On activation of the non-equilibrium vibrational dissociation of CO_2 in plasma chemistry

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The plasma-chemical splitting of CO_2 has been intensively studied in the last decade in view of its potential applications for Power-2-X technologies. Dissociation from upper vibrational states at relatively low translational-rotational temperatures T <1000 K in conditions of strong non-equilibrium between vibrational and translational-rotational modes was considered in the past as the most efficient mechanism of the CO_2 plasma conversion [1]. Indeed, for reduced fields and average electron energies typical for microwave plasmas the electron energy shall go predominantly into excitation of vibrational states of CO_2 [3]. Nevertheless, no solid confirmation of the non-equilibrium mechanism has been found so far in the modern day experiments which rather focus on thermal quenching [2]. In the present work the role of vibrational relaxation in activating the process has been investigated theoretically and computationally.

For dissociation from the upper vibrational states to be efficient their population must be sufficiently high. Subsequently, a vibrational distribution has to build up with a certain high average vibrational energy per CO_2 molecule E^*_{vibr}. The condition for reaching the required level of non-equilibrium can be expressed by the following inequality:

$$\frac{Q}{n_0^2} > \left(\frac{Q}{n_0^2}\right)_{crit} = R_{VT}(T)\left[E^*_{vibr} - E^{eq}_{vibr}(T)\right] \tag{1}$$

Here Q is the specific power (per unit volume) which goes into excitation of vibrational states and n_0 is the initial number density of CO_2 molecules. The right hand side is the expression for the vibrational energy relaxation known from the shock tube and sound absorption experiments [4]. $R_{VT}(T)$ is the empiric relaxation rate coefficient, T is the translational-rotational temperature, $E^{eq}_{vibr}(T)$ is vibrational energy per molecule calculated for Boltzmann distribution of vibrational states with temperature T.

To obtain quantitative estimates (1) is extended and verified by the simulations performed with the state-to-state vibrational kinetics model [5]. This is a coarse-grained model which uses 2-modes approximation, the dissociation process is represented by introducing unstable vibrational states with total energy larger than the prescribed dissociation limit E_{diss} =5.5 eV.

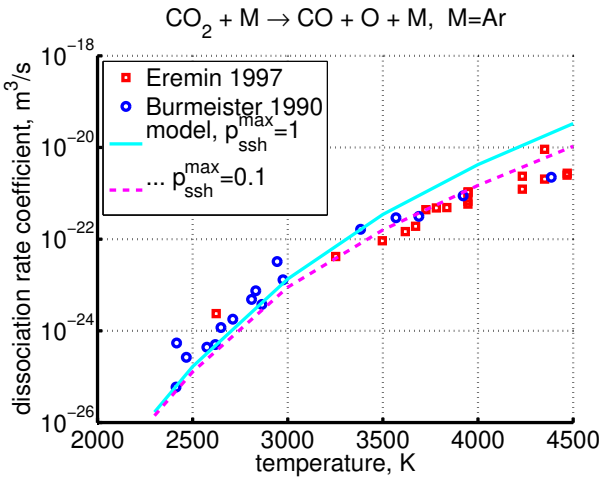

Figure 1: Comparing the CO_2 vibrational kinetics model with shock tube measurements [6, 7]

To confirm that this model is capable of producing the realistic dissociation rates the calculations are compared with shock tube measurements. The agreement with the data for CO_2 diluted in Ar [6, 7] is relatively good, see figure 1. However, in that benchmark vibrational-vibrational transitions are effectively disabled and not tested. There are no direct measurements for M=CO_2, the rate coefficients found in the literature are those for M=Ar multiplied by enhancement factor estimated from experimental data. The reference model calculations for pure CO_2 were found to overestimate the literature rate coefficients [8, 9] by an order of magnitude. Good agreement can only be achieved when the parameter p_{SSH}^{max} is reduced from its nominal value 1 to 0.1. This parameter is an artificial limit imposed for all transition probabilities calculated by the Schwartz-Slawski-Herzfeld (SSH) theory [10], see [5]. It had to be introduce because SSH is the 1st order perturbation theory and can grossly overestimate transition probabilities. In the subsequent numerical experiments the p_{SSH}^{max}=0.1 case was always part of sensitivity tests. Comparison with shock tubes data validates the model, but only partly because in shock tube conditions T >2000 K which is above the range relevant for the gas discharge studies.

The results of 0D simulations for a model system which mimics microwave induced plasmas where vibrational states are excited by electron impact are shown in figure 2. The electron temperature T_e in those simulations is a prescribed parameter varied from 0.5 to 3 eV. Same governing parameter Q/n_0^2 as in (1) can be introduced for master equations of the state-to-state model by translating them into following variables: molar fractions related to n_0 instead of densities, and Specific Energy Input (SEI) Qt/n_0 ($Q = const$) instead of time t. The plotted quantity is the conversion rate χ defined as the amount of

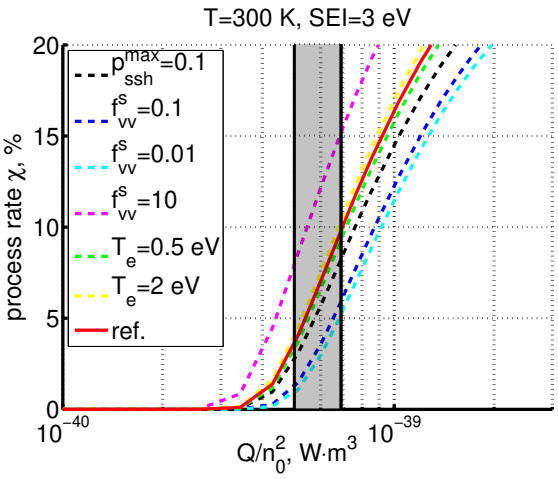

Figure 2: Results of 0D vibrational kinetics simulations for microwave plasmas

CO molecules at the end of the process divided by the amount of CO_2 in the beginning. The present model only includes the primary dissociation process $CO_2 + M \rightarrow CO + O + M$. Therefore, only regimes with low χ are investigated with the aim to find the position in terms of Q/n_0^2 where the non-equilibrium dissociation starts to work.

Different curves in figure 2 correspond to different model assumptions. One can see that for all of them the process rate is zero at low Q/n_0^2, and then starts to increase monotonically as Q/n_0^2 is increased. The steepness of the χ grow varies strongly depending on the model parameters, but not the position where the grow starts. This latter can be well approximated by (1): the shaded rectangle in figure 2 is $\left(Q/n_0^2\right)_{crit}$ calculated by applying (1) with E^*_{vibr} extracted from the simulation results. Technically E^*_{vibr} is estimated by taking the losses of vibrational energy into dissociation Q_{diss} and losses into translational-rotational modes Q_{VT} as their appear in the simulation results as functions of E_{vibr}. E^*_{vibr} is then defined as E_{vibr} for which $Q_{diss} = 0.1 Q_{VT}$. Variation of E^*_{vibr} estimated in this way is not large and is translated into relatively small variation of $\left(Q/n_0^2\right)_{crit}$, figure 1. $R_{VT}(T)$ is taken from [12]. Of note is that the vibrational kinetics model of [5] is calibrated is such way that for shock wave conditions it reproduces this experimental $R_{VT}(T)$ with good accuracy, see [11].

To compare with plasma experiments it is more convenient to write Q/n_0^2 in terms of pressure p. Critical values of the parameter Q/p^2 calculated for different T applying (1) are shown in table 1. Also shown is the vibrational temperature T^*_{vibr} estimated as described above. The temperature is used instead of $E^*_{vibr} = E^{eq}_{vibr}\left(T^*_{vibr}\right)$ as more illustrative quantity. One can see that $\left(Q/p^2\right)_{crit}$ always increases with increased T.

Table 1: Estimate of the critical values of the governing parameter Q/p^2

T, K	T^*_{vibr}, K	$\left(\frac{Q}{p^2}\right)_{crit}$, $\frac{\mathrm{W}}{\mathrm{m^3Pa^2}}$
300	2500..3200	30..40
500	2900..4300	40..60
800	3300..5000	50..90
1200	3700..5500	60..100

Calculation of the volume averaged values of Q/p^2 for the IPP Garching plasma torch experiment [13] gives the following results. In homogeneous mode before contraction the assumption that the plasma occupies the whole diameter of discharge tube yields for the smallest pressure 20 mbar: Q/p^2=30 W/(m^{3}Pa^2). In contracting mode for the plasma size estimated from radiation intensity it is always $Q/p^2 <$6 W/(m^{3}Pa^2).

Accurate reconstructions of the spacial distribution of input power Q have been published for the surfaguide CO_2 plasma conversion experiment at DIFFER. In figure 3 peak values of Q/p^2 calculated taken the data from [14, 15, 16] are shown. One can see that there are only two points which are marginally above $\left(Q/p^2\right)_{crit}$ at T=300 K, one of them at very low pressure 10 mbar.

$Q/p^2 = \left(Q/p^2\right)_{crit}$ merely means that the non-equilibrium vibrational dissociation starts to be visible. One would expect that for this process to be efficient it must be $Q/p^2 = (5..10)\left(Q/p^2\right)_{crit}$. Thus, according to the theory there should be no significant non-equilibrium dissociation in experiments [13, 14, 15, 16] even if the gas temperature would be keep around 300 K. Indeed, in the experiments $T_{vibr} \approx T$, the gas is heated above 2000 K, and CO_2 conversion is largely explained by thermal quenching. To conclude, one can formulate a hypothesis that the non-equilibrium vibrational dissociation is not observed in microwave experiments because Q/p^2 there is too low. In other words, because the specific input power per unit volume Q is not high enough for this process to be activated.

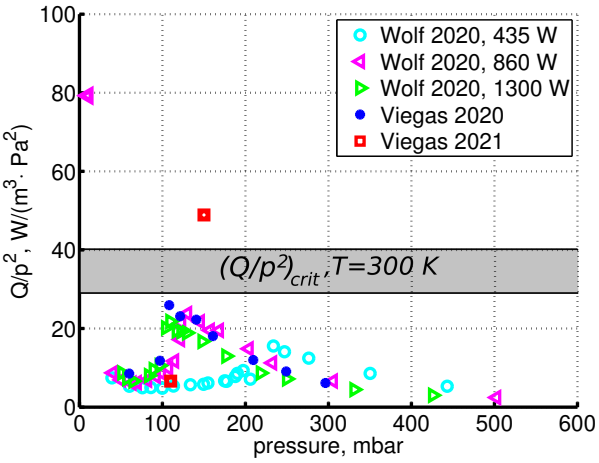

Figure 3: Peak values of Q/p^2 in 2.45 GHz surfaguide experiments [14, 15, 16]

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