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CO₂ conversion in a microwave plasma reactor in the presence of N₂: Elucidating the role of vibrational levels

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Abstract

A chemical kinetics model is developed for a CO₂/N₂ microwave plasma, focusing especially on the vibrational levels of both CO₂ and N₂. The model is used to calculate the CO₂ and N₂ conversion, as well as the energy efficiency of CO₂ conversion, for different power densities and for N₂ fractions in the CO₂/N₂ gas mixture ranging from 0 till 90%. The calculation results are compared with measurements, and agreements within 23% and 33% are generally found for the CO₂ conversion and N₂ conversion, respectively. To explain the observed trends, the destruction and formation processes of both CO₂ and N₂ are analyzed, as well as the vibrational distribution functions of both CO₂ and N₂. The results indicate that N₂ contributes in populating the lower asymmetric levels of CO₂, leading to a higher absolute CO₂ conversion upon increasing N₂ fraction. However, the effective CO₂ conversion drops, because there is less CO₂ initially present in the gas mixture, and thus also the energy efficiency drops with rising N₂ fraction.

1. Introduction

In recent years, there is considerable interest in the plasma-based conversion of CO₂ into value-added chemicals or fuels, by means of different types of plasmas^{1–23}. A microwave (MW) plasma is gaining increasing interest^{5–12}, because of the high energy efficiencies reported under some conditions^{1,13,14}. Most experiments are carried out in pure CO₂^{3–9}, or in combination with CH₄ (i.e., dry reforming)^{11,12,15–19}, H₂^{20,21}, H₂O¹⁰ or an inert gas^{22,23}. However, in real gas emissions from combustion or the chemical industry, the CO₂ will not be in pure form, but it will be mixed with other gases, such as N₂. It is therefore crucial to study the effect of N₂ on the CO₂ conversion and on the energy efficiency of the process. A few experiments have been performed for CO₂/N₂ mixtures, more specifically in a gliding arc⁴ and a glow discharge²⁴. In both cases, a higher CO₂ conversion was found when adding N₂. However, the exact mechanisms for the conversion of CO₂ and N₂ were not discussed, and to our knowledge, no experiments are performed yet for CO₂/N₂ mixtures in a microwave discharge.

Computer modeling can be very useful to provide more insight in the underlying reaction mechanisms of the effect of N₂ on CO₂ conversion. The modelling of CO₂/N₂ plasmas was initially motivated by the application of CO₂ lasers^{25,26}. However, these early models did not

include the vibrational levels of the molecules, which are stated to be important in certain plasmas, especially in a microwave plasma, and for the application of CO₂ conversion¹. For pure N₂, or N₂/O₂ mixtures, there are several papers presenting kinetic models with a complex description of vibrational and electronic levels, e.g.^{27,28}. The diatomic molecules are significantly easier to model than CO₂, because it is possible to include all (i.e., several tens of) vibrational levels of their single vibrational mode in a straightforward manner. Also, there are more reliable reaction rate coefficients available from various experiments and ab-initio calculations. Nevertheless, the various mechanisms that contribute to the dissociation of N₂ in a microwave plasma seem not to be completely elucidated²⁹.

For the dissociation of pure CO₂ in a plasma, Rusanov and Fridman presented a model combining a kinetic description of the chemical reactions and a temperature-based description of the vibrational distribution functions of CO₂ and CO^{1,13}. Based on their work, we have presented a reaction kinetics model for the dissociation of CO₂ in a MW plasma and a dielectric barrier discharge^{30,31}, which includes state-to-state reactions of vibrational levels of CO₂ and CO in a similar manner as was done for N₂ in the above mentioned works. However, to our knowledge, there exist no models yet for a CO₂/N₂ plasma, including the vibrational levels.

In the present paper, we show the results of such a computer model developed for studying the effect of N₂ on the CO₂ conversion in a MW plasma, taking into account the vibrational levels of both CO₂ and N₂. Indeed, it is known that the CO₂ vibrational levels are very important for energy efficient CO₂ conversion in a MW plasma^{1,30,31}. Therefore, we will focus especially on the behavior of the CO₂ vibrational levels, and how they are affected by the presence of N₂ (and their vibrational levels), and consequently, how this influences the CO₂ conversion and energy efficiency in the MW plasma.

2. Model description

The model used for this study is a zero-dimensional (0D) chemical kinetics model, called ZDPlaskin³². In this model, the time-evolution of the species densities is calculated by balance equations, taking into account the various production and loss terms by chemical reactions. Transport processes are not considered and hence, the species densities are assumed to be constant in the entire simulation volume. The rate coefficients of these reactions are assumed constant and adopted from literature for the heavy particle reactions, whereas the rate coefficients for the electron impact reactions are calculated with a Boltzmann solver, BOLSIG+³³, which is integrated into ZDPlaskin. This Boltzmann routine uses the two-term approximation, which is less accurate than using multi-term Boltzmann routines^{34,35}. Typically, the rate constants calculated using the two-term approximation show an error of approximately 30%³⁶⁻³⁸. Furthermore, the uncertainty in the rate constants of the most important neutral reactions (see section 4.3 below) is typically around 100%³⁹⁻⁴¹. Therefore, we performed a sensitivity analysis to check whether variations of 30% in electron impact reaction rate constants and variations of 100% in neutral reaction rate constants have a significant effect on the CO₂ and N₂ conversion and on the vibrational kinetics (see Supporting Information). The results indicate that these variations do not affect the results to a large extent. More information about the model can be found in³². In the following sections we will describe in a bit more detail the general reaction chemistry assumed in the model (section 2.1), with special emphasis on the vibrational levels

(section 2.2), and we conclude with explaining how we apply this 0D model to a MW reactor (section 2.3).

2.1. General reaction chemistry

The species taken into account in our model for the CO₂/N₂ mixture, are listed in Table 1. These species include various neutral molecules in the ground state, as well as several electronic and vibrationally excited levels, various radicals, positive and negative ions, and the electrons. Besides the input gases (CO₂ and N₂), also various formed products are included, such as CO, O₂, O₃, several NO_x compounds, as well as some other CO₂-derived compounds, N-C and N-C-O compounds. CO₂(V) and CO₂(E) indicate the vibrational and electronic excited levels of CO₂. Because the asymmetric mode levels are most important for the splitting of CO₂^{1,42}, all these levels up to the dissociation limit are included in the model (i.e., 21 levels), whereas only a few symmetric model levels are incorporated, following the example of the model developed by Kozák et al.³⁰. Similarly, CO(V), CO(E), O₂(V) and O₂(E) indicate the vibrational and electronic excited levels of CO and O₂, which are sometimes comprised of several individual levels. The detailed notations of these vibrational and electronic excited levels are summarized in Table 2.

Table 1: Overview of the species included in the model

CO₂ compounds	CO ₂ , CO ₂ (Va), CO ₂ (Vb), CO ₂ (Vc), CO ₂ (Vd), CO ₂ (V1-V21), CO ₂ (E1), CO ₂ (E2), CO ₂ ⁺
Derived CO₂ compounds	C ₂ O, C ₂ O ₂ ⁺ , C ₂ O ₃ ⁺ , C ₂ O ₄ ⁺ , C ₂ , C ₂ ⁺ , C, C ⁺
CO compounds	CO, CO(V1-V10), CO(E1), CO(E2), CO(E3), CO(E4), CO ⁺ , CO ₃ ⁻ , CO ₄ ⁻ , CO ₄ ⁺
O₃, O₂ and O compounds	O ₂ , O ₂ (V1), O ₂ (V2), O ₂ (V3), O ₂ (V4), O ₂ (E1), O ₂ (E2), O ₂ ⁺ , O ₂ ⁻ , O, O ⁺ , O ⁻ , O ₄ ⁻ , O ₄ ⁺ , O ₃ , O ₃ ⁻
Pure N-compounds	N ₂ , N ₂ (V1-V14), N ₂ (C ³ Π _u), N ₂ (A ³ +Σ _u ⁻), N ₂ (a' ¹ Σ _u ⁻), N ₂ (B ³ Π _g), N ⁺ , N ₂ ⁺ , N ₃ ⁺ , N ₄ ⁺ , N, N(2D), N(2P)
N-O-compounds	NO, N ₂ O, NO ₂ , NO ₃ , N ₂ O ₅ , NO ⁺ , N ₂ O ⁺ , NO ₂ ⁺ , NO ⁻ , N ₂ O ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , N ₂ O ₂ ⁺
N-O-C-compounds and N-C-compounds	CN, ONCN, NCO, C ₂ N ₂ , NCN
Electrons	e ⁻

Table 2: Explanation of the notations for the vibrational and electronic excited levels of CO₂, CO and O₂.

CO ₂ levels	CO levels	O ₂ levels
CO ₂ (Va)=(010)	CO(E1)=CO(A ³ Π)	O ₂ (E1)=sum of the A ¹ Δ and b ¹ Σ states
CO ₂ (Vb)=(100),(020)	CO(E2)=CO(A ¹ Π)	O ₂ (E2)=O ₂ (B ³ Σ) and higher triplet states
CO ₂ (Vc)=(110),(030)	CO(E3)=CO(A ³ Σ),	
CO ₂ (Vd)=(040),(120),(200)	CO(D ³ Δ),	
CO ₂ (Vn)=(00n) with n=1...21	CO(E ³ Σ), CO(B ³ Σ)	
CO ₂ (E1)=CO ₂ (¹ Π _g)	CO(E4)=CO(C ¹ Σ), CO(E ¹ Π),	
CO ₂ (E2)=CO ₂ (¹ Δ _u)	CO(B ¹ Σ), CO(Γ ¹ Σ),	
	CO(D ¹ Δ)	

All these species undergo a large number of chemical reactions, like electron impact collisions with neutral species, leading to excitation, ionization, dissociation and electron-attachment, electron-ion recombination reactions, as well as many heavy-particle chemical reactions (i.e., between neutral species and/or ions).

The chemical reaction set described in this model, is partly based on the model by Kozák et al.³⁰ (i.e., for the entire CO₂ chemistry, including the vibrational levels of CO₂, CO and O₂) and the work of Pancheshnyi et al.³² (for the N₂/O₂ chemistry); hence, all details of the reactions and the corresponding rate coefficients can be found in these references. The coupling reactions between CO₂ and N₂ and their reaction products, mostly in the ground state or electronically excited, were not included in the above chemistry sets, and were therefore added in our work to complete the reaction set for the CO₂/N₂ mixture. These extra reactions, as well as the corresponding rate coefficients, are listed in the Supporting Information (Tables A1-A4). Note that the reactions or relaxation processes and their rate coefficients are tabulated for the ground state or lowest vibrational state, respectively. The same processes are also included for the higher vibrational levels, and the corresponding rate coefficients are calculated with the theories explained in section 2.2 below.

2.2. Description of the vibrational levels

Because the vibrationally excited species play an important role in the CO₂ conversion in a MW plasma, as mentioned above, we pay special attention to their kinetics. In the following sections, we therefore describe the different vibrational levels included in the model, as well as the methods to calculate their rate coefficients.

2.2.1. Vibrational levels taken into account

CO₂ has three vibration modes, the symmetric stretch mode, the bending mode (which is double degenerate) and the asymmetric stretch mode. As mentioned above, the asymmetric stretch mode is most important for the CO₂ dissociation^{1,42}, so for this mode all levels up to the dissociation limit of 5.5 eV are taken into account, whereas only four effective vibrational levels of the symmetric modes are included, in the same way as was described by Kozák et al.; so for details we refer to³⁰.

For the diatomic molecules, i.e., CO, N₂ and O₂, the energies of the various vibrational levels are calculated as:

$$\frac{E(\xi)}{hc} = \omega_e \xi - \omega_e x_e \xi^2 + \omega_e y_e \xi^3 + \omega_e z_e \xi^4 \quad (1)$$

In this equation, ω_e , $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$ are spectroscopic constants (in cm^{-1}) that are characteristic for the molecule, and $\xi = \left(v + \frac{1}{2}\right)$ with v being the vibrational quantum number. The values of the spectroscopic constants are listed in Table 3. 10 vibrational levels are taken into account for CO, and 4 levels for O₂, like in Kozák et al.³⁰. For N₂, 14 vibrational levels are included, because the populations of the higher levels are negligible, as will be demonstrated in section 4.5 below.

Table 3: Spectroscopic constants used for calculating the energies of the various vibrational levels of CO, N₂ and O₂.

	CO	N ₂	O ₂
ω_e	2170,21	2372,45	1580,19
$\omega_e x_e$	13,46	18,1017	11,98
$\omega_e y_e$	0,0308	$1,27552 \times 10^{-2}$	0,0474
$\omega_e z_e$	0,0	$-7,95949 \times 10^{-5}$	$-1,27 \times 10^{-3}$

2.2.2. Processes of the vibrational levels considered in the model

(a) Vibrational excitation

Electron impact vibrational excitation is very important to populate the lower vibrational levels. The rate coefficients of this process for the lower vibrational levels are calculated from the cross sections adopted from the LXCAT database. To obtain the cross sections for electron impact vibrational excitation to the higher vibrational levels, we use the Fridman approximation¹, which is based on the following semi-empirical formula:

$$\sigma_{nm}(\varepsilon) = \exp\left(\frac{-\alpha(m-n-1)}{1+\beta n}\right) \sigma_{01}(\varepsilon + E_{01} - E_{nm}) \quad (2)$$

In this formula $E_{01} = E_1 - E_0$ and $E_{nm} = E_m - E_n$ are the threshold energies for excitation from level $v = 0$ to $v = 1$ and for excitation from level $v = n$ to $v = m$, respectively. Hence, the cross sections $\sigma_{nm}(\varepsilon)$ are calculated from the cross section $\sigma_{01}(\varepsilon)$ for excitation from the ground state to the first vibrational level, by shifting this cross section $\sigma_{01}(\varepsilon)$ over an energy of $E_{01} - E_{nm}$ and by adapting the value with an exponential factor. The parameters α and β are specific for each plasma species. For CO₂ α is taken as 0.5 and β is 0³⁰, whereas for N₂ α is taken as 0.7 and β is 0.05¹. For CO and O₂ we don't need to use this formula, as the cross sections are described in literature; more information can be found in Kozák et al.³⁰.

(b) VT relaxation processes of the vibrational levels

In VT relaxation, or vibrational-translational relaxation, the internal vibrational energy is transferred into translational energy, upon collision of a vibrationally excited species with another species. In the case of CO₂ splitting, this process should be avoided, because it lowers the population of the higher vibrational levels, which otherwise give rise to dissociation (see

below). As the rate coefficient of VT relaxation is determined by the gas temperature, this process can be reduced by using a lower gas temperature in the plasma¹.

We assume in our model that at maximum one quantum of vibrational energy is transferred between the collision partners in VT relaxation processes, because so-called multi-quantum processes typically have a rate that is two orders of magnitude lower³⁰. The rate coefficients for VT relaxation of the CO₂ vibrational levels upon collision with other CO₂ molecules, or with CO or O₂ molecules are adopted from Kozák et al.³⁰. As described in³⁰, the rate coefficient for collisions with CO and O₂ molecules was taken equal as the rate coefficient for collisions with CO₂, but multiplied with a factor 0.3 (for CO) and 0.4 (for O₂)⁴³. The same approach is used here for collisions with N₂ molecules, i.e., the rate coefficient is taken equal as the rate coefficient for collisions with CO₂, but multiplied with a factor 0.3⁴³. The rate coefficients for VT relaxation of the CO vibrational levels with CO, CO₂ and O₂ are also adopted from³⁰. For collisions with N₂ the rate coefficients are taken the same as for collisions with O₂, based on⁴³.

For the higher vibrational levels of CO₂ and CO, the rate coefficients are calculated with a scaling law, based on the Schwartz–Slawsky–Herzfeld (SSH) theory for collisions between two anharmonic oscillators⁴⁴, as described in detail in³⁰. The rate coefficients for VT relaxation of the N₂ and O₂ vibrational levels with either CO₂, CO, O₂ or N₂, are calculated with the Forced Harmonic Oscillator (FHO) model,^{45,46} which compares well with exact quantum methods⁴⁷.

More details about the VT relaxation processes and the corresponding rate coefficients can be found in³⁰, as well as in Table A1 of the Supporting Information, for the VT reactions that were incorporated in this model for the CO₂/N₂ mixture.

(c) VV relaxation processes of the vibrational levels

In VV relaxation, or vibrational-vibrational relaxation, the internal vibrational energy of one species is transferred to another species upon collision. This process is very important in CO₂ splitting, as it populates the higher vibrational levels out of the lower levels, which are populated by electron impact excitation (see above)¹.

Like for VT relaxation, we assume again that at maximum one quantum of vibrational energy is transferred between the collision partners in VV relaxation³⁰. The rate coefficients for the lower vibrational levels are again adopted from literature^{30,44}. For the higher vibrational levels, we use again the SSH theory to calculate the rate coefficients of VV relaxation for collisions between two CO₂ vibrational levels and between CO₂ and CO levels, assuming that only short-range interactions are important. For collisions of CO₂-N₂ and CO-CO, we have to take into account both long-range and short-range interactions, and therefore we use a combination of the SSH theory and Sharma-Brau (SB) theory⁴⁸ for calculating the rate coefficients of VV relaxation of the higher vibrational levels. The rate coefficients for VV relaxation between two O₂ levels and two N₂ levels are again calculated with the FHO model^{45,46}. The other combinations of VV relaxation (i.e., N₂-CO, N₂-O₂, CO-O₂ and CO₂-O₂) are not considered in our model, as they are assumed to be less important. Indeed, for the first three types of reactions, we have calculated the VV rate constants using the FHO model to find out that they are more than two orders of magnitude lower than the rate constants of the above mentioned reactions. Moreover, the reactants CO and O₂ have typically lower densities than the inlet gases CO₂ and N₂. Their density is comparable to the densities of CO₂ and N₂ only later in the simulations and for high power densities.

Again, the details about the VV relaxation processes and the corresponding rate coefficients can be found in ³⁰, as well as in Table A2 of the Supporting Information, for the extra VV reactions included in this model for the CO₂/N₂ mixture.

(d) Chemical reactions of the vibrational levels

Finally, also chemical reactions of the vibrational levels need to be taken into account. Their rate coefficients are typically calculated from the corresponding rate coefficients of the collisions from the ground state atoms, by multiplying with an exponential factor, according to the Fridman-Macheret α -model ¹. This yields the following formula:

$$k_R(E_v, T) = A * \exp\left(\frac{-E_A - \alpha E_v}{T}\right) \quad (3)$$

where A is the pre-exponential factor, E_A is the activation energy, E_v is the vibrational energy, T is the gas temperature and α represents the efficiency of the vibrational level to lower the activation energy, adopted from ^{1,30}. For reactions where no α could be found, we make the same assumptions as described by Fridman ¹, i.e.,

- When no bond breaking occurs, α is taken equal to a very low value (0.03).
- When bond breaking occurs in the vibrationally excited species, α is taken as 0.9.
- When in addition to the bond breaking also an atom is transferred, α is taken as 1.0.

2.3. Application of the 0D model to a MW reactor

As mentioned in the beginning of this section, a 0D model only calculates the species densities as a function of time, and it neglects spatial variations. However, the time evolution can be translated into a spatial evolution (i.e., as a function of position in the MW reactor), by means of the gas flow rate. Indeed, the MW reactor can be considered as a tubular reactor, in which the densities only vary in the axial direction, but remain constant in the radial direction. The plasma reactor is thus treated as a plug flow reactor. In this way, axial variations in power density can be implemented in the model without adding to the computational cost. The electron density in the radial direction may change with a factor 2 or 3 in the bulk plasma ⁴⁹⁻⁵². These fluctuations in electron density, however, don't affect the plasma chemistry, as is shown in the Supporting information. The CO₂/N₂ gas mixture is inserted at the inlet of the tubular reactor and on their way throughout the reactor, the gases will gradually be converted into the reaction products, which leave the reactor at the other side. In other words, the time has the meaning of residence time of the species in the reactor.

The electric power in the MW plasma is applied to the electrons by setting a certain value for the reduced electric field, assuming the electric field frequency equal to 2.45 GHz. The reduced electric field is calculated at each time step to obtain the desired axial distribution of the power density and the desired total power deposition. The maximum of the power density is applied in the centre of the reactor (where the waveguide crosses the reactor tube in reality). Furthermore, we assume that the power density decreases linearly towards both ends of the discharge tube in accordance with theoretical calculations ⁵³. This is illustrated in Figure 1 for the three different power density values investigated, i.e., 30, 50 and 80 W/cm³.

The operating conditions assumed in the model, i.e., power density, gas flow rate, pressure, temperature) are exactly the same as used in the experiments (see section 3 below). The gas flow rate is 5 slm for a MW reactor length of 10 cm. The pressure is taken as 2660 Pa^{6,7} and the gas temperature at the inlet is set at 300K. Because the gas absorbs most power in the centre of the reactor, we assume that the gas temperature rises linearly between 3.3 and 8 cm, from 300K till 1000K (see solid curve in Figure 1), based on our earlier findings^{7,31}.

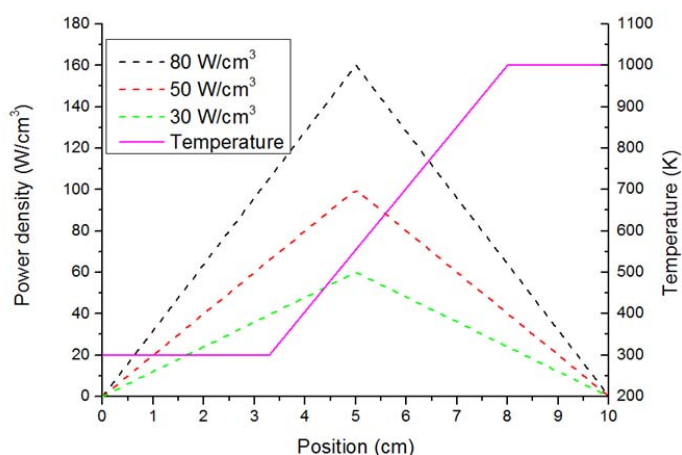


Figure 1: Power density profile (dashed curves; left axis) and temperature profile (solid curve; right axis) used in the simulations.

3. Experimental setup

The surfaguide-type microwave discharge was generated at a frequency of 915 MHz in a double-walled quartz tube with 14 mm inner diameter and about 20 cm length, cooled down during the measurements by 10 °C silicon oil flow (see Figure 2). The gas mixture injected from the top of the system was regulated by electronic mass flow controllers. The whole system was surrounded by a grounded aluminum grid to prevent any leak of microwave radiation into outer space. At the bottom of the quartz tube, an additional diaphragm was installed to maintain the pressure difference between the discharge and the post-discharge regions.

The concentrations of CO₂, CO and N₂ were analyzed by a gas chromatograph (Bruker) equipped with a carbon molecular sieve column and a Molecular sieve 5A column in series and connected to a thermal conductivity detector with argon used as a carrier gas (see Figure 2). As the discharge worked in reduced pressure regime, a sampling system was used between the post discharge and the gas chromatograph. The low pressure sample is diluted with neutral gas prior to its injection in the chromatograph.

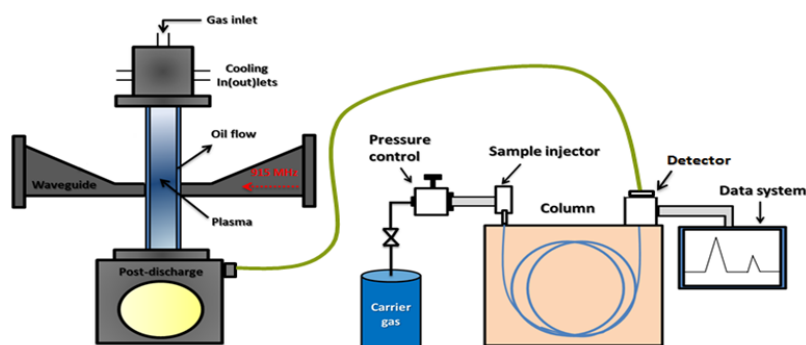


Figure 2: Schematic representation of the microwave generator and the gas chromatograph.

4. Results and discussion

4.1. CO_2 and N_2 conversion

The (absolute) conversion (X_A) of a compound (CO_2 or N_2) is calculated from the number densities before and after the simulation:

$$\chi_A = 1 - \frac{n_A}{n_{A0}} \quad (4)$$

On the other hand, the effective conversion of a compound ($X_{A,\text{eff}}$) denotes how much effectively is converted, and takes into account the fraction of the compound in the gas mixture, e.g., when only 10% CO_2 is present in the gas mixture, the absolute conversion needs to be multiplied with a factor 0.1. In this section, we will show both the absolute and effective conversion for both CO_2 and N_2 .

Figure 3 illustrates the calculated and measured absolute and effective CO_2 conversions as a function of N_2 fraction in the gas mixture, for the three different values of power density investigated, i.e., 30, 50 and 80 W/cm^3 . In general, agreements within 23% with the measured values are obtained. The largest deviations occur at N_2 fractions below 10%, with discrepancies till 70%. However, the overall evolution of the calculated CO_2 conversion with rising N_2 fraction follows the experimental results. This indicates that the plasma chemistry and vibrational kinetics occurring in the microwave plasma are quite realistically described in our model.

It is clear that the absolute conversion (Figure 3(a)) increases with N_2 fraction, both in the model and the experiments, indicating that N_2 has a beneficial effect on the conversion, as will be discussed in sections 4.3 and 4.4 below. However, at the higher power densities, a slight drop in the calculated CO_2 conversion is seen between 0% and 10% N_2 , which can be explained by the model, based on the relative contributions of the CO_2 destruction mechanisms, as will be elaborated in section 4.3 below. This slight drop is however not so visible in the experimental data, so it might be overestimated in the model.

The effective CO_2 conversion (Figure 3(b)) generally drops upon increasing N_2 fraction, which is as expected, because there is less CO_2 initially present in the gas mixture. However, this drop is not very pronounced, especially not between 10 and 60 % N_2 , because of the rising absolute conversion, as observed in Figure 3(a). In general, the CO_2 conversion is very high (i.e., 10-80% absolute conversion and 5-53% effective conversion, depending on power and N_2 fraction) and it increases clearly with rising power density, as expected.

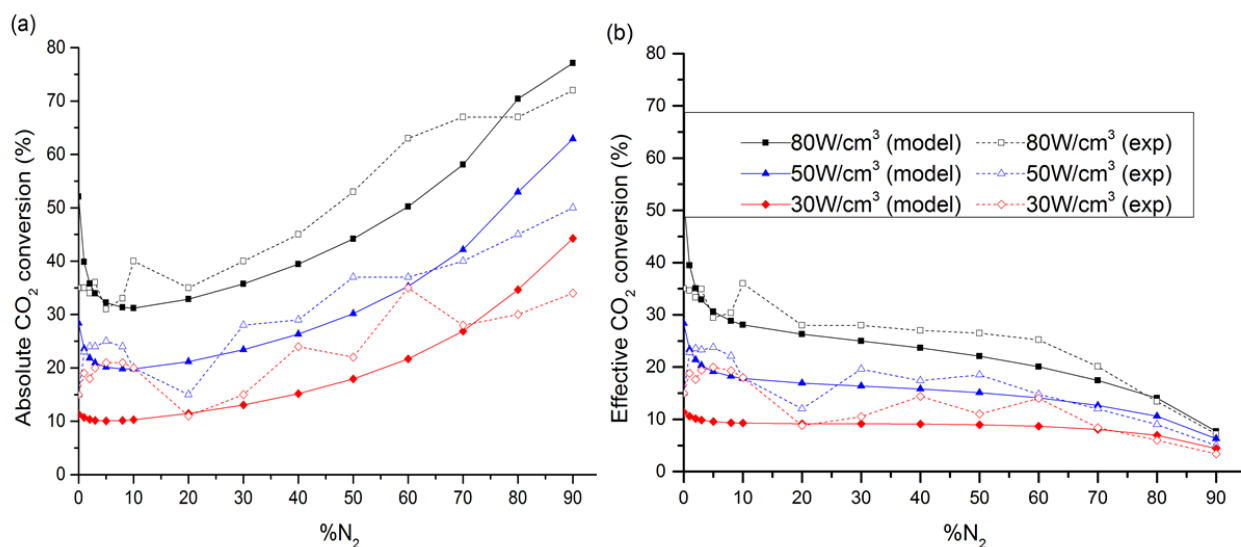


Figure 3: Calculated (solid lines) and measured (dashed lines) absolute (a) and effective (b) CO₂ conversion as a function of N₂ fraction in the gas mixture, for three different power densities, a pressure of 2660 Pa, and a residence time of 9.13 ms.

The calculated and measured absolute and effective N₂ conversions are plotted as a function of N₂ fraction in the gas mixture in Figure 4, for the three different values of power density. Agreements between calculated and measured results are generally within 33%, and thus somewhat worse than for the CO₂ conversion. The largest deviations (i.e. up to 130%) occur at 80% N₂ where the model systematically predicts higher values than the experiments. This indicates that the model might still need further improvement, although the experiments are also subject to uncertainties. However, the focus of this paper is more on obtaining a better insight in how N₂ interacts with CO₂, especially its effect on the vibrational kinetics, and less on the N₂ conversion itself.

The N₂ conversion increases again clearly with power density, as expected. The absolute N₂ conversion is rather constant for all power values, up to 50% N₂ fraction, and then it rises up to 70-80% N₂ fraction, followed by a significant drop towards 90% N₂ fraction in the gas mixture. In the model, this trend is explained by the fact that the most important formation processes for N₂ are reactions between reactive N-compounds, which originate from the destruction of N₂ (see section 4.3 below).

The effective N₂ conversion generally rises with N₂ fraction, which is logical, as there is more N₂ initially present in the gas mixture, but the same drop is observed above 70-80 % N₂ fraction, which follows of course the behavior of the absolute conversion. The highest effective N₂ conversion is around 15% (calculated) and 9% (measured) at the highest power density and a N₂ fraction of 70%. This indicates that under these conditions the formation of reactive N-compounds will be at maximum, including also NO_x species.

Indeed, our model predicts that above 70% N₂ addition, some reactive N-compounds are formed. The most abundant is NO, with a relative percentage (among the formed products) of 40-50%, followed by C₂N₂ and CN, with relative percentages of 15-20% and 5-10%,

respectively. Other NO_x compounds, like NO₂, NO₃, N₂O and N₂O₅, were found to be negligible, as predicted by the model.

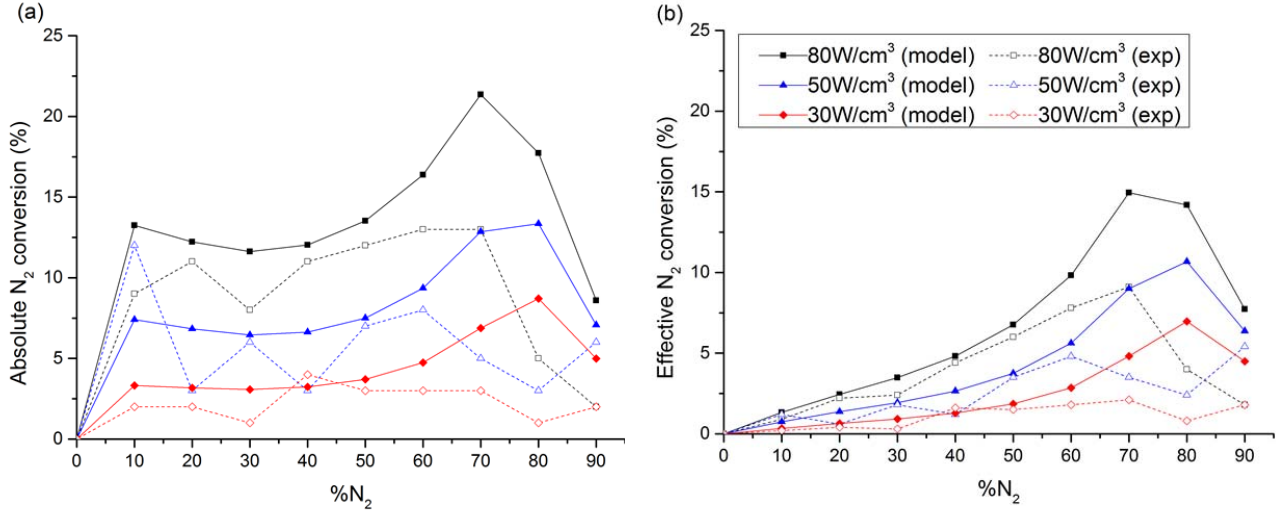


Figure 4: Calculated (solid lines) and measured (dashed lines) absolute (a) and effective (b) N₂ conversion as a function of N₂ fraction in the gas mixture, for the same conditions as in Figure 3.

4.2. Energy efficiency

The energy efficiency will only be presented for the CO₂ conversion, because this is the process of major importance in this study. It is calculated from the effective CO₂ conversion as:

$$\eta = \chi_{A,eff} \frac{\Delta H}{SEI} \quad (5)$$

where ΔH is the theoretical reaction enthalpy for CO₂ splitting ($\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$), i.e., 2.9 eV/molec, and SEI is the specific energy input for the process. The latter is calculated in the model by integrating the power deposition (P_d , in W/cm³) over the residence time (t_r):

$$SEI \left(\frac{J}{\text{cm}^3} \right) = \int_0^{t_r} P_d dt = \int_0^{t_r} e * E/N * v_d * n_e * N dt \quad (6)$$

e is $1,6 \times 10^{-19}$ J/(eV), E/N is the reduced electric field (in Td or 10^{-17} V cm²), v_d is the drift velocity of the electrons (cm s⁻¹), n_e is the electron number density (cm⁻³) and N is the number density of the neutral species (cm⁻³). The SEI in eV/molec is calculated as follows:

$$SEI \left(\frac{eV}{\text{molecule}} \right) = \frac{SEI \left(\frac{J}{\text{cm}^3} \right)}{e * t_r * Q_n} \quad (7)$$

where Q_n is the gas density flow rate (#molec/(cm³s)), which is calculated as:

$$Q_n = \frac{p}{t_r * k_B * T_{gas} * 10^6} \quad (8)$$

p is the gas pressure (Pa), k_b is the Boltzmann constant and T_{gas} is the neutral gas temperature (K). The factor 10^6 is used to transfer Q_n from #molec/(m³s) to #molec/(cm³s). The three power densities investigated, i.e., 30, 50 and 80W/cm³, correspond to SEI values of 2.66, 4.44 and 7.1 eV/molec, respectively.

Figure 5 illustrates the calculated and measured energy efficiencies for CO₂ conversion for the three different power densities and the entire range of CO₂/N₂ gas mixing ratios. Agreements within 23% are obtained between model and experiments. The largest deviations (i.e. 70%) occur at low N₂ fractions, similar to the results of the effective CO₂ conversion, which is logical, considering eq. 5.

The energy efficiency is in the order of 8-15%, except at the highest N₂ fractions, where it drops to 3%. Furthermore, the calculated values slightly drop from 0 to 10% N₂ fraction at the lowest power density (i.e., by ~2%) and this drop is more significant for 50W/cm³ and 80W/cm³ (i.e., around 7% and 10%, respectively). However, this trend was not observed in the experiments, mainly due to a rather high measurement error in this case. Between 10% and 60% N₂ fraction, the energy efficiency drops slightly, but at higher N₂ fractions, the drop is again a bit more pronounced. These trends can again be explained based on the relative contributions of the CO₂ destruction processes, as discussed in section 4.3 below. The calculated energy efficiency at low N₂ fractions is highest for the higher power densities, whereas the opposite trend is seen for the high N₂ fractions, although the differences are small. This behavior will also be explained in sections 4.3 and 4.4 below.

When comparing these energy efficiencies with values from literature, albeit for pure CO₂ MW plasmas, we can conclude that the maximum obtained calculated energy efficiency (i.e., 21% at 80 W/cm³ or an SEI of 7.1 eV/molec) is similar to the value predicted by Kozák et al.³⁰ (i.e., 23%; the small difference is attributed to the use of a different 0D code, with other approximations³⁰). Several years ago, Fridman and colleagues^{1,13,14} reported much higher values of 90% for a MW reactor, but the latter was operating under supersonic flow conditions. However, at normal flow conditions, similar values as obtained here were also reported^{1,7}. Indeed, for a pressure of 50 Torr (or 6664 Pa), a value of 20% was obtained¹. Furthermore, earlier experiments by Silva et al.⁷ yielded energy efficiencies of 12% for a pulsed MW plasma at a pressure in the range of 133-1333 Pa and a SEI in the range of 25-40 eV/molecule.

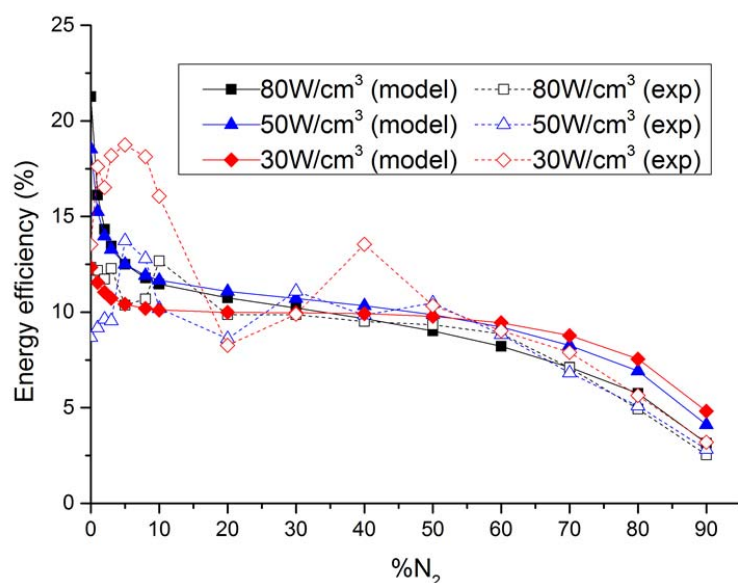


Figure 5: Calculated (solid lines) and measured (dashed lines) energy efficiencies for CO_2 conversion as a function of N_2 fraction in the gas mixture, for the same conditions as in Figure 3.

4.3. Destruction and formation processes of CO_2 and N_2

From the comparison between calculated and experimental data, we can conclude that the model is in general able to qualitatively and even quantitatively describe the most important chemical reactions in the CO_2/N_2 plasma, and can thus be used for explaining the underlying mechanisms responsible for the experimental trends in CO_2 and N_2 conversion and in the energy efficiency. This will be elaborated here and in the following sections.

To explain the trends in the CO_2 and N_2 conversion, we plot in Figure 6 the relative contributions of the most important destruction processes of CO_2 , as a function of N_2 fraction, for 30 W/cm^3 and 80 W/cm^3 . The results of 50 W/cm^3 are in between, so they are not explicitly presented.

At the two highest power densities, the destruction of CO_2 is mainly attributed to the dissociation of vibrationally excited CO_2 by collision with any molecule in the plasma (denoted as M). At 30 W/cm^3 , this process is also important for N_2 fractions above 30%. At lower N_2 fractions, electron impact dissociation from ground state CO_2 , and especially from vibrationally excited CO_2 , are more important, with a contribution of 25% and 42%, respectively. At 50 W/cm^3 and 80 W/cm^3 and N_2 fractions below 20%, electron impact dissociation from vibrationally excited CO_2 is also very important for the CO_2 destruction, with a contribution of about 33% around 10% N_2 , at both 50 W/cm^3 and 80 W/cm^3 . At higher N_2 fractions, these processes gradually become less important upon increasing N_2 fraction.

Because electron impact dissociation from the CO_2 ground state requires considerable more energy than the dissociation energy of CO_2 , this explains the lower energy efficiency at 30 W/cm^3 and low N_2 fractions, as shown in Figure 5 above.

Finally, the reaction between vibrationally excited CO₂ and an O atom is also significant, with a contribution of 10-28%, slightly increasing for higher N₂ fractions. The difference between this process and the dissociation reaction with any molecule M is that in the first process the formed O atoms recombine with the reactant O atoms, forming O₂, whereas in the latter process no such recombination of O atoms occurs. Note that this first reaction is essential for the total CO₂ conversion into CO and O₂, which is in fact the combination of two subsequent steps:

- 1) CO₂ → CO + O (upon collision of an electron, followed by VV relaxation (i.e., so-called ladder climbing), or upon collision with any neutral molecule)
- 2) CO₂ + O → CO + O₂

It is the combination of these two steps that is considered for the calculation of the energy efficiency. Indeed, the reaction enthalpy needed for the first reaction is 5.5 eV/molec, while for the second reaction only 0.3 eV/molec is needed¹. In total, this gives a reaction enthalpy of 2.9 eV/molecule per one CO₂ molecule, which is the value used for calculating the energy efficiency (see section 4.2 above).

For the three power densities investigated, the contribution of the neutral reactions with vibrationally excited CO₂ (i.e., either by collision with M or O atoms) is slightly lower at 10% N₂ fraction than for the pure CO₂ plasma, but it increases again for higher N₂ fractions. The reason for this drop between 0 and 10% N₂ fraction will be clarified based on the vibrational distribution functions, shown in section 4.4 below. This drop also explains the calculated drop in both the absolute and effective CO₂ conversion from 0% to 10% N₂, as illustrated in Figure 3 above. At 30 W/cm³, this drop in effective and absolute CO₂ conversion was barely visible (~1%), because of the lower contribution of this reaction (see Figure 6(a)).

Neutral reactions with vibrationally excited species are more energy efficient than electron impact dissociation¹. Therefore, a drop in the contribution of the reaction (CO₂(V) + M → CO + O) also explains the drop in energy efficiency, predicted by the model, between 0% and 10% N₂ at the higher power densities, where this process is dominant, as was illustrated in Figure 5 above.

The fact that the effective CO₂ conversion and energy efficiency remain constant between 10% and 60% at 30 W/cm³, and drop to some extent in the same interval at 50 and 80 W/cm³, as shown in Figures 3 and 5 above, can be explained based on the fact that the sum of the relative contributions of the three reactions with vibrationally excited CO₂ (which are most beneficial for the energy efficiency) rises faster or slower with increasing N₂ fraction than the drop in the contribution of the less energy-efficient electron impact dissociation from the ground state. Indeed, at 50 and 80 W/cm³, there is a clear drop in effective CO₂ conversion and energy efficiency, because the relative contribution of electron impact dissociation drops faster with rising N₂ fraction than the rise in relative contributions of the three reactions with vibrationally excited CO₂. This results in a higher contribution of very energy-inefficient processes, like the reactions between ions, and ionization of the N₂ fraction, and hence in a more pronounced drop of the energy efficiency for CO₂ splitting. This effect is the strongest at 80W/cm³ as can be seen in Figure 5. On the other hand, at 30 W/cm³, the contribution of the vibrational reactions increases to the same extent as the drop in electron impact dissociation from the ground state, so the effective CO₂ conversion and energy efficiency remain more or less constant upon rising N₂ fraction, as was indeed illustrated in Figures 3 and 5 above.

Above 60% N₂, the contribution of the vibrational reactions will rise more slowly than the drop in the contribution of electron impact dissociation from the ground state, for all three

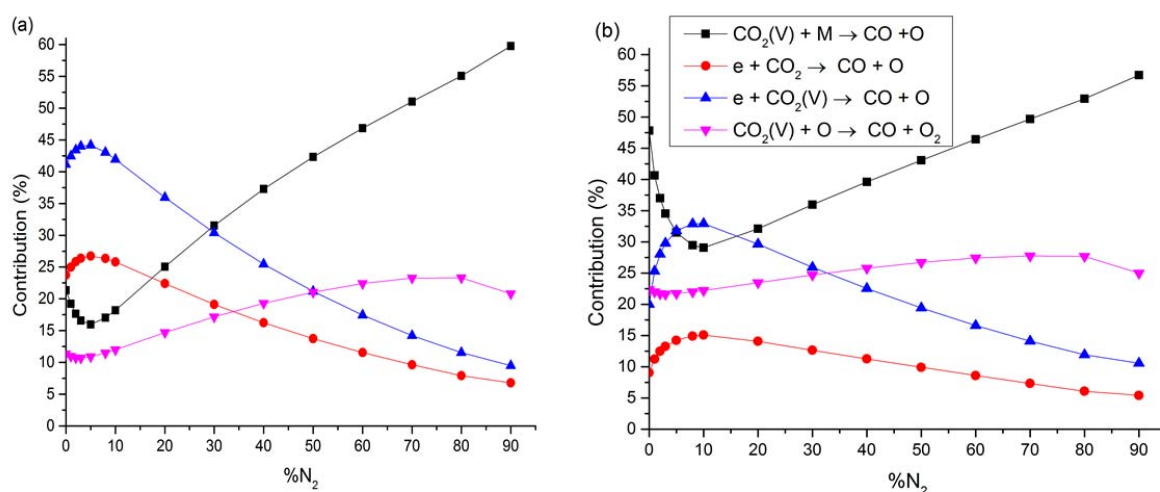


Figure 6: Relative contributions of the most important destruction processes of CO₂, as a function of N₂ fraction in the gas mixture, for the same conditions as in Figure 3, for the power density of 30 W/cm³ (a) and 80 W/cm³ (b).

Figure 7 illustrates the relative contributions of the most important formation processes of CO₂, as a function of N₂ fraction, again for 30 W/cm³ and 80 W/cm³. At 80 W/cm³, the reaction between (ground state or vibrational) CO and O⁻ ions, with the formation of CO₂ and an electron, is the most important formation process in almost the entire range of N₂ fractions (see Figure 7(b)). This is also the case for 50 W/cm³, at least between 20% and 70% N₂ (not shown). For the lower N₂ fractions (i.e. < 20% N₂ at 50 W/cm³ and < 2% N₂ at 80 W/cm³) the reactions of C₂O₄⁺ or C₂O₃⁺ ions with CO are more important. At 30 W/cm³, these two reactions are by far the most important below 60% N₂ (see Figure 7(a)). Finally, the reaction between NCO and NO, with the formation of CO₂ and N₂, is the dominant formation process at very high N₂ fractions, when there are enough reactive N-compounds present. However, it should be mentioned that the relative contribution of the formation processes should not be overestimated, as the total formation rate of CO₂ is two orders of magnitude lower than the total destruction rate.

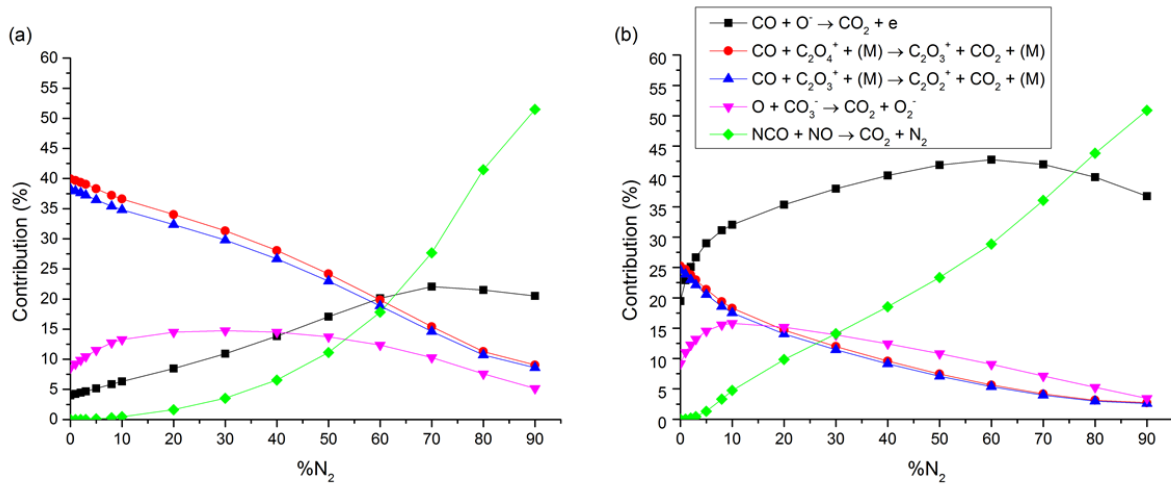


Figure 7: Relative contributions of the most important formation processes of CO₂, as a function of N₂ fraction in the gas mixture, for the same conditions as in Figure 3, for the power density of 30 W/cm³ (a) and 80 W/cm³ (b).

N₂ is almost exclusively destroyed by the reaction between vibrationally excited N₂ molecules and O atoms, yielding the formation of N and NO. The relative contribution of this process is above 95% for all N₂ fractions and power densities investigated. The contributions of the three most important formation processes are depicted in Figure 7, for 30 and 80 W/cm³. The reaction of N atoms with either NO or NO₂, yielding O atoms or O₂ molecules, besides the N₂ molecules, is the dominant formation process, for all power densities investigated and for N₂ fractions above 10%. At lower fractions, N₂ is mainly formed by the reaction of N(2D) with NO or N₂O, forming O atoms or NO radicals, besides N₂, and at 80 W/cm³, the reaction between NCO and NO, forming N₂ and either CO₂ or CO and O atoms, also plays a role.

Note that, in contrast to CO₂, the total formation rate of N₂ is not so much lower than the total destruction rate, i.e., it is at maximum a factor 3 lower at 20 % N₂, and the difference becomes even smaller with rising N₂ fraction, i.e., at the highest N₂ fraction investigated, the total formation and destruction rates are almost equal to each other. The net destruction rate (i.e., destruction rate minus formation rate) increases with rising N₂ fraction, up to 70% N₂ at the power density of 80 W/cm³, and up to 80% N₂ at the lower power densities, but it decreases for still higher N₂ fractions, because of the higher densities of reactive N-compounds (N, NO, NO₂), responsible for forming N₂ again. This explains the calculated drop in N₂ conversion above 70% N₂ (for 80 W/cm³) and above 80% N₂ (for the lower power densities), shown in Figure 4 above.

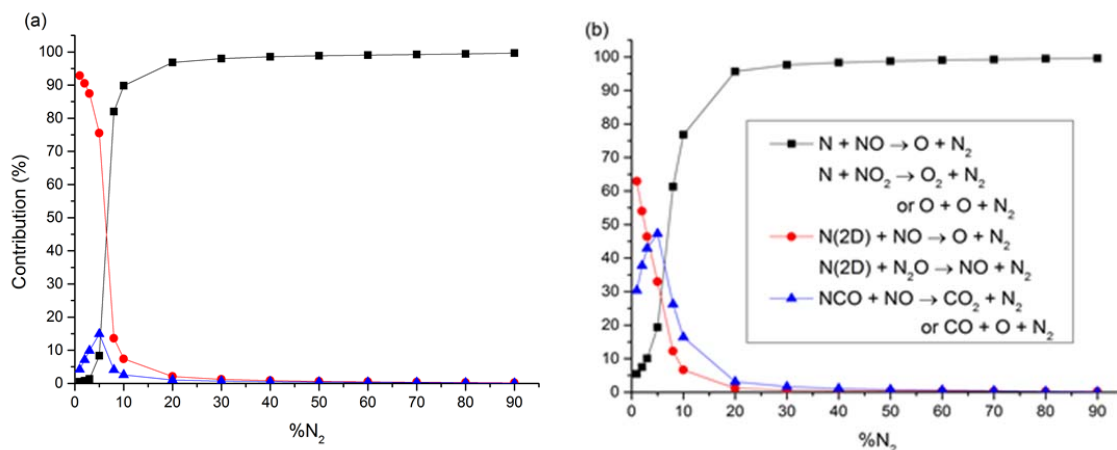


Figure 8: Relative contributions of the most important formation processes of N₂, as a function of N₂ fraction in the gas mixture, for the same conditions as in Figure 3, for the power density of 30 W/cm³ (a) and 80 W/cm³ (b).

4.4. Vibrational analysis of CO₂

It is clear from previous section that the vibrational levels of CO₂ play a crucial role in the CO₂ splitting process. Therefore, it is important to investigate the vibrational distribution function (VDF) of CO₂ at the various power densities, and to elucidate which processes are responsible for populating these vibrational levels, and whether N₂ will play a role in determining the VDF of CO₂. As the asymmetric mode vibrational levels are most important for the dissociation of CO₂, we will focus only on the VDF of these 21 asymmetric mode levels. In Figure 9 the VDFs, obtained at a position of 10 cm, are depicted for the three different power densities, at N₂ fractions of 0% (a), 10%, 50% and 90% (b).

At 0% N₂ the populations of the higher vibrational levels are much lower at 30 W/cm³ than at 50 and 80 W/cm³. The total percentage of vibrationally excited CO₂ is 60% at 30 W/cm³, while it is 72% and 77% at 50 and 80 W/cm³. This explains why vibrationally excited CO₂ is so important for CO₂ splitting in a MW plasma, especially at the higher power densities (cf. Figure 6 above).

At 10% N₂ (Figure 9(b)), the VDFs are very close to each other for the three power densities investigated, with only a slightly higher population of the highest vibrational levels upon increasing power density. The fractions of the vibrational levels are 56%, 55% and 55% at the power densities of 30, 50 and 80 W/cm³. This is lower than at 0% N₂, which explains the drop in the contribution of the reaction between CO₂(v) and neutral molecules M (i.e., CO₂(v) + M → CO + O + M), compared to the pure CO₂ case, as was illustrated in Figure 6 above.

At 50% N₂, the difference between the VDFs obtained at the different power densities is even lower than at 10% N₂, and at 90% N₂, they are almost equal to each other, as appears also from Figure 9(b). The fractions of vibrationally excited CO₂ for the three different power densities are calculated to be 63%, 63% and 64% at 50% N₂, and 73%, 73% and 74% at 90% N₂. It is curious that in the case of 90% N₂ at 80W/cm³ the percentage of vibrationally excited CO₂ is lower than at the same power density at 0% N₂, and yet the contribution of neutral reactions with

vibrationally excited CO_2 is higher. This is due to the fact that at 0% N_2 a lower fraction of the vibrationally excited CO_2 is found in the higher levels, when compared to 90% N_2 . This again stresses the importance of the high vibrationally excited CO_2 levels. In the other cases, more vibrationally excited CO_2 also means more highly vibrationally excited CO_2 , and this gives rise to higher contributions of the destruction reactions involving vibrationally excited CO_2 (see Figure 6 above).

Because the VDFs of the different power densities are nearly equal to each other at 90% N_2 , the importance of the vibrationally excited CO_2 levels is also equally important for the CO_2 splitting, as was clear from Figure 5 above. Therefore, at this higher N_2 fraction, the power density of 30 W/cm^3 will yield a higher energy efficiency (cf. Figure 5 above), because the vibrational levels are equally important, but the SEI is significantly lower.

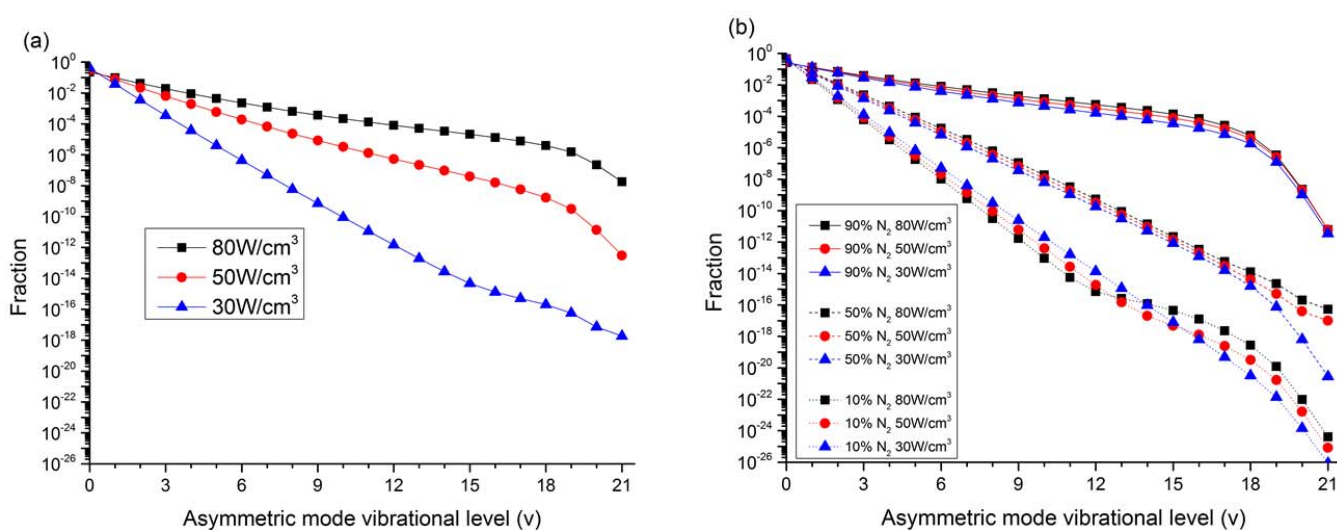


Figure 9: Vibrational distribution functions (VDFs) of the asymmetric mode vibrational levels of CO_2 , obtained at the end of the simulations (i.e. a position of 10 cm), for three different power densities, and N_2 fractions of 0% (a), 10%, 50% and 90% (b).

To explain the VDFs at the various N_2 fractions and power densities, we make here an analysis of the processes responsible for the population of these vibrational levels. The relative contributions of the various mechanisms are plotted in Figure 10, as a function of the vibrational level, at 80 W/cm^3 and various N_2 fractions. The results at the other power densities are almost equal, and are therefore not shown.

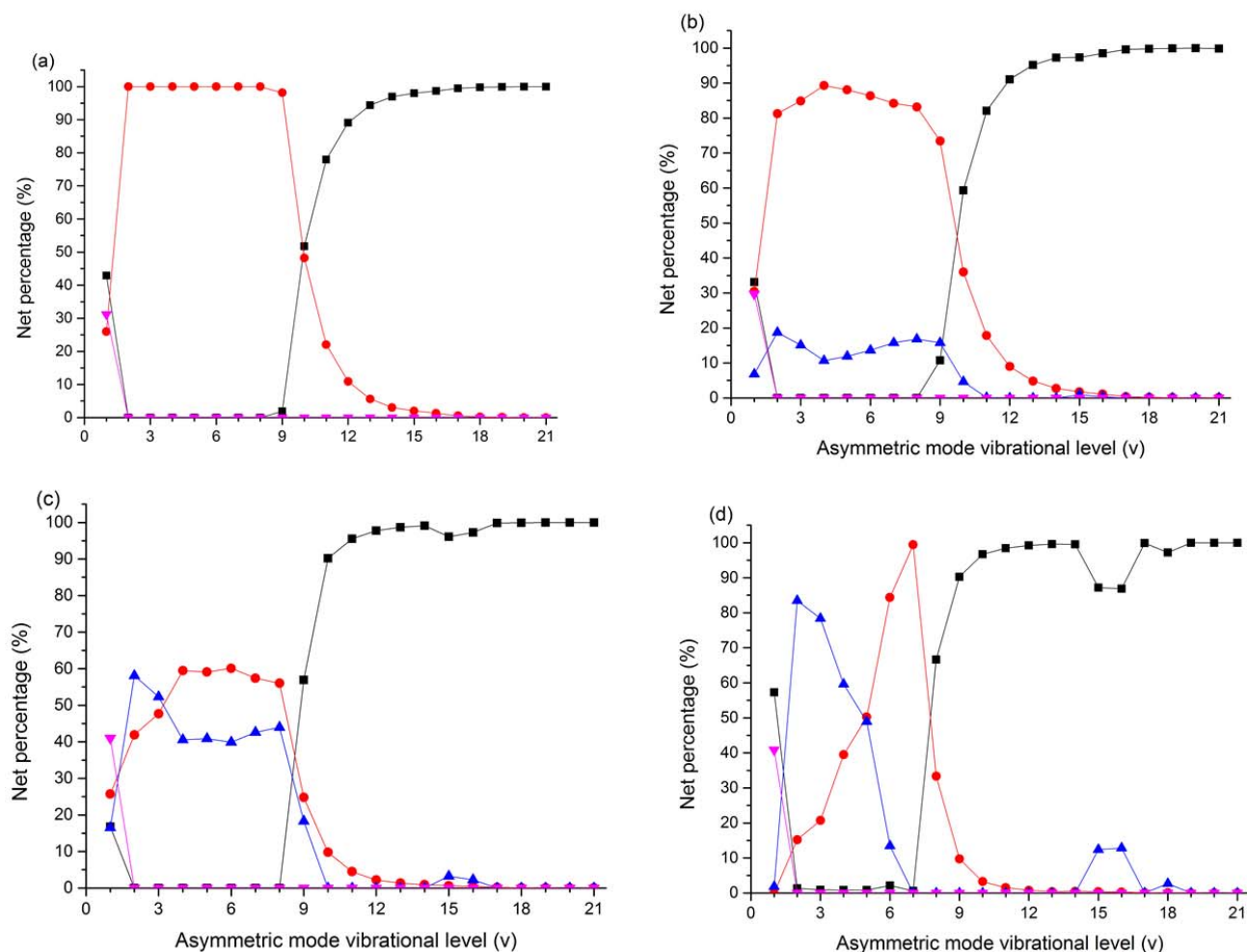


Figure 10: Relative contributions of the various processes responsible for the population of the asymmetric mode vibrational levels of CO_2 , at 80 W/cm^3 and N_2 fractions of 0% (a), 10% (b), 50% (c) and 90% (d).

At 0% N_2 (Figure 10(a)), the most important mechanisms for population of the higher levels, which are important for CO_2 splitting, are the VV relaxation processes with either CO_2 or CO vibrational levels. This was also reported by Kozák et al.³⁰. For the lower levels (i.e., levels 2-9), electron impact vibrational excitation is the most important population mechanism, whereas the first vibrational level appears to be mainly populated by VT and VV relaxation from the higher levels.

At 10% N_2 (Figure 10(b)) we observe the same behavior: electron impact vibrational excitation is most important for the lower levels, and VV relaxation with CO_2 or CO vibrational levels is dominant for the higher levels. However, VV relaxation with N_2 now also contributes to some extent ($\sim 15\%$), especially for the lower levels, so that the relative contribution of electron impact vibrational excitation slightly drops.

At 50% N_2 , the contribution of VV relaxation with N_2 becomes comparable to electron impact vibrational excitation for the lower levels, and it is even slightly more important for the

levels 2-4 at the highest power density of 80 W/cm^3 (which is effectively illustrated in Figure 10(c)). This is logical, because a higher power density yields more vibrational excitation of N_2 (see section 4.5 below). The higher vibrational levels of CO_2 , on the other hand, are still almost exclusively populated by VV relaxation with CO_2 and CO .

Finally, at 90% N_2 , VV relaxation with N_2 becomes the dominant population mechanism for the lower CO_2 vibrational levels (level 2-4), at all power densities. For the higher levels, VV relaxation with CO_2 and CO is still most important, as is clear from Figure 10(d). VT relaxation, although in general an important process, e.g., for the net vibrational energy losses and the associated heating of the gas, appears to be negligible for the net population of the vibrational levels at all power densities and N_2 fractions investigated, because the VV-rates are much faster than the VT-rates.

Hence, we can conclude that for all power densities investigated, N_2 plays an important role in the population of the lower (asymmetric mode) vibrational levels of CO_2 , especially at higher N_2 fractions. The reason is that at higher N_2 concentrations in the mixture, there is more electron impact vibrational excitation of N_2 compared to CO_2 , and thus also a higher vibrational energy transfer rate between N_2 and CO_2 . Subsequently, VV relaxation with CO and CO_2 will (partially) convert these lower levels into the higher vibrational levels, which are essential for energy efficient CO_2 splitting.

4.5. Vibrational analysis of N_2

As the vibrational levels of N_2 are quite important (~15-85% contribution) for populating the CO_2 vibrational levels, and therefore for CO_2 splitting, we present in Figure 11 the VDFs of N_2 , again obtained at a position of 10 cm, for 10%, 50% and 90% N_2 in the gas mixture, and at the power density of 80 W/cm^3 . The results for the other power densities were virtually the same, and are therefore not presented. This confirms that the role of vibrationally excited N_2 in populating the asymmetric mode vibrational levels for CO_2 will almost be the same for the different power densities (see previous section). As mentioned in section 2.2 above, only the lowest 14 levels of N_2 are considered, as the higher levels are negligible; this is indeed clear from Figure 11.

We can deduce from Figure 11 that the VDFs look very similar to each other, except at the higher vibrational levels, where the population becomes somewhat higher with increasing N_2 fraction. Nevertheless, the percentage of vibrationally excited N_2 rises with increasing N_2 fraction, and is calculated to be 26%, 43% and 59% for 10, 50 and 90% N_2 , respectively. The reason for this rather large difference in the percentage of vibrationally excited N_2 , although the VDF's seem similar, is because there is still a small, yet significant rise in the population of the lower levels with increasing N_2 fraction. These levels are generally much more populated than the highest levels due to lower energy barriers, and a small change in their populations causes therefore a significant change in the total population in vibrationally excited N_2 . The VDFs drop only slightly upon increasing level for the levels 1-11, but the populations of the higher levels are much lower. The reason is that for these higher levels, chemical reactions with vibrationally excited N_2 are important, which depopulate these levels, whereas the populations of the lower levels are mainly affected by electron impact excitation (see below), which do not give rise to such a drastic drop in the populations.

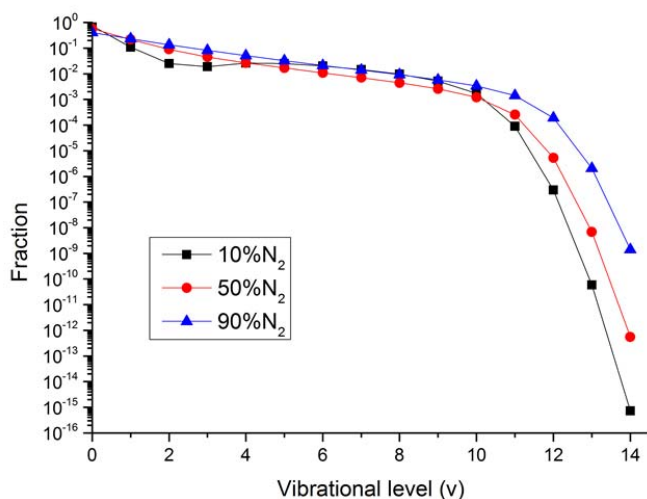


Figure 11: Vibrational distribution functions (VDFs) of N₂, obtained at the end of the simulations (i.e. a position of 10 cm), for N₂ fractions of 10%, 50% and 90%, and a power density of 80 W/cm³.

The relative contributions of the different processes responsible for the population of the various vibrational levels of N₂ are plotted in Figure 12, again for 80 W/cm³ and for 10% and 90% N₂. The results at intermediate N₂ fractions are not shown, as they are very much the same as for 90% N₂. Likewise, the results at the lower power densities are very similar as for 80 W/cm³, and are therefore not shown either. The most important population mechanism for the lower and intermediate vibrational levels (i.e., up to level 8-9) is electron impact vibrational excitation, with a contribution close to 100%, at all N₂ fractions and power densities investigated, while the higher levels are mainly populated by VV relaxation with either CO₂ or N₂. We want to stress the fact that the net contributions are plotted. The absolute contributions of the different populating and depopulating mechanisms for the intermediate and higher levels are dominated by VV relaxation with CO₂ and N₂. This means that when one of these levels is populated through VV relaxation with CO₂ and N₂ or vibrational excitation, depopulation immediately occurs by the same VV relaxation mechanisms or by chemical reactions. Therefore, averaged over the simulation time, the population due to VV relaxation is compensated by depopulation by the same mechanism because of the fast exchange of vibrational energy. This explains why vibrational excitation is even crucial as net population mechanism for the intermediate levels of N₂.

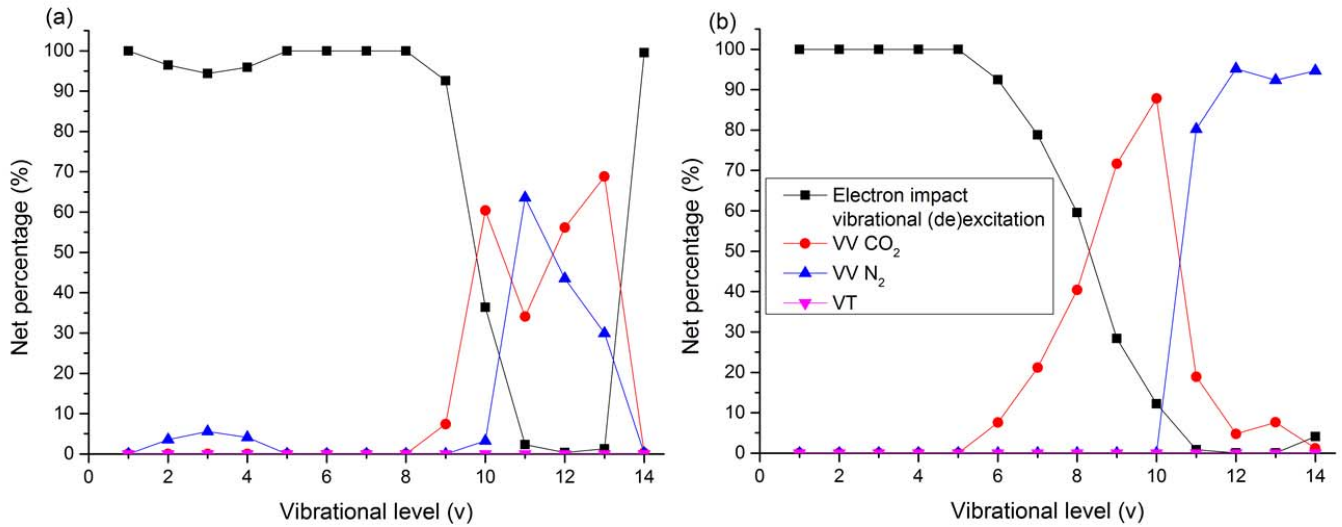


Figure 12: Relative contributions of the various processes responsible for the population of the N_2 vibrational levels, at 80 W/cm^3 and N_2 fractions of 10% (a) and 90% (b).

We can deduce from Figure 12 that when the N_2 fraction in the gas mixture increases, VV relaxation with the CO_2 vibrational levels becomes more and more important for the N_2 levels 9-10. This is at first sight counterintuitive, because we would expect that VV relaxation with the N_2 levels would become more important at higher N_2 fractions. The reason is that for higher N_2 fractions VV relaxation with N_2 vibrational levels becomes the most important depopulation mechanism for those levels, while VV relaxation with CO_2 and CO is relatively more important for depopulating the N_2 levels at lower N_2 fractions. This makes that at higher N_2 fractions VV relaxation with CO_2 and CO becomes more important as net population mechanism. For the highest N_2 vibrational levels, on the other hand, VV relaxation with N_2 vibrational levels is the dominant net population mechanism at higher N_2 fractions ($>50\% N_2$), as expected. However, as the populations of these levels are very low (see Figure 10), the absolute importance of these processes is almost negligible. Finally, like for CO_2 , VT relaxation is found to be negligible for all vibrational levels and at all N_2 fractions and power densities investigated, due to the faster VV-rates.

5. Conclusions

In this paper, we presented a 0D chemical kinetics model for a CO_2/N_2 microwave plasma, with special emphasis on the vibrational levels of both CO_2 and N_2 . For CO_2 , 4 effective symmetric mode energy levels as well as 21 asymmetric mode levels, i.e., up to the dissociation limit, are taken into account, whereas for N_2 14 vibrational levels are included. Besides, also 10 CO vibrational levels and 4 O_2 vibrational levels are considered. A detailed description of the vibrational processes, including vibrational excitation, VT and VV relaxation, and chemical reactions of the vibrational levels, is included.

The model is used to calculate the CO_2 and N_2 conversion, as well as the energy efficiency for CO_2 conversion, at a gas pressure of 2660 Pa and a gas inlet temperature of 300 K,

for three different values of power density in the range of 30-80 W/cm³, and for N₂ fractions in the gas mixture ranging from 0 till 90%. The absolute CO₂ conversion is in the order of 10-80%, rising with power density and with N₂ fraction. This indicates that N₂ has a beneficial effect on the CO₂ conversion. The effective CO₂ conversion, on the other hand, remains constant or drops slightly upon rising N₂ fraction, as there is less CO₂ present in the gas mixture.

The absolute N₂ conversion is calculated to be in the order of 2-20% at the conditions under study. It remains more or less constant or rises slightly upon increasing N₂ fraction, except in the higher range of N₂ fractions, where it clearly drops. The reason is that many reactive N-compounds are formed, which give again rise to the formation of N₂, thereby limiting the net N₂ conversion. The effective N₂ conversion generally increases, as there is more N₂ initially present, except again at the highest N₂ fractions, for the reason explained above.

The energy efficiency is in the order of 8-15%, and remains more or less constant when varying the N₂ fraction, except in the low or high range of N₂ fractions. At low N₂ fractions, the energy efficiency is the highest for the higher power density, whereas at high N₂ fractions, the opposite behavior is observed, i.e., the energy efficiency is highest for the lowest power density.

The calculated CO₂ and N₂ conversions and the energy efficiencies are compared with experimental data, measured for exactly the same conditions, and generally, agreements within 23% and 33% are obtained, indicating that the model can already qualitatively describe the underlying plasma physics and chemistry in CO₂/N₂ microwave discharges.

To explain the observed trends, we have analyzed the destruction and formation processes of both CO₂ and N₂, as well as their vibrational distribution functions (VDFs). The major destruction process for CO₂ is dissociation of vibrationally excited CO₂ upon collision with any molecule or atom in the plasma, especially at the higher power densities. At the lowest power density investigated and low N₂ fractions, electron impact dissociation from CO₂, both in the ground state and vibrationally excited levels, are more important. Because dissociation from the ground state requires a significant amount of energy, this explains the somewhat lower energy efficiency obtained at the lowest power density and low N₂ fractions. CO₂ will also be formed again, e.g., by reactions between reactive N-compounds (NCO and NO) at the highest N₂ fractions, and by reactions with ions or with CO and O⁻ at lower N₂ fractions, but these processes are of minor importance, as the total formation rate of CO₂ is two orders of magnitude lower than the total destruction rate.

N₂ is almost exclusively destroyed by the reaction between vibrationally excited N₂ molecules and O atoms, yielding the formation of N and NO, at all conditions investigated. However, the reverse process, i.e., the reaction of N with NO (or with NO₂), yielding O atoms (or O₂ molecules) and N₂ molecules, is also an important formation mechanism. In contrast to CO₂, the total formation rate of N₂ is typically only a factor 1.1-3 lower than the total destruction rate, explaining the lower conversion compared to CO₂.

Finally, the VDFs of CO₂ and N₂ are calculated. The VDFs of N₂ are virtually equal to each other at all N₂ fractions and power densities investigated; they drop slightly upon increasing level number for the levels 1-11, but the populations of the higher levels are much lower. The calculated VDFs of CO₂ illustrate that the vibrational levels of CO₂ are important at all power densities investigated, especially at high N₂ fractions. As a result, the importance of the vibrationally excited CO₂ levels is also equally important for the CO₂ destruction at these high N₂ fractions, and this explains why the power density of 30 W/cm³ will yield a higher energy efficiency. Our calculations reveal that the lower CO₂ vibrational levels are mainly populated by

electron impact vibrational excitation at low N₂ fractions, but at high N₂ fractions, VV relaxation with N₂ becomes increasingly important. Subsequently, VV relaxation with CO and CO₂ will (partially) convert these lower levels into the higher vibrational levels, which are essential for energy efficient CO₂ splitting. This illustrates the important role of N₂ in populating the CO₂ vibrational levels, and explains the higher CO₂ conversion upon addition of N₂. In general, we can conclude that both the CO₂ and N₂ vibrational levels play a very important role in the (energy-efficient) CO₂ conversion.

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Supporting Information Available: The following material can be found in the Supporting Information:

- The extra coupling reactions between CO₂ and N₂, as well as the corresponding rate coefficients;
- A sensitivity analysis of the most important reactions;
- Validation of the 0D approach.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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