

Experimental investigation and kinetic modeling of CO₂-CH₄ plasmas

Rodolfo Simões^{1,*}

¹*IPFN, Departamento de Física, Instituto Superior Técnico,
Universidade de Lisboa, Avenida Rovisco Pais 1, 1049 Lisboa, Portugal*

Understanding CO₂/CH₄ plasmas can help us address one of today's most pressing scientific issues: To dissolve carbon dioxide molecules efficiently and lower the amount of greenhouse gases in the atmosphere. It is critical to gain a firm understanding of the inner workings of the plasma for this. An experimental investigation of the chemical composition of the plasma, its gas temperature, and its emission spectrum was done to contribute to this effort. Furthermore, a kinetic model capable of replicating plasma behavior under various conditions was developed, allowing for a quantitative examination of the plasma parameters and the corresponding equilibrium concentrations.

I. INTRODUCTION

The generation of energy from fossil fuels was an achievement that had a massive influence on nearly every area of our lives and society. Although fossil fuels facilitated significant scientific breakthroughs in industry, engineering, medicine, and other fields, we now are reliant on nonrenewable energy sources, which harm our ecosystem. Indeed, if major adjustments are not made, many of contemporary society's recent accomplishments begin to be threatened.

Renewable energy sources are commonly presented as the solution for this problem, but to this day, they are unable to create enough electrical power today because of their inconsistency and the imbalance between supply and demand [1]. For this reason, it is vital that we figure out how we can store the energy so that we can use it when there's a necessity. The creation of an energy storage strategy, which converts transient electrical energy into valuable chemical molecules, like a fuel, could be one answer to this problem. The power-to-gas approach to this problem suggests that the excess of energy produced by renewable energy sources is used to dissociate CO₂ molecules, and lead to the production of Synthesis Gas (Syngas) which can be utilized in the manufacturing of hydrocarbon fuels or in the chemical industry.

One of the most difficult tasks in implementing this idea is properly disassociating the relatively stable CO₂ molecule, since CO₂ dissociation is an highly endothermic reaction. Under classical industrial conditions, this reaction is limited by the rate of heat transfer. Consequently, this leads to high production costs, which turns the whole CO₂ conversion chain economically unreasonable. And this is where plasma applications can make a difference.

Plasmas are commonly referred to as the fourth state

of matter and it consists of a gas of ions – atoms or molecules which have orbital electrons removed, and free electrons. In particular, low temperature plasmas are characterized by non-equilibrium conditions under which electrons, ions and neutral species have different translational and-in case of molecules-internal (ro-vibrational) energies.

Low temperature plasmas have the unique ability to activate the vibrational excitation of CO₂ molecules because of the characteristic low electron energies with 1-2 eV. In this temperature range, it has been estimated that about 95% of all the discharge energy is transferred from plasma electrons to the vibrations of CO₂ molecules (see figure 1). This helps to accumulate energy that can be used to decompose the CO₂ molecules via vibrational climbing [2], which is a much more efficient method of dissociating the CO₂ molecule.

The ultimate aim of this master thesis is to widen our understanding on plasmas used for chemical conversion. In particular, we are interested in studying the potential of plasmas to generate hydrocarbons from CO₂-CH₄ mixtures in order to create fuels and chemical feedstock. In this vision of the future, plasma can act as a processor of electricity into chemistry, providing pathways that are environmentally friendly. The current work relies on the systematic investigation of key points important for the efficient decomposition of CO₂-CH₄ mixtures in plasmas, through studying the basic plasma parameters, namely dissociation degree, gas temperature and vibrational excitation, both by conducting experimental investigation and by kinetic modelling.

*Electronic address: rodolfo.m.simoes@tecnico.ulisboa.pt

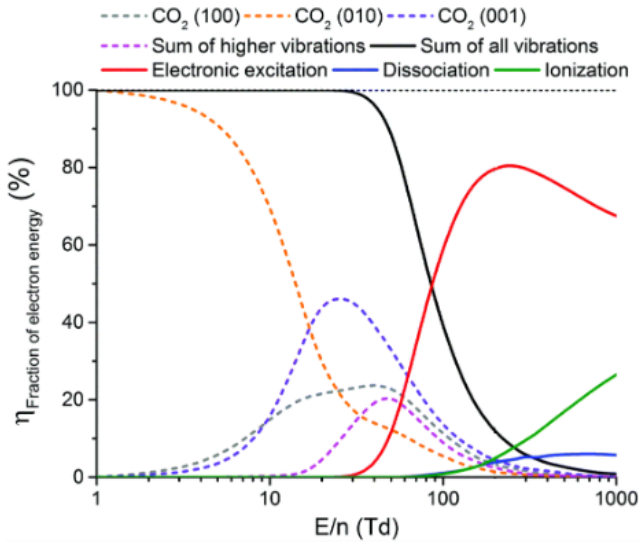


FIG. 1: Fraction of energy transferred through the different energy channels of CO_2 , as a function of the reduced electric field. From [3]

II. BASIC CONCEPTS

A. CO_2 conversion

CO_2 is a triatomic, linear and symmetric molecule. This leads to three vibrational modes - the symmetric stretching mode (v_1), the double degenerate bending mode (v_2), and the asymmetrical stretching mode (v_3). These modes (illustrated in figure 2) are typically represented using the Herzberg notation $\text{CO}_2(v_1, v_2^{l_2}, v_3)$, where l_2 is the projection of the momentum of bending vibrations onto the axis of the molecule. It can take the values $l_2 = v_2, v_2 - 2, v_2 - 4, \dots, 1$ or 0 , depending on whether v_2 is odd or even.

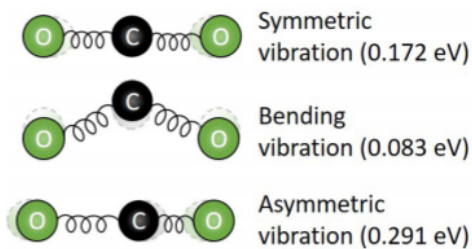
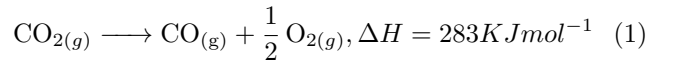


FIG. 2: Vibrational modes for the CO_2 molecule. [4]

Since CO_2 is a highly stable molecule, the conversion of CO_2 to $\text{CO} + \text{O}$ is not an easy task. The enthalpy variation of the reaction is very considerable, as shown in equation 1. CO_2 conversion can be accomplished through thermal conversion, at high temperatures but overall the

effective conversion rate is not sufficiently high to allow its industrial application[3].



In Figure 3 a representation of the energy levels of the CO_2 molecule is given. This figure provides a good illustration of two possible ways of dissociating CO_2 : either by a step-wise vibrational excitation (also referred to as vv up-pumping mechanism), or direct dissociation (equivalent process in equation 1). In the first, the CO_2 vibrational levels are excited one by one, and the energy of the molecule increases until it dissociates into CO and O . On the other hand, in the direct dissociation, an electron collides with the CO_2 molecule, causing the separation into CO and O , without any vibrational excitation. As it is shown in figure 3, the vibrational pumping mechanism requires less energy than the electron impact dissociation (5.5eV compared to 7.5eV), which is very important if our goal is to maximize the energetic efficiency of this process.

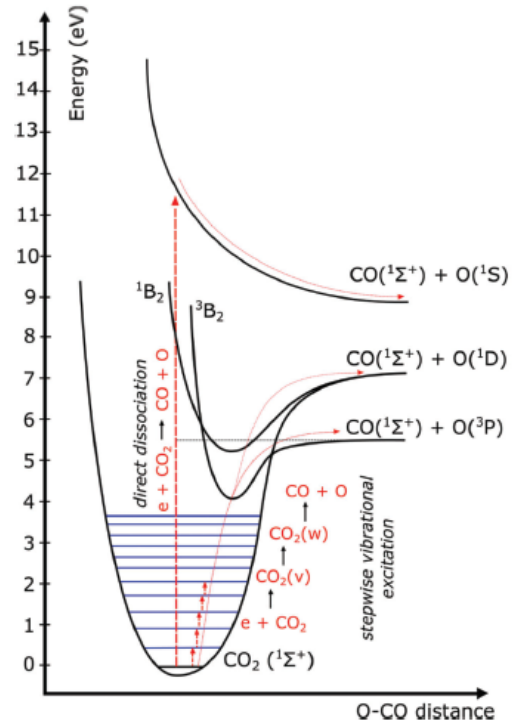
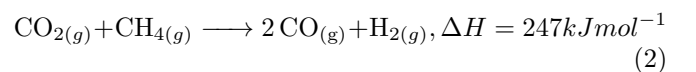


FIG. 3: Potential energy values of electronic states of CO_2 , as a function of the internuclear distance [2]

Another very important process for CO_2 conversion is dry reforming methane (DRM), which converts CH_4 and CO_2 into synthesis gas:



It is well known that CH_4 is also a greenhouse gas which also needs to be recycled. Just like the CO_2 dissociation, this reaction is highly endothermic, which means that high temperatures (≈ 1000 K), are necessary to have this process run in an efficient manner. Furthermore, a lot of side reactions occur simultaneously with this process, which promotes the creation of carbon deposits that deactivate the catalysts, preventing this reaction from being used in an industrial scale.

B. Plasma applications for CO_2 conversion

Plasma-based dissociation of CO_2 is a topic that has been experimentally studied in detail for more than 40 years. Two parameters are usually used to quantify the dissociation process: the energy efficiency η and the conversion rate α . In this context, it is worth mentioning that earlier results obtained in the Sovietic Union [5], [6] gave highly promising results, in the context of CO_2 dissociation under a non-equilibrium microwave discharge. Under supersonic expansion gas conditions, these studies revealed an energy efficiency of 80% - 90%. These remarkable levels of energetic efficiency, however, have not been replicated to this day, since the highest energy efficiency values recently reported are around 50-60 % [7]

With regards to dry reforming of methane many different types of plasma reactors for this process have been used, some with promising results. It is worth mentioning the very recent work of Montesano et al [8], using nanosecond repetitively pulsed discharges. It was shown that it is possible to achieve a conversion rate between 40 % and 50 % for CH_4 and CO_2 and an energetic efficiency between 50 and 65 %. Another promising experimental setup is the atmospheric pressure glow discharge plasmas (APGLD). In [9], the dry methane reforming was studied using this setup and it was possible to achieve a conversion of 98.52 % and 90.3 % of CH_4 and CO_2 respectively with a conversion ability was of 12.21 mmol/kJ.

C. DC Glow Discharge

The DC glow discharge will be the experimental setup used in work to explore the properties of CO_2/CH_4 plasmas. To form a DC glow discharge plasma it is necessary to apply a potential difference between two parallel electrodes placed in a gas-filled reactor (see figure 4). If the applied electric field is strong enough, certain molecules in the gas will break up into positive ions and electrons, resulting in gas breakdown. The applied electric field accelerates free electrons towards the anode, where they may collide with gas molecules, resulting in ionization, excitation, and dissociation. Former collisions generate new electrons and ions. The electric field accelerates the ions towards the cathode, where they generate secondary electron emission. The newly formed electrons may then

cause more ionization collisions. This series of events results in self-sustaining plasma.

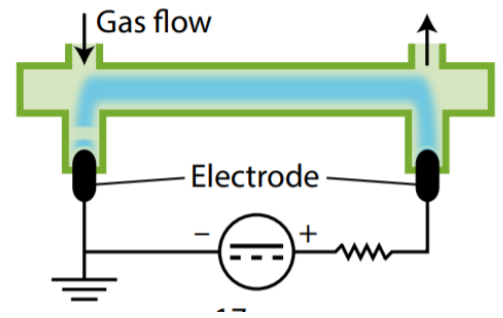


FIG. 4: Experimental setup for a low temperature, glow discharge plasma. Adapted from [10].

Because electrons have a relatively tiny mass in comparison to positive ions, they are quickly accelerated by the electric field, therefore their temperature will be significantly higher than that of the heavier species. Thus, whereas heavy ions have temperatures similar to neutral molecules, electrons have temperatures in the order of 10 000 K. Collisions will generate excited molecules, which can decay to lower energy levels and emit light, which is one of the plasma's distinctive features.

D. Modelling - LoKI

In order to accurately simulate our low temperature plasma and compare our experimental results, the LibOn KInetics Simulation Tool (LoKI) was used [11]. Plasmas are a notoriously complex environment, due to the non-linearity of the equations that govern it. Overall, the LoKI software is able to solve a two-term homogeneous electron Boltzmann (LoKI-B) and also to determine the chemistry of the various neutral and charged species present in the plasma (LoKI-C).

It's possible to write the electron Boltzmann equation as:

$$\frac{\partial f_e}{\partial t} + \vec{v}_e \cdot \vec{\nabla}_{\vec{r}} f_e + \frac{\vec{F}_e}{m_e} \cdot \vec{\nabla}_{\vec{v}_e} f_e = \left(\frac{\partial f_e}{\partial t} \right)_{coll}, \quad (3)$$

where f_e is the electron energy distribution function (EEDF), \vec{v}_e is the electron velocity, \vec{r} is the electron position, \vec{F}_e is the total force applied on the electron, $\left(\frac{\partial f_e}{\partial t} \right)_{coll}$ is the variation of the EEDF due to the collision between electrons and heavy species

The LoKI-B algorithm is responsible to solve this equation. Since this is a difficult task, many approximations are used. To learn more about the assumptions/approximations used in the LoKI-B Boltzmann solver, see Tejero-del-Caz et al [11].

On the other hand, LoKI-C is concerned with the processes that occur in the plasma that include heavy

species. So, for each heavy atom in plasma, including transport effects, the algorithm solves the zero-dimensional rate-balance equations (volume averaged). This is the rate balance equation for the general species i :

$$\frac{dn_i}{dt} = \sum_j \left(\frac{dn_i}{dt} \right)_j = 0 \quad (4)$$

Heavy-species chemistry reactions are classified into four categories: electron-heavy species (e-H), heavy species (H-H), diffusion to the wall (H-w), and reactor inlet and outlet flow. More details about the algorithm can be found in [11].

III. DIAGNOSTIC TECHNIQUES

Plasma diagnostics are a collection of methodologies, tools, and experimental techniques used to evaluate plasma characteristics such as density, temperature, spatial distributions. First we will describe optical emission spectroscopy and its potential for temperature measurements in plasmas. OES will also be used to analyze the broadband emission associated to the chemiluminescence from recombination of CO and O. After, we present the Fourier-transform infrared spectroscopy techniques, that were used to obtain the chemical composition of the plasma.

A. Optical Emission Spectroscopy

Optical Emission Spectroscopy (OES) is a non-intrusive optical technique that relies on the light produced by the relaxation of excited species in plasma. Because of its ease of use and great sensitivity, this method is perhaps the most commonly utilized diagnostic in plasmas. It is a qualitative way of measuring the plasma composition and it allows for several species to be detected at the same time. To characterize the emission spectrum obtained in OES, the following intensity equation can be used [12]:

$$I(p, q) = \frac{h\nu_{pq}}{4\pi} n(p) A(p, q) l \quad (5)$$

where $I(p, q)$ is the intensity line of the state transition $p \rightarrow q$, $h\nu_{pq}$ is the energy difference between the p and q state, p is the most energetic level, $n(p)$ the density of the q state, $A(p, q)$ the transition probability and l the line-segment of the plasma along which radiation is collected.

B. Rotational Temperature Fit - CO angstrom rotational band

Gas temperature measurements in plasmas through rotational temperature is a very common method provided that translational-rotational equilibrium exists. With this in mind, the objective of this diagnostic is to fit the emission spectrum of a rotational emission band, to obtain the rotational temperature. The method used will be based on the work of Silva et al [13] and Du et al [14]. The intensity distribution I_{rot} in a rotational emission band, associated to the vibrational transition between v_i and v_j , assuming a Boltzmann distribution, is given by [15]:

$$I_{rot} = \frac{C_{rot} S_{J_i J_j}}{Q_{rot} \lambda_{J_i J_j}^4} \exp\left(-\frac{F(J_i)hc}{k_B T_{rot}}\right) \quad (6)$$

where C_{rot} is a constant that combines all the terms not dependent on J states, Q_{rot} the statistical sum, $S_{J_i J_j}$ the Hönl-London factor (taken from [14]) and $\lambda_{J_i J_j}$ the transition wavelength, $F(J_i)$ the rotational energy term, which can be found in [14] and h , the Planck constant, k_B the Boltzmann constant and c the speed of light. Using a fitting script, that takes the experimental data collected and the FIT function of MATLAB, from the Curve Fitting Toolbox, a least-square fit is made and it provides the value for T_{rot} .

C. FTIR spectroscopy

Infrared Spectroscopy consists essentially in the study of the interaction of infrared light with matter. This can be achieved through an Infrared Spectrometer. Using IR absorption spectroscopy it is possible to determine with a high accuracy the density of the plasma species and its vibrational states.

A fitting algorithm was used to fit the transmittance spectrum obtained through the Infrared Spectrometer. This procedure was based on the algorithm developed by Klarenaar et al [16] and the later adaptations done by Henrique in [17]. In essence, using the Beer-Lambert law to calculate the transmittance, in the region $\nu \in [1000, 4000] \text{cm}^{-1}$, it is possible to fit the densities of the species present in table I

Molecules		
CO2	CO	CH4
C2H2	H2O	C2H6
C2H4		

TABLE I: Molecules included in the fitting algorithm

IV. RESULTS

We now present the results of this work, in three different sections: First, the experimental results coming from optical emission spectroscopy; Second, the experimental results coming from the fourier transform infrared spectroscopy; Finally, the results coming from the simulation developed. Experimental measurements for this work were all done in a glow discharge plasma.

A. Optical emission Spectroscopy - Experimental Results

In this section we will analyze the results related to optical emission spectroscopy. In particular we will analyze the potential of the Angstrom band to measure gas temperature and the applicability of broadband acquisition to quantify the reduced electric field of the discharge. The experimental measurements made using OES shared the same experimental setup, a glow discharge plasma similar to the one presented in figure 4. The pressure in the tube was varied between 0.5 and 5 Torr, with a constant total gas flow of 7.83 sccm using gas from bottles of pure CO₂, CH₄ and Ar. The discharge current was varied between 10 and 50 mA. All measurements were taken at the axial centre of the positive column of the glow discharge. Two different spectrometers were used in throughout the measures one wide range spectrum, where $\lambda \in [200, 900]nm$ and another for precise measurements, where the $\lambda \in [474, 484]$.

1. Broadband Study

The emission spectra analyzed in this work are characterized not only by the characteristics bands of CO₂, CO and atomic oxygen lines, but also by a continuum-like shape. This continuum is usually measured between 250 and 800 nm with a maximum intensity around 400 nm (see figure 5)

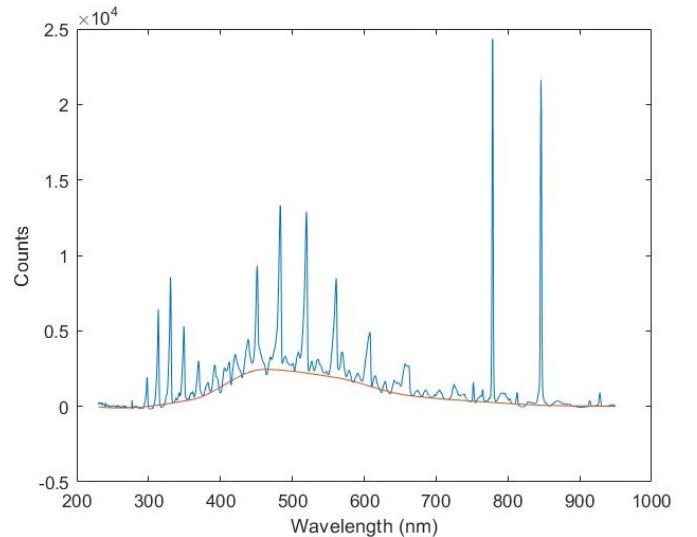


FIG. 5: Intensity spectrum measured for a DC glow discharge plasma with current of 40 mA, pressure of 3 Torr, and with gas composition of input flow of 7.40 sccm of CO₂ and 0.39 sccm of Ar.

To understand what is the process underlying this continuum, it is necessary to calculate its total intensity, which can be done by integrating the baseline of the spectrum over the full wavelength range. After this is done, we can analyse its dependence on the plasma parameters.

This emission is similar to the process of CO + O chemiluminescence reaction, proposed by Slack in [18]. However, it was found that rate coefficients in [18] were not suited to describe the experimental data. Since we are in the energy region that promotes CO₂ dissociation via electronic excitation due to high values of reduced electric field [2], in this work we propose that this is the main mechanism responsible for the continuum emission. Considering that the electron temperature is proportional to the change in reduced electric field, we can propose an expression for the intensity measured

$$k_{el} = a \cdot \exp\left(-\frac{c_{el}}{(E/N)}\right) \quad (7)$$

$$I = k_{el}[\text{CO}_2] \quad (8)$$

$$\log_{10}\left(\frac{I}{[\text{CO}_2]}\right) = -\frac{c_{el}}{(E/N)} + b \quad (9)$$

where a , b and c_{el} are constant values, (E/N) is the reduced electric field and $[\text{CO}_2]$ the CO₂ concentration. Equation 9 is used to fit the experimental data, as seen in figure 6.

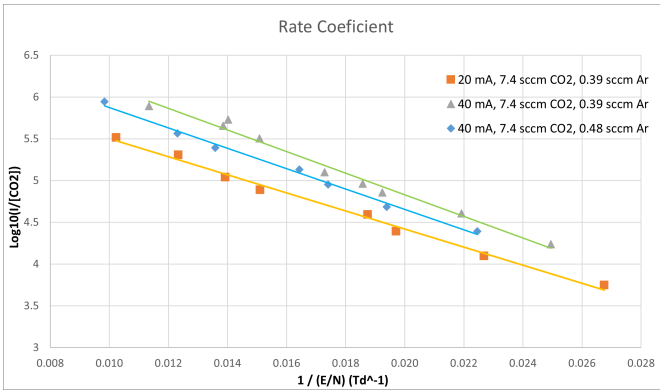


FIG. 6: Variation of the logarithm of broadband intensity divided by the CO_2 concentration, measured for different gas mixtures, as a function of the reduced electric field.

The results show a clear dependence of the intensity of the broadband emission on the electronic excitation of the CO_2 molecule. From figure 6 it is evident the linear dependence of the variables, from which we can conclude that the reduced electric field and the CO_2 concentration are the main parameters that determine the intensity of this emission.

Overall, the method developed in this section offers an easy-to-handle solution if quick reduced electric field measurements are required in CO_2 discharges, provided access to the broadband emission. This approach should be further studied and validated in future works. In particular, next studies should analyze the dependence of b and c_{el} constants with the plasma conditions (e.g. discharge current and flow rate).

2. Gas temperature measurements

The measurements for the CO rotational angstrom band were made in a much smaller wavelength range than in chapter IV A 1, and so a more precise spectrometer was used, where $\lambda \in [477, 484]$. As described in section , the intensity spectrum was fitted and the gas temperature was obtained, for different experimental conditions. Figures 7 and 8 show the evolution of the gas temperature as a function of the current and pressure, respectively.

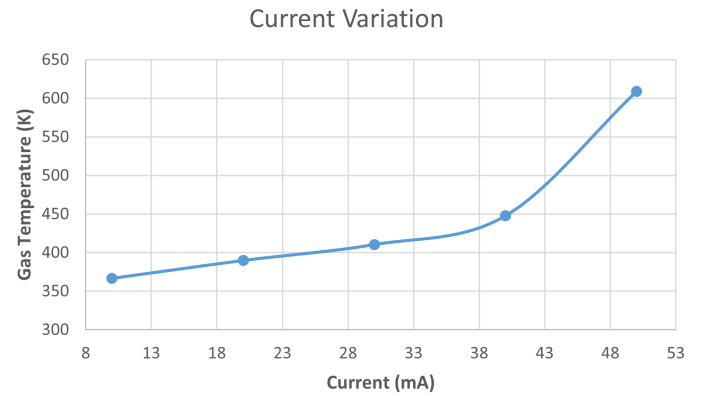


FIG. 7: Variation of the gas temperature with current, measured for a DC glow discharge plasma with pressure of 3 Torr, and with input flow of 3.7 sccm of CO_2 and 3.7 sccm of CH_4 .

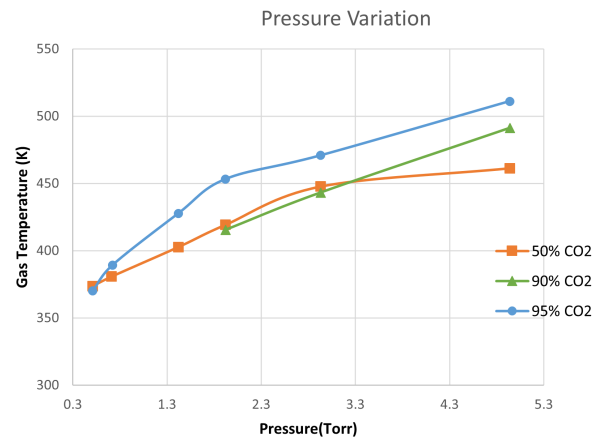


FIG. 8: Variation of the gas temperature with pressure, for a DC glow discharge plasma with a current of 40 mA, and varying input flows.

These results are consistent with the measurements that were made in the PhD thesis of A. S. Morillo-Candas in [19], in which the gas temperature was measured in CO_2 plasmas (but without CH_4), and also increased with the current and pressure values. Note that in [19] the gas temperature was obtained through FTIR measurements. In this work we have demonstrated that OES offers an easy-to-handle solution if T_{gas} measurements are required in CO_2 discharges, provided access to the emission of CO Angstrom band. To further validate this approach, it would be necessary to compare gas temperature measurements through FTIR measurements and through the rotational temperature fit.

B. DC Glow Discharge - Downstream FTIR measurements

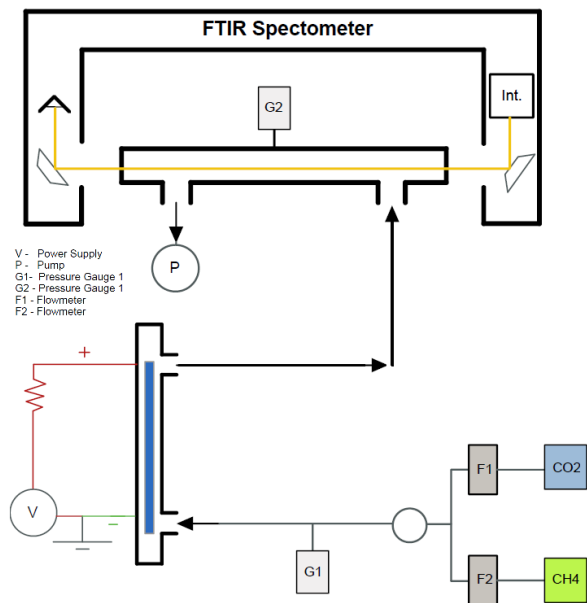


FIG. 9: Experimental setup for the DC Glow Discharge plasma, used for FTIR measurements.

In this section we analyze the concentration of species downstream the DC discharge, ignited with mixtures of CO_2 and CH_4 (see figure 9). More specifically, we will analyze the fraction of CO_2 , CO , CH_4 , H_2O , since these are the most abundant molecules on the plasma, as function of various parameters, namely gas pressure, initial CO_2 fraction and total gas flow. The input gas consists of CO_2 and CH_4 , whose flows are controlled by the respective flowmeters, in the range between 3.7 sccm to 7.40 sccm. The gas is pumped into the reactor, where the plasma is created as a result of the high voltage applied between the cathode and anode, with a low current (typically ≤ 50 mA). Finally, since this is a downstream measurement, the second reactor acts as a measurement cell for the post-plasma gas, and this is where the FTIR measurements will be made.

The results of the equilibrium chemical composition from the spectrum transmittance fitting are shown in figures 10 to 15. The simulated results are also present in the figures, and will be explored in section IV C. We can make the following general comments about each molecule:

- CO_2 is one of the most present molecules in the mixture. Overall, its concentration decreases with the increase in discharge current. Furthermore, its concentration increases with the increase in the amount of initial CO_2 in the mixture.
- CO is also one of the most present species in the mixture, for all of the conditions shown. The con-

centration of CO shows great increase with the rise of the discharge current.

- CH_4 concentration is generally not as high as CO_2 and CO . Furthermore, when initial flow of CO_2 is $\geq 90\%$, almost all CH_4 completely destroyed in the mixture.
- H_2O is present in the mixture and its concentration generally increases with the increase in pressure. Furthermore, there is an increase of the measured H_2O with the increase in the initial flow of CO_2 , but when the flow is 100 % CO_2 , the amount of H_2O vanishes (there are no H atoms).

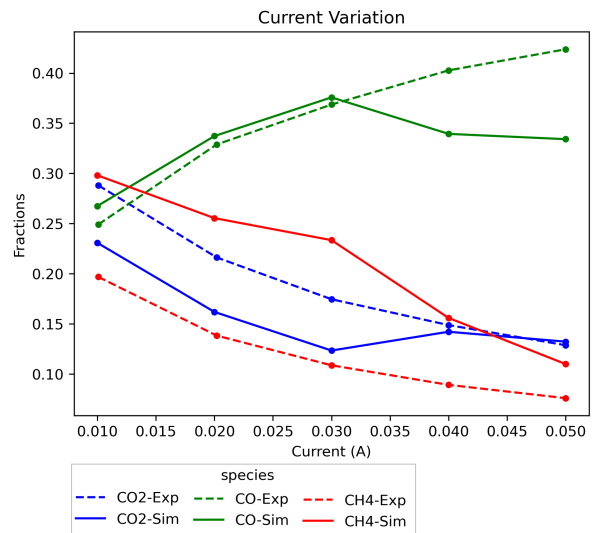


FIG. 10: Experimental and simulation equilibrium concentration values for CO_2 , CO , CH_4 , with varying current, at 3 Torr, with a 50/50% CO_2/CH_4 mixture and with total flow at 2.89 sccm.

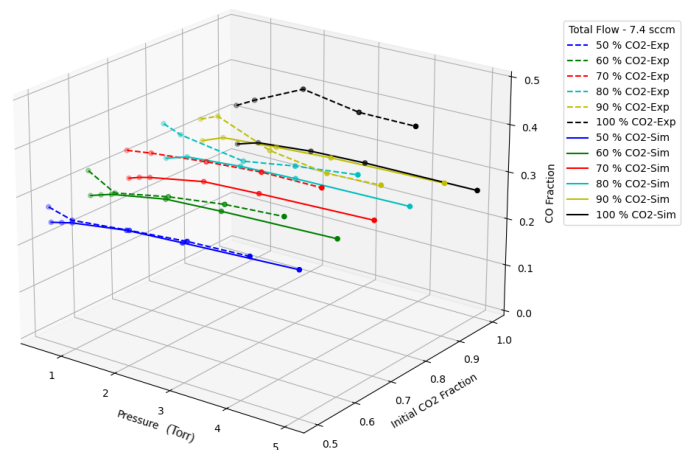


FIG. 13: Experimental and simulation equilibrium concentration values for CO , with varying pressure, current of 40 mA and with a total flow of 7.40sccm.

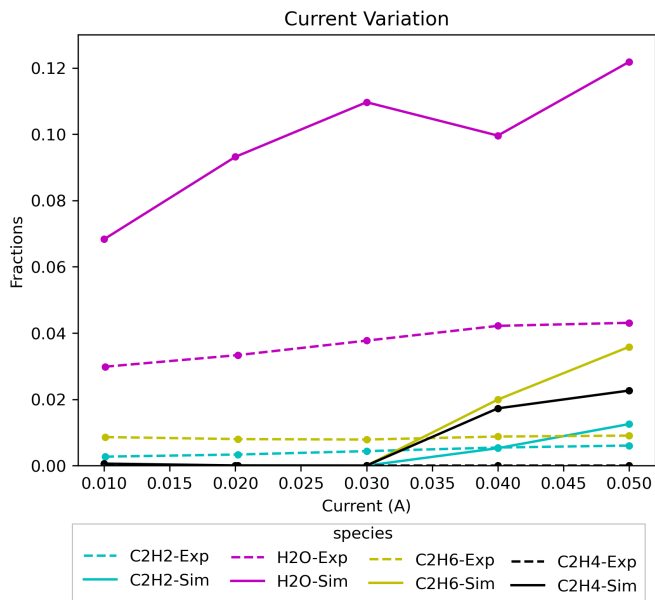


FIG. 11: Experimental and simulation equilibrium concentration values for H_2O , C_2H_2 , C_2H_4 and C_2H_6 , with varying current, at 3 Torr, with a 50/50% CO_2/CH_4 mixture and with total flow at 2.89 sccm.

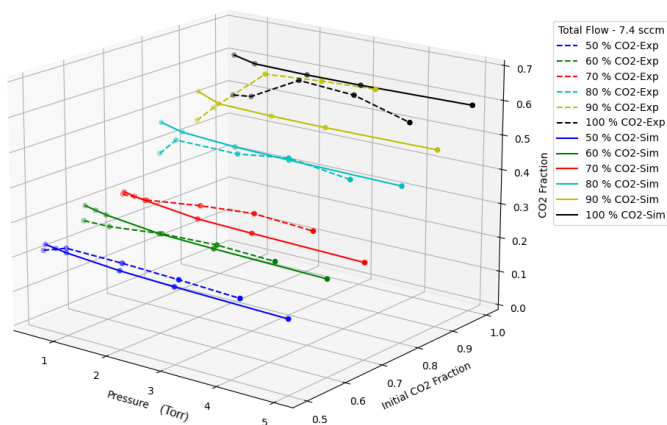


FIG. 12: Experimental and simulation equilibrium concentration values for CO_2 , with current of 40mA and varying pressure, with a total flow of 7.40sccm.

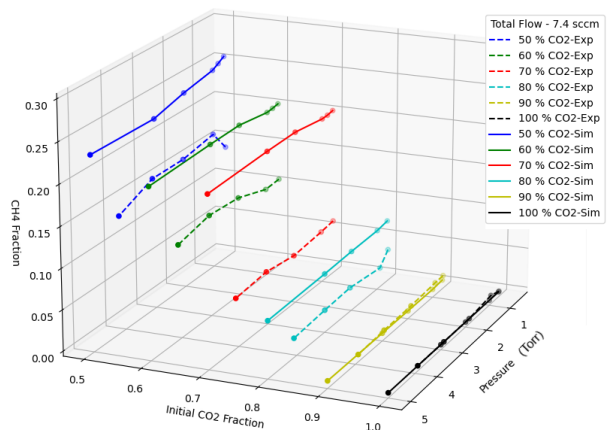


FIG. 14: Experimental and simulation equilibrium concentration values for CH_4 , with varying pressure, current of 40 mA and with a total flow of 7.40sccm.

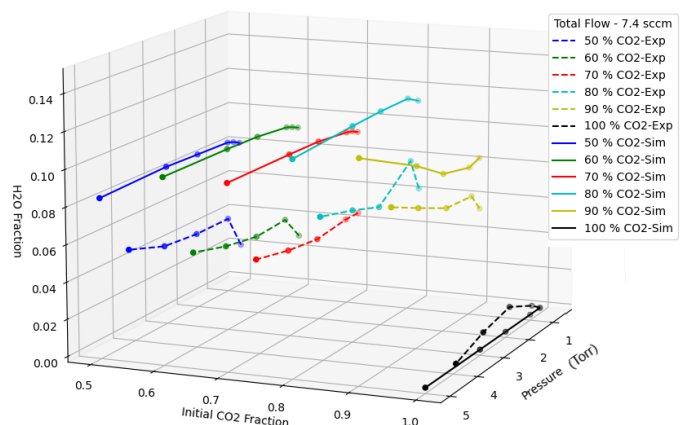


FIG. 15: Experimental and simulation equilibrium concentration values for H_2O , with varying pressure, current of 40 mA and with a total flow of 7.40sccm.

C. Simulation Results

In order to simulate the CO_2/CH_4 plasma and replicate the experimental data, several steps were necessary. First, it was necessary to select the proper cross sections to correctly simulate the electron kinetics of this system. This was validated using the IST Lisbon Database [20] and Dutton Database [21] to compare the swarm parameters, and very good agreement with the experimental data was obtained.

Having done this validation, we move to creating a model for the chemistry of our system. This was done by testing different reactions between the species present in the plasma and different rate coefficients, that were found in the literature. The model includes 23 species (present in table II) and more than 250 reactions. The complete set of reactions and rate coefficients is presented in the

full version of the thesis. After this, the model was tested for numerous plasmas conditions, to try to replicate our experimental data. The results of the equilibrium chemical composition from the spectrum transmittance fitting are shown in figures 10 to 15.

O ₂	O	O ₃	H ₂	H
CO ₂	CO	CH ₄	CH ₃	CH ₂
HCO	OH	H ₂ O	CH ₂ O	CH
C	C ₂	C ₂ H	C ₂ H ₂	C ₂ H ₃
C ₂ H ₄	C ₂ H ₅	C ₂ H ₆		

TABLE II: Molecules included in the kinetic model

Overall, the simulation results of the density are satisfactory. It was possible to simulate all the relevant species and the dependence with plasma parameters. The model was especially good at replicating the experimental conditions when the initial CO₂ was $\leq 90\%$. Although the agreement with experiment was not always very good, the predicted orders of magnitude and several general trends were correctly described. For most conditions, the errors between the experimental and simulated concentrations were between 2% and 10%. Furthermore, for some of the species, like CH₄ and H₂O, an error of about 5% to 15% in the concentration was consistently found, which is where major improvements in the model can happen.

V. CONCLUSIONS

In this work, we carried out an experimental and modelling study of CO₂-CH₄ plasmas. During the experi-

mental campaign we investigated several parameters, including the gas temperature and the plasma composition. These parameters were investigated as function of input gas pressure, gas flow and initial gas mixture. In respect to gas temperature analysis, the results revealed that the emission of CO molecules (measured through OES) can be used as a thermometer to characterize the discharge heating. This is particularly relevant for CO₂ non-thermal discharges given that CO is expected to be a direct product of the CO₂ decomposition.

Regarding the broadband continuous emission of CO₂-CH₄ plasmas, an easy-to-handle solution to measure the reduced electric field was developed, in the case of easy access to the broadband emission.

Regarding the studies associated to plasma composition, it is worth noticing that in this work we used FTIR to follow the evolution of not only CO₂ and CH₄ species, but also several decomposition products, including C_xH_y. These results are particularly relevant to the validation of future models focused on CO₂-CH₄ plasma chemistry.

On the modeling section, a kinetic model for CO₂/CH₄ was developed, which included 23 species and more than 250 reactions. This model was then used to replicate the experimental conditions and good agreement between experimental results and modelling was obtained. Despite the fact that the agreement with experiment was not always excellent, the expected orders of magnitude and some broad patterns were accurately characterized.

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