Numerical modelling of the CO_2 dissociation in gas discharges including full vibrational kinetics

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The plasma chemical decomposition $CO_2 \to CO+\frac{1}{2}O_2$ is a potentially important upstream process for conversion of electricity into fuels (Power-2-X). One of the possible mechanisms is the non-equilibrium vibrational conversion at relatively low translational-rotational temperature $T \lesssim 1000$ K and high vibrational temperature $T_{vibr} \gg T$ [1, 2]. In the present contribution an estimate of the efficiency of this mechanism by means of model extrapolation is addressed.

The number of vibrational states $CO_2\left(v_1, v_2^l, v_3\right)$ is too large to directly apply the state-to-state approach even in 0D/1D simulations. This problem is solved here by gathering the states with close vibrational energies into 'combined' states $CO_2\left[v_s, v_a\right]$, where $v_a = v_3$, and $v_s = 2v_1 + v_2$ is the good quantum number of symmetric vibrations. In this way the number of master equations to solve is reduced from $\approx 10^5$ down to ≈ 800. The model is described in detail in [3, 4], for completeness the list of transitions is reproduced in Table 1. The calculation of transition probabilities is mainly based on the Schwartz-Slawski-Herzfeld (SSH) theory [5, 6, 7], the absolute values of the rate coefficients are adjusted with available experimental data.

The rate coefficients of vibrational-translational (VT) process V1 can be calibrated against the shock tube and sound absorption experiments. Behind the shock fronts a very rapid increase of T is followed by a relatively slow increase of T_{vibr}. For diatomic molecules a simple equation can be derived for relaxation of vibrational energy under the following assumptions (see [8], Chapter 19): i) the molecules are linear oscillators; ii) the probabilities of VT-transitions obey the SSH or Landau-Teller relations; iii) the number of vibrational states is infinite. This derivation has been modified for CO_2 assuming that the process V1 (in Table 1) dominates the VT-transfer, see [9]. The resulting energy relaxation equation reads:

$$\frac{dE_{vibr}}{dt} = R_{10}N\left(1-e^{-\frac{\hbar\omega_2}{T}}\right)\left[E^{eq}_{vibr-2}(T)N - E_{vibr-2}N\right], \quad E^{eq}_{vibr-2}(T) = \frac{2\hbar\omega_2}{e^{\frac{\hbar\omega_2}{T}}-1} \qquad (1)$$

Here E_{vibr} is the total vibrational energy in a unit control volume, E_{vibr-2} is the energy (per one molecule) stored in the double degenerate bending mode v_2^l, $E^{eq}_{vibr-2}(T)$ is the value at thermal equilibrium with Boltzmann temperature T (see e.g. [10], Eq. (49.3)), N is the number density of molecules, $\hbar\omega_2$ is the vibrational quantum of the mode v_2, R_{10} is the rate coefficient of the process $CO_2\left(01^10\right)$+M $\to$ $CO_2\left(00^00\right)$+M.

Table 1: List of vibrational transitions included in the model

V1	$CO_2[v_s,v_a]+M \leftrightarrows CO_2[v_s-1,v_a]+M$
V2a	$CO_2[v_s,v_a]+M \leftrightarrows CO_2[v_s+3,v_a-1]+M$
V2b	$CO_2[v_s,v_a]+M \leftrightarrows CO_2[v_s+2,v_a-1]+M$
V7a	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s+1,v_a-1]+CO_2[u_s+2,u_a]$
V7b	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s+2,v_a-1]+CO_2[u_s+1,u_a]$
V7c	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s+2,v_a-1]+CO_2[u_s+2,u_a]$
V7d	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s,v_a-1]+CO_2[u_s+2,u_a]$
V7e	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s,v_a-1]+CO_2[u_s+3,u_a]$
V7f	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s+1,v_a-1]+CO_2[u_s+3,u_a]$
V7g	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s+3,v_a-1]+CO_2[u_s+1,u_a]$
V8	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s,v_a-1]+CO_2[u_s,u_a+1]$
V11	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s-1,v_a]+CO_2[u_s+1,u_a]$
V12	$CO_2[v_s,v_a]+CO_2[u_s,u_a] \leftrightarrows CO_2[v_s-2,v_a]+CO_2[u_s+2,u_a]$

If the distribution of vibrational levels is Boltzmann with temperature T_{vibr}, then (1) can be transformed into an equation which can be readily integrated (here $N = const$):

$$\frac{dT_{vibr}}{dt} = R_{10}N\frac{\left(1-e^{-\frac{\hbar\omega_2}{T}}\right)}{c_v^{vibr}\left(T_{vibr}\right)}\left[E^{eq}_{vibr-2}\left(T\right)-E_{vibr-2}\left(T_{vibr}\right)\right] \tag{2}$$

Here c_v^{vibr} is the heat capacity due to vibrational degrees of freedom (see e.g. Eq. (49.4) in [10]):

$$c_v^{vibr} = c_1+c_2+c_3, \quad c_{1,3} = \frac{\left(\hbar\omega_{1,3}\right)^2\exp\left(\frac{\hbar\omega_{1,3}}{T_{vibr}}\right)}{T^2_{vibr}\left[\exp\left(\frac{\hbar\omega_{1,3}}{T_{vibr}}\right)-1\right]^2}, \quad c_2 = \frac{2\left(\hbar\omega_2\right)^2\exp\left(\frac{\hbar\omega_2}{T_{vibr}}\right)}{T^2_{vibr}\left[\exp\left(\frac{\hbar\omega_2}{T_{vibr}}\right)-1\right]^2}$$

The comparison between the equation (2) and numerical simulations with the full vibrational kinetics of Table 1 is summarized in Table 2. In both cases T is a fixed parameter and the initial T_{vibr} equals 300 K. In Table 2, ε_1 is the maximum relative difference of the two solutions (energies E_{vibr} per molecule are compared), and η_{V1} is the fraction of process V1 in the energy transfer between translational-rotational and vibrational degrees of freedom. One can see, indeed, a very good agreement for $T <$2000 K when the process V1 dominates.

The rate coefficients R_{10} published in the literature are typically obtained from the experimental time τ_{VT} applying the equations derived for diatomic molecules, see e.g. [11]:

$$\frac{dE_{vibr}}{dt} = \frac{1}{\tau_{VT}}\left[E^{eq}_{vibr}\left(T\right)-E_{vibr}\right], \quad \tau_{VT} = \frac{1}{R_{10}N\left(1-e^{-\frac{\hbar\omega_2}{T}}\right)} \tag{3}$$

It has been found empirically that for T <2000 K equation (3) can match the numerical solution as well as (2) when τ_{VT} is taken as:

$$\tau_{VT} = \frac{c_v^{vibr}\left(\bar{T}_{vibr}\right)}{c_2\left(\bar{T}_{vibr}\right)} \cdot \frac{1}{R_{10}N\left(1-e^{-\frac{\hbar\omega_2}{T}}\right)}, \quad \bar{T}_{vibr} = \frac{300\,\mathrm{K}+T}{2} \tag{4}$$

The relative difference between the numerical results and the exponential decay with τ_{VT} according to (4) is given in Table 2 as ε_2. Equation (4) allows to calibrate the basis rate coefficient R_{10} of process V1 such that the model of Table 1 will reproduce the vibrational relaxation times measured in gas-dynamic and acoustic experiments.

R_{10} from [12] (Table IIIa, $(01^10) \rightarrow (00^00)$) used in the present work was calculated applying the τ_{VT} defined by (3). The error introduced when (3) is used instead of (4) is not large: the factor $\frac{c_v^{vibr}(\bar{T}_{vibr})}{c_2(\bar{T}_{vibr})}$ only varies from 1 at low T to 2 at high T, which could be within the experimental uncertainty.

Table 2: *Results of the VT-relaxation test*

T, K	ε_1, %	ε_2, %	η_{V1}, %
400	0.3	0.7	99.9
500	0.3	1.6	99.8
600	0.3	2.5	99.6
800	0.3	3.8	98.9
1000	0.9	4.1	97.7
1200	2.1	3.4	95.5
1500	5.2	0.9	89.6
2000	15.7	12.5	71.9
2500	34.0	33.1	48.8

The dissociation process itself is included in the model by introducing unstable states with vibrational energies > E_{diss}=5.5 eV, for which a very fast decay is assumed. To prove that this approach is realistic a comparison was made with the shock tube measurements [13, 14] of the dissociation rate of CO_2 diluted in Ar in conditions of thermal equilibrium $T_{vibr} = T$, see [4]. Good agreement was found only for T <3000 K. The reason of an order of magnitude disagreement at higher T is thought to be the known shortcoming of the SSH theory - that it overestimates the transition probabilities p_{SSH} at high T and for high excited states, and can even yield $p_{SSH} > 1$. In the present work to avoid especially this latter issue an artificial upper limit $p_{SSH}^{max} = 1$ was imposed to all p_{SSH}. Calculations with $p_{SSH}^{max} = 0.1$ for the shock wave conditions showed, indeed, a better match with experimental data [13, 14] at high T.

The CO_2 vibrational kinetics model verified, calibrated and (partially) validated as described above was used to provide extrapolation to the conditions of microwave plasmas where vibrationally excited states are produced by electron impact. Only pure CO_2 and the primary dissociation step CO_2 + M → CO + O + M are considered. The results are discussed in detail in [4] and are only briefly outlined here.

The model shows that at T=300 K and degree of ionization $r = n_e/N$ around 10^{-5} strong vibrational non-equilibrium can be achieved. Despite initially 76-80 % of input energy goes into excitation of asymmetric modes ν_3 the fast inter-mode redistribution leads for low lying vibrational states to the energy distribution close to Boltzmann with single temperature T_{vibr}, Fig. 1. The populations of high vibrational states close to E_{diss} lie far above the Boltzmann level. The main reason for the observed shape is found to be the ladder-like electron impact excitation, while vibrational-vibrational transitions are only playing a minor role.

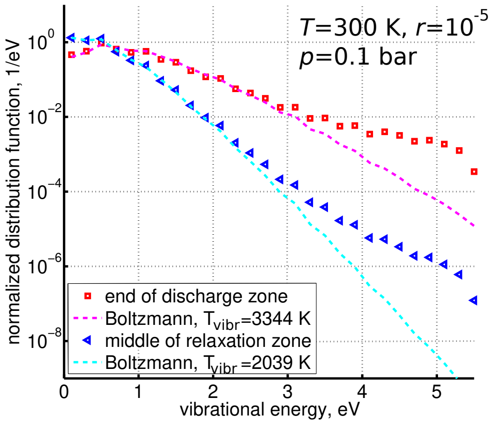

Figure 1: *Example of vibrational distribution function of CO_2 calculated for conditions of microwave plasma discharges*

The calculated chemical energy efficiency η obtained for T=300 K and r=10^{-5} (pressure p=0.1 bar) is 42..56 % depending on the assumed p_{SSH}^{max} and rate coefficients of processes V11, V12 for which no solid experimental data were found. The η is reduced at elevated T and smaller r, and eventually vanishes (at T >500 K, $r < 3 \cdot 10^{-6}$). This result implies that the non-equilibrium vibrational mechanism of CO_2 conversion is going to be difficult to achieve in condition of real microwave discharges because of inevitable heating of the gas.

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