

LETTER

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Letter

Electron impact dissociation of CO₂

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Abstract

Several CO₂ electron impact dissociation cross sections are available in the literature, different in magnitude and threshold, hindering the understanding of CO₂ dissociation mechanisms under gas discharges. This work reports the experimental validation of the electron impact CO₂ dissociation cross section using two complementary methods: through the comparison of the measured rate coefficients with those derived from cross sections available in literature; and through the comparison of the experimental time evolution of the dissociation fraction with the simulations of a 0D model. A careful experimental approach was designed to avoid any influence from other dissociation mechanisms or chemical reactions. The experimental results match remarkably well the theoretical predictions from Polak and Slovetsky and establish the validity of the dissociation rate coefficients derived from their cross section. This validation supports the use of Polak and Slovetsky's cross section in any theoretical or modelling approach involving CO₂ molecules under electrical discharges.

Keywords: CO₂ dissociation, CO₂ plasma, low temperature plasma, electron impact dissociation cross section, rate coefficient, glow discharge

CO₂ plasmas have been attracting growing interest for the last few years. CO₂ emissions could be reused to produce different fuels and chemicals [1], contributing to mitigate the climate change. In this regard, low-temperature plasmas are potentially more efficient than thermal dissociation [2] (reported efficiencies are close to 90% [3]) and allow an easy use of intermittent energy sources, such as renewable energies [4, 5]. The study of CO₂ plasmas is also important for space mission research to simulate the entry in the atmospheres of Mars and Venus [6], where CO₂ is the dominant compound. A related hot topic focus on the *in situ* resource utilization on Mars for future missions, such as oxygen production from Mars atmosphere [7, 8]. The use of plasmas for surface treatment processes on carbon-containing substrates such as

polymers [9], glassy carbon [10], carbon nano-structures [11, 12] or graphene [13, 14] is also a new and interesting subject. Surface treatment processes can either use CO₂ plasma, or O₂ plasma forming CO₂ molecules at the surface [15]. For all these applications understanding the CO₂ dissociation mechanism is essential to control the induced chemistry.

CO₂ can be dissociated in low-temperature plasmas by direct electron impact. This process has an energy threshold above 7 eV, producing CO or O in an electronically excited state (the production of ground state CO(X¹Σ⁺) + O(³P) is spin-forbidden). An indirect dissociation route is the so-called vibrational up-pumping mechanism, where the energy given by low energy electrons ~1 eV is transferred to the asymmetric stretch vibrational mode of CO₂ [16, 17]. The exchange of vibrational quanta between molecules may lead

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to highly vibrational excited molecules, reaching the dissociation level (~ 5.5 eV) [3] and producing ground state CO and O atoms. Nevertheless, in many plasma regimes electron impact dissociation is the main path for the CO₂ dissociation and it is a key process in any CO₂-containing gas discharge. The cross section for this process is reported by several authors. However, the proposed values differ significantly both in threshold and in magnitude as a function of the electron energy [18]. Consequently, the derived rate coefficients are orders of magnitude different, which has a direct impact in the modelling predictions [19].

A detailed review of the available electron impact cross sections is given by Grofulović *et al* [18]. In summary, Itikawa [20, 21] reports a single mechanism with a threshold energy around 11.9 eV, leading to the production of O(¹S), based on measurements by LeClair and McConkey [22]. This cross section was adopted for example in [23, 24]. Similar variation as a function of the reduced electric field, although up to a factor 5 larger, and with slightly higher energy threshold is given by Cosby and Helm [25], obtained by crossed beam experiments and claimed to correspond to two dissociation channels giving CO(X¹Σ⁺) + O(¹S) and CO(a³Π) + O(³P) and it is used in [26].

The cross sections reported by Phelps [27, 28] are widely used in the literature [29–33]. Phelps' cross section was derived from the comparison between predicted and measured swarm parameters (transport coefficients) for pure CO₂ and CO₂ laser gas mixtures (CO₂–He–N₂) [34, 35]. The set contains two electronic excitation cross sections, with thresholds at 7 and 10.5 eV. The 7 eV cross section is often used to calculate the dissociation rate coefficient [29–33]. The cross section calculated theoretically by Polak and Slovetsky [36], used in [3, 18], also includes two excitation/dissociation channels, but smaller in magnitude and with thresholds shifted towards higher energy values (~ 7.5 and 11.9 eV). Corvin and Corrigan [37] built a cross section from their measured rate coefficient assuming a Maxwellian distribution of electron energies, defining a single process with threshold at 6 eV. The corresponding rate coefficient falls in between those calculated using Phelps' and Polak's cross section for the high reduced electric field (E/N , where E is the electric field and N the gas density) range, but they are up to two orders of magnitude higher for low E/N [18].

This short compilation illustrates the discrepancies found in the literature for the CO₂ electron-impact dissociation cross section. The lack of experimental data and validation for this cross section is a bottleneck for the understanding of CO₂-containing plasmas [26]. The objective of this work is to provide an experimental validation of the CO₂ electron impact dissociation cross section. To this aim, we have designed an experiment, so-called 'building-up', performed in static conditions (closed reactor, without gas flow), which allows to follow the evolution of a fixed amount of CO₂ molecules and the dissociation products. We compare our experimental values for the rate coefficient with those derived from various cross sections available in literature. A comparison with results of a 0D model [38, 39] provides an alternative validation and reinforces the experimental conclusions.

In the building-up experiment, a defined number of plasma pulses is ignited while consecutive measurements of the CO and CO₂ concentrations by infra-red absorption provide the time evolution of the dissociation fraction up to the steady-state value. A glow discharge was chosen as plasma source because of the homogeneity of its positive column [40], which leads to several diagnostic advantages: (1) the determination of the electric field is straightforward, allowing an easy and accurate estimation of the electron density, (2) the plasma volume is well defined and constrained between the electrodes, and (3) it allows line-of-sight integrated diagnostics, such as *in situ* Fourier transform infra-red (FTIR) absorption spectroscopy [41, 42]. These characteristics led to a successful comparison with a 0D kinetic model discussing the electron and vibrational kinetics of CO₂ under negligible CO₂ dissociation conditions [38, 39]. In this study, we make use of experimental data from previous works obtained in similar conditions concerning O atom densities [43], vibrational kinetics in the discharge and the time evolution of the gas temperature along a plasma pulse [41, 44].

The pulsed DC glow discharge was ignited at pressures between 0.4 and 5 Torr and currents between 20 and 50 mA, in a cylindrical Pyrex (2 cm inner diameter and 23 cm length) tube positioned in the sample compartment of a FTIR spectrometer (Bruker, Vertex 70) with a spectral resolution of 0.2 cm⁻¹, as shown schematically in figure 1(a). In static conditions at the working pressures a pre-treatment of the reactor walls is required to achieve good reproducibility. The pre-treatment consisted in 15 minutes of pure O₂ continuous DC plasma at 40 mA, 1.5 Torr [45], with a constant 7.4 sccm gas flow, followed by 10 minutes of CO₂ gas flow (no plasma) at similar pressure and flow. Following this procedure, the measurements start always with the same surface conditions and very good reproducibility was achieved.

The reactor is then filled with pure CO₂ at the targeted pressure and closed. A trigger signal provided by the FTIR, operated in rapid scan mode, triggers a train of plasma pulses, whose characteristics are defined by two signal generators (SG): SG1, triggered by the FTIR, defines the number of pulses within a train by adjusting the gate duration; SG2, gated by SG1, controls the pulse duration and the delay between pulses within a train, and triggers the DC pulsed power supply. After every train, an IR absorption measurement with the plasma OFF (the gas in thermal equilibrium) is acquired before the next trigger. The default train configuration is 10 pulses of $t_p^{\text{ON}} = 5$ ms plasma ON and $t_p^{\text{OFF}} = 10$ ms plasma OFF, which gives a total plasma ON per train $t_{\text{tr}}^{\text{ON}} = \sum t_p^{\text{ON}} = 50$ ms. This procedure, schematically presented in figure 1(b), is repeated until the total accumulated plasma ON time $T^{\text{ON}} = \sum t_{\text{tr}}^{\text{ON}}$ is around 25 s (500 trains). The obtained spectra are analysed using an algorithm described in [41] providing the molecular densities of CO and CO₂. For the calculation of the reduced electric field the values of the gas temperature during the plasma pulse measured in similar experimental conditions [43, 44] were used. The axial electric field was obtained from the voltage drop across the positive column of the glow discharge between two tungsten probes embedded in the Pyrex tube and matches the modelling predictions [39].

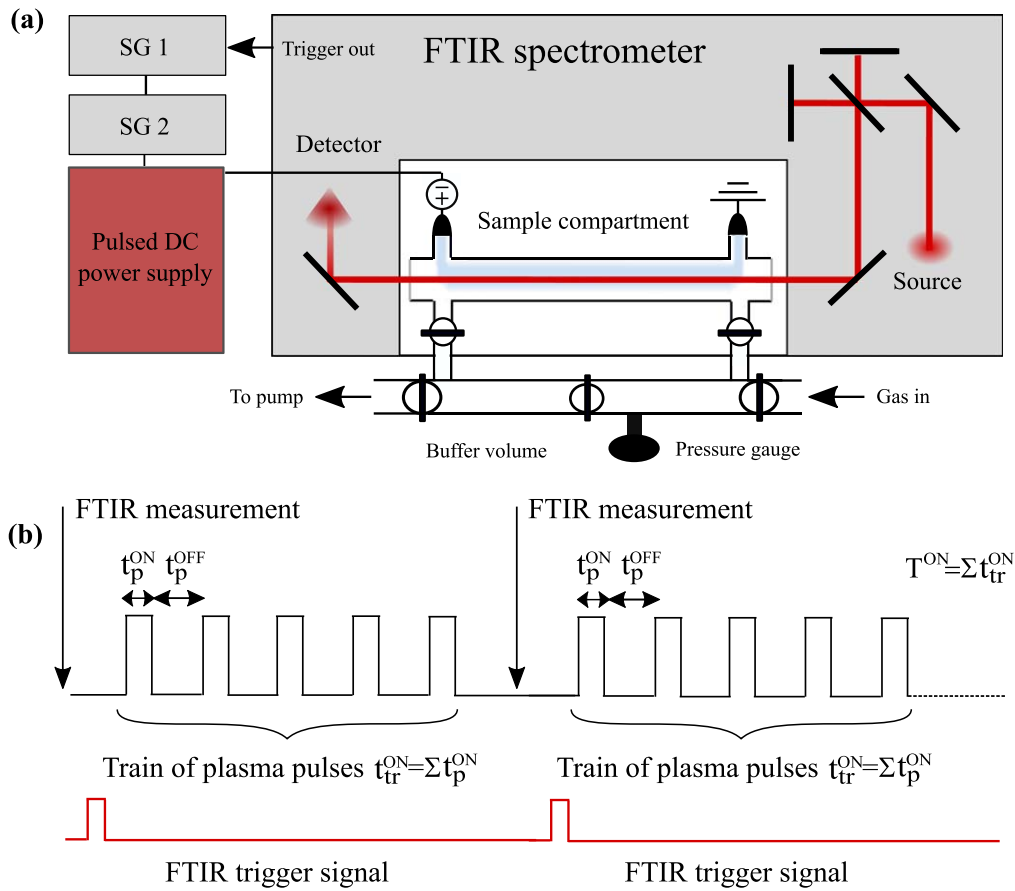


Figure 1. Experimental set-up (a) and measurement scheme (b).

The time evolution of the dissociation fraction, represented by the parameter $\alpha = \frac{CO}{CO + CO_2}$, is shown in figure 2. For every plasma condition, α shows an initial fast increase followed by a saturation towards longer T^{ON} times. Figure 2(a) plots the variation of α as a function of T^{ON} for two pressures, 1 and 2 Torr, and three discharge currents: 20, 30 and 40 mA. Evidently, higher currents make the time evolution, i.e. the kinetics of the discharge, faster. This graph includes two measurements for the same condition, 2 Torr and 40 mA, to show the reproducibility reached in the experiment. Figure 2(b) presents the time evolution of α for several different pressures at a given current (40 mA). Lower pressures show a faster and sharper increase of the dissociation fraction; consequently, the final equilibrium concentration is reached for shorter T^{ON} than at higher pressures. The effect of the current can be explained mostly by the increase of the electron density when the current increases, along with a small contribution of the slightly higher reduced electric field. In these conditions the electric field decreases slightly as a function of current but the reduced electric field still increases due to the higher gas temperature [43]. The time variation of α for different pressures is mostly dominated by the effect of the reduced electric field. Although the electric field increases as a function of pressure, the reduced electric field decreases significantly [43].

It is noticeable that for short total plasma ON times (typically $T^{ON} < 0.6$ s), the evolution of the dissociation fraction with time is *quasi* linear (small deviations for low pressures are discussed below). This behaviour can be explained by a first-order process: electron impact dissociation of CO_2 : $e^- + CO_2 \rightarrow CO + O$, which can be described by the first-order rate equation:

$$\frac{d[CO]}{dt} = K_{diss} \cdot n_e \cdot [CO_2] \rightarrow [CO] = n_e \cdot K_{diss} \cdot [CO_2] \cdot T^{ON}, \quad (1)$$

where n_e is the electron density, K_{diss} the dissociation rate coefficient, $[CO_2]$ and $[CO]$ the measured CO_2 and CO densities at each time point and T^{ON} is the plasma ON time.

In order to be sure that the initial slope is defined only by the CO_2 electron impact dissociation and can be used to determine the corresponding rate coefficient, we must verify that neither the dissociation through vibrational up-pumping nor the possible occurrence of recombination reactions, such as that between CO and O , affect the measured CO and CO_2 densities in the relevant time range. Firstly, the dissociation through vibrational up-pumping is not expected to show a linear time evolution since it is not a first order process. In addition, the density of the individual vibrationally excited levels was measured in similar experimental conditions [38, 39, 44], and was shown to be relatively low, as expected

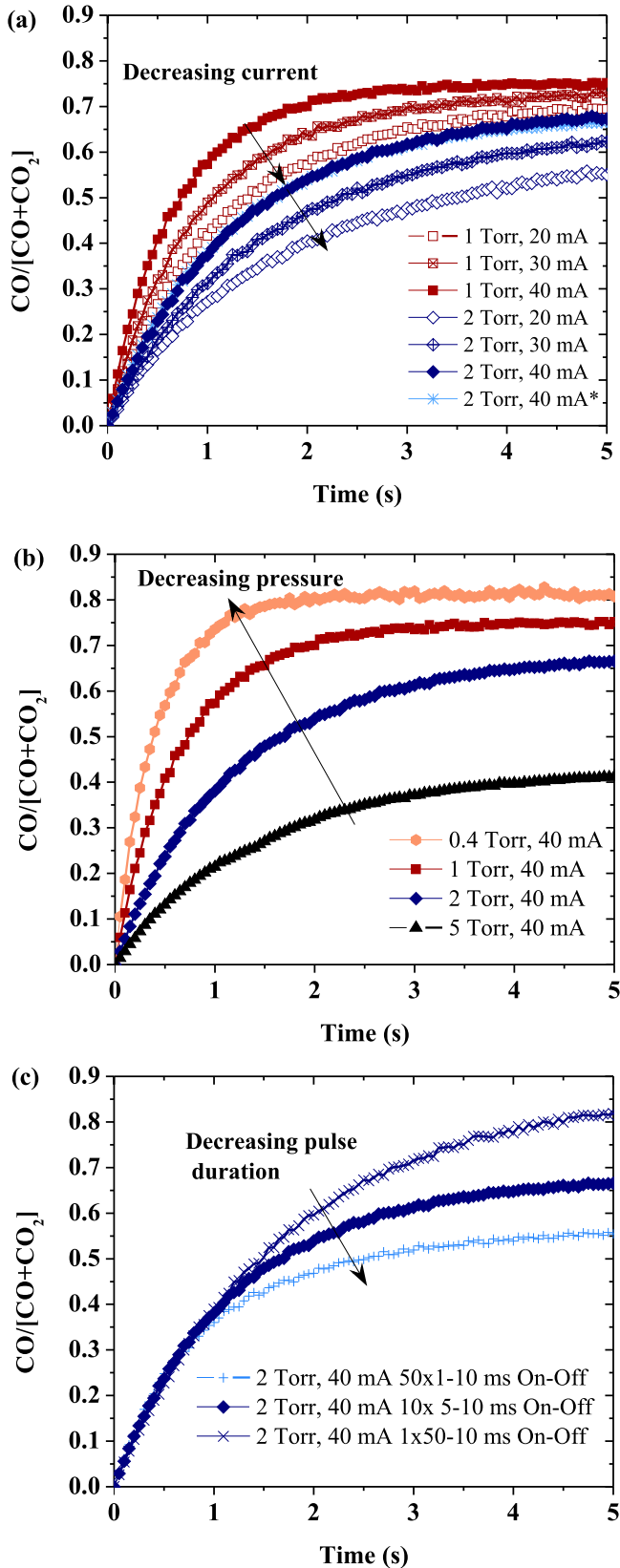


Figure 2. Time evolution of the dissociation fraction (a) for two pressures (1 and 2 Torr) and three different currents 20, 30 and 40 mA, and (b) for different pressures at 40 mA (c) for different pulse durations at 2 Torr, 40 mA.

in a glow discharge regime. The maximum of vibrational excitation in the asymmetric stretch mode of CO_2 was reached ~ 1 ms after the beginning of the plasma pulse, followed by a relaxation due to vibrational–translational (V–T) energy exchanges [39, 44]. As example, at 5 Torr 50 mA, at the maximum of vibrational excitation the density of CO_2 molecules in $\nu_3 = 1$ was found to be 0.018 times the density in ground state ($\nu_3 = 0$). For $\text{CO}_2(\nu_3 = 2)$ is 3.4×10^{-4} times the ground state density. To confirm the negligible role of vibrationally induced dissociation for the conditions under study, we varied the pulse duration in our experiment for one discharge condition (2 Torr and 40 mA) igniting 50 pulses $\times t_p^{\text{ON}} = 1$ ms ON – $t_p^{\text{OFF}} = 10$ ms OFF and 1 pulse $\times t_p^{\text{ON}} = 50$ ms ON – $t_p^{\text{OFF}} = 10$ ms OFF per train. The measured time evolution of α for these conditions is shown in figure 2(c). Despite the different average vibrational excitation [44], the initial slope for short T^{ON} is unchanged. Contrary to the initial slope, the dissociation fraction for long T^{ON} is significantly affected by the pulse duration. This is probably related with the occurrence of recombination reactions, involving CO and oxygen, and producing back CO_2 . We therefore conclude that the dissociation through vibrational up-pumping does not contribute to the dissociation fraction in the present discharge conditions for short T^{ON} .

Concerning the recombination rate between CO and O, it was found to be at least two orders of magnitude lower than the recombination of O atoms into O_2 in similar conditions [43], according to the rate coefficients from NIST, widely used in literature [32, 46]. This rate increases with temperature, which increases with pressure [43, 44]. However, the largest concentrations of CO in our discharge are for very low pressures. In addition, by choosing to run experiments with a limited number of trains of plasma pulses, we limit the accumulation of O atoms, since they get recombined in between trains (the time between trains is ~ 2 s, whereas the O atom life-time is ~ 50 – 100 ms [43]). Additional tests with O_2 add-mixtures in a similar experimental set-up and similar excitation regime, but with a radio frequency discharge showed that adding O_2 to the initial gas mixture (even for 25% CO_2 –75% O_2) had no effect on the initial slope, whereas a clear effect starts to be noticeable after a certain time point, ~ 0.4 s of T^{ON} [47]. Hence, only data corresponding to $T^{\text{ON}} < 0.3$ s were kept for the calculation of the rate coefficient. Lastly, the high amount of CO for low pressures could suggest the possibility of CO dissociation by electron impact. However, it is not expected to be very relevant due to the high energy threshold, estimated to be above 10 eV [36], and the typical electron energy distribution function (EEDF) in our conditions [18]. Still, only data with a CO/N ratio below 30% and showing a clearly linear time variation in α versus T^{ON} were kept to insure a minimal influence of other processes on the determination of the rate coefficients.

The electric field was measured for each data point matching these conditions. Note that CO affects significantly the electric field in the discharge, being especially important at

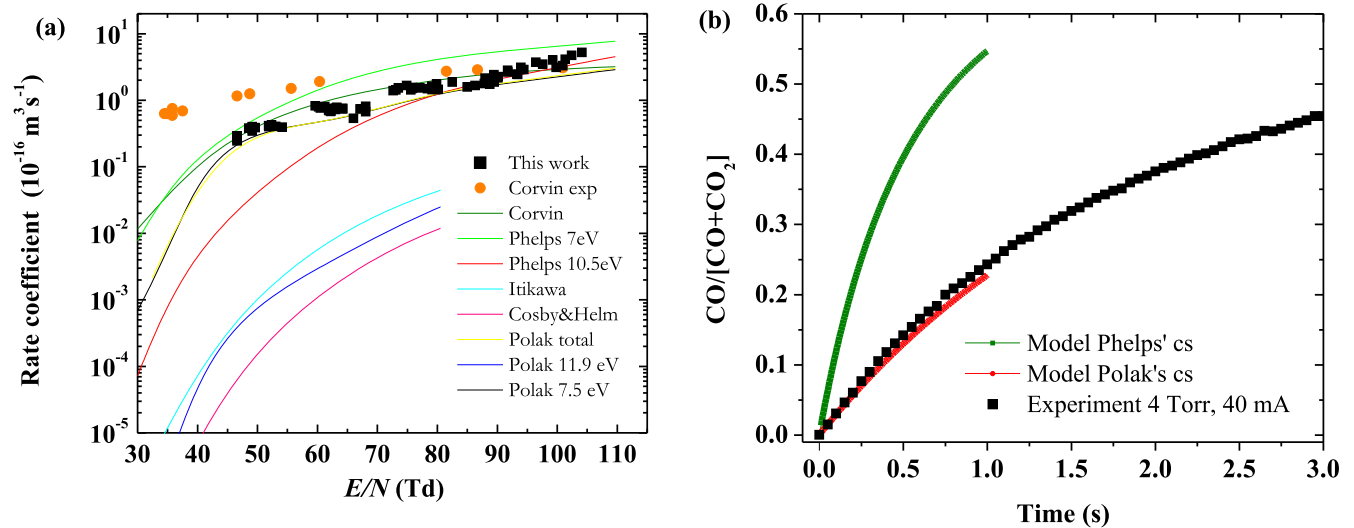


Figure 3. (a) Rate coefficients for the electron impact dissociation of CO_2 calculated from the experimental data compared with values obtained from theoretical cross section from literature [18]. (b) Comparison of experimental data at 4 Torr 40 mA with a 0D model using Polak's or Phelps' electron impact dissociation cross sections.

low pressures. As example, at 1 Torr, 20 mA the electric field changes from 19.3 V cm^{-1} at $T^{\text{ON}} = 0.05 \text{ s}$ to 16.4 V cm^{-1} at $T^{\text{ON}} = 0.3 \text{ s}$. From the reduced electric field (E/N), we calculate the electron drift velocity through a fitting of data available in LXCat database [48]. The electron density is calculated with:

$$n_e = \frac{J}{e \cdot v_d}, \quad (2)$$

where J is the current density ($J = \frac{I}{S}$, I being the discharge current and S the transversal area of the plasma reactor), e is the electron charge and v_d the electron drift velocity. For low pressures, the first 2 or 3 trains of pulses present a certain over-shoot in the discharge current ($\sim 20\%$ higher than targeted). The real current was recorded by the oscilloscope and taken into account in the calculations. Substituting the measured CO and CO_2 densities and the calculated n_e values in equation (1) we obtained the rate coefficients for the electron impact dissociation of CO_2 . These values are plotted in figure 3(a) along with the rate coefficients calculated from the available cross sections by direct integration over the EEDF in [18].

The agreement between the experimental rate coefficients and the values obtained from the cross section proposed by Polak and Slovetsky 'Polak total' [36] is remarkable. The main contribution to the total cross section comes from the cross section with threshold at $\sim 7.5 \text{ eV}$, which includes excitations of allowed and forbidden transitions between 7 and 9 eV [36]. A significantly smaller contribution is due the dissociation mechanism leading to the formation of the $\text{CO}(a^3\Pi)$, at $\sim 11.9 \text{ eV}$. The experimental rate coefficients are significantly lower than those calculated from the 7 eV cross section from Phelps. Note that the precision on the determination of CO_2 and CO densities is in the order of 10^{19} m^{-3} , to be compared with absolute densities in the order of $10^{21}\text{--}10^{23} \text{ m}^{-3}$. The error associated with the experimental rate coefficients is then mostly related to the determination of the electron density. The reproducibility error on the E/N determination is around 7.2%, which leads to an average error

in the rate coefficients around 2.5%. Apart from the error derived from the determination of E/N , the use of the data from [48] for pure CO_2 could be a source of error in the calculation of the drift velocity from the reduced electric field. The error in this case is maximum for the lowest E/N (highest pressures), but even at $\sim 50 \text{ Td}$ and considering 20% of CO in the gas mixture, it is still below 3% [51]. We therefore consider that the experimental error does not affect the conclusions on the CO_2 electron impact dissociation cross section. The obtained experimental rate coefficients are also relatively close to those calculated from the cross section proposed by Corvin and Corrigan, derived assuming a Maxwellian distribution of electron energies. However, they are significantly different to their experimental rate coefficients [37] particularly in the range of low E/N . The reasons for this discrepancy are unclear but could be related to the larger uncertainties of the methods used to measure the CO_2 and CO densities, based on the change of pressure due to the dissociation products. The method used to determine the reduced electric field by varying the distance between the electrodes or differences in the calculation of the EEDF could also explain these discrepancies. As final comment, in the present experimental conditions it was difficult to ignite the glow discharge at pressures above 5 Torr. Consequently it was not possible to explore E/N values below $\sim 45 \text{ Td}$, which would require a significant increase of the initial pressure [43].

The same conclusions extracted from the comparison between the experimental rate coefficients and those derived from available cross sections is obtained when comparing the time-evolution of the dissociation fraction with the predictions of a 0D kinetic model. The calculations are based on a model previously validated that solves on time the electron and vibrational kinetics of CO_2 and takes into account the time evolution of the gas temperature and the electric field along a plasma pulse [38, 39], to which a simple set of reactions describing CO_2 dissociation and recombination (detailed in table 1) was added for completeness. We have

Table 1. Set of chemical reactions included in the model. Reactions accounting for the electron and vibrational kinetics of CO₂ are detailed in [38, 39].

Reaction	References
$e^- + \text{CO}_2(v^*) \rightarrow e^- + \text{CO} + \text{O}$	[36] or [28]
$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2(000) + \text{M}$	[26, 46]
$e^- + \text{O}_2 \rightarrow e^- + \text{O} + \text{O}$	[49]
$\text{O} + \text{wall} \rightarrow 1/2 \text{O}_2$	[43]
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	[50]

verified that the inclusion of these reactions leads to differences in the modelled evolution of less than 1% up to $T^{\text{ON}} = 0.4$ s. The model considers the average experimental E/N value, which for the condition plotted in figure 3(b) varies between ~ 52 and 55 Td. The electron density profile along the plasma pulse was considered either constant or similar to that discussed in [39], having no influence in the modelled time evolution. Electron impact dissociation from vibrationally excited molecules was taken into account in the model either with the same rate coefficient as from the ground (000) state or using a threshold shift in the cross section [32]. The results are not affected by the assumption considered. Indeed, the only vibrational level with a significant population density is the first level of the bending vibrational mode, CO₂(010), with maximum values up to 0.29 times the density of the ground state, for the highest pressures and currents [39]. However, the inclusion of this level in the calculations has a negligible effect in the modelled dissociation due to its low energy, ~ 0.08 eV, above the ground state. As shown in figure 3(b), the model reproduces very well the experimental data for short T^{ON} when using Polak's CO₂ electron impact dissociation cross section, whereas Phelps' over-estimates the dissociation. The general trend of a much better agreement with the experimental data when using Polak's cross section is extended to the other conditions of this study. For instance, at 1 Torr 40 mA the dissociation fraction obtained using Phelps' cross section is always larger than twice the experimental values, whereas with Polak's cross section, the obtained values are similar to the experiment within an error $\sim 25\%$. The larger error in this case is due to the assumption of a constant E/N in the model, which is more realistic at the higher pressures, where the variation of E/N due to the increasing CO content is small, but is less accurate at the lower pressures for which the CO and the E/N variation is larger.

Summarizing, a careful experimental approach allowed to establish the validity of the CO₂ electron impact dissociation cross section calculated by Polak and Slovetsky by two complementary methods: (1) comparing directly the experimental electron impact dissociation rate coefficients with those derived from their calculation by direct integration of the available cross sections over the EEDF; (2) comparing the experimental time evolution of the dissociation fraction with the results of a 0D model. This validation suggests and

agrees with the hypothesis that the cross sections proposed by Phelps probably include energy loss processes besides dissociation [18]. The authors therefore recommend the use of Polak and Slovetsky's cross section for the calculation of the CO₂ electron impact dissociation rate under discharge conditions.

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