# Dissociation of $CO_2$ in nonequilibrium conditions:

## comparison of state-to-state and step-ladder approaches

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# Introduction

The peculiarity of high-temperature chemical reactions is the vibrationally nonequilibrium distribution of participating molecules, which can influence considerably on the rates of transformations. The bright example is the dissociation in vibrationally nonequilibrium conditions, when the vibrational relaxation times are comparable with the dissociation time itself.

The most complicated problem for numerical simulation of these processes is the description of vibration-dissociation coupling of polyatomic molecules, especially in conditions of considerable depletion of vibrational distributions, or in multi-mode nonequilibrium conditions. In all these cases the kinetic master equations (KME) for the dissociating molecules are to be solved.

There exist two different approaches to the solution of KME: exact method based on the state-tostate approach, and approximative one in terms of smooth energetical distributions. The state-to-state distributions may be reduced to the quasi-stationary ones when some kinds of the vibrational energy exchanges occur more rapid compared to the other ones and dissociation-recombination process. Theoretical models of vibration-dissociation coupling of di-atomic molecules, based on the state-to-state kinetics are developed by many authors, we follow here the model given in [1]. The nonequilibrium quasistationary distributions for tri-atomic molecules are derived in [2]. To describe distributions of populations of highly excited states (HES) of dissociating polyatomic molecules the different kinds of diffusion assumptions are used, such as so-called "step-ladder" model, first proposed in [3] and developed in [4].

The main goal of this study is to expand the possibilities given by state-to-state method on the description of vibration-dissociation coupling of tri-atomic molecule like CO<sub>2</sub>, and to compare results with step-ladder solution. This comparison could give the region of the step-ladder approximation applicability and check the results given by this approach. The validity of the quasi-stationary solution is also discussed in the paper. The results of calculations are verified on the experiments [5] in which the multi-mode vibrational nonequilibrium in shock heated mixtures  $CO_2 / N_2 / Ar$  was created and accurate extraction of  $CO_2$  dissociation rate coefficients  $k_{dis}$  by the time-resolved atomic resonance absorption spectroscopy (ARAS) measurements of O-atom formation was carried out. These data are obtained for mixtures 2000 ppm  $CO_2 + N_2$  and 2000ppm  $CO_2 + 10\%N_2 + Ar$  at equilibrium temperatures Teq=2326 - 2855K and pressures P= 0.75 - 2.59 bar. In typical experimental conditions the yield of oxygen atoms was registered during about 100--1000  $\mu$ s after the reflected shock wave arrival (see Fig.1). For the other hand, according to [5], vibrational relaxation times of different modes takes in these conditions up to few hundreds  $\mu$ s.

At first, to describe qualitatively O-atom yields at CO<sub>2</sub> dissociation in vibrationally nonequilibrium conditions the simple simulations with  $k_{dis}$  assumed to be the function of translational (T), symmetric vibrational (T<sub>2</sub>) or asymmetric vibrational (T<sub>3</sub>) temperatures were made. The time profiles of T, T<sub>2</sub>, T<sub>3</sub> were calculated by well known "4-temperature" model for vibrational relaxation in CO<sub>2</sub> + N<sub>2</sub> mixtures [6]. These evaluations revealed that  $k_{dis}$ = f(T) gives O atom yield at a factor of 100 greater and faster than experimental one,  $k_{dis}$ = f(T<sub>2</sub>) - at a factor of 10 more and faster. At the same time  $k_{dis}$ = f(T<sub>3</sub>) fits experimental data within 10-20% (Fig.1). Qualitative explanation of this fact is that the HES of asymmetric mode (v<sub>3</sub>) are on the reaction coordinate. But this result is in contrast with the assumption of mixing of HES of all modes [6].

Hence to analyze results of  $CO_2$  dissociation obtained at vibrational nonequilibrium conditions the time-behavior of various vibrational levels of  $CO_2$  behind shock waves in  $CO_2 / N_2 / Ar$  mixtures have to be studied.



Fig.1. Oxygen atoms concentration time dependence behind the reflected shock waves in mixtures: (a) – 2000 ppm  $CO_2 + N_2$ ,  $T_{eq} = 2754$ K,  $p_{eq} = 2.09$  bar; (b) – 2000ppm  $CO_2 + 10\%N_2 + Ar$ ,  $T_{eq} = 2595$ K,  $p_{eq} = 0.78$  bar. Curves marked  $O(T_3)$  and  $O(T_2)$  – numerical simulations of O - atoms formation in assumptions  $k_{dis} = f(T_3)$  and  $k_{dis} = f(T_2)$  correspondently.

#### State-to-state model

In the state-to-state approximation the equations for the vibrational level populations  $n_i$  are coupled with the conservation equations and form the closed system for the gas flow parameters:  $n_i$ , macroscopic velocity **v** and gas temperature T. The state-to-state distributions in CO<sub>2</sub> depend on the vibrational levels of three modes  $n_{i1i2i3}$  which are strongly coupled due to anharmonism of vibrations. Anharmonic effects become important even at low levels of CO<sub>2</sub> molecules. The equations for  $n_{i1i2i3}$  contain the state-to-state rates of dissociation, recombination and vibrational energy transitions due to the energy exchange within each mode, between different modes and vibration-translation energy transfer. The fixed number of excited levels in each mode has been considered, and the state-to-state distributions have been computed using the Gear method.

The quasi-stationary solution of KME is obtained taking into account the different rates of vibrational energy exchanges and assuming the relaxation time of the most rapid process to be equal to zero. Thus, it is known that in the vibrationally excited gas the relaxation times of VV exchange within modes are much shorter compared to the characteristic times of other processes. In this case the level populations  $n_{i1i2i3}$  can be expressed in terms of the vibrational temperature of the first level in all three modes and the translational temperature (four-temperature approach, [2]). Instead of KME for a big number of vibrational levels the relaxation equations for the vibrational temperatures should be solved together with the conservation equations.

Moreover, the exchange of vibrational energy between the symmetric and bending modes proceeds more rapidly than the exchange with the asymmetric mode due to the Fermi resonance. Using this assumption the four-temperature approach may be reduced to the three-temperature one because the temperatures of the symmetric and bending modes are not independent.

### **Mode-ladder model**

The step-ladder approach was applied to these conditions as mode-ladder model by the following way: 1) all modes were considered separately as independent "ladders" with all possible processes of energy transfer between them; 2) low-lying levels in each mode and rate constants of transitions between them were described exactly; 3) higher levels were taken in "step-ladder" approximation for each ladder with the model energetical density of states  $\rho(i)$  [4].

The CO<sub>2</sub> molecule was considered as a system with two types of vibrations: 1) symmetric vibrations -- symmetric ( $v_1$ ) and bending ( $v_2$ ) CO<sub>2</sub> own modes; 2) asymmetric vibrations -- CO<sub>2</sub> asymmetric mode ( $v_3$ ). All CO<sub>2</sub> vibrations were considered to be harmonic oscillators, N<sub>2</sub> molecule was simulated as Morse oscillator with vibrational frequency  $v_4$ . The following physical vibrational levels were considered separately: 3 lower levels of symmetric vibrations which correspond to 3 levels of bending vibrations; 1st level of asymmetric vibrations and 1st level of N<sub>2</sub> vibrations.

The next energy-exchange processes and chemical reactions were included into the kinetical scheme:

1. The conventional V-T, V-V and V-V'-relaxation of low-lying vibrational levels of different modes;

2. Step-ladder excitation of higher vibrational levels with the united step-size for each mode  $\Delta E$  and rate constants, written for actual numbers n of the corresponding physical vibrational levels in Landau-Teller approximation;

3. The energy-exchange processes between HES:

(a)  $CO_2(i,j,k) + M \rightarrow CO_2(i,j-3,k+1) + M$ 

(b)  $CO_2(i,j,k) + N_2(l) \rightarrow CO_2(i,j,k-1) + N_2(l+1);$ 

4. The spontaneous decay of over-barrier HES in RRKM approximation .

At conditions of experiments performed the CO<sub>2</sub> dissociation was assumed to proceed only through the lowest spin-forbidden channel  $CO_2(X^1\Sigma) \rightarrow CO_2({}^{3}B_2) \rightarrow O + O({}^{3}P)$ . The fast reactions of O-atoms with  $N_2$  and secondary bimolecular reactions in the system of O-C-N-atoms were considered. For the reaction  $O + N_2 \rightarrow N + NO$  the activation energy was reduced by the mean vibration energy of nitrogen molecules (mode  $v_4$ ). The details of mode-ladder model one can find in [5].

### **Results and discussion**

The nonequilibrium vibrational distributions of  $CO_2$  molecules have been computed taking into account dissociation and different vibrational energy exchanges. The most rigorous state-to-state model is based on the KME for level populations of different modes and takes into account strong coupling between modes due to anharmonism of vibrations. The quasi-stationary models are much more simple and are based on the multi-temperature nonequilibrium distributions over vibrational levels. The four-temperature and three-temperature models have been considered. These distributions are not valid in the beginning of the relaxation zone behind shock waves and are established under the conditions of rapid vibrational energy exchange within all three modes and between the symmetric and bending modes.

The vibrational relaxation coupled with the thermal dissociation of three-atomic molecule could be well described by the mode-ladder model also. The kinetic mechanism of HES of  $CO_2$  and  $N_2$  interaction is proposed and the rate constants of the microscopic processes considered are deduced by the fitting of calculations and experimental data (Fig. 1). The essence of the mechanism proposed is as following:

-- decomposition of  $CO_2$  molecules occurs from the HES of the asymmetric mode, by the "weak" collisions mechanism;

-- the effective interaction between near-threshold states of symmetric and asymmetric modes exists and at vibrationally equilibrium conditions this leads to equalizing of the both mode temperatures;

-- the strong energy-exchange between HES of asymmetric mode and with  $N_2$  vibrations is also essential and at nonequilibrium conditions this leads to considerable depletion of decomposing states populations and hence to decrease of dissociation rate.

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