Activation of Carbon Dioxide and Methane by Non-Equilibrium Plasmas.

Henrique Ferreira Carvalho Leal Rodrigues
henrique.leal.rodrigues@ist.utl.pt

Instituto Superior Técnico, Lisboa, Portugal
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Abstract

Through line-of-sight, spatially resolved measurements of the transmission spectrum of a low-pressure glow discharge plasma through FTIR, a parametric study of the vibrational temperatures and molecular concentrations of the various species in a CO₂/CH₄ plasma was carried out. A model consisting of over 1500 different reactions and 100 species was then developed for this system which allowed for a deeper understanding of the main mechanisms of interaction in a CO₂/CH₄ plasma and to determine the influence of adding methane with regards to the excitation of the vibrational energy levels of carbon dioxide.

Keywords: CO₂/CH₄, Glow Discharge Plasma, Vibrational Kinetics, Dry Reforming of Methane.

1. Introduction

Fossil fuels have been directly responsible for unprecedented development rates in human evolution. Nevertheless, while the benefits reaped from the use of fossil fuels have been vast and profound, so have its consequences. Indeed, perhaps the foremost issue plaguing today’s society consists in the accumulation of anthropogenic greenhouse gases in the Earth’s atmosphere. Due to this, the depletion of natural resources and countries’ need for energetic security it is clearly imperative that an alternative non-pollutant and sustainable energy source be found. One viable path consists in the use of CO₂ Neutral Fuels, which is an umbrella-term for the creation of an energetically neutral closed cycle powered by non-polluting energy sources which hinges upon the capture and conversion of CO₂ into fuel and subsequent emission of CO₂ to be captured restarting the cycle [1].

One of the most promising avenues towards the production of this cycle consists in the use of Non-Thermal Low-Temperature Plasmas (LTPs). Plasmas by their very nature contain an extremely high concentration of chemically active species such as electrons, ions, excited states and radicals. Compound with avoiding unnecessary spending of energy in gas heating, this leads LTPs to exhibit great conversion rates as well as incredible energetic efficiency. Not only that, but possible end products for plasma processes include syngas, methanol and other value-added chemicals, whose chemical bonds are an extremely advantageous way of storing energy for later use. Finally, unlike fossil fuels, plasmas result in near-zero emissions.

Nevertheless pure CO₂ plasmas are not efficient enough to allow further large-scale implementations. To surmount this obstacle, two distinct approaches are being developed. The first is rooted in the study of the vibrational levels of CO₂ because the highly energetic electrons in a plasma are responsible for exciting the vibrational levels of CO₂, and vibrationally excited CO₂ is more easily dissociated [2, 3]. The second consists in the simultaneous conversion of CO₂ and CH₄ and is named Dry Reforming of Methane (DRM). This process is characterized by the production of syngas, a mixture of CO and H₂. There are two different types of DRM process which can be stimulated through plasmas: Direct Oxidative Plasma Liquefaction (DOPL) - where the final products are molecules which are already value-added fuels; and Indirect Oxidative Plasma Liquefaction (IOPL) - in which the final products are syngas and other molecules and which, through means such as the Fischer-Tropsch process, can be converted into liquid hydrocarbons. The threshold in regards to energetic efficiency is 60% for IOPL and circa 20% for DOPL (the difference amounts to the energy spent to convert the products into value-added fuels in the case of IOPL).

A comparison between the conversion rates and energetic efficiencies relative to both the pure CO₂ and the DRM reactions can be found in Fig 1. It is immediately clear from the figures that not only is the peak energetic efficiency higher for DRM (al-
most 70% whereas it was below 50% for pure CO\textsubscript{2}, it also occurs for a much lower temperature, which means that less energy is required to heat the gas

![Figure 1: Comparison of theoretical thermal conversion (left axis) and energetic efficiency (right axis) of CO\textsubscript{2} splitting (above) and DRM splitting (below). Adapted from [4]](image)

We present in Fig. 2 a comparison of all the data collected from the literature for DRM regarding the different plasma types which was carried out by Snoeckx et al [4], showing the energy cost as a function of the conversion. As per their own words, (...) the thermal equilibrium limit and the target energy cost of 4.27 eV per molecule for the production of syngas (corresponding to a 60% efficiency target) are also indicated.. Besides Plasma-driven means, several other methods have been developed in the last decades to counteract the shortcomings of more traditional CO\textsubscript{2} dissociation processes [5, 6], but they have thus far proved inferior to the solutions presented by plasma-based alternatives.

The aim of this thesis is twofold: to develop a deeper understanding of the main mechanisms of interaction in a CO\textsubscript{2}/CH\textsubscript{4} plasma and to determine the influence of adding methane with regards to the excitation of the vibrational energy levels of carbon dioxide. In order to achieve this, the work was divided into two parts: an experimental part done at LPP in Ecole Polytechnique de Paris, and a modelling part done at IST.

Regarding the experimental work, line-of-sight, spatially resolved measurements of the transmission spectrum of a glow discharge plasma through FTIR were obtained. The use of a low-pressure glow discharge instead of other plasma types allows for an easier understanding of the vibrational excitations which others would lack. A code partially developed allowed for the pre-treatment and fitting of this spectrum whilst correcting for factors such as the plasma’s own emission radiation and the emission curve of the lamp used for the measurements. In-situ measurements allow for the determination of the plasma working conditions - pressure, electric field and gas temperature, as well as the various vibrational temperatures of CO\textsubscript{2} and CO, hence their vibrational population distribution - and downstream measurements determine the plasma chemistry. Finally, by using a pulsed plasma, the time-dependent evolution of the plasma various quantities can be determined.

The modelling part was carried out utilizing the LoKI code [7], more specifically the two modules LoKI-B and LoKI-C. LoKI-B solves the two-term electron Boltzmann equation, whereas LoKI-C provides the solution to the 0-dimensional system of rate equations for all species present in the plasma [7]. When coupled together, upon finding agreeing results between the experimental and modelling values, it should be clear exactly what the main mechanism of interaction in the plasma are, and how to optimize configurations with regards to CO\textsubscript{2} splitting.

2. Theoretical Concepts

There are three main distinct contributions to the energy levels of molecules (one can neglect at the relevant temperature ranges the contribution from the nuclear energy levels since it is much smaller than all the others): the electronic excitation, which depends on the energy level of the electrons in their orbitals (\(n\)); the vibrational excitation, which corresponds to the vibrational normal modes of the molecules (\(\nu\)); and the rotational energy, which stems from the total angular momentum of the
molecule when thought of as a whole (J) [8]. Normally, in molecular spectroscopy, these are decoupled under what is called the Born-Oppenheimer Approximation, allowing one to write [9]

\[ E_{n,v,J} = E_e(n) + E_{vib}(v) + E_{rot}(J) := E_n + E_v + E_J. \]  

(1)

To actually model these energy level dependencies, several assumptions have to be imposed. In the simplest possible approximation, upon decoupling these terms, the rotational term corresponds to a quantized rigid rotor whereas the vibrational levels correspond to an harmonic oscillator.

2.1. The CO₂ and CH₄ Molecules

The CO₂ molecule is a linear triatomic molecule. A linear polyatomic molecule with N atoms usually possesses 3 Translational degrees of freedom, 2 Rotational degrees of freedom and 3N-5 vibrational degrees of freedom. In this case, this means 4 vibrational degrees of freedom. However, due to the symmetry inherent to the CO₂ molecule that arises in view of having two oxygen atoms, two of these modes are degenerate.

Therefore, the CO₂ molecule possesses three vibrational modes: the non-degenerate symmetric stretching mode \( \nu_1 \), the double-degenerate bending mode \( \nu_2 \) and the asymmetric stretching mode \( \nu_3 \). These are present in Figure 3.

![Figure 3: Vibrational Modes of CO₂. Source: [10]](image)

Using these three modes and the projection of the angular momentum of the bending mode onto the axis of the molecule \( I_2 \), it is possible to refer to the rovibrational state of the CO₂ molecule using the so-called Herzberg form \( \text{CO}_2(\nu_1, \nu_2^2, \nu_3) \). One final important point to raise with regards to the CO₂ molecule deals with the occurrence of Fermi Resonance for rovibrational levels which couples them together. Indeed, for a Fermi Resonance to occur, it is necessary that not only two states have almost the same energy (in other words, that a transition from one given level to either of these two have approximately the same wavelength), but the two vibrational states must also possess the same symmetries, that is, have the same Mullikian symbol. It can easily be seen that, since \( \omega_1 \approx 2\omega_2 \), the levels \( \text{CO}_2(\nu_1, \nu_2^2, \nu_3) \) and \( \text{CO}_2(\nu_1 - 1, (\nu_2 + 2)^2, \nu_3) \) will possess approximately the same energy. Furthermore, since they are degenerate, it follows that they must exhibit the same symmetries, leading to a fermi coupling between these two levels. In essence, one experiences a resonance phenomenon of the type

\[ (\nu_1, \nu_2^2, \nu_3) \rightarrow (\nu_1 \pm 1, (\nu_2 \pm 2)^2, \nu_3). \]  

(2)

To deal with this, one considers a state whose degeneracy corresponds to the sum of the degeneracy of the two states coupled and whose energy is an average of their energies.

![Figure 4: Idealized Fermi Resonance representation](image)

The CH₄ molecule is a polyatomic molecule somewhat more complex than the carbon dioxide one. Indeed, it is a tetrahedral molecule possessing 15 degrees of freedom: 3 Translational degrees of freedom, 3 Rotational degrees of freedom and 9 Vibrational degrees of freedom. Nevertheless, due both to its inherent geometry and the fact that all the vertices are H atoms, these vibrational modes are degenerate. Indeed, after coupling the degenerate modes together, methane possesses solely 4 distinct vibrational modes. Thus, the vibrational state of a methane molecule can be expressed as \( \text{CH}_4(\nu_1, \nu_2, \nu_3, \nu_4) \) with degeneracies \( (1, 2, 3, 3) \).

2.2. Glow Discharges and RF Discharges

A glow discharge is, essentially, a self-sustained gas discharge in a region between a charged anode and cathode caused by a high enough voltage, during which the cathode emits electrons due predominantly to bombardment by positive ions [11], and whose name arises from the characteristic light emission. The glow discharge has two distinct regions depending on the applied voltage. In the normal regime, the voltage is approximately constant and independent of the discharge current over several orders of magnitude [12]. A glow discharge presents a very characteristic division in alternating dark and luminescent regions, whose distribution is independent of the conditions under which it is operating but whose relative size is extremely dependent on these conditions. This stratification can be seen in Fig. 5.

![Figure 5: Glow Discharge](image)

2.3. Diagnostic Techniques - 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. FTIR Spectroscopy - Fourier Transform Infrared Spectroscopy - is a specific case where, instead of utilizing a monochromatic incident light,
Figure 5: Various regions within a glow discharge, partially adapted from [11]

A polychromatic beam of incident light containing several frequencies is shined upon a target, after which it is modified to contain a new array of frequencies. This process is repeated as desired until, at the end, the raw data - denoted interferogram - is put through a Fourier transform enabling one to obtain the final desired spectrum, which in essence translates a plot of measured intensity of the light as a function of one of its characteristics, for instance, the relative intensity of the light’s absorption by the molecules for each incident wavelength [13]. The actual inner workings of FTIR are, nevertheless, rather simple, as exemplified in Fig. 6.

Figure 6: Scheme of an Interferometer utilized for FTIR

The interferometer is composed of two perpendicular plane mirrors, one of which is fixed whereas the remaining can be moved. A beamsplitter is utilized so as to cause the incoming laserbeam to divide itself and travel two different paths to each mirror, after which they will be reflected. Upon recombining, interference will occur due to the two rays of light having travelled different lengths, and the new laserbeam will move towards the detector. Taking into account the plasma radiation emission, one can write for the transmission spectrum:

$$T = \frac{I_T}{I_0} = \frac{I_{T_0} - I_p}{I_0},$$

where $T$ is the transmittance, $I_0$ is the intensity of the spectral profile of the IR source - which is obtained after purging the reactor with nitrogen and operating the FTIR spectrometer in its conventional mode - and $I_T$ is the transmitted light intensity obtained after subtracting the intensity $I_p$ of the plasma’s radiation, which takes into account both the radiation directly emitted towards the detector as well as the one that is detected after travelling through the interferometer, from the measured intensity $I_{T_0}$. This transmittance is obtained for each incident wavelength after being Fourier-transformed, allowing one to obtain the transmittance spectrum.

2.3.1 In-Situ

Figure 7: Flowchart of the fitting procedure adapted from [14]

The flowchart above serves as a guideline for the fitting procedure utilized for the in-situ measurements. This procedure is based on an algorithm developed by Klareenar et al. This algorithm considers the region $\nu \in [1975, 2400] \text{cm}^{-1}$ and fits the CO vibrational lines and the CO$_2$ asymmetric lines present in this spectral region. Regarding the downstream measurement fitting procedure, a similar algorithm was developed and extended from a previous existing one also developed by Klareenar et al to the region $\nu \in [1000, 4000] \text{cm}^{-1}$, taking into account all the possible molecules that could be viable...
in a CO₂/CH₄ mixture and whose information was present in the HITRAN database. Regarding the In-Situ measurements fitting, one starts by defining the fitting parameters as per table 1.

2.4. Modelling

The LisbOn Kinetics (LoKI) Code is the simulation tool utilized throughout this work. It is made up of two distinct blocks which can be coupled: a two-term homogeneous electron Boltzmann equation solver on one hand, and a 0D chemical solver for the various neutral and charged species present in the plasma. Under the working approximations of Steady State, Plasma Homogeneity, no magnetization and small anisotropic regime we can write the electron’s boltzmann equation solved for in LoKI-B as

\[ \frac{\partial f_e}{\partial t} = \frac{eE}{m_e} \cdot \nabla_v f_e = \left( \frac{\partial f_e}{\partial t} \right)_{\text{coll}}, \]  

where the RHS includes collisions with other electrons, ions and neutral species. In our case, we shall neglect collisions with other electrons and retain the other two terms. Regarding the kinetics of the remaining species present in the plasma, several reaction types are considered: firstly, electron-neutral reactions, divided into four main cases: elastic collisions, electron impact dissociation, electron impact ionization, and electron attachment, for which the rate coefficients were calculated by integrating the specific reaction’s cross section with the EEDF calculated through LoKI-B, where the cross section was adjusted by an energy shift for the excited species; secondly, electron-ion recombinantion and detachment reactions, whose rates was found in the literature; thirdly, neutral-neutral, ion-neutral and ion-ion reactions whose rates were obtained also in the literature. In the case of involving vibrational species, the Fridmann approximation [2] was utilized, which asserts that for a given particle in state \( i \), the reaction rate can be scaled from the ground state reaction rate \( k_0 \) according to

\[ K(E_i, T_g) = k_0 e^{\alpha_F g_{\text{rot}}}, \]  

where \( E_i \) denotes the particle’s energy, \( T_g \) the gas temperature and \( \alpha_F \) is a parameter that can be approximated by \( \alpha_F = \frac{E_i^{(1)} + E_i^{(2)}}{E_i^{(1)} + E_i^{(2)}}, \) where \( E_i^{(1,2)} \) correspond to the arrenhius energy of the direct and inverse reactions respectively.

Also considered in the model were VT transfers, VV transfers, eV transfers and spontaneous emission. The eV reaction rates were calculated self-consistently by integrating the tabulated cross sections found in the literature during the LoKI-B modulus when such data was available. Otherwise, all these rates were obtained directly from the pre-existing literature [3, 15, 16, 17]. In order to calculate the inverse reactions for binnary heavy-particle

<table>
<thead>
<tr>
<th>Variable</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{rot}} )</td>
<td>Rotational Temp.</td>
</tr>
<tr>
<td>( T_{12} )</td>
<td>CO₂ vib. modes ( \nu_{1,2} ) Temp.</td>
</tr>
<tr>
<td>( T_3 )</td>
<td>CO₂ vib. mode ( \nu_3 ) Temp.</td>
</tr>
<tr>
<td>( T_{\text{CO}} )</td>
<td>CO vib. Temp.</td>
</tr>
<tr>
<td>( c_{T_i} )</td>
<td>Thermal Variable</td>
</tr>
<tr>
<td>( \alpha = \frac{[\text{CO}]}{[\text{CO}]+[\text{CO}_2]} )</td>
<td>CO₂ Conversion Factor</td>
</tr>
<tr>
<td>( p )</td>
<td>Pressure</td>
</tr>
</tbody>
</table>

Table 1: Fitting Parameters

Several assumptions and simplifications are carried out:

1. \( T_{\text{rot}} \approx T_{\text{gas}} \) is identical for all molecules.
2. \( T_{\nu_1} = T_{\nu_2} = T_{12} \)
3. The plasma is divided into a thermal and a non-thermal region. The thermalized fraction is considered to be \( f_t = 26\% \).
4. The pressure \( p \) for both non-thermal and thermal regions is the same. However, while \( T_{\text{int}} = T_{\text{rot}} \), \( T_i = c_{T_i}(T_{\text{rot}} - 273) + 273 \) where \( c_{T_i} \in [0,1] \), that is, the thermal temperature ranges from 273K to the same temperature as the non-thermal part.
5. The relative proportion of CO and CO₂ is identical for the thermal and non-thermal regions.

Due to the measurements being downstream, the gas is completely thermalized; hence, the fitting parameters now become the gas temperature \( T_g \), the pressure \( p \) and the concentrations of the various molecules. Furthermore, both the vibrational and the rotational distributions are now assumed to be a boltzmann distribution. The molecules included are presented in table 2.

<table>
<thead>
<tr>
<th>Molecule</th>
<th></th>
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<tbody>
<tr>
<td>CO₂, CO, O₃</td>
<td></td>
</tr>
<tr>
<td>CH₄, H₂O₂, OH, C₂H₂</td>
<td></td>
</tr>
<tr>
<td>H₂O, CH₂O, C₂H₆, HCOOH</td>
<td></td>
</tr>
<tr>
<td>C₂H₄, CH₃OH, C₄H₂</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Molecules included in the fitting algorithm
collisions, we utilized the detailed balance principle:

\[ k_{kl \rightarrow ij} = \frac{k_{ij \rightarrow kl} g_i g_j \exp\left(\frac{(E_k + E_l - E_i - E_j)}{k_B T}\right)}{k_{ij}} \]

where \( E_x \) and \( g_x \) denote the energy and degeneracy of a given state \( x \) and \( T \) corresponds to a given temperature which will be reaction dependent - for instance, in the case of eV reactions, it shall be the electron temperature, whereas for the VV and VT reactions the temperature utilized was the gas temperature.

Regarding transport phenomena, for neutral species the reaction rate utilized takes into account Fickian diffusion and the interaction with the walls of the reactor, and is given by the inverse of a characteristic time \( \tau_i \) given by [18]

\[ \tau_i = \frac{A^2}{D_i} + \frac{V}{A} \frac{4 - 2 \gamma_i}{\gamma_i v_{th_i}} \]

where \( V \) and \( A \) are the chamber volume and area respectively, \( v_{th_i} \) is the thermal velocity of species \( i \) in the plasma, \( \gamma_i \) is the probability of destruction of the species at the wall, and \( D_i \) is the diffusion coefficient obtained through the Chapman-Enskog equation as in [19] after correcting for the different background gases through Blanc’s Law: \( \frac{1}{D_i} = \sum_j \frac{n_j}{D_{ij}} \).

Regarding charged species we also considered ambipolar diffusion transport phenomena, with the rate coefficient given by [20]

\[ k_{a,i} = \frac{A^2}{\mu_i} \sum_{j=1}^{n+1} n_j \mu_j \frac{\sum_{j=1}^{n+1} n_j D_j}{\mu_i} \]

where the characteristic length \( A \) is dependent upon the reactor’s geometry, \( \mu_i \) is the ion’s mobility obtained through Blanc’s Law from the self diffusion mobilities obtained through the low electric field Langevin’s mobility expansion \( \mu_{i,j} = 0.515 \frac{e \alpha_i}{m_i} \gamma_j \)

with \( m_{i,j} \) the reduced mass and \( \alpha_i \) the polarizability, and \( D_j \) is related to \( mu_j \) through Einstein’s relation \( D_j = \frac{k_B T}{e^2 \mu_j} \).

3. Results

3.1. Experimental Results

Regarding the In-Situ measurements, the parametric dependendency of the various temperatures \( T_{rot} \), \( T_{12} \) and \( T_3 \) are present in Fig 8, Fig 9 and Fig 10 respectively.

The overall trend of the rotational temperature seems to be independent of the amount of CH\(_4\) present in the initial mixture, increasing with pressure and with the current acting as an offset. The higher the amount of CH\(_4\), the lower the temperature at a given pressure and current condition - whereas the current seems not to have an equally large effect. One possible explanation resides in the fact that the energetic threshold for the most common ionization and dissociation processes by electron impact is lower for CH\(_4\) than for CO\(_2\) and the overall effect of these is also more pronounced, leading to the creation of lower energetic neutrals and ionic species in the plasma at the same working conditions. The scenario is nearly identical with regards to \( T_{12} \), with the major difference being that the quenching of the symmetric vibrational modes of CO\(_2\) in the CO\(_2\)/CH\(_4\) plasma with relation to the pure CO\(_2\) case is more pronounced than the decrease in gas temperature. With regards to \( T_3 \),
the overall behaviour upon adding CH\textsubscript{4} to the initial gas mixture seems once again to stay the same, with a decrease in the temperature - therefore a quenching of the vibrational population - with increasing amounts of methane. Also like before, the current seems to play a much smaller role than the initial mixing ratio. It is important to notice, however, that the quenching is smaller for the asymmetric mode $\nu_3$ than for the symmetric modes $\nu_1$ and $\nu_2$.

Regarding the downstream results, the various molecular concentrations were determined. Amongst these, the dissociation parameter $\alpha$, the CH\textsubscript{4} concentration, the H\textsubscript{2}O concentration, and the C\textsubscript{2}H\textsubscript{6} concentration can be seen in Fig 11, Fig 12, Fig 13 and Fig 14 respectively. The only other molecule present was C\textsubscript{2}H\textsubscript{2}, albeit in smaller quantities and only for large initial CH\textsubscript{4} fractions - not including undetectable species such as H\textsubscript{2}, H, O\textsubscript{2} and O, which were found to be present by studying the C, O and H atom balance.

It is patently obvious that CH\textsubscript{4} increases the $\alpha$ parameter, which comes from an increase in CO production. Like for the In-Situ case, the higher the current the higher the $\alpha$ parameter; For CH\textsubscript{4}, a higher current leads to a higher dissociation. However, an increase of the CH\textsubscript{4} concentration in the initial mixture leads from a situation where methane is either completely or very nearly so consumed for high enough currents to a situation where it is always present in the final mixture. This occurs at the same initial mixture for which $\alpha$ drops sharply, which indicates a correlation. Finally, it is noticeable that the influence of the current increases with the amount of methane in the gas - in fact, the spacing between CH\textsubscript{4}'s concentration for different currents increases significantly. C\textsubscript{2}H\textsubscript{6} becomes relevant at circa 70% CH\textsubscript{4} in the gas mixture, and exhibits an increase with pressure. The behaviour of H\textsubscript{2}O is radically different - with regards to current, a higher current leads to a higher formation of H\textsubscript{2}O (which implies that electron impact leads to a higher production rate of H and O radicals that can then form water than dissociation.
of water molecules). Initially, the production of water is the main chemical reaction channel but this changes with an increase in CH$_4$ in the gas mixture, instead leaving the hydrocarbons and other undetectable particles such as H$_2$ as its main end products. It also exhibits an increase with pressure.

3.2. Modelling Results
Under our model, the procedure developed so as to simulate the experimental results was the following (note that the residence time is determined from the flow, the fitted pressure and the fitted temperatures in the plasma):

1. Take as inputs the experimental gas temperature $T_g$ and pressure $p$.
2. Use the measured electric field and concentrations of molecules in a run of LoKI-B to calculate the electron density $n_e$, which acts as an input.
3. Run LoKI until an end time such that the system converges $t_f = \tau_\infty$.
4. Use the resulting self-consistently calculated reduced electric field $\vec{E}$ as an input for another LoKI run with $t_f = \tau_R$ the residence time and with the quasineutrality cycle disabled.
5. Take the ensuing input as the in situ results and run a single iteration of the pressure cycle with $E = 0$ to recreate the downstream conditions.

In order to test whether the electron kinetics results were accurate, a study of the swarm parameters was carried out. Simulations were run utilizing LoKI-B and the resulting quantities were benchmarked against known results when such were available. The results were all in agreement with the known values.

3.2.1 Pure CO$_2$ Plasma

A Non-Vibrational model which excludes the vibrational species from the chemistry and a Vibrational model were developed and the results compared with the experiment and between themselves. The results obtained are presented in Fig 15. It is evident that, for both models, the results are extremely good, especially with regards to the no-vibrations model. However, upon the addition of the vibrations, the dissociation becomes enhanced in such a manner that it actually deviates from the experimental results. Tests carried out eliminated as possibilities the approximation for the vibrational states’ dissociation cross sections, which yielded a maximum difference in $\alpha$ below 5%, and the difference in the EEDF caused by the change in the vibrational populations of CO$_2$ and CO for the vibrational model, but that too yielded little influence upon being tested. One final possibility is the description of the vibrational mode’s chemistry being flawed.

With regards to the vibrational temperatures, the results can be found in 16. While $T_{12}$ matches up nearly perfectly with the experimental values, the same is not true for $T_3$. The reason for this is, we believe, found in the CO description. Indeed, the CO vibrational temperature is quite different from the experimental value, and the VV interactions between the assymmetric CO$_2$ vibrational mode $\nu_3$ and the CO vibrational modes are extremely important.

3.2.2 CO$_2$/CH$_4$

The comparison between the model and the experiment come mainly from CH$_4$ and H$_2$O, since these are abundant enough to be comparable but are not affected by the issues present with the fitting script being unable to account for the carbon atoms that come from CH$_4$ with regards to the calculation of $\alpha$. These molecule’s concentrations can be seen in Fig 17 and Fig 18.

Our model seems to display, overall, a good agreement with the experiment, albeit not close to the same degree that the pure CO$_2$ model was. The main molecules predicted are the ones that are verified experimentally and broadly speaking their parametric dependencies follow the same trends with slight hiccups and exceptions along the way. Finally, regarding the temperatures, the results can be seen in Fig 19 and Fig 20. For $T_{12}$, the results are in good agreement with the experimental values, especially with respect to the current and pressure dependencies. However, modelling results are somewhat bracketed by the experimental ones, which allows us to conclude that our model underestimates the vibrational temperature’s decrease with the CH$_4$ concentration in the initial mixture. The same is not true for $T_3$, where although both the pressure and current’s dependency seem to be taken into account correctly, the dependency on the initial gas mixture is wrong. To proceed, one should review the pure CO$_2$ VV interactions for the assymmetric mode, given the already pre-existing issues remarked upon at length in the pure CO$_2$ analysis, especially with regards to H$_2$ and CH$_4$ interactions.

4. Conclusions

The results obtained were overwhelmingly positive, excluding the assymmetric mode’s vibrational temperature’s dependence on the initial gas mixture. The developed model accurately reproduced within reasonable deviations the experimental results from a chemical standpoint, comparable to the molecu-
Figure 15: Comparison of $\alpha$ for the experimental values, non-vibrational model values and vibrational model values.

Figure 16: Vibrational and Experimental Comparison of the $T_{12}$, $T_3$ and $T_{CO}$ vibrational temperatures.

Figure 17: In Situ CH$_4$ concentration parametric study.

Figure 18: In Situ H$_2$O concentration parametric study.

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