

Combining CO₂ conversion and N₂ fixation in a gliding arc plasmatron

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Description of the experiments

Product analysis

The feed gases and main product gases (CO₂, N₂, CO, O₂) were analyzed by a three-channel compact gas chromatograph (CGC) from Interscience. This device has three different ovens, each with their own column and detector. A Molsieve 5A and Rt-Q-Bond column were used to separate O₂, N₂ and CO, which were detected with a thermal conductivity detector (TCD). The other channel was equipped with a Rt-Q-Bond column and TCD for the measurement of CO₂. The absolute conversion of CO₂, X_{abs,CO_2} , is defined as:

$$X_{abs,CO_2}(\%) = \frac{\dot{n}_{CO_2(in)} - \dot{n}_{CO_2(out)}}{\dot{n}_{CO_2(in)}} \times 100\% \quad (1)$$

where $\dot{n}_{CO_2(in)}$ and $\dot{n}_{CO_2(out)}$ are the molar flow rate of CO₂ without and with plasma, respectively. As the method mentioned above does not account for the gas expansion due to CO₂ splitting, a correction factor is used, which is explained in ref. 1.

The effective conversion, X_{eff,CO_2} , accounts for the fraction of CO₂ in the initial gas mixture:

$$X_{eff,CO_2}(\%) = X_{abs,CO_2}(\%) \times fraction_{CO_2} \quad (2)$$

To calculate the energy cost and energy efficiency of CO₂ conversion, the specific energy input (SEI) in the plasma is defined as:

$$SEI \left(\frac{kJ}{L} \right) = \frac{Plasma\ power\ (kW)}{Flow\ rate\ \left(\frac{L_n}{min} \right)} \times 60 \left(\frac{s}{min} \right) \quad (3)$$

where the flow rate is expressed in L_n/min (liters normal per minute) with reference conditions at a temperature of 0 °C and a pressure of 1 atm.

The energy cost (EC) for converting CO₂ is calculated as follows:

$$EC_{CO_2} \left(\frac{kJ}{L} \right) = \frac{SEI \left(\frac{kJ}{L} \right)}{X_{eff,CO_2}} \quad (4)$$

Likewise, the energy efficiency, η , is calculated as:

$$\eta(\%) = \frac{\Delta H_R \left(\frac{kJ}{mol} \right) \times X_{eff,CO_2}(\%)}{SEI \left(\frac{kJ}{L} \right) \times 22.4 \left(\frac{L}{mol} \right)} \quad (5)$$

where ΔH_R is the reaction enthalpy of CO₂ splitting (i.e., 279.8 kJ/mol), and 22.4 L/mol is the molar volume at 0 °C and 1 atm.

During the experiments, the concentrations of NO, NO₂, and other NO_x compounds were monitored almost in real-time using a Nicolet 380 Fourier Transform Infrared (FTIR) Spectrometer (Thermo Fischer Scientific, Waltham, MA) equipped with a 2m heated gas cell with ZnSe windows and a DTGS detector. Based on the height of the bands, different species were monitored at the following wavenumbers: NO with $\nu(\text{NO})$ at 1900 cm⁻¹ and NO₂ with $\nu_{as}(\text{NO}_2)$ at 1597 cm⁻¹. Note that N₂O with $\nu(\text{NN})$ at 2234 cm⁻¹, N₂O₃ with $\nu_s(\text{NO}_2)$ at 1309 cm⁻¹, N₂O₅ with $\nu_s(\text{NO}_2)$ at 1245 cm⁻¹, O₃ with ν_s at 1054 cm⁻¹ were never detected with the FTIR spectrometer. To quantify these results, the concentrations were determined using a CT5800 Analyzer (Emerson, Stirling, UK) based on Quantum Cascade Laser Technology, allowing to accurately measure different N-containing molecules simultaneously. The monitored compounds were NO, NO₂, N₂O and NH₃, with the following detection limits: 1.5 ppm, 0.5 ppm, 1 ppm and 1 ppm, respectively.

Description of the model

Details of the 0D model

The 0D model is based on solving equation (6):

$$\frac{\partial n_s}{\partial t} = \sum_{i=1}^j [(a_{s,i}^R - a_{s,i}^L) R_i] \quad (6)$$

where n_s is the density of species s (in m⁻³), j the total number of reactions, $a_{s,i}^L$ and $a_{s,i}^R$ the stoichiometric coefficients at the left hand side and right hand side of the reaction and R_i the rate of reaction (in m⁻³ s⁻¹), given by:

$$R_i = k_i \prod_s n_s^{\alpha_{s,i}} \quad (7)$$

where k_i is the rate coefficient (in m³ s⁻¹ or m⁶ s⁻¹ for two-body or three-body reactions, respectively). The rate coefficients of the heavy particle reactions are either constant or dependent on the gas temperature, whereas the rate coefficients of the electron impact reactions depend on the electron temperature T_e or the reduced electric field E/N (i.e., the electric field E divided by the number density of all neutral species N , usually expressed in Td = 10⁻²¹ V m²). The rate coefficients of the electron impact reactions are generally calculated according to the following equation:

$$k_i = \int_{\varepsilon_{th}}^{\infty} \sigma_i(\varepsilon) v(\varepsilon) f(\varepsilon) d\varepsilon \quad (8)$$

with ε the electron energy (usually in eV), ε_{th} the minimum threshold energy needed to induce the reaction, $v(\varepsilon)$ the velocity of the electrons (in m s⁻¹), $\sigma_i(\varepsilon)$ the cross section of collision i (in m²), and $f(\varepsilon)$ the normalized electron energy distribution function (EEDF; in eV⁻¹) calculated using a Boltzmann solver. In this work we use the ZDPlasKin² code to solve the balance equations (equation (6)) of all species, which has a built-in Boltzmann solver, called BOLSIG+³, to calculate the EEDF and the rate coefficients of the electron impact reactions based on a set of cross sections, the plasma composition, the gas temperature and the reduced electric field (E/N). The electric field (E ; in V m⁻¹) is calculated from a given power density, using the so-called local field approximation⁴:

$$E = \sqrt{\frac{P}{\sigma}} \quad (9)$$

with P the input power density (in W m^{-3}) and σ the plasma conductivity ($\text{A V}^{-1} \text{m}^{-1}$). The plasma conductivity is estimated at the beginning of the simulations as ⁴:

$$\sigma = \frac{e^2 n_{e,init}}{m_e \nu_m} \quad (10)$$

with e the elementary charge ($1.6022 \times 10^{-19} \text{ C}$), $n_{e,init}$ the initial electron density (in m^{-3}), m_e the electron mass ($9.1094 \times 10^{-31} \text{ kg}$) and ν_m the collision frequency (in s^{-1}) calculated using BOLSIG+ ³. During the simulation the plasma conductivity is calculated as ⁴:

$$\sigma = \frac{e \nu_d n_e}{\left(\frac{E}{N}\right)_{prev} n_0} \quad (11)$$

with ν_d the electron drift velocity (in m s^{-1}), which is calculated using BOLSIG+ ³ implemented in ZDPlasKin, and $\left(\frac{E}{N}\right)_{prev}$ the reduced electric field at the previous time step (in V m^2).

The balance equation for the gas temperature T_g (in K) is also solved, but for pure CO_2 . We only do this to estimate when the maximum gas temperature is reached (i.e. 3140 K), which is derived from 3D fluid dynamics simulations⁵ and experiments ⁶. The same approach was also used in 7,8. We assume that the temperature profile will not significantly change when adding N_2 to the mixture ⁶.

The balance equation for the gas temperature is:

$$N \frac{\gamma k}{\gamma-1} \frac{dT_g}{dt} = P_{e,el} + \sum_j R_j \Delta H_j - P_{ext} \quad (12)$$

where $N = \sum n_i$ is the total neutral species density, γ is the specific heat ratio of the total gas mixture, k is the Boltzmann constant (in J K^{-1}), $P_{e,el}$ is the gas heating power density due to elastic electron-neutral collisions (in W m^{-3}), R_j is the rate of reaction j (in $\text{m}^{-3} \text{s}^{-1}$), ΔH_j is the heat released (or consumed when this value is negative) by reaction j (in J) and P_{ext} is the heat loss due to energy exchange with the surroundings (in W m^{-3}). The specific heat ratio of the total (ideal) gas mixture is calculated from the specific heat ratios of the individual species in the model, γ_i , using the formula:

$$N \frac{\gamma}{\gamma-1} = \sum_i n_i \frac{\gamma_i}{\gamma_i-1} \quad (13)$$

where n_i are the densities of the individual species i . The individual specific heat ratios, γ_i , can be calculated from the specific heat capacity at constant pressure $c_{p,i}$ (in $\text{J K}^{-1} \text{kg}^{-1}$) using the relation:

$$c_{p,i} = \frac{\gamma_i}{\gamma_i-1} \frac{k}{M} \quad (14)$$

where k is the Boltzmann constant and M is the molar weight of CO_2 (in kg). Since the vibrational levels are treated as separate species (see Table S1), only the heat capacity due to translational and rotational degrees of freedom and, in the case of CO_2 , also the heat capacity due to the symmetric vibrational modes, which are not treated as individual species, should be taken into account ^{9,10}. A classical partitioning between the translational and rotational degrees of freedom is assumed, which gives a value for the specific heat ratio, at room temperature and above, of 1.67 for the atomic species and 1.40 for the diatomic molecules (CO , O_2 and C_2). For O_3 , a value of 1.27 was taken ^{9,11}. Details about the calculation of the total heat capacity and the resulting specific heat ratio for CO_2 , calculated using equation (14), can be found in 9.

Modeling the GAP with a 0D approach

The model is applied to the GAP reactor used for the experiments, using exactly the same dimensions and operating conditions as in the experiments. A schematic diagram of the GAP, including the dimensions, is presented in Figure S1. The arc plasma column inside the GAP is illustrated by the red rectangle. Because the gas enters the GAP reactor by tangential inlets, it follows a vortex flow pattern. As the outlet (anode) diameter is smaller than the reactor body (cathode part) (see Figure S1), the gas will first move upwards in a so-called forward vortex flow (indicated in Figure S1 by the solid spiral) and when it arrives at the top of the reactor, it will have lost some speed by friction and inertia, so that it will travel downwards in a smaller so-called reverse vortex flow, which is more or less captured by the arc column (see dashed spiral in figure S1). This vortex flow results in stabilization of the arc column in the center of the GAP reactor, as predicted by 3D fluid dynamics modeling^{5,12}. Since the plasma confined in the inner vortex gas flow is more or less uniform,^{5,12} we can assume a constant power density applied to the gas, during its residence time in the plasma column. Hence, 0D modeling of this kind of plasma is justified. Indeed, the 0D model calculates the species densities as a function of time, and spatial variation by means of transport is not considered. Nevertheless, by means of the gas flow rate, we can convert the temporal variation calculated in the model into a spatial variation in the arc plasma column, and vice versa. The arc plasma column is thus considered as a plug flow reactor, where the plasma characteristics vary as a function of distance travelled by the gas within a certain residence time, in the same way as they would vary as a function of time in a batch reactor. 2D fluid dynamics simulation results of Trenchev et al. for a GAP in argon^{5,12} revealed that the arc radius is typically around 1 mm. However, the temperature just outside this arc region is still high enough to induce plasma, especially in a molecular plasma where vibration-translation (VT) relaxation causes gas heating. Therefore, we assumed an arc radius of 2 mm in our simulations. Combined with the length of the cathode (10.20 mm) and anode (16.30 mm) and the inlet of 3 mm (see Figure S1), this yields a plasma volume of 0.37 cm³. These approaches were also successfully used in 1,7,8.

The CO₂ conversion after passing through the arc, $X_{CO_2,arc}$, is defined as:

$$X_{CO_2,arc}(\%) = 100\% \left(1 - \frac{n_{CO_2,e} v_e}{n_{CO_2,i} v_i} \right) \quad (15)$$

where $n_{CO_2,e}$ and v_e are the CO₂ density (in m⁻³) and gas velocity (in m s⁻¹) at the end of the arc region near the outlet (fixed at 3140 K), and $n_{CO_2,i}$ and v_i are the CO₂ density (in m⁻³) and gas velocity (in m s⁻¹) at the beginning, right before entering the arc region, i.e., at room temperature.

Since not all gas in the reactor passes through the arc region, the total CO₂ conversion in the reactor, which is also measured experimentally, will be lower than the CO₂ conversion after passing through the arc region, as we also need to account for the unconverted CO₂ in the reactor. This total conversion, $X_{CO_2,tot}$, is defined as:

$$X_{CO_2,tot}(\%) = 100\% \left(1 - \frac{Q_{CO_2,arc} + Q_{CO_2,rest}}{Q_{CO_2,in}} \right) \quad (16)$$

where $Q_{CO_2,in}$, $Q_{CO_2,arc}$ and $Q_{CO_2,rest}$ are the CO₂ fluxes (in s⁻¹) entering the reactor, exiting the arc region at the outlet and exiting the reactor without passing through the arc, hence without being converted. This means that we need to define the fraction of CO₂ that passes through the arc region, which is explained below.

The CO₂ flux entering the reactor $Q_{CO_2,in}$ is defined as:

$$Q_{CO_2,in} = n_{CO_2,i} \dot{V} \quad (17)$$

where $n_{CO_2,i}$ is the CO₂ density (in m⁻³) at the inlet of the reactor (at room temperature) and $\dot{V}$ the volumetric flow rate (in m³ s⁻¹). The CO₂ flux exiting the arc region at the outlet $Q_{CO_2,arc}$ is defined as:

$$Q_{CO_2,arc} = n_{CO_2,e} v_e A_{arc} \quad (18)$$

with $n_{CO_2,e}$ and v_e the CO₂ density (in m⁻³) and gas velocity (in m s⁻¹) at the end of the arc region near the outlet, and A_{arc} the cross sectional area of the arc region, i.e. 12.57 mm². Finally, due to conservation of mass, the CO₂ flux $Q_{CO_2,rest}$ which is not treated by the plasma, is given by:

$$Q_{CO_2,rest} = Q_{CO_2,in} - n_{CO_2,i} v_i A_{arc} \quad (19)$$

Hence, the fraction of CO₂ that passes through the arc region is defined by the mass flow rate through the arc, and is 14.8 % of the total mass flow rate through the reactor. The remaining 85.2% does not pass through the arc, and will not be converted.

The N₂ conversion is calculated in exactly the same way as the CO₂ conversion.

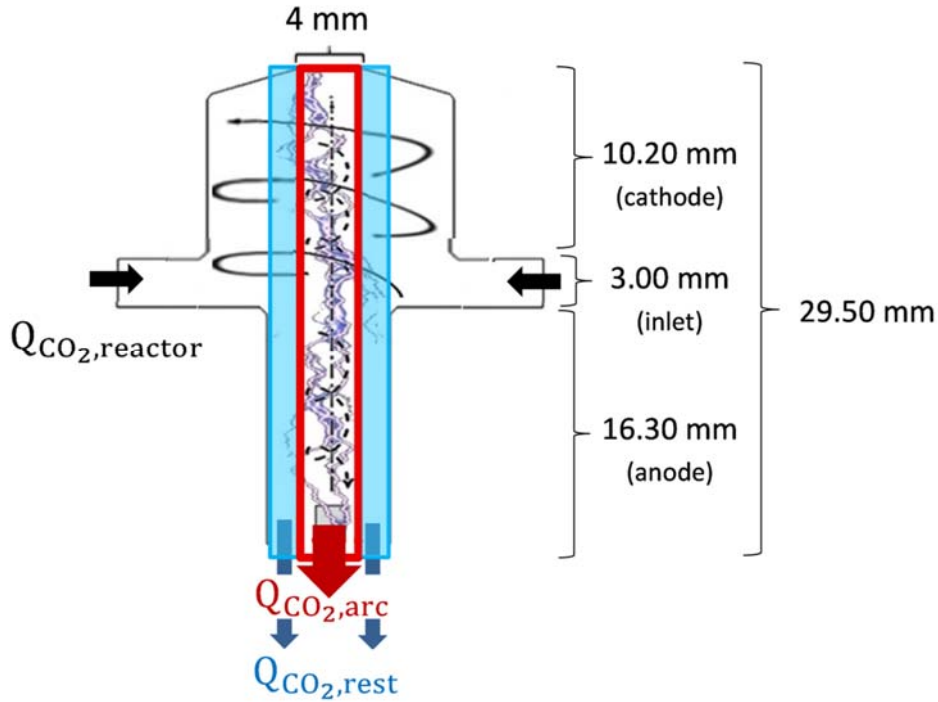


Figure S1. Schematic picture of the GAP, with indication of the dimensions, as well as the outer vortex (solid spiral) and inner (reverse) vortex (dashed spiral). The red frame indicates the arc plasma column, while the blue part indicates the region where the gas is untreated in the reverse vortex.

Chemistry set

The chemistry set used in this study is based on the papers of Heijkers et al.¹³, Snoeckx et al.¹⁴ and Wang et al.¹⁵. The species included in the model are listed in Table S1. The symbol 'V' between brackets for N₂, CO₂, CO and O₂ and the symbol 'E' between brackets for CO₂, CO and O₂ represent the vibrationally and electronically excited levels of these species, respectively. More information about the notation of the vibrationally and electronically excited levels of CO₂, CO and O₂ can be found in¹⁶.

For CO₂, all 21 levels of the asymmetric mode till the dissociation limit (5.5 eV) are taken into account, since they are crucial for storing vibrational energy for efficient CO₂ dissociation¹⁷. In addition, four effective low-lying symmetric stretching and bending mode levels are included in the model, i.e. CO₂ (Va-Vd). For N₂, up to 24 vibrational levels are included (till 5.8 eV), which is more than enough to describe vibration induced dissociation in the GAP, since most dissociation occurs from the lowest levels (see Figure S2), which is also the case for pure CO₂, as revealed in 8.

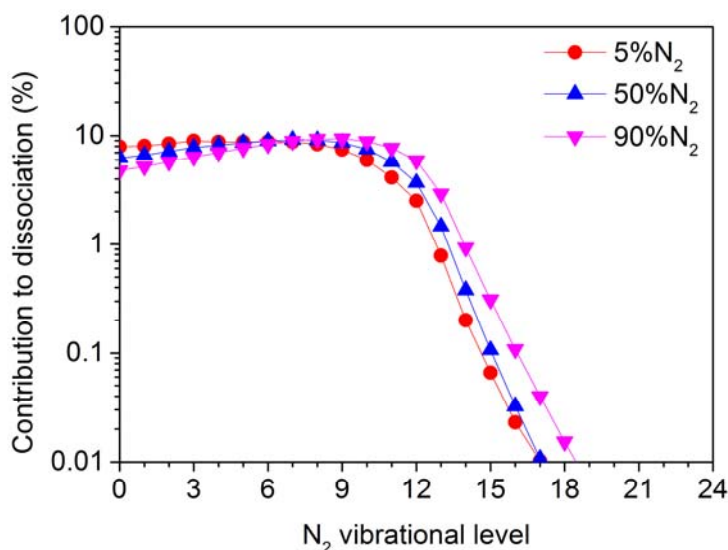


Figure S2. Contribution of the different vibrational levels of N₂ to the total dissociation of N₂ at three different N₂ fractions in the mixture.

The major difference with the sets in 13–15 is that we use the cross section set of Phelps, with the 7 eV threshold excitation reaction used for dissociation, for the electron impact reactions with CO₂^{18–20}, as suggested by Grofulovic et al.²¹, Bogaerts et al.²² and Pietanza et al.^{23–25}. Furthermore, to account for the high temperature and atmospheric pressure conditions in the GAP, some extra reactions, which become significant at these conditions, are included, and the rate coefficients for some existing reactions are also updated (see Table S2).

Therefore, a large chemistry set (containing 18180 reactions and 134 species, consisting of 14 molecules, 30 charged species, 9 radicals and 81 excited species) is created, including electron impact reactions, electron-ion recombination reactions, ion-ion, ion-neutral and neutral-neutral reactions, as well as vibration-translation (VT) and vibration-vibration (VV) relaxation reactions.

Table S1. Species taken into account in the chemistry set for modeling the GAP.

Molecules	Charged species	Radicals	Excited species
CO ₂ , CO, N ₂ , N, NO, N ₂ O, NO ₂ , NO ₃ , N ₂ O ₅ , N ₂ O ₃ , N ₂ O ₄ , C ₂ N ₂	CO ₂ ⁺ , CO ₄ ⁺ , CO ⁺ , C ₂ O ₂ ⁺ , C ₂ O ₃ ⁺ , C ₂ O ₄ ⁺ , C ₂ ⁺ , C ⁺ , CO ₃ ⁻ , CO ₄ ⁻ , N ⁺ , N ₂ ⁺ , N ₃ ⁺ , N ₄ ⁺ , NO ⁺ , N ₂ O ⁺ , NO ₂ ⁺ , NO ⁻ , N ₂ O ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , O ₂ ⁺ N ₂	C ₂ O, C, C ₂ , CN, ONCN, NCO, NCN, C ₂ N	CO ₂ (Va, Vb, Vc, Vd), CO ₂ (V1-V21), CO ₂ (E1), CO(V1-V10), CO(E1-E4), N ₂ (V1-V24), N ₂ (C ³ Π _u), N ₂ (A ³ Σ _u), N ₂ (a ¹ Σ _u), N ₂ (A ¹ Π _g), N ₂ (B ³ Π _g), N ₂ (W ³ Δ _u), N ₂ (B ³ Σ _u), N ₂ (E ³ Σ _g), N ₂ (W ¹ Δ _u), N ₂ (A ¹ Σ _g), N(² D), N(² P)
O ₂ , O ₃	O ⁺ , O ₂ ⁺ , O ₄ ⁺ , O ⁻ , O ₂ ⁻ , O ₃ ⁻ , O ₄ ⁻	O	O ₂ (V1-V3), O ₂ (E1-E2)
	electrons		

Table S2. The reactions included in the model are taken from refs. 13–15, but some extra reactions are added, and the rate coefficients of some other reactions are updated, as listed in this table, to account for the high pressure and temperature conditions in the GAP. The rate coefficients are given in cm³ s⁻¹ and cm⁶ s⁻¹ for two-body and three-body reactions, respectively. *R* is the gas constant and *T* the gas temperature (in K).

Reaction	Rate coefficient	Reference
N + NO → N ₂ + O	1.66x10 ⁻¹¹	26
N + O ₂ → O + NO	2.36x10 ⁻¹¹ exp(- $\frac{44.23}{RT}$)	27
O + NO ₂ → NO + O ₂	9.05x10 ⁻¹² ($\frac{T}{298}$) ^{-0.52}	28
NO + NO + O ₂ → NO ₂ + NO ₂	3.30x10 ⁻³⁹ exp($\frac{4.41}{RT}$)	29
N ₂ O + M → N ₂ + O + M	1.20x10 ⁻⁹ exp(- $\frac{240.00}{RT}$)	30
NO + O → NO ₂	3.01x10 ⁻¹¹ ($\frac{T}{298}$) ^{-0.75}	31
NO ₂ + M → NO + O + M	9.40x10 ⁻⁵ ($\frac{T}{298}$) ^{-2.66} exp(- $\frac{311.00}{RT}$)	31
NO ₂ + O + CO ₂ → NO ₃ + CO ₂	6.59x10 ⁻³⁰ ($\frac{T}{298}$) ^{-3.94} exp(- $\frac{9.56}{RT}$)	31

$\text{NO}_2 + \text{O} + \text{N}_2 \rightarrow \text{NO}_3 + \text{N}_2$	$3.31 \times 10^{-30} \left(\frac{T}{298} \right)^{-4.08} \exp\left(-\frac{10.31}{RT}\right)$	31
$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$2.10 \times 10^{-11} \left(\frac{T}{300} \right)^{3.50} \exp\left(-\frac{91.46}{RT}\right)$	32
$\text{CO}_2 + \text{NO} \rightarrow \text{CO} + \text{NO}_2$	$\left(\frac{1}{30}\right) \times 10^{(-10.59 - (\frac{32500}{4.58T}))}$	33
$\text{C} + \text{N}_2 \rightarrow \text{CN} + \text{N}$	$8.70 \times 10^{-11} \exp\left(-\frac{188.00}{RT}\right)$	34
$\text{C} + \text{NO} \rightarrow \text{CN} + \text{O}$	3.32×10^{-11}	35
$\text{CN} + \text{O} \rightarrow \text{CO} + \text{N}$	$\left(\frac{1}{5}\right) \times 1.69 \times 10^{-11}$	36
$\text{CO} + \text{N} \rightarrow \text{CN} + \text{O}$	$3.84 \times 10^{-9} \exp\left(-\frac{275.05}{RT}\right)$	37,38
$\text{C}_2\text{N}_2 + \text{M} \rightarrow \text{CN} + \text{CN} + \text{M}$	$3.65 \times 10^{-1} \left(\frac{T}{298} \right)^{-4.32} \exp\left(-\frac{545.00}{RT}\right)$	39
$\text{CN} + \text{NO}_2 \rightarrow \text{NO} + \text{NCO}$	$1.02 \times 10^{-8} (T)^{-0.80} \exp\left(-\frac{173.63}{T}\right)$	40
$\text{N} + \text{NCO} \rightarrow \text{CN} + \text{NO}$	1.66×10^{-12}	41
$\text{N} + \text{NCO} \rightarrow \text{CO} + \text{N}_2$	3.30×10^{-11}	36
$\text{CN} + \text{O}_2 \rightarrow \text{O} + \text{NCO}$	$\left(\frac{1}{2.77}\right) 1.16 \times 10^{-11}$	42
$\text{O} + \text{NCO} \rightarrow \text{CN} + \text{O}_2$	$4.05 \times 10^{-10} \left(\frac{T}{298} \right)^{-1.43} \exp\left(-\frac{29.10}{RT}\right)$	43
$\text{O} + \text{NCO} \rightarrow \text{CO} + \text{NO}$	7.51×10^{-11}	43
$\text{CO}_2 + \text{CN} \rightarrow \text{CO} + \text{NCO}$	$1.35 \times 10^{-12} \left(\frac{T}{298} \right)^{2.16} \exp\left(-\frac{112.0}{RT}\right)$	44
$\text{NCO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO}$	$5.15 \times 10^{-11} \left(\frac{T}{298} \right)^{-1.34} \exp\left(-\frac{2.99}{RT}\right)$	45
$\text{NCO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$	$1.29 \times 10^{-10} \left(\frac{T}{298} \right)^{-1.97} \exp\left(-\frac{4.66}{RT}\right)$	45
$\text{NCO} + \text{NO} \rightarrow \text{CO} + \text{N}_2 + \text{O}$	$0.23 \times 1.69 \times 10^{-11} \exp\left(\frac{1.63}{RT}\right)$	43
$\text{NCO} + \text{NO}_2 \rightarrow \text{CO} + \text{NO} + \text{NO}$	1.30×10^{-12}	46

$\text{NCO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{N}_2\text{O}$	$5.40 \times 10^{-12} \exp\left(-\frac{354.81}{T}\right)$	40
$\text{NCO} + \text{NCO} \rightarrow \text{N}_2 + \text{CO} + \text{CO}$	3.01×10^{-11}	43
$\text{NCO} + \text{M} \rightarrow \text{N} + \text{CO} + \text{M}$	$1.69 \times 10^{-9} \exp\left(-\frac{195.0}{RT}\right)$	36
$\text{N}_2\text{O} + \text{NCO} \rightarrow \text{CO} + \text{N}_2 + \text{NO}$	$1.50 \times 10^{-10} \exp\left(-\frac{116.0}{RT}\right)$	43
$\text{NCN} + \text{O} \rightarrow \text{N} + \text{NCO}$	$4.02 \times 10^{-14} \left(\frac{T}{298}\right)^{0.42} \exp\left(\frac{0.66}{RT}\right)$	47
$\text{NCN} + \text{O} \rightarrow \text{N}_2 + \text{CO}$	$2.22 \times 10^{-16} \left(\frac{T}{298}\right)^{2.32} \exp\left(\frac{4.75}{RT}\right)$	47
$\text{NCN} + \text{O} \rightarrow \text{CN} + \text{NO}$	$1.54 \times 10^{-10} \exp\left(-\frac{5.80}{RT}\right)$	48
$\text{NCN} + \text{NO} \rightarrow \text{CN} + \text{N}_2\text{O}$	$3.16 \times 10^{-12} \exp\left(-\frac{26.30}{RT}\right)$	49
$\text{NCN} + \text{O}_2 \rightarrow \text{NO} + \text{NCO}$	$1.15 \times 10^{-13} \left(\frac{T}{298}\right)^{0.51} \exp\left(-\frac{103.00}{RT}\right)$	50
$\text{NCN} + \text{NCN} \rightarrow \text{CN} + \text{CN} + \text{N}_2$	6.14×10^{-12}	48
$\text{NCN} + \text{M} \rightarrow \text{C} + \text{N}_2 + \text{M}$	$1.48 \times 10^{-9} \exp\left(-\frac{260.00}{RT}\right)$	48
$\text{NO} + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_3 + \text{M}$	$3.09 \times 10^{-34} \left(\frac{T}{298}\right)^{-7.70}$	32
$\text{N}_2\text{O}_3 + \text{M} \rightarrow \text{NO} + \text{NO}_2 + \text{M}$	$1.91 \times 10^{-7} \left(\frac{T}{298}\right)^{-8.70} \exp\left(-\frac{40.57}{RT}\right)$	32
$\text{NO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$	$1.40 \times 10^{-33} \left(\frac{T}{298}\right)^{-3.80}$	32
$\text{N}_2\text{O}_4 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_2 + \text{M}$	$1.30 \times 10^{-5} \left(\frac{T}{298}\right)^{-3.80} \exp\left(-\frac{53.21}{RT}\right)$	32
$\text{CO}_2 + \text{N} \rightarrow \text{CO} + \text{NO}$	5.00×10^{-16}	51
$\text{CO}_2 + \text{N}(^2\text{D}) \rightarrow \text{CO} + \text{NO}$	3.60×10^{-13}	52
$\text{CO} + \text{N}_2\text{O} \rightarrow \text{CO}_2 + \text{N}_2$	$5.30 \times 10^{-13} \exp\left(-\frac{84.81}{RT}\right)$	31

$\text{NO}_3 + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{O}_2$	1.00×10^{-17}	53
$\text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M}$	$1.52 \times 10^{-4} \left(\frac{T}{298} \right)^{-3.10} \exp\left(-\frac{1073.00}{RT}\right)$	54
$\text{C} + \text{NO} \rightarrow \text{CO} + \text{N}$	4.82×10^{-11}	55
$\text{CN} + \text{NO}_2 \rightarrow \text{CO} + \text{N}_2\text{O}$	$0.08 \times 5.01 \times 10^{-11} \exp\left(\frac{1.42}{RT}\right)$	56
$\text{CN} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{N}_2$	$0.06 \times 5.01 \times 10^{-11} \exp\left(\frac{1.42}{RT}\right)$	56
$\text{N} + \text{CN} + \text{M} \rightarrow \text{NCN} + \text{M}$	2.76×10^{-32}	57
$\text{CN} + \text{N}_2\text{O} \rightarrow \text{NCN} + \text{NO}$	$1.73 \times 10^{-14} \left(\frac{T}{298} \right)^{2.60} \exp\left(-\frac{15.46}{RT}\right)$	43
$\text{NCN} + \text{NO}_2 \rightarrow \text{ONCN} + \text{NO}$	$7.80 \times 10^{-12} \exp\left(-\frac{38.00}{RT}\right)$	49
$\text{C}_2\text{N}_2 + \text{O} \rightarrow \text{CN} + \text{NCO}$	$4.15 \times 10^{-11} \exp\left(-\frac{45.73}{RT}\right)$	58
$\text{C}_2\text{N}_2 + \text{O} \rightarrow \text{NCN} + \text{CO}$	$2.31 \times 10^{-10} \exp\left(-\frac{7540.00}{T}\right)$	59
$\text{C}_2\text{N} + \text{N} \rightarrow \text{CN} + \text{CN}$	1.0×10^{-10}	60
$\text{C}_2\text{N} + \text{O} \rightarrow \text{CN} + \text{CO}$	5.99×10^{-12}	61
$\text{C}_2 + \text{NO} \rightarrow \text{C}_2\text{N} + \text{O}$	$0.70 \times 1.25 \times 10^{-10} \exp\left(-\frac{36.17}{RT}\right)$	62
$\text{C}_2\text{N}_2 + \text{C} \rightarrow \text{CN} + \text{C}_2\text{N}$	3.01×10^{-11}	60
$\text{C}_2\text{N}_2 + \text{N} \rightarrow \text{C}_2\text{N} + \text{N}_2$	$4.98 \times 10^{-8} \exp\left(-\frac{17500.00}{T}\right)$	63
$\text{N}_2\text{O}_5 + \text{O} \rightarrow \text{N}_2 + \text{O}_2 + \text{O}_2 + \text{O}_2$	$3.00 \times 10^{-16} \left(\frac{T}{300} \right)^{0.50}$	64
$\text{CN} + \text{NO} \rightarrow \text{NCN} + \text{O}$	$2.99 \times 10^{-11} \exp\left(-\frac{19220.00}{T}\right)$	65
$\text{CN} + \text{NCN} \rightarrow \text{N} + \text{C}_2\text{N}_2$	3.32×10^{-11}	65
$\text{N} + \text{NCN} \rightarrow \text{N}_2 + \text{CN}$	1.66×10^{-11}	65
$\text{NCN} + \text{M} \rightarrow \text{N} + \text{CN} + \text{M}$	$8.47 \times 10^{-9} \exp\left(-\frac{53300.00}{T}\right)$	65
$\text{C} + \text{NCN} \rightarrow \text{CN} + \text{CN}$	1.66×10^{-11}	65

$C + NCO \rightarrow CN + CO$	1.66×10^{-11}	65
$NCN + NCO \rightarrow CN + N_2 + CO$	1.66×10^{-11}	65

Results and discussion

CO₂ conversion, energy cost and energy efficiency

Table S3. Concentrations, as well as the carbon and oxygen balance. Note that the C-balance is always lower and the O-balance is always higher than 100 %, which can be explained by the accuracy of the calibration method within the gas chromatograph.

IN (%)		OUT (%)				OUT (ppm)		C-balance (%)	O-balance (%)
CO ₂	N ₂	CO ₂	N ₂	CO	O ₂	NO	NO ₂		
99.53	0.08	92.04	0.04	5.71	2.90	0	0	98.21	101.12
94.50	5.33	85.69	5.10	6.27	3.07	1023.1	9.60	97.31	100.56
89.82	10.33	82.28	10.05	6.24	3.01	3178	54.6	98.56	101.90
80.39	20.46	72.24	19.88	5.94	2.78	5545	170.1	97.26	100.72
69.37	30.59	63.21	29.94	5.79	2.65	6408	264.6	99.47	103.29
59.99	40.60	53.44	39.67	5.64	2.52	6453	307.3	98.50	102.71
50.46	50.63	44.32	49.68	5.21	2.25	5998	316.9	98.15	102.60
40.29	60.76	35.28	59.82	4.63	1.99	5275	286	99.06	103.99
30.31	70.89	25.99	70.17	3.86	1.62	4507	241	98.49	103.83
19.74	80.42	16.37	80.18	2.92	1.21	3620	201.3	97.76	103.91
9.20	89.45	7.34	89.70	1.73	0.72	2136	143.5	98.63	106.49
3.79	94.61	2.80	95.12	0.96	0.44	1524.4	108.17	99.15	110.79

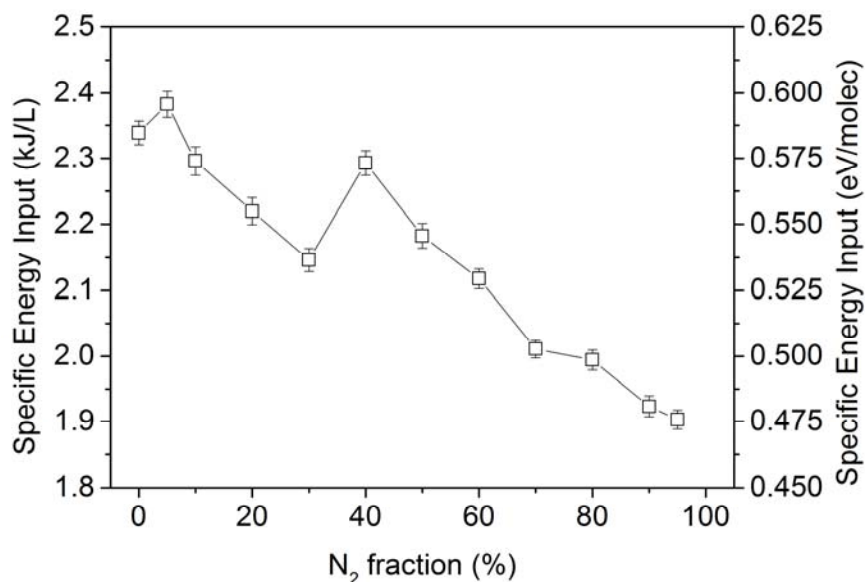


Figure S3. There is a small drop in specific energy input (SEI) upon N₂ addition.

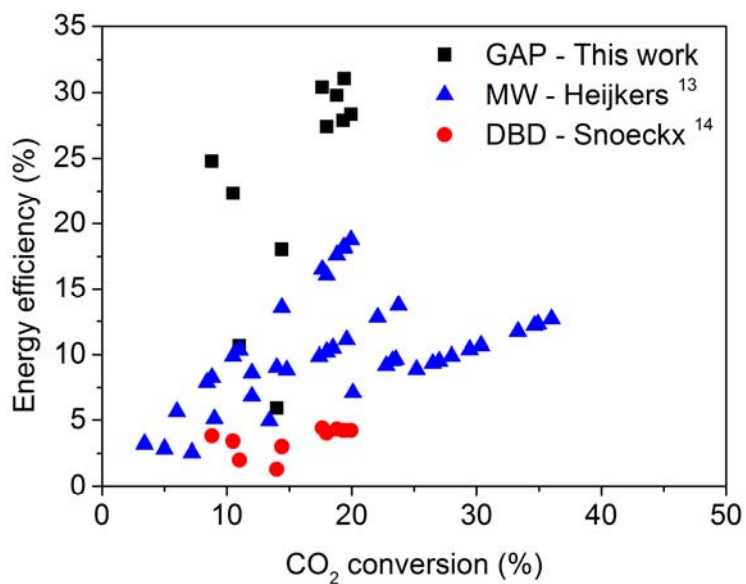


Figure S4. Comparison of the energy efficiency versus CO₂ conversion in three different types of plasma reactors mostly studied for CO₂ conversion: gliding arc plasmatron (GAP; this work), microwave plasma (MW; Heijkers¹³) and dielectric barrier discharge (DBD; Snoeckx¹⁴).

In general, most studies for CO₂ conversion are carried out in these three plasma types⁶⁶, but studies with addition of N₂ are still limited to these two references and our current work.

Analysis of the byproducts - NO_x concentrations

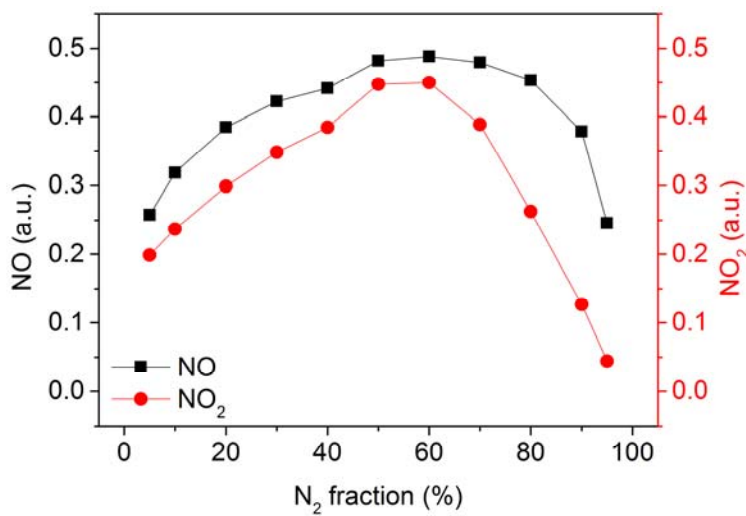


Figure S5. NO and NO₂ concentration in arbitrary units as a function of N₂ fraction, as obtained from the FTIR measurements.

Table S4. NO and NO₂ concentration and calculated error, in parts per million, as obtained from the QCL measurements.

N ₂ fraction (%)	NO (ppm)		NO ₂ (ppm)	
	Value	Error	Value	Error
5	1524.4	0.8	108.17	0.09
10	2136	1	143.5	0.2
20	3620	8	201.3	0.4
30	4507	19	241	1
40	5275	21	286	1
50	5998	8	316.9	0.5
60	6453	14	307.3	0.7
70	6408	10	264.6	0.4
80	5545	9	170.1	0.3
90	3178	7	54.6	0.1
95	1023.1	0.3	9.60	0.02

The maximum total NO_x concentration obtained is 6761 ppm at 60 % N₂. To make the process effective for N₂ fixation, the NO_x concentration should be above 1%, as stated in the main paper. For this purpose, we should enhance the CO₂ conversion in the GAP. To realize the latter, the fraction of gas passing through the arc should be increased to 22%. This can be explained as follows: from previous fluid dynamics calculations we know that the fraction of gas passing through the arc is 14.8 % ⁷ (used in equation 20). Based on this number, we calculated that the conversion inside the arc is about 71 % (equation 21).

$$X_{CO_2}^{Absolute}(\%) = X_{CO_2,arc}(\%) \times 0.148 \quad (20)$$

$$X_{CO_2,arc}(\%) = \frac{X_{CO_2}^{Absolute}(\%)}{0.148} = \frac{10.5\%}{0.148} = 71\% \quad (21)$$

As we now obtain a maximum NO_x concentration of 6761 ppm at 60 % N₂, and when this must be increased up to 1 %, we need an increase of $X_{CO_2}^{Absolute}$ up to 16 %. Assuming that we have 71 % CO₂ conversion in the arc and we need an absolute CO₂ conversion of 16 %, we need a fraction of 22 % passing through the arc (equation 22).

$$fraction_{arc} = \frac{X_{CO_2}^{Absolute}(\%)}{X_{CO_2,arc}(\%)} = \frac{16\%}{71\%} = 0.22 \quad (22)$$

Underlying mechanisms as revealed by computer simulations

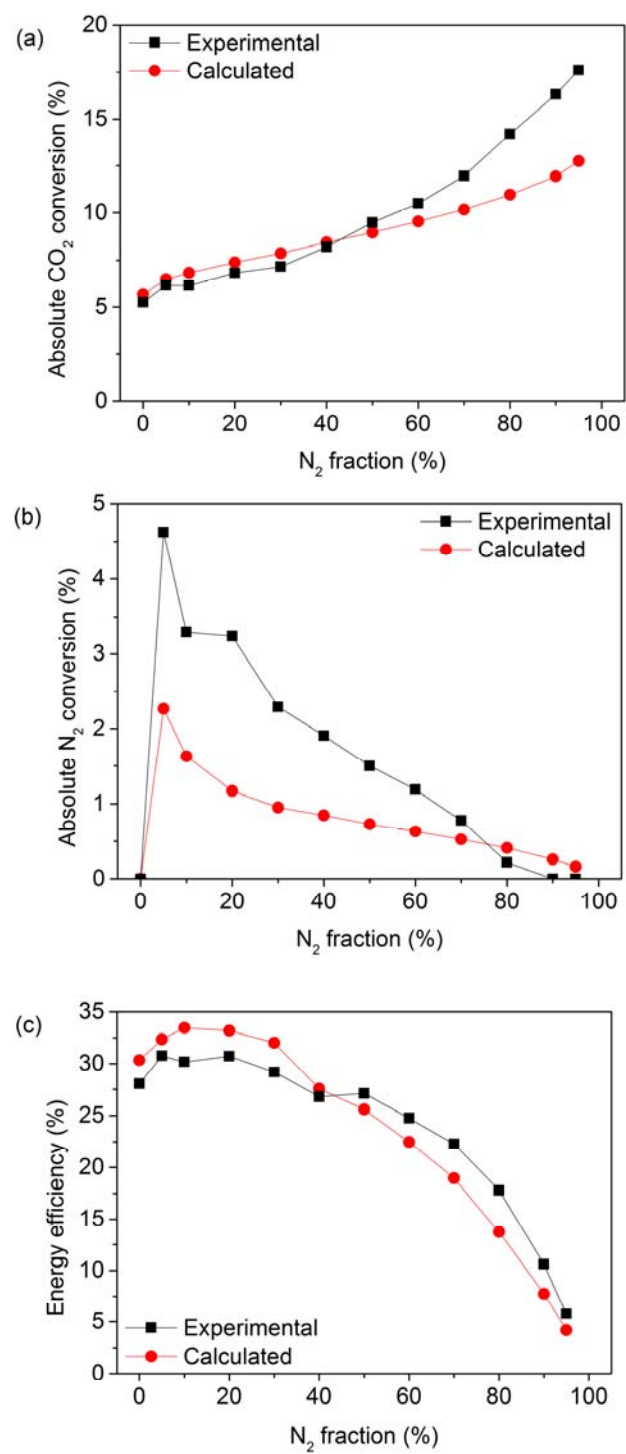


Figure S6. Experimental and calculated results for CO₂ conversion (a), N₂ conversion (b) and energy efficiency (c).

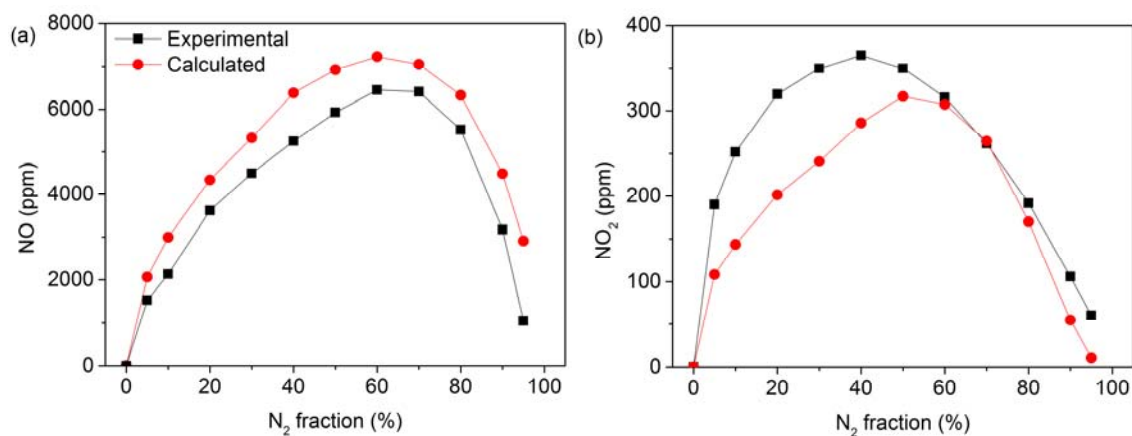


Figure S7. Experimental and calculated results for NO (a) and NO₂ (b) concentration (in parts per million).

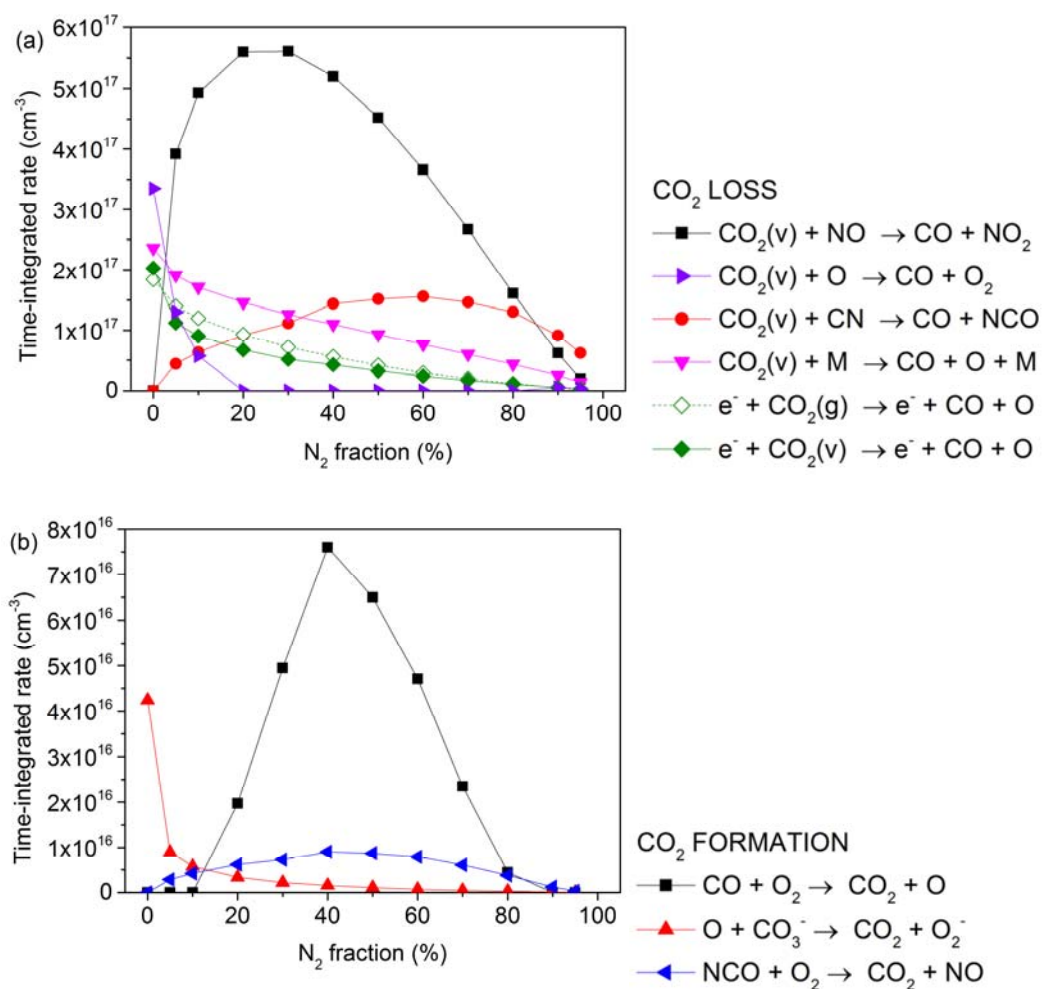


Figure S8. Time-integrated rate for the most important CO₂ loss (a) and CO₂ formation (b) mechanisms as a function of N₂ fraction. Note that the time-integrated formation rate is an order of magnitude lower than the time-integrated loss rate.

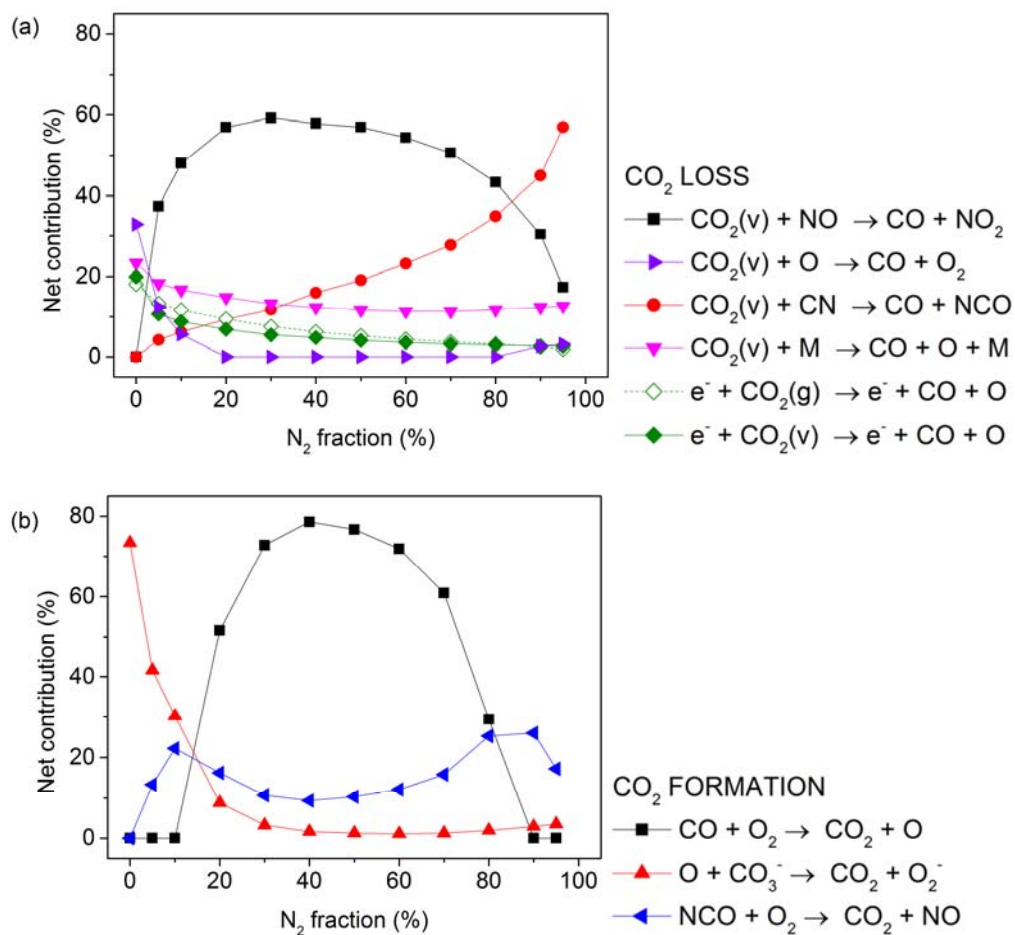
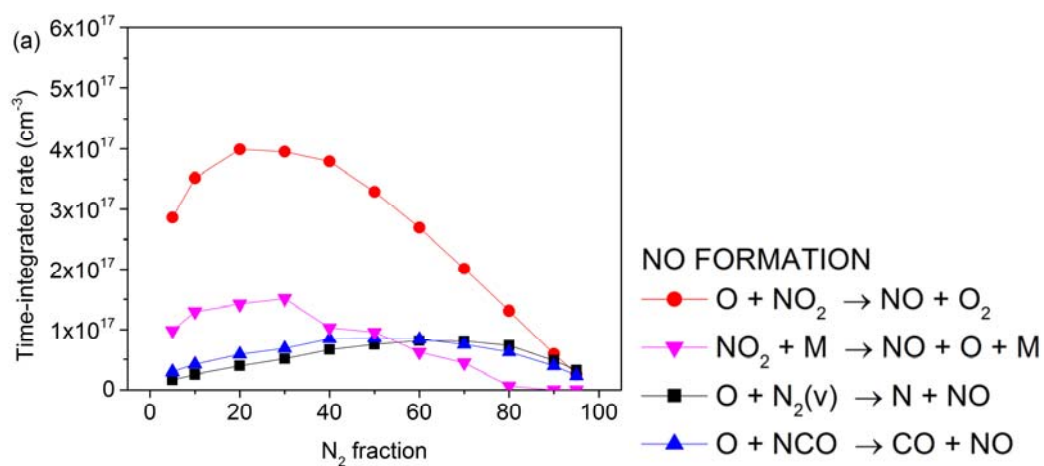


Figure S9. Net contribution of the most important loss (a) and formation (b) reactions of CO₂.



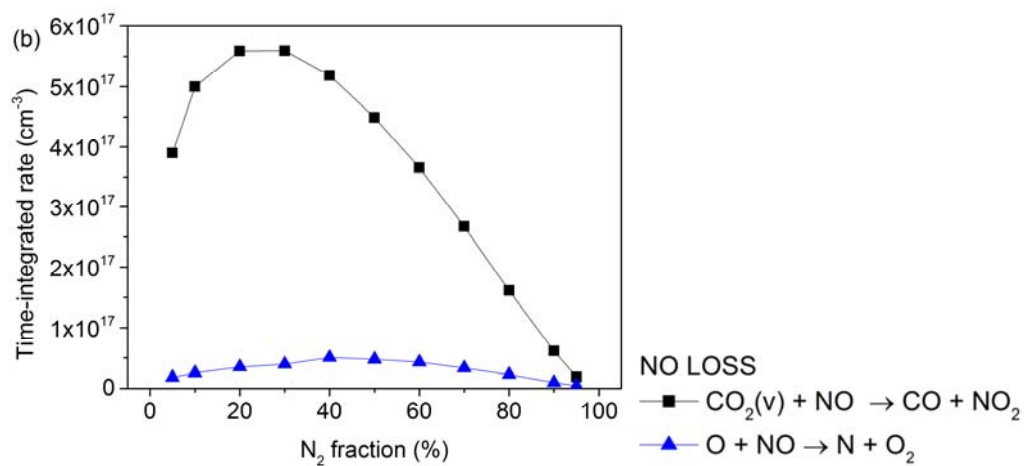


Figure S10. Time-integrated rate for the most important NO formation (a) and NO loss (b) mechanisms as a function of N₂ fraction.

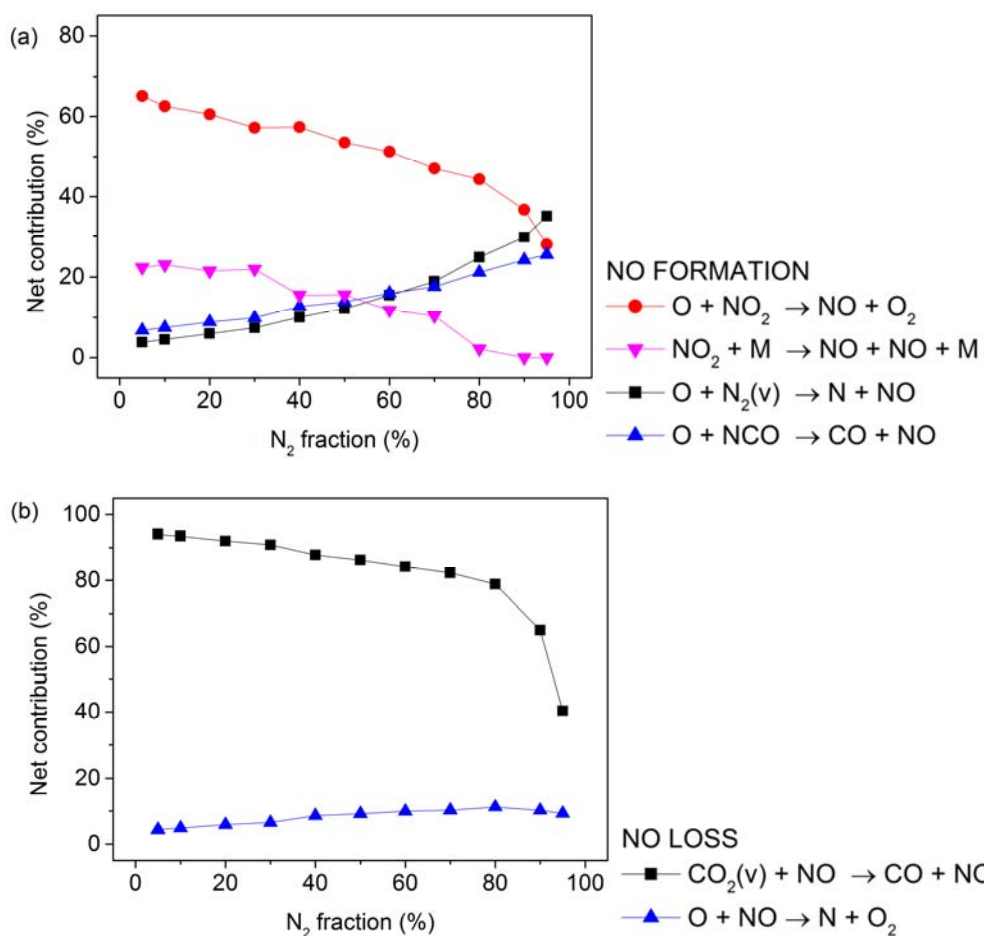


Figure S11. Net contribution of the most important formation (a) and loss (b) reactions of NO.

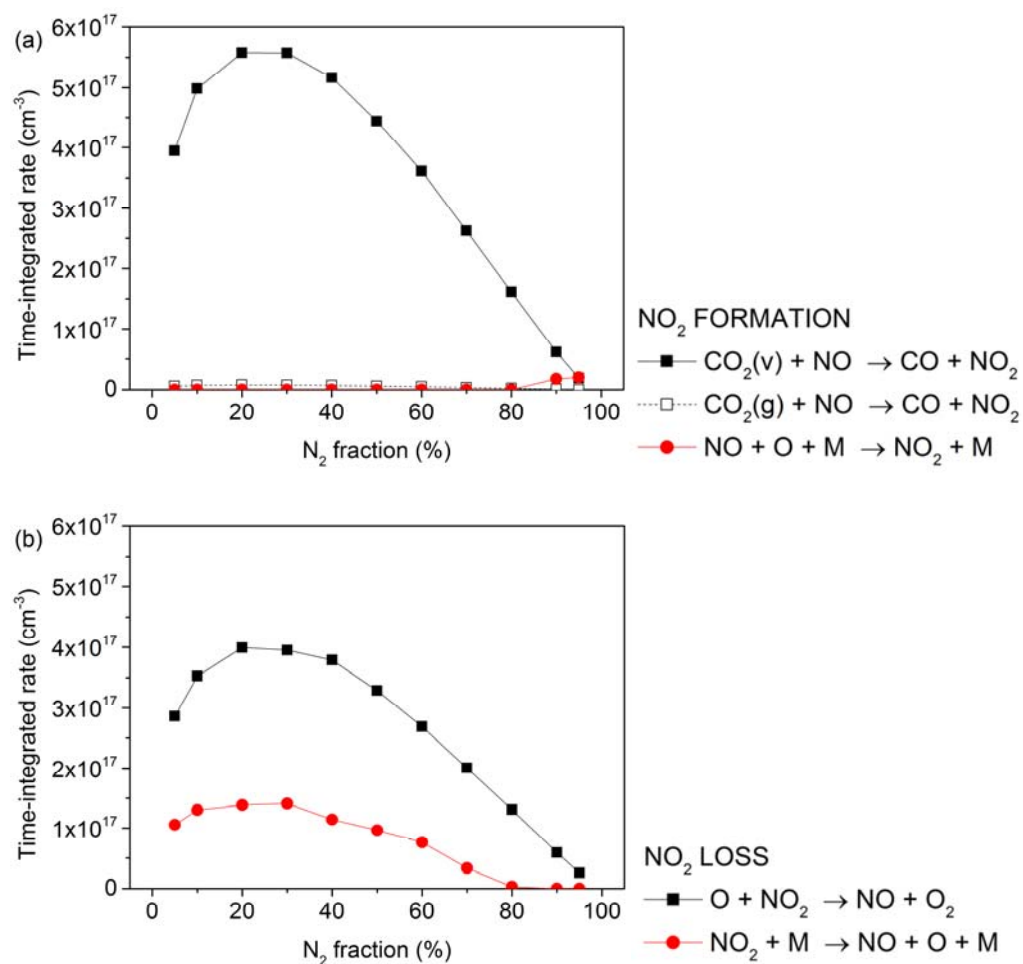


Figure S12. Time-integrated rate for the most important NO₂ formation (a) and NO₂ loss (b) mechanisms as a function of N₂ fraction.

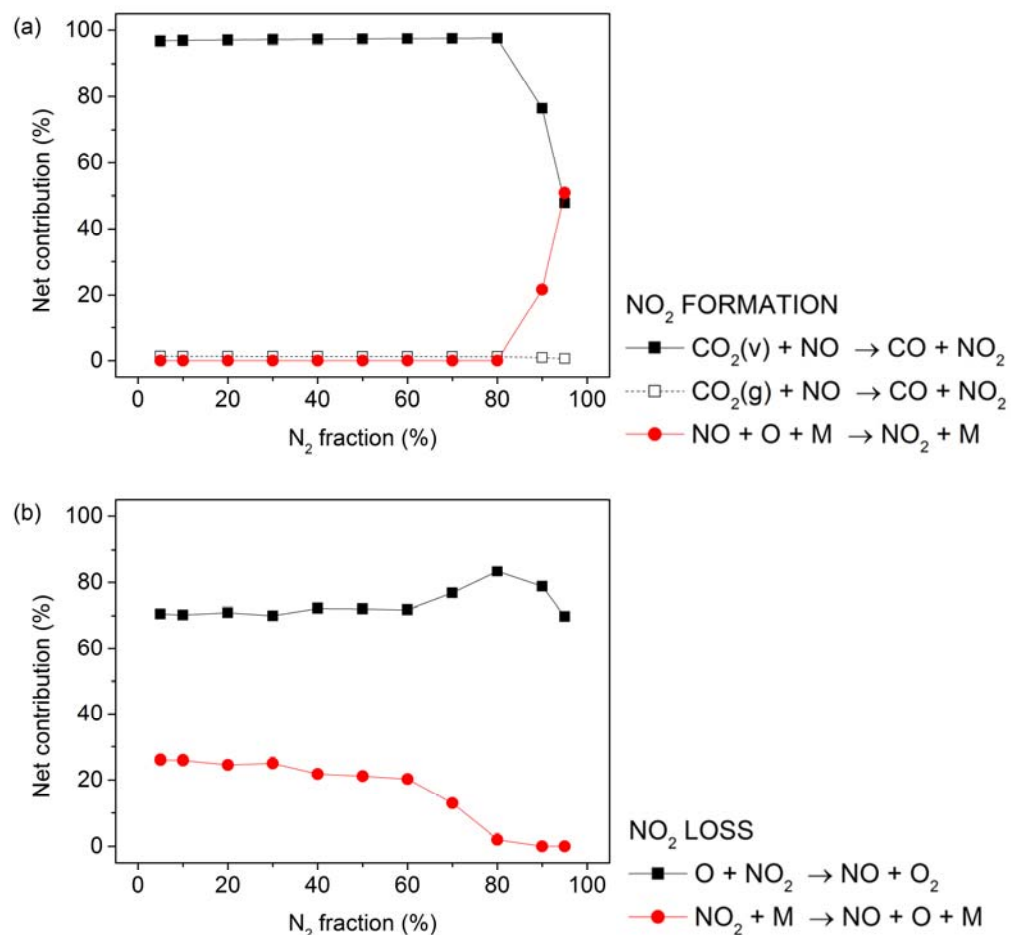


Figure S13. Net contribution of the most important formation (a) and loss (b) reactions of NO₂.

Table S5. Most important reactions, ranked by importance based on the average time-integrated rate.

Reactions	Average time-integrated rate (cm ⁻³)
CO ₂ + NO → CO + NO ₂	3.55 x10 ¹⁷
O + NO ₂ → NO + O ₂	2.57 x10 ¹⁷
CO + N → CN + O	1.38 x10 ¹⁷
e ⁻ + CO ₂ → e ⁻ + CO + O	1.19 x10 ¹⁷
CO ₂ + M → CO + O + M	1.16 x10 ¹⁷
CO ₂ + CN → CO + NCO	1.15 x10 ¹⁷
NO ₂ + M → NO + O + M	7.63 x10 ¹⁶
NCO + M → N + CO + M	5.96 x10 ¹⁶
O + N ₂ → N + NO	5.93 x10 ¹⁶
O + NCO → CO + NO	5.92 x10 ¹⁶
CO + O ₂ → CO ₂ + O	3.17 x10 ¹⁶
NCO + NO → CO + N ₂ + O	6.61 x10 ¹⁵
N ₂ O + M → N ₂ + O + M	6.49 x10 ¹⁵
N + NO ₂ → N ₂ O + O	3.78 x10 ¹⁵
NCO + NO → N ₂ O + CO	3.13 x10 ¹⁵
NO ₂ + NO ₃ + M → N ₂ O ₅ + M	6.88 x10 ¹³
NO ₂ + NO ₂ + M → N ₂ O ₄ + M	9.34 x10 ⁸
NO + NO ₂ + M → N ₂ O ₃ + M	4.28 x10 ⁷

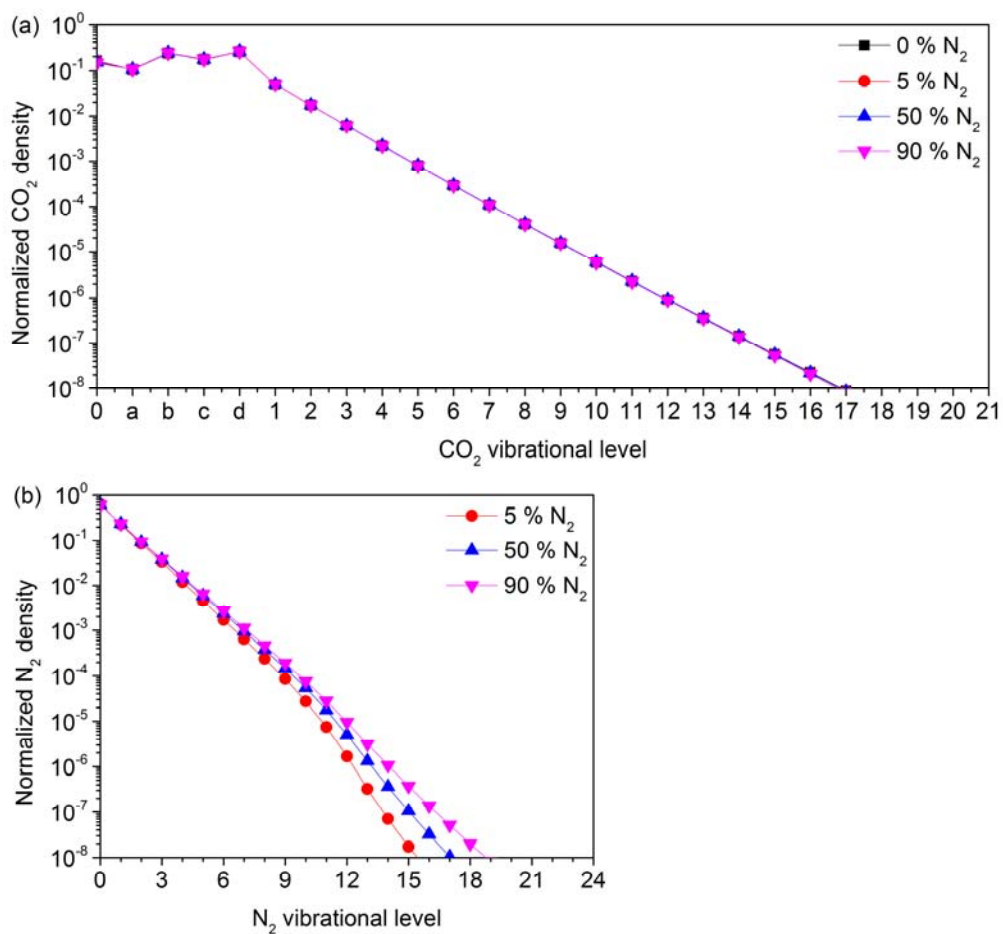


Figure S14. The calculated vibrational distribution of CO₂ (a) and N₂ (b) are nearly thermal, in the entire range of N₂ fractions in the mixture.

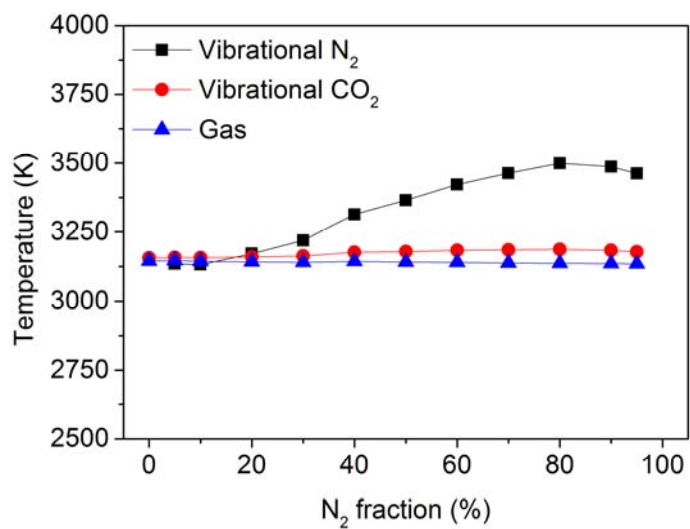


Figure S15. The average gas temperature is 3140 K, while the average vibrational temperature of CO₂ and N₂ are 3174 K and 3333 K, respectively.

Comparison of gliding arc plasmatron with dielectric barrier discharge

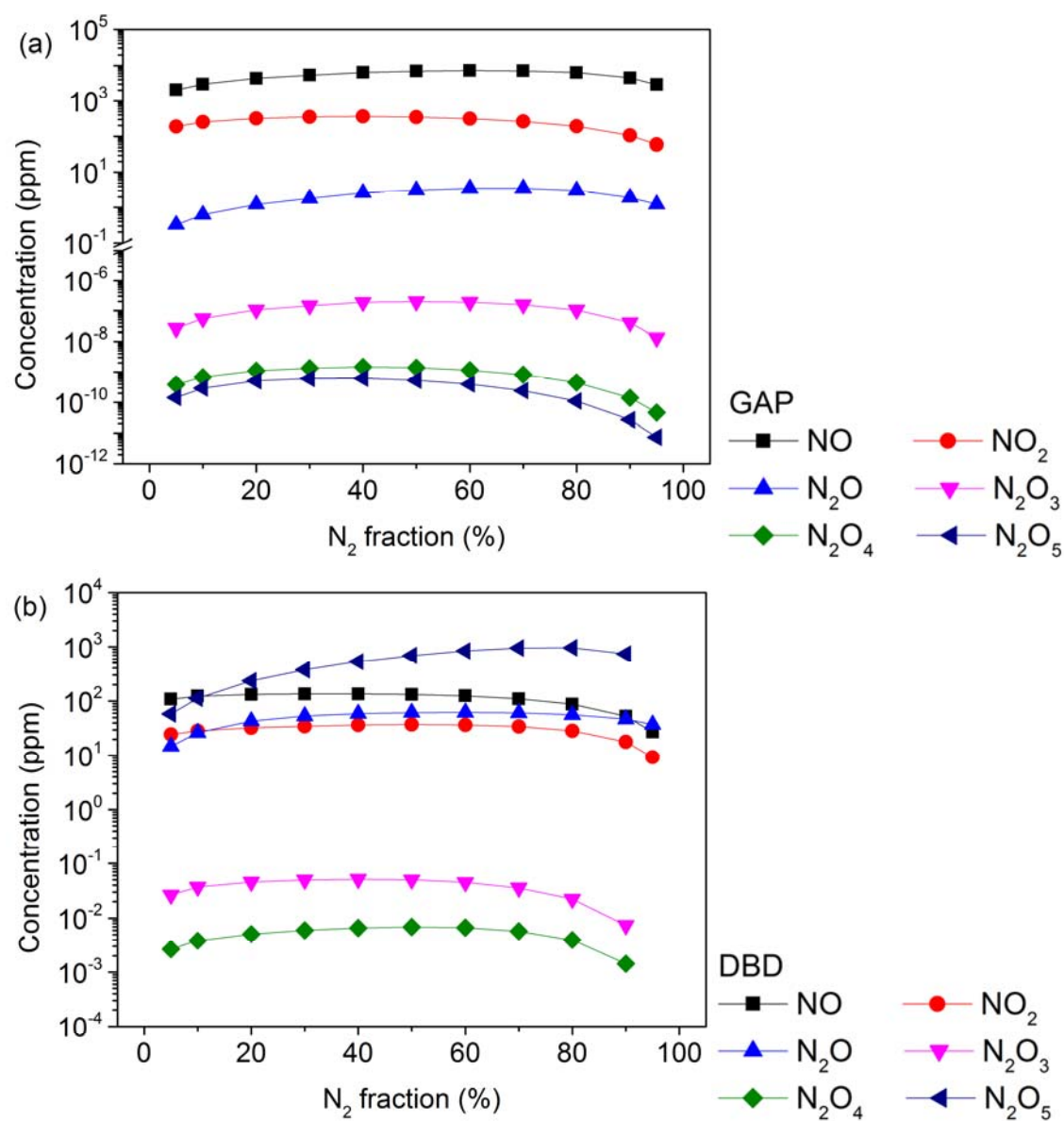


Figure S16. Concentration of the most important byproducts in the GAP (a) and DBD (b) as a function of N_2 fraction, obtained by modeling.

In Figure S17, we plot the total time-integrated net formation (a) and loss (b) rates of N_2O , N_2O_3 , N_2O_4 and N_2O_5 , in both a GAP and DBD. It is clear that the total formation rate is lower than the total loss rate in the GAP, while it is higher in the DBD, explaining why these species have a much higher concentration in the DBD than in the GAP.

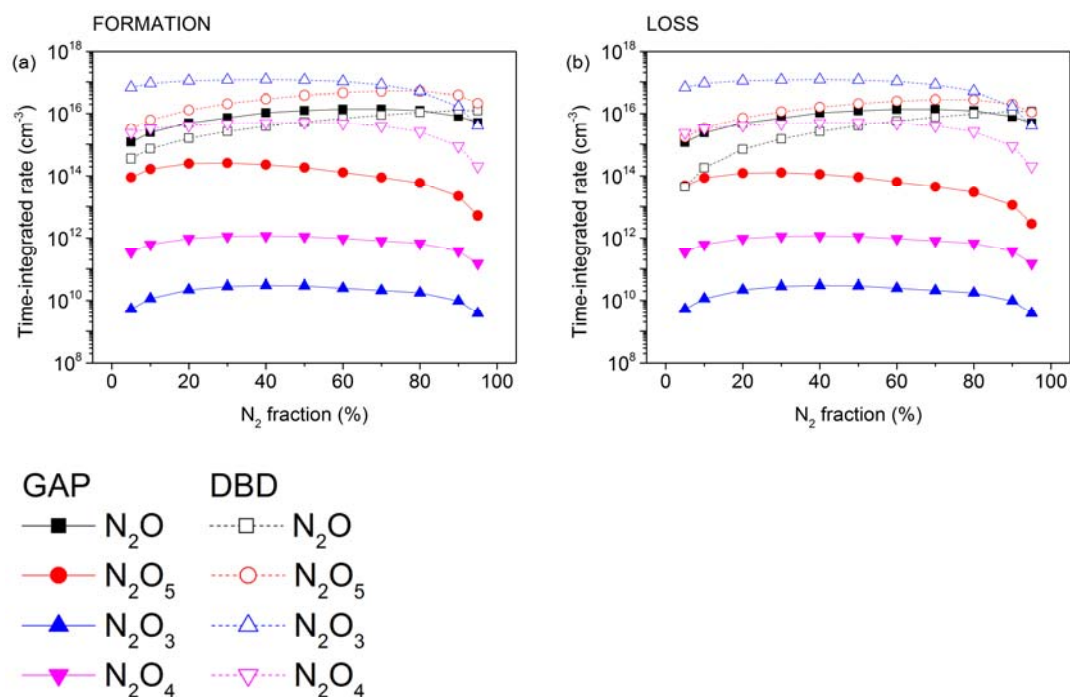


Figure S17. Total time-integrated net formation (a) and loss (b) rates of N₂O, N₂O₃, N₂O₄, N₂O₅, in both a GAP and DBD.

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