Insights into the limitations to vibrational excitation of CO_2: validation of a kinetic model with pulsed glow discharge experiments

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ABSTRACT

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]. Extensive research has been conducted during the last decades to find out the optimal conditions to obtain energy-efficient conversion of CO_2 and make the technology attractive to the industrial sector while concurring to reduce our carbon footprint.
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. Such favorable conditions can 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].
In this perspective, we developed a zero-dimensional (0D) kinetic model to reproduce the evolution of the gas and vibrational temperature measured by Klarenaar *et al.* [6] in a pulsed glow discharge and determine the underlying heating dynamics. The kinetic scheme was established upon our previous modelling efforts and includes an extensive description of the CO_2 vibrational chemistry (101 vibrational levels) and the main gas heating pathways. The successful validation of our kinetic scheme (see Figure 1) enabled the resolution of the heating dynamics (see Figure 2), disclosing the importance of the symmetric vibrational levels and electronic excitation of CO_2. Finally, this study provides useful insights into the limitations to the stepwise excitation and lays the foundation to

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clarify its possible contribution to the dissociation of CO_2 in future modelling efforts.

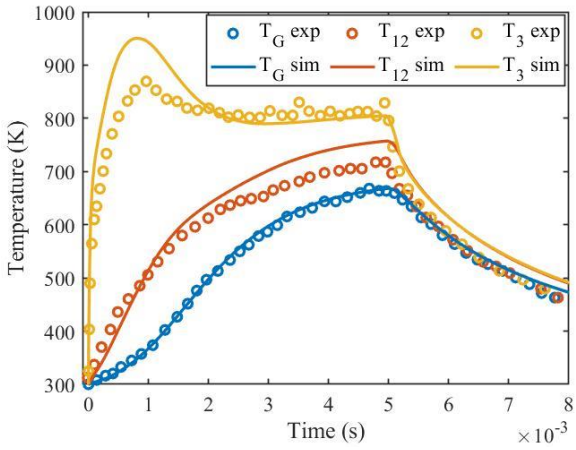

Fig. 1: Experimental (circles) [6] and simulated (solid curves) gas (T_G) and vibrational (symmetric (T_{12}) and asymmetric (T_3)) temperatures as a function of time. Note that the pulse time is 5 ms; for t > 5 ms, the plasma is turned off.

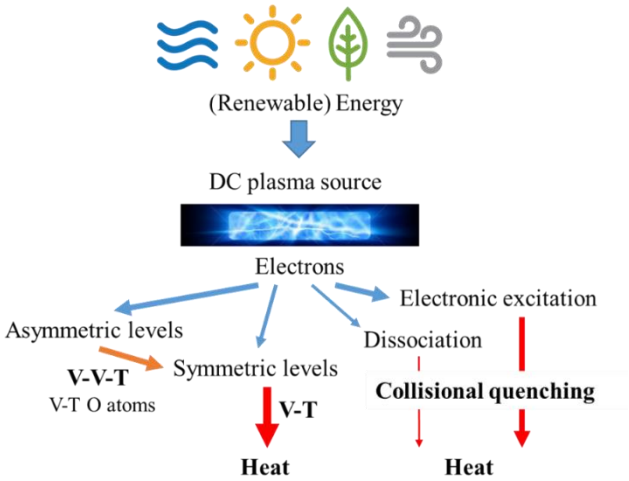

Fig. 2: Schematic overview of the flow of energy in a pure CO_2 low-pressure discharge. The red arrows stand for the main heating mechanisms involved: vibration-vibration-translation (V-V-T) relaxation, vibration-translation (V-T) and deactivation by collisions with oxygen atoms (V-T O atoms) and collisional quenching of electronic states coming from direct excitation or electron-impact dissociation of CO_2.

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