A parametric Boltzmann equation analysis of CO₂ dissociation in cold plasmas and afterglows

L.D. Pietanza, M. Capitelli, G. Colonna, G. D’Ammando and A. Laricchiuta

CNR-IMIP, via Orabona 4, 70126 Bari, Italy

Abstract: CO₂ dissociation has been studied in discharge and post discharge conditions by comparing direct electron impact dissociation rates with those rates obtained by considering a pure vibrational dissociation mechanism in which excitation of vibrational modes of CO₂ is taken into account. Results have been obtained by solving a Boltzmann equation including elastic, inelastic, superelastic and electron electron collisions.

Keywords: CO₂, dissociation, superelastic collisions, vibrational mode excitation

Plasma processing of CO₂ under non-equilibrium conditions is nowadays considered a promising substitute to conventional routes to specifically tackle the rate-limiting dissociation into CO [1-4]. The idea to use cold, i.e. non-equilibrium plasma, for the CO₂ dissociation has a long history started with the works of Russian [5, 6] and Italian groups [7, 8], at the beginning of plasma-chemistry activities. The basic idea was the impossibility to rationalize experimental dissociation rates of CO₂ by using the direct electron impact dissociation process. On the contrary, especially at low electron temperature ($T_e\sim 1 eV$), the input of electrical energy goes through the excitation of vibrational modes of CO₂ (in particular the asymmetric one), followed by VV energy exchange processes able to spread the low lying vibrational quanta over the whole vibrational ladder of CO₂, ending in the dissociation process. The upper limit to the dissociation rate of this mechanism, called pure vibrational mechanisms, can be obtained by the simplified equation

$$K_d^{(IPV)} = \frac{1}{v_{max}} K_e\nu(000 \rightarrow 001) \quad (1)$$

where $K_e\nu(000 \rightarrow 001)$ is the rate of the resonant vibrational excitation process and $v_{max}$ the number of vibrational quanta contained in the vibrational ladder of CO₂ (to a first approximation we can imagine to pump vibrational energy selectively on the asymmetric mode of CO₂). This rate can be several orders of magnitude higher than the corresponding dissociation process induced by electron impact. These simple considerations are at the basis of the numerous experimental attempts to use vibrational energy in the dissociation process rather than the direct electronic process with the belief that the activation energy of the vibrational excitation process is much less than the corresponding electron impact process. Unfortunately, the situation is much more complicated than that given by Eq. (1), which completely disregards the relaxation of the vibrational energy by VT energy exchange processes. Moreover, the possible enhancement of the direct electron impact dissociation process due to the presence of vibrationally excited molecules should be taken into account. The last has a twofold effect on the direct dissociation process: 1) it enlarges the electron energy distribution function (eedf) through the effect of superelastic vibrational and electronically excited state collisions, increasing at the same time the direct dissociation rate; and 2) it increases the dissociation rate due to the lowering of the energy threshold of dissociation, decreasing with vibrational quantum number. The first point has been considered in the past to understand the dissociation of CO₂ in laser mixtures [9], this aspect being reiterated more recently for the same aim [10]. The second point has been recently reinvestigated in the case of nitrogen plasmas [11].

To better understand these points, we report in Fig. 1 the dissociation rate of CO₂ as a function of vibrational temperature of CO₂ at E/N 30 Td calculated in different approximations: 1) according to Eq. (1); 2) considering only the direct electronic excitiation-dissociation from the CO₂ ground state, $K_d(000)$; and 3) including the effect of vibrational levels in direct dissociation according

$$K_d(\text{all}) = \sum_{\nu} \nu_{\max} \exp\left[\sum_{\nu=0}^{\nu_{\max}} \left(\frac{1}{v_{\nu}} - \frac{1}{v_{\nu_{\max}}}\right)\right] k_d(000) \quad (2)$$

$v_{\max}$ being the maximum value of vibrational levels in the asymmetric stretching ladder, i.e., 21 according to [3]. This equation results from the crude assumption of a shift of cross-section threshold for excited vibrational levels, and Boltzmann distribution function of VDF and EEDF at $T_v$ and $T_e$ temperatures, respectively, reducing to $K_d(\text{all}) = v_{\max} k_d(000)$ for the case $T_v = T_e$ as reported by [12]; 4) including the effect of vibrational levels in the pure vibrational mechanism

$$K_d^{(IPV)}(\text{all}) = \frac{1}{v_{\max}} \sum_{\nu=1}^{\nu_{\max}} \frac{\nu_{\nu}}{e^{\nu_{\nu}/k_B T_v}} e^{\nu_{\nu}/k_B T_e} k_e(0 \rightarrow \nu_{\nu}) \quad (3)$$

where $\nu_{\nu}$ are the excited vibrational levels belonging to different normal CO₂ modes, as reported in Table 1. $k_d(000)$ and $k_e(0 \rightarrow \nu_{\nu})$ rate coefficients have been calculated from the solution of the Boltzmann equation including vibrational and electronic superelastic collisions, considering a parametric change of the
temperatures associated to the different vibrational normal modes, $T_{\nu}$ for the asymmetric stretching and $T_{\nu}'$ for the symmetric and bending modes, imposing $T_{\nu} > T_{\nu}'$ following what observed in CO$_2$ laser physics. Moreover, the concentration of the CO$_2$(e$_2$) electronically excited state has been set at equilibrium with the symmetric and bending modes ($T_{\nu}'$), while, only in the post discharge regime, a fixed concentration of $10^{-5}$ has been imposed. Finally, the electron-electron Coulomb collisions have been inserted with different electron ionization degrees. All the cross-section data entering the Boltzmann equation have been taken from [13], while superelastic cross sections have been derived by detailed balance principle. Note that in the corresponding database [13], the 7 eV threshold process is considered as a dissociative channel, while the electronic excitation is limited to a process with energy threshold of 10.5 eV. The addition of further excitation levels [3, 5] can improve the accuracy of the present results, without altering their qualitative validity.

Inspection of Fig. 1 shows that the pure vibrational mechanisms including all vibrational channels are dominant at lower $T_v$ vibrational temperature, while direct dissociation channels become competitive at higher vibrational temperatures. In any case, at $E/N = 30$ Td, direct dissociation strongly increases with $T_v$ as a result of the corresponding behaviour of the eedf (see Fig. 2). At the same time, the pure vibrational mechanisms become more and more important as the reduced field decreases ($E/N < 30$ Td), the reverse being true for $E/N > 30$ Td. These points nowadays are practically forgotten when trying to rationalize the experimental results of CO$_2$ dissociation. Attempt in this direction should take into account the strong coupling between eedf and non-equilibrium vibrational kinetics, including electronic (dissociative and excitation) transitions involving vibrational excited states as shown in Fig. 1. The above reported scenario applies mainly in the low-electron temperature plasmas dominated by the excitation of vibrational modes, a situation that can occur in microwave (Mw) discharges operating at moderate pressures. Microwave (Mw) driven CO$_2$ plasma at sub-atmospheric pressures can reach energy efficiencies as high as 60% at low specific injected energies (around 1 eV/molecule CO$_2$) thus confirming the importance of vibrational excitation in the dissociation process [4]. The use of atmospheric DBD pulsed discharges revealed an energy efficiency of about 10% [3, 4].

Another interesting case could be the use of nanosecond high-voltage discharges operating at atmospheric pressure. The situation in this case is completely different from the Mw case because during the pulse one creates very elevate electron temperatures, able to excite electronic states of CO$_2$ rather than vibrational states. However, in the post-discharge following the pulse, the electronically excited states can create structures in the eedf due to superelastic collisions between cold electrons and electronically excited states, increasing the dissociation rate of CO$_2$ also in the post-discharge regime [14]. In Fig. 3 we report the electron energy distribution function at different vibrational temperatures in the post-discharge regime ($E/N = 0$ Td).

![Fig. 1. Rate coefficients for dissociation channels in CO$_2$ plasma, as a function of vibrational temperature of asymmetric mode (on the upper axis the corresponding values of characteristic energy $E_c$ are reported), at $E/N = 30$ Td.](image_url)
by elastic and inelastic relevant collisions, including electron-electron collisions not considered by [14]. The plateau length strongly decreases with the increase of vibrational temperatures. It should be pointed out that in ns pulsed discharges the realistic values of vibrational temperatures do not exceed 3000 K, while the selected values of the electronic state and electron concentrations are typical of ns pulsed discharges. In Fig. 4, the rate coefficients for the dissociative channels are reported in the post-discharge regime (E/N = 0 Td). In this case, the pure vibrational mechanisms dominate the direct dissociation channels in the whole T_v vibrational temperature range. In any case, the direct dissociation channels cannot be neglected and should be included in the description of post-discharge regime.

Fig. 4. Rate coefficients for dissociative channels in CO_2 plasma, as a function of vibrational temperature of asymmetric mode (on the upper axis the corresponding values of characteristic energy E_c are reported), in the post-discharge regime (E/N = 0 Td).

The results reported in this abstract should be taken in the present case from a qualitative point of view. Improvements of the vibrational ladder as well as of the dynamical information for the corresponding inelastic channels should require a not trivial effort. On the other hand, a state-to-state vibrationally and electronically excited state kinetics coupled to a self-consistent Boltzmann equation should be developed. Particular care should be devoted to the VV and VT processes involving a realistic vibrational CO_2 ladder [15]. Moreover we should insert these modules in a more complex one describing the plasma chemistry occurring in the discharge [3]. Dedicated experiments are then expected...
to validate the theoretical model to transform it in a predictive tool.

1. References


