CO_2 plasmas: from solar fuels to oxygen production on Mars

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Abstract: The similarities and differences between CO_2 plasmas to produce solar fuels on Earth and to produce oxygen on Mars are discussed. The investigation comprises a theoretical study based on simulations from a detailed kinetic model, and an experimental campaign to address the influence of Martian conditions in CO_2 dissociation. The theoretical predictions suggest that Mars has excellent conditions for in-situ resource utilisation on Mars by plasmas and are corroborated by the experimental measurements.

Keywords: CO_2 dissociation, vibrational excitation, Mars, oxygen production, ISRU.

1. Introduction

The continuous growth of fossil fuel consumption in the last decades has led to a steady increase of anthropogenic greenhouse gas emissions [1], with planetary impact [2]. This has motivated the scientific community to investigate how to replace fossil fuels by *solar fuels*, *i.e.*, the production of synthetic fuels from renewable electricity, using CO_2 as a raw material. The combustion of these fuels would result in a CO_2-neutral cycle. The bottleneck in this scheme is achieving an efficient CO_2 dissociation, in a process compatible with the geographic constraints and intermittency of renewable energy sources.

Low-temperature plasmas provide a very interesting possibility to address the problem. There are many advantages of plasmas, such as the possibility of instant start and stop of operation and scalability. In this rich medium, the high-energy electrons created can directly dissociate the CO_2 molecule, high-power plasma sources can significantly heat the gas and enhance thermal dissociation, and in typical conditions found for operation of various discharges the electrons can efficiently transfer their energy into the vibrational excitation of CO_2, that can be subsequently up-pumped along the asymmetric stretching mode to high levels and enhance dissociation via non-equilibrium processes [3]. The latter process is essential to achieve high energy efficiencies for CO_2 conversion, above those obtainable under thermally-driven processes.

In this context of a vast research effort aiming at understanding the basic phenomena ruling the global behaviour and the dissociation of CO_2 plasmas, a new application was recently proposed: the use of plasmas as a technology for *in-situ resource utilisation* (ISRU) on Mars [4,5]. As the Martian atmosphere is mostly composed of CO_2, plasmas can be used to decompose the molecule and produce oxygen directly from the atmosphere on the red planet, remaining available for breathing on future manned missions and as a component of fuels to be used to get back on Earth.

It was suggested that the red planet has nearly ideal conditions for CO_2 dissociation by plasmas [4]. In particular, it was advocated that the cold Martian atmosphere may enhance vibration-vibration (V-V) up-pumping and hinder vibration-translation (V-T) deactivation, thus leading to a higher degree of non-equilibrium, and that N_2 and Ar may help pumping the CO_2 asymmetric stretching mode and shift the electron energy to higher energies, respectively, contributing as well to favour dissociation [4]. Furthermore, the pressure on Mars (~4.5 Torr) is very suitable for plasma operation.

Herein we develop a joint experimental and theoretical investigation to discuss the similarities and differences between CO_2 plasmas operating on Earth and on Mars and to assess the validity of the ideas advanced in [4,5].

2. Model and experiment

The system under analysis consists of a DC discharge operating both in pulsed and continuous regimes, at pressures in the range p=0.5-5 Torr, discharge currents I=10-50 mA, initial gas temperature of either 300 K or approximately 200 K, created in pure CO_2 and in a 96%CO_2-2%N_2-2%Ar mixture. This set of parameters allows to mimic the conditions on the surface of Mars and to investigate the separate influence of different factors. In addition, the homogeneity of the discharge makes it more accessible to diagnostics and to models describing a complex kinetics.

The self-consistent model for CO_2 DC pulsed plasmas described in detail in [6,7] is used in this investigation. It follows the LoKI (LisbOn KInetics) approach [8], by coupling the electron Boltzmann equation with a system of rate balance equations describing the creation and loss of about 70 individual vibration levels of CO_2. In addition, *in-situ* Fourier Transform Infrared (FTIR) spectroscopy is used to measure the characteristic vibrational temperature of the asymmetric stretching mode, T_3, the common vibrational temperature of the symmetric stretching and bending modes, T_{12}, the rotational temperature, T_{rot} (assumed to represent the gas temperature, T_g) and the conversion factor, α, defined as α=[CO]/([CO]+[CO_2]) [9]. To impose the Martian low gas temperature, $T_g \approx 200$ K, the reactor is placed inside a bath of solid CO_2 (dry ice) and ethanol.

3. Results and discussion

Figure 1 shows the results of a first modelling study, where the ratios of the different characteristic temperatures, T_3/T_g, T_3/T_{12} and T_{12}/T_g are calculated in pulsed DC discharges at p=5 Torr and I=50 mA, when the gas temperature is initially 300 K (Earth) and 200 K (Mars). It can be seen that the degree of non-equilibrium, *i.e.*, the enhancement of T_3 over T_{12} and T_g, is higher for the conditions on Mars than those on Earth, promising an enhanced dissociation in discharges favouring vibrational dissociation.

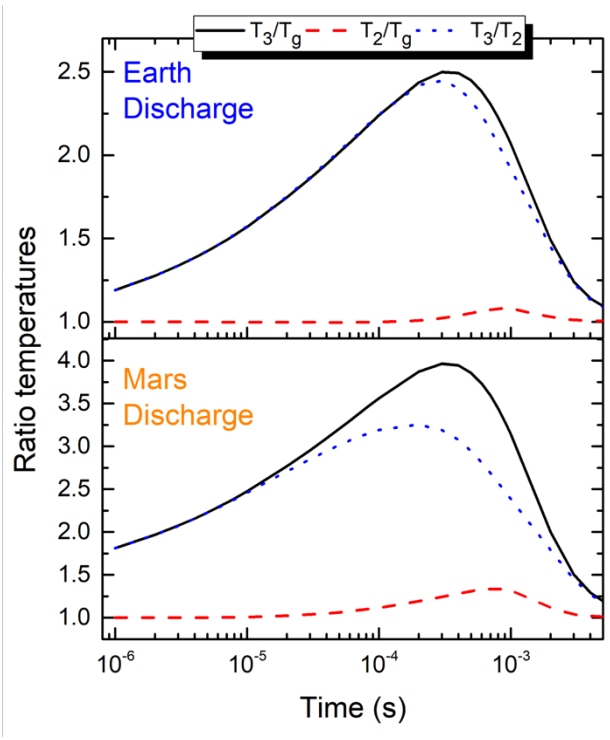

Fig. 1. Calculated ratios of different characteristic temperatures, for a 5 ms DC pulsed discharge at p=5 Torr and I=50 mA, when the gas temperature is initially 300 K (Earth) and 200 K (Mars).

Figure 2 shows similar ratios as in figure 1, measured in a continuous DC discharge at p=2 Torr as a function of the discharge current. The experimental results reveal an increase in the degree of non-equilibrium T_3/T_g going from Terrestrial to Martian conditions of the order of 1.2. Although the conditions in both figures are not the same, the experimental results are very much in line with the theoretical predictions from figure 1, which show an increase up to a factor of 1.6. However, at the conditions investigated the stronger degree of non-equilibrium in Martian conditions does not lead to a higher production of CO and oxygen. This is likely to be related to the discharge type used in this study, where vibrational dissociation is probably not playing a significant role.

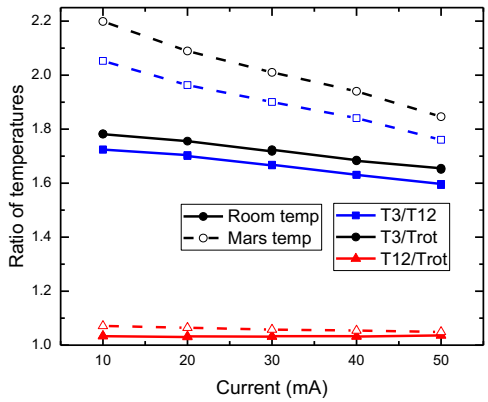

Fig. 2. Measured ratios of different characteristic temperatures, for a continuous DC discharge at p=2 Torr, when the gas temperature is initially 300 K (Earth, full curves) and 200 K (Mars, dashed curves).

Finally, figure 3 shows the conversion factor α as a function of pressure, for various currents and the gas initially at 300 K, measured in a pure CO_2 discharge and in a mixture containing 2% of Ar and 2% of N_2. The experimental results corroborate the conjecture of a positive effect of the Martian atmospheric composition on dissociation advanced in [4], confirming the potential of plasma technologies for oxygen production on Mars.

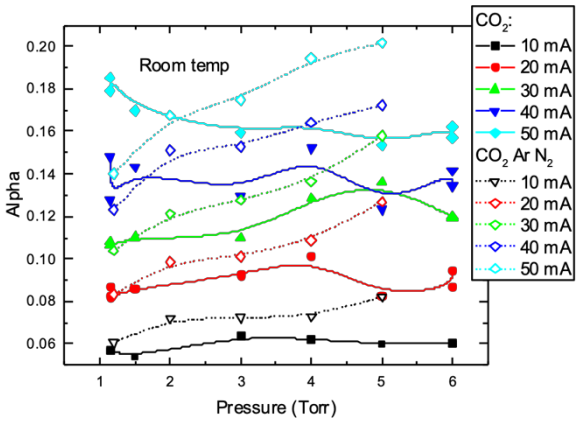

Fig. 3. Influence of the atmospheric composition (2%Ar+2%N_2) on dissociation, when the gas is initially at 300 K.

4. References

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