Understanding the electron and vibration kinetics in CO_2 plasmas

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This work focuses on the modeling of CO_2-containing discharges in order to describe the input and relaxation of vibrational energy. The vibrational energy exchanges are investigated through a self-consistent model describing the time evolution of the population of individual vibrational levels. The model is validated by comparing the calculated densities of vibrationally excited CO_2 molecules with experimental data obtained in a pulsed CO_2 glow discharge.

The emission of CO_2 into the atmosphere is frequently viewed as one of the major concerns for the 21st century. This environmental issue calls for an urgent energy transition based on renewable technologies [1]. However, at the current stage, renewable sources alone cannot cost-effectively generate electrical power due to their intermittent nature [1]. A promising solution to this problem is the development of a suitable energy storage scheme that converts temporary electrical energy into hydrocarbon-based chemical fuels. One such scheme is the power-to-gas approach, in which excess of wind or solar power is used to convert feedstock of CO_2 and H_2O into fuels [1]. One challenge within this approach is the maximization of CO_2 and H_2O conversion at a low energy cost. Indeed, this step involves highly endothermic reactions, which are difficult to stimulate by conventional thermal processes. To overcome this issue, previous research [2] has shown that molecular decomposition can be significantly improved by non-thermal plasma technology, which allows the coexistence of energetic electrons with relatively cold gas molecules. It is under such conditions, far from thermodynamic equilibrium, that it is possible to intensify traditional chemical processes and to achieve molecular decomposition with highest energy efficiencies.

This vision of using plasma as vehicle to transform electricity into chemistry is well recognized by the international plasma chemistry community [3]. Consequently, many research groups are currently investigating CO_2-containing discharges through both modeling studies [4] and experimental works [5] in order to understand and enhance the molecular decomposition. Nevertheless, despite these efforts, questions related with the optimal plasma operation conditions (pressure, reactor geometry, etc.) still raise many questions and the complete pathways of CO_2 and H_2O dissociation are far from being understood. The response to these last points will contribute towards the industrial implementation of an efficient recycling plasma device for fuel production.

This work presents a modeling and experimental investigation of CO_2 discharges, operating at pressures around 1 Torr. In regards of the modeling part, we have developed a state-to-state kinetic model that couples the electron Boltzmann equation [6] to the rate balance equations describing the creation and loss of the different vibrational levels. The vibrational kinetics accounts for electron-vibration (e-V), vibration-vibration (V-V) and vibration-translation (V-T) exchanges, dissociation, recombination and deactivation of vibrationally excited states to the plasma reactor wall. The modeling results are compared against *in situ* Fourier transform infrared spectroscopy data obtained in a pulsed DC glow discharge and its afterglow [7]. Among other important plasma parameters, this investigation allows accessing the time-resolved evolution of the various CO_2 vibrational levels along the discharge pulse. The basis of the model, together with the comparison against experimental data can be found in [8].

Typical results are shown in Fig. 1. Here we exhibit the characteristic temperature (T_3) of the asymmetric mode of CO_2, together with the gas temperature (T_{gas}) for a pulsed DC pure CO_2 glow discharge at p = 5 Torr, I = 50 mA and on-time of 5 ms. Note that T_{gas} was experimentally measured [6], while T_3 was both measured and determined from a distribution involving the calculated densities of the various CO_2 levels associated with the asymmetric mode of vibration [8]. Under these experimental conditions we can clearly see the deviation from thermal equilibrium during the on-time of the pulse discharge. In fact, T_3 rapidly increases at the beginning of the pulse with a maximum before 1 ms, while T_{gas} presents a slower growth till the start of the afterglow. On the other hand, the plasma-off time is characterized by a quick thermalization as the value of T_3 equals the T_{gas}.

It is worth noting that these results also show a very good agreement between the model predictions and the experimental results. However, this validation has been mostly obtained for pure CO_2 discharges under low-excitation regime (see [7-8]). Work is in progress in order to complete the plasma chemistry related with pure CO_2 discharges. At the same time, a special attention is also given to the inclusion of N_2 and H_2O species. The inclusion of N_2 is used to study the vibrational energy transfer from N_2 to the CO_2 asymmetric stretching mode (see [9]), while the addition of H_2O allows the investigation of hydrocarbons production.

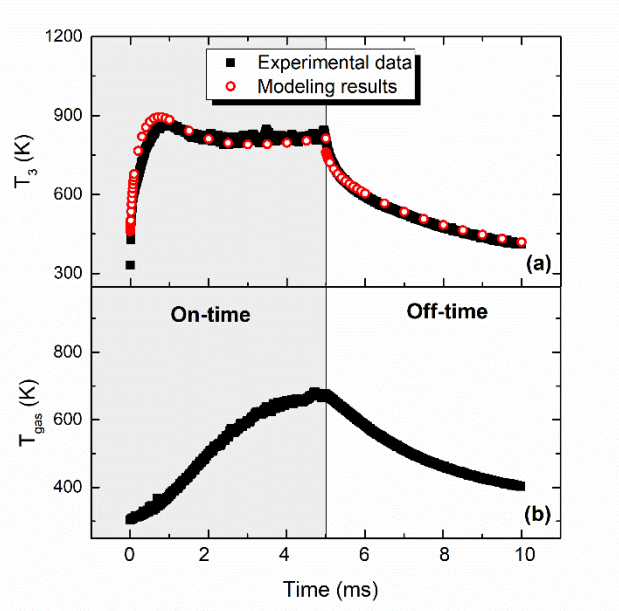

Fig. 1: (a) Comparison between the experimental (closed symbols) and model (open symbols) vibrational temperature T_3. (b) Experimentally measured gas temperature. Experimental conditions: DC glow discharge in pure CO_2 at p=5 Torr, I=50 mA

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