From non-equilibrium to thermal plasma opportunities

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Abstract: The energy transition justifies research into plasma gas conversion. Plasma offers compatibility with (intermittent) sustainable energy and unique opportunities for efficiency and/or selectivity in reactions with CO_2, N_2, and CH_4. Vibrational excitation effects have been generally embraced as key to success. This work invokes vibrational laser excitation to determine its limits. *In situ* plasma temperature and species measurements confirm a thermal regime instead. The results are extrapolated to opportunities for industrial application.

Keywords: CO_2 utilization, CH_4 coupling, N_2 fixation, Process Electrification

1. Introduction

A truly carbon neutral and circular economy means that no new fossil resources such as naphtha or natural gas are added to the carbon cycle. Instead, waste materials and biomass are used as feedstock for the production of new materials. Moreover, the energy input must be of zero carbon footprint, which currently implies that it concerns electric energy input that is intermittently available.

Plasma technology carries the following distinct advantages and/or promises that make it suitable to make an impact in the transition to such a circular economy [1]:

- Low inertia, meaning that the process can rapidly be switched on or off, which makes it perfect for coupling with intermittent renewable power sources.
- High power density, meaning that the system size is small, generally transferring in low CAPEX and hence opportunities to depart from 24-7 productivity and to economically allow intermittent operation.
- No scarce materials, implying scalability to a level that is relevant to the scale of the CO_2 emissions.
- High energy efficiency, a claim that originates from early work on CO_2 [2]. As the early records have not been confirmed in recent work, their absolute values are no longer relied upon. Nevertheless, plasma technology still offers competitiveness to other CO_2 utilization technologies [2], and distinct opportunities for N_2 [3] and CH_4 chemistry [4].

Those early records of 80-90% energy efficiency for CO_2 dissociation were explained as a consequence of the initial energy transfer of the free plasma electrons to vibrational modes of the CO_2 molecule (see Fig. 1) [5]. In this view, collisional energy exchange dominates over vibration-translation energy transfer and is effective to carry CO_2 molecules over the vibrational ladder up to the dissociation limit. The potential energy carried by the oxygen radical is supposed to be harvested back in a reaction with another CO_2 molecule to realize the overall record efficiency of ~3.5 eV which is lower than the dissociation energy of 5.5 eV.

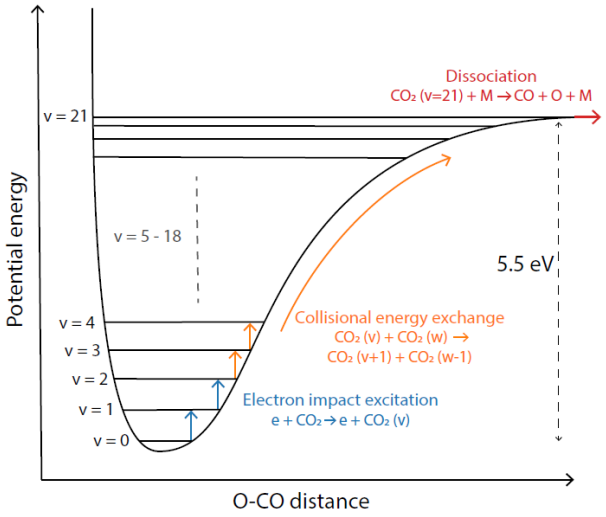

Fig. 1. Schematic of vibrational ladder climbing due to plasma excitation of the lowest levels that is followed by collisional energy exchange carrying molecules up to the dissociation limit (reproduced from [5]).

However, our earlier work in pulsed microwave plasma has shown that the prerequisite for vibrational ladder climbing, i.e. a thermal non-equilibrium in which vibrational levels are strongly over-populated and translational heating remains low, is only met at the ~0.1 ms timescale after which thermalization sets in [6]. Instead, thermal dissociation is observed to dominate under our conditions that are most relevant in view of performance, i.e. for energy efficiencies approaching 50% [7,8].

In this contribution, we will build upon these works to address the existence of the vibrational ladder climbing mechanism in a well-defined laser excitation experiment. Modelling of these experiments shows the fundamental limitations of the vibrational non-equilibrium lifetime. Subsequently, the earlier pulsed microwave plasma excitation experiments are revisited to show that the actual non-equilibrium can be increased, but its lifetime not. Maps of species and temperature distributions throughout the reactor from *in situ* Raman scattering are used to infer the importance of heat and mass transfer and the

opportunities for their control in view of reactor performance.

2. Ladder Climbing unraveled

To study the potential CO_2 dissociation by mode-selective collisional energy exchanges, we measure CO production upon selective excitation of CO_2 (99.995% purity) to the first vibrational level of v3, as schematically shown in Fig. 2.

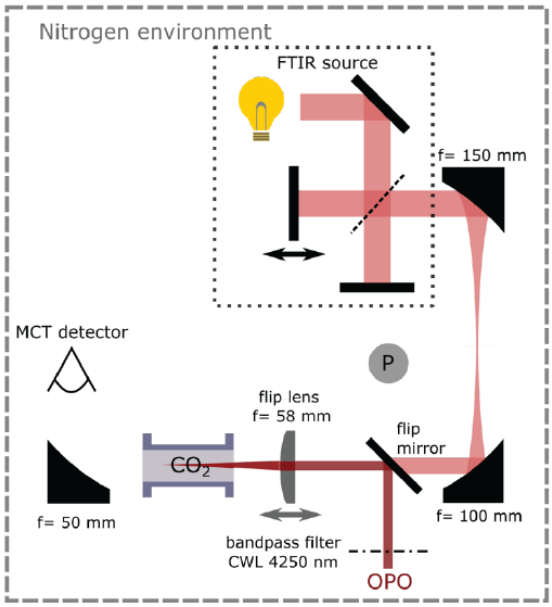

Fig. 2. Experimental configuration of the mid-infrared laser excitation experiments in which the output of a ns pulsed YAG-pumped OPO is focused into a gas cell filled with pure CO_2. FTIR is employed for quantification of dissociation products after 5-20 min laser irradiation.

Indeed, CO formation was observed upon exclusively exciting the asymmetric stretch vibration from its ground state to the first excited level. Fig. 3 shows the experimentally determined values of energy efficiency η in parametric scans of laser fluence as well as simulations of the experiment. The simulations will be discussed in detail to explain the observed experimental trends as well as to infer the fundamental limits to the mechanism.

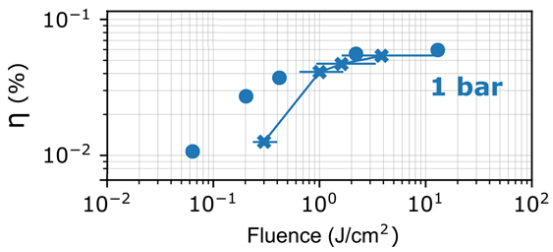

Fig. 3. Measured (crosses) and modelled (circles) energy efficiency of CO_2 dissociation η upon mid-IR pulsed laser irradiation versus photon fluence at 1 bar pressure of pure CO_2.

3. Vibrational excitation dynamics in pulsed microwave plasma

Pulsing of the microwave power gives the opportunity to observe population (and relaxation) of the vibrational levels over time with synchronized vibrational Raman spectroscopy. In addition, having each new pulse ignite in a replenished gas volume allows to start the experiment from effectively room temperature. This approach was the basis of our earlier work [6]. However, the Raman measurements require data collection over many ignitions. It appears that these ignitions are not perfect repetitions and a strong stochastic nature is observed instead. Fig. 4 shows the light emission of the plasma filament 40 µs after ignition for an arbitrary set of 4 ignitions which emphasizes this stochastic nature.

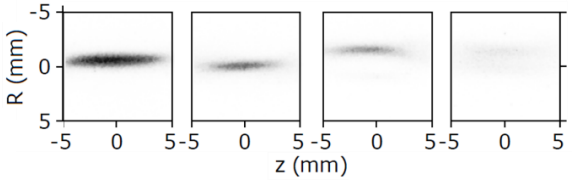

Fig. 4. Four plasma emission images taken 40 µs after ignition, emphasizing the stochastic nature in position and intensity.

It is evident that averaging over such a set of ignitions will yield some sort of non-representing lower average temperature due to cold background gas contributing to the measurements. In fact, the averaging is strongly non-linear, making the effect stronger. In our new measurements, we analyzed single shot Raman data so that we only included plasma data in the analysis. We found a much stronger non-equilibrium after 60 µs than before: ~3000 K in vibrations compared to ~1000 K gas temperature, while before the system was observed to thermalize at that timescale to ~1000 K. In terms of energy efficiency of conversion, of course no difference was found. As the gas temperature is too low for thermal dissociation and the vibrational temperature too low for significant ladder climbing, all observed dissociation is due to dissociative electron excitation.

4. Discharge contraction versus temperature control

As pressure is increased in microwave discharges, the plasma is generally observed to confine to smaller volumes. This effect is generally described as a temperature instability induced contraction [9]. However, we compared, forward and reverse vortex configuration CO_2 discharges in which we kept remaining operational parameters equal. Fig. 5 shows the gas temperature profile measured with Raman scattering as well as the plasma spontaneous emission. We explain the difference in gas temperature as a result of a difference in central flow speed and hence different heat transfer [10]. The emission is not scaling with temperature according to the temperature instability explanation. The higher gas temperature causes

plasma broadening instead. We interpret the effect due to ambipolar diffusion that is balanced with recombination in the plasma edge. In such a picture, pressure reduces and temperature increases diffusion rates.

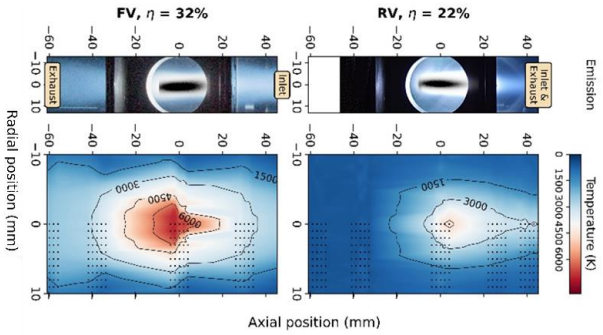

Fig. 5. Comparison of gas temperature and plasma emission in Forward Vortex flow (left) and Reverse Vortex flow (right).

5. Extrapolation to industrial applications

In the presentation, we will highlight specific opportunities that connect to CO_2, CH_4, and N_2 chemistry for electrification of the chemical industry on basis of the new insights highlighted above. In particular, we will relate to kinetic effects that can be exploited by balancing power density with heat transport. In effect, we depart from the narrative that vibrational excitation is the key to success for gas conversion in microwave plasma.

6. References

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