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Investigation of filamentary and diffuse DBD in CO₂ by means of *in-situ* FTIR absorption spectroscopy

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Abstract

This work investigates CO₂ dielectric barrier discharges at atmospheric pressure in the filamentary and diffuse regimes for the first time using *in situ* FTIR absorption measurements. The conversion factor of CO₂ is determined and is consistent with the results obtained for DBDs in the literature. Vibrational temperatures for CO₂ and CO molecules are also determined, as well as the rotational temperature. The ordering of the different temperatures is similar to the reported results for other CO₂ discharges. The evolution of the measured parameters as a function of the specific energy input is discussed and a comparison of the two different regimes is carried out.

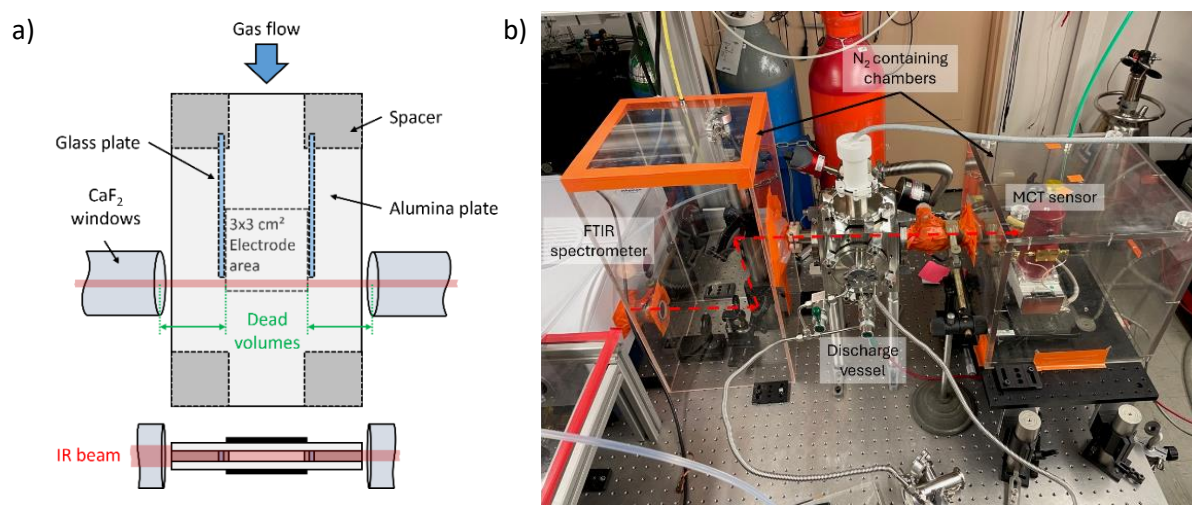
Introduction

Interest in CO₂ plasmas started from the studies of CO₂ lasers in the 60's [1]. Further studies were dedicated to astrophysical observations [2,3] or to spacecraft shield design for atmosphere re-entry [4–6]. In the 70's, Fridman [7] and Capezzuto [8] were among the first to take advantage of the capability of non-equilibrium plasmas to induce chemistry in gases and to study the dissociation of CO₂ molecules. Non-equilibrium plasma discharges are an excellent way to produce oxygen from CO₂ during space missions [9–11], especially on Mars, where the atmosphere is composed of 95 % of CO₂. In addition, the current context, where global warming is a significant concern, motivates studies on CO₂ conversion into value-added products, for example, the production of methane from CO₂ and H₂ [12], or energy storage by the production of CO-H₂ "syngas" from CO₂ and CH₄, to reform hydrocarbons later [13,14]. Dielectric barrier discharges (DBDs) are interesting because they work at atmospheric pressure, are easy to set up, scalable and can be coupled with catalytic materials to improve CO₂ conversion. At this pressure, barrier discharges generally work in the well-known filamentary regime. However, it was demonstrated that obtaining a diffuse discharge in CO₂ at atmospheric pressure is possible as well [15]. This diffuse type of discharge works in the well-known atmospheric pressure Townsend regime (APTD), as it was initially reported in N₂ and later also in air [16–18]. In the Townsend regime, the electric field is almost constant along the gas gap [19,20]. It can be easily determined from the knowledge of the gas gap voltage, which can be determined by electrical measurements. This regime constitutes an exciting way to study the discharge mechanisms involved in CO₂ discharges because of the easy determination of the reduced electric field. In such APTD regime barrier discharge, it changes on relatively slow microsecond scales and peaks at low fields of approximately 120-140 Td, which represents another uniqueness in discharge conditions for CO₂ plasma study. Infrared absorption spectroscopy (FTIR) was used in low-pressure glow discharge [21–24], DBD [25] and recently in atmospheric pressure RF jets [26,27] to determine the dissociation rate of CO₂, and measure the energy distribution in the CO₂ and CO vibrational levels associated with their own temperature. The conversion rate of the CO₂ molecule into CO appears to be a function of the energy dissipated within the discharge. A non-equilibrium between the temperatures of the different vibrational modes of CO₂ was observed in the different discharge configurations, and a higher vibrational temperature of CO compared to vibrational temperatures of CO₂ was reported. In addition, the works of Morillo-Candas *et al.* [23,24] highlighted the importance of the CO(a) metastable and oxygen species, such as O₂ and atomic oxygen

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3 in the discharge kinetic. In this work, *in-situ* FTIR absorption spectroscopy is used for the first time in
4 CO₂ DBDs at atmospheric pressure in both diffuse (also referred as Townsend) and filamentary regimes.
5 The results obtained for both regimes are then compared.
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10 1. Experimental setup

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12 The experimental setup used for this work is similar to the one used in [15]. The DBD cell, shown
13 schematically in Figure 1a, was composed of two alumina plates 115x50 mm with a squared electrode
14 of 3x3 cm painted on the outer side using a silver-based conductor painting (ESL 9916-G). The gas gap
15 of 2 mm was set using four printed pieces, which maintain a glass plate to ensure a laminar gas flow.
16 The glass plates were cut 5 mm before the electrode output allowing the IR beam to pass through the
17 discharge.
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38 Figure 1: a) Top view diagram and b) picture of the experimental setup.

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41 Before each experiment, the primary pump allows to reach a pressure of 10^{-3} mbar within the vessel.
42 The vessel was filled with CO₂ Alphagaz 1 from Air Liquide[®], with a purity of 99.999 %, for the
43 experiments. The gas flow was set using a mass flow controller. An electronically controlled valve
44 associated with a diaphragm pump was used to maintain a constant pressure of 1015 mbar during the
45 experiments. The discharge cell was supplied by a low-frequency generator Keysight 33210A coupled
46 to an audio amplifier connected to a high-voltage transformer. The applied voltage was measured using
47 a Tektronix P6015A probe, and the current was measured through a shunt resistor placed in series with
48 the discharge cell using a Rohde & Schwarz RT-ZP03 probe. Electrical characteristics were acquired
49 using an oscilloscope Rohde & Schwarz RTB2004 with a bandwidth of 300 MHz. The discharge power
50 was calculated by integrating the product of the measured voltage and current over one period. The
51 gas voltage was determined from electrical measurements using an equivalent electrical circuit [28].
52 As the electric field is almost constant for a Townsend discharge, the electric field and then the reduced
53 electric field E/N can be easily determined from the gas voltage, i.e. voltage over the gas gap
54 (sometimes referred to as gap voltage).
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59 The FTIR measurement setup was composed of a FTIR spectrometer Bruker V70 coupled with a MCT
60 sensor cooled with liquid nitrogen. The IR beam of the spectrometer was guided through the discharge

cell by a set of mirrors and collected on the other side by the MCT sensor. The FTIR beam was collimated to pass through the gas gap. However, due to the large section of the IR beam, a part of it is cut, and only a fraction of the incident beam is collected by the MCT sensor. The absorption signal therefore corresponds to an average over the inter-electrode space, at the end of the plasma in the direction of the gas flow. At atmospheric pressure, the large amount of CO₂ molecules can be responsible for a total extinction of the IR beam in given spectral regions. To limit this saturation effect, the length of the optical path containing CO₂ was reduced using dedicated CaF₂ windows disposed as close as possible to the discharge cell (Figure 1a). In addition, the optical path from the FTIR spectrometer to the MCT sensor was purged with nitrogen circulation (see Figure 1b). Only the volume between the windows and the discharge area, called dead volume, contains pure CO₂ unexposed to the discharge. It must, therefore, be considered during the analysis of the absorption spectra. IR measurements were repeated for each condition until a steady state was reached.

Using the method described in [21], the IR spectra (Figure 2) were fitted to determine the vibrational temperatures of CO (T_{CO}) and CO₂ (T_{12} and T_3), the rotational temperature (T_{rot}) and the conversion factor α given in equation (1):

$$\alpha = \frac{[CO]}{[CO] + [CO_2]} \quad (1)$$

where $[CO]$ and $[CO_2]$ are the CO and CO₂ densities, respectively. The vibrational kinetic of the CO₂ molecule is described in [7]. The CO₂ molecule has three vibrational modes: a symmetric stretching mode ν_1 , a double degenerate bending mode ν_2 and an asymmetric stretching mode ν_3 associated with the vibrational temperatures T_1 , T_2 and T_3 , respectively. The temperatures of the symmetric and bending modes of CO₂ are considered in Fermi equilibrium ($\hbar\nu_1 = 2\hbar\nu_2$), and consequently, a single temperature T_{12} is used to describe them. The temperature of the asymmetric mode T_3 is considered independently. A Treanor distribution is assumed for the population densities of the vibrational levels. The rotational temperature (T_{rot}) is assumed to be the same for all vibrational modes of CO₂ and CO. In the dead volumes, unlike in the plasma volume, the vibrational temperatures are assumed to be equal to T_{rot} , but the value of T_{rot} is not fixed. A similar gas composition is considered in both plasma volume and dead volume. The temperatures are determined with an error estimated to 30 K for CO₂ and around 100 K for CO using a sensitivity analysis by varying T_{rot} , T_{12} , T_3 and T_{CO} individually, as described in [21].

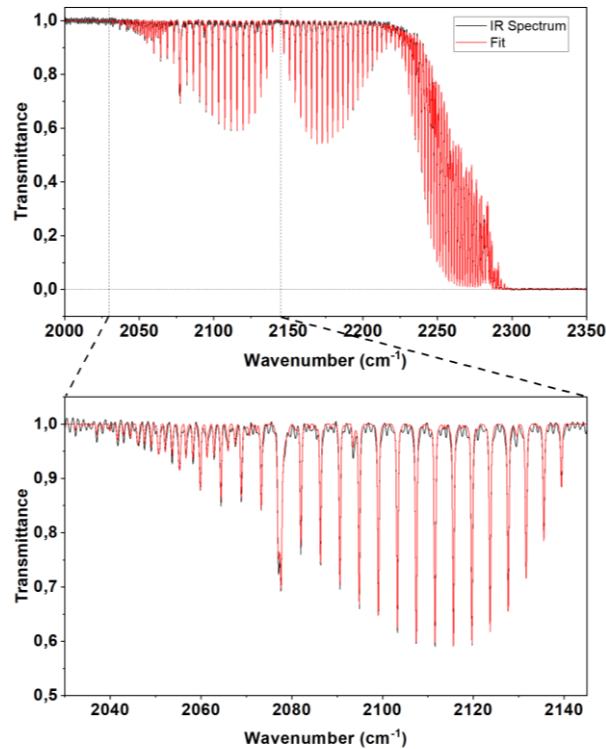


Figure 2: Example of a fitted IR spectrum. The IR spectrum is represented in black and the calculated spectrum in red ($f = 2$ kHz, $V = 17$ kVpp, gas gap = 2 mm, gas flow = 200 sccm).

2. Results and discussion

2.1. Specific energy input

This study investigates and compares the diffuse regime with a classical filamentary discharge regime. The frequency of the sine voltage is chosen as a parameter to switch from one discharge regime to the other. Indeed, for an amplitude of the applied voltage lower than 17 kV_{pp}, the discharge is systematically diffuse for a frequency of 1 kHz and filamentary for higher frequencies (2 kHz and 3 kHz). The influence of the amplitude of the applied voltage and the gas flow will be discussed later. The effect of all these parameters can be considered using the specific energy input (SEI), which represents the amount of energy dissipated within a defined volume of gas during its interaction with the discharge. Then, many authors use SEI as a scaling parameter for CO conversion to compare discharges with different geometry, pressure, and electrical excitation [25,29–31]. The SEI is calculated using equation (2).

$$SEI = \frac{P}{\Phi} \cdot \frac{p_0 T_g}{p T_0} = \frac{\tau \times P}{V} \quad (2)$$

with P the discharge power, Φ the gas flow injected through the discharge, p_0 and T_0 the standard conditions of pressure and temperature, T_g the gas temperature and p the experimental pressure. $\tau = \frac{V}{\Phi}$ is the residence time of the gas and V the volume of the discharge obtained by multiplying the area of the electrodes by the gas gap value.

To check the possible influence of the gas flow parameter on the dissipated plasma power in the discharge, we have conducted the following analysis. Figure 3a shows the discharge power as a function of the gas flow. For each excitation condition (frequency and amplitude of the applied voltage), the discharge power is almost independent of the gas flow in the explored range. It is worth mentioning that for an APTD generated in N_2 with small admixtures of oxidising gases such as O_2 (tens of ppm), some processes in the gas phase, such as associative ionisation reactions, occur [32]. Then, in N_2 , a change in the gas flow rate while keeping the electrical parameters unchanged, induces a change in the discharge power. Whereas, in CO_2 APTD, the gas chemistry seems to have almost no influence. This is in good agreement with previous results provided in [15], where the memory effect was found to be independent of the species in the volume.

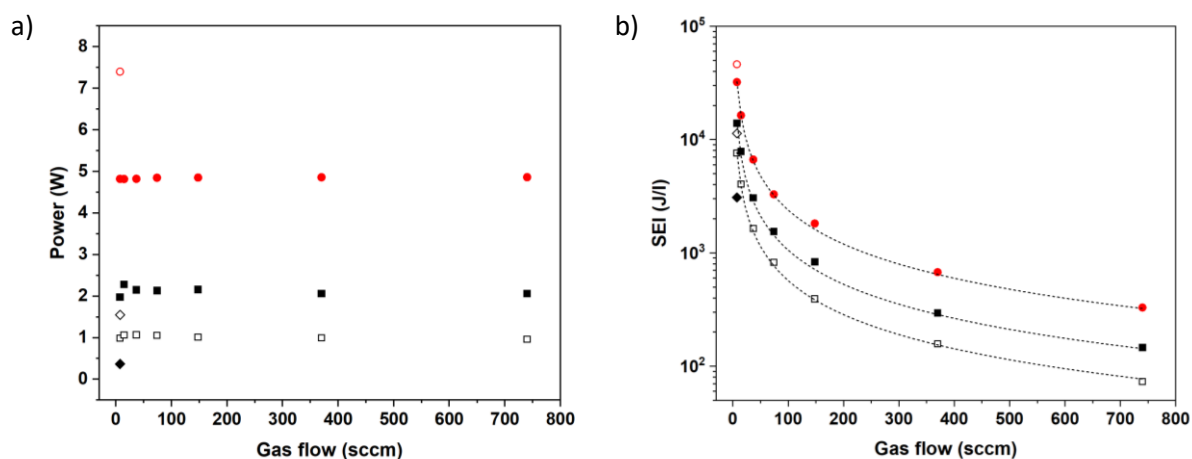


Figure 3: a) Discharge power and b) specific energy input (SEI) as a function of the gas flow for both diffuse regime (Townsend): black shapes (\blacklozenge : 1 kHz 14 kV_{pp}, \blacksquare : 1 kHz 15 kV_{pp}, \blacklozenge : 1 kHz 16 kV_{pp}, \blacksquare : 1 kHz 17 kV_{pp}) and filamentary regime: red shapes (\bullet : 2 kHz 17 kV_{pp} and \circ : 3 kHz 17 kV_{pp}).

The specific energy as a function of the gas flow for the different conditions of electrical excitation is represented in Figure 3b. SEI falls rapidly by two orders of magnitude when the gas flow increases from 7.4 sccm to 740 sccm, or residence time decreases from 14.6 s to 146 ms. The higher the gas flow, the lower the residence time of the gas and the lower the SEI for a similar electrical excitation condition. The moderate increase of the gas temperature with SEI (see section 2.3), as well as the independence of the discharge power regarding the gas flow, makes the SEI just inversely proportional to the gas flow. The SEI can thus be modified by changing the discharge power for a given gas flow, or by changing the gas flow for a given power, or by combining both approaches.

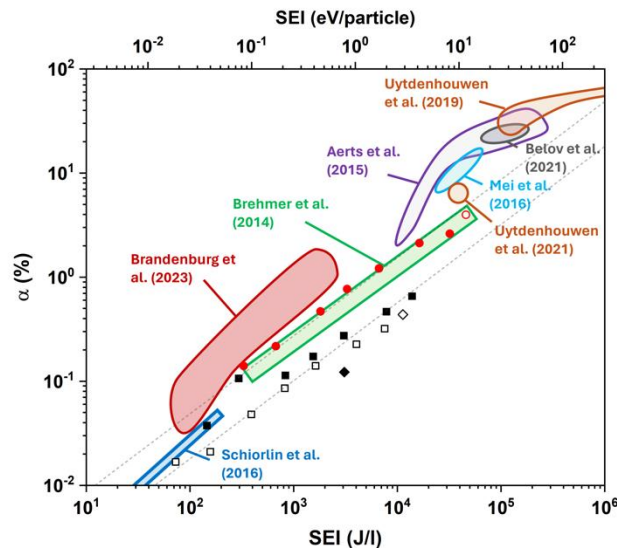


Figure 4: Conversion ratio α as a function of specific energy input (SEI). Our results were added to the figure reproduced from [29]. The dashed lines correspond to the fit of the experimental results obtained in the present work by imposing a slope of 0.75 for the diffuse regime (Townsend): black shapes (\blacklozenge : 1 kHz 14 kV_{pp}, \square : 1 kHz 15 kV_{pp}, \diamond : 1 kHz 16 kV_{pp}, \blacksquare : 1 kHz 17 kV_{pp}) and filamentary regime: red shapes (\bullet : 2 kHz 17 kV_{pp} and \circ : 3 kHz 17 kV_{pp}).

2.2. CO₂ conversion factor

Figure 4 is reproduced from an article by Brandenburg *et al.* [29] and summarises the results obtained by different groups in CO₂ DBDs together with the results of this work. The conversion factor is shown as a function of the SEI. Red circles correspond to conditions for which the discharge works in the filamentary regime, whereas black squares are related to the diffuse discharge regime. The conversion ratio does not exceed a few percents, as it is reported in the literature for different barrier discharge configurations [33]. It is important to note that the discharge did not cover the whole electrode surface for the diffuse conditions at 14 kV_{pp} and 15 kV_{pp}. Then, the spreading of the discharge along the gas flow was estimated from the electrical measurements and imaging performed during additional dedicated measurements (see *e.g.* [34,35]). According to the obtained results, measurements at 15 kV_{pp} were still done within the discharge zone, whereas for the condition at 14 kV_{pp}, the measurements were done at the boundary between the discharge and the very beginning of the post-discharge. In the following, the SEI and residence time calculations were done considering the real discharge volume *i.e.* considering the spreading of the discharge. The values of α for the filamentary regime are in good agreement with the *ex-situ* measurements results obtained by Brehmer *et al.* [25] in atmospheric pressure DBD with quartz dielectrics and a gas gap of 1 mm (half of the gap used in this work). For a given SEI, the α factor is always higher for the filamentary regime than for the diffuse one. Indeed, it is now well accepted that in DBDs the CO₂ dissociation mainly occurs through direct electron impact with a low contribution of the vibrational ladder climbing [36]. Then, electrons with high energy in the tail of the energy distribution function play a significant role. The dissociation fraction results from a balance between the production and destruction of CO molecules. Considering that both regimes share rather similar conditions (pressure, nature of the surface, gas composition...) and assuming that the dominant production and destruction mechanisms are the same in both regimes (see discussion further), the lower dissociation degree observed in the diffuse regime could be explained by the lower reduced electric field values in this regime, which in turn is responsible for a lower population of energetic electrons. Indeed, E/N in the diffuse mode remains in the range 120-140

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3 Td for all conditions, compared to the filamentary regimes where E/N values within the micro-
4 discharges can reach values around 500 Td in the gas bulk [37,38]. Note that increasing the applied
5 voltage in the Townsend regime (*i.e.* at a frequency of 1 kHz), does not result in an increase of the gas
6 gap voltage, which remains close to the breakdown voltage, keeping unchanged the E/N value. Instead,
7 it causes the discharge current and, thus, the electron density to increase, resulting in a slight increase
8 of the discharge power (Figure 3) and thus of the dissociation fraction α (Figure 4). Conversion factor α
9 grows when SEI increases. Both diffuse and filamentary results can be fitted by a straight line in log-log
10 scale (which is similar to a power law in linear scale) *i.e.* $\alpha = k \times SEI^n$. A corresponding slope of $n =$
11 0.67 is found for both the filamentary and the diffuse regimes with R-squared values $R^2 = 0.99$ and
12 $R^2 = 0.94$ respectively. Aerts *et al.* [39] have already shown using their numerical model that the
13 conversion factor α in DBDs follows such a power law as a function of the SEI. In their review article,
14 Brandenburg *et al.* [29] observed the same behaviour for SEI lower than 10 eV per particle by
15 comparing the results of several works for different dielectric barrier discharge configurations. In his
16 article Brehmer *et al.* reported a slope of $n = 0.75$ and developed a simple model considering the
17 dissociation of CO_2 by collisions with electrons as a source term for CO production, and surface and
18 volume recombination of CO as a loss term. If there are no losses, then $n = 1$, whereas including
19 recombination losses leads to a lower value of the exponent. More recently, Douat *et al.* [30] reported
20 a similar power law dependence with $n = 0.75$ for a discharge in pin-to-pin configuration at lower SEI.
21 They attributed the power-law dependence to the fact that the number of filaments in filamentary
22 DBDs also follows a power law. Nevertheless, the fact that this behaviour is also observed in purely
23 diffuse DBD challenges this hypothesis and suggests that it is probably much more the result of a
24 balance between gain and loss processes. Our value of the exponent $n = 0.67$ would thus suggest
25 slightly higher CO losses than those of Brehmer and Douat, as discussed later. However, fitting our data
26 by imposing $n = 0.75$ results in a good agreement for filamentary ($R^2 = 0.98$) and diffuse ($R^2 = 0.91$)
27 regimes (see dashed lines on Figure 4). This shows that our results and the previously published ones
28 remain close to each other. One of the possible explanations for this slight difference might be related
29 to the lower number of measurements in our study.

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37 The three-body recombination, see equation (3), is efficient only at high temperature or at the wall
38 [36,40], equation (4) (in this case, M represents the wall itself).



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43 In our conditions, the gas temperature remains moderate (see [28] and next part), thus if this reaction
44 plays a role, it will likely occur at the surface. The rate of wall recombination is difficult to assess but
45 one can estimate the characteristic diffusion time τ_{diff} of O and CO to the walls and the associated
46 frequency. Due to the small gas gap compared to the dimension of the system, τ_{diff} can be
47 approximated to $\tau_{diff} = \frac{d^2}{\pi^2 D}$ where $d = 2mm$ is the gap length and D the diffusion coefficient of the
48 specie of interest. Morillo-Candas *et al.* [41] reported two different diffusion coefficients for atomic
49 oxygen, coming from Cenian *et al.* [42] and Klarenaar *et al.* [22]. Under our conditions, τ_{diff} for O
50 atoms is in the range of 9 – 15 ms using the diffusion coefficient from Cenian, and 2 times larger
51 according to Klarenaar. For CO, estimated τ_{diff} ranges between 18 and 28 ms where the diffusion
52 coefficient of CO was calculated according to [43]. These values are well below the lower value of the
53 residence time τ in our conditions which is about 140 ms. It means that particles have enough time to
54 reach the surface by diffusion during their stay within the gas flow. Brehmer *et al.* used coefficient rates
55 from [42] to study the backreaction mechanisms in gas phase, see equation (3), and at the surfaces,
56 eq. (4), and reported a similar rate coefficient $k \approx 1.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. Our results are comparable to
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[25] in terms of α , gap length and gas temperature (see next section). Therefore, we assume a similar coefficient rate for both reaction mechanisms. Considering only these backreaction mechanisms as CO loss channels is consistent with behaviour similar to that observed by Brehmer *et al.*. Note that also other mechanisms are suspected to be of major importance in the backreactions mechanisms in CO₂ plasmas, such as the metastable species O(¹D) or CO(^a3Π), which could react with CO and/or O₂ to form CO₂ again, or O₂(^a1Δ_g) and O₂(^b1Σ_g⁺) [36]. Despite an impossible estimation of their contribution with the available data, the fact that the slope of the $\alpha = f(SEI)$ curve is the same for both discharge regimes suggests that the dominant mechanisms are the same whether they are gain or loss processes, and that their relative importance does not strongly vary with the E/N value in the range covered by the present study.

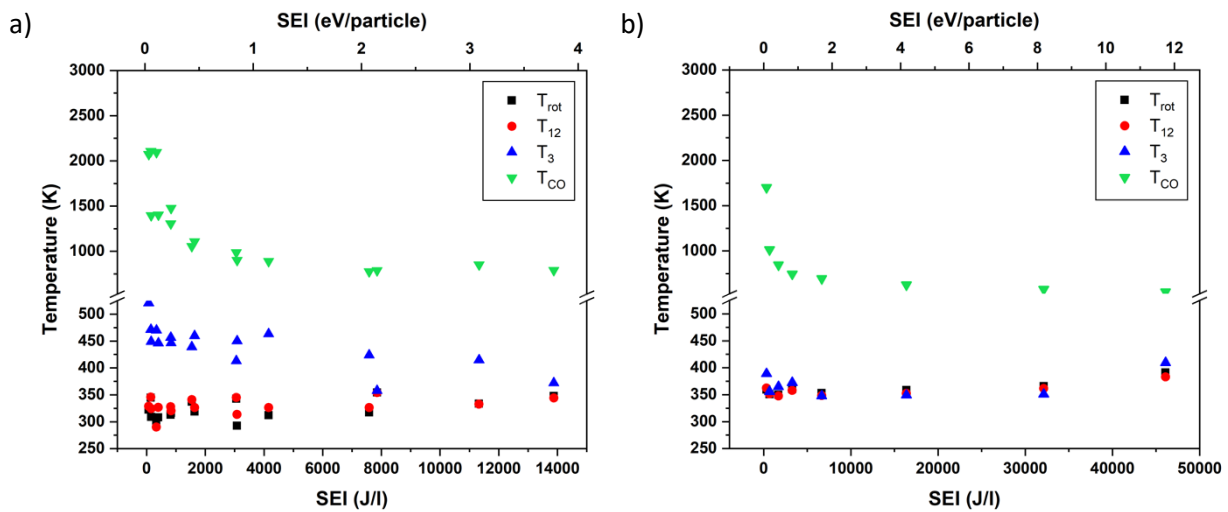


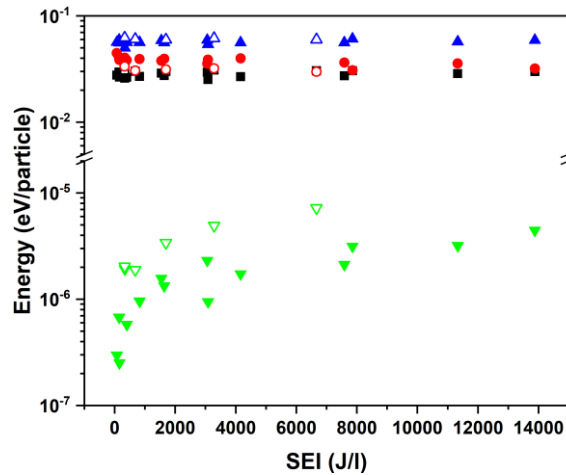
Figure 5: Rotational temperature (T_{rot} : ■) and vibrational temperature of CO₂ and CO (T_{12} : ●, T_3 : ▲ and T_{CO} : ▼) as a function of the SEI in a) Diffuse regime (Townsend) and b) filamentary regime.

2.3. Vibrational kinetic

As explained in section 1, due to the Fermi resonance between ν_1 and ν_2 , important energy transfers occur between these two modes, which are thus strongly coupled and can be considered as a triple degenerate mode associated with a single vibrational temperature denoted hereafter as T_{12} . The CO molecule has only one vibration mode associated with temperature T_{CO} . Figure 5 shows the rotational temperature T_{rot} , the vibrational temperature of the symmetric-bending mode of CO₂ (T_{12}), the vibrational temperature of the asymmetric mode of CO₂ (T_3) and the vibrational temperature of CO (T_{CO}) obtained for both studied discharge regimes. Let us first discuss the results obtained for the diffuse regime (Figure 5a), whereas the results obtained for the filamentary regime (Figure 5b) will be discussed at the end of this section.

The general ordering of the different temperatures: $T_{CO} > T_3 > T_{12} \approx T_{rot}$ is consistent with the results reported in several works [36,44] except that under our conditions, the difference between T_{CO} and T_3 is very large, with T_{CO} being at least 500 K higher. Due to the short energy gap between the vibrational levels of symmetric stretching and bending modes of CO₂, the V-T relaxation mechanisms are efficient. The energy of the vibrational levels ν_1 and ν_2 is thus easily lost in gas heating, and consequently, T_{12} remains close to T_{rot} . On the contrary, the energy gap between the vibrational levels of the asymmetric mode is larger, and thus, the V-T relaxation mechanisms are less efficient. This

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 3 difference results in a non-equilibrium between symmetric-bending mode (T_{12}) and asymmetric
 4 stretching mode (T_3). This non-equilibrium is generally favoured by the resonance between the
 5 vibrational level of CO and the asymmetric stretching mode of CO_2 , which can result in vibrational
 6 energy transfer from CO to the ν_3 mode of CO_2 . Nevertheless, in our conditions, the dissociation
 7 fraction is too low for these energy transfers to significantly contribute to a rise of T_3 . This is especially
 8 true for low SEI for which T_{CO} exceeds T_3 by more than 2000 K in the diffuse regime and can at least
 9 partly explain why $T_{CO} \gg T_3$. Energy stored in the different vibrational modes can be estimated by the
 10 product $\varepsilon = nk_B T$, where n is the density of CO_2 or CO, k_B the Boltzmann constant and T the
 11 temperature associated to the vibrational mode under study. Corresponding results are represented in
 12 Figure 6 for diffuse and filamentary regimes. Note that here $\varepsilon_{12} = 2 \times n_{\text{CO}_2} k_B T_{12}$. It is clearly visible
 13 that the energy of the CO vibrations is very low regarding to the CO_2 vibrational modes. Indeed, ε_{CO}
 14 represents less than 1 % of the total vibrational energy. It confirms that even if there is a resonance
 15 between CO and the asymmetric mode of CO_2 , the amount of energy stored in the vibrational modes
 16 of CO is too low to significantly impact T_3 . Other phenomena can also be responsible for this large
 17 difference between T_3 and T_{CO} . Vibrational intermodal exchanges occur between the asymmetric
 18 mode of CO_2 and the symmetric stretching and bending modes (V-V' exchanges), while these V-V'
 19 exchanges do not exist for the CO molecule. Also, according to [23], the V-T relaxation processes are
 20 slightly more efficient for the ν_3 mode of CO_2 compared to CO, whereas vibrational excitation by
 21 collision with electronically excited species as $\text{CO}(a^3\Pi)$ and $\text{O}(^1D)$, which are products of the CO_2
 22 dissociation by direct electron impact, could be more efficient for CO. Fromentin *et al.* [44] also
 23 reported an unusually large cross section for the excitation of the vibrational levels of CO which is
 24 related to a resonance effect with short-lived negative ions CO^- [45]. In conclusion, the higher value of
 25 T_{CO} compared to T_3 probably results from a combination of several mechanisms, including: 1) limited
 26 vibrational energy transfer from CO to CO_2 , 2) V-V' transfers and higher VT relaxation for ν_3 compared
 27 to CO and 3) higher energy transfers towards the vibrational levels of CO.



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 51 Figure 6: Energies associated to the vibrational temperatures T_{rot} : ■, T_{12} : ▲, T_3 : ● and T_{CO} : ▲ as a function of
 52 the SEI for diffuse regime (filled shapes) and filamentary regime (empty shapes).

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 56 Another interesting phenomenon is the evolution of the temperatures with the SEI, and especially T_{CO} .
 57 The trends are similar for both regimes. As SEI increases, T_{CO} rapidly decreases. In the diffuse regime,
 58 it drops from 2073 K at 73 J/l to 986 K at 3058 J/l. The decrease is less pronounced for T_3 . Indeed, on
 59 the same range of SEI, it only decreases from 520 K to 413 K. Whereas T_{12} only slightly increases from
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room temperature (300 K) for the lower SEI to 348 K for 13877 J/l. Having in mind that the dissociation fraction α in both regimes is different, it is interesting to have a look at the evolution of the temperatures as a function of α . Figure 7 shows the evolution of T_{CO} with α . All the experimental data for both regimes are aligned on the same curve, indicating that α is a relevant parameter and suggesting that the dissociation products O and/or CO can play a role in this evolution. Atomic oxygen is known to be a good quencher of vibrational levels and the V-T relaxations of CO₂ and CO molecules by collision with O atoms are dominant [23]. Figure 8 shows the quenching frequencies of the vibrational levels of CO and CO₂ (ν_2 and ν_3) by O atoms as a function of α . These frequencies were determined by multiplying the quenching rate coefficient k taken from the literature [23,44] by the density of O atoms, which is estimated from the dissociation fraction using the ideal gas law and the measured rotational temperature. The O atoms density was considered equal to the CO density, thus neglecting recombination. In this way, atomic oxygen density is overestimated, and the computation provides an upper limit of the quenching rate. V-T relaxation rate by CO₂, which is the dominant species within the discharge, is added for direct comparison. The quenching rate coefficient of CO₂ symmetric and asymmetric stretching modes were found in [23,44] from the work of [46–48]. The rate coefficient for the quenching of CO($\nu = 1$) by collision with O atoms came from [49] and the rate coefficient for V-T relaxation of CO(ν) through collisions with CO₂ was obtained using the same method as described in [44]. Due to the large number of CO₂ molecules in our conditions (low dissociation rate), deexcitation frequencies of CO₂ by collision with another CO₂ molecule are almost constant independently of the conversion factor. The calculated quenching frequencies by O atoms increase rapidly for low values of α with the apparition of CO and O. The results clearly show that V-T processes of CO are dominated by collisions with O atoms. The deexcitation frequency is thus directly related to the O atom density. It is thus reasonable to assume that for very low SEI, the appearance of O atoms in the discharge is responsible for a significant increase of the VT processes of CO, leading to the observed drop of T_{CO} in the diffuse and filamentary regimes. In addition, due to the large amount of CO₂, V-T relaxations of CO₂ vibrations by collision with another CO₂ molecule are efficient, which could explain why T_3 and T_{12} remain low whatever the dissociation degree. A large difference between the vibrational temperatures of CO and the asymmetric mode of CO₂ was also observed in noble gases with an admixture of CO₂ [26,27]. In these works, the dilution of CO₂ into noble gas limits the transfer between T_{CO} and T_3 as it is in our conditions due to the low amount of CO. It also reduces the quenching rate of CO vibrations by atomic oxygen.

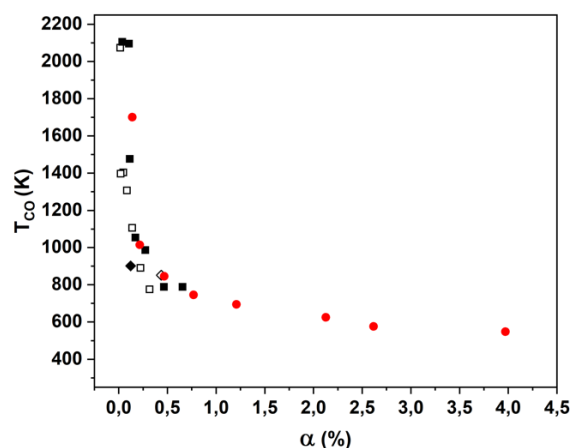


Figure 7: Vibrational temperature of CO as a function of α . Diffuse regime (Townsend): black shapes (\blacklozenge : 1 kHz 14 kV_{pp}, \blacksquare : 1 kHz 15 kV_{pp}, \blacklozenge : 1 kHz 16 kV_{pp}, \blacksquare : 1 kHz 17 kV_{pp}) and filamentary regime: red shapes (\bullet : 2 kHz 17 kV_{pp} and \circ : 3 kHz 17 kV_{pp}).

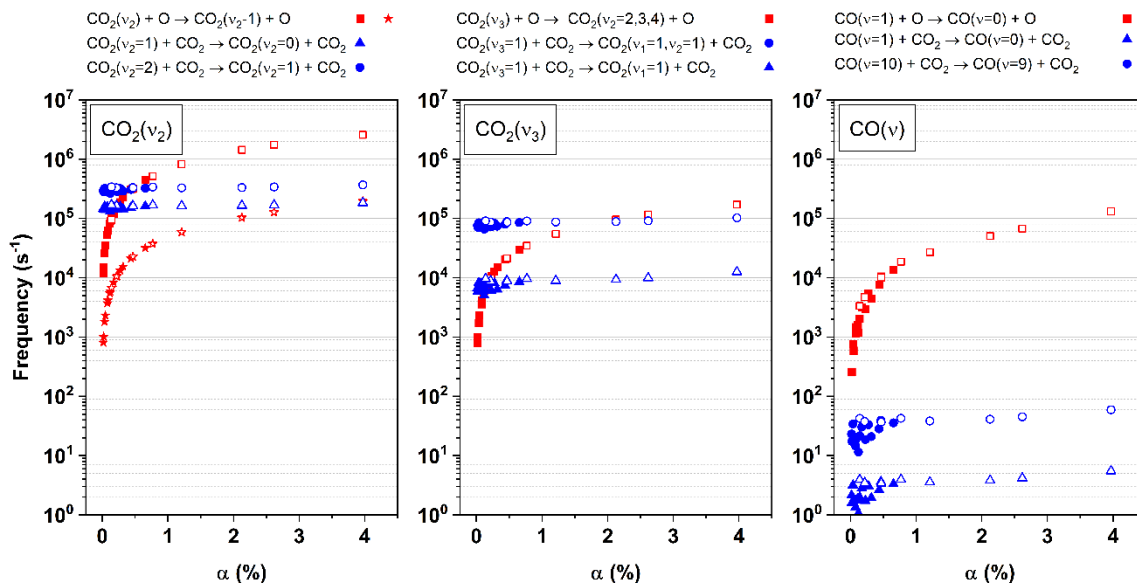


Figure 8: V-T relaxation frequencies of the vibrational levels of CO₂(v₂ and v₃) and CO(v) by collision with O and CO₂ as a function of α . Diffuse regime (Townsend) corresponds to filled shapes and filamentary regime is associated to empty shapes. The reactions involving atomic oxygen are represented in red and those involving CO₂ molecule as collision partner are in blue. Two different reaction rates, coming from [23] (■) and [44] (★), were used for the calculation of the V-T frequencies by collision with O for the symmetric bending mode (v₂).

In the filamentary regime (Figure 5b), the main difference with the results obtained in the diffuse regime concerns T_3 which is equal to T_{12} and T_{rot} . The general ordering becomes $T_{CO} > T_3 \approx T_{12} \approx T_{rot}$. Note that in addition for a given SEI, T_{CO} is systematically lower compared to the diffuse regime (from 300 K at lower SEI to 150 K i.e. above the error bar). One of the possible explanations is related to the measurement technique itself. Indeed, FTIR absorption measurements are integrated over space (along the beam path and the width of the beam) and over time. The filamentary discharge being made of numerous plasma filaments randomly distributed in time and space, an average is done during the measurements between the gas contained within the filaments and the cold gas located around. Another hypothesis is that in the filamentary regime, the dissociation of CO₂ molecules occurs within the volume of a plasma filament, which means that the local density of the dissociation products can reach high values during the filament lifetime. The aforementioned V-T processes related *e.g.* to oxygen atoms can thus be significantly higher compared to the diffuse discharge, explaining both the lower T_{CO} and T_3 even for very small SEI. This V-T processes probably also plays a role in the diffuse regime but to a lower extent: T_3 continuously decreases when increasing the SEI and approaches the value of T_{12} only for the largest SEI investigated. As a conclusion, the observed equilibrium between T_3 , T_{12} and T_{rot} in the filamentary regime probably results both from an averaging effect during the measurement and from strong V-T energy transfers due to a high O atoms density within the plasma filaments.

To go further in this discussion, an accurate determination of the O atom density is thus necessary as well as the use of a detailed modelling of the vibrational kinetics.

3. Summary and conclusion

In-situ FTIR measurements were performed in pure CO₂ DBD at atmospheric pressure in the diffuse and filamentary regimes. The results were analysed to get the dissociation fraction and the vibrational

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3 excitation of CO₂ and CO through the determination of the vibrational temperatures T_3 , T_{12} and T_{CO} of
4 the CO₂ and CO molecules, respectively. The dissociation fraction follows a power law with respect to
5 the specific energy input (SEI) with an exponent of 0.67 for both the diffuse and the filamentary
6 regimes. It is close to value of 0.75 already published in the literature [25,30]. This power law is
7 probably the result of the complex chemistry taking place in CO₂ discharges. The maximum conversion
8 rate in the investigated range of specific energy input (SEI) was about 4% at 46 000 J/l (≈ 10 eV/particle).
9 For a given SEI, the dissociation was found to be more efficient in the filamentary regime, probably due
10 to higher values of the reduced electric field. In the diffuse regime, the ordering of the different
11 temperatures is similar to what has already been reported in the literature: $T_{CO} > T_3 > T_{12} \approx T_{rot}$.
12 Nevertheless, we observed an unexpectedly significant difference between T_3 and the temperature T_{CO} .
13 Part of the explanation probably relies on the low density of CO molecules limiting the transfer between
14 vibrations of CO and the asymmetric mode of CO₂. In addition, a significant drop of T_{CO} with SEI was
15 observed for low SEI values in both discharge regimes, which was attributed to VT transfers with oxygen
16 atoms. Surprisingly in the filamentary regime, T_3 is found to be equal to T_{12} over the whole range of
17 SEI investigated. It can result from an averaging effect between the excited gas within the plasma
18 filaments and the surrounding cold gas during the absorption measurements and to strong VT transfers
19 in the filaments due to the higher density of O atoms. To go further, the possible role played by ground
20 state and excited species, such as CO($a^3\Pi$) or metastable states of molecular oxygen, would require a
21 numerical model to be investigated. In addition, the determination of the O atoms density would be
22 beneficial to definitely validate the aforementioned hypothesis, which will be the topic of future work.
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26
27
28
29
30
31
32

- 33 [1] Witteman W J 2013 *CO₂ Laser* (S.l.: Springer Berlin Heidelberg)
- 34 [2] D'Hendecourt L B and Jourdain de Muizon M 1989 The discovery of interstellar carbon dioxide.
35 *Astronomy and Astrophysics* **223** L5–8
- 36 [3] Wyckoff S and Theobald J 1989 Molecular ions in comets *Advances in Space Research* **9** 157–61
- 37 [4] Herdrich G, Auweter-Kurtz M, Kurtz H L, Laux T and Winter M 2002 Operational Behavior of
38 Inductively Heated Plasma Source IPG3 for Entry Simulations *Journal of Thermophysics and Heat*
39 *Transfer* **16** 440–9
- 40 [5] Vacher D, Lino da Silva M, André P, Faure G and Dudeck M 2008 Radiation from an equilibrium
41 CO₂-N₂ plasma in the [250–850 nm] spectral region: I. Experiment *Plasma Sources Science and*
42 *Technology* **17** 035012
- 43 [6] Lin X, Chen L Z, Li J P, Li F and Yu X L 2018 Experimental and Numerical Study of Carbon-
44 Dioxide Dissociation for Mars Atmospheric Entry *Journal of Thermophysics and Heat Transfer* **32**
45 503–13
- 46 [7] Fridman A A 2008 *Plasma chemistry* (Cambridge University Press)
- 47 [8] Capezzuto P, Cramarossa F, D'Agostino R and Molinari E 1976 Contribution of vibrational
48 excitation to the rate of carbon dioxide dissociation in electrical discharges *The Journal of Physical*
49 *Chemistry* **80** 882–8
- 50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 [9] Guerra V, Silva T, Ogloblina P, Grofulović M, Terraz L, Silva M L D, Pintassilgo C D, Alves L L
4 and Guaitella O 2017 The case for in situ resource utilisation for oxygen production on Mars by
5 non-equilibrium plasmas *Plasma Sources Science and Technology* **26**
6
- 7 [10] Premathilake D, Outlaw R A, Quinlan R A and Byvik C E 2019 Oxygen Generation by Carbon
8 Dioxide Glow Discharge and Separation by Permeation Through Ultrathin Silver Membranes *Earth
9 and Space Science* **6** 557–64
10
- 11 [11] Ogloblina P, Morillo-Candas A S, Silva A F, Silva T, Tejero-Del-Caz A, Alves L L, Guaitella O
12 and Guerra V 2021 Mars in situ oxygen and propellant production by non-equilibrium plasmas
13 *Plasma Sources Science and Technology* **30**
14
- 15 [12] Sivachandiran L, Costa P D and Khacef A 2020 CO₂ reforming in CH₄ over Ni/ γ -Al₂O₃ nano
16 catalyst: Effect of cold plasma surface discharge *Applied Surface Science* **501** 144175
17
- 18 [13] Ozkan A, Dufour T, Arnoult G, De Keyzer P, Bogaerts A and Reniers F 2015 CO₂–CH₄
19 conversion and syngas formation at atmospheric pressure using a multi-electrode dielectric barrier
20 discharge *Journal of CO₂ Utilization* **9** 74–81
21
- 22 [14] Bogaerts A, De Bie C, Snoeckx R and Kozák T 2017 Plasma based CO₂ and CH₄ conversion: A
23 modeling perspective *Plasma Processes and Polymers* **14** 1600070
24
- 25 [15] Bajon C, Dap S, Belinger A, Guaitella O, Hoder T and Naudé N 2023 Homogeneous dielectric
26 barrier discharge in CO₂ *Plasma Sources Science and Technology* **32** 045012
27
- 28 [16] Massines F, Gherardi N, Naudé N and Ségur P 2005 Glow and Townsend dielectric barrier
29 discharge in various atmosphere *Plasma Physics and Controlled Fusion* **47** B577–88
30
- 31 [17] Osawa N, Takashi A, Yoshioka Y and Hanaoka R 2013 Generation of high pressure homogeneous
32 dielectric barrier discharge in air *The European Physical Journal Applied Physics* **61** 24317
33
- 34 [18] Tyl C, Lin X, Bouzidi M C, Dap S, Caquineau H, Ségur P, Gherardi N and Naudé N 2018
35 Investigation of memory effect in atmospheric pressure dielectric barrier discharge in nitrogen with
36 small oxygen or nitric oxide addition *Journal of Physics D: Applied Physics* **51**
37
- 38 [19] Mrkvić M 2023 Electric field in APTD in nitrogen determined by EFISH, FNS/SPS ratio, α -fitting
39 and electrical equivalent circuit model *Plasma Sources Sci. Technol.*
40
- 41 [20] Massines F, Ségur P, Gherardi N, Khamphan C and Ricard A 2003 Physics and chemistry in a glow
42 dielectric barrier discharge at atmospheric pressure: diagnostics and modelling *Surface and
43 Coatings Technology* **174–175** 8–14
44
- 45 [21] Klarenaar B L M, Engeln R, van den Bekerom D C M, van de Sanden M C M, Morillo-Candas A
46 S and Guaitella O 2017 Time evolution of vibrational temperatures in a CO₂ glow discharge
47 measured with infrared absorption spectroscopy *Plasma Sources Science and Technology* **26**
48 115008
49
- 50 [22] Klarenaar B L M, Morillo-Candas A S, Grofulović M, Sanden M C M van de, Engeln R and
51 Guaitella O 2019 Excitation and relaxation of the asymmetric stretch mode of CO₂ in a pulsed glow
52 discharge *Plasma Sources Science and Technology* **28** 035011
53
- 54 [23] Morillo-Candas A S, Klarenaar B L M, Amoedo C, Guerra V and Guaitella O 2020 Effect of
55 oxygen atoms on the vibrational kinetics of CO₂ and CO revealed by the use of a large surface area
56 material *Journal of Physics D: Applied Physics* **54**
57
58
59
60

- 1
2
3 [24] Morillo-Candas A S, Guerra V and Guaitella O 2020 Time Evolution of the Dissociation Fraction
4 in rf CO₂ Plasmas: Impact and Nature of Back-Reaction Mechanisms *Journal of Physical Chemistry*
5 *C* **124** 17459–75
6
7 [25] Brehmer F, Welzel S, Van De Sanden M C M and Engeln R 2014 CO and byproduct formation
8 during CO₂ reduction in dielectric barrier discharges *Journal of Applied Physics* **116**
9
10 [26] Urbanietz T, Böke M, Schulz-von der Gathen V and von Keudell A 2018 Non-equilibrium
11 excitation of CO₂ in an atmospheric pressure helium plasma jet *Journal of Physics D: Applied*
12 *Physics* **51** 345202
13
14 [27] Stewig C, Schüttler S, Urbanietz T, Böke M and von Keudell A 2020 Excitation and dissociation
15 of CO₂ heavily diluted in noble gas atmospheric pressure plasma *Journal of Physics D: Applied*
16 *Physics* **53** 125205
17
18 [28] Naudé N, Cambronner J-P, Gherardi N and Massines F 2005 Electrical model and analysis of the
19 transition from an atmospheric pressure Townsend discharge to a filamentary discharge *Journal of*
20 *Physics D: Applied Physics* **38** 530–8
21
22 [29] Brandenburg R, Schiorlin M, Schmidt M, Höft H, Pipa A V and Brüser V 2023 Plane Parallel
23 Barrier Discharges for Carbon Dioxide Splitting: Influence of Discharge Arrangement on Carbon
24 Monoxide Formation *Plasma* **6** 162–80
25
26 [30] Douat C, Ponduri S, Boumans T, Guaitella O, Welzel S, Carbone E and Engeln R 2023 The role
27 of the number of filaments in the dissociation of CO₂ in dielectric barrier discharges *Plasma*
28 *Sources Science and Technology* **32** 055001
29
30 [31] Salden A, Budde M, Garcia-Soto C A, Biondo O, Barauna J, Faedda M, Musig B, Fromentin C,
31 Nguyen-Quang M, Philpott H, Hasrack G, Aceto D, Cai Y, Jury F A, Bogaerts A, Da Costa P,
32 Engeln R, Gálvez M E, Gans T, Garcia T, Guerra V, Henriques C, Motak M, Navarro M V,
33 Parvulescu V I, Van Rooij G, Samojeden B, Sobota A, Tosi P, Tu X and Guaitella O 2023 Meta-
34 analysis of CO₂ conversion, energy efficiency, and other performance data of plasma-catalysis
35 reactors with the open access PIONEER database *Journal of Energy Chemistry* **86** 318–42
36
37 [32] Lin X, Tyl C, Naudé N, Gherardi N, Popov N A and Dap S 2020 The role of associative ionization
38 reactions in the memory effect of atmospheric pressure Townsend discharges in N₂ with a small O
39 ₂ addition *Journal of Physics D: Applied Physics* **53** 205201
40
41 [33] Snoeckx R and Bogaerts A 2017 Plasma technology-a novel solution for CO₂ conversion?
42
43 [34] Tyl C, Martin S, Combettes C, Brillat G, Bley V, Belinger A, Dap S, Brandenburg R and Naudé N
44 2021 New local electrical diagnostic tool for dielectric barrier discharge (DBD) *Review of Scientific*
45 *Instruments* **92** 053552
46
47 [35] Belinger A, Dap S and Naudé N 2022 Influence of the dielectric thickness on the homogeneity of
48 a diffuse dielectric barrier discharge in air *J. Phys. D: Appl. Phys.* **55** 465201
49
50 [36] Pietanza L D, Guaitella O, Aquilanti V, Armenise I, Bogaerts A, Capitelli M, Colonna G, Guerra
51 V, Engeln R, Kustova E, Lombardi A, Palazzetti F and Silva T 2021 Advances in non-equilibrium
52 CO₂ plasma kinetics: a theoretical and experimental review
53
54 [37] Ponduri S, Becker M M, Welzel S, Van De Sanden M C M, Loffhagen D and Engeln R 2016 Fluid
55 modelling of CO₂ dissociation in a dielectric barrier discharge *Journal of Applied Physics* **119**
56
57
58
59
60

- 1
2
3 [38] Jánský J, Bessiéres D, Brandenburg R, Paillol J and Hoder T 2021 Electric field development in
4 positive and negative streamers on dielectric surface *Plasma Sources Science and Technology* **30**
5 105008
6
- 7 [39] Aerts R, Somers W and Bogaerts A 2015 Carbon Dioxide Splitting in a Dielectric Barrier Discharge
8 Plasma: A Combined Experimental and Computational Study *ChemSusChem* **8** 702–16
9
- 10 [40] Otorbaev D K 1995 Catalytic properties of surfaces with respect to generation of CO₂ molecules
11 in the plasma *Chemical Physics* **196** 543–50
12
- 13 [41] Morillo-Candas A S, Drag C, Booth J P, Dias T C, Guerra V and Guaitella O 2019 Oxygen atom
14 kinetics in CO₂ plasmas ignited in a DC glow discharge *Plasma Sources Science and Technology*
15 **28**
16
- 17 [42] Cenian A, Chernukho A, Borodin V and Śliwiński G 1994 Modeling of Plasma-Chemical
18 Reactions in Gas Mixture of CO₂ Lasers I. Gas Decomposition in Pure CO₂ Glow Discharge
19 *Contributions to Plasma Physics* **34** 25–37
20
- 21 [43] Bird R B, Stewart W E and Lightfoot E N 2007 *Transport phenomena* (New York: Wiley)
22
- 23 [44] Fromentin C, Silva T, Dias T C, Morillo-Candas A S, Biondo O, Guaitella O and Guerra V 2023
24 Study of vibrational kinetics of CO₂ and CO in CO₂–O₂ plasmas under non-equilibrium conditions
25 *Plasma Sources Science and Technology* **32** 024001
26
- 27 [45] Ehrhardt H, Langhans L, Linder F and Taylor H S 1968 Resonance Scattering of Slow Electrons
28 from H₂ and CO Angular Distributions *Physical Review* **173** 222–30
29
- 30 [46] Lopez-Puertas M and Taylor F W 2001 *Non-LTE radiative transfer in the atmosphere* (Singapore:
31 World Scientific Publ. Co)
32
- 33 [47] López-Puertas M, Rodrigo R, Molina A and Taylor F W 1986 A non-LTE radiative transfer model
34 for infrared bands in the middle atmosphere. I. Theoretical basis and application to CO₂ 15 μm
35 bands *Journal of Atmospheric and Terrestrial Physics* **48** 729–48
36
- 37 [48] Blauer J and Nickerson G 1974 A survey of vibrational relaxation rate data for processes
38 important to CO₂-N₂-H₂O infrared plume radiation *7th Fluid and Plasma Dynamics Conference* 7th
39 Fluid and Plasma Dynamics Conference (Palo Alto, CA, U.S.A.: American Institute of Aeronautics
40 and Astronautics)
41
- 42 [49] Capitelli M, Ferreira C M, Gordiets B F and Osipov A I 2000 *Plasma Kinetics in Atmospheric*
43 *Gases*
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60