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CO and byproduct formation during CO2 reduction in dielectric barrier discharges

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The dissociation of CO2 and the formation of CO, O, and O2 were studied in a dielectric barrier discharge (DBD) at atmospheric pressure by means of ex-situ infrared absorption spectroscopy. CO mixing ratios of 0.1%–4.4% were determined for specific injected energies between 0.1 and 20 eV per molecule (0.3–70 kJ/l). A lower limit of the gas temperature of 320–480 K was estimated from the wall temperature of the quartz reactor as measured with an infrared camera. The formation of CO in the DBD could be described as function of the total number of transferred charges during the residence time of the gas in the active plasma zone. An almost stoichiometric CO:O2 ratio of 2:1 was observed along with a strongly temperature dependent O2 production up to 0.075%. Although the ideal range for an efficient CO2 dissociation in plasmas of 1 eV per molecule for the specific injected energy was covered, the energy efficiency remained below 5% for all conditions. The present results indicate a reaction mechanism which is initiated by electron impact processes followed by charge transfer reactions and non-negligible surface enhanced O and CO recombinations. While electron-driven CO2 dissociation is relatively energy inefficient by itself, fast O recombination and the low gas temperatures inhibit the synergistic reuse of atomic oxygen in a secondary CO2 + O dissociation step. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

The decrease in fossil fuel consumption is undoubtedly one of the most demanding missions in the next decades to cut down the emission of greenhouse gases and to reduce the reliance on fossil fuels, along with energy security and geopolitical issues. Obviously, both the transport and the industrial sectors will play key roles during the transformation into a low-carbon, energy-efficient society. However, the intermittency of renewable sources in conjunction with the absence of useful storage solutions hamper presently an integration of wind or photovoltaics into energy-intensive industries. Additionally, the direct introduction of sustainable energy into, e.g., the value chain of chemical industry remains challenging: Heat is the desired form of energy, whereas renewables are frequently harvested in the form of electricity.1

Therefore, carbon dioxide is often considered as the key molecule, also called energy vector, in many strategies to replace conventional energy sources by renewable ones. Although the dissociation of CO2 is a strongly endothermic process, a sustainable production of CO or synthesis gas (syngas, CO + H2) would be an elegant route to implement renewable energy into the chemical production chain while adding value to the waste gas CO2.1,2 At the same time, renewable energy would be stored in high energy-density chemical fuels, also known as solar or CO2-neutral fuels, which can straightforwardly be integrated into the existing transport infrastructure. Carbon capture will thereby help closing the carbon cycle and reducing the global CO2 emissions.3,4

Promising candidates to dissociate CO2 energy-efficiently in the gas phase are cold, non-thermal plasmas.2 These electrical discharges are characterized by non-equilibrium conditions under which electrons, ions, and neutral species have different translational and — in case of molecules — internal energies. The corresponding energy distribution functions may be described by separate temperature functions with unequal electron, gas, and vibrational temperatures provide an entirely different environment for chemical reactions than known from conventional processing under thermal equilibrium. Thus, particularly for endothermic chemical processes increased energy efficiencies or conversion yields may be obtained.5,6

Already in 1925 Wendt and Farnsworth reported such effects in a corona discharge used for the dissociation of CO2.7 The most promising energy efficiencies and dissociation degrees of CO2 in non-equilibrium plasmas were shown in the in the 1970s using radio frequency and microwave discharges at sub-atmospheric pressure conditions. These studies tried to highlight the importance of vibrationally excited states, more specifically of the asymmetric stretch vibration, in order to efficiently dissociate CO2 and obtain energy efficiencies as high as 80%.8–10 Later, the experimental results were theoretically supported.11,12 According to this theory, the energy efficiency can be maximized at specific injected energies in the range of 0.5–2 eV per molecule (1.9–7.7 kJ/l) while keeping the averaged electron kinetic energies relatively low at around 1–2 eV.

Although such low electron energies are difficult to achieve in Dielectric Barrier Discharges (DBDs) the
CO$_2$ dissociation studies in DBDs at atmospheric pressure have a long history: the probably first experiments carried out by Thenard date back to 1872. Thénard observed 4%–8% CO$_2$ dissociation in a classical ozonizer and could increase the CO yield to 26.5%. Unfortunately, the reaction products were de-ozonized with potassium hydroxide solution while separating them from CO$_2$. Brodie corrected for this and found a dissociation degree of 1.5%–2.7%, in which an average of 50% of the produced oxygen was ozonized. Interestingly, this study initially aimed at increasing the O$_3$ yield in a DBD by using a gas that was expected to be inert, namely, CO$_2$, as substitute for O$_2$. However, the final gas mixtures contained more O$_2$ than injected into the discharge tube. The apparent net production of O$_2$ triggered experiments on undiluted CO$_2$. More systematic studies on the dissociation of CO$_2$ in a sealed ozonizer under static gas conditions followed in 1909. Holt observed a CO concentration of 2.6% at 860 mbar that increased at lower pressure and smaller discharge gap. Surprisingly, Chapman et al. detected the same dissociation degree when exposing the gas for several hours to ultraviolet radiation only.

The majority of these early studies do not provide values for energy consumed by the processes. Progress in understanding of the non-equilibrium properties of plasmas in general and of DBDs, in particular, led in the 1960s to renewed interest in their capability to boost endothermic chemical reactions, like the reduction of CO$_2$. Dissociation degrees around 30% were reported by Andrew and co-workers for values of the specific injected energy up to 250 eV per molecule (970 kJ/l). The decomposition under flowing gas conditions was found to be dependent on the (controlled) temperature of the reactor wall. A significant influence of the detected O$_3$ on the plasma chemistry was suggested. To further elucidate the processes, the plasma reactor was modified to establish a recirculating gas flow. Gas samples were taken and analysed in intervals of a few minutes. The temperature independent conversion degree saturated at slightly reduced levels as compared to the non-circulating experiments. A complementary study on the formation of CO$_2$ from CO and O$_2$ carried out by the same authors in 1966 led to an explanation of the ozone behaviour in the recirculation reactor: first, the oxygen from the dissociation of CO$_2$ is mainly converted into O$_3$. Second, after a few minutes of recirculation, the O$_3$ seemed to be decomposed by electron impact into O$_2$.

The plasma chemistry of CO$_2$ containing DBDs attracted again new attention in the 1990s in the framework of dry reforming of methane. Kogelschatz and co-workers studied plasma-catalytic effects in a cylindrical reactor both experimentally and theoretically. The theoretical treatment showed that a maximum of 40% of the electron energy could be used for dissociation of CO$_2$. The discharges were operated in the mid-frequency range (10–30 kHz) encompassing the option of sinusoidal and pulsed excitation. The reaction products were quantified ex-situ by means of gas chromatography. For plasmas containing undiluted CO$_2$ conversion yields and energy efficiencies were determined to be between 1.8%–13% and 0.2%–3%, respectively. More importantly, a temperature dependent decrease in conversion rate and energy efficiency was recognized as soon as catalytic materials were inserted into the discharge gap. These results imply an undesirable catalytically enhanced re-oxidation of CO to CO$_2$. Notably, gas discharges in mixtures of CO$_2$/CH$_4$ are more complex and behave considerably different than “clean” CO$_2$ plasmas. In the aforementioned studies, CO$_2$ discharges were considered as extreme case of a dry reforming mixture. To reduce complexity this paper will focus on CO$_2$ plasmas without admixtures of additional gases.

More recently Paulussen et al. have developed a sinusoidally driven cylindrical DBD reactor. The exhaust of the plasma was analyzed by gas chromatography which inherently hinders the determination of ozone concentrations. Interestingly, the reported CO yields are smaller than the decrease in CO$_2$ suggesting another sink of carbon in their system. The energy efficiency was around 2% and did not change significantly while tuning the excitation frequency between 30 and 90 kHz. Aerts et al. established thereupon a numerical model to scrutinize the trends observed in these experiments. Based on the assumption that the CO$_2$ dissociation occurs dominantly through electron impact processes, an energy efficiency around 4% was predicted. Probably due to a lack of appropriate cross sections the kinetics of higher vibrational levels, specifically of the asymmetric stretch mode, was not implemented.

Despite the meanwhile numerous experimental studies on CO$_2$ dissociation at various excitation frequencies, gas flow rates, and reactor configurations, there still is a lack of fundamental knowledge on the prevailing mechanisms occurring in CO$_2$ DBDs at atmospheric pressure. Conversion rates and energy efficiencies are frequently below 10%. Experimental in-situ studies of the spatially and temporally highly transient plasmas are highly desirable. On the other hand they are challenging as well. Additionally, the question remains as to whether vibrational excitation, as proposed by Ref. for discharges using higher excitation frequencies, plays a dominant role in atmospheric pressure DBDs.

The aim of the present study is thus two-fold. First, a flow-tube reactor, particularly optimized for optical access to the active discharge zone, is established and characterized electrically. The reactor facilitates in-situ studies at high spatial or temporal resolution where required. Quartz, known as chemically relatively inert surface, was chosen as dielectric material for the symmetric DBD reactor to reduce potential surface-catalytic effects to a minimum. Second, quantitative Fourier-Transform Infrared (FT-IR) absorption spectroscopy is applied at the exhaust of the reactor to determine the CO$_2$ conversion yield and energy efficiency. Special care is thereby taken to quantify the ozone...
production. In this way, links to earlier studies focusing on the O₂ formation at low residence times as well as on the CO production in DBDs operated in the mid-frequency range are provided.

The material presented in this paper is organized as follows: the DBD reactor is described in Sec. II. Data processing of the results obtained with the applied diagnostic methods are detailed in Sec. III. Among them are the electrical characterization of the system (Sec. III A), optical emission spectroscopy (Sec. III B), and ex-situ infrared absorption spectroscopy (Sec. III C). In Sec. IV, the dissociation of CO₂ into CO and by-products is qualitatively discussed. Potential reaction mechanisms are suggested and summarized in Sec. V.

II. EXPERIMENTAL SETUP

The plasma reactor is designed as a flow tube of about 250 mm total length and is entirely made of quartz. Since quartz is known to be relatively inert, a catalytic enhancement of the inevitable plasma-surface interactions is minimized. Carbon deposits have never been observed on the surface of the flow tube reactor even after hours of operation and at elevated surface temperatures. A symmetric parallel plate configuration with dielectric barriers of equal thickness is chosen for the active discharge zone with a gap width, d_{gap}, of 1 mm. Flat metal electrodes are glued to the outside of the plates. The active plasma phase of 70 mm length is centered between two quartz pipes (Figure 1). The total discharge volume is nearly 2 cm³. Several flow tube reactors with thicknesses of the dielectric barriers between 1 and 2 mm and a constant d_{gap} were manufactured. More details on the plasma reactor are collected in Table I.

Standard stainless steel tubes serve as gas connections at inlet and exhaust of the reactor. The entire system is sealed and continuously pumped by a rotary pump to establish well-defined gas conditions and to avoid gas exchange with laboratory air. The base pressure of the reactor is typically less than 100 Pa. CO₂ (Linde, 4 l foodgrade, 99.9%) is injected along the tube axis through a mass flow controller (Bronkhorst, El-Flow F-201C) at gas flow rates, \( \Phi \), of 0.058, 0.15, 0.52, and 1.7 slm (standard liter per minute). The total pressure in the reactor, which is atmospheric throughout all experiments, is controlled by means of a regulating valve that adjusts the effective pumping speed to the above mentioned CO₂ flow rates. Residence times in the active discharge zone of \( \tau = 2070, 800, 230, \) and 70 ns are achieved.

Figure 1 shows a schematic diagram of the electric resonance circuit that is used to excite the plasma together with the accompanying diagnostics used to characterize the I-V behaviour. The power supply (AFS, G10S-500K) is coupled resonantly to the primary side of a transformer. The secondary coil of the transformer determines the main characteristics and thus the frequency range of the resonance circuit. Fine adjustment of the resonance frequency is achieved by a high voltage vacuum capacitor (C_M) through which the resonance can be tuned steplessly. In this study excitation frequencies of \( f = 60, 90, \) and 130 kHz are used. The specifications of individual electrical components are summarized in Table I.

The voltage amplitude applied to the reactor (\( U_{appl} \)) is measured by a custom-made voltage divider (10000:1), which also serves as electronic trigger device (E.T. in Figure 2) to synchronize the diagnostic equipment to the plasma excitation. The discharge current (\( I_{meas} \)) is measured by means of two different methods: A current transformer (Pearson, model 6585) at the high voltage side is used to measure the current directly. Additionally, transferred charges are collected on a capacitor (\( C_Q \)) and are detected by the use of a commercial voltage probe (Testec, TT-HV 250, 100:1). All signals are recorded using a fast digitizing oscilloscope (LeCroy, WaveRunner 610Zi).

To study the plasma chemistry ex-situ, infrared (IR) absorption spectroscopy is applied. For this purpose, a 49 cm long stainless steel cell is used downstream the plasma reactor (Figure 2). The effluent of the discharge is pumped at the same gas flow rate and total pressure through the cell to avoid artificially induced changes in the gas composition during the sampling process. The pressure drop across the

### Table I. Relevant measures and values of used components.

<table>
<thead>
<tr>
<th>Discharge zone</th>
<th>Symbol</th>
<th>Value</th>
<th>Thickness of quartz plates</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>( ... )</td>
<td>70 mm</td>
<td>( d_{barrier} )</td>
<td>( ... )</td>
<td>1/1.5/2 mm</td>
</tr>
<tr>
<td>Width</td>
<td>( ... )</td>
<td>28 mm</td>
<td></td>
<td>( C_M )</td>
<td>18–762 pF</td>
</tr>
<tr>
<td>Gap distance ( d_{gap} )</td>
<td>( ... )</td>
<td>1 mm</td>
<td></td>
<td>( C_Q )</td>
<td>595 pF</td>
</tr>
<tr>
<td>Volume</td>
<td>( V )</td>
<td>1960 mm³</td>
<td></td>
<td>( C_{Q} )</td>
<td>1.2 pF</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Symbol</th>
<th>Value</th>
<th>Resonance frequency ( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>( ... )</td>
<td>70 mm</td>
<td>30–135 kHz</td>
</tr>
<tr>
<td>Width</td>
<td>( ... )</td>
<td>16 mm</td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>( ... )</td>
<td>ca. 1060 mm²</td>
<td></td>
</tr>
</tbody>
</table>

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enlarge this fibre-optic based approach enables the gas connections to be kept as short as possible, i.e., to mount the absorption cell as close as possible to the plasma reactor. On the other hand, the gas temperature in the absorption cell can be considered to be room-temperature which simplifies the analysis of the absorption spectra as the temperature dependence of spectroscopic line data can be neglected.

Additionally, the wall temperature of the reactor is monitored using an IR camera (FLIR, A320). Although emissivity of the entire setup is unknown, which may induce a systematic error to the temperature measurements, these values provide a lower limit for both wall and gas temperature. The discharge reactor is constantly air-cooled by a fan, but the wall temperature could not actively be controlled. Therefore, the individual FT-IR measurements are delayed until a steady state of the reactor wall temperature is achieved after ignition of the plasma.

For advanced optical access to the active discharge zone the flow tube design as depicted in Figure 1 was slightly modified by two cylindrical quartz viewports which were added perpendicular to the gas flow (Figure 2). The optical emission from the plasma was recorded with a spatial resolution of ~400 µm. Two spherical lenses with focal lengths of 40 mm and 150 mm, respectively, formed a telescope configuration that was applied to image the emission of excited states in the plasma onto an optical fibre of about 100 µm diameter. A Czerny-Turner grating spectrometer (Andor, Shamrock, SR-303i-A) was used to spectrally resolve the radiation collected by the optical fibre. For the detection of survey spectra, a grating with 150 lines per mm blazed at 500 nm was employed along with an intensified CCD (I-CCD) camera (Andor, iStar, DH734-18U-03). Synchronization to individual AC cycles of the applied voltage is provided by the custom-made electronic trigger unit (E.T., Figure 2). To account for the wavelength dependence of both the transmission characteristics of the optical components and the sensitivity of the I-CCD chip, the spectrometer was calibrated relatively in intensity using a tungsten ribbon band lamp (λ > 350 nm) and a deuterium lamp (λ < 400 nm).

III. CHARACTERIZATION OF THE PLASMA REACTOR

A. Electrical characterization

The analysis of the current and voltage characteristics of the reactor is mainly based on the algorithm described by Pipa et al.\textsuperscript{33} The injected energy per AC cycle, \( E_{\text{cycle}} \), is calculated from a Q-V-plot (Figure 3(a)) where the transferred charges are plotted against the applied voltage, as originally proposed 1943 by Manley\textsuperscript{34} and generalized later (see, e.g., Refs. 33 and 35). The area enclosed by a loop, which is formed during one AC cycle, represents \( E_{\text{cycle}} \) and is directly proportional to the injected power \( P \) via the excitation frequency \( f (P = E_{\text{cycle}} \cdot f) \). As indicated in Figure 3(a), the charges transferred through the discharge during one half of an AC cycle, \( q_{\text{max}} \), can be inferred from the Q-V-Plot as well.\textsuperscript{36} The voltage across the discharge gap \( u_{\text{gap}}(t) \) and the plasma current \( i_{\text{plasma}}(t) \) (Figure 3(b)) are derived from the recorded signals \( U_{\text{app}}(t) \) and \( I_{\text{meas}}(t) \) (Figure 1). As can be further seen from \( i_{\text{plasma}}(t) \) in Figure 3(b), the nature of a DBD in CO\textsubscript{2} at atmospheric pressure is highly transient in time.

As the determination of the reduced electrical field, \( E/n \), is experimentally challenging, an approximation is employed here: the reduced electrical field at the time \( t_0 \), just before breakdown in each half-cycle, can be found from \( u_{\text{gap}} \), the size of the discharge gap \( d_{\text{gap}} \) and the neutral gas density \( n_{\text{tot}} \):

\[
\frac{E}{n} \approx \frac{u_{\text{gap}}(t = t_0)}{d_{\text{gap}} n_{\text{tot}}}. \tag{1}
\]

It is clear that such an estimate neglects the filamentary character of the plasma. The use of \( u_{\text{gap}} \) in Eq. (1) should be therefore considered as an estimate for \( E/n \) (at \( t = t_0 \)). A more detailed treatment, e.g., of local effects, is outside the scope of this paper and not necessary for the qualitative discussion below. Strictly speaking, the neutral gas density, \( n_{\text{tot}} \), is a function of the gas temperature. As this calculation serves only as approximation of the order of magnitude of \( E/n \), a gas temperature, \( T_n \), of 300 K is assumed. Thus, a reduced electrical field in the range between \( E/n \approx 90–150 \) Td is obtained for all the flow tubes of 1.0 mm gap width used in this study. These \( E/n \) values should be considered as lower limit since any increase in gas temperature will change the electrical field accordingly.

To assess the efficiency of plasma chemical processes the specific injected energy per particle, \( E_{\text{spec}} \), is frequently applied. It follows from the injected energy per AC cycle:

\[
E_{\text{spec}} = \frac{E_{\text{cycle}} f}{\Phi} = \frac{P}{\Phi}. \tag{2}
\]

Note that the gas flow rate, \( \Phi \), refers to norm conditions (\( T_0 = 273.15 \) K, \( p_0 = 1013.25 \) mbar) throughout this paper and is measured in standard litres per unit time. The specific injected energy \( E_{\text{spec}} \) is usually expressed in J/l and may easily be converted into eV per molecule. Basically, \( E_{\text{spec}} \)}
represents the average amount of energy that is spent on each molecule of CO2 thereby neglecting whether it is dissociated or not. For reasons that will become clear later throughout the discussion of the results it can be useful to express $E_{\text{spec}}$ differently using the residence time, $\tau$, of the gas in the active plasma volume $V$

$$\tau = \frac{V}{\Phi} \frac{pT_0}{p_0T_g},$$

where index “0” is used for norm conditions. With the above mentioned simplification of $T_g = 300 \text{ K} \approx T_0$ and $p = p_0$ for all experiments $\tau \approx V/\Phi$ and Eq. (2) simplifies to

$$E_{\text{spec}} = \frac{P\tau}{V}.$$  

Specific injected energies of 0.4–72.7 kJ/l (0.1–18.8 eV per molecule) are used in this study. The parameters to vary $E_{\text{spec}}$ are the applied voltage, $U_{\text{appl}}$, and the gas flow rate, $\Phi$. The plasma power $P$ was controlled via $U_{\text{appl}}$ in a range of 5–80 W. High values of $E_{\text{spec}}$ are achieved by low gas flow rates leading simultaneously to increased residence times.

B. Optical emission spectroscopy

The emission collected from the plasma is typically very faint under all experimental conditions. Hence, undesirably long integration times were required in case commercially available CCD-based spectrometers were employed. To facilitate more detailed optical emission spectroscopy (OES) studies in the future the plasma reactor is equipped with a gated I-CCD mounted to a spectrograph of medium base length (0.3 m). Vertical binning of camera pixels is applied to further increase the signal-to-noise ratio of the spectra. A typical survey spectrum of a CO2 plasma at atmospheric pressure is shown in Figure 4. The spectrum contains the time-averaged emission detected during one full AC cycle.

The observed emission is typically concentrated in the UV spectral range between 280 nm and 420 nm. Similar spectra of this characteristic shape have been reported earlier for CO2 discharges at elevated pressures.37 Main spectroscopic features in the observed spectral window are electronically excited states of CO2$^+$ (A, B).38 Surprisingly, excited states of CO, even the long-living CO(a) state, are not observed. The lifetime of the latter is probably efficiently reduced to below 1 ns by collisions.39 On the other hand, these recorded CO2$^+$ features suggest a non-negligible high energy tail of the electron energy distribution function (EEDF) since excitation into both the A and B state require at least 17.31 eV and 18.08 eV, respectively40 (and references therein). A detailed analysis of excitation and de-excitation channels requires better knowledge of the EEDF and electron density and will be subject of future spatially and phase-resolved emission studies.

C. FT-IR absorption spectroscopy

The focus of this paper is on the formation of (stable) species in the plasma. Therefore the number densities of CO and O3 are quantified by FT-IR spectroscopy in the exhaust of the discharge. Typical transmission spectra of carbon monoxide and ozone are shown in Figure 5 which also depicts the steps carried out during the data processing. Although the beam path for the IR radiation was purged, absorption features from laboratory air are inevitably present. Thus, a spectrum under plasma-off conditions is firstly measured. When the wall temperature of the plasma reactor
is stabilized, an FT-IR spectrum is acquired under plasma-on conditions. Thermal equilibration of the reactor after changing the conditions is usually of the order of a few minutes and takes thus longer than the gas renewal of the flow system, i.e., plasma-on measurements reflect the gas mixture in the DBD reactor. The entire system consisting of flow tube reactor and sampling cell is then evacuated and refilled for the next experimental condition. Accumulation of, e.g., ozone has been carefully avoided through sufficiently long pumping intervals. Finally, the ratio of the plasma-on and plasma-off spectra was determined and fit to transmission graphs that are calculated on the basis of spectroscopic data as given in the HITRAN database.41 Commercially available software (Q-MACS Soft HITRAN Tool, neoplas control) is used to calculate sample spectra of CO and O3 in well-defined, interference-free spectral windows of a few wave-numbers. These spectra are compared with those ones obtained from experiments to determine molecular concentrations. The approach outlined here requires knowledge of the instrumental broadening of the spectrometer that was carefully calibrated on a well-defined N2O gas sample. The instrumental broadening, which was 0.15 cm\(^{-1}\) in this case, clearly exceeds any other line-broadening mechanisms, even at atmospheric pressures, and hinders therefore a straightforward treatment of the acquired transmission spectra. A direct calculation of the absorbance, ln(\(I_0/I\)), would neglect the convolution with the transmission function of the instrument. The approach chosen for the present study is only applicable to molecular species where spectroscopic line data are available. As molecular oxygen is not infrared active, O2 number densities will be established on the basis of an oxygen balance. Since the measurements were performed with an initial gas composition of 100% CO2, the ro-vibrational transitions belonging to the strong asymmetric stretch vibration at 4.3 \(\mu\)m are saturated. As will be shown below, the DBD dissociates CO2 only weakly. The changes in the CO2 concentration of a few percent are therefore not detectable in the recorded spectra.

FIG. 5. FT-IR transmission spectra of stable CO2 conversion products (1700 sccm, 1004.5 mbar, 61.7 kHz, 22 W): O3 (110 ppm, upper) and CO (2100 ppm, lower). Plasma-off measurements (grey) exhibit transitions of different vibrational bands of CO2. Plasma-on spectra corrected for these features (black, bold) were used to quantify CO and O3 through comparison with calculated spectra (orange, thin).

FIG. 6. Number densities (\(n\)) and corresponding mixing ratios (\(n/\rho\)) determined for CO (full) and O3 (open) in different flow tube reactors as function of specific energy (\(E_{\text{spec}}\)). The reactors were characterized by different dielectric barrier thicknesses (square: 2 mm, circle: 1.5 mm, triangle: 1 mm). The applied frequency was varied between 60 kHz (red), 90 kHz (black), and 130 kHz (orange). The dotted line indicates the detection limit of the FT-IR spectrometer for O3 which is at 50 ppm. The symbols in Figure 6 correspond to different types of flow tube reactors. As mentioned earlier the thickness of the dielectric barriers used in this study are 2, 1.5, and 1 mm. Different colours symbolize the applied frequencies between 60 kHz and 130 kHz. The yield of CO increases monotonously with \(E_{\text{spec}}\) and varies between 0.1% and 4.4% for specific injected energies between 0.4 and 72.7 kJ/l (0.1–18.8 eV per molecule, Figure 6). The CO2 conversion is thereby independent of the barrier thickness and the excitation frequency. Clearly, as the injected power and thus the specific injected energy are linear functions of the frequency, any change will affect \(E_{\text{spec}}\), i.e., the x-axis in Figure 6. Surprisingly, the corresponding CO mixing ratio follows exactly the same trend that is established by other excitation frequencies. Ozone is clearly visible for the majority of discharge conditions. Mixing ratios up to 750 ppm (parts per million) are detected. However, scatter in the O3 data is more pronounced than for CO. The uncertainties of the O3 data cannot explain such behaviour.

IV. RESULTS AND DISCUSSION

In this section, the results obtained experimentally and possible reaction mechanisms will be discussed in more detail. First, the energy efficiency of the dissociation process in a DBD is assessed (Sec. IV A). Second, the behaviour of ozone is examined (Sec. IV B), and finally, the production of carbon monoxide will be scrutinized (Sec. IV C).

A. Energy efficiency

An important aspect with respect to the conversion of CO2 is the energy efficiency of the CO production process.
Throughout this paper the term energy efficiency is defined as the ratio of the dissociation enthalpy of CO$_2$ (\(\Delta H\)) and the injected energy per CO molecule produced in the plasma (\(E_{\text{CO}}\)):

\[
\eta = \frac{\Delta H}{E_{\text{CO}}}. \tag{5}
\]

The total dissociation enthalpy, \(\Delta H\), in Eq. (5) is dependent on the reaction mechanism. The most desirable chemical route to produce CO from CO$_2$ would be obviously a process or a sequence of processes requiring the smallest amount of energy for this endothermic reaction. Conversion through vibrationally excited CO$_2$ is suggested as such a route.

\[
\text{CO}_2 \rightarrow \text{CO} + \text{O}; \quad \Delta H_6 = 5.5 \text{ eV}. \tag{6}
\]

In case the atomic oxygen produced in step (6) is recycled, dissociation of a second vibrationally excited CO$_2$ molecule may occur

\[
\text{O} + \text{CO}_2 \rightarrow \text{CO} + \text{O}_2; \quad \Delta H_7 = 0.3 \text{ eV}. \tag{7}
\]

The net reaction for the dissociation of one molecule of CO$_2$ yields then

\[
\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2; \quad \Delta H_8 = 2.9 \text{ eV}. \tag{8}
\]

Hence the enthalpy value that is used to calculate the energy efficiency in Eq. (5) is \(\Delta H_8 = 2.9 \text{ eV per molecule (279.8 kJ/mol)}. A complete discussion on this reaction mechanism may be found in Ref. 11.

It is essential to distinguish between \(E_{\text{CO}}\) in Eq. (5) and the specific energy injected to the plasma, which is linked to the total number of CO$_2$ molecules. \(E_{\text{CO}}\) is calculated from the specific energy input \(E_{\text{spec}}\) as detailed in Sec. III A and the mixing ratio \(m_r = n_{\text{CO}_2}/n_{\text{tot}}\):

\[
E_{\text{CO}} = \frac{E_{\text{spec}}}{m_r} = \frac{P \tau}{m_r n_{\text{tot}} V}. \tag{9}
\]

Applying the aforementioned considerations, the equation to calculate the energy efficiency transforms into

\[
\eta = \frac{m_r}{E_{\text{spec}}} \cdot \Delta H_8. \tag{10}
\]

For the experimental data displayed in Figure 6, the CO mixing ratios of \(m_r < 4.4\%\) convert into energy efficiencies of \(\eta < 5\%\).

**B. Ozone production**

In what follows the ozone densities shown in Figure 6 are assessed. Although the upper limit of the O$_3$ densities as function of \(E_{\text{spec}}\) follows a similar trend as observed for CO, the O$_3$ data show a (weak) dependency on the excitation frequency. Moreover, even for a constant frequency a significant scatter in the data can be seen, that (i) clearly exceeds the deviations detected for CO, and (ii) is bigger than the estimated uncertainties. Since the air-cooling of the reactor is not adjusted the wall temperature stabilizes at a given equilibrium between injected power (heating) and external cooling capacity. It is well-known that both the formation and destruction of ozone are temperature dependent. Therefore, the correlation between the wall temperature of the reactor and the O$_3$ number density, \(n(O_3)\), is examined.

In Figure 7, a colour map of the apparent wall temperatures measured with the IR camera is depicted. It is merged with an enlarged plot of the O$_3$ densities taken from Figure 6 as a function of the specific injected energy \(E_{\text{spec}}\). The temperatures between the experimental data points are linearly interpolated. Since \(E_{\text{spec}}\) is proportional to the injected power and hence the excitation frequency, a change in frequency leads to a variation of \(E_{\text{spec}}\), assuming all other parameters (such as flow rate and applied voltage) are kept constant. Higher excitation frequencies, and thus higher \(E_{\text{spec}}\), enhance the CO (and O) production (Figure 6) and would suggest an increase in O$_3$ densities. However, Figure 7 clearly shows temperature gradients for elevated \(E_{\text{spec}}\), i.e., heat accumulation effects become more pronounced in the reactor. More importantly, the ozone densities are reduced as soon as frequency and temperature are rising although at least the O production is enhanced as confirmed by the trend in CO. A similar effect can be observed for reduced thicknesses of the dielectric barrier. The O$_3$ densities for the reactor with 1 mm wall thickness, for which considerably higher temperatures are recorded, are frequently below the detection limit of 50 ppm (cf. Sec. III C).

A similar behaviour was reported earlier for a recirculating system. Semiokhin and Andreev found decreasing levels of ozone at higher wall temperatures as well. In their case the reactor wall was actively temperature controlled. The comparison of O$_2$ and O$_3$ densities led to the conclusion that the oxygen from the dissociation of CO$_2$ is initially converted into O$_3$, which is then subsequently decomposed by electron impact into O$_2$ after a few minutes recirculation. Since the timescales between the formation and decomposition of O$_3$ in...
their study are much longer than the residence times used in the present study, the proposed formation and destruction routes cannot explain the scatter in the ozone data in Figures 6 and 7. It should be mentioned that Andreev et al. observed a temperature dependent degree of dissociation of CO$_2$ into CO while working with a reactor equipped with an actively controlled wall temperature. This observation suggests a significant contribution of surface processes (i) to the primary dissociation and the re-association of CO$_2$ in a DBD at atmospheric pressures, and (ii) especially to the ozone production. The latter fact was suggested by Andreev et al., however, confirmation by experimental data on O$_3$ was absent at that time.

On the other hand, it is obvious that an increase in the reactor wall temperature correlates with higher gas temperatures. The apparent reactor temperatures shown in Figure 7 should be considered as a lower limit for the gas temperature (320–480 K) in the active plasma zone. Assuming a gas temperature of $T_g = 450$ K the rate for the dominant formation mechanism of ozone

$$O + O_2 + O_2 \rightarrow O_3 + O_2,$$

where $k_{11} = 6 \times 10^{-34} (T_g/300)^{-2.8} \text{cm}^6 \text{s}^{-1}$ decreases by a factor of 3 compared to room temperature while the rates for the majority of quenching reactions

$$O_3 + X \rightarrow O_2 + \text{products},$$

exhibit an increase of at least a factor of 10 or more. Although their individual contribution might be relatively small, the most efficient quenchers, X, are O$_2$(1Σ), O$_2$(1Δ), O$_2$, and O. Note that the present ex-situ measurements are not suitable to conclude whether the formation is hindered or the destruction is enhanced. Nevertheless, these two competing mechanisms may also explain the (wall) temperature dependence of the ozone levels in the recirculating system used by Semiokhin and Andreev in Ref. 25.

C. Carbon monoxide formation

1. Macrokinetics and scaling parameter

In this sub-section, the measured data are used to discuss the plasma chemistry of CO formation globally. A more detailed treatment would require a thorough modelling which is beyond the scope of this paper. Based on the experimental results in Ref. 29 an attempt has recently been made to model the CO$_2$ dissociation in a DBD. Aerts et al. used a single 30 ns microdischarge to study important reaction channels in the plasma and its afterglow. A direct comparison of these zero-dimensional numerical results with experimental ones obtained in a filamentary discharge of cylindrical or parallel-plate geometry, such as used here, is difficult. Moreover, the model in Ref. 30 does not include surface reactions which makes a comparison between the quartz flow tube, where both electrodes of the DBD reactor were covered, and the DBD employed by Paulussen et al. even more challenging. In the latter case one electrode was still metallic, so that the surfaces exposed to the CO$_2$ plasma were of stainless steel and alumina. From fundamental studies on heat shields it is known that the chemistry of metal and dielectric surfaces in mixtures of CO and O is considerably different. Although the model used by Aerts et al. might be not suitable for a direct comparison with the present measurements, links will be made where appropriate.

The specific injected energy $E_{\text{spec}} = \frac{\tau}{V} \cdot (E_{\text{cyc}}/N \cdot f)$ (Eqs. (2) and (4)) is the typical global parameter used to describe plasma-assisted conversion processes. It embodies three different time scales in the form of individual microdischarges (nanoseconds), the AC cycle (microseconds), and the residence time (milliseconds). As can be seen in Figure 3(b) recorded at 60 kHz, microdischarges at atmospheric pressure were usually present for about 4 μs per AC half-cycle. A change in the excitation frequency from 60 and 130 kHz very likely does not change the individual microdischarges, but reduces the effective length of the “on-phase,” in which they appear, by about 50%. Similarly, the “off-phase” per half-cycle will become shorter. However, it turned out that changes in frequency at constant τ had no influence on the CO concentration as long as $(E_{\text{cyc}} \cdot f)$ was constant. Doubling the excitation frequency is then accompanied by a reduction of the injected energy per cycle $E_{\text{cyc}}$ to 50%, probably due to fewer microdischarges per cycle. In other words, the CO production does not seem to be dependent on reactions that are occurring on the microsecond time-scale or in the “off-phase.” The CO yield remained unchanged when the power was injected in one phase (4 μs) in a half-cycle or in subsequent phases (2 μs per half-cycle) with short afterglow periods in between. On the other hand, the “off-phase” was still insufficiently long to sustain a reasonable level of vibrationally excited CO$_2$ that would facilitate dissociation through vibrationally excited CO$_2$. An estimate of typical lifetimes of vibrational levels yields a few microseconds and agrees with recent calculation. Note that the residence time, τ, of CO$_2$ molecules in the active plasma was τ ≳ 1/f for all conditions, i.e., a CO$_2$ molecule will encounter tens or hundreds of AC cycles while travelling through the active discharge.

Next, the application of the specific injected energy as key parameter suggests to assess a macrokinetic description as introduced by Rutscher and Wagner. This approach also allows the identification of potential scaling parameters. Sonnenfeld et al. successfully applied scaling parameters to the plasma-assisted CO$_2$ decomposition over the entire range from low to elevated pressures (200 mbar). Interestingly, an extrapolation of their CO yields to the presently used (pressure) conditions would lead to the same dissociation efficiencies of a few percent. To link typical scaling parameters with the specific energy and measured quantities, Eqs. (2) and (4) are rewritten in the form

$$E_{\text{spec}} = \frac{\tau}{V} \cdot f \cdot E_{\text{cyc}} = \frac{\tau}{V} \cdot f \cdot \left[ \int_{0}^{\tau} (u_{\text{gap}}(t) \cdot I_{\text{plasma}}(t)) \, dt \right].$$

In a simplified evaluation of Eq. (13), the injected power per full AC cycle of period $T = f^{-1}$ is expressed as twice the average power per half-cycle,
The integrated plasma current per half-cycle corresponds to $q_{\text{max}}$, i.e., the number of transferred charges (Figure 3(a)), as introduced by Pipa et al.\textsuperscript{36} Therefore, $E_{\text{spec}}$ in (14) transforms into

$$E_{\text{spec}} = \frac{\tau}{V} \cdot 2\cdot f \cdot \int_0^{\tau/2} (\hat{u}_{\text{gap}} \cdot i_{\text{plasma}}(t)) \, dt,$$

where $\hat{u}_{\text{gap}}$ is an average voltage across the discharge gap. The integrated plasma current per half-cycle corresponds to $q_{\text{max}}$, i.e., the number of transferred charges (Figure 3(a)), as introduced by Pipa et al.\textsuperscript{36} Therefore, $E_{\text{spec}}$ in (14) transforms into

$$E_{\text{spec}} = 2\hat{u}_{\text{gap}} \cdot \left( f \cdot \frac{q_{\text{max}}}{V} \cdot \tau \right) = 2\hat{u}_{\text{gap}} \cdot \Xi,$$

where $\Xi$ expresses the total number of transferred charges during the residence time of CO$_2$ molecules in the active discharge zone. Furthermore, $q_{\text{max}}/V$ might be considered as time- and volume-averaged electron density $\langle n_e \rangle$, neglecting the influence of (negative) ions. In Figure 8, the same experimental data as in Figure 6 are displayed, but now as function of $\Xi$ (bottom axis). Obviously, a single trend is established for all experimental conditions leading to three conclusions:

(I) The CO mixing ratio ($n_{\text{CO}}$) in the DBD reactor can be described for all conditions studied here by the parameter $\Xi \sim \langle n_e \rangle \tau$, which is a well-known scaling parameter in plasma-chemistry as long as certain conditions are fulfilled.\textsuperscript{48,50} Note, that the frequency dependence of $\Xi$ accounts for the fact that $f^{-1} \ll \tau$, as outlined earlier.

(II) The influence of the gap voltage, $\hat{u}_{\text{gap}}$, and thus of the electron energy seems to be negligible in this macrokinetic description.

(III) The slope observed in the double-logarithmic plot (Figure 8) is 0.75, i.e., $n_{\text{CO}} \sim \langle n_e \rangle^{0.75}$. The upper and lower limits of the slope correspond to the absence of any CO loss channels ($\sim \langle n_e \rangle \tau$) or the presence of CO + O recombination ($\sim \langle n_e \rangle^{0.75}$). Both cases are indicated in Figure 8 and will be further discussed in Sec. IV C 4.

Particularly (II) is an important criterion for the application of the scaling parameter $\langle n_e \rangle \tau$ as it requires that the rate coefficients, that are governing the reaction mechanisms, are only weakly dependent on the EEDF, gas pressure and gas temperature.\textsuperscript{50} While the gas pressure was kept constant in this study, the gas temperature and reduced electrical field (that determines the EEDF) were in the range between 320–480 K and 90–150 Td, respectively. In case $\Xi$ is normalised to the total molecular number density, $n_{\text{gap}}$, a slightly more intuitive value can be derived, namely, the number of required charges per injected CO$_2$ molecule to produce a CO molecule. The values for $\Xi/n_{\text{gap}}$ are added as top axis in Figure 8 and are directly linked to the “reactor parameter,” $R$, which weighs the energy spent per precursor molecule in the active discharge zone against its thermal energy.\textsuperscript{50} Notably, the presently obtained CO$_2$ dissociation efficiencies are in good agreement with results reported by Dernier in a DC glow discharge at 30 mbar at similar $R$.\textsuperscript{50} Dernier also discusses the constriction of the plasma at increasing pressure which can limit in parts the uniform description of the plasma chemistry in terms of the macrokinetic approach.

The application of the scaling parameters such as $\Xi$ and $R$ to DBDs neglects the physics of individual microdischarges. In the present case, the behaviour of the microdischarges is accounted for in the number of transferred charges per half-cycle, $q_{\text{max}}$. It was reported that the transferred charges per microdischarge are (statistically) a function of the discharge gap, $d_{\text{gap}}$, along with permittivity and thickness of the dielectric barriers ($d_{\text{barrier}}$).\textsuperscript{31} Since $d_{\text{gap}}$ was constant and SiO$_2$ was used as barrier material for all experiments, the transferred charges per microdischarge should only change with $d_{\text{barrier}}^{-1}$. As can be seen in Figure 6 (and Fig. 8), the CO yield follows the same trend although the barrier thickness was varied by a factor 2 (1–2 mm).

To conclude, the total number of transferred charges during the residence time is the essential criterion for CO$_2$ to CO conversion in a DBD while the energy and density of electrons in individual microdischarges are apparently of reduced importance. This fact also justifies the use of scaling parameters. It is further interesting to note that—apart from all details involved—the numerical modelling of successive pulses of 30 ns microdischarge in Ref. 30 suggests an almost linear increase in CO density with the number of plasma pulses. An oversimplified extrapolation of the CO density after one microdischarge to the presently used 4 $\mu$s long plasma “on-phase” in one half AC cycle at 60 kHz leads to the same order of magnitude in CO yield ($\sim 10^{17}$ cm$^{-3}$). This coincidence might be closely connected with the (unique) dependence on the number of transferred charges.

2. Reaction mechanisms

The previous discussion supports the assumption that the plasma-chemical CO$_2$ conversion in the DBD reactor employed is determined by electron-induced reactions. Due

![Figure 8](image-url)
to residence times of the order of milliseconds up to seconds, discrimination between excitation in microdischarges and potentially slower follow-up reactions is difficult or impossible on the basis of the available data and the applied diagnostics. Detailed time-resolved measurements that are preferably carried out in situ along with modelling would be required. Nevertheless, a few potential reaction mechanisms that could explain the low conversion and energy efficiencies are discussed in what follows.

Among the electronically induced CO$_2$ decomposition channels dissociative attachment

$$\text{CO}_2(X) + e \rightarrow \text{CO} + O^- \quad (16)$$

has the lowest energy barrier and is most efficient at electron energies around 4 eV (380 kJ/mol) and 8 eV (770 kJ/mol).$^{52}$ Electronic impact excitation (CO$_2$(X) + e → CO$_2$* + e) or ionisation (CO$_2$(X) + e → CO$_2$* + 2e) require at least about 6.2 eV (600 kJ/mol) or more than 13 eV (1250 kJ/mol). Both processes are therefore strongly dependent on the high energy tail of the EEDF. Due to the excess energy of the intermediate excited or ionised states, the dissociation products (CO*, O*) are frequently formed in (electronically) excited states$^{32}$-$^{34}$

$$\text{CO}_2^+ \rightarrow \text{CO} + O^+, \quad (17)$$
$$\text{CO}_2^+ \rightarrow \text{CO}^+ + O, \quad (18)$$
$$\text{CO}_2^{++} + e \rightarrow \text{CO}^+ + O, \quad (19)$$
$$\text{CO}_2^{2+} \rightarrow \text{CO}^{2+} + O. \quad (20)$$

In cases where CO(a) is not directly formed the decay of higher CO* states may progress via CO(a). However, the role of CO(a) for the plasma chemistry is unclear: Cenian et al. discuss its significance for the CO$_2$ recombination in glow discharges,$^{55}$ whereas Sonnenfeld considers the influence of CO(a) as negligible in similar systems.$^{56}$ Additionally, at elevated pressures the lifetime of electronically excited CO falls below the radiative lifetime due to quenching (e.g., as short as $\sim$200 ps for CO(B) at 1000 mbar (Ref. 39)). This could explain the absence of CO features in the optical emission spectra and may reduce the influence of CO(a) on the kinetics. Excited oxygen is reported to be quickly deactivated by ground state CO (Ref. 57) which led Hokazono et al. to the conclusion that the three-body recombination

$$\text{O} + \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M} \quad (21)$$

is the dominant CO$_2$ reforming process at atmospheric pressure.$^{58}$ Other processes encompassing CO + O*, CO* + O, and CO(n) + CO(n') were considered as significantly slower. For the present conditions the rate coefficient for reaction (21) in excess of CO$_2$ (= M) would be $k_{21} = 1.5 \times 10^{-15} \text{ cm}^3 \text{s}^{-1}$.$^{59}$ Particularly, surface recombination

$$\text{O} + \text{CO} + \text{wall} \rightarrow \text{CO}_2 + \text{wall} \quad (22)$$

is frequently neglected. However, due to spin-mismatch the recombination in the gas phase (21) is relatively slow compared to other gas mixtures,$^{32}$ so that surface recombination of CO could play a non-negligible role in the backconversion to CO$_2$. Unfortunately, reliable loss frequencies for CO on quartz surfaces are barely available in literature. To estimate the effect of wall recombination, an effective rate coefficient for plasma conditions given by Cenian et al. is chosen here.$^{59,60}$ As the selected reference does not distinguish between the two channels CO(g) + O(s) + wall and CO(s) + O(g) + wall, the effective rate coefficient cannot straightforwardly be traced back to a sticking coefficient. The (diffusion limited) effective rate coefficient is inversely proportional to the distance of the walls, $l_{\text{diff}}$: $k_{22} = 7.4 \times 10^{-17} / l_{\text{diff}} \text{cm}^4 \text{s}^{-1}$. By contrast to typical CO$_2$ (laser) discharge tubes,$^{58,59}$ the reactor walls for the present DBD are about a factor of 500 closer and the rate coefficient becomes comparable to the three-body recombination (21), i.e., $k_{21} \approx k_{22} = 1.5 \times 10^{-15} \text{ cm}^3 \text{s}^{-1}$. This conclusion is even valid in case the surface recombination is only diffusion limited and faster transport effects such as convection in, e.g., microdischarges are neglected at first. The (classical) diffusion time, $t_{\text{diff}}$, at atmospheric pressure would be approximately

$$t_{\text{diff}} = \frac{L^2}{D}, \quad (23)$$

where $L = d_{\text{gap}}/2$, i.e., half the discharge gap, and $D$ is the diffusion coefficient. The value for the diffusion of CO in CO$_2$ ($D = 0.283 \text{ cm}^2 \text{s}^{-1}$ at 400 K (Ref. 61)) leads to a diffusion time of $t_{\text{diff}} = 10 \text{ ms}$ which is at least an order of magnitude smaller than the residence time in the active discharge zone. CO molecules may therefore reach the surface sufficiently fast.

Another important loss channel for the injected energy would be charge exchange reactions and CO$_2^+$ clustering. Already in 1923 Lind (qualitatively) suggested clustering of CO$_2^+$ followed by decay into CO$_2$

$$\text{CO}_2^+ + \text{CO}_2 \rightarrow [(\text{CO})_2]^{3+}, \quad (24)$$

$$[(\text{CO}_2)_3]^{7+} + e \rightarrow 2 \text{CO}_2, \quad (25)$$

which was known from experiments using alpha particle radiation to ionize CO$_2$. Such a mechanism effectively reduces the energy efficiency of the CO production. Through reactions (24) and (25) CO$_2^+$, which is produced at high energy costs, remains chemically inert. More recently and based on experiments at low-pressure, Schildcrout et al. and Ellis et al. discuss the formation of C$_2$O$_4^+$ in (24) in more detail as a four-body process$^{62,63}$

$$\text{CO}_2^+ + \text{CO}_2 + \text{M} + \text{M'} \rightarrow \text{C}_2\text{O}_4^+ + \text{M} + \text{M'}, \quad (26)$$

where M, M', are CO$_2$ or may possibly be O$_2$ and CO.$^{63}$ First, an intermediate activated molecular complex is formed which needs a subsequent collision with at least another molecule to stabilise the product

$$\text{CO}_2^+ + \text{CO}_2 \rightarrow \text{C}_2\text{O}_4^+, \quad (27)$$
$$\text{C}_2\text{O}_4^+ + \text{M} \rightarrow \text{C}_2\text{O}_4^+ + \text{M}. \quad (28)$$
Such three-body ion-molecule reactions usually have no activation energy and are fast. The total rate coefficient for an ion-molecule reaction, \( k_{27+28} \), given by Cenian considers a 3-body process (i.e., without \( M^+ \) in (26)) and \( CO_2 \) as collisional partner at 1000 mbar: \( k_{27+28} = 7 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \). Although the clustering process seems not very well understood, Ellis reported for elevated pressures, such as used here, a temperature sensitive cluster formation through one parent ion that is surrounded by \( CO_2 \) molecules. 

\[
CO_2^+ + O_2 \rightarrow CO_2 + O_2^+ \tag{29}
\]

As will be estimated in Sec. IV C 3 for the present experiments, the \( O_2 \) mixing ratios are indeed not significantly higher than 1%.

To sum up, the relatively low conversion and energy efficiencies that were obtained can be caused by inefficient dissociation channels and fast recombination, respectively. Particularly, a considerable fraction of the energy carried by electrons in the high-energy tail of the EEDF might be effectively lost for the CO production due to fast charge exchange and clustering reactions. These are especially favoured at elevated pressures since they are strongly dependent on the collision frequency. In the model of Aerts et al. such ionic reactions were calculated to hamper the net rate of \( CO_2 \) dissociation: the effect of electron impact ionisation and dissociative ionisation channels was compensated to a large extent by ionic reactions.

### 3. Byproducts and oxygen balance

It is clear from Figure 6 and the discussion in Sec. IV B that \( O_3 \) formation is only one reaction channel to recycle the oxygen produced in the DBD. Therefore, a straightforward oxygen balance was established based on the measured molecular densities. \( CO_2 \) was assumed to be the only source of oxygen and \( CO, O_3, \) and \( O_2 \) were considered as stable reaction products. The corresponding number density of molecular oxygen as estimated by

\[
n(O_2) = \frac{1}{2} [n(CO) - 3n(O_3)] \tag{30}
\]

is added to Figure 8. Despite the non-equilibrium conditions in the DBD, \( CO \) and \( O_2 \) are present in an almost stoichiometric ratio of 2:1 that are to be expected under chemical and thermal equilibrium.

Since the ozone density is about 1–2 orders of magnitude smaller than \( CO \) the scatter in the \( O_3 \) data does not transfer to the \( O_2 \) data in Figure 8. On the other hand, the experiments clearly show that the observation of a stoichiometric \( CO/O_2 \) ratio does not imply that \( O_3 \) is not present. A direct comparison with the modelling results for \( O_3 \) obtained in Ref. 30 is more challenging here than for \( CO \). Ozone formation progresses in several steps and is relatively slow. Therefore, the ozone calculations for successive plasma pulses in Ref. 30 do not lead to a “ladder-like” increase in density as for \( CO \). A linear extrapolation of the results in Ref. 30 to, e.g., our 4 \( \mu s \) long “on-phase” per half-cycle at 60 kHz would therefore fall far short of the values obtained experimentally.

In a slightly more generalised 3-body-recombination than given by (11), \( O_3 \) will be formed through

\[
O + O_2 + M \rightarrow O_3 + M, \tag{31}
\]

where \( M = O_2 \) yields reaction (11) with corresponding rate coefficient of \( k_{11} \sim 5 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \) for the estimated \( O_2 \) densities. However, in case of \( M = CO_2 \), with a mixing ratio of almost 100%, \( k_{31} \sim 2 \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \) i.e., recycling of atomic oxygen and subsequent ozone formation is about an order of magnitude faster than \( CO \) recombination via reactions (21) and (22).

An energy efficient \( CO_2 \) dissociation would require the recycling of oxygen through reaction (7) which is partially hindered by competing mechanisms such as the aforementioned ozone formation. Additionally, due to high activation energy the rate coefficient for the synergistic \( CO_2 \) dissociation via \( O \) is very small at low gas temperatures, \( k_7 \sim 10^{-33} - 10^{-37} \text{ cm}^3 \text{s}^{-1} \) (Refs. 59 and 65) and thus unlikely to occur.

### 4. Macroscopic model of \( CO_2 \) dissociation

The \( CO \) production as function of the scaling parameter \( \Xi \) shows a trend proportional to \( [\langle n_i \rangle \tau]^m \) (Figure 8). To qualitatively understand the value of \( m = 0.75 \) mentioned in Sec. IV C 1 , a simplified (macroscopic) model is used. Based on the previous discussion three dominant reactions are taken into account: direct electron-impact dissociation of \( CO_2 \)

\[
CO_2 + e \rightarrow CO + O + e, \tag{32}
\]

as well as \( CO \) recombination in the gas phase and on the reactor walls (reactions (21) and (22)) together with their corresponding rate coefficients \( k_{32}, k_{21}, \) and \( k_{22} \). Since the main source of \( O \) is assumed to be \( CO_2 \) and hence the same as for \( CO \) (reaction (32)), an ansatz in the form of \( n_{CO} = n_{O} (p < 1) \) is chosen to describe the \( O \) density. This ansatz also accounts for additional \( O \) recombination products such as \( O_2 \) or \( O_3 \). The \( CO \) production rate is then

\[
\frac{dn_{CO}}{dt} = k_{32}n_{CO}/n_e - \left( \frac{k_{21} + k_{22}}{\alpha} \right) n^2_{CO}, \tag{33}
\]

from which two limiting cases for the exponent \( m \) can be derived. If loss processes are absent (\( k_{32} = \text{const.}, k_{21} = k_{22} = 0 \)), the solution of (33) yields \( n_{CO}(t) \sim \langle n_i \rangle \tau \). Assuming that \( CO_2 \) molecules spend the residence time \( \tau \) in the active discharge zone \( (n_{CO}/n_{tot})(\tau) \sim \langle n_i \rangle \tau \) and thus \( \log(n_{CO}/n_{tot}) \sim m_{\text{max}} = 1 \). In case loss processes are present (\( k_{32} = \text{const.}, k_{21}, k_{22} = \text{const.} \neq 0 \)), Eq. (33) can be transformed for the steady state, which is assumed to be achieved after residence time \( \tau \), into

\[
\frac{n_{CO}}{n_{tot}} (t \geq \tau) = \sqrt{\frac{zk_{32}}{k_{21}}} \times \left( 1 + \frac{k_{22}}{k_{21}} \right)^{-\frac{t}{\tau}} \sqrt{\frac{n_e}{n_{tot}}} \tag{34}
\]
and the exponent \( \log(n_{CO}/n_{tot}) \sim m_{\text{min}} \) becomes 0.5. Both, the upper and lower limits of \( m \) are displayed in Figure 8. Obviously, the experiments suggest a different behaviour with \( 0.5 \leq m \leq 1 \) which means that CO loss processes are less pronounced than assumed in the simplified model consisting of reactions (32), (21), and (22). A loss process that is (weakly) dependent on the number of transferred charges could cause the observed trend, e.g., \( k_{21} = \text{const.} \), \( k_{21} = \text{const.} \neq 0 \), \( k_{22} (\langle n_e \rangle) \neq \text{const.} \neq 0 \). From Eq. (34)

\[
\log \left( \frac{n_{CO}}{n_{tot}} \right) = \text{const.} + \log \left[ \left( 1 + \frac{k_{22}}{k_{21}} \right)^{-1} \sqrt{\frac{n_{CO}}{n_{tot}}} \right] \tag{35}
\]

and comparison with the experimentally obtained slope \( m = 0.75 \) the rate coefficient for surface recombination of CO, \( k_{22} (\langle n_e \rangle) \), can be estimated to

\[
k_{22} \approx k_{21} \left( \sqrt{\frac{n_{tot}}{\langle n_e \rangle}} - 1 \right). \tag{36}
\]

Especially at high specific injected energies (i.e., increased \( \langle n_e \rangle \) values) surface reactions \( k_{22} \sim \langle n_e \rangle^{-1/2} \) become relatively less important compared to gas phase recombination of CO. Such effects could be indeed explained as CO typically forms stronger bonds than O on (dielectric) surfaces. At increased \( \langle n_e \rangle \) values more CO will be produced and hence the ratio of surface adsorbed CO/O would shift towards CO which in turn hampers CO + O recombination (reaction (22)). Similarly, the (thermal) power deposited on the reactor wall increases (as can be seen in Figure 7). Since surface recombination of oxygen (O + O + wall → O₂ + wall) depends on the CO concentration, an increase in wall temperature would favour CO desorption and simultaneously reduce CO to CO₂ recombination on the wall as loss channel.

To conclude, the CO yield as function of the scaling parameter \( \langle n_e \rangle \) clearly indicates a regime in which O as main species for CO recombination is less efficient (\( m > 0.5 \), Figure 8) than predicted by the simplified model used here. An explanation for this behaviour could be a charge-mediated reactor wall coverage with CO and O.

V. SUMMARY AND CONCLUSION

The dissociation of CO₂ into CO and by-products was studied at atmospheric pressure by means of ex-situ FTIR spectroscopy. For this purpose a symmetric, parallel-plate like DBD reactor was designed and electrically characterised. The specific input energies \( E_{\text{spec}} \) were varied in the range of 0.1–20 eV per molecule (0.3–70 kJ/l). Fine adjustment of \( E_{\text{spec}} \) was implemented – additionally and independently from gas flow variations – by using different applied voltages and barrier thicknesses. CO densities between \( 10^{16} \) and \( 10^{18} \text{cm}^{-3} \) were observed which are in good agreement with values reported earlier by, e.g., Andreev for a cylindrical, but otherwise similar system (quartz walls, flowing gas conditions). The experiments of Andreev were targeted on considerably high specific input energies of up to 250 eV per molecule (≈1000 kJ/l). However, the high values of injected energy are a result of extended residence times of up to 4 min (285 s) that lead to saturation effects in chemical conversion and higher degrees of dissociation (~30%) in conjunction with low energy efficiency. The present experiments were especially carried out in a specific energy range (0.5–2.0 eV per molecule) where high dissociation and energy efficiencies are predicted due to preferential vibrational excitation. An extrapolation of the dissociation efficiencies reported in Ref. 23 to presently applied \( E_{\text{spec}} \) values lead to the same CO yields. More recent studies in undiluted CO₂ employing mid-frequency (i.e., tens of kHz) driven DBDs described similar energy and dissociation efficiencies of a few percent. Paulussen et al. observed less than 5% CO yield for gas flow rates and thus residence times comparable to those used here. A significant increase was only detected for enhanced residence times, whereas the effect of frequency changes between 10 and 90 kHz was negligible.

It transpires that the relatively low efficiencies are independent of the design details of the (DBD) reactor which implies a more fundamental explanation linked with the reaction mechanism. In this study, the specific injected energy was adjusted to around 1 eV per molecule (3.9 kJ/l) while maintaining gas flow rates that may allow relevant throughput. Nevertheless, the energy efficiencies fell short by at least one order of magnitude compared to discharge types for which the aforementioned criterion for \( E_{\text{spec}} \) was established. This may suggest that vibrational excitation and dissociation via highly vibrationally excited states are absent or at least of reduced importance in DBDs. This assumption is supported by the estimated lower limit of the reduced electrical field (≥90 Td). For such relatively high values of \( E/n \) a non-negligible contribution of directly electron-driven dissociation channels (electron-impact dissociation, excitation, and ionisation) has to be considered. The presence of O₃ in the exhaust gas directly indicates that the atomic oxygen produced during the dissociation of CO₂ molecules is partially not recycled. The loss of O atoms in by-product formation processes reduces the possibility of sequential CO₂ splitting as proposed in reaction (7) and increases the total energy cost per CO formation in the DBD. Apart from the inefficient CO₂ activation in form of excitation or ionisation, competing reaction mechanisms such as charge exchange, clustering, and O recombination additionally hamper the CO production. Clustering or the formation of ionic complexes might be controlled through their small binding energy, i.e., their sensitivity to the gas temperature. Recombination of CO and O in the gas phase is hindered by spin-mismatch and therefore unusually slow for a molecular plasma at elevated pressures. Surface recombination of CO would be equally fast and is non-negligible. On the other hand, O recombination on quartz is even faster and will therefore (i) reduce the surface loss of CO and (ii) further frustrate the recycling of O with CO₂ in the gas phase, which has an almost negligible rate coefficient at the low gas temperatures that were estimated to be around 400 K.
A macroscopic description, that neglects the details of the filamentary character of the discharge, reveals that the CO production in the DBD follows a single trend as function of the specific injected energy for all different conditions applied. More importantly, the application of the scaling parameter \( (n_i) \tau \), that is well-known from low-pressure plasma processing, is applicable: the CO production in the presently employed DBD depends only on the total number of charges that are transferred through the discharge during the residence time of the gas. The analysis of the observed trend as function of the scaling parameter suggests a charge-mediated reactor wall coverage with CO/O which in turn influences the recombination and hence loss of CO.

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