# Kinetic mechanisms in vibrationally excited CO<sub>2</sub> plasmas

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#### Introduction

A very promising approach for the mitigation of climate change is the use of non-thermal plasmas (NTP) for CO<sub>2</sub> conversion, benefiting from non-equilibrium conditions. However, the different processes occurring in CO<sub>2</sub> plasmas are not yet well understood, thus further work is necessary to reach a better comprehension and higher conversion and energy efficiency of the dissociation of CO<sub>2</sub>. Recent measurements of the gas temperature T<sub>g</sub>, vibrational temperatures of CO<sub>2</sub> and CO, reduced field (E/N), densities of O(3P), CO(X<sup>1</sup>\Sigma<sup>+</sup>) and CO<sub>2</sub>(X<sup>1</sup>\Sigma<sup>+</sup>) and O(<sup>3</sup>P) loss frequencies performed in low-pressure DC discharges provide an ideal set of constraints for validating numerical simulations from a **0D self-consistent kinetic model**. Dominant elementary processes with impact on the overall coupled kinetics can be studied but the focus will be on the vibrational kinetics of CO<sub>2</sub> and CO.

Investigating the impact of CO on the vibrational temperature of the different CO<sub>2</sub> vibrational modes and on the plasma chemistry is relevant as it is a product of the dissociation. It will therefore be present in the discharge and vibrationally energy transfers between CO and CO<sub>2</sub> are known to be effective [1]. Indeed, CO vibrations can promote CO<sub>2</sub> vibrational excitation and eventually, molecular dissociation through the so-called ladder climbing mechanism.

**N**<sup>P</sup>RIME

#### **Experimental setup**

DC glow discharge



# Simulations results and comparison with experiment

• The vibrational temperatures for the different modes of CO<sub>2</sub> and CO obtained from the model are in good agreement with the experimental data (Fig. 2).

- Pyrex tube of radius 1cm and length 23cm. Flow of 7.4 sccm, current of 20 mA and pressure in the range of 1-5 Torr.
- FTIR spectrometry to obtain rotational and vibrational temperatures of the different modes of CO<sub>2</sub> and CO, and the CO<sub>2</sub> dissociation fraction, as described in [2]. Actinometry to obtain O/N [3].

## Modelling

- Lisbon kinetics (LoKI) simulation tool [4]:
  - Loki-B: solves time and space independent electron Boltzmann equation within the two terms approximation, for non-magnetised non-equilibrium low-temperature plasmas excited by DC/HF electric fields for different gases or gas mixtures.
  - LoKI-C: solves system of zero-dimensional rate balance equations for the heavy species (charged
  - and neutral). Describes transport and wall reactions.
- Kinetic models developed in N-PRIME group [5-7] to which we added the vibrational kinetics of CO including the vibrational to vibrational (V-V) transfer between CO<sub>2</sub> and CO.

## Focus on the CO<sub>2</sub>-CO V-V exchange

- Vibrationally excited CO molecules can transfer energy to the asymmetric stretching mode  $(v_3)$  of CO<sub>2</sub> via:  $CO_2(v_3) + CO(w) \leftrightarrow CO_2(v_3 - 1) + CO(w + 1)$  (1)
  - Energy difference between the first vibrational level of CO, CO(w=1), and the first asymmetric stretch

For all the conditions under study,  $T_{1.2}$  is almost in equilibrium with  $T_{rot}$  ( $T_g$ ) but  $T_{CO}$ is higher than  $T_3$  which is higher than  $T_{1,2}$ :  $T_{CO} > T_3 > T_{1,2}$ 



vibrational level of CO<sub>2</sub>, CO<sub>2</sub>( $v_3$ =1), is only 25 meV, which is smaller than the average kinetic energy [1].

- Large cross sections of electron impact excitation of molecular vibrations of CO, due to the resonance effect of short-lived negative ions CO<sup>-</sup>[8].



 $CO_2(00^011) + CO(0) \rightarrow CO_2(00^001) + CO(1)$  used in this work (—) against the experimental results for the asymmetric stretch, and similarly for the other (symbols) from Seery et al. [10], Rosser et al. [11], Starr et al. [12] and Stephenson et al. [13].

• Procedure to obtain accurate rate coefficients for the V-V transfer between CO<sub>2</sub> and CO from Kustova et al. [9]:

- Rate coefficients of vibrational energy transitions between the lowest vibrational states are computed using the expression:

 $k_{0 \to 1} = \frac{kI}{P_{\tau}}$ , with  $P\tau = 10^{A_0 + A_1 T^{-1/3} + A_2 T^{-2/3}}$  (2)

and A<sub>n</sub> constants can be found in table 1 of [9] and compared with experimental data from the literature (Fig. 1).

- Remaining rate coefficients (for higher levels) are calculated on the basis of the harmonic oscillator modified for polyatomic molecules:

Figure 1: rate coefficients for the process:  $k(w \to w + 1)(v_3 + 1 \to v_3) = k_{0 \to 1} * (v_3 + 1) * (w + 1) (3)$ 

modes.

Figure 2: Experimental values ( $\Delta$ ) and calculated values (o) of the common vibrational temperature of the CO<sub>2</sub> bending and symmetric modes  $T_{1,2}$ , the vibrational temperature of the asymmetric stretching mode T<sub>3</sub>, the CO vibrational temperature T<sub>CO</sub>, dissociation fraction  $\alpha$  and the reduced atomic oxygen density O/N, when a discharge is ignited in  $CO_2$ , at current = 20 mA and as a function of pressure. The error bars (~357K) are not indicated for T<sub>CO</sub> to facilitate the reading of the figures. The model calculations were done including (-) and excluding (--) the CO<sub>2</sub>-CO V-V transfer.

- $T_{co} > T_3$  can be explained by the different rate coefficients for V-T relaxation, the lack of inter-mode V–V relaxation processes for CO but affecting  $CO_2(v_3)$  $(CO_2(v_3)+CO_2(v_{1,2}) \rightarrow CO_2(v_3-1)+CO_2(v_{1,2}+1))$ , and more efficient vibrational excitation through electron-to-vibrational energy transfers for CO.
- $T_3 > T_{1,2}$  since the asymmetric stretch has a relatively long lifetime and its relaxation is thus much slower than that of the symmetric stretch and bending modes [14].
- Similar trend with pressure for  $T_{CO}$  and  $T_3$ , even when there is no  $CO_2$ -CO V-V transfer included, could be explained by the variations of the rate coefficients for the quenching with O atoms with T<sub>g</sub>.
- Increase of T<sub>g</sub> (not shown in Fig. 2) with pressure because of the higher power necessary to keep the same current, which explains the trend for  $T_{1,2}$  (since  $T_{1,2} \sim T_g$ ).
- All temperatures tend to converge for higher pressures because of higher relaxation rate.
- Decrease of  $T_3$  and  $T_{1,2}$  and increase of  $T_{CO}$  when  $CO_2$ -CO V-V is not included but the  $CO_2$  dissociation fraction  $\alpha$  and the reduced atomic oxygen density O/N are not affected.

#### Conclusion

The comparison of the model predictions with the experimental data contributes to develop the existing models [5-7] and to better control and enhance plasma-assisted CO<sub>2</sub> conversion. Our model was further refined to include a self-consistent description of the CO vibrational kinetics and more specifically the CO<sub>2</sub>-CO V-V transfer to study the vibrational energy transfers between CO and the asymmetric stretching mode of CO<sub>2</sub>. This transfer greatly influences the vibrational temperatures but very slightly the dissociation fraction. Indeed, the vibrationally excited CO does not influence the plasma chemistry, in our conditions, where the dissociation mainly occurs by electron impact (on the ground state of CO<sub>2</sub>). Indeed, CO is mostly involved in back reactions via its electronically excited state CO(a<sup>3</sup>Π<sub>r</sub>) in collision with  $O_2$  or CO to create back  $CO_2$  or with  $CO_2$  leading to dissociation.

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