must be interpreted through a holistic analysis that considers the full thermochemical and gas-dynamic context.

The quality of the predictions of any plasma-chemistry model depends on the set of reactions and corresponding rate coefficients it considers. Therefore, we now examine whether the conclusions obtained thus far depend on the particular plasma-chemistry scheme adopted or on specific choices of individual reaction rate coefficients. Fig. 16 compares the results for the CO₂ dissociation fraction and gas temperature from our reference model and when we use the rate coefficients for the thermally activated heavy-particle CO₂ dissociation reactions and for the corresponding reverse 3-body recombination processes (direct and reverse reactions R44–R47 in Table C.3 in Appendix C) from Kozák and Bogaerts [5]. We note that the kinetics of recombining CO₂ plasma flows was recently identified to depend on the rate coefficients of these reactions [65]. From Fig. 16 we can verify that the general behavior of the system is similar regardless of the choice of the chemistry scheme, despite some quantitative differences in the calculation of the peak value of CO₂ dissociation. Moreover, the details

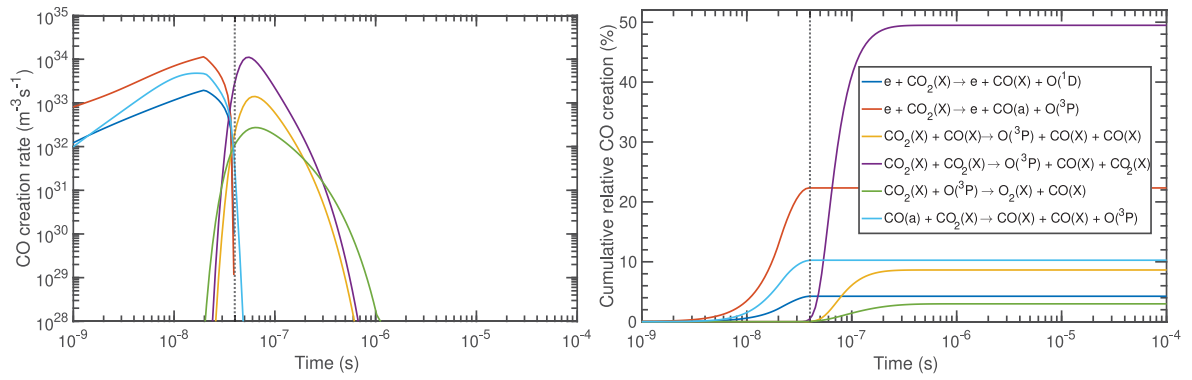


Fig. 9. Instantaneous (left) and cumulative relative (right) CO creation rates. The dashed vertical line indicates the end of the discharge.

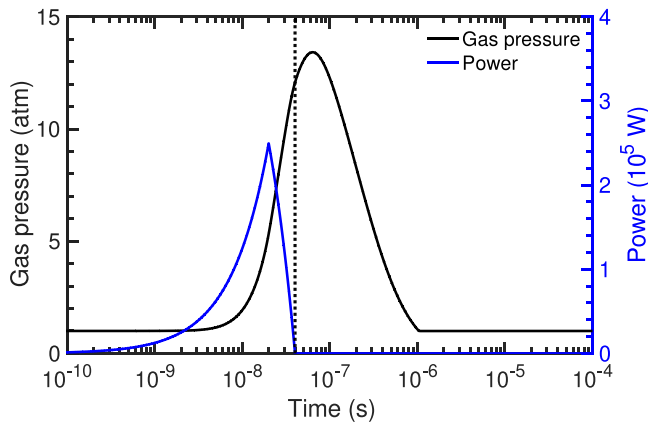


Fig. 10. Gas pressure as a function of time (—). To guide the eye the power pulse is also represented (—, right axis) and a dashed vertical line indicates the end of the discharge.

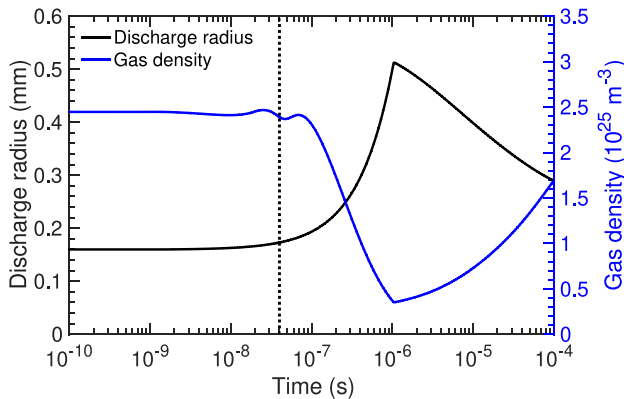


Fig. 11. Discharge radius (—, left axis) and total gas density (—, right axis) as a function of time. The dashed vertical line indicates the end of the discharge.

of the main pathways for heavy-particle CO₂ dissociation according to Eq. (7) predicted by the two models are somewhat different. In particular, in our reference model, CO₂ dissociation involving CO₂, CO and O as collision partners contributes about 50%, 8% and 5%, respectively. In contrast, when using the rate coefficients from [5], dissociation through CO₂+CO collisions accounts for about 37%, through CO₂+O about 6%, while CO₂+CO₂ collisions make a negligible contribution to the total dissociation. As a result, in the latter case, electron-impact dissociation during the discharge pulse contributes about 38% to the

overall dissociation, compared with ~25% in our reference model (cf. Fig. 9 and corresponding discussion). This discussion illustrates both the ability of our relatively simple model to identify the origin of the delayed CO₂ dissociation mechanism and its limitations in capturing the microscopic details of the underlying processes.

The onset of gas heating is due to the quenching of the electronically excited states (see Fig. 7). However, there are several uncertainties related to these processes. First, in our scheme the electronically excited states are assumed to be de-excited directly to the ground state, which is somewhat unlikely specially for CO₂(e₁) and CO(a), given the relatively large amount of energy that would need to be transferred directly into translational modes. A more plausible pathway is that the excess energy is first converted into a vibrationally excited state, which then relaxes to the ground state through V-T deactivation [46]. Consequently, although the amount of energy transferred into gas heating is nearly the same in both views, the dynamics of this transfer is different. Second, some rate coefficients are known only at room temperature, in a limited range of temperatures, or simply assumed by analogy with other reactions [46,66], making them less reliable in the whole range of gas temperatures covered by this work. Finally, here we do not consider the kinetics of the O(¹S) metastable state. This state was shown to give a significant contribution to fast gas heating in low-pressure (10–20 mbar) nanosecond capillary discharges [58], albeit its role was not noteworthy in DC pulsed discharges at 4–7 mbar [46,66]. To estimate the impact these uncertainties may have in our model, Fig. 17 depicts the simulations made when all the rate coefficients of quenching of electronically excited states are either divided or multiplied by a factor of 10, together with the results from the reference model and the experimental data. The general trends of the dissociation fraction and gas temperature remain largely unchanged. However, as expected, larger quenching rate coefficients result in faster gas heating, leading to higher gas temperatures and more pronounced CO₂ dissociation. Conversely, if the quenching of the electronically excited states is less efficient, the delay between the end of the discharge pulse and the onset of CO₂ dissociation increases, as does the time required for the dissociation to reach its peak value.

While Fig. 17 addresses the stage of fast gas heating associated with the quenching of electronically excited states, Fig. 18 examines the subsequent heating stage, associated with V-T relaxation (see Fig. 8 and accompanying discussion), by comparing simulations carried out assuming different relaxation times, τ_{VT} . It can be confirmed that the relaxation of vibrationally excited states has a noticeable effect in the gas heating during the post-discharge, in agreement with the results in Fig. 7, with stronger V-T relaxation inducing a faster and larger gas-heating, and vice-versa. Furthermore, the present results indicate that the estimate of τ_{VT} from [50] used in our reference model is appropriate to describe vibrational relaxation under the conditions considered here.

Our analysis of the impact of different assumptions of the model on the main results finalizes with an evaluation of the influence of

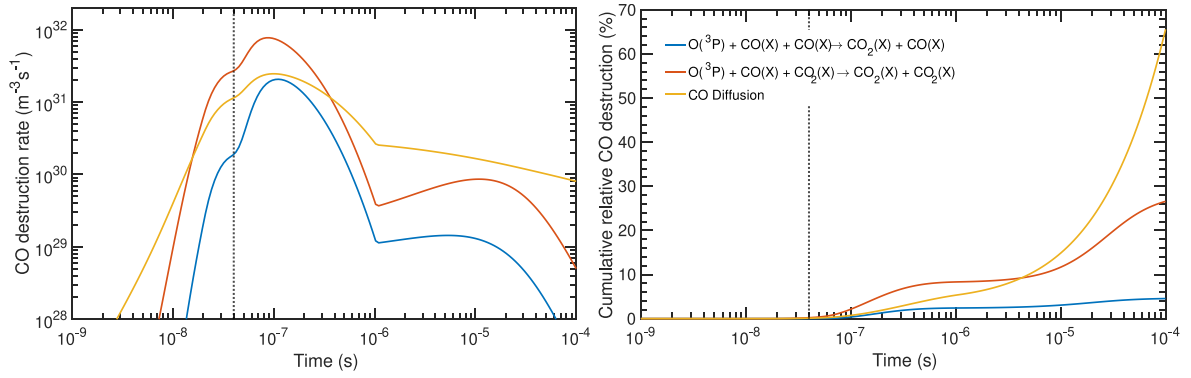


Fig. 12. Instantaneous (left) and cumulative relative (right) CO destruction rates. The dashed vertical line indicates the end of the discharge.

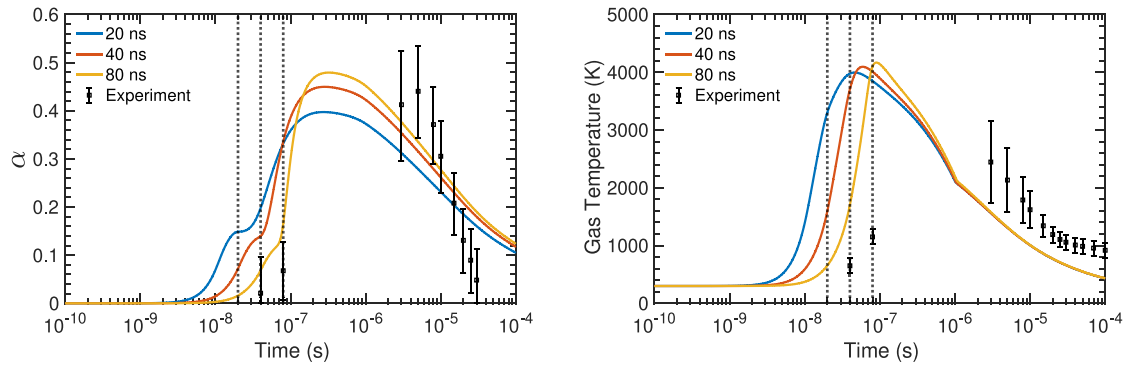


Fig. 13. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated for a discharge pulse of 20 ns (—), 40 ns (reference model, —) and 80 ns (—), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

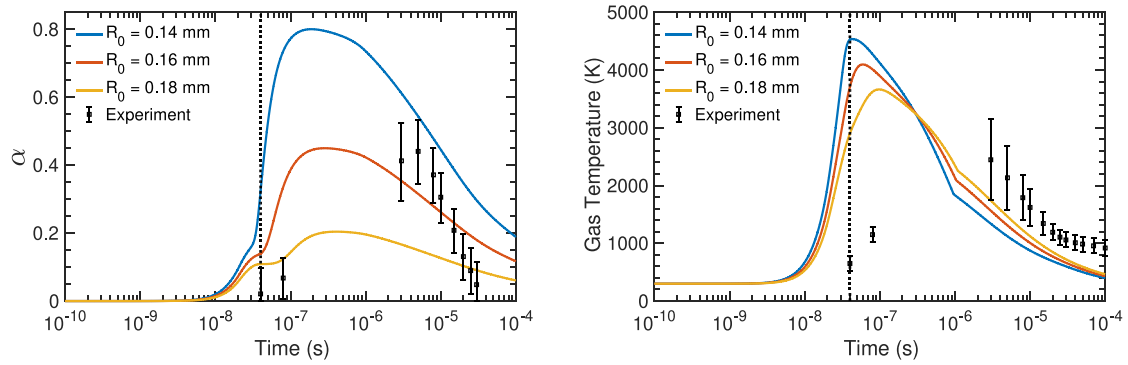


Fig. 14. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated for an initial discharge radius of 0.14 mm (—), 0.16 mm (reference model, —) and 0.18 mm (—), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

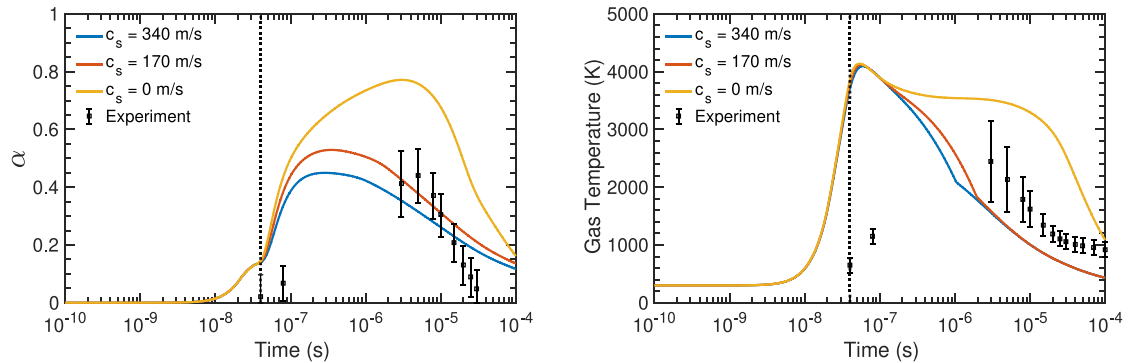


Fig. 15. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated for a sound speed c_s of 340 m/s (reference model, —), 170 m/s (—) and 0 m/s (no discharge expansion/contraction, —), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

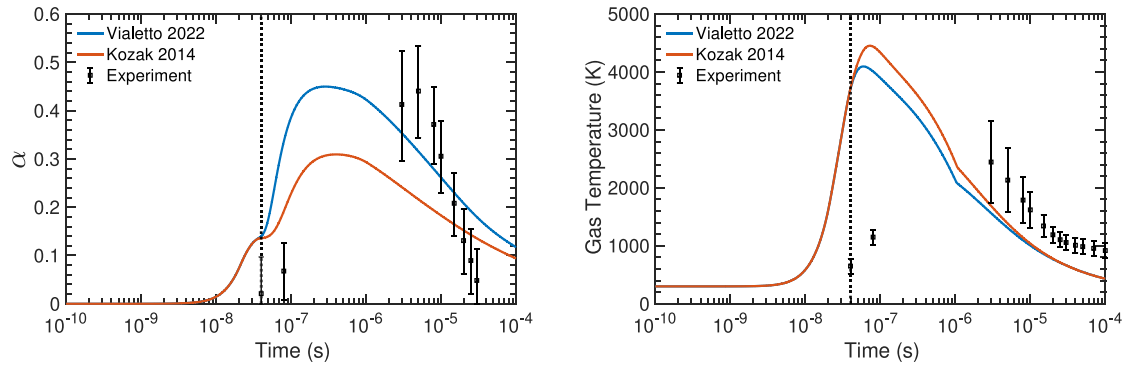


Fig. 16. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated with the plasma chemistry set from our reference model (Vialetto 2022, —) and with CO₂ dissociation/recombination heavy-particle reactions from [5] (Kozak 2014, —), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

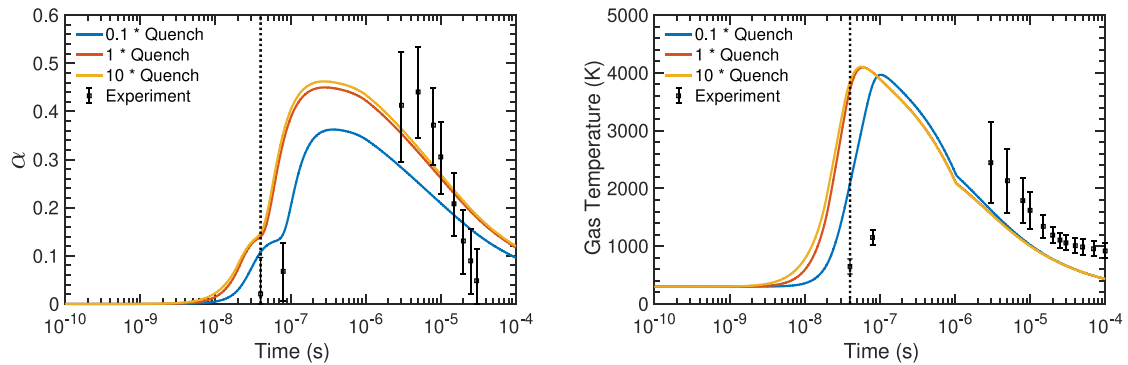


Fig. 17. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated by assuming all the rate coefficients of quenching of the electronically excited states 10 times smaller than in the reference model (—), as in the reference model (—) and 10 times larger than in the reference model (—), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

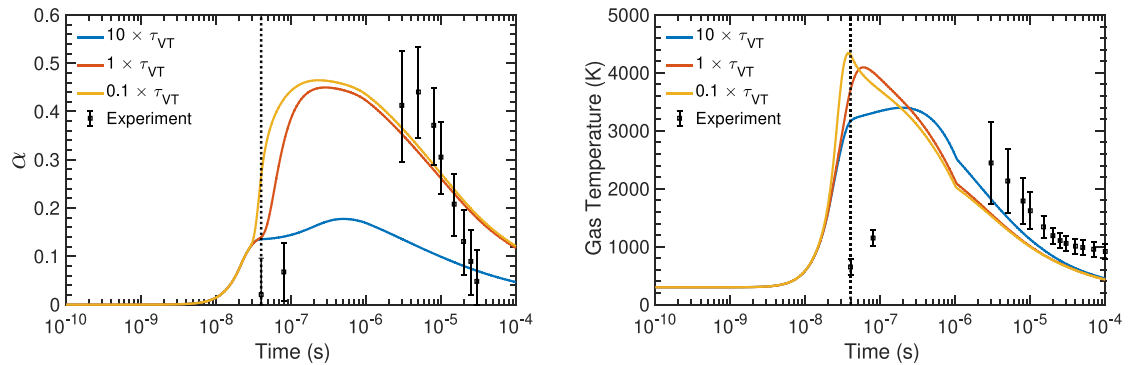


Fig. 18. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated when the V-T relaxation time, τ_{VT} , is 10 times larger than in the reference model (—), as in the reference model (—) and 10 times smaller than in the reference model (—), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

the rate of radial diffusion outside the discharge channel, which is an important mechanism of loss of CO molecules for times above $\sim 1 \mu\text{s}$ (cf. Fig. 12). We recall that the treatment of diffusion in the model is inherently approximate, relying on assumptions regarding the radial profile, boundary conditions, and the use of volume-averaged species densities and gas temperature, as detailed in Section 2.1. Inspection of Fig. 19 shows that altering the diffusion coefficients of all neutral species induces only some changes in the decay profile of the CO number density at the longer afterglow times considered here, but has no impact in the delayed dissociation mechanism. Indeed, the increase in [CO] during the discharge and throughout the first instants of the post-discharge, until it reaches its peak value, are not affected by the

hypotheses made for CO diffusion, which occurs with a substantially longer characteristic timescale.

4. Conclusions

CO₂ plasmas are of great interest because they enable the controlled activation and dissociation of a very stable molecule, opening pathways for efficient CO₂ conversion into value-added products such as CO, O₂ and synthetic fuels. While CO₂ dissociation by direct electron impact is not energy-efficient, plasmas can benefit from non-equilibrium conditions to offer alternative routes to dissociation. Unambiguous experimental evidence of such an alternative pathway to dissociation was

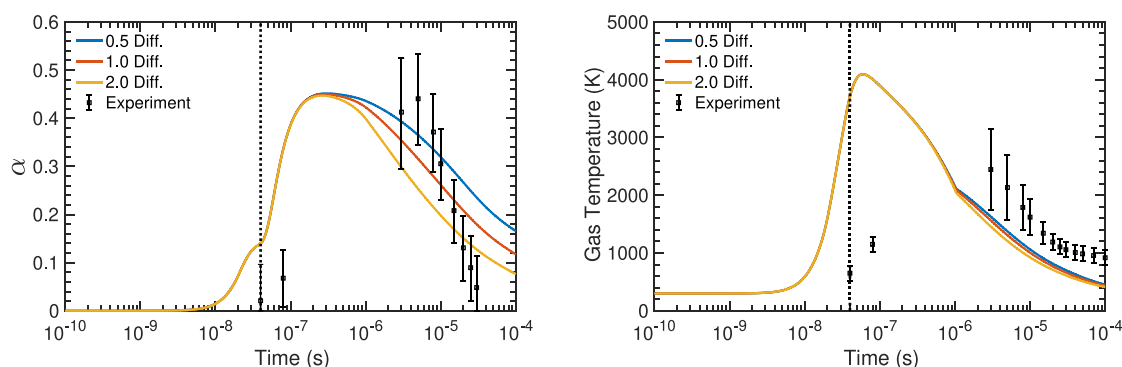


Fig. 19. CO₂ conversion α (left) and gas temperature (right) as a function of time, calculated when the diffusion coefficients of all neutral species are 2 times smaller than in the reference model (—), as in the reference model (—) and 2 times larger than in the reference model (—), and experimental data from [23] (■). The dashed vertical lines indicate the end of the discharge.

recently obtained by the group at the University of Trento [23]. Using an atmospheric pressure CO₂ pin-to-pin nanosecond repetitively pulsed discharge, they have demonstrated the existence of a delayed CO₂ dissociation mechanism, where the dissociation fraction peaks after the discharge pulse, when the electron density has already decayed and electron impact dissociation is vanishingly small.

In this work, we elucidate the phenomena underlying the delayed CO₂ dissociation mechanism. They involve three phases, that can be summarized as follows. First, during the discharge phase the electron density grows rapidly and there is a strong population of electronically and vibrationally excited states by direct electron impact. The electronically excited states are quickly quenched and barely survive at the end of the discharge pulse, leading to fast gas heating and an initial increase in the gas temperature. In this phase, CO₂ is dissociated by electron impact and the dissociation fraction reaches $\sim 20 - 25\%$ of its maximum value. Second, in the first instants of the afterglow, the vibrationally excited states release their energy into gas heating, due to vibration-translation relaxation. As an outcome, the gas temperature continues to increase, up to values of the order of 4000 K, and temperature activated CO₂ dissociation reactions involving heavy-particles, CO₂+M $\rightarrow$ CO+O+M, take place, microseconds after the discharge. Accordingly, there is a continuous increase of the dissociation fraction until it reaches its peak value. Finally, the high temperatures attained in the afterglow are associated with a substantial increase of the pressure inside the discharge channel, inducing its expansion and correlated gas cooling. As the temperature drops, CO begins to recombine in three body reactions, CO+O+M $\rightarrow$ CO₂+M, mainly with CO₂ and/or CO acting as the third body. As the gas cooling progresses, the hot gas channel eventually contracts, with CO+O recombination continuing throughout this phase.

Our analysis is based on a new 0.5D formulation to study pin-to-pin nanosecond discharges operating at atmospheric pressure. In this approach, the particle continuity and gas energy balance equations are radially averaged, while the discharge channel is allowed to have a time-varying radius that expands or contracts in response to local pressure changes. We show that molecular collision driven dissociation is governed by the peak gas temperature attained in the channel: only when sufficiently high temperatures are reached does the molecular pathway become dominant, whereas at lower power densities dissociation is instead controlled by direct electron-impact processes. Furthermore, we demonstrate that accounting for the channel dynamics is essential to accurately describe the recombination kinetics along the afterglow.

We tested the sensitivity of our predictions against the key assumptions of the model and uncertainties in elementary data and concluded that, despite some differences in the details, the general picture and identification of the main phenomena ruling the delayed dissociation outlined above are robust and largely independent of the

model assumptions. In fact, the quantitative agreement with experiment could be improved by tuning uncertain model parameters, but such an exercise would not be meaningful here. The comparison with the experiment should not be quantitative and serves only to rationalize the experimental findings at a fundamental level, given that neither the measurements nor the idealized 0.5D model capture the complexity of the development of the discharge. While the actual discharge is highly inhomogeneous in space and time, measurements were taken at the centre of the gap and are therefore localized to that area. Conversely, the 0.5D model averages over the entire discharge volume. Nevertheless, the simulations describe accurately both the trend and order of magnitude of the experimental observations, supporting the validity of our approach and conclusions.

It must be noted that the experiments in [23] were conducted at repetition rates up to 30 KHz and have shown a dependence of the subsequent pulses on the interpulse time. While our simulations correspond to a single discharge pulse and are compared with the first pulse in the burst, so that there is no residual influence from previous pulses, future work should evaluate the influence of having a second discharge pulse on a partially pre-dissociated gas. In addition, since product separation remains a major challenge for the practical deployment of plasma-based CO₂ conversion, it would be highly valuable to investigate what are the appropriate pulse patterns and reactor geometries that enhance dissociation and product extraction in prospective systems coupling plasmas with separation membranes.

Our finding that molecular rather than electron collisions are responsible for dissociation contrasts with the conventional wisdom that direct electron-impact dissociation is the primary mechanism in nanosecond gas discharges. These results are in line with the very recent work by Van Rompey et al. [67], who used a 0D model to study CH₄ conversion in nanosecond pulsed plasmas and highlight the interplay between plasma-induced and thermal processes during the nanosecond pulse and in the afterglow, respectively. By demonstrating the dominance of molecular collision-driven pathways, these works point towards a paradigm shift in the interpretation of nanosecond pulsed discharges and open new avenues for research into the design and control of plasma-induced gas conversion. Finally, performing experiments at different initial pressures would change the characteristic times of the different phenomena at play and would provide additional insight to further refine and validate our analysis.

CRedit authorship contribution statement

Tiago C. Dias: Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis. **Luca Matteo Martini:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Paolo Tosi:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Vasco Guerra:** Writing – original draft, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

VG was partially supported by the Portuguese FCT - Fundação para a Ciência e a Tecnologia, Portugal, under project's references UID/50010/2023, UID/PRR/50010/2025, LA/P/0061/2020 (DOI: 10.54499/LA/P/0061/2020) and PTDC/FIS-PLA/1616/2021 (DOI: 10.54499/PTDC/FISPLA/1616/2021). LMM and PT acknowledge the financial support by the European Union under NextGenerationEU Mission 4 Component 2 CUP E53D23002330006 PRIN 2022 PLASMODD Prot. n. 2022J5NBBN. TCD is indebted to Duarte Gonçalves for discussions on the 0.5D model.

Appendix A. Derivation of the continuity equation

Consider a control volume V , bounded by a control surface A moving with velocity $\mathbf{V}_c$. Reynolds transport theorem reads

$$\frac{d}{dt} \int_V f dV = \int_V \frac{\partial f}{\partial t} dV + \oint_A (f \mathbf{V}_c) \cdot \mathbf{n} dA, \quad (\text{A.1})$$

where $\frac{d}{dt}$ denotes the total derivative, f is a quantity being integrated over the control volume, and $\mathbf{n}$ is the outward normal unit vector to the control surface.

Applying the theorem to $f = n_i$ and using Eq. (1),

$$\frac{d}{dt} \int_V n_i dV = \int_V (-\nabla \cdot (n_i \mathbf{v}) + \nabla \cdot (D_i \nabla n_i) + S_i) dV + \oint_A (n_i \mathbf{V}_c) \cdot \mathbf{n} dA. \quad (\text{A.2})$$

Considering a control surface moving with the same velocity as the fluid ($\mathbf{V}_c = \mathbf{v}$), Eq. (A.2) simplifies to

$$\frac{d}{dt} \int_V n_i dV = \oint_A (D_i \nabla n_i) \cdot \mathbf{n} dA + \int_V S_i dV. \quad (\text{A.3})$$

The total derivative of the volume averaged density of species i ,

$$\bar{n}_i \equiv \frac{1}{V} \int_V n_i dV, \quad (\text{A.4})$$

can be written as

$$\frac{d\bar{n}_i}{dt} = \frac{1}{V} \frac{d}{dt} \int_V n_i dV - \frac{1}{V} \frac{dV}{dt} \bar{n}_i. \quad (\text{A.5})$$

Replacing in Eq. (A.3),

$$\frac{d\bar{n}_i}{dt} = \frac{1}{V} \oint_A (D_i \nabla n_i) \cdot \mathbf{n} dA + \bar{S}_i - \frac{1}{V} \frac{dV}{dt} \bar{n}_i, \quad (\text{A.6})$$

where we have defined

$$\bar{S}_i \equiv \frac{1}{V} \int_V S_i dV. \quad (\text{A.7})$$

For an axisymmetric control volume $V(t) = \pi R^2(t)L$ expanding radially with velocity v (cf. Section 2.1), $\frac{dV(t)}{dt} = 2\pi R(t)L = A(t)v$. Assuming a zero-order Bessel function J_0 for the radial profile of the species' densities, corresponding to the lowest-order solution of the diffusion equation, with the boundary condition $n_i(R) = n_{0,i}$, ensuring that the density of species i at the border of the control volume is equal to its density in the surrounding medium, we have

$$n_i(r) = n_{0,i} + [n_i(0) - n_{0,i}] J_0(r/\lambda) = n_{0,i} + (\bar{n}_i - n_{0,i}) \frac{R/\lambda}{2J_1(R/\lambda)} J_0(r/\lambda), \quad (\text{A.8})$$

Table C.1

List of species included in the kinetic scheme considered in this work. $\text{CO}_2(\text{e}_1)$, $\text{O}_2(\text{Hz})$ and O_3^* denote, respectively, lumped CO_2 states with energy thresholds around 8 eV [68], an effective sum of the Herzberg states $\text{O}_2(\text{c}^1\Sigma_u^-, \text{A}^3\Sigma_u^+, \text{A}'^3\Delta_u)$ [69], and an effective state representing vibrationally-excited ozone [70].

$\text{CO}_2(\text{X}^1\Sigma_g^+)$	$\text{CO}_2(\text{e}_1)$	CO_2^*		
$\text{CO}(\text{X}^1\Sigma^+)$	$\text{CO}(\text{a}^3\Pi_t)$	CO^+		
$\text{O}_2(\text{X}^3\Sigma_g^-)$	$\text{O}_2(\text{a}^1\Delta_g)$	$\text{O}_2(\text{b}^1\Sigma_g^+)$	$\text{O}_2(\text{Hz})$	O_2^*
O^3P	O^1D	O^+	O^-	
$\text{O}_3(\text{X}^1\text{A}_1)$	O_3^*			
C^3P	C^+			

where $\lambda = R/2.405$ and $r \in [0, R]$. Therefore, the average rate of change of the density of species i in the control volume due to diffusion is

$$\frac{1}{V} \int_V (D_i \nabla n_i) \cdot \mathbf{e}_r dA = -\frac{D_i}{\lambda^2} (\bar{n}_i - n_{0,i}). \quad (\text{A.9})$$

Replacing in (A.6) we obtain Eq. (2), where D_i and $\bar{S}_i$ are calculated as described in Section 2.1.

Appendix B. Derivation of the gas energy equation

Using Reynolds transport theorem (A.1) with $f = NC_V T$ and integrating over a control volume whose surface expands with the fluid velocity, as it was done in Appendix A for the continuity equation, we have

$$\frac{d}{dt} \int_V (NC_V T) dV = \oint_A (\lambda \nabla T) \cdot \mathbf{n} dA - \int_V p \nabla \cdot \mathbf{v} dV + \int_V \sum_m R_m \Delta H_m dV, \quad (\text{B.1})$$

where we have used (4). Using the relation expressed by (A.5) (applied to $\overline{NC_V T}$ instead of $\bar{n}_i$), we can write

$$\frac{d}{dt} \overline{NC_V T} = \frac{1}{V} \oint_A (\lambda \nabla T) \cdot \mathbf{n} dA - \frac{1}{V} \int_V p \nabla \cdot \mathbf{v} dV + \sum_m \overline{R_m \Delta H_m} - \frac{1}{V} \frac{dV}{dt} \overline{NC_V T}. \quad (\text{B.2})$$

The first term in (B.2) describes thermal conduction to the periphery of the discharge channel and can be simplified assuming that the thermal conductivity, λ , can be approximated by a uniform value over the control volume with its value calculated at the average gas temperature, $\bar{T}$. Heat losses by convection are neglected. Further assuming a parabolic gas temperature profile,

$$T(r) \simeq T(0) - [T(0) - T_0] \frac{r^2}{R^2} = 2\bar{T} - T_0 - 2(\bar{T} - T_0) \frac{r^2}{R^2}, \quad (\text{B.3})$$

we have the usual conduction term

$$\frac{1}{V} \oint_A (\lambda \nabla T) \cdot \mathbf{n} dA = -\frac{8\lambda}{R^2} (\bar{T} - T_0). \quad (\text{B.4})$$

In the second term on the r.h.s of (B.2) we assume $\bar{p} \simeq k_B \bar{N} \bar{T}$, so that

$$-\frac{1}{V} \int_V p \nabla \cdot \mathbf{v} dV \simeq -\frac{\bar{p}}{V} \int_V \nabla \cdot \mathbf{v} dV = -\frac{\bar{p}}{V} \oint_A \mathbf{v} \cdot \mathbf{n} dA = -\frac{2v\bar{p}}{R}. \quad (\text{B.5})$$

Finally, if we additionally assume that the heat capacity can be considered uniform over the control volume and calculated at the average gas temperature, $\bar{T}$, we arrive at the expression for the energy conservation equation used in this work, expressed by (5).

Appendix C. Kinetic scheme

See Tables C.1–C.3.

Table C.2

List of electron-impact processes considered in this work for the chemical kinetics of CO₂ discharges. The rate coefficients for two- and three- body reactions are in m³s⁻¹ and m⁶s⁻¹, respectively. T_e and $T_{e,K}$ are the electron temperature in eV and K, respectively. For rate coefficients labeled with $f(T_e)$, the value is calculated from the integration of the corresponding cross section over the EEDF.

Reaction	Rate coefficient (m ³ s ⁻¹ , m ⁶ s ⁻¹)	Ref.
<i>Electron-impact ionization</i>		
R1 $e + \text{CO}_2(\text{X}) \rightarrow e + e + \text{CO}_2^+$	$f(T_e)$	[46]
R2 $e + \text{CO}_2(\text{X}) \rightarrow e + e + \text{O}^+ + \text{CO}(\text{X})$	$f(T_e)$	[45,71]
R3 $e + \text{CO}_2(\text{X}) \rightarrow e + e + \text{C}^+ + \text{O}_2(\text{X})$	$f(T_e)$	[45,71]
R4 $e + \text{CO}_2(\text{X}) \rightarrow e + e + \text{CO}^+ + \text{O}(\text{^3P})$	$f(T_e)$	[45,71]
R5 $e + \text{CO}_2(\text{X}) \rightarrow e + e + \text{O}_2^+ + \text{C}(\text{^3P})$	$7 \times 10^{-19} (1 + 1.3 \times 10^{-5} T_{e,K}) T_{e,K}^{0.5} \exp\left(\frac{-1.5 \times 10^5}{T_{e,K}}\right)$	[45,72]
R6 $e + \text{CO}(\text{X}) \rightarrow e + e + \text{CO}^+$	$f(T_e)$	[46,73]
R7 $e + \text{CO}(\text{X}) \rightarrow e + e + \text{C}^+ + \text{O}(\text{^3P})$	$f(T_e)$	[46,73]
R8 $e + \text{CO}(\text{X}) \rightarrow e + e + \text{O}^+ + \text{C}(\text{^3P})$	$f(T_e)$	[46,73]
R9 $e + \text{O}_2(\text{X}) \rightarrow e + e + \text{O}_2^+$	$f(T_e)$	[48,74]
R10 $e + \text{O}_2(\text{X}) \rightarrow e + e + \text{O}^+ + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]
R11 $e + \text{O}(\text{^3P}) \rightarrow e + e + \text{O}^+$	$f(T_e)$	[48,75]
R12 $e + \text{C}(\text{^3P}) \rightarrow e + e + \text{C}^+$	$f(T_e)$	[45,72]
<i>Electron-impact detachment</i>		
R13 $e + \text{CO}_2(\text{X}) \rightarrow \text{O}^- + \text{CO}(\text{X})$	$f(T_e)$	[46]
R14 $e + \text{CO}(\text{X}) \rightarrow \text{O}^- + \text{C}(\text{^3P})$	$f(T_e)$	[46,76]
R15 $e + \text{O}_2(\text{X}) \rightarrow \text{O}^- + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]
R16 $e + \text{O}(\text{^3P}) + \text{M} \rightarrow \text{O}^- + \text{M}$	10^{-43}	[45,59]
<i>Electron-impact dissociation</i>		
R17 $e + \text{CO}_2(\text{X}) \rightarrow e + \text{CO}(\text{X}) + \text{O}(\text{^1D})$	$f(T_e)$	[46]
R18 $e + \text{CO}_2(\text{X}) \rightarrow e + \text{CO}(\text{a}) + \text{O}(\text{^3P})$	$f(T_e)$	[46]
R19 $e + \text{CO}(\text{X}) \rightarrow e + \text{C}(\text{^3P}) + \text{O}(\text{^3P})$	$f(T_e)$	[46,73]
R20 $e + \text{O}_2(\text{X}) \rightarrow e + \text{O}(\text{^3P}) + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]
R21 $e + \text{O}_2(\text{X}) \rightarrow e + \text{O}(\text{^3P}) + \text{O}(\text{^1D})$	$f(T_e)$	[48,74]
<i>Electron-impact recombination</i>		
R22 $e + \text{CO}_2^+ \rightarrow \text{CO}(\text{X}) + \text{O}(\text{^3P})$	$3.94 \times 10^{-13} T_e^{-0.4}$	[45,72]
R23 $e + \text{CO}_2^+ \rightarrow \text{C}(\text{^3P}) + \text{O}_2(\text{X})$	$3.94 \times 10^{-13} T_e^{-0.4}$	[45,72]
R24 $e + \text{CO}^+ \rightarrow \text{C}(\text{^3P}) + \text{O}(\text{^3P})$	$1.57 \times 10^{-13} T_e^{-0.4}$	[45,72]
R25 $e + \text{O}_2^+ + \text{M} \rightarrow \text{O}(\text{^3P}) + \text{O}(\text{^3P}) + \text{M}$	$1.61 \times 10^{-39} T_e^{-0.5}$	[45,72]
R26 $e + \text{O}_2^+ \rightarrow \text{O}(\text{^3P}) + \text{O}(\text{^3P})$	$5.17 \times 10^{-15} T_e^{-1} + 1.51 \times 10^{-14} T_e^{-0.7}$	[48]
R27 $e + \text{O}^+ + \text{M} \rightarrow \text{O}(\text{^3P}) + \text{M}$	$2.49 \times 10^{-41} T_e^{-1.5}$	[45,72]
<i>Electron-impact involving electronically-excited states</i>		
R28 $e + \text{CO}_2(\text{X}) \leftrightarrow e + \text{CO}_2(\text{e1})$	$f(T_e)$	[46]
R29 $e + \text{CO}(\text{X}) \leftrightarrow e + \text{CO}(\text{a})$	$f(T_e)$	[46,73]
R30 $e + \text{O}_2(\text{X}) \leftrightarrow e + \text{O}_2(\text{a})$	$f(T_e)$	[48,74]
R31 $e + \text{O}_2(\text{X}) \leftrightarrow e + \text{O}_2(\text{b})$	$f(T_e)$	[48,74]
R32 $e + \text{O}_2(\text{a}) \leftrightarrow e + \text{O}_2(\text{b})$	$f(T_e)$	[48,74]
R33 $e + \text{O}(\text{^3P}) \leftrightarrow e + \text{O}(\text{^1D})$	$f(T_e)$	[48,75]
R34 $e + \text{O}_2(\text{X}) \leftrightarrow e + \text{O}_2(\text{Hz})$	$f(T_e)$	[48,74]
R35 $e + \text{O}_2(\text{a}) \rightarrow e + \text{O}(\text{^3P}) + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]
R36 $e + \text{O}_2(\text{a}) \rightarrow e + \text{O}(\text{^3P}) + \text{O}(\text{^1D})$	$f(T_e)$	[48,74]
R37 $e + \text{O}_2(\text{b}) \rightarrow e + \text{O}(\text{^3P}) + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]
R38 $e + \text{O}_2(\text{b}) \rightarrow e + \text{O}(\text{^3P}) + \text{O}(\text{^1D})$	$f(T_e)$	[48,74]
R39 $e + \text{O}_2(\text{a}) \rightarrow e + e + \text{O}_2^+$	$f(T_e)$	[48,74]
R40 $e + \text{O}_2(\text{a}) \rightarrow e + e + \text{O}^+ + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]
R41 $e + \text{O}_2(\text{a}) \rightarrow e + e + \text{O}^- + \text{O}(\text{^3P})$	$f(T_e)$	[48,74]

Table C.3

List of neutral-species processes considered in this work for CO₂ discharges. The rate coefficients for two- and three- body reactions are in m³s⁻¹ and m⁶s⁻¹, respectively. N is total number density in m⁻³, P_r is the reduced pressure as defined in [47], and T_g is the gas temperature in K.

Reaction	Rate coefficient (m ³ s ⁻¹ , m ⁶ s ⁻¹)	Ref.
<i>Neutral thermal chemistry reactions</i>		
R42 $\text{O}(\text{^3P}) + \text{O}(\text{^3P}) + \text{CO}(\text{X}) \leftrightarrow \text{O}_2(\text{X}) + \text{CO}(\text{X})$	$5.79 \times 10^{-43} T_g^{-1}$	[45,47]
R43 $\text{O}(\text{^3P}) + \text{O}(\text{^3P}) + \text{CO}_2(\text{X}) \leftrightarrow \text{O}_2(\text{X}) + \text{CO}_2(\text{X})$	$11.92 \times 10^{-43} T_g^{-1}$	[45,47]
R44 $\text{O}(\text{^3P}) + \text{CO}(\text{X}) + \text{CO}(\text{X}) \leftrightarrow \text{CO}_2(\text{X}) + \text{CO}(\text{X})$	$4.49 \times 10^{-20} \exp(-1195.27/T_g) \cdot \frac{P_r}{N(1+P_r)}$	[45,47]
R45 $\text{O}(\text{^3P}) + \text{CO}(\text{X}) + \text{CO}_2(\text{X}) \leftrightarrow \text{CO}_2(\text{X}) + \text{CO}_2(\text{X})$	$10.47 \times 10^{-20} \exp(-1195.27/T_g) \cdot \frac{P_r}{N(1+P_r)}$	[45,47]
R46 $\text{O}(\text{^3P}) + \text{CO}(\text{X}) + \text{O}_2(\text{X}) \leftrightarrow \text{CO}_2(\text{X}) + \text{O}_2(\text{X})$	$17.94 \times 10^{-20} \exp(-1195.27/T_g) \cdot \frac{P_r}{N(1+P_r)}$	[45,47]
R47 $\text{O}_2(\text{X}) + \text{CO}(\text{X}) \leftrightarrow \text{O}(\text{^3P}) + \text{CO}_2(\text{X})$	$4.15 \times 10^{-18} \exp(-24021.37/T_g)$	[45,47]
R48 $\text{CO}(\text{X}) + \text{CO}(\text{X}) \leftrightarrow \text{CO}_2(\text{X}) + \text{C}(\text{^3P})$	$6.31 \times 10^{-17} \exp(-97013.83/T_g)$	[45,47]
R49 $\text{CO}(\text{X}) + \text{O}(\text{^3P}) \leftrightarrow \text{O}(\text{^3P}) + \text{C}(\text{^3P}) + \text{O}(\text{^3P})$	$3.57 \times 10^{-3} T_g^{-3.1} \exp(-1288.10/T_g)$	[45,47]
R50 $\text{CO}(\text{X}) + \text{O}_2(\text{X}) \leftrightarrow \text{O}(\text{^3P}) + \text{C}(\text{^3P}) + \text{O}_2(\text{X})$	$3.57 \times 10^{-3} T_g^{-3.1} \exp(-1288.10/T_g)$	[45,47]
R51 $\text{CO}(\text{X}) + \text{CO}(\text{X}) \leftrightarrow \text{O}(\text{^3P}) + \text{C}(\text{^3P}) + \text{CO}(\text{X})$	$14.28 \times 10^{-3} T_g^{-3.1} \exp(-1288.10/T_g)$	[45,47]
R52 $\text{CO}(\text{X}) + \text{CO}_2(\text{X}) \leftrightarrow \text{O}(\text{^3P}) + \text{C}(\text{^3P}) + \text{CO}_2(\text{X})$	$7.14 \times 10^{-3} T_g^{-3.1} \exp(-1288.10/T_g)$	[45,47]
R53 $\text{C}(\text{^3P}) + \text{O}_2(\text{X}) \leftrightarrow \text{CO}(\text{X}) + \text{O}(\text{^3P})$	$5.36 \times 10^{-18} T_g^{0.41} \exp(26.92/T_g)$	[45,47]

(continued on next page)

Table C.3 (continued).

Reaction	Rate coefficient ($\text{m}^3\text{s}^{-1}, \text{m}^6\text{s}^{-1}$)	Ref.
<i>Relaxation of electronically-excited states</i>		
R54 $\text{CO}_2(\text{e}1) + \text{M} \rightarrow \text{CO}_2(\text{X}) + \text{M}$	10^{-17}	[46,66]
R55 $\text{O}_2(\text{b}) + \text{CO}_2(\text{X}) \rightarrow \text{O}_2(\text{X}) + \text{CO}_2(\text{X})$	$1.18 \times 10^{-23} T_g^{1.5} \exp(595/T_g)$	[12,77]
R56 $\text{O}_2(\text{b}) + \text{CO}(\text{X}) \rightarrow \text{O}_2(\text{X}) + \text{CO}(\text{X})$	3.74×10^{-21}	[12,78]
R57 $\text{O}(\text{D}) + \text{CO}_2(\text{X}) \rightarrow \text{O}(\text{P}) + \text{CO}_2(\text{X})$	$7.4 \times 10^{-17} \times \exp(133/T_g)$	[12,79]
R58 $\text{CO}(\text{a}) + \text{O}_2(\text{X}) \rightarrow \text{CO}(\text{X}) + \text{O}_2(\text{X})$	$0.4 \times 6 \times 10^{-17}$	[12,80]
R59 $\text{CO}(\text{a}) + \text{O}_2(\text{X}) \rightarrow \text{CO}(\text{X}) + \text{O}(\text{P}) + \text{O}(\text{P})$	$0.4 \times 6 \times 10^{-17}$	[12,80]
R60 $\text{CO}(\text{a}) + \text{O}_2(\text{X}) \rightarrow \text{CO}_2(\text{X}) + \text{O}(\text{P})$	$0.2 \times 6 \times 10^{-17}$	[12,80]
R61 $\text{CO}(\text{a}) + \text{CO}(\text{X}) \rightarrow \text{CO}_2(\text{X}) + \text{C}(\text{P})$	$0.016 \times 5.7 \times 10^{-17}$	[12,80]
R62 $\text{CO}(\text{a}) + \text{CO}(\text{X}) \rightarrow \text{CO}(\text{X}) + \text{CO}(\text{X})$	$0.984 \times 5.7 \times 10^{-17}$	[12,80]
R63 $\text{CO}(\text{a}) + \text{CO}_2(\text{X}) \rightarrow \text{CO}(\text{X}) + \text{CO}_2(\text{X})$	0.5×10^{-17}	[12,81]
R64 $\text{CO}(\text{a}) + \text{CO}_2(\text{X}) \rightarrow \text{CO}(\text{X}) + \text{CO}(\text{X}) + \text{O}(\text{P})$	0.5×10^{-17}	[12,81]
R65 $\text{CO}(\text{a}) + \text{O}(\text{P}) \rightarrow \text{CO}(\text{X}) + \text{O}(\text{P})$	1.9×10^{-16}	[12,82]
R66 $\text{O}_2(\text{a}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{X}) + \text{O}(\text{P})$	7×10^{-22}	[48,83]
R67 $\text{O}_2(\text{a}) + \text{O}(\text{P}) + \text{O}_2(\text{X}) \rightarrow \text{O}_2(\text{X}) + \text{O}(\text{P}) + \text{O}_2(\text{X})$	3×10^{-44}	[48,84]
R68 $\text{O}_2(\text{a}) + \text{O}_2(\text{a}) \rightarrow \text{O}_2(\text{b}) + \text{O}_2(\text{X})$	$1.81 \times 10^{-24} \times (T_g/300)^{3.8} \exp(700/T_g)$	[48,85]
R69 $\text{O}_2(\text{a}) + \text{O}_2(\text{X}) \rightarrow \text{O}_2(\text{X}) + \text{O}_2(\text{X})$	$2.2 \times 10^{-24} (T_g/300)^{0.8}$	[48,83]
R70 $\text{O}_2(\text{b}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{a}) + \text{O}(\text{P})$	4×10^{-20}	[48,86]
R71 $\text{O}_2(\text{b}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{X}) + \text{O}(\text{P})$	$4 \times 10^{-20} + 10^{-16} \exp(-3700/T_g)$	[48,87]
R72 $\text{O}_2(\text{b}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{X}) + \text{O}(\text{D})$	$3.39 \times 10^{-17} \times (300/T_g)^{0.1} \exp(-4201/T_g)$	[48,88]
R73 $\text{O}_2(\text{Hz}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{X}) + \text{O}(\text{P})$	4.95×10^{-18}	[48,69]
R74 $\text{O}_2(\text{Hz}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{a}) + \text{O}(\text{D})$	2.7×10^{-18}	[48,69]
R75 $\text{O}_2(\text{Hz}) + \text{O}(\text{P}) \rightarrow \text{O}_2(\text{b}) + \text{O}(\text{D})$	1.35×10^{-18}	[48,69]
R76 $\text{O}_2(\text{Hz}) + \text{O}_2(\text{X}) \rightarrow \text{O}_2(\text{X}) + \text{O}_2(\text{X})$	0.23×10^{-19}	[48,69]
R77 $\text{O}_2(\text{Hz}) + \text{O}_2(\text{X}) \rightarrow \text{O}_2(\text{a}) + \text{O}_2(\text{X})$	1.86×10^{-19}	[48,69]
R78 $\text{O}_2(\text{Hz}) + \text{O}_2(\text{X}) \rightarrow \text{O}_2(\text{b}) + \text{O}_2(\text{X})$	0.21×10^{-19}	[48,69]
R79 $\text{O}(\text{D}) + \text{O}(\text{P}) \rightarrow \text{O}(\text{P}) + \text{O}(\text{P})$	8×10^{-18}	[48,89]
R80 $\text{O}(\text{D}) + \text{O}_2(\text{X}) \rightarrow \text{O}(\text{P}) + \text{O}_2(\text{X})$	$7 \times 10^{-18} \exp(67/T_g)$	[48,89]
R81 $\text{O}(\text{D}) + \text{O}_2(\text{X}) \rightarrow \text{O}(\text{P}) + \text{O}_2(\text{a})$	$8 \times 10^{-19} \exp(67/T_g)$	[48,90]
R82 $\text{O}(\text{D}) + \text{O}_2(\text{X}) \rightarrow \text{O}(\text{P}) + \text{O}_2(\text{b})$	$2.56 \times 10^{-17} \exp(67/T_g)$	[48,89]

Data availability

Data will be made available on request.

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