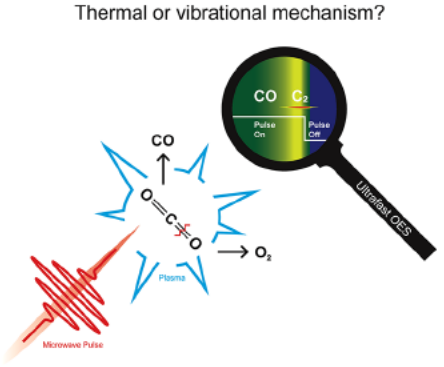
Time-Resolved Optical Emission Spectroscopy Reveals Nonequilibrium Conditions for CO_2 Splitting in Atmospheric Plasma Sustained with Ultrafast Microwave Pulsation

Sergey Soldatov, Guido Link, Lucas Silberer, Clara Marie Schmedt, Emile Carbone, Federico D'Isa, John Jelonnek, Roland Dittmeyer, and Alexander Navarrete*

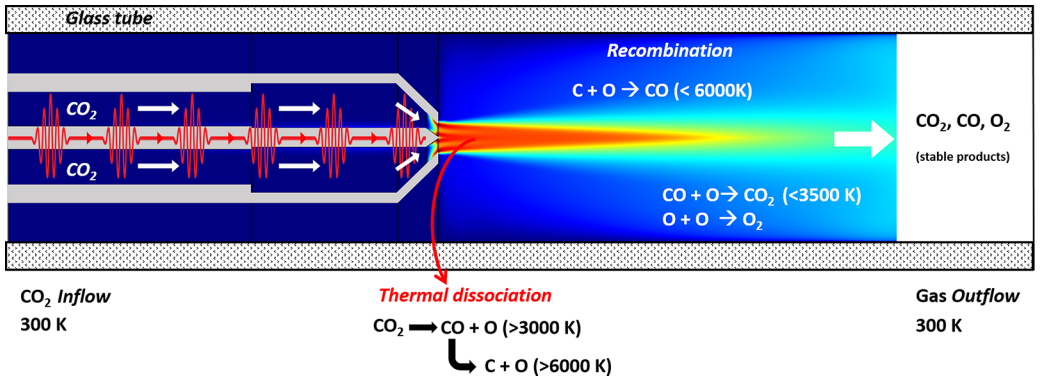
ABSTRACT: Among the pool of Power to X technologies, plasmas show high potential for the efficient use of intermittent renewable energies. High efficiencies of CO_2 conversion have been reported while using microwave plasmas at vacuum conditions which are, however, not suitable for CO_2 mitigation at industrial scales. Here we show that ultrafast pulsation of microwaves allow significant improvements of energy efficiencies during CO_2 splitting at atmospheric pressure as compared to continuous wave operation of the microwave source. Moreover, by the interrogation of the plasma with time resolved optical emission spectroscopy we can, for the first time, observe the evolution of the vibrational and rotational temperatures and define a time window where nonequilibrium can be expected at the beginning of the pulse of an atmospheric CO_2 microwave plasma. In spite of the evidence of nonequilibrium in our system, thermal mechanism appears to dominate the CO_2 dissociation. It is shown that a fine control of the energy deposition in the plasma is possible with ultrafast pulsation of the microwave energy supply.



Early in the 21st century, the COVID 19 pandemic is teaching us the importance of addressing challenges early and based on science.[1] According to the Intergovernmental Panel on Climate Change (IPCC) global warming is already happening and we have around three decades left to drastically reduce our greenhouse gas emissions and remain in the target scenario of 1.5 °C above preindustrial levels, set in the Paris Agreement.[2] The prescription to achieve this target involves measures such as increasing the efficiency of the everyday energy use, actively removing carbon dioxide from the atmosphere and reducing our consumption of fossil fuels while shifting either to renewable energies or to nuclear energy. The latter finds nowadays decreasing acceptance due to high potential risk and high system cost including deconstruction and waste disposal and storage. The intermittency and increasing availability of renewables in the energy mix create, however, the need for technologies that store the excess energy produced during one period and save it for another.[3] However, the dimension of the problem calls for not only technologies propelled by renewable energy but also technologies that are scalable and sustainable. Precisely for these reasons, recent efforts have been put in the commonly known Power to X technologies. One example of such technologies considers capturing CO_2 from point sources or directly from the atmosphere and subsequently transforming it into valuable products such as fuels and chemical precursors using renewable electrical energy.[4−8]

In particular, plasma technology offers the possibility of dealing with an intermittent availability of electricity by instantaneously switching on or off the process.[8] Moreover, an efficient chemical conversion of thermodynamically stable molecules such as CO_2 is possible with plasmas.[9,10] In these possibilities, the green electricity based plasma assisted conversion of CO_2 into synthetic fuels is increasingly being explored as a promising approach for mitigation of CO_2 emissions and for energy storage.[9,11,12] A key figure of merit

Scheme 1. Schematic Representation of CO_2 Splitting in an Atmospheric Microwave Plasma Torch under Ultrafast Pulsation



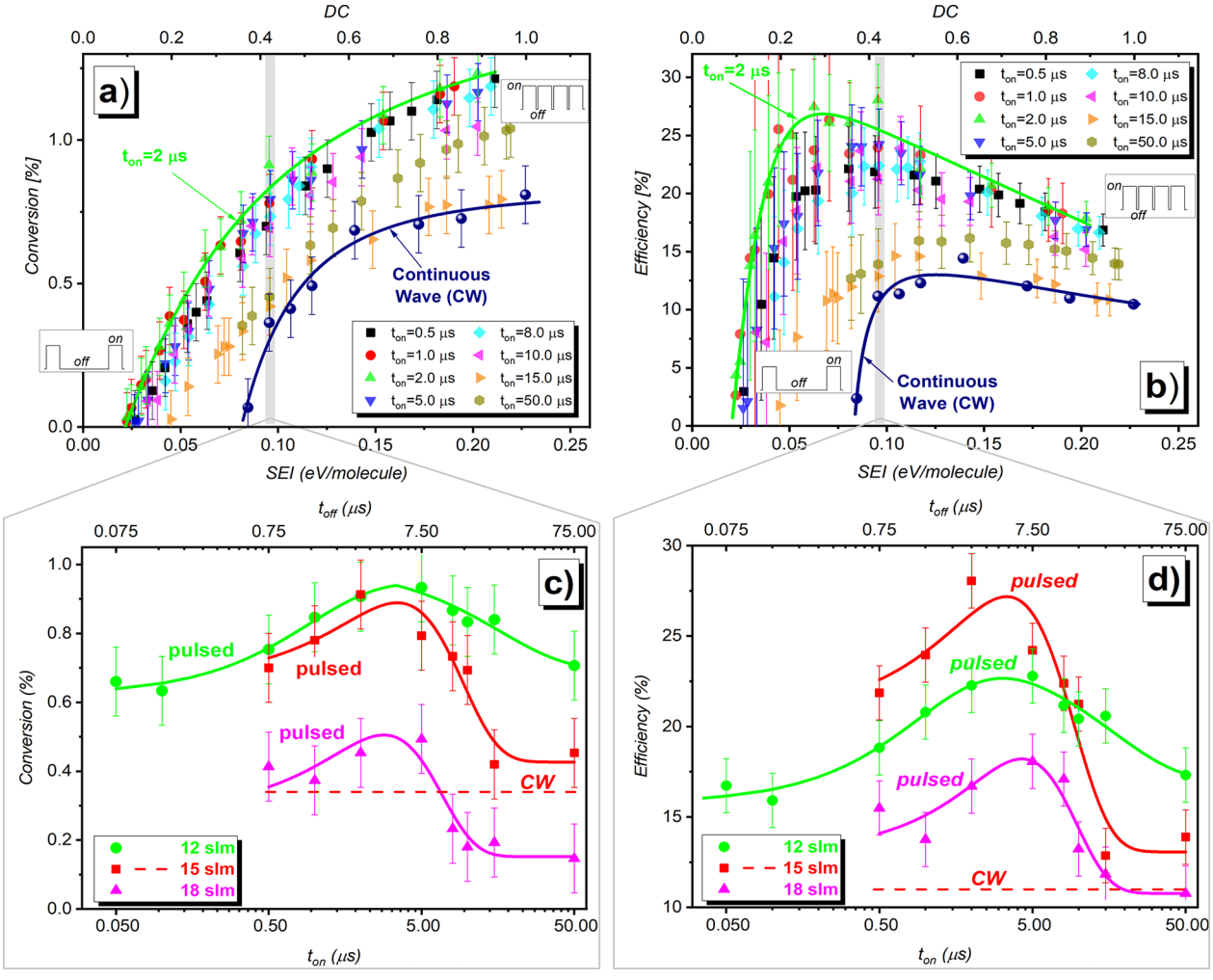


Figure 1. CO_2 atmospheric plasma sustained with continuous (CW) and pulsed microwave with different pulse t_{on} and interpulse t_{off} times. (a) and (b) show conversion and efficiency versus specific energy input (SEI) and duty cycle (DC) at 15 slm gas inflow. Guides for the eye for CW and t_{on} = 2 μs are shown with dark blue and green thick solid lines, respectively. The gray rectangles in (a) and (b) highlight the data plotted in (c) and (d). Small insets show schematically the pulse form for the lowest and highest SEI. (c) and (d) show the conversion and efficiency for three inflows and $P_{abs} \approx 94$ W (DC $\approx$ 0.4) as a function of t_{on} and t_{off}. The solid lines are guides for the eye and the dashed lines correspond to CW data at 15 slm.

to consider in the use of renewable energy is efficiency. Microwave sustained plasmas have been defined as the most promising ones with record efficiencies for CO_2 splitting (reactions R1 and R2) up to 90%, albeit the experimental details were not fully given.[13−16]

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \quad \text{(R1)}$$

$$CO_2 + O \rightarrow CO + O_2 \quad \text{(R2)}$$

The ruling hypothesis behind highly efficient CO_2 splitting in microwave plasmas is the preferential vibrational excitation

of the CO_2 molecule, which leads to its dissociation.[17] This route requires a high vibrational−translational (VT) non equilibrium, which is achieved when low pressures, low gas temperature, and high power densities plasmas are produced.[18] At pressures of typically 100 mbar and above, thermal dissociation has been recently demonstrated as the predom inant mechanism for CO_2 dissociation in microwave plasmas.[19−21] On the basis of these findings, precise power deposition and temperature control are necessary in the plasma and afterglow to achieve efficient CO_2 conversion. Yet, in order to achieve high efficiencies, most of the experimental and modeling reports deal with the use of a vacuum, which allows researchers to reach easily nonequilibrium.[22−29] Low pressure operation is, however, undesirable for future large scale deployable technology for CO_2 conversion because of high device volume requirements and energy costs to enable high throughput.

Looking to extend the potential benefits of microwave plasma activation to the atmospheric pressure realm, ultrafast pulsation of the microwave field as a means to manage the efficiency of CO_2 splitting is proposed in this Letter (Scheme 1). Indeed, power pulsation has the potential to create VT nonequilibrium states during suitable on times[27,31−34] and decrease energy deposited in the plasma and therefore improve the efficiency by selecting suitable off times.[20,27,30−35]

Here, we report the first known time resolved experimental observation of VT nonequilibrium in atmospheric CO_2 microwave plasmas. We follow the vibrational and rotational temperature evolution of the plasma species with nanosecond time resolution Optical Emission Spectroscopy (OES). The plasma size and shape are investigated with a short gated ICCD camera. To analyze the effect of pulsations on the reaction, we followed the composition and efficiency changes as a function of energy supplied per single CO_2 molecule (specific energy input) with in line gas analytics. The specific energy input (SEI) reads as

$$\mathrm{SEI} = \frac{P_{\mathrm{abs}} \cdot V_{\mathrm{m}}}{\nu_{\mathrm{inp}} \cdot N_{\mathrm{A}}}$$

where ν_{inp} is the CO_2 gas flow, P_{abs} is the mean microwave power absorbed in the system and is proportional to the duty cycle, DC = $t_{\mathrm{on}}/(t_{\mathrm{on}} + t_{\mathrm{off}})$ (see the Supporting Information), V_{m} is the molar gas volume set to 24.47 L/mol, and N_{A} is the Avogadro constant. Thus, SEI depends on both t_{on} and t_{off} times, which were systematically varied throughout the experiment. In addition, the efficiency is expressed as follows:

$$\eta = \frac{\chi \cdot \Delta H_{\mathrm{R}}^{0}}{\mathrm{SEI}}$$

where $\Delta H_{\mathrm{R}}^{0}$ is the reaction enthalpy, which is 2.93 eV/molecule for reaction R1, and χ is the molar degree of CO_2 conversion into CO.

The experiments are performed in a custom setup that comprises a compact coaxial plasma torch and an advanced solid state microwave generator that enables independent control of pulse time (t_{on}) and interpulse time (t_{off}) in the range 50 ns to 200 μs, as well as the frequency within the range 2.4−2.5 GHz (additional details in the Supporting Informa tion). Throughout the experiment in the pulsed regime, the peak power and microwave frequency were kept at 220 W and 2.45 GHz, respectively. In the CW regime, the power was scanned from 220 W down to 80 W (the minimum power at which the plasma can be sustained). Panels a and b of Figure 1 show the CO_2 conversion and efficiency as a function of SEI for different pulse duration, varied between 0.5 and 50 μs. Plots c and d show the results at fixed SEI (i.e., fixed DC) with variation of pulse widths down to 50 ns for different gas flows.

Power pulsation promotes conversions and efficiencies better than those found in the continuous microwave mode. At SEI $\approx$ 0.1 eV/molecule, the conversion with pulsation almost doubles the one measured in the continuous wave (CW) mode. The conversion initially increases gradually with the energy provided to the molecules, but after a certain SEI level, it starts to saturate. This stabilization of the conversion with SEI can be explained by the influence of the recombination mechanisms during dissociation, which in creases with SEI and is promoted by the atmospheric pressure of our system.[17,18] Yet, the observed saturation effect is much less pronounced in the pulsed mode compared to that in the CW mode. Interestingly, the efficiency behaves as expected if either vibrational activation or (thermal) quenching was present. We can see that energy efficiency peaks at a maximum of $\eta \approx 27\%$ obtained for a SEI = 0.077 $\pm$ 0.014 eV/molecule and 0.25 < DC < 0.4. This concave behavior has been described by some works as characteristic of reactions under vibrational activation.[36] Efficiency maxima have also been reported when experiments include fast quenching to control the evolution of thermal dissociation.[16,23]

Two important observations have to be underlined. First, in the pulsed mode it is possible to sustain the plasma at lower SEI compared to the CW mode; i.e., the operation window increases (CW plasma dies away at SEI < 0.075 eV/molecule). Second, at very short energy interruptions compared to the pulse length, when $t_{\mathrm{off}} \ll t_{\mathrm{on}}$ (see Figure 1a,b at maximum SEI), the pulsations still promote the CO_2 conversion, though, energetically, such a plasma (DC $\approx$ 0.95) is almost equivalent to the CW (DC = 1) plasma. This can be related to the changes in power coupling due to variation in residual electron densities left over from the previous pulse[33] that leads to a reduction of electron temperatures down to a range where vibrationally driven dissociation is more efficient.[17]

The optimal pulse parameters were found for three different gas flows by varying the t_{on} and t_{off} times at fixed DC $\approx$ 0.4 (Figure 1c,d). The maximum conversion and efficiency are found for pulse and interpulse lengths in the ranges 2.0−5.0 μs and 3.0−7.5 μs, respectively. The independence of this optimum on the gas flow is due to the much longer time scales of gas flow dynamics as compared to the power pulsations. The found optimum can be explained by a trade off between optimal gas cooling (quenching), which deteriorates toward shorter t_{off} times, and optimal gas treatment, which, at too long t_{off} times, tends to be less efficient because the gas residence time in the reactor becomes comparable with t_{off} (see the Supporting Information). Additionally, too much drop in electron density would result in a harder ignition.

Yet, the question remains: which phenomena are actually controlling the presently reported behavior of CO_2 dissociation in atmospheric pressure plasma? To answer this question, we looked along the pulse at the nanosecond scale using both ultrafast imaging and OES (see the Supporting Information for details). As the efficiency peaked in pulse durations between 2 and 3 μs and duty cycles between 0.25 and 0.40, a pulse duration of 2.5 μs and interpulse time of 7.5 μs (DC = 0.25) were chosen for this investigation.

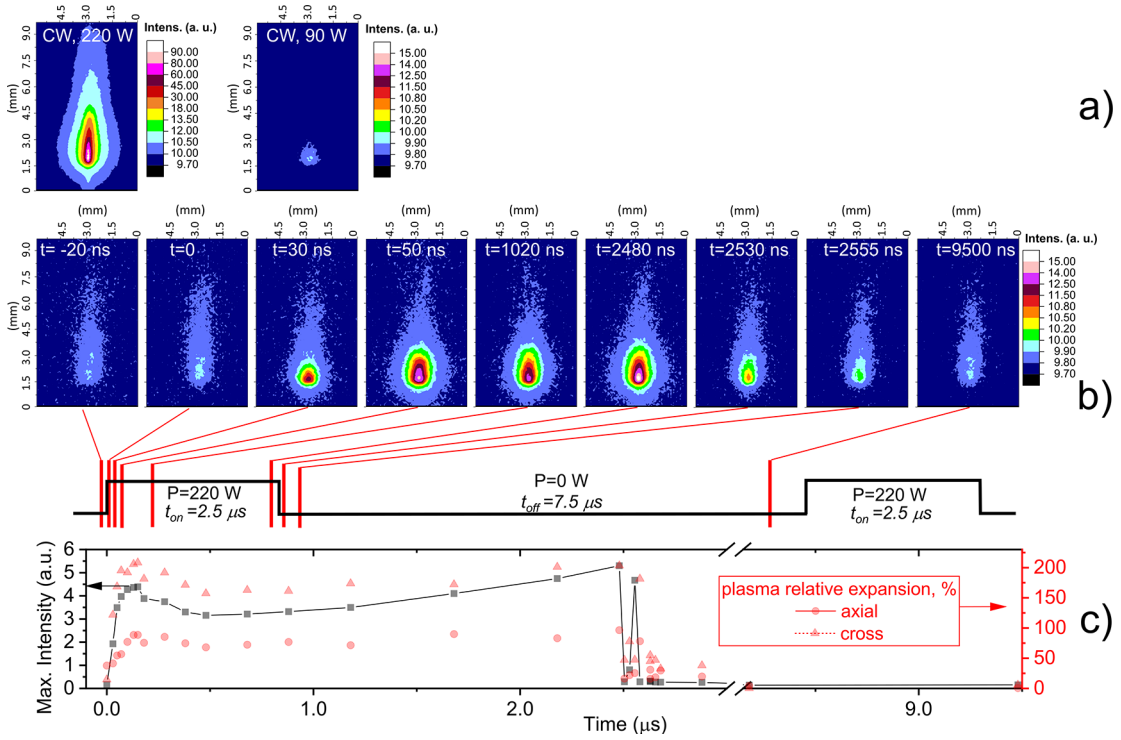


Figure 2. Fast imaging of CO_2 plasma performed with an iCCD camera gated with 25 ns. (a) Reference data for continuous wave (CW) plasma with 220 and 90 W (lowest stable CW plasma) of input microwave power. (b) Selected plasma images whose acquisition times are schematically related to the microwave pulse timing. (c) Maximum light intensity above background is given in black (left axis). Plasma expansion in axial and cross direction taken at fixed intensity level relative to minimal size of plasma (t = 9.5 μs). Parameters: P_{peak} = 220 W, t_{on} = 2.5 μs, t_{off} = 7.5 μs, DC = 0.25, and gas flow rate of 12 slm.

Interestingly, the volume of plasma sustained with a mean power of 55 W (=P_{peak}·DC) is much larger than the one in CW mode at 90 W (Figure 2a,b). Thus, a much larger volume of CO_2 is treated in the pulsed mode, which explains the increase of CO yield as observed in Figure 1a. Before the pulse, a weak light remaining from the previous pulse due to recombination processes in the plasma afterglow is registered. After switching on the power, both plasma intensity and plasma axial and cross dimensions increase rapidly and by 130 ns attain the local maximum (see Figure 2c). Given that the expansion in the axial direction is additionally contributed by axial flow, which is constant in both on and off phases, the expansion in cross section better characterizes the modulated microwave power. For the same reason, the relative expansion in cross section is much larger than the expansion in the axial direction. After 150 ns, both the emission pattern and the intensity decrease gradually and stabilize after about 1 μs. Once the power has been switched off, the light intensity and the dimensions of the emitting pattern fall abruptly by factors of 20 and 5, respectively. Interestingly, this fall is followed (after about 60 ns) by a short intense flash of light, which can be explained by an ion recombination event.[35] Within the off phase, the afterglow intensity and its size remain negligible until the following pulse.

To characterize the state of VT nonequilibrium, the acquired emission spectra are used to obtain the vibrational (T_{vib}) and rotational (T_{rot}) temperatures by fitting of the molecular bands of CO and C_2 species with synthetic spectra using MassiveOES[37,38] (see the Supporting Information). Figure 3a shows the evolution of the OES spectra together with T_{vib} and T_{rot} along the 2.5 μs pulse. In the following analysis, rotational and gas temperatures are assumed equivalent ($T_{rot} \approx T_g$) due to subnanosecond rotational−translational relaxation at atmospheric pressure.[39] For the first time in atmospheric microwave plasma, two distinct regimes were observed along the energy pulses for the selected conditions: a nonequilibrium regime existing at the beginning of the pulse and a thermal equilibrium regime when the pulse surpasses approximately 1.6 μs of duration. This observation implies that longer pulses would not then maintain nonequilibrium. VT nonequilibrium is observed at the onset of the power pulsing with $T_{vib}/T_{rot} \approx 2$ (see also Figure S7). After 75 ns, the vibrational temperature determined from the first two vibrational states of the CO ($B^1\Sigma^+$) is already 6900 K and then stays relatively constant along the pulse (7000 K < T_{vib} < 8000 K). This prompt vibrational activation can be attributed to an efficient CO vibrational excitation by electron collisions.[30] Simultaneously, rotational (or gas) temperature starts at $T_{rot} \approx$ 3500 K and stays constant until around 1 μs. After this time, the gas temperature increases and after the pulse surpasses around 1.6 μs the plasma reaches VT equilibrium. This correlates with the increase in light intensity after ≈1 μs observed in Figure 2c. After the pulse, the rotational and vibrational temperatures start cooling down and 0.8 μs later attain ≈5700 K, which corresponds to a thermal quenching of ≈2×10^9 K/s, which is in the optimal range to preserve the reaction species.[10] However, at later postdischarge times, this high cooling rate deteriorates; thus, the gas cools down to temperatures not less than or equal to 3500 K as observed at the beginning of the next pulse. Further temperature monitoring was not feasible given the drop of plasma emission below the detection limit for after pulse times longer than 0.6 μs.

As mentioned earlier, efficient use of renewable energy is decisive for Power to X technologies such as plasma assisted

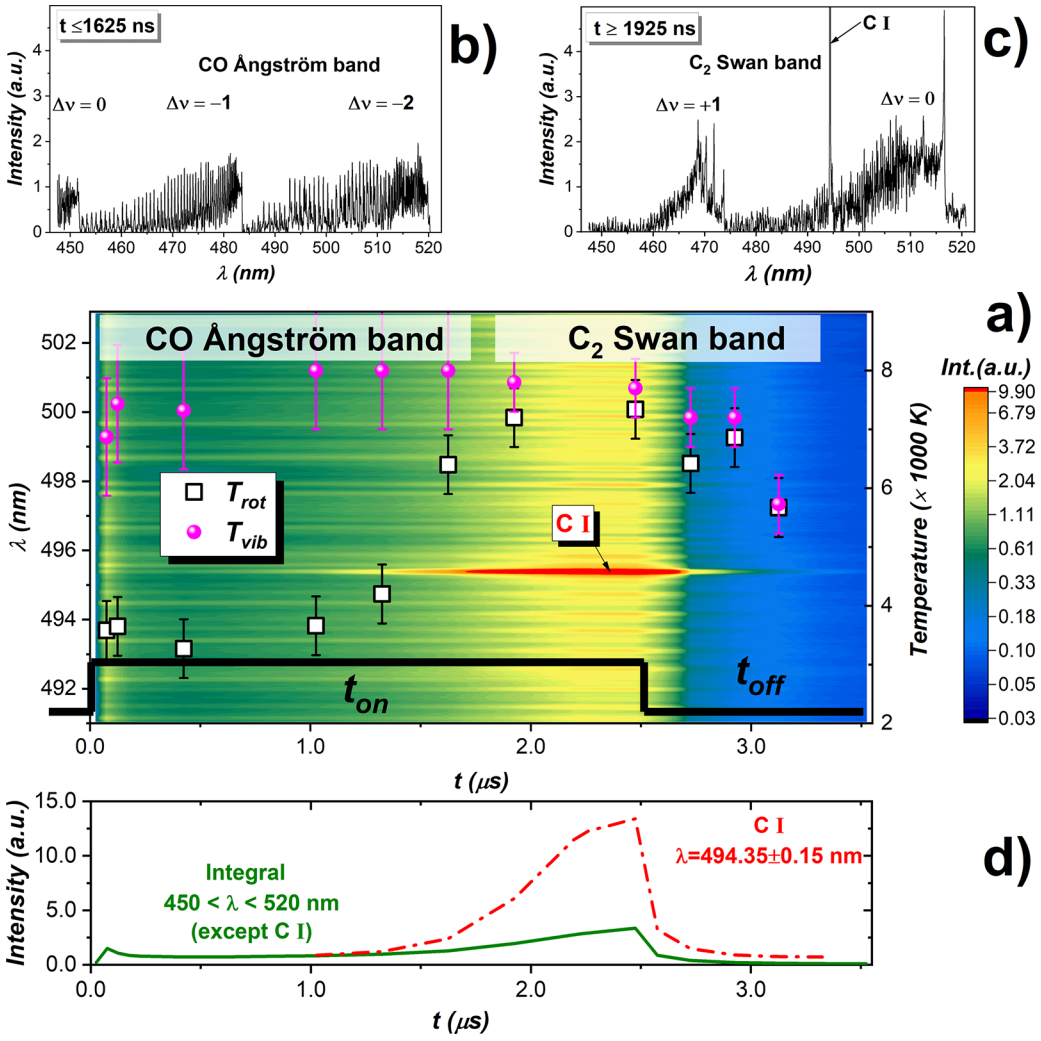


Figure 3. Dynamics of microwave CO_2 plasma emission and related rotational (T_{rot}) and vibrational (T_{vib}) temperatures (a) in pulsed regime with t_{on} = 2.5 μs, t_{off} = 7.5 μs and a gas flow rate of 12 slm. (b) and (c) show the typical emission spectra dominated by CO Ångström bands and by C_2 Swan bands before and after thermalization, respectively. The thick solid line in (a) indicates the microwave pulse. The evolution of integral emission within the 450−520 nm spectral range and the intensity of a carbon atomic line are plotted in (d) on the same time scale.

CO_2 conversion. The temperature evolution suggests (when applying the Kirchhoff's law for enthalpy correction) that the efficiency is overestimated by the use of standard reaction enthalpies.[40] In the future, a more accurate approach should take into account this fact for warm plasmas. But, which regime favors an efficient CO_2 splitting into CO in the present experiments at atmospheric pressure? Thermal equilibrium or nonequilibrium? To determine which temperature range suits best for CO production at the high gas temperatures observed, thermodynamic calculations with the National Aeronautics and Space Administration (NASA) computer program Chemical Equilibrium with Applications (CEA)[41] were performed (Figure S8). The model shows that CO concentration is highest within the 3000−6000 K range. This agrees with the CO band dominated spectra observed in this temperature interval (Figure 3b) before equilibration (75−1625 ns). Such band indicates electron impact dissociation and excitation processes of CO_2 and CO. However, after thermal equilibration within 1625−3325 ns, the CO band dominated emission is fully replaced by C_2 Swan band emission (Figure 3c) thus evidencing a change in chemistry. The transition from CO to C_2 dominating spectra was also reported recently for experiments with CW microwave plasmas where pressure was scanned from low to moderate vacuum by D'Isa et al.[19] They observed that once the VT equilibrium is reached with temperatures $T_{vib} \approx T_g \approx 6000$ K, the energy from the plasma is spent on thermal dissociation of CO into C and O.[42] In the present experiments, thermal dissociation of CO is also evident not only from the C_2 emission spectrum but also from a pronounced C emission peak around 494.3 nm (second order spectrum of the C (2p ^{1}S→ 3s ^{1}P) atomic transition) whose amplitude in pulse (Figure 3d) correlates nicely with the thermodynamic calculations (see Figure S8). Such observations are related to an excessive power density deposited in the plasmas. Thus, remaining inside the nonequilibrium regime with a gas temperature that thermodynamically favors CO production increases the energy efficiency of the process. Therefore, even at the low SEI and consequently low conversion obtained here, the ultrafast pulsation of microwave plasmas is a very promising tool to promote the conversion and efficiency of CO_2 splitting into CO in atmospheric

pressure systems owing to its ability to control energy deposition modes and gas heating.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c01983.

Apparatus, nanosecond time resolved optical emission spectroscopy (OES), fast imaging of plasma discharge, measurement of absorbed microwave power, measure ment of partial gas concentrations, experiment arrange ment, table of t_{on} settings, conversion and efficiency of CO_2 splitting, effect of finite residence time, dynamics of vibrational nonequilibrium on the pulse time scale, T_{vib}/T_{rot} vs time, thermal calculations of plasma species composition (PDF)

AUTHOR INFORMATION

Corresponding Author

Alexander Navarrete − *Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany;* orcid.org/0000 0002 4354 2227; Phone: +49 721 608 2665; Email: alexander.navarrete@kit.edu

Authors

Sergey Soldatov − *Institute for Pulsed Power and Microwave Technology (IHM), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany*

Guido Link − *Institute for Pulsed Power and Microwave Technology (IHM), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany*

Lucas Silberer − *Institute for Pulsed Power and Microwave Technology (IHM), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany*

Clara Marie Schmedt − *Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany*

Emile Carbone − *Max Planck Institute for Plasma Physics, D 85748 Garching, Germany*

Federico D'Isa − *Max Planck Institute for Plasma Physics, D 85748 Garching, Germany*

John Jelonnek − *Institute for Pulsed Power and Microwave Technology (IHM) and Institute of Microwaves and Electronics (IHE)., Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany*

Roland Dittmeyer − *Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein Leopoldshafen, Germany;* orcid.org/0000 0002 3110 6989

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

HBH Microwave GmbH is kindly acknowledged for supplying the microwave source. This research was partly funded by the Federal Ministry for Economic Affairs and Energy of Germany in the project ZF4204602PR6. Annette Hürter is kindly acknowledged for her support to this work with the graphic design.

REFERENCES

(1) Jin, S. COVID 19, Climate Change, and Renewable Energy Research: We Are All in This Together, and the Time to Act Is Now. *Acs Energy Lett.* **2020**, *5*, 1709.

(2) IPCC *Global Warming of 1.5 °C*. An IPCC Special Report on the impacts of global warming of 1.5 °C above preindustrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty, 2018.

(3) IEA. *More of a good thing − is surplus renewable electricity an opportunity for early decarbonisation?*; International Energy Agency, 2019; Vol. *2020*.

(4) Breyer, C.; Fasihi, M.; Bajamundi, C.; Creutzig, F. Direct Air Capture of CO_2: A Key Technology for Ambitious Climate Change Mitigation. *Joule* **2019**, *3*, 2053.

(5) Jarvis, S. M.; Samsatli, S. Technologies and infrastructures underpinning future CO_2 value chains: A comprehensive review and comparative analysis. *Renewable Sustainable Energy Rev.* **2018**, *85*, 46.

(6) Smith, W. A.; Burdyny, T.; Vermaas, D. A.; Geerlings, H. Pathways to Industrial Scale Fuel Out of Thin Air from CO_2 Electrolysis. *Joule* **2019**, *3*, 1822.

(7) Jouny, M.; Luc, W.; Jiao, F. General Techno Economic Analysis of CO_2 Electrolysis Systems. *Ind. Eng. Chem. Res.* **2018**, *57*, 2165.

(8) Martens, J. A.; Bogaerts, A.; De Kimpe, N.; Jacobs, P. A.; Marin, G. B.; Rabaey, K.; Saeys, M.; Verhelst, S. The Chemical Route to a Carbon Dioxide Neutral World. *ChemSusChem* **2017**, *10*, 1039.

(9) Bogaerts, A.; Neyts, E. C. Plasma Technology: An Emerging Technology for Energy Storage. *Acs Energy Lett.* **2018**, *3*, 1013.

(10) Bongers, W.; Bouwmeester, H.; Wolf, B.; Peeters, F.; Welzel, S.; van den Bekerom, D.; den Harder, N.; Goede, A.; Graswinckel, M.; Groen, P. W.; Kopecki, J.; Leins, M.; van Rooij, G.; Schulz, A.; Walker, M.; van de Sanden, R. Plasma driven dissociation of CO_2 for fuel synthesis. *Plasma Processes Polym.* **2017**, *14*, 1600126.

(11) Navarrete, A.; Centi, G.; Bogaerts, A.; Martin, A.; York, A.; Stefanidis, G. D. Harvesting Renewable Energy for Carbon Dioxide Catalysis. *Energy Technol Ger* **2017**, *5*, 796.

(12) Snoeckx, R.; Bogaerts, A. Plasma technology a novel solution for CO_2 conversion? *Chem. Soc. Rev.* **2017**, *46*, 5805.

(13) Rusanov, V. D.; Fridman, A. A.; Sholin, G. V. CO_2 dissociation in a nonequilibrium plasma. *Sov. Phys. Tech. Phys. (Engl. Transl.)* **1979**, *24*, 1195.

(14) Butylkin, Y. P. Z.; Krasheninnikov, E. G.; Krotov, M. F.; Rusanov, V. D.; Tarasov, Y. V.; Fridman, A. A. Dissociation of CO_2 by a plasma chemical process in a nonequilibrium microwave discharge. *Sov. Phys. Tech. Phys.* **1981**, *26*.

(15) Asisov, R.; Givotov, V.; Krasheninnikov, E.; Potapkin, B.; Rusanov, V.; Fridman, A. Carbon Dioxide Dissociation in Non Equilibrium Plasma. In *Proc. 5th Int. Symp. Plasma Chemistry* **1981**; Vol. *2*.

(16) Legasov, V. A.; Zhivotov, V. K.; Krasheninnikov, E. G.; Kroto, M. F.; Patrushev, B. I.; Rusanov, V. D.; Rykunov, G. V.; Spektor, A. M.; Fridman, A. A.; Shoiin, G. V. A nonequilibrium plasma chemical process of CO_2 dissociation in high frequency and ultrahigh frequency discharges. *Sov. Phys. Dokl.* **1978**, *23*, 44.

(17) Fridman, A. *Plasma chemistry*; Cambridge University Press, 2008.

(18) Berthelot, A.; Bogaerts, A. Modeling of CO_2 Splitting in a Microwave Plasma: How to Improve the Conversion and Energy Efficiency. *J. Phys. Chem. C* **2017**, *121*, 8236.

(19) D'Isa, F.; Carbone, E.; Hecimovic, A.; Fantz, U. Performance analysis of a 2.45 GHz microwave plasma torch for CO_2 decomposition in gas swirl configuration. *Plasma Sources Sci. Technol.* **2020**, *29*, 105009.

(20) van den Bekerom, D. C. M.; Linares, J. M. P.; Verreycken, T.; van Veldhuizen, E. M.; Nijdam, S.; Berden, G.; Bongers, W. A.; van de Sanden, M. C. M.; van Rooij, G. J. The importance of thermal

dissociation in CO_2 microwave discharges investigated by power pulsing and rotational Raman scattering. *Plasma Sources Sci. Technol.* **2019**, *28*, 055015.
(21) Wolf, A J; Righart, T W H; Peeters, F J J; Bongers, W A; van de Sanden, M C M Implications of thermo chemical instability on the contracted modes in CO_2 microwave plasmas. *Plasma Sources Sci. Technol.* **2020**, *29*, 025005.
(22) van Rooij, G. J.; van den Bekerom, D. C. M.; den Harder, N.; Minea, T.; Berden, G.; Bongers, W. A.; Engeln, R.; Graswinckel, M. F.; Zoethout, E.; van de Sanden, M. C. M. Taming microwave plasma to beat thermodynamics in CO_2 dissociation. *Faraday Discuss.* **2015**, *183*, 233.
(23) den Harder, N.; van den Bekerom, D. C. M.; Al, R. S.; Graswinckel, M. F.; Palomares, J. M.; Peeters, F. J. J.; Ponduri, S.; Minea, T.; Bongers, W. A.; van de Sanden, M. C. M.; van Rooij, G. J. Homogeneous CO_2 conversion by microwave plasma: Wave propagation and diagnostics. *Plasma Processes Polym.* **2017**, *14*, 1600120.
(24) Kotov, V.; Koelman, P. M. J. Plug flow reactor model of the plasma chemical conversion of CO_2. *Plasma Sources Sci. Technol.* **2019**, *28*, 095002.
(25) Pietanza, L. D.; Colonna, G.; Capitelli, M. Kinetics versus thermodynamics on CO_2 dissociation in high temperature microwave discharges. *Plasma Sources Sci. Technol.* **2020**, *29*, 035022.
(26) Pietanza, L. D.; Colonna, G.; D'Ammando, G.; Laricchiuta, A.; Capitelli, M. Vibrational excitation and dissociation mechanisms of CO_2 under non equilibrium discharge and post discharge conditions. *Plasma Sources Sci. Technol.* **2015**, *24*, 042002.
(27) Kozák, T.; Bogaerts, A. Splitting of CO_2 by vibrational excitation in non equilibrium plasmas: a reaction kinetics model. *Plasma Sources Sci. Technol.* **2014**, *23*, 045004.
(28) Silva, T.; Britun, N.; Godfroid, T.; Snyders, R. Understanding CO_2 decomposition in microwave plasma by means of optical diagnostics. *Plasma Processes Polym.* **2017**, *14*, 1600103.
(29) Silva, T.; Grofulović, M.; Klarenaar, B. L. M.; Morillo Candas, A. S.; Guaitella, O.; Engeln, R.; Pintassilgo, C. D.; Guerra, V. Kinetic study of low temperature CO_2 plasmas under non equilibrium conditions. I. Relaxation of vibrational energy. *Plasma Sources Sci. Technol.* **2018**, *27*, 015019.
(30) Vermeiren, V.; Bogaerts, A. Improving the Energy Efficiency of CO_2 Conversion in Nonequilibrium Plasmas through Pulsing. *J. Phys. Chem. C* **2019**, *123*, 17650.
(31) Britun, N.; Silva, T.; Chen, G.; Godfroid, T.; van der Mullen, J.; Snyders, R. Plasma assisted CO_2 conversion: optimizing performance via microwave power modulation. *J. Phys. D: Appl. Phys.* **2018**, *51*, 144002.
(32) Van Alphen, S.; Vermeiren, V.; Butterworth, T.; van den Bekerom, D. C. M.; van Rooij, G. J.; Bogaerts, A. Power Pulsing To Maximize Vibrational Excitation Efficiency in N_2 Microwave Plasma: A Combined Experimental and Computational Study. *J. Phys. Chem. C* **2020**, *124*, 1765.
(33) Carbone, E.; Nijdam, S. Ultra fast pulsed microwave plasma breakdown: evidence of various ignition modes. *Plasma Sources Sci. Technol.* **2014**, *23*, 012001.
(34) Kabouzi, Y.; Moisan, M. Pulsed microwave discharges sustained at atmospheric pressure: study of the contraction and filamentation phenomena. *IEEE Trans. Plasma Sci.* **2005**, *33*, 292.
(35) Carbone, E.; Sadeghi, N.; Vos, E.; Hübner, S.; van Veldhuizen, E.; van Dijk, J.; Nijdam, S.; Kroesen, G. Spatio temporal dynamics of a pulsed microwave argon plasma: ignition and afterglow. *Plasma Sources Sci. Technol.* **2015**, *24*, 015015.
(36) Givotov, V. K.; Fridman, A. A.; Krotov, M. F.; Krasheninnikov, E. G.; Patrushev, B. I.; Rusanov, V. D.; Sholin, G. V. Plasmochemical methods of hydrogen production. *Int. J. Hydrogen Energy* **1981**, *6*, 441.
(37) Voráč, J.; Synek, P.; Potočňáková, L.; Hnilica, J.; Kudrle, V. Batch processing of overlapping molecular spectra as a tool for spatio temporal diagnostics of power modulated microwave plasma jet. *Plasma Sources Sci. Technol.* **2017**, *26*, 025010.
(38) Voráč, J.; Synek, P.; Procházka, V.; Hoder, T. State by state emission spectra fitting for non equilibrium plasmas: OH spectra of surface barrier discharge at argon/water interface. *J. Phys. D: Appl. Phys.* **2017**, *50*, 294002.
(39) Bruggeman, P. J.; Iza, F.; Brandenburg, R. Foundations of atmospheric pressure non equilibrium plasmas. *Plasma Sources Sci. Technol.* **2017**, *26*, 123002.
(40) Atkins, P. W.; De Paula, J. *Elements of physical chemistry*, 6th ed.; Oxford University Press: Oxford, 2013.
(41) NASA Glenn Research Centre. *Chemical Equilibrium with Applications*. https://grc.nasa.gov/WWW/CEAWeb/.
(42) Carbone, E.; D'Isa, F.; Hecimovic, A.; Fantz, U. Analysis of the C_2 ($d^3\Pi_g$ $a^3\Pi_u$) Swan bands as a thermometric probe in CO_2 microwave plasmas. *Plasma Sources Sci. Technol.* **2020**, *29*, 055003.