Microwave plasma activation of CO_2 - accessing vibrational non-equilibrium

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Abstract: Plasma is considered as a promising candidate for transforming electric power into chemical energy in general and for the reduction of CO_2 in particular. This presentation reviews the experimental investigations at DIFFER in microwave plasma and focusses on CO_2 reduction performance, importance of thermal dissociation, the existence of vibrational non-equilibrium, and the potential role for vibrational excitation to go beyond thermal equilibrium performance.

Keywords: CO_2 utilization, vibrational excitation, non-equilibrium, thermal conversion, microwave plasma

1. Introduction

Conversion from electricity to chemicals is desirable for future energy grids that are powered 100% by renewables to mitigate intermittency issues. Furthermore, the production of synthetic fuels from renewable energy enables sector integration as it could make sustainable energy available for e.g. transport and industry. Plasma is considered as a promising candidate for transforming electric power into chemical energy. This contribution addresses the role of vibrational excitation in the dissociation of CO_2 in microwave plasma.

The highest energy efficiencies in CO_2 conversion have been reported for microwave plasma: values close to 90% were reached in supersonic flow reactors [1], which is significantly higher than the thermodynamic limit of roughly 50% at these conditions [2]. These record efficiencies were explained on the basis of ideal electron kinetics that drive a strong non-equilibrium between particularly vibrational excitation and the gas kinetic temperature [3]. In this picture, plasma electrons gain their energy from the microwaves and preferentially transfer the energy to vibrational modes in the molecule. More than 65% of the electron energy can be transferred to vibrational modes in this way [4]. Of the three vibrational modes of CO_2, special interest is given to the asymmetric stretch, as this motion strongly correlates with the reaction coordinate of one oxygen atom separating to form a CO molecule, which corresponds to the lowest dissociation energy. This is opposed to the bending mode that would split off an oxygen molecule, and the symmetric stretch that would split off two oxygen atoms. Moreover, the asymmetric stretch quanta are largest, therefore difficult to convert via collisions into kinetic energy, and hence best suited to exhibit a strong non-equilibrium.

The efficient vibrational pumping in CO_2 leads to a situation in which higher vibrational modes are much more populated than they would be in a thermal equilibrium, ultimately producing the so-called Treanor distribution [5]. The condition for achieving overpopulation of the higher vibrational levels is that the Vibration-Vibration (V-V) relaxation rates are much higher than Vibration-Translation (V-T) relaxation rates. This is the case for the asymmetric stretch mode of CO_2. The V-V relaxation rates decrease with increasing gas temperature, while the V-T rates increase. Since the V-T relaxations increase the gas temperature, a positive feedback mechanism can produce a runaway V-T relaxation, leading to the destruction of the overpopulation of higher vibrational levels. In other words, low gas temperatures are prerequisite for a strongly non-thermal distribution.

Faced with a resurgence of interest in CO_2 utilisation due to climate change, a number of groups is investigating the maximally achievable energy efficiency for reduction of CO_2 in plasma [6]. So far none of these efforts has come close to the reported 90% energy efficiency.

Among the highest efficiencies that were measured in recent years is the value of 50% as was reported by den Harder et al. [6]. However, here gas temperature estimates on the basis of Rayleigh scattering revealing neutral gas densities in combination with pressure measurements were reported to be in excess of 3500K in the core, which seems to be incompatible with a strong vibrational non-equilibrium. Such high temperatures suggest that thermal equilibrium conversion is significantly contributing to the conversion.

In this contribution, we will review the experimental investigations at DIFFER in terms of CO_2 reduction performance, importance of thermal dissociation, the existence of vibrational non-equilibrium, and the potential role for vibrational excitation to go beyond thermal equilibrium performance. The present extended abstract focusses on pulsed microwave plasma experiments. The relationship between gas temperature and reduction performance is investigated and the heating dynamics of CO_2 plasma are established with laser Raman scattering and Fourier transform infrared spectroscopy as main diagnostics.

2. Experimental

The experimental layout is schematically depicted in Fig. 1. Microwave power (2.45 GHz) is generated either cw with a 1kW magnetron or pulsed with a solid-state microwave source with a peak power of 600 W and

modulated with a frequency up to 3MHz and a variable duty cycle from 0 to 100%. The microwaves are launched into a rectangular waveguide through which an 18 mm inner diameter quartz tube is inserted. A mass-flow controller is used to select the gas flow between 1.0 and 5.0 slm. Pure CO_2 gas is tangentially injected to induce a vortex which stabilizes the plasma and prevents contact with the wall. The length of the plasma is typically around 3 cm, but varies for different settings. Similarly, the axial position of the plasma relative to the quartz tube varies for different settings of pressure, power and tuning of the microwave cavity. The processed gas is pumped through a variable restriction that controls the pressure and exhausted through a few meters of bellows into an FTIR sample cell for composition measurements.

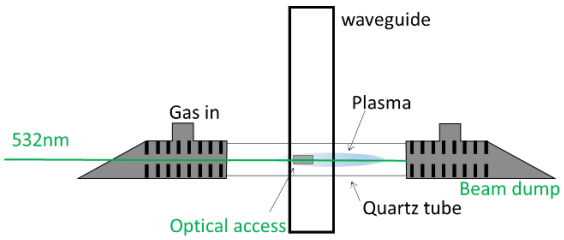

Fig. 1: Schematic of the experimental layout. Plasma is produced in the centre of the cell by launching microwave power through a waveguide intersected with a flow tube. Laser scattering is performed in the plasma region to infer gas temperatures and vibrational excitation. Fourier Transform Infrared (FTIR) absorption spectroscopy is used to determine the species composition in the exhaust.

Laser scattering is performed for temperature and vibrational excitation measurements. The frequency doubled output of a Nd:YAG laser (6W, 10 Hz) is focused in the centre of the plasma discharge. Scattered light is relayed with a fibre bundle into an in-house built spectrometer in Littrow arrangement (f=1m, f/10). An ICCD camera gated to the laser pulse records the spectra with a spatial resolution of 1 mm.

3. Results

The importance of thermal dissociation in CO_2 microwave discharges was investigated by power modulation. Power modulation creates an extra degree of freedom by decoupling peak and average power, and allows for the study of dynamic effects e.g. at ignition or after the plasma pulse. The time evolution of the rotational temperature was inferred from rotational Raman scattering as a proxy for the gas kinetic temperature in a 2.5 kHz pulsed plasma. Measured temperature profiles are shown for different duty cycles in Fig, 2, in each case both for the end of the power off phase (denoted "OFF") and the end of the power on phase ("ON"). It is observed that higher temperatures and broader temperature profiles are achieved in the centre of the discharge region as the duty cycle is decreased. Furthermore, the pulsing causes

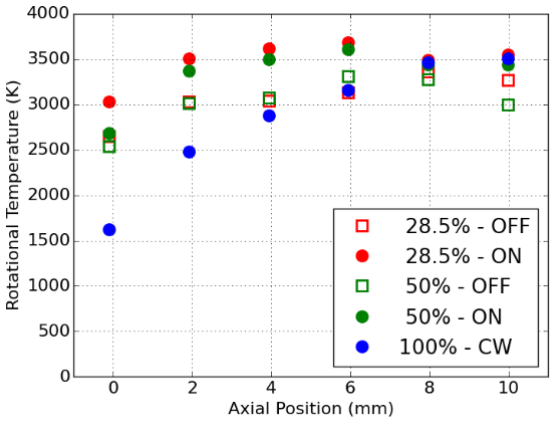

Fig. 2: Axial temperature profiles for different duty cycles at constant mean power at a constant average power of 150 W. Systematic error on the absolute temperature determination by fitting the rotational Raman spectra was for this case estimated to be ~500 K.

temperature oscillations of roughly 500 K. In any case, the temperature regime that is observed is where thermal dissociation of CO_2 is significant and fast, as was also established in our earlier cw work [2,7]. It means that the conditions in the radial centre of the discharge were still unfavourable for significant vibrational non-equilibrium which would require temperatures of at least 1000 K lower.

Also, radial profiles were measured (data not shown), which exhibited strong temperature differences between the edge (500K) and core (~3000K) of the plasma. Tangential gas injection is suspected to separate the core and edge layers, and thus supporting the strong thermal gradient.

Energy efficiency was inferred from the FTIR composition measurements in the effluent. It revealed that the energy efficiency increased with decreasing duty cycle, and thus, given the constant average power, with increasing peak power. At 28.5% duty cycle, the 8% efficiency at cw was doubled at 30% duty cycle. We explain the increase in efficiency as to result from the temperature increase, which alters the competition between radial heat transport (i.e. energy losses) and chemistry. The CO_2 reduction rate increases exponentially with temperature and thus becomes much more effective with a slight temperature increase.

The duty cycle was reduced to the lowest value at which it is still possible to ignite the plasma to investigate the vibrational, rotational, and gas heating dynamics were studied. At 25 mbar and 4 slm flow, the ON and OFF times that still delivered reproducible operation were 100 µs and 33 ms, respectively. The long OFF-time was selected to allow the gas to be fully replaced between pulses, so that each pulse starts at room temperature. In effect, we ensured

a low enough gas temperature to minimize quenching of vibrational excitation.

As plasma density was increasing during the power pulse, also the plasma impedance changed, which made it impossible to keep the cavity tuned to zero reflected power. As a compromise, the cavity was tuned to minimal reflected power just after ignition, of course also beneficial for ignition. Reflected power slowly increased during the pulse, from 600W absorbed power at the beginning resulting to 200W at the end of the pulse.

A spectral model was developed for fitting vibrational Raman spectra to directly determine the vibrational

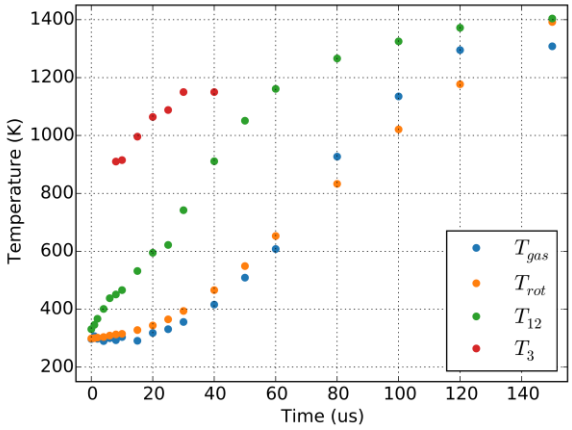

Fig. 3: Evolution of the vibrational, rotational and gas temperature inferred from vibrational Raman, rotational Raman and Rayleigh scattering, respectively.

temperatures of CO_2. The Fermi-resonance between symmetric stretching mode (v1) and the bending mode (v2) resulted in two separate branches in the symmetric stretch vibrational spectrum. The 1388 cm^{-1} branch was selected for spectral as it offers spectral separation of the symmetric stretch and bending peaks from the asymmetric stretch feature. In effect, we were able to determine the vibrational temperature for the symmetric and bending mode (which are assumed to be in equilibrium, denoted $T_{1,2}$) and the asymmetric stretch mode (T_3) separately. In addition, rotational temperatures were obtained as before, from fitting the rotational Raman spectra, and the translational (gas), and gas kinetic temperatures were inferred by relating Rayleigh scattering intensities and pressure measurements. The results are presented in Fig. 3. It illustrates that initially a strong $T_{1,2}$ –T_3 non-equilibrium is established. After 50 µs, the sensitive is not sufficient anymore (gas heating decreases density and thus scattering) to resolve the asymmetric stretch spectral feature, hence no further data on T_3 could be included. The vibrational temperature remains higher than the rotational temperature until 130 µs, which is after the input power is switched off. The maximum temperature difference at 60 µs, where $T_{1,2}$ = 1150K and T_{gas} = 600K. The rotational temperature remains in equilibrium with the translational temperature throughout the pulse and justifies the assumption of such an equilibrium in the previous analysis above.

The CO_2 reduction performance was also measured for these short pulse discharges. The discharge duration was varied from 20 µs to 100 µs and it was found that the energy efficiency was approximately 3%, irrespective of the discharge duration and thus independent of the degree of non-equilibrium that was established. This low value indicates that only ion processes and dissociative electron excitation were effectively responsible for the observed dissociation, similar as what is generally found for DBD discharges. The low gas kinetic temperatures indicate that thermal decomposition could not have been significant in these measurements. Apparently, the vibrational excitation density was not yet sufficient to effectively drive dissociation via ladder climbing, the mechanism that is generally assumed to be at play in microwave plasma.

4. Discussion and conclusions

Further analysis of the heating dynamics learns that the observed gas heating rate is much slower than what would be expected on the basis of the local power input. The latter yielded a time constant of 2.8 µs for thermal heating. The slow heating rate could be the result of radial transport, which would reduce the effective local power input.

The initial rise in vibrational temperature can be used to determine the power fraction that is deposited in the two vibrational modes. Underlying is a simulation of the power transfer fractions to estimate the reduced electric field and electron temperature in the discharge. At 10 µs, the fraction of power deposited to the asymmetric stretch was 27%. This power fraction corresponds to a lower limit for the reduced electric field of ~6×10^{-16} Vcm^2, which is much higher than the 2–2.5×10^{-16} Vcm^2 at which the power fraction deposited to the asymmetric stretch is maximized.

The findings reported here show that although a vibrational non-equilibrium can be achieved at the discharge onset, thermal equilibrium conversion might have a significantly larger contribution to dissociation than has been recognized traditionally.

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