GAS HEATING DYNAMICS IN A CO_2 PULSED GLOW DISCHARGE RESOLVED BY KINETIC MODELING

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Introduction

Renewable energy is a fast-growing market and is expected to become the largest power source by 2040 [1]. However, its intermittent nature makes a full exploitation of the natural energy sources hardly achievable [2]. Moreover, climate change is putting increasing pressure onto society and actions to drastically reduce our CO_2 emissions are more than ever needed. Therefore, the development of technologies able to simultaneously reduce CO_2 emissions and store the excess of renewable energy into chemical bonds of fuels is of vital importance. To this end, plasma technology stands out as a viable tool to achieve splitting of CO_2, which opens up to the different chemical routes to convert the undesirable waste product into valuable chemicals or fuels [3]. Vibrational excitation of the asymmetric stretch mode of CO_2 to its dissociation limit is believed to be an efficient channel for splitting, having the lowest threshold energy amongst the possible dissociation pathways [4]. However, the stepwise excitation up to the dissociation threshold, also called "ladder-climbing", is typically sustained only at limited reduced electric fields (E/N) and low gas temperature. Ideally, such favorable conditions may be offered by pulsed low-pressure discharges, where the modulation of the pulse and inter-pulse time allows to selectivity trigger the vibrational chemistry while limiting the gas heating [5].

Aim of the work

- Development and validation of a kinetic scheme valid for pure CO_2, pulsed plasma discharges, with low dissociation degree
- Disclosure of the mechanisms underlying gas heating
- Insights into the limitations to a prominent vibrational excitation of CO_2 and, therefore, to the energy efficiency in low-temperature conditions
- Paving the way towards the modeling of a wider range of conditions (i.e. with higher power density and dissociation degree) with self-consistent calculation of gas and vibrational temperature

Zero-Dimensional (0D) kinetic model

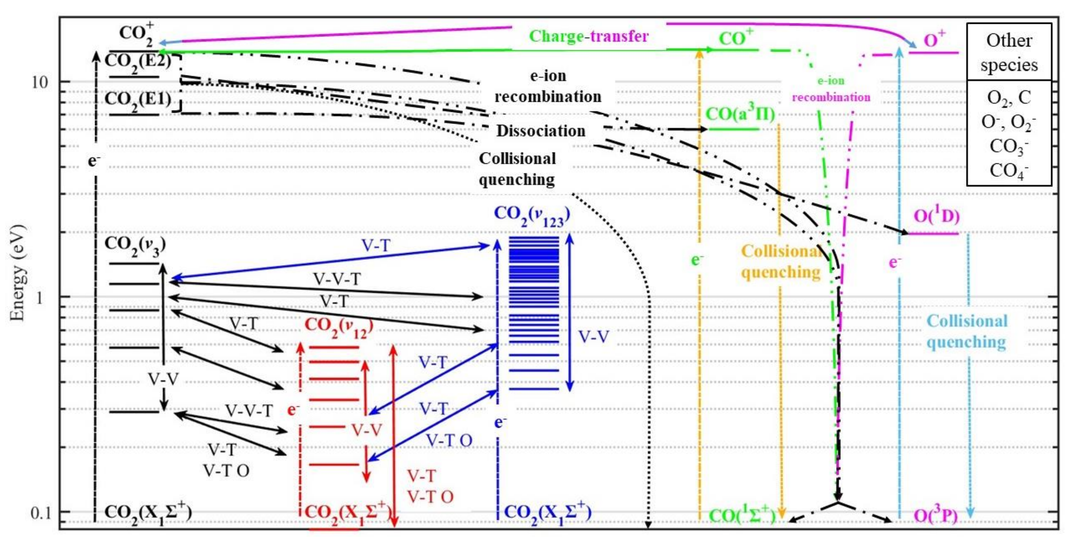

Figure 1. Species and main corresponding reactions included in the model, with vibration-vibration (V-V), vibration-vibration-translation (V-V-T), vibration-translation (V-T) and V-T by collision with O atoms (V-T O) relaxation reactions.

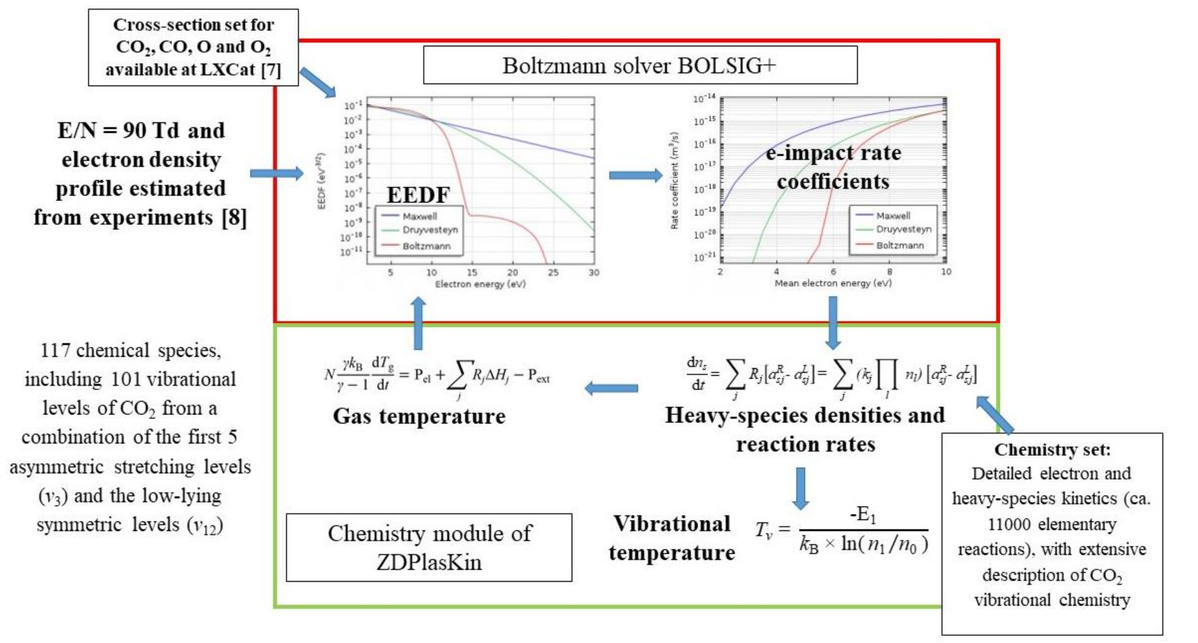

Figure 2. Main components of ZDPlasKin [6] simulation tool and main steps composing the iterative solution of the 0D kinetic model.

Validation with experiments

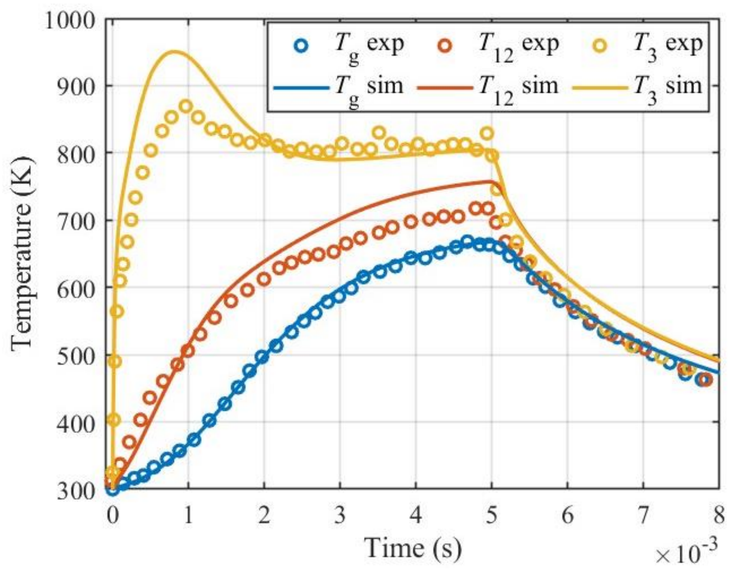

Figure 3. Experimental (circles) [8] and simulated (solid curves) gas (T_g) and vibrational (symmetric (T_{12}) and asymmetric (T_3)) temperatures as a function of time. Note that the pulse time is 5 ms; for $t > 5$ ms, the plasma is turned off.

Gas heating dynamics

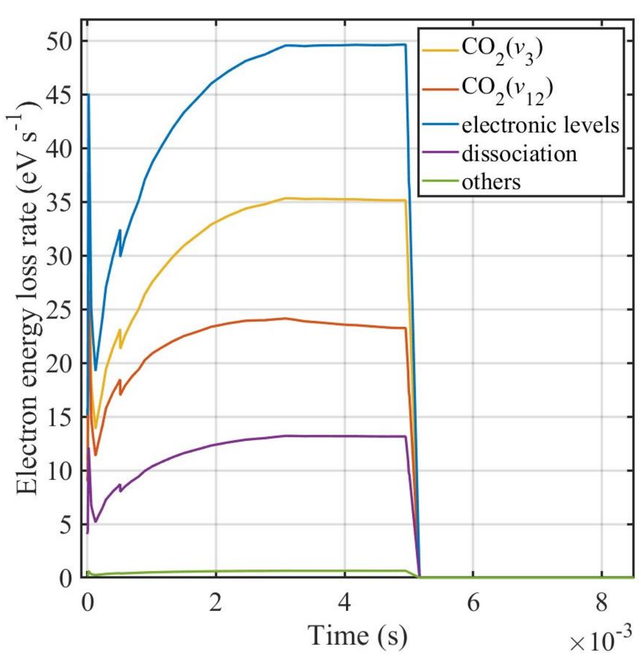

Figure 4. Electron energy loss rate to different excitation processes, with ionization, attachment and elastic scattering grouped under "others".

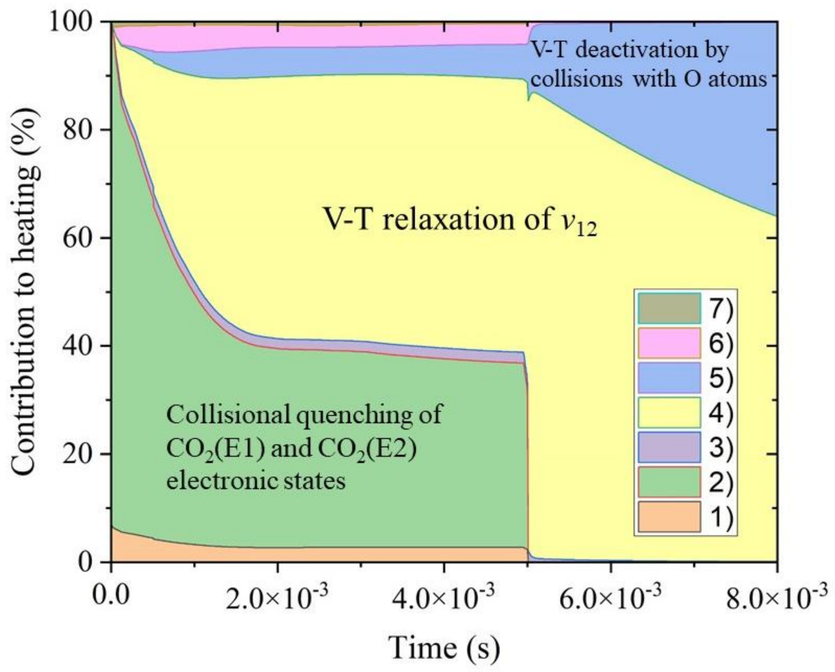

Figure 5. Percentage contribution to the gas heating rate from: (1) relaxation of $CO(a^3\Pi)$ and $O(^1D)$; (2) relaxation of CO_2(E1) and CO_2(E2) electronic states; (3) V-T relaxation from v_3 to v_{12}; (4) V-T relaxation of v_{12}; (5) V-T deactivation by collisions with O atoms; (6) V-V-T relaxation; (7) other reactions (namely electron-ion recombination, ion-neutral, V-V relaxation and thermal reactions and electron-neutral elastic scattering). Note that the contributions are stacked in order from (1) to (7).

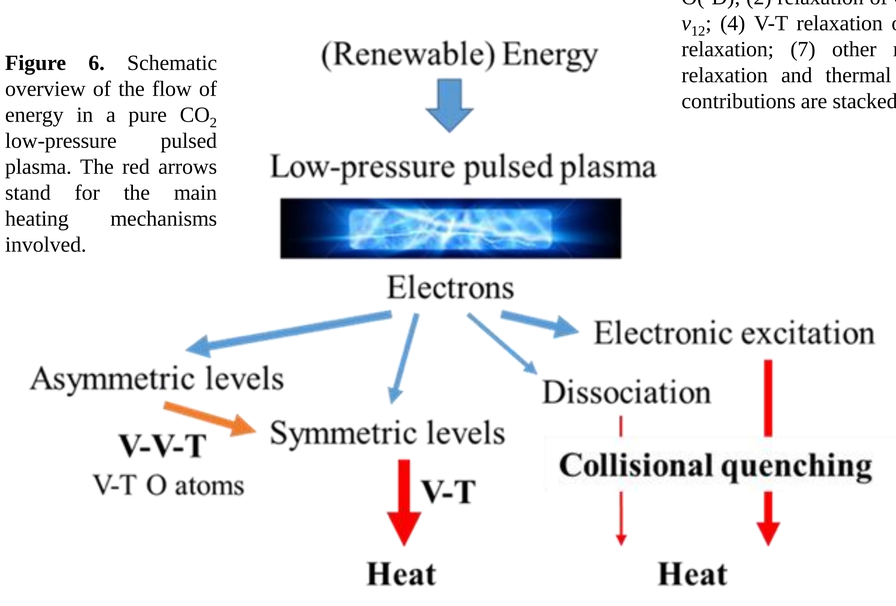

Figure 6. Schematic overview of the flow of energy in a pure CO_2 low-pressure pulsed plasma. The red arrows stand for the main heating mechanisms involved.

- Key role of V-V-T relaxation in coupling the kinetics of v_3 and v_{12}
- V-T relaxation alone cannot fully describe the heating dynamics under typical experimental conditions: contribution of ca. 35 % to gas heating from electronic relaxation, and even up to nearly 100% during the onset of the discharge
- O atom kinetics plays an important role in the heating dynamics as well, becoming essential to describe the energy transfers in the afterglow, where electron kinetics is quenched

Implications

Presence of multiple channels for gas heating reduces extent and timeframe to exploit V-T non-equilibrium in CO_2 plasmas. The polyatomic nature of CO_2 and, therefore, the existence of low-lying symmetric stretching and bending levels besides the asymmetric levels is a major constraint to a strong V-T non-equilibrium. Additional limitation is posed by fast loss of energy into electronic states and, subsequently, heat, which seems to be unavoidable in pulsed regimes. Moreover, the presence of dissociation products (e.g. O atoms, as demonstrated in this study) can alter the vibrational distribution and the heating dynamics during the active phase of the discharge and in the afterglow. Therefore, the redefinition of the conditions suitable for a consistent and exploitable vibrational excitation, as well as its possible role into dissociation, is highly desirable.

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