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Fluid modelling of CO₂ dissociation in a dielectric barrier discharge

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The dissociation of CO₂ in a geometrically symmetric dielectric barrier discharge has been analysed by means of numerical modelling. A time- and space-dependent fluid model has been used, taking into account the spatial variation of the plasma between the plane-parallel dielectrics covering the electrodes. The main features of the model, including an extensive reaction kinetics for the vibrational states of CO₂, are given. The modelling studies have been performed for different applied voltages, discharge frequencies, pressures, gas temperatures, and relative permittivities of the dielectrics. The model calculations show that the discharges in the positive and negative half-cycles are different for the considered standard condition, leading to a spatially asymmetric distribution of the stable neutrals like CO molecules and O atoms. The generation of CO mainly takes place during the discharge pulses, and it is dominated by electron impact dissociation. The specific energy input obtained for the broad range of parameters considered and determined for residence times reported in the literature agrees well with the corresponding experimental values. In accordance with these experiments, the calculated degree of CO₂ conversion has been found to increase almost linearly with the specific energy input. Remaining discrepancies between the measured and calculated energy efficiencies are discussed. © 2016 AIP Publishing LLC.

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I. INTRODUCTION

Electricity from renewable energy can be directly used to make synthetic fuels sustainable if electrical discharges could be used to generate CO from CO₂ in an energy efficient manner.^{1,2} Research done in the 1970s and 1980s established that non-equilibrium plasmas, i.e., certain kinds of electrical discharges, are capable of dissociating CO₂ with very high energy efficiencies of up to 90%^{3–6} albeit at low throughputs. The advantage of non-equilibrium plasma is that it possesses high electron temperature and vibrational temperature, which promote dissociation reactions, even endothermic reactions, while simultaneously it has a low gas temperature, which prevents backward recombination reactions.⁶ In this context, many different non-equilibrium plasma routes have been tested to see if high energy efficiencies can be reproduced. For example, in recent years, there were reports on using a micro-plasma reactor,⁷ low-pressure RF discharges,⁸ a gliding arc plasmatron at atmospheric pressure,⁹ and an atmospheric pressure microwave plasma/catalyst system,¹⁰ among others, for CO₂ dissociation. In addition, dielectric barrier discharges (DBDs) in CO₂ have become subject of recent works^{11–19} because their simplicity in operation and potential for scalability offer immense promise for producing CO in industrial scales.

In order to understand the mechanisms of dissociation and to support the prediction of optimal operational parameters, numerical simulations are very important. Different modelling approaches are employed for the theoretical investigation of gas discharge plasmas, including fluid models,

methods that involve a fully kinetic treatment of the charge carriers, and the so-called hybrid methods.²⁰ The modelling of discharges in CO₂ has been generally done by means of global reaction kinetic models for the analysis of the dissociation mechanisms. In these models, the corresponding set of rate equations for the different species has been solved to analyse low-pressure rf discharges,²¹ dc glow discharges,²² and microwave discharges at moderate pressures^{16,23} in pure CO₂. In addition, various global modelling studies were done for CO₂ laser discharge plasmas^{24–31} in different mixtures and dc He-CO₂ glow discharges.⁷ In these modelling studies, a more or less extended reaction kinetics was used, where the vibrational relaxation processes of CO₂ were generally not considered.

However, the number of reported works on modelling of the CO₂ dissociation in DBD is rather limited. It has been a subject of only a few earlier works³² and has started receiving attention only recently.^{16,17,33,34} In these recent works, a zero-dimensional fluid model has been used, including an extensive reaction kinetics, which takes the vibrational kinetics of CO₂ into account. In contrast, the study reported in Ref. 32 used a time-dependent, spatially two-dimensional model solving the continuity equation for the charged particles and Poisson's equation to compute the local electric field, where a simplified set of reactions was taken into account.

Among the various experimental results reported in the literature, the operational parameter space varies significantly and is mainly determined by the reactor size and the power source used. To harmonize these results with each

other and also with modelling results, two macroscopic parameters, namely, the conversion degree

$$\alpha = \frac{n_{\text{CO}}}{n_{\text{CO}_2}} \quad (1)$$

and the specific energy input

$$\text{SEI} = \frac{P}{\Phi} = \frac{P t_r}{V} \quad (2)$$

are commonly used to quantify the CO_2 dissociation in a DBD.^{6,15} The conversion degree (1) is given by the ratio of the particle density n_{CO} of CO produced in a certain period of time and the density n_{CO_2} of CO_2 . The specific energy input (2) is defined as the ratio of power P absorbed by the discharge and the gas flow rate Φ , which can be related to the residence time t_r of a CO_2 molecule in the active plasma volume V according to $t_r = V/\Phi$.¹⁵ The specific energy input is frequently used in plasma processing³⁵ and is a measure of the energy density of the plasma. From the quantities α and SEI, the efficiency of CO production η can be calculated according to¹⁵

$$\eta = \alpha \frac{\Delta H_{\text{CO}_2}}{\text{SEI}}, \quad (3)$$

where ΔH_{CO_2} specifies the dissociation enthalpy of CO_2 .

Using a flow reactor, Brehmer *et al.*¹⁵ have recently established that the CO production from CO_2 dissociation in terms of α increases monotonically with the SEI. They also showed that the specific energy input can be considered as the universal scaling parameter for CO_2 conversion to CO. That is, no matter how a given SEI is attained, i.e., using any combination of applied voltage, flow condition, frequency, and dielectric thickness, the production of CO from CO_2 dissociation remains almost constant for that specific energy input.¹⁵ Very similar experimental results about the CO production were reported in Ref. 17.

The present paper deals with numerical modelling related to the DBD reactor used in Ref. 15 and aims to analyse and explain in more detail the discharge behaviour and the observed trends for similar experimental conditions. A time-dependent, spatially one-dimensional fluid model, taking into account an extended vibrational kinetics of CO_2 , is employed. The main features of the fluid model and the reaction kinetics used are represented. The fluid model is applied to characterize the spatiotemporal behaviour of discharges taking place in the DBD arrangement under consideration with a special focus on the electrical discharge characteristics and the mechanisms of the CO_2 dissociation. In addition, modelling results for a large range of operational parameters are utilized to analyse the CO_2 conversion and energy efficiency and their relation to the specific energy input.

II. DESCRIPTION OF THE MODEL

The modelling studies presented in this paper are related to the geometrically symmetric DBD built in a flow reactor configuration used in Ref. 15. A schematic representation of this plasma reactor is shown in Figure 1(a). It consists of a tube that directs the gas flow into the gap between two planar electrodes, which form the active zone. The active zone of

FIG. 1. Schematic of the flow reactor geometry used in Ref. 15 (a) and the spatially one-dimensional discharge geometry (b) with gap width d and thickness of dielectric layers Δ .

the DBD is seamlessly connected with another tube, which is used to pump out the gas that has been processed between the dielectrics. The reactor configuration is optimized for different experimental diagnostics, e.g., measurement of the CO produced. Several flow tube reactors with thicknesses Δ of the dielectric barriers between 1 and 2 mm and a constant gap width d of 1 mm were used in the experiments. Further details are given in Ref. 15.

A typical DBD is generally composed of many filaments that are distributed stochastically across the surface of the dielectrics. Thus, a spatially two- or even three-dimensional model including a stochastic description of the filament generation is needed to theoretically describe discharges in this flow reactor configuration. As a step towards such a complex modelling, here a time-dependent, spatially one-dimensional approach has been used to model and analyse the spatiotemporal discharge dynamics of the active zone. The corresponding discharge geometry considering the axial component x of the plasma between the plane-parallel, dielectric covered electrodes is displayed in Figure 1(b). Such a spatially one-dimensional treatment is well suited for the analysis of DBD operating in the homogeneous or glow mode⁶ and has been successfully applied for the analysis of single microdischarges, e.g., in Refs. 36 and 37. Here, the one dimensional description is justified by the fact that the time scales inherent in the discharge plasma are much shorter than the residence time of a unit gas volume in the active plasma zone for the flow rates considered in Ref. 15.

A. Basic relations

For the theoretical description and analysis of the symmetric DBD in CO_2 under consideration, a time-dependent,

spatially one-dimensional fluid model, based on the one reported in Ref. 36, was adapted. The fluid model consists of particle balance equations for the densities n_j of electrons ($j = e$) and several neutral and charged heavy particles, the electron energy balance equation to determine the mean energy U_e of the electrons, and Poisson's equation providing the electric potential ϕ and electric field $E(x, t) = -\partial\phi(x, t)/\partial x$. It is represented by the relations

$$\frac{\partial}{\partial t} n_j(x, t) + \frac{\partial}{\partial x} \Gamma_j(x, t) = S_j(x, t), \quad (4)$$

$$\frac{\partial}{\partial t} (n_e(x, t) U_e(x, t)) + \frac{\partial}{\partial x} Q_e(x, t) = -e_0 \Gamma_e(x, t) E(x, t) + P_e(x, t), \quad (5)$$

$$-\frac{\partial^2}{\partial x^2} \phi(x, t) = \frac{e_0}{\epsilon_0} \sum_j Z_j n_j(x, t), \quad (6)$$

where e_0 , ϵ_0 , and Z_j denote the elementary charge, vacuum permittivity, and particle charge number, respectively. The particle fluxes Γ_j in (4) and the electron energy flux Q_e in (5) in the x -direction are expressed by the drift-diffusion approximation according to

$$\Gamma_j(x, t) = \text{sgn}(Z_j) b_j(x, t) n_j(x, t) E(x, t) - \frac{\partial}{\partial x} (D_j(x, t) n_j(x, t)), \quad (7)$$

$$Q_e(x, t) = -\tilde{b}_e(x, t) n_e(x, t) E(x, t) - \frac{\partial}{\partial x} (\tilde{D}_e(x, t) n_e(x, t)). \quad (8)$$

Here, b_j and D_j are the mobility and diffusion coefficient of species j , $\tilde{b}_e$ and $\tilde{D}_e$ designate the mobility and diffusion coefficients of electron energy transport, and the function $\text{sgn}(Z_j)$ yields the sign of Z_j . Furthermore, the term S_j on the right-hand side of (4) describes the gain and loss of particles in the plasma due to collisional and radiative processes, and the terms $-e_0 \Gamma_e E$ and P_e in (5) denote the power input from the electric field and the gain and loss of electron energy resulting from the various collision processes, respectively. The collisional power gain is caused by superelastic electron collisions as well as collisional and associative detachment processes. The collisional power loss considered is due to elastic collisions, electron impact excitation, dissociation, ionization and detachment, electron attachment, and electron-ion recombination. A detailed description of these terms can be found, e.g., in Refs. 38 and 39. In particular, the power gain rate resulting from collisional and associative detachment P^{cd} is given by

$$P^{\text{cd}}(x, t) = \sum_p n_p^{(1)}(x, t) n_p^{(2)}(x, t) k_p U_p \quad (9)$$

with the rate coefficient k_p and power gain U_p by an individual detachment process p . Furthermore, the power loss rates due to elastic collisions P^{el} , inelastic collisions P^{in} leading to excitation, dissociation, ionization, and detachment as well as two-body electron attachment P^{at} are determined according to

$$P^{\text{el}}(x, t) = n_e(x, t) \sum_j n_j(x, t) K_j^{\text{el}}, \quad (10)$$

$$P^{\text{in}}(x, t) = n_e(x, t) \sum_j n_j(x, t) \sum_m U_{j,m}^{\text{in}} k_{j,m}^{\text{in}}, \quad (11)$$

$$P^{\text{at}}(x, t) = n_e(x, t) \sum_j n_j(x, t) K_j^{\text{at}}, \quad (12)$$

where the rate coefficient K_j^{el} for energy dissipation in elastic collisions with species j of mass m_j , the rate coefficient $k_{j,m}^{\text{in}}$ of the m th inelastic collision processes of electrons with neutral species j , and the individual energy rate coefficients K_j^{at} for two-body electron attachment are given by

$$K_j^{\text{el}} = 2 \frac{m_e}{m_j} \sqrt{\frac{2}{m_e}} \int_0^\infty U^2 Q_j^{\text{d}}(U) \left(f_0(U) + k_B T_g \frac{d}{dU} f_0(U) \right) dU, \quad (13)$$

$$k_{j,m}^{\text{in}} = \sqrt{\frac{2}{m_e}} \int_0^\infty U Q_{j,m}^{\text{in}}(U) f_0(U) dU, \quad (14)$$

$$K_j^{\text{at}} = \sqrt{\frac{2}{m_e}} \int_0^\infty U^2 Q_j^{\text{at}}(U) f_0(U) dU. \quad (15)$$

These rate coefficients are determined by an integration of the product of electron collision cross section and isotropic part $f_0(U)$ of the electron velocity distribution function (EVDF) over the kinetic energy U of the electrons, where Q_j^{d} , $Q_{j,m}^{\text{in}}$, and Q_j^{at} are the cross section for momentum transfer in elastic collisions, for the inelastic collision process considered with the energy loss $U_{j,m}^{\text{in}}$, and for electron attachment, respectively, k_B and T_g denote the Boltzmann constant and gas temperature, respectively, and $f_0(U)$ is normalized according to $\int_0^\infty \sqrt{U} f_0(U) dU = 1$.

B. Reaction kinetics model

In addition to the electron component, the reaction kinetics model includes the 42 heavy particle species listed in Table I. As products of dissociation reactions of CO_2 , CO , molecular oxygen (O_2), ozone (O_3), and atomic oxygen (O) are taken into account (species 2–5 in Table I). Because up to 97% of electron energy can be injected into vibrational excitation in molecular plasmas,⁵ vibrationally excited states in CO_2 plasmas are particularly important as they are expected to enhance the dissociation rates.⁶ Thus, 28 vibrationally excited species (species 6–33 in Table I) are considered to describe the evolution of electron energy accurately and to analyse their role in the CO_2 dissociation. The corresponding statistical weights of the undegenerated vibrational states in the symmetry-stretching (e.g., $\text{CO}_2(\nu_{2a})$) and the asymmetric-stretching ($\text{CO}_2(\nu_{3i})$ with $i = 1, \dots, 20$) modes are 1 and those of the n th doubly degenerated state $\text{CO}_2(0n0)$ in the bending mode are $n+1$.⁴⁰ For the mixed vibrational levels $\text{CO}_2(\nu_j)$ with $j = 4, \dots, 7$, the statistical weights for the individual states were added, and $\text{CO}_2(\nu_8)$ is assumed to be in a pure bending mode with 31 quanta so that its statistical weight is 32. Furthermore, two electronically excited states of CO_2 , assigned by $^3\Sigma_u^+$ and $^1\Sigma_u^+$, as well as the positive ion of CO_2 in its ground state $\text{X}^2\Pi_g$ and in the two excited states $\text{A}^2\Pi_u$

TABLE I. List of heavy particle species considered. For excited species and positive ions, the excitation/ionization energy threshold is listed, and for negative ions the electron affinity is given in the last column.

Number	Species	State	Statistical weight	Energy (eV)
<i>Neutral species in ground state</i>				
1	CO ₂ (v ₀)	(0 0 0)	1	0.0
2	CO	...	1	0.0
3	O ₂	...	1	0.0
4	O ₃	...	1	0.0
5	O	...	1	0.0
<i>Vibrationally excited species</i>				
6	CO ₂ (v ₁)	(0 1 0)	2	0.083
7	CO ₂ (v _{2a})	(1 0 0)	1	0.172
8	CO ₂ (v _{2b})	(0 2 0)	3	0.159
9	CO ₂ (v ₃₁)	(0 0 1)	1	0.291
10	CO ₂ (v ₃₂)	(0 0 2)	1	0.579
11	CO ₂ (v ₄)	(0 3 0) + (1 1 0)	6	0.252
12	CO ₂ (v ₅)	(0 4 0) + (1 2 0) + (2 0 0)	9	0.339
13	CO ₂ (v ₆)	(1 3 0) + (2 1 0) + (0 5 0)	12	0.442
14	CO ₂ (v ₇)	(1 4 0) + (2 2 0) + (3 0 0)	9	0.505
15	CO ₂ (v ₈)	Sum of higher states	32	2.5
16–33	CO ₂ (v ₃₃)–CO ₂ (v ₃₂₀)	(0 0 3)–(0 0 20)	1	0.87–5.24
<i>Electronically excited species</i>				
34	CO ₂ [*]	³ Σ _u ⁺	3	7.0
35	CO ₂ ^{**}	¹ Σ _u ⁺	1	10.5
<i>Positive ions</i>				
36	CO ₂ ⁺	X ² Π _g	4	13.8
37	CO ₂ ⁺ (A)	A ² Π _u	4	17.6
38	CO ₂ ⁺ (B)	B ² Σ _u ⁺	2	18.1
<i>Negative ions</i>				
39	O [−]	...	...	1.46
40	O ₂ [−]	...	...	0.45
41	CO ₃ [−]	...	...	3.5
42	CO ₄ [−]	...	...	...

and B²Σ_u⁺, are taken into consideration. The excited ionic states are introduced to allow for comparison with optional measurements of their optical emission. In addition, the four negative ions O[−], O₂[−], CO₃[−], and CO₄[−] are included in the reaction kinetics model.

The reaction kinetic scheme takes into account 56 electron impact collision processes with heavy particles. These reactions are given in Table II. In addition to elastic collisions contributing directly to the electron energy balance (5), exciting, de-exciting, ionizing, detaching, attaching, and recombining electron collision processes with heavy particles are taken into consideration where the corresponding rate coefficients depend on the mean energy U_e of the electrons. For their determination, the collision cross section data of the respective reference were used. In particular, the collision cross sections for electron impact de-excitation processes are determined by the use of the principle of detailed balancing using the statistical weights given in Table I. In addition, four collisional or associative detachment processes are included and listed in Table II, which also contribute to the electron energy balance (5). Notice that the interaction of electrons only with CO₂ is taken into account in the present reaction kinetics scheme. This approach is justified by the low conversion degrees of less than 5% observed in

corresponding experiments^{12,15} and leads to a decrease in the number of species to be considered in comparison with other recent studies reported, e.g., in Ref. 16.

In addition to the collision processes involving electrons, further 257 heavy particle collision processes and two radiation processes are considered. In order to allow for an analysis of the vibrational energy transfer, an extended set of reactions describing the vibrational-translational (VT) and vibrational-vibrational (VV) relaxation processes is used. The corresponding reactions and rate coefficients are listed in Tables III and IV. Furthermore, 16 collisions between neutrals in their ground state, non-detaching ion-neutral reactions such as charge transfer reactions as well as ion-ion recombination processes, are taken into account, as given in Table V. The two radiation processes (from excited ions) are also listed in Table V.

C. Transport and electron rate coefficients

In order to describe the flux of particles and electron energy according to (7) and (8), the corresponding transport coefficients are required. The mobility of the positive and negative ions specified in Table I is determined as a function of the reduced electric field E/N , where N is the number density

TABLE II. Electron impact reactions considered in the model. The rate coefficients of reactions E1–E53 are obtained from the solution of the electron Boltzmann equation as a function of the mean electron energy U_e using the cross section data of the respective reference given. The energy rate coefficient for elastic collisions K_1^{el} and the energy rate coefficients for two-body attachment K_j^{at} with $j=47$ –53 are given in $\text{eVm}^3\text{s}^{-1}$. All other rate coefficients k_j^{in} with $j=2$ –53 for inelastic (in) two-body electron collision processes are given in m^3s^{-1} , where electron impact excitation (ex), de-excitation (sc—superelastic collision), dissociation (di), ionization (io), detachment (de), and attachment (at) are distinguished. $T_e = 2U_e/(3k_B)$ is the electron temperature in K, and T_g is the gas temperature in K.

Number	Reaction	Rate coefficient	Reference
<i>Elastic electron collisions</i>			
E1	$\text{CO}_2(v_0) + e \rightarrow \text{CO}_2(v_0) + e$	$K_1^{\text{el}}(U_e)$	41
<i>Electron impact excitation and de-excitation of vibrational levels</i>			
E2, E3	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_1) + e$	$k_2^{\text{ex}}(U_e), k_3^{\text{sc}}(U_e)$	42
E4, E5	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_{2a}) + e$	$k_4^{\text{ex}}(U_e), k_5^{\text{sc}}(U_e)$	42, 43
E6, E7	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_{2b}) + e$	$k_6^{\text{ex}}(U_e), k_7^{\text{sc}}(U_e)$	43
E8, E9	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_{31}) + e$	$k_8^{\text{ex}}(U_e), k_9^{\text{sc}}(U_e)$	42
E10, E11	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_{32}) + e$	$k_{10}^{\text{ex}}(U_e), k_{11}^{\text{sc}}(U_e)$	44
E12, E13	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_4) + e$	$k_{12}^{\text{ex}}(U_e), k_{13}^{\text{sc}}(U_e)$	42
E14, E15	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_5) + e$	$k_{14}^{\text{ex}}(U_e), k_{15}^{\text{sc}}(U_e)$	42
E16, E17	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_6) + e$	$k_{16}^{\text{ex}}(U_e), k_{17}^{\text{sc}}(U_e)$	42
E18, E19	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_7) + e$	$k_{18}^{\text{ex}}(U_e), k_{19}^{\text{sc}}(U_e)$	42
E20, E21	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2(v_8) + e$	$k_{20}^{\text{ex}}(U_e), k_{21}^{\text{sc}}(U_e)$	42
E22, E23	$\text{CO}_2(v_1) + e \rightleftharpoons \text{CO}_2(v_{2b}) + e$	$k_{22}^{\text{ex}}(U_e), k_{23}^{\text{sc}}(U_e)$	Analogous to E2 (Ref. 42)
E24, E25	$\text{CO}_2(v_1) + e \rightleftharpoons \text{CO}_2(v_4) + e$	$k_{24}^{\text{ex}}(U_e), k_{25}^{\text{sc}}(U_e)$	Analogous to E6 (Ref. 43)
E26, E27	$\text{CO}_2(v_1) + e \rightleftharpoons \text{CO}_2(v_5) + e$	$k_{26}^{\text{ex}}(U_e), k_{27}^{\text{sc}}(U_e)$	Analogous to E12 (Ref. 42)
E28, E29	$\text{CO}_2(v_{2a}) + e \rightleftharpoons \text{CO}_2(v_5) + e$	$k_{28}^{\text{ex}}(U_e), k_{29}^{\text{sc}}(U_e)$	Analogous to E4 (Refs. 42 and 43)
E30, E31	$\text{CO}_2(v_{2b}) + e \rightleftharpoons \text{CO}_2(v_4) + e$	$k_{30}^{\text{ex}}(U_e), k_{31}^{\text{sc}}(U_e)$	Analogous to E2 (Ref. 42)
E32, E33	$\text{CO}_2(v_{2b}) + e \rightleftharpoons \text{CO}_2(v_5) + e$	$k_{32}^{\text{ex}}(U_e), k_{33}^{\text{sc}}(U_e)$	Analogous to E4 + E6 (Ref. 42)
E34, E35	$\text{CO}_2(v_{31}) + e \rightleftharpoons \text{CO}_2(v_{32}) + e$	$k_{34}^{\text{ex}}(U_e), k_{35}^{\text{sc}}(U_e)$	Analogous to E8 (Ref. 42)
E36, E37	$\text{CO}_2(v_4) + e \rightleftharpoons \text{CO}_2(v_5) + e$	$k_{36}^{\text{ex}}(U_e), k_{37}^{\text{sc}}(U_e)$	Analogous to E2 (Ref. 42)
<i>Electron impact excitation and de-excitation of electronically excited states</i>			
E38, E39	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2^* + e$	$k_{38}^{\text{ex}}(U_e), k_{39}^{\text{sc}}(U_e)$	42
E40, E41	$\text{CO}_2(v_0) + e \rightleftharpoons \text{CO}_2^{*+} + e$	$k_{40}^{\text{ex}}(U_e), k_{41}^{\text{sc}}(U_e)$	42
<i>Electron impact dissociation</i>			
E42	$\text{CO}_2(v_0) + e \rightarrow \text{CO} + \text{O} + e$	$k_{42}^{\text{di}}(U_e)$	41
<i>Electron impact ionization and detachment</i>			
E43	$\text{CO}_2(v_0) + e \rightarrow \text{CO}_2^+ + e + e$	$k_{43}^{\text{io}}(U_e)$	41
E44	$\text{CO}_2(v_0) + e \rightarrow \text{CO}_2^+(A) + e + e$	$k_{44}^{\text{io}}(U_e)$	41
E45	$\text{CO}_2(v_0) + e \rightarrow \text{CO}_2^+(B) + e + e$	$k_{45}^{\text{io}}(U_e)$	41
E46	$\text{O}^- + e \rightarrow \text{O} + e + e$	$k_{46}^{\text{de}}(U_e)$	45, 46
<i>Dissociative electron attachment</i>			
E47	$\text{CO}_2(v_0) + e \rightarrow \text{CO} + \text{O}^-$	$k_{47}^{\text{at}}(U_e), K_{47}^{\text{at}}(U_e)$	47
E48	$\text{CO}_2(v_1) + e \rightarrow \text{CO} + \text{O}^-$	$k_{48}^{\text{at}}(U_e), K_{48}^{\text{at}}(U_e)$	47 ^a
E49	$\text{CO}_2(v_{2a}) + e \rightarrow \text{CO} + \text{O}^-$	$k_{49}^{\text{at}}(U_e), K_{49}^{\text{at}}(U_e)$	47 ^a
E50	$\text{CO}_2(v_{2b}) + e \rightarrow \text{CO} + \text{O}^-$	$k_{50}^{\text{at}}(U_e), K_{50}^{\text{at}}(U_e)$	47 ^a
E51	$\text{CO}_2(v_{31}) + e \rightarrow \text{CO} + \text{O}^-$	$k_{51}^{\text{at}}(U_e), K_{51}^{\text{at}}(U_e)$	47 ^a
E52	$\text{CO}_2(v_4) + e \rightarrow \text{CO} + \text{O}^-$	$k_{52}^{\text{at}}(U_e), K_{52}^{\text{at}}(U_e)$	47 ^a
E53	$\text{CO}_2(v_5) + e \rightarrow \text{CO} + \text{O}^-$	$k_{53}^{\text{at}}(U_e), K_{53}^{\text{at}}(U_e)$	47 ^a
<i>Dissociative electron-ion recombination</i>			
E54	$\text{CO}_2^+ + e \rightarrow \text{CO} + \text{O}$	$4.2 \times 10^{-13} (T_e/300)^{-0.75}$	48
E55	$\text{CO}_2^+(A) + e \rightarrow \text{CO} + \text{O}$	$4.2 \times 10^{-13} (T_e/300)^{-0.75}$	48
E56	$\text{CO}_2^+(B) + e \rightarrow \text{CO} + \text{O}$	$4.2 \times 10^{-13} (T_e/300)^{-0.75}$	48
<i>Collisional and associative detachment</i>			
E57	$\text{O}^- + \text{CO}_2(v_0) \rightarrow \text{O} + \text{CO}_2(v_0) + e$	4.0×10^{-18}	30
E58	$\text{O}^- + \text{CO} \rightarrow \text{CO}_2(v_{2b}) + e$	$5.8 \times 10^{-15} (T_g)^{-0.4}$	49
E59	$\text{O}^- + \text{O} \rightarrow \text{O}_2 + e$	2.3×10^{-16}	50
E60	$\text{O}_2^- + \text{O} \rightarrow \text{O}_3 + e$	1.5×10^{-16}	29

^aAnalogous to E47 and shifted by threshold energy.

of the neutral gas. Here, the mobility of CO_2^+ in CO_2 given in Ref. 56 and of O^- and CO_3^- in CO_2 according to Ref. 57 is employed. The mobility of O_2^- and CO_4^- is assumed to be the same as that of O^- and CO_3^- , respectively. The

corresponding diffusion coefficients are calculated using the Einstein relation.⁶ Regarding the neutral species, the diffusion coefficient of CO_2 in CO_2 is taken from the relation $ND_{\text{CO}_2} = 3.07 \times 10^{20} \text{ m}^{-1}\text{s}^{-1}$ according to Ref. 58, where

TABLE III. Vibrational-translational relaxation reactions considered in the model. The rate coefficients refer to a gas temperature of 400 K and are given in m^3s^{-1} .

Number	Reaction	Rate coefficient	Reference
VT1	$\text{CO}_2(\text{v}_1) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0)$	1.06×10^{-20}	51
VT2	$\text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_1) + \text{CO}_2(\text{v}_0)$	2.15×10^{-20}	51
VT3	$\text{CO}_2(\text{v}_{2a}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0)$	9.68×10^{-20}	51, 52
VT4	$\text{CO}_2(\text{v}_{2a}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_0)$	6.92×10^{-17}	52
VT5	$\text{CO}_2(\text{v}_{31}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0)$	1.0×10^{-23}	6
VT6	$\text{CO}_2(\text{v}_{31}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_1) + \text{CO}_2(\text{v}_0)$	1.66×10^{-23}	51
VT7	$\text{CO}_2(\text{v}_{31}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_0)$	6.04×10^{-21}	51
VT8	$\text{CO}_2(\text{v}_{32}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_{31}) + \text{CO}_2(\text{v}_0)$	5.0×10^{-23}	6
VT9	$\text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_0)$	3.20×10^{-20}	51
VT10	$\text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_1) + \text{CO}_2(\text{v}_0)$	8.96×10^{-24}	51
VT11	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_0)$	6.46×10^{-20}	51
VT12	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_{31}) + \text{CO}_2(\text{v}_0)$	1.72×10^{-22}	51
VT13	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_0)$	5.95×10^{-26}	51
VT14	$\text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_0)$	9.62×10^{-20}	51
VT15	$\text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_0)$	2.65×10^{-23}	51
VT16	$\text{CO}_2(\text{v}_7) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_0)$	2.12×10^{-20}	51
VT17	$\text{CO}_2(\text{v}_8) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_7) + \text{CO}_2(\text{v}_0)$	3.18×10^{-20}	51
VT18–VT35	$\text{CO}_2(\text{v}_{3j}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_{3(j-1)}) + \text{CO}_2(\text{v}_0)$	$c_j \times 10^{-22}$	6 ^a

^a $j = 3, \dots, 20$; $c_j = j - 2$.

the same value is also used for all vibrationally and the electronically excited states. Furthermore, the coefficients $ND_{\text{CO}} = 9.86 \times 10^{18} \text{m}^{-1}\text{s}^{-1}$,⁵⁹ $ND_{\text{O}_2} = 7.3 \times 10^{20} \text{m}^{-1}\text{s}^{-1}$,⁵⁹ and $ND_{\text{O}} = 6.5 \times 10^{18} \text{m}^{-1}\text{s}^{-1}$ ¹²² are used, and the diffusion coefficient of O_3 in CO_2 is assumed to be the same as that of O_2 .

In the framework of the present fluid model, the local-mean-energy approximation is used for the description of the electron properties.⁶⁰ That is, the transport and rate coefficients of the electrons including the coefficients (13) and (15) are determined in advance from the solution of the steady-state, spatially homogeneous electron Boltzmann equation using the collision cross section data according to

Table II. The kinetic equation of the electrons has been solved for given reduced electric field, gas temperature, and cross section data in multiterm approximation of the EVDF expansion in Legendre polynomials using a generalized version of the method described in Ref. 61 adapted to take non-conservative electron collisions and the random motion of gas particles into account. The resulting coefficients have subsequently been put into look-up tables as a function of the mean electron energy U_e and used in the model calculations. Notice that the consistent coefficients $\hat{b}_e$ and $\hat{D}_e$ of the electron energy transport have been utilized, instead of the frequently used simplified expressions $\tilde{b}_e = 5U_e b_e/3$ and $\tilde{D}_e = 5U_e D_e/3$.⁶²

TABLE IV. Table of vibrational energy exchange reactions used in the model. The rate coefficients refer to a gas temperature of 400 K and are given in m^3s^{-1} . $c_i = 10$ for $i \leq 9$; $c_i = (19 - i)$ for $10 \leq i \leq 15$; $c_i = (20 - i)$ for $16 \leq i \leq 19$.

Number	Reaction	Rate coefficient	Reference
VV1	$\text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_1) + \text{CO}_2(\text{v}_1)$	1.01×10^{-18}	51
VV2	$\text{CO}_2(\text{v}_{31}) + \text{CO}_2(\text{v}_{31}) \rightarrow \text{CO}_2(\text{v}_{32}) + \text{CO}_2(\text{v}_0)$	1.0×10^{-16}	6
VV3	$\text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_1) \rightarrow \text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_{2b})$	2.99×10^{-18}	51
VV4	$\text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_4) \rightarrow \text{CO}_2(\text{v}_{2b}) + \text{CO}_2(\text{v}_5)$	8.30×10^{-17}	52
VV5	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_1)$	3.07×10^{-18}	51
VV6	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_1) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_{2b})$	6.03×10^{-18}	51
VV7	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_{2b}) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_4)$	9.24×10^{-18}	51
VV8	$\text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_5) \rightarrow \text{CO}_2(\text{v}_4) + \text{CO}_2(\text{v}_6)$	1.30×10^{-15}	52
VV9	$\text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_1)$	4.58×10^{-18}	51
VV10	$\text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_1) \rightarrow \text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_{2b})$	9.24×10^{-18}	51
VV11	$\text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_{2b}) \rightarrow \text{CO}_2(\text{v}_5) + \text{CO}_2(\text{v}_4)$	1.52×10^{-17}	51
VV12	$\text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_6) \rightarrow \text{CO}_2(\text{v}_7) + \text{CO}_2(\text{v}_5)$	1.30×10^{-15}	52
VV13	$\text{CO}_2(\text{v}_7) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_1)$	2.76×10^{-16}	52
VV14	$\text{CO}_2(\text{v}_7) + \text{CO}_2(\text{v}_1) \rightarrow \text{CO}_2(\text{v}_6) + \text{CO}_2(\text{v}_{2b})$	5.53×10^{-16}	52
VV15	$\text{CO}_2(\text{v}_8) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_7) + \text{CO}_2(\text{v}_1)$	1.31×10^{-15}	52
VV16–VV33	$\text{CO}_2(\text{v}_{3i}) + \text{CO}_2(\text{v}_{31}) \rightarrow \text{CO}_2(\text{v}_{3(i+1)}) + \text{CO}_2(\text{v}_0)$	1.0×10^{-16}	6 ^a
VV34–VV204	$\text{CO}_2(\text{v}_{3i}) + \text{CO}_2(\text{v}_{3j}) \rightarrow \text{CO}_2(\text{v}_{3(i+1)}) + \text{CO}_2(\text{v}_{3(j-1)})$	$c_i \times 10^{-17}$	6 ^{a,b}

^a $i = 2, \dots, 19$.

^b $j = 2, \dots, i$.

TABLE V. Neutral-neutral, ion-neutral, and ion-ion collision processes, as well as radiative transition processes, used in the model. The rate-coefficients have the units of m^3s^{-1} for two-body collisions, m^6s^{-1} for three-body collisions, and s^{-1} for radiative transitions. The gas temperature T_g is given in K.

Number	Reaction	Rate coefficient	Reference
<i>Neutral kinetics of ground state particles</i>			
N1	$\text{CO}_2(\text{v}_0) + \text{O} \rightarrow \text{CO} + \text{O}_2$	$2.8 \times 10^{-17} \exp(-26500/T_g)$	53
N2	$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2(\text{v}_0) + \text{O}$	$4.2 \times 10^{-18} \exp(-24000/T_g)$	53
N3	$\text{CO} + \text{O} + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0)$	$1.6 \times 10^{-45} \exp(-1510/T_g)$	22
N4	$\text{O}_2 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}$	$7.26 \times 10^{-16} \exp(-11400/T_g)$	50
N5	$\text{O}_2 + \text{O} + \text{CO}_2(\text{v}_0) \rightarrow \text{O}_3 + \text{CO}_2(\text{v}_0) \rightarrow 1.7 \times 10^{-42} T_g^{-1.2}$	22	
N6	$\text{O}_2 + \text{O} + \text{O}_2 \rightarrow \text{O}_3 + \text{O}_2$	$8.61 \times 10^{-43} T_g^{-1.25}$	54
N7	$\text{O}_2 + \text{O} + \text{O} \rightarrow \text{O}_3 + \text{O}$	$2.15 \times 10^{-40} \exp(345/T_g)$	50
N8	$\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$	$1.81 \times 10^{-17} \exp(-2300/T_g)$	54
N9	$\text{O} + \text{O} + \text{CO}_2(\text{v}_0) \rightarrow \text{O}_2 + \text{CO}_2(\text{v}_0)$	$3.81 \times 10^{-42} T_g^{-1.0} \exp(-170/T_g)$	33
<i>Ion-atom and ion-molecule reactions (including charge transfer)</i>			
I1	$\text{O}^- + \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_3^- + \text{CO}_2(\text{v}_0)$	9.0×10^{-41}	25
I2	$\text{O}_2^- + \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0) \rightarrow \text{CO}_4^- + \text{CO}_2(\text{v}_0)$	1.2×10^{-40}	29
I3	$\text{O}_2^- + \text{O} \rightarrow \text{O}_2 + \text{O}^-$	1.5×10^{-16}	29
I4	$\text{CO}_3^- + \text{O} \rightarrow \text{O}_2^- + \text{CO}_2(\text{v}_0)$	1.1×10^{-16}	29
I5	$\text{CO}_4^- + \text{O} \rightarrow \text{CO}_3^- + \text{O}_2$	1.4×10^{-16}	29
<i>Ion-ion recombination</i>			
I6	$\text{CO}_2^+ + \text{CO}_3^- \rightarrow \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0) + \text{O}$	5.0×10^{-13}	25
I7	$\text{CO}_2^+ + \text{CO}_4^- \rightarrow \text{CO}_2(\text{v}_0) + \text{CO}_2(\text{v}_0) + \text{O}_2$	5.0×10^{-13}	25
<i>Radiative transitions</i>			
R1	$\text{CO}_2^+(A) \rightarrow \text{CO}_2^+ + h\nu$	6.1×10^6	55
R2	$\text{CO}_2^+(B) \rightarrow \text{CO}_2^+ + h\nu$	7.2×10^6	55

Based on the solution of the electron Boltzmann equation, it is also possible to get an impression of the fraction of power transferred from plasma electrons to different channels of collisions of the CO_2 molecule. Using equations (13), (14), and (15), the fraction of transferred power can be calculated by dividing the energy rate coefficient $K_{\text{CO}_2}^{\text{el}}$ for elastic collisions, the individual energy rate coefficient $\bar{U}_{\text{CO}_2,m}^{\text{in}} k_{\text{CO}_2,m}^{\text{in}}$ for the m th inelastic collision process, and the energy rate coefficient $K_{\text{CO}_2}^{\text{at}}$ for two-body electron attachment, respectively, by the total energy rate coefficient $K_{\text{CO}_2}^{\text{el}} + \sum_m \bar{U}_{\text{CO}_2,m}^{\text{in}} k_{\text{CO}_2,m}^{\text{in}} + K_{\text{CO}_2}^{\text{at}}$. The resulting fractions of power transferred to different channels as a function of the mean electron energy are shown in Figure 2.

It is found that almost all power is dissipated in vibrational excitation of CO_2 for mean energies below about

1.2 eV, where the excitation of the asymmetric mode level $\text{CO}_2(\text{v}_{31})$, i.e., $\text{CO}_2(0\ 0\ 1)$, is generally the dominant one. The contribution of this vibrational excitation decreases for larger mean energies, and the electron impact excitation of the electronically excited states $\text{CO}_2(^3\Sigma_u^+)$ and $\text{CO}_2(^1\Sigma_u^+)$ becomes predominant above about $U_e = 3$ eV. The electron impact dissociation of CO_2 ground state molecules consumes 1% of power transferred at a mean energy of 3.5 eV increasing to about 5% at larger U_e . The fraction of power dissipated in ionizing collisions increases continuously above about 2.0 eV and becomes larger than the dissociation for $U_e = 3.8$ eV. At the same time, the contribution of the momentum transfer in elastic collisions and the dissociative electron attachment are of minor importance in general. These results show great similarity with those presented, e.g., in Refs. 6 and 33, where an analysis with respect to the reduced electric field dependence is represented.

This global consideration indicates that low mean energies (and reduced electric fields) are favourable for CO_2 dissociation that is induced by vibrational up-pumping along the asymmetric mode. Nonetheless, for vibrational up-pumping to contribute significantly to CO_2 dissociation, a remarkable population of vibrational levels is required, which, in turn, leads to modifications of the discussion due to the expected impact of superelastic electron collisions of the distribution function similar to the results for nitrogen reported in Ref. 63.

D. Boundary conditions and solution method

The system of partial differential equations (4)–(6) including the fluxes (7) and (8) is completed by appropriate boundary conditions. For the heavy particles, the electrons

FIG. 2. Fraction of power transferred into important channels as a function of mean electron energy at $T_g = 400$ K. Selected reduced electric field values are also added. Only important channels are shown for the sake of clarity.

and the electron energy density, the flux boundary conditions are employed at the dielectric surfaces in front of the electrodes at $x=0$ and $x=d$ (cf. Figure 1(b)), taking into account partial reflection of the particles with reflection coefficients of 0.3 for electrons and neutral species and 0.001 for ions. Additionally, the emission of secondary electrons caused by positive ions impinging onto the surface is considered assuming a secondary electron emission coefficient of 0.02. Further details of these boundary conditions are given in Ref. 36.

For the determination of the electric potential and electric field in the gap, a sinusoidal voltage $U_0(t) = V_0 \sin(2\pi ft)$ with an amplitude V_0 and a frequency f is applied at the powered electrode ($x = -\Delta$) and the potential at the grounded electrode ($x = d + \Delta$) is zero. To describe adequately the accumulation of surface charges on the dielectrics, the condition^{36,64}

$$\epsilon_r \epsilon_0 E_{\text{diel}}(x_0, t) \cdot \nu - \epsilon_0 E(x_0, t) \cdot \nu = \sigma(x_0, t) \quad (16)$$

is used at the plasma boundaries, where the parameter ν is given by $\nu = -1$ at $x_0 = 0$ and $\nu = 1$ at $x_0 = d$, respectively. The electric field E_{diel} inside the dielectrics with relative permittivity ϵ_r is obtained from the assumption of an immediate drop of the space charges inside the dielectrics by the Laplace equation and the temporal variation of the surface charge density σ results from the particle currents impinging onto the dielectrics.³⁶

The numerical solution of the resulting set of equation has been realized using the finite-difference method according to Refs. 36 and 65. In particular, an adaptive time stepping is used for the model calculation performed using 500 non-equidistant intervals with logarithmic meshing for the spatial grid. The calculations were done on Intel® Xeon® processors E5-2603 with a processing speed of 1.8 GHz. A typical calculation of 20 voltage cycles at a discharge frequency of 130 kHz lasted about 5 days.

III. RESULTS AND DISCUSSION

In order to analyse the behaviour of the CO₂ DBD in the reactor configuration used in Ref. 15 by means of numerical modelling, a number of different operational parameters have been considered. These values are listed in Table VI and were selected on the basis of the experimental conditions studied in Ref. 15. The standard condition represents typical discharge parameters and was chosen as a reference to illustrate the main discharge features and the importance of different processes responsible for CO production. Note that the

values for the relative permittivity of the dielectrics are a representative of quartz. Beginning with the standard condition, usually one parameter is changed for the respective parameter variation while keeping the other parameters constant. For all conditions, a gap width of $d = 1$ mm and a dielectric thickness of $\Delta = 2$ mm are used.

The model calculations start at the time $t = 0$ from a spatially homogeneous distribution of the particle densities assuming a quasineutral plasma with a particle density of $1.0 \times 10^3 \text{ cm}^{-3}$ for the positive ions and the electron component with an initial mean energy of 2.0 eV and of $5.0 \times 10^2 \text{ cm}^{-3}$ for the negative ions. The spatiotemporal evolution of the DBD has usually been calculated for 20 voltage cycles of the respective frequency, which corresponds to about 0.154 ms at the standard condition. This time is chosen such that there are enough cycles to get good average properties while simultaneously keeping the assumption that electrons mainly interact only with CO₂.

In the following, results for the DBD at standard condition are discussed at first. Then, the results obtained by model calculations for the different operational parameters given in Table VI are analysed with a special focus on the conversion degree and energy efficiency and their relation to the specific energy input, which can be considered as the universal scaling parameter for CO₂ conversion to CO according to the related experimental work of Ref. 15.

A. Discharge behaviour at standard condition

The analysis of the behaviour of the DBD at standard condition focuses on the electrical discharge characteristics and the mechanisms of the CO₂ dissociation.

1. Electrical discharge characteristics

The temporal evolution of the applied voltage, the gap voltage, and the discharge current density, as well as the spatiotemporal evolution of the electron density, mean electron energy, and reduced electric field are shown in Figure 3. Because already after few cycles a quasi-periodic state is established for these properties at the discharge conditions considered, here the three cycles 18 to 20 are shown, where the electrical characteristics are identical in every cycle. Since a sinusoidal voltage signal is applied to the powered electrode of the DBD, each electrode alternates between being a cathode and an anode. That is, for half of the period, one electrode is the instantaneous cathode (lower voltage compared to the other electrode), and for the next half-period, it is the instantaneous anode (higher voltage compared to the other electrode). On the basis of this alternating nature of a DBD, another classification is generally made, where a voltage cycle is divided into positive and negative half-cycle. The positive half-cycle takes place when a positive voltage is applied at the powered electrode, while the negative half-cycle occurs when a negative voltage is applied. These classifications are helpful in simplifying the following discussion.

It can be seen from the characteristics of the voltage and discharge current density displayed in Figure 3(a) that there

TABLE VI. Standard condition and parameter variations used for the model calculations.

Parameter	Standard condition	Parameter variation
Frequency (kHz)	130	60, 90
Pressure (mbar)	1000	600, 700, 800, 900
Voltage amplitude (kV)	10.0	8.0, 8.5, 9.0, 9.5, 10.5, 11.0
Gas temperature (K)	400	300, 350, 450, 500
Dielectric permittivity	3.8	4.5, 6.0

FIG. 3. Temporal variation of applied voltage (---), gap voltage (—) and discharge current density (a), and spatiotemporal distribution of electron density in logarithmic scale (b), mean electron energy (c), and electric field magnitude (d) for the standard condition given in Table VI with $T = 1/f = 7.69 \mu\text{s}$. The black lines in (d) mark the positions at which the sign (direction) of the electric field changes. The direction of the electric field is also identified.

is one discharge event every half-cycle. Each peak in the discharge current density

$$J(t) = \frac{1}{d} \int_0^d \left[\epsilon_0 \frac{\partial}{\partial t} E(x, t) + e_0 \sum_i Z_i \Gamma_i(x, t) \right] dx \quad (17)$$

corresponds to a discharge event, which lasts approximately 100–200 ns. The gap voltage

$$V_g(t) = \phi(0, t) - \phi(d, t) \quad (18)$$

increases until the breakdown voltage of 2.4 kV in the positive and 2.7 kV in the negative half-periods is reached. In both half-cycles, the discharge starts with an ionization wave from the instantaneous anode, which reaches the instantaneous cathode after few nanoseconds. There is an increase in the electron density and mean electron energy (cf. Figures 3(b) and 3(c)) during ignition of the discharge at a large electric field (Figure 3(d)) and a subsequent decline once the ionization wave approaches to the opposite electrode.

As it can be seen from Figure 3(b), the electron density starts to increase at the instantaneous anode and reaches a maximum at a certain distance from the instantaneous cathode during the discharge event. This distance at which the maximum electron density occurs during the positive and negative half-cycles is denoted as d_0 and corresponds to the thickness of the cathode fall region. It is approximately 200 μm for the standard condition. After breakdown, the electrons drift towards the anode where they are partly absorbed. Note that in the negative half-cycles, not all electrons reach the anode before the polarity changes. The remaining electrons drift back to the former cathode as it becomes the anode in the following discharge. Figures 3(c) and 3(d) show that the mean electron energy as well as the electric field have their maxima in the cathode-fall region.

However, the electron density in front of the cathode is small, and thus, the highest electron induced CO_2 dissociation is expected to occur in the cathode sheath to plasma transition region. Plasma electrons, i.e., electrons not in the sheath, have a low mean energy of less than 1 eV, and thus, the CO_2 dissociation in collisions with plasma electrons is of minor importance (cf. Figure 2).

As it can be noticed from all the discharge characteristics, there is a difference in the positive and negative half-cycles. Discharges occurring in the negative half-cycles are characterized by a higher breakdown voltage, stronger current peak, and longer period with higher electron density compared to discharges in the positive half-cycles. This asymmetry is caused by the relatively high frequency of 130 kHz, which does not allow the charge carriers to recombine completely between subsequent discharge events. The resulting volume memory effect leads to a mutual influence of the discharges occurring in the positive and negative half-cycles. Golubovskii *et al.*⁶⁶ have observed a similar difference between the positive and negative half-cycles in a helium discharge. In their model, they attributed this difference to the slow recombination of He_2^+ ions. They could reduce the memory effect and thus the differences between the positive and negative half-cycles by using an artificially increased recombination rate coefficient for electron-ion recombination.

In order to understand the influence of the charged particles on the observed asymmetry in the discharge evolution, the spatiotemporal behaviour of the densities of charged particles is plotted in Figure 4. Instead of three cycles as in Figure 3, only one representative cycle (18.45–19.45) is chosen to capture the important features of both half-cycles. Obviously, there is a clear difference in the spatiotemporal evolution of the charged particles between the positive and negative half-cycles. The density of the CO_2^+ ions shown in Figure 4(a) decays slowly after ignition of discharges in the

FIG. 4. Spatiotemporal behaviour of the density of CO_2^+ ions, including its excited states (a) and density of all negative ions (surface) and electrons (grid lines) (b) in logarithmic scale for the standard condition given in Table IV with $T = 1/f = 7.69 \mu\text{s}$. The white line in (a) marks the discharge current for a better understanding of the temporal position. In (b), the electron density exceeds the density of negative ions in regions where grid lines are shown.

negative half-cycle due to electron-ion recombination according to processes E54–E56 in Table II. Note that the density of the excited ionic states $\text{CO}_2^+(\text{A})$ and $\text{CO}_2^+(\text{B})$ amounts only to 10% of the total positive ion density during the discharge phase and is smaller than 2% of the total positive ion density in the off-phase. Since the time between subsequent discharges of about $3.7 \mu\text{s}$ at $f = 130 \text{ kHz}$ is much smaller than the recombination time, which is in the range of milliseconds, the positive ion density decays by less than one order of magnitude until ignition of the following discharge in the positive half-cycle. During the positive half-cycle, electron-ion recombination is less important due to the lower density of electrons. Because the magnitude of the electric field between the electrodes is larger during the positive half-cycle compared to the negative half-cycle (cf. Figure 3(d)), a pronounced positive ion drift to the instantaneous cathode ($x = d$) occurs, and thus, the positive ion density in the gap decreases stronger compared to the negative half-cycle. At $t/T = 19.2$, few new positive ions are generated in front of the instantaneous anode at $x = 0$ because the mean electron energy slightly exceeds the threshold for ionization of CO_2 molecules in electron collisions at this position (cf. Figure 3(c)).

Even larger differences between the negative and the positive half-cycle are found in the spatiotemporal evolution of the negative charge carriers shown in Figure 4(b). In the negative half-cycle, electrons are the dominant negatively charged species in the plasma region, whereas the negative ions dominate in the cathode-fall region. Here, CO_3^- is the dominant negative ion because of its efficient generation from O^- according to reaction I1 in Table V. Its particle density contributes to more than 95% to the total density of negative ions during the entire period. Due to their larger mass compared to the electron component, the negative ions respond more inertly to the change in the electric field direction at $t/T \approx 18.8$ (cf. Figure 3(d)). As a result, most negative ions remain in the gap until re-ignition of the discharge in the positive half-cycle and constitute the dominant negatively charged species here in contrast to the dominance of electrons during the negative half-cycle. Ion-ion recombination according to the processes I6 and I7 in Table V is the dominant loss channel of negative ions. But, it is too slow for a marked reduction in their particle density within one voltage half-cycle. Note that CO_3^- has also been found to be the dominant negative ion in pure CO_2 plasmas at the respective conditions studied by experiments⁶⁷ and modelling.³³

2. Mechanisms of CO_2 dissociation

In order to analyse the mechanisms of CO_2 dissociation generating CO and O, the spatiotemporal distributions of CO and O particle densities are displayed in Figure 5 for the standard condition. Starting from a spatially homogeneous distribution of these species with an initial particle density of $1.0 \times 10^3 \text{ cm}^{-3}$, the densities of CO and O gradually increase in time. Both these species are mainly generated around d_0 . The slight asymmetry of their spatial density distribution is a consequence of the differences in the discharge behaviour during the positive and negative half-cycle

FIG. 5. Spatiotemporal behaviour of the particle density of CO (a) and O (b) calculated for the standard condition with $T = 1/f = 7.69 \mu\text{s}$.

(cf. Figure 3). At the end of the calculation, the density of CO is slightly larger than that of O because the dissociative electron attachment to CO_2 according to reaction E47 in Table II leads to an additional generation of CO, while it does not produce O. Furthermore, the loss processes of CO and O in Table V due to heavy particle collisions are comparatively inefficient during the period of time considered, and the diffusion of both these species takes place with comparable velocity.

To analyse the contribution of the different CO production channels, the rates of CO production due to electron impact dissociation (reaction E42 in Table II), dissociative electron attachment to CO_2 (reactions E47–E53 in Table II), and dissociative electron-ion recombination (reactions E54–E56 in Table II) are shown in Figure 6 together with the temporal variation of the discharge current density and the spatially integrated CO density over one representative voltage cycle ($t/T = 18.45$ – 19.45 in Figure 3). It is found that the CO density shows a step-like increase during the short discharge events, while it remains almost constant for the rest of the cycle (Figure 6(a)). The representation of the CO production rates in Figure 6(b) points out that the steep increase during the current pulses results mainly from electron impact dissociation with weaker contributions caused by dissociative electron attachment. Immediately after breakdown, electron-ion recombination weakly contributes to the CO_2 splitting in the plasma region as well. In contrast to the

FIG. 6. Temporal variation of current density and spatially integrated CO density (a) and spatiotemporal change of the CO production (b) due to electron impact dissociation (black grid lines), dissociative attachment (grey grid lines), and dissociative recombination (surface without grid lines) over one representative voltage cycle. In blank regions, the CO production rates are smaller than $1.0 \times 10^{14} \text{ cm}^{-3} \text{ s}^{-1}$.

negative half-cycle, a second weaker increase in the CO density occurs in the positive half-cycle at $t/T \approx 19.2$ (cf. Figure 6(a)) because of a further marked increase in the electron impact dissociation rate (cf. Figure 6(b)), in accordance with the spatiotemporal change of the mean energy and particle density of the electrons in Figure 3.

A quantification of the different contributions of the electron processes to the CO production can be obtained by considering the period-integrated density production of CO at every position in the gap. The particle density $N_{j,m}(x)$ of a species j generated by the two-body electron collision process m during the period $T = 1/f$ is given by

$$N_{j,m}(x) = \int_{t_0}^{t_0+T} n_e(x, t) n_m(x, t) k_{j,m}(U_e(x, t)) dt \quad (19)$$

in the framework of the fluid model, where n_m denotes the density of the collision partner in the process m , $k_{j,m}$ is the corresponding collision rate coefficient depending on the mean electron energy (cf. equation (14)), and t_0 denotes a certain instant of the periodic state. The resulting densities of CO generated by electron impact dissociation (reaction E42 in Table II), by dissociative electron attachment to CO₂ (reactions E47–E53), by dissociative electron-ion recombination (reactions E54–E56), respectively, and in total during one voltage cycle are shown in Figure 7.

The results confirm that the CO₂ dissociation in electron collisions is the dominant CO production channel. Furthermore, it becomes obvious that dissociative attachment and recombination processes contribute with almost equal parts of about 10% to the CO production. Figure 7 also highlights the spatial asymmetry of the CO production, which is caused by the differences in the negative and positive half-cycles. In particular, it becomes obvious that the asymmetry of the CO density shown in Figure 5(a) is

FIG. 7. Spatial variation of the CO molecules generated during one voltage cycle by electron impact dissociation, dissociative electron attachment, dissociative electron-ion recombination, and, in total, respectively, during one voltage cycle.

mainly caused by different contributions of electron-ion recombination in the positive and negative half-cycles.

Apart from electron collision processes, the collision process between the ground state CO₂ and oxygen atoms (reaction N1 in Table V) can lead to a generation of CO in the framework of the present model. However, the corresponding rate coefficient is smaller in the gas temperature range considering that its contribution is negligible.

Another reaction chain that can become relevant for the CO₂ dissociation is the vibrational up-pumping along the asymmetric stretch according to the reactions VV2 and VV16–VV204 in Table IV. Since the vibrational energy exchange among the levels of the asymmetric mode reaction channel is comparatively fast, it can lead to considerable densities of highly excited states of this mode, where finally the dissociation energy of CO₂ of 5.5 eV is exceeded and dissociation takes place. Here, the state CO₂(v₃₂₀) is close to the dissociation energy, and its density is considered as a representative for CO generated by vibrational up-pumping. In Figure 8, the temporal evolution of the spatially averaged

FIG. 8. Temporal evolution of the spatially averaged particle density of CO₂(v₃₂₀) generated by vibrational up-pumping at the standard condition.

particle density of $\text{CO}_2(v_{320})$ is illustrated. When comparing this result with the CO density generated by electron impact dissociation, dissociative electron attachment, and dissociative electron-ion recombination, it becomes immediately obvious that vibrational up-pumping is negligible for the discharge conditions and period of time considered. This finding is in agreement with the results of zero-dimensional modelling studies of a DBD at atmospheric pressure recently reported in Ref. 16, where a similar chain of vibrational up-pumping reactions was considered.

B. Universal scaling parameter of CO_2 dissociation

According to the analysis of the related DBD experiment given in Ref. 15, the specific energy input (2) can be considered as the universal scaling parameter for the CO_2 conversion to CO. Because a flow of the gas transverse to the direction of the discharge is not considered in the spatially one-dimensional model and thus the residence time t_r of gas molecules in the active plasma zone is an open parameter, the power spent per CO_2 molecule

$$P_{\text{CO}_2} = \frac{P_d}{n_{\text{CO}_2}} \quad (20)$$

is introduced and correlated with the CO_2 conversion frequency $\Delta n_{\text{CO}}/(n_{\text{CO}_2}T)$ in Figure 9. Here, the average power density P_d is determined by

$$P_d = \frac{f}{d} \int_{t_0}^{t_0+T} J(t)V_g(t) dt \quad (21)$$

and Δn_{CO} denotes the increase of the spatially averaged CO density during one voltage cycle of length $T = 1/f$. The results represented in Figure 9 have been obtained by a number of model calculations for the operational parameters given in Table VI, where only one parameter with respect to the standard condition was changed for the respective parameter variation. Obviously, a linear dependence of the conversion frequency on the power spent per CO_2 molecule is obtained for all discharge conditions considered. In particular, the CO_2

conversion frequency increases linearly with increasing temperature, voltage, and frequency, respectively, while the gas pressure has an inverse effect. A decrease in the pressure leads to higher power per CO_2 molecule and at the same time to a higher CO_2 conversion. Furthermore, a markedly higher power density with raised conversion frequency is obtained for dielectrics with a relative permittivity of 6.

The linear dependence of the CO_2 conversion on the power spent per CO_2 molecule predicted by the model calculations for the variation of five parameters is in good agreement with the experimental results reported in Ref. 15. For the range of SEI reported in Ref. 15, a similar scaling of the CO_2 conversion has also been observed in Ref. 16, where a global time-dependent model was applied for the theoretical description of an atmospheric pressure DBD using a constant average power density and gas temperature as input.

A parameter that allows the direct comparison of the modelling results with experimental data is the energy efficiency of CO production η according to equation (3). It is defined as the ratio of the dissociation enthalpy $\Delta H_{\text{CO}_2} = 2.9 \text{ eV}^{15,16}$ of CO_2 and the energy that is consumed to generate one CO molecule. The division of the conversion frequencies represented in Figure 9 by the corresponding power values yields values for η in the range between 0.2 and 0.3%. These values are about one order of magnitude smaller than the efficiencies found in the experiment.¹⁵ A possible reason for the comparatively low energy efficiency obtained by the model calculations consists in an overestimation of the electron energy loss due to vibrational and/or electronic excitation as a consequence of insufficient cross section data.⁴¹ Furthermore, once a CO_2 molecule is electronically excited, it often dissociates into neutral fragments like CO and O, but the knowledge about these processes leading to an increase in CO and O is improvable as well. When assuming that both the electronically excited states CO_2^* and CO_2^{**} undergo a very rapid dissociation to give a CO molecule and an O atom,⁶⁸ an energy efficiency of 7.6% is obtained by the present model calculations for the standard condition. When following Pietanza *et al.*⁶⁹ and supposing that only the electronically excited state CO_2^* contributes directly to the CO_2 dissociation, energy efficiencies η in the range between 4% and 5% are predicted by the present model calculations for the parameter conditions of Table VI. These values are in good agreement with the energy efficiencies of $\eta < 5\%$ measured in Ref. 15. They are also in conformity with the value obtained by global modelling in Ref. 16. However, the electronically excited state CO_2^* is not mentioned to contribute to the dissociation in that paper. Note that the change of the reaction E38 in Table II into a direct dissociation process does not affect the discharge characteristics except for the densities of CO and O.

In order to compare the present modelling results directly with the measured CO_2 conversion degree and specific energy input from Brehmer *et al.*¹⁵ for the same discharge conditions as used here, the parameters α and SEI are determined according to

$$\alpha = \frac{\Delta n_{\text{CO}} t_r}{n_{\text{CO}_2} T} \quad (22)$$

FIG. 9. CO_2 conversion frequency as a function of P_{CO_2} for the parameter conditions of Table IV.

$$SEI = \frac{P_d}{n_{CO_2}} t_r \quad (23)$$

for the measured residence times t_r of 70, 230, and 800 ms,¹⁵ respectively. Figure 10 shows that the scaling of the modelling results with the experimental residence times leads to a fair agreement of the specific energy input from the experiment and the SEI predicted by the model. From this fact, it can be concluded that the considered self-consistent time- and space-dependent fluid model provides a good prediction of the electrical characteristics of the discharge.

Furthermore, Figure 10 shows that the slope of the increase in the conversion degree with increasing SEI is well predicted by the present model, while the conversion degree α is underestimated by one order of magnitude if the contribution of CO_2^* to the CO_2 dissociation according to Pietanza *et al.*⁶⁹ is not taken into account. Inclusion of the latter leads to a slight overestimation of the conversion degree for a given SEI by roughly a factor of two. That is, further work is needed in order to clarify the role of the different reaction channels contributing to the CO_2 dissociation. For example, further additional processes not included in the present reaction kinetics model could also lead to the production of CO. Here, especially CO_2 reactions with various ions are to mention which were found to contribute to 60% to the dissociation of CO_2 in the atmospheric pressure DBD with a frequency of 35 kHz and power density of 10.6 W cm^{-3} studied by a global time-dependent model in Ref. 16. This global modelling was done for residence times between 0.5 and 5 s. However, these processes are negligible for the discharge conditions and period of time considered in the present time- and space-dependent fluid modelling. This finding is in accordance with Ref. 33, where up to five pulses in an atmospheric pressure DBD with a frequency of 50 kHz and a power of 150 W were analysed by a global model including an extensive plasma chemistry model, and electron impact reactions were found to dominate the splitting of CO_2 . Moreover, more recent global modelling studies of CO_2

dielectric barrier discharges reported in Ref. 17 also show the predominance of the electron impact reactions for the dissociation of CO_2 . The extension of the present fluid model to take CO_2 reactions with various ions and further processes into account to clarify the influence of heavy particle collisions on the CO production will be the subject of future studies.

The description of the CO_2 conversion degree in terms of the universal scaling parameter SEI becomes possible because most of the energy is injected into the DBD plasma during the formation of the filaments and is dissipated almost immediately due to different electron collision processes for the most part according to the fractional power shown in Figure 2. This situation takes place in the case of CO_2 dissociation, i.e., net CO production, at the cold conditions used in a typical DBD in pure CO_2 , because the CO produced is very stable and cannot be easily oxidized or reduced so that loss processes of CO are slow. For example, one of the expected loss reactions is the recombination of CO and O back to CO_2 . This reaction is spin forbidden⁷⁰ and occurs only very slowly in the gas phase (reactions N2 and N3 in Table V) or on non-catalytic surfaces like quartz. The loss of CO due to electron impact dissociation is negligible because it requires about twice as much energy than the electron impact dissociation of CO_2 and the electron impact ionization of CO was found to be less important for conversion degrees less than 15%.¹⁷

As an extension, it can be expected that a description of an electron induced production process in terms of the specific energy input is fairly general independent of the gas mixture. That is, if the fractional power transferred is the determining variable, the density of a chemical species produced by an electron impact collision process with ground state molecules should scale only with the specific energy input in a filamentary dielectric barrier discharge. One example is the ozone generation in dielectric barrier discharges.^{71,72} However, here the ozone yield scales with the specific energy input only over a limited parameter range because of the thermal destruction of ozone at elevated temperatures.⁷²

IV. SUMMARY

The conversion of CO_2 into CO and by-products was investigated by means of a self-consistent fluid modelling approach. Model calculations were performed for a wide range of discharge conditions related to the DBD reactor used by Brehmer *et al.*¹⁵ The analysis of the discharge behaviour and the general features of CO production can be summarized as follows.

For the standard condition, comprising a voltage amplitude of 10 kV at a frequency of 130 kHz, a gas pressure of 1 bar at a gas temperature of 400 K, and a gap width of 1 mm with 2 mm thick quartz dielectrics on both sides, differences in the discharge evolution in the positive and negative voltage half-cycles appear. It was found that discharges occurring in the negative half-cycles of the applied voltage are characterized by a higher breakdown voltage, stronger current peaks, and longer period with higher electron density

FIG. 10. Calculated CO_2 conversion degree as a function of the specific energy input for residence times of 70, 230, and 800 ms in comparison with the measured data of Brehmer *et al.*¹⁵ for a dielectric barrier thicknesses of 2 mm without (full symbols) and with (open symbols) the contribution of CO_2^* to the CO_2 dissociation according to Pietanza *et al.*⁶⁹

compared to discharges in the positive half-cycles. The differences between the positive and negative half-cycles were ascribed to the occurrence of volume memory effects, which lead to a mutual influencing of sequent discharge events. In particular, the high inertia of negative ions compared to the electron component and the relatively high frequency result in a predominance of CO_3^- in positive half-cycles, while electrons constitute the dominant negatively charged species in negative half-cycles. It was also shown that the different properties of the individual discharge events in positive and negative half-cycles lead to a spatially asymmetric distribution of the stable neutrals like CO molecules and O atoms in the gap.

The exploration of the CO_2 dissociation mechanisms revealed that for the present discharge conditions, the electron impact dissociation is the dominant CO production channel (contribution of about 80% to the total dissociation), while dissociative electron attachment and recombination processes contribute only weakly to the CO_2 dissociation (contribution of about 10% from each). The analysis of the spatiotemporal change of the different dissociation channels showed that the electron impact dissociation has its maxima at the sheath edges as a result of the spatial distribution of the electron density and the mean electron energy at the instants of maximum current while the rate of dissociative electron attachment is almost equally distributed over the gap. The dissociative recombination processes occur exclusively in the quasi-neutral plasma region. Furthermore, the CO production in heavy particle collision processes and due to vibrational up-pumping along the asymmetric stretch was found to be negligible in the gas temperature range considered.

The total CO production rate was found to be largest for a short duration of a few nanoseconds during breakdown as a consequence of the dramatic increase in the electron density with ignition of the individual discharge events. This leads to a step-wise increase in the line integrated CO density in the gap of about $1.5 \times 10^{11} \text{ cm}^{-2}$ during each discharge pulse.

Besides the standard condition, model calculations for different pressures, gas temperatures, voltage amplitudes, frequencies, and permittivities of the dielectrics were performed. Here, one parameter was changed for the respective parameter variation while keeping the other parameters constant. A different power density coupled into the plasma and a different CO_2 conversion frequency were obtained for each parameter set. In accordance with the experimental results of Brehmer *et al.*,¹⁵ it was found that the CO_2 conversion frequency depends linearly on the power spent per CO_2 molecule but it does not depend directly on any of the investigated input parameters.

In order to compare the CO production predicted by the fluid model directly with measured conversion degrees in dependence on the specific energy input, the respective properties obtained for the different discharge conditions were scaled by the experimental residence times of a gas volume in the active plasma zone. From this approach, a fairly good agreement of the measured SEI and the SEI predicted by the model was obtained. In addition, the slope of the linear increase in the conversion degree with increasing SEI in log-log scale obtained from the modelling results for the

different parameter sets does coincide with that reported in Ref. 15 to a large extent.

However, the conversion degree obtained from the present model for a given SEI and thus the energy efficiency of CO production turned out to be smaller than the experimental values by about one order of magnitude. As a possible reason for this drawback, the immediate dissociation of the electronically excited states CO_2^* and CO_2^{**} as additional CO_2 conversion channels according to Refs. 68 and 69 was discussed and tested. It was also verified that the change in the excitation reactions into direct dissociation channels does not have any influence on other discharge properties than the densities of the dissociation products CO and O.

A strong overestimation of the energy efficiency was obtained when assuming that both the electronically excited states undergo a very rapid dissociation to give a CO molecule and an O atom. When following Pietanza *et al.*⁶⁹ and supposing that only the electronically excited state CO_2^* contributes directly to the CO_2 dissociation, energy efficiencies in the range of $\eta = 4\ldots 5\%$ are predicted for the considered data range. These values are in the same order of magnitude as the energy efficiencies of $\eta = 1.5\ldots 3.5\%$ obtained experimentally by Brehmer *et al.*¹⁵ and also coincide roughly with the results of a global reaction kinetics model in Ref. 16, which does not include the direct dissociation of CO_2^* as a CO production channel. In that paper, other processes occurring mainly at higher dissociation degrees are mentioned to contribute markedly to the CO production. The extension of the present fluid model to take CO_2 reactions with various ions and further processes into account to clarify the influence of heavy particle collisions at higher dissociation degrees on the CO production will be subject of future studies.

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