

Electron and vibration kinetics in CO₂/CO mixtures

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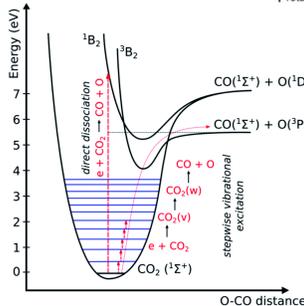
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Motivation

Carbon dioxide (CO₂) is an important trace gas in Earth's atmosphere, as a major cause of the climate change, and is the main component of the atmospheres of Mars and Venus. The use of plasmas for CO₂ dissociation is a hot topic nowadays, being discussed in different contexts, from CO₂ gas mixtures in Earth for the production of solar fuels [1] to Mars low-temperature and low-pressure atmospheric conditions for oxygen production [2]. Non-equilibrium plasmas can promote CO₂ dissociation by direct electron impact or through vibrational excitation [3]. The study of electron kinetics is essential, allowing to understand how the energy gained by the electrons is transferred to the different heavy-particles.

The products of dissociation of carbon dioxide are CO and atomic oxygen. Even small concentrations of these gases can change the behaviour of the discharge [4].

Herein we discuss the influence of CO on the electron kinetics of a CO₂ discharge. To this purpose, we use the Boltzmann solver of the LibOn Knetics simulation tool (LoKI) [5] to calculate the electron energy distribution function (EEDF), transport coefficients, reaction rate coefficients and power balance in CO-CO₂ mixtures.



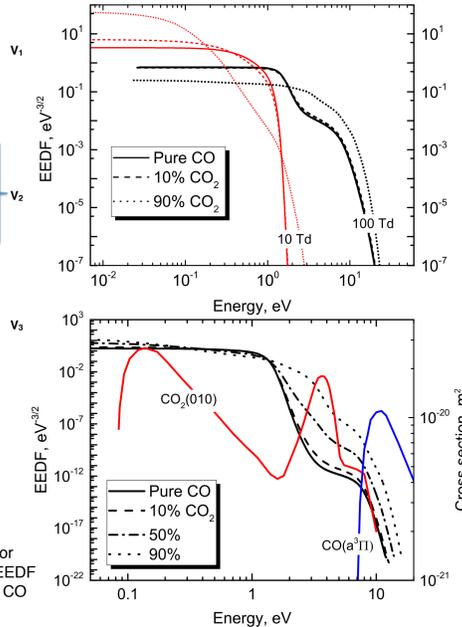
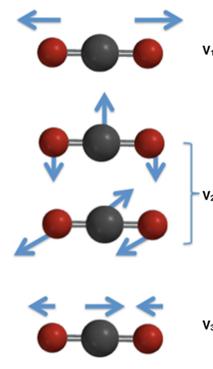
Schematic representation of the energy exchange processes relevant for CO₂ molecular dissociation based on the literature data. The arrow thickness is roughly proportional to the process rate [6].

Ladder climbing mechanism for CO₂ dissociation [7].

CO₂/CO mixture kinetics - EEDF

The addition of small concentrations of CO₂ introduces only small changes in the shape of EEDF. For the pure CO and 10% CO₂ cases, we can notice a strong depletion of the EEDF around 1-2 eV. This is due to the resonant part of the vibrational cross sections of CO and CO₂ bending mode, which makes it difficult for electrons to reach higher energies. At low E/N the role of electronic excitation in shaping the EEDF is negligible, but it starts to be noticeable at higher reduced fields, with the appearance of second depletion region at 7-8 eV. The outcome is an opposite behaviour of the EEDF with CO₂ addition in the electron energy region $u < 0.2$ eV for low and high E/N .

Electron energy distribution functions versus electron energy for different values of reduced field. On the right the evolution of EEDF with concentration of CO₂ plotted together with CO₂ (010) and CO (a³Π) cross section. Reduced field for this case is 20 Td.

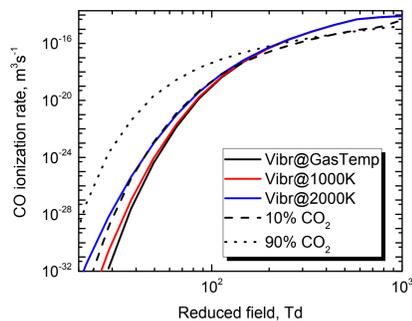
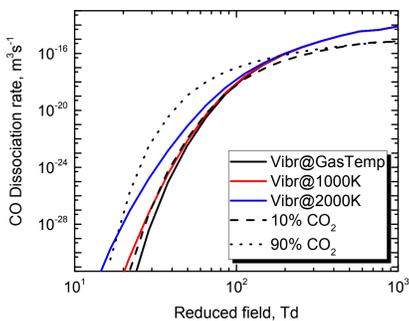
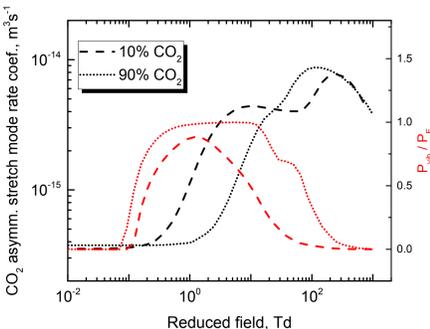
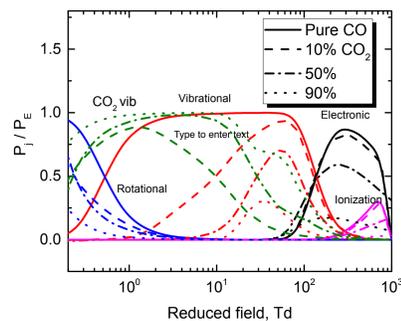


CO₂/CO mixture kinetics - power transfer and rate coefficients

Figures on the right report the fractional power losses dissipated in the different channels as a function of E/N for different concentrations of CO₂. These fractional power losses have been calculated as the ratio between the electron energy transferred from electrons to different CO excitation channels, vibrational, dissociative, electronic, and ionization, to the electron energy gained by the electrons from the electric field.

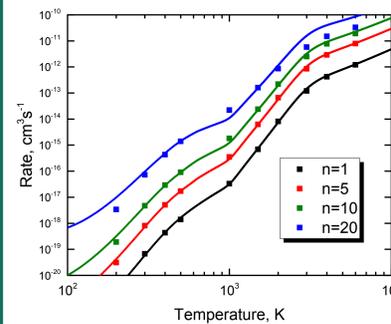
The addition of the small fraction of CO₂ in to the CO discharge promotes great increase of pumping CO₂ vibrational channels - especially CO₂(010) bending mode.

The rate coefficients of excitation of the asymmetric stretching mode are a manifestation of the changes in the EEDF and power transfer discussed above. This figure reveals that finding the ideal working conditions to enhance CO₂ dissociation is not straightforward, as the dissociation products modify the ideal reduced fields for discharge operation, implying that the optimisation of a CO₂ plasma must take into account the kinetics of the formed CO in some detail, as also pointed out in [4].



Vibrational kinetics plays very important role in the CO₂ dissociation. In microwave discharge the temperature can rise up to 1500K [6]. This includes the rise of the vibrational temperature as well. The affect of the vibrational temperature for pure CO discharge is depicted above. For the reduced field 60 Td the dissociation rate increases by more than 10 times for vibrational temperature 2000 Td and a bit less than 2 times for 1000 K comparing with the case where the vibrational temperature is equal to gas temperature. For example, adding only 10% of CO₂ can increase the dissociation rate by a factor of 2.2. And if we have the mixture where 90% is CO₂ and only 10 % is CO the enhancement of the rate will be almost 3 orders of the magnitude. For dissociations and ionization rates, we can see that increase of the rate happening for the reduced field lower than 100 Td. For higher fields - the dissociation rate is decreasing with any admixture of CO₂ and remains the same for different vibrational temperatures.

CO vibrational kinetics - VT



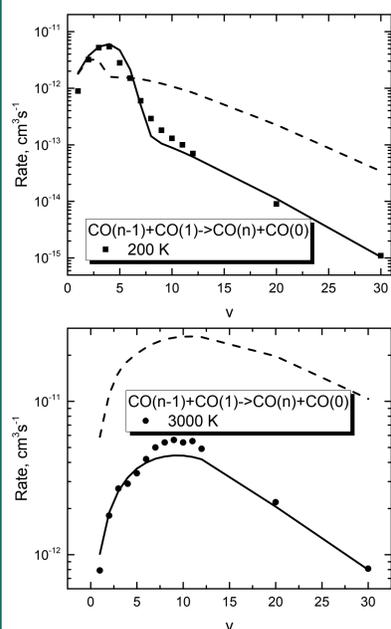
CO(n) + CO -> CO(n-1) + CO

- Based on Schwartz-Slawsky-Herzfeld (SSH) theory
- Adapted to the results of close-coupled trajectory calculations

SSH theory is widely used to describe VT transitions for different molecules, but it doesn't accurately describe the results obtained with more sophisticated and complex close-coupled trajectory calculations. In order to get accurate fitting of these rates we fitted the CC calculations for $n = 1$ and scaled all our results for higher values of n .

$$K^{n,n-1} = K^{1,0} \cdot \frac{B^{1,0}}{P^{1,0}}$$

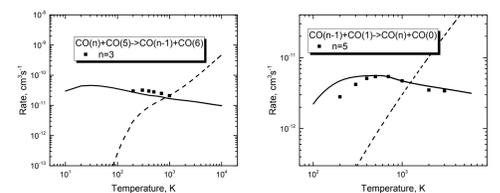
CO vibrational kinetics - VV



CO(n-1) + CO(m) -> CO(n) + CO(m-1)

- Based on SSH and Sharma-Brau theories
- Adapted to the results of close-coupled trajectory calculations (200-3000K)

In this case of VV rate coefficients to obtain quite good agreement the dependency on the vibrational quanta was studied. In this way, it was easier to find some patterns create fitting functions that will depend on temperature, not on vibrational quanta.



$$k_{v+1,v}^{w,w+1} = 3.4 \times \left(\frac{T}{300}\right)^{1/2} \times [S_{10}^{01} \times G_S(v+1, w+1) + L_{10}^{01} \times G_L(v+1, w+1)]$$

$$G_L(v+1, w+1) \approx Z_{v+1} Z_{w+1} \exp\left[-\frac{(\Delta E)^2 (v-w)^2}{bT}\right]$$

In original theory it was suggested using constant value $b = 39.9$ for CO molecule. We are proposing to use linear function dependant on temperature: $b = 5 \cdot T + 1.5 \cdot 10^3$.

Some other changes were implemented into the SSH and Sharma-Brau theory. For example, we had to increase the adiabatic function F for the low temperatures and implement the multiplication factor m to the whole rate coefficient, which can be seen on the figure above, where VV rate for temperature 3000 K is depicted.

Conclusions

The model that will describe the dissociation of the CO₂ is being developed in IST in Lisbon together with collaborators. It should include proper description of electron, vibrational kinetics, chemistry and influence of the products of dissociation on the plasma discharge.

This contribution addresses the electron kinetics in CO₂/CO mixtures, in order to evaluate the influence of the CO created as a result of CO₂ dissociation in a plasma discharge. It is shown that vibrational excitation of CO has a significant role in shaping the electron energy distribution function (EEDF) and that CO influences in a complex way the low-energy region of the EEDF, of significant importance to control the energy input into the CO₂ asymmetric stretching vibration mode.

The vibrational kinetics of CO is another block that will be added into the model. The modifications to the existing theories presented in the current work more accurately describe the semiclassical trajectory calculations

References & Acknowledgements

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