LETTER

The case for *in situ* resource utilisation for oxygen production on Mars by non-equilibrium plasmas

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The case for *in situ* resource utilisation for oxygen production on Mars by non-equilibrium plasmas

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Abstract
Herein, it is argued that Mars has nearly ideal conditions for CO_2 decomposition by non-equilibrium plasmas. It is shown that the pressure and temperature ranges in the $\sim$96% CO_2 Martian atmosphere favour the vibrational excitation and subsequent up-pumping of the asymmetric stretching mode, which is believed to be a key factor for an efficient plasma dissociation, at the expense of the excitation of the other modes. Therefore, gas discharges operating at atmospheric pressure on Mars are extremely strong candidates to produce O_2 efficiently from the locally available resources.

Keywords: plasma, CO_2 dissociation, Mars, in situ resource utilisation, gas discharge, oxygen production, vibrational kinetics

1. Introduction

Mankind has been exploring space for decades, stimulating the imagination and expanding the horizons of knowledge. Mars is the next step of the voyage into the Universe. For instance, the European Space Agency (ESA) has established the ExoMars programme to investigate the Martian environment and atmospheric trace gases [1]. On the other hand, NASA, in cooperation with SpaceX, has launched the programme 'Red Dragon', which aims to land on Mars within the next few years. This mission claims to be the first Mars settlement programme and optimistic scenarios foresee manned missions to an asteroid by 2025 and to Mars in the 2030s [2].

The red planet has resources that can be used for a sustainable settlement. In particular, the local production of oxygen (O_2) on Mars may help solve the problems of manufacturing fuel for coming back to Earth and of creating a breathable environment for a future outpost. In fact, the main component of the Martian atmosphere is carbon dioxide (CO_2) (95.9%), with smaller percentages of Ar (1.9%), N_2 (1.9%) and other gases. CO_2 can be converted into O_2 and carbon monoxide (CO), which were proposed to be used in a propellant mixture in rocket vehicles [3–6]. Such *in-situ* resource utilisation (ISRU) will diminish the needs of additional launch or lander mass. Accordingly, it will minimise risks to the crew and mission, as well as reduce logistics, making it possible to increase the space-craft shielding and provide increased self-sufficiency. Moreover, it will reduce costs by demanding less launch vehicles to complete the mission [3–6].

Plasma reforming of CO_2 on Earth is also a growing field of research, prompted by the problems of climate change and the production of solar fuels [7, 8]. Indeed, low-temperature plasmas constitute one of the best media for CO_2 dissociation, both by direct electron impact and, especially, by transferring electron energy into vibrational excitation [8–12]. The latter mechanism takes advantage of the non-equilibrium nature of low-temperature plasmas, with the activation of the plasma at a relatively low energy-cost, because it is possible to benefit from the energy stored in the vibrational levels. As a matter of fact, an efficient excitation of the vibrational levels can be achieved with a non-thermal plasma source with low mean electron energy (1–2 eV); if the electron energy can be selectively channelled into the asymmetric stretching mode, i.e. minimising the losses on the excitation of the other vibration modes and on gas heating, the subsequent V-V (vibration-to-vibration) up-pumping on the asymmetric stretching mode provides a unique way to efficiently break the C=O bond and dissociate the CO_2 molecule [9, 10]. Accordingly, one critical parameter to efficiently dissociate CO_2 seems to be the ratio T_3/T_g, where T_3 is the characteristic temperature of the asymmetric stretching mode and T_g is the gas temperature, characterising the degree of non-equilibrium of the plasma [13]. By the same reasoning, the ratio T_3/T_2, where T_2 is the characteristic temperature of the bending mode (which is typically very similar to the characteristic temperature of the symmetric stretching mode), is another interesting parameter to maximise.

The knowledge acquired from these investigations on Earth can be transposed to a large extent to ISRU on Mars, with the additional benefit of not requiring carbon capture. Besides, there are several other reasons why Mars seems to have excellent conditions for ISRU by plasma: first, of course, Mars has a CO_2 atmosphere and, if O_2 is to be produced locally on Mars, then there is no other available O_2 source than the atmospheric CO_2; the cold surrounding atmosphere (on average $T_g \leqslant 210$ K) may induce a stronger vibrational up-pumping than what can be achieved on Earth (see below); additionally, the cold atmosphere will somewhat freeze the chemistry, slowing the back reactions and giving additional time for the separation of products; the average atmospheric pressure on Mars, of about 600 Pa ($\simeq 4.5$ Torr), is in the good range for plasma reforming [10], allowing the operation of a discharge without the need to use vacuum pumps or compressors; traces of Ar and N_2 can only help, the former by slightly shifting the electron energy distribution function (EEDF) to higher energies [14], the latter by transferring vibrational energy from the N_2 to the CO_2 molecules as in a CO_2 laser; the required power for discharge operation is typically ~100 W and can be as low as ~20 W, which is perfectly feasible on Mars (e.g. the Mars Exploration Rover solar arrays generate, when fully illuminated, about 140 watts of power for up to four hours per sol).

In this context, CO_2 vibrational kinetics play an important role, to the extent that the energy stored in the vibrationally excited states activates the plasma and contributes to an increase in dissociation efficiency, helping low-temperature plasmas to surpass competing technologies, such as electrolysis

and thermo-chemistry. The conjecture of an exceptional V-V up-pumping and subsequent CO_2 dissociation on Mars is supported by the opposite dependences of the V-T (vibration-to-translation) and V-V energy transfer rate coefficients when the gas temperature goes down: on the one hand, the V-T reaction rates decrease and, accordingly, V-T deactivation is likely to be hindered; in contrast, on the other hand, the near resonant V-V rates *increase* as a result of the long-range attractive forces [15], favouring the V-V up-pumping. The purpose of this work is to start building a case for *in situ* resource utilisation on Mars using non-equilbrium plasmas, by investigating the similarities and differences of the vibrational energy input and relaxation in CO_2 plasmas for typical conditions on Earth and on Mars.

2. Results and discussion

Pulsed DC discharges constitute an ideal system for fundamental studies, since their simple geometry and homogeneity makes them accessible to a series of diagnostics and suitable for the development of 0D self-consistent kinetic models, accounting for very complex vibrational and chemical kinetics. CO_2 pulsed discharges have been very recently investigated, both experimentally [16, 17] and theoretically [18, 19], for a Pyrex cylindrical plasma reactor (23cm length, 2 cm diameter), operated under flowing conditions in the millibar range, with a pulsed 10–50 mA plasma current at 5/10 ms on/off. In particular, the time-resolved populations of the vibrational levels $\nu_1 \leqslant 2$, $\nu_2 \leqslant 6$ and $\nu_3 \leqslant 5$—where ν_1, ν_2 and ν_3 correspond to the quanta of vibration in the symmetric stretching, bending and asymmetric stretching modes, respectively—were measured by IR absorption [16, 17] and calculated from a detailed self-consistent kinetic model accounting for e-V, V-T and V-V transfers involving ~70 vibrational levels [18, 19], whose predictions are in excellent agreement with the experimental results.

Herein, the model developed in [18, 19], where the self-consistent coupling between the electron and vibrational kinetics is made as described in [20], is used to assess the capability of non-equilibrium plasmas to efficiently up-pump CO_2 vibrational quanta in Martian conditions. For this purpose, we focus on a DC pulsed discharge operating at discharge current $I = 50$ mA, pulse length $\Delta t = 5$ ms and gas pressure $p = 5$ Torr, corresponding to one of the conditions on Earth reported in [16, 18] and to the relevant pressure on Mars. The gas temperature profile for the Earth simulations was taken from the experiment [16] (see figure 1). The same profile was assumed for Mars, simply shifted down by 100 K, as a consequence of a similar shift in the boundary condition. This assumption was shown to be valid by self-consistent gas temperature calculations for the case of N_2-O_2 DC pulsed discharges at similar pressures and discharge currents [20]. Therefore, the simulations take as the input the discharge geometry (R), discharge operating parameters (I, Δt and p) and, additionally, the temporal profile of the gas temperature (T_g). The self-consistently calculated reduced electric fields are $E/N \simeq 63.5$ Td and $E/N \simeq 59.5$ Td, respectively
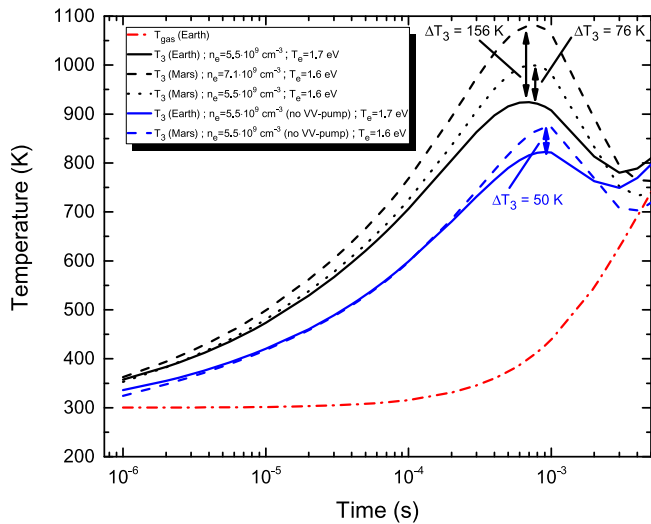
Figure 1. Time evolution of the gas ($-\cdot$) and the T_3 characteristic temperature for a DC pulsed discharge at $p = 5$ Torr, $I = 50$ mA, $\Delta t = 5$ ms: (——) Earth; (– –) Mars; (···) the same as 'Mars,' but with $n_e = 5.5 \times 10^9$ cm^{-3}; (——) Earth without V-V up-pumping; (– –) Mars without V-V up-pumping.

Figure 2. Logarithm of the normalised populations of the first level of the symmetric stretching, bending and asymmetric stretching modes, for a DC pulsed discharge at $p = 5$ Torr, $I = 50$ mA, $\Delta t = 5$ ms: on (——) Mars; on (– –) Earth.

for Earth and for Mars, corresponding to electron kinetic temperatures of about 1.7 and 1.6 eV, respectively, with calculated electron densities $n_e = 5.5 \times 10^9$ cm^{-3} and $n_e = 7.1 \times 10^9$ cm^{-3}, respectively.

It is worth noting that the system under analysis corresponds to a low excitation regime, where only the first few vibrational levels get excited, no significant CO_2 dissociation takes place [18, 19] and, accordingly, the kinetics of CO molecules and O atoms play a negligible role. It is therefore a perfect arrangement to study the input of electron energy into the vibrational levels and its initial redistribution among the lower levels, which are crucial to determine T_3 and the ratios T_3/T_g and T_3/T_2 [13].

Figure 1 shows the calculated time-dependence of the effective vibrational temperature between the first vibrational level of the asymmetric stretching mode ν_3 and the ground state, T_3, as a function of time, for a DC pulsed discharge in the conditions described above. The full and dashed black curves reveal that T_3 is strongly enhanced on Mars during the discharge pulse in comparison to the same discharge made on Earth. However, at the end of the discharge pulse, this effect vanishes (see figure 3 and the respective discussion), which suggests that, when pulsing appropriately, the discharge may maximise the vibrational temperature T_3. The black dotted curve corresponds to the same conditions as in the calculation for Mars, with the exception of the value of the electron density, which is taken the same as on Earth, $n_e = 5.5 \times 10^9$ cm^{-3}. This curve shows that the increase in T_3 on Mars is not due solely to the slightly larger electron density and an enhancement of electron impact vibrational excitation (e-V processes), but it is also an outcome of the complex vibrational kinetics. This is further confirmed by inspection of the blue curves in figure 1, corresponding to simulations performed without taking into account V-V energy exchanges. As can be seen, in this case, the
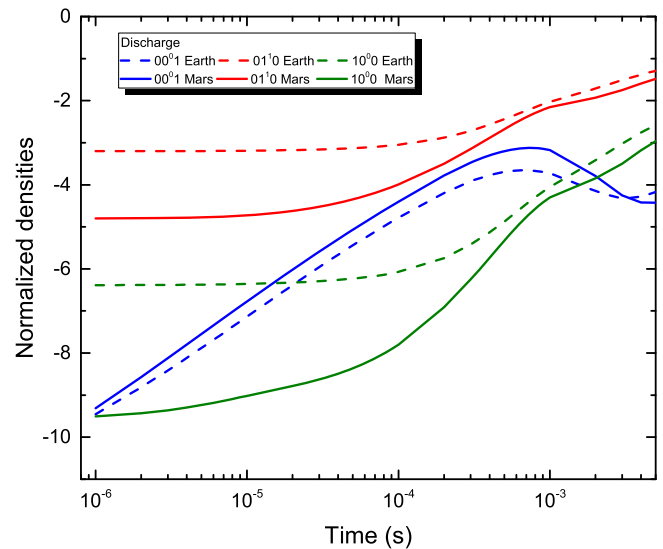
temperatures T_3 for the conditions on Earth and on Mars remain very close and much lower than the actual values, which demonstrates the important role of the V-V transfers in the buildup of T_3.

The time-evolution of the populations of the first level of each of the vibration modes during the pulse—denoted here, according to Herzberg's notation [21], as (10^00) for the symmetric stretching mode (green curves), (01^10) for the bending mode (red curves) and (00^01) for the asymmetric stretching mode (blue curves)—is shown in figure 2, depicting the logarithm of the normalised populations in respect to the ground state (00^00), divided by the statistical weight. This figure discloses a very interesting effect. As a matter of fact, besides the efficient pumping of the asymmetric-stretching mode, verified by the higher population of the (00^01) level on Mars than on Earth, the Martian conditions also promote a stronger internal non-equilibrium, since, on the contrary, both levels (10^00) and (01^10) are more populated on Earth than on Mars. Accordingly, advantageous conditions for using non-equilibrium plasmas for CO_2 dissociation can be fulfilled easier on Mars.

For completeness, figure 3 represents the non-equilibrium parameter T_3/T_g, suggested in [13] as an important measure of the impact of vibrational kinetics to dissociation, as well as the ratios T_2/T_g and T_3/T_2, where T_2 is the characteristic temperature of the bending mode. It can be immediately verified that a discharge on Martian atmospheric conditions is very suitable to induce vibrational non-equilibrium, with a larger difference between T_3 and both T_g and T_2, anticipating a positive impact on CO_2 dissociation. As noted in figure 1, the strongest non-equilibrium is verified for an on-time $\sim$0.5 ms, decreasing for longer times. Nevertheless, the ratio T_3/T_g remains higher for Mars than for Earth, even at the end of the 5 ms pulse.
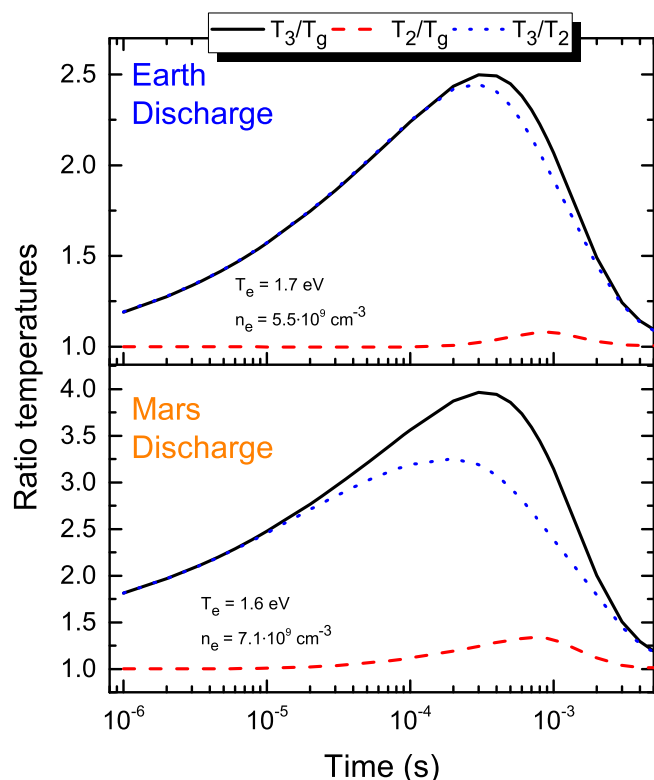
Figure 3. Time evolution of the ratio of different characteristic temperatures on a DC pulsed discharge at $p = 5$ Torr, $I = 50$ mA, $\Delta t = 5$ ms: (——) T_3/T_2; (— —) T_2/T_g; (· · ·) T_3/T_2.

3. Conclusions

The present analysis strongly suggests the possibility of an efficient CO_2 plasma dissociation from the Martian atmosphere, as the low-temperature and low-pressure on Mars trigger a more efficient up-pumping of vibrational quanta into the asymmetric stretching mode and higher ratios of T_3/T_g and T_3/T_2 than from typical conditions on Earth. Accordingly, the reasonableness of using non-equilibrium plasmas for efficient oxygen production on Mars is established.

Plasma technologies for CO_2 reforming on Earth are already competitive nowadays with solid oxide electroliser cells (SOEC). Therefore, our investigation evinces that a non-equilibrium plasma process can probably perform better than SOEC for O_2 production on Mars, the technology proposed by the exciting MOXIE programme [22]. In fact, while the efficiency of plasma dissociation of CO_2 on Mars is likely to increase compared to that on Earth, as demonstrated in this work, the efficiency of solid oxide electrolysis is likely to decrease, because extra energy is necessary to heat the gas up to ~ 1100 K and to compress it up to ~ 1 atm [22]. In addition, any estimation based on typical gas flows and CO_2 conversion rates obtained on Earth [8] points out that the throughput anticipated by the MOXIE experiment, of about 10 g per hour for a power of 300 W, is perfectly within the reach of an optimised plasma device.

Evidently, there are still many open challenges and directions for research, like finding the actual impact of

vibrational excitation in the degree and efficiency of dissociation; how the kinetics of CO and O may affect the vibrational distribution function, e.g. due to V-V CO_2-CO and V-T CO_2-O collisions, and the EEDF (questions raised as well in the very recent paper by Capitelli *et al* [23], in the framework of a self-consistent study of the electron and vibrational kinetics in CO_2 plasmas); what are the optimal discharge types, configurations and operating conditions; deeply understanding the role of the gas temperature and temperature gradients; and solving the question of the separation of the products of dissociation (an open problem on Earth as well). Nevertheless, the current indications are already extremely promising and are enough to justify further theoretical and experimental research, constituting the first step to build a case for non-equilibrium plasma *in situ* resource utilisation on Mars.

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