

Advanced Models of Vibration-Dissociation Kinetics in Mixtures Containing CO₂

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Abstract. In the present paper, vibration-dissociation kinetics in strongly non-equilibrium flows of mixtures containing CO₂ molecules is studied. Quasi-stationary approaches of the kinetic theory are used, and a self-consistent closed description of a gas flow is proposed for different relations between relaxation times of considered processes. Gas dynamic equations are coupled to the equations of multi-temperature vibrational-chemical kinetics in a flow. The main attention is focused on the four-temperature approximation for CO₂/N₂ mixture. The source terms in the kinetic equations are expressed in terms of state-dependent rate coefficients which can be calculated using experimental data or elementary processes theory. The model is applied for calculation of gas dynamic parameters, non-equilibrium distributions and mixture composition in a relaxation zone behind shock waves. The influence of strongly non-equilibrium kinetics on gas dynamics is evaluated.

Keywords: Carbon dioxide, Non-equilibrium vibration-chemical kinetics, Inter-mode exchange, Shock heated flow

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INTRODUCTION

A problem of correct simulation of vibration-dissociation kinetics in CO₂ mixtures is widely discussed in the literature [1, 2, 3, 4, 5, 6, 7, 8] but still remains to be far from the complete resolution. It is well known that CO₂ molecules possess several vibrational modes (symmetric, bending and asymmetric ones), and therefore vibrational relaxation proceeds through numerous relaxation channels including intra-mode VV transitions, inter-mode VV' transfers and VT exchanges. The rates of these processes vary with temperature according to different laws, and under specific flow conditions various relaxation mechanisms can prevail. Moreover, anharmonism of molecular vibrations can play a significant role in CO₂ kinetics. These peculiarities should be taken into account to develop an accurate model of vibration-dissociation kinetics of polyatomic gas mixtures. Nevertheless, the majority of computational fluid dynamics (CFD) codes use rather simple descriptions of CO₂ kinetics such as a one-temperature model assuming vibrational degrees of freedom to be in thermal equilibrium, or a model with indistinguishable vibrational modes, which assigns a single vibrational temperature to all CO₂ modes. In the majority of CO₂ models used in CFD, anharmonic effects of vibrations are neglected.

The objective of this study is to develop and compare more realistic approaches taking into account complex CO₂ structure, anharmonism of vibrations and different rates of vibrational transitions. The most detailed state-to-state description considered in [7] appears to be rather precise but hardly realizable in engineering applications due to the high computational cost. Therefore it is important to introduce reliable multi-temperature models providing a satisfactory description of a non-equilibrium flow under specific conditions; one can find some ideas on different quasi-stationary approaches in [5, 6, 7, 8]. A choice of a model depends on relations between relaxation times of considered kinetic and gas dynamic processes. In the present contribution, several models are considered for CO₂/N₂ mixture. The main attention is focused on the four-temperature model introducing a single vibrational temperature T_{12} for coupled symmetric and bending CO₂ modes and vibrational temperatures T_3 and T_4 for CO₂ asymmetric mode and N₂ respectively.

In the frame of this model, we have developed a self-consistent closed flow description including coupling of conservation and relaxation equations and correct expressions for the production terms. In the existing multi-temperature approaches, the vibrational production terms are usually written in terms of relaxation times of slow processes, which can be found from experimental data. In the case of CO₂ mixtures, direct measurements of numerous relaxation times of intra-, inter-mode and VT transitions are not feasible. In order to eliminate this problem, we use here some advantages of the state-to-state model: the production terms in the relaxation equations are expressed in terms of the

state-dependent rate coefficients calculated using experimental data and analytical SSH theory. Similar improvement is introduced for the calculation of dissociation source terms: the state-dependent Treanor-Marrone dissociation rate coefficients [7] are averaged with the corresponding vibrational distribution. Developed models are applied for the investigation of CO₂/N₂ flows behind shock waves; the influence of complex kinetics on the flow parameters is evaluated; ranges of various models applicability are determined.

THEORETICAL MODELS

Under strong non-equilibrium conditions some of kinetic processes proceed in the gasdynamic time scale and therefore gas dynamic equations should be considered together with the equations of non-equilibrium kinetics in a flow. The most rigorous kinetic model is the state-to-state one. This model is appropriate for the conditions when all vibrational energy exchanges and chemical reactions proceed simultaneously with gas dynamic processes and occur slower than transitions of translational and rotational energies. In the frame of this approach conservation equations for macroscopic parameters are coupled to the equations for state-to-state distributions. This approach has been successfully developed during last years and used for different gas dynamic problems for diatomic gases. For CO₂/N₂ mixtures, the flow equations in the state-to-state approximation are given in [7]. Compared to diatomic gases, practical implementation of such a model to CFD codes for polyatomic gases appears to be too numerically expensive due to the necessity of including many vibrational levels for each CO₂ mode and consequently solving many equations for level populations. More simple multi-temperature models are based on quasi-stationary distributions.

A five-temperature model is based on the assumption of rapid intra-mode VV relaxation compared to inter-mode VV' and VT processes. In this case all CO₂, N₂ level populations are expressed in terms of vibrational temperatures of the first levels of three CO₂ modes T_m ($m = 1, 2, 3$) and T_4 for N₂. The equations for T_m ($m = 1, 2, 3, 4$), gas temperature T , velocity \mathbf{v} and mixture composition represent a closed set of flow equations in the 5-temperature approximation.

This model can be simplified using an assumption about rapid VV' ₁₋₂ exchange between symmetric and bending modes, which allows for introducing the combined vibrational temperature of these modes T_{12} . The set of macroscopic parameters in this case consists of T_{12} , T_3 , T_4 , T , \mathbf{v} and number densities of species n_c . A three temperature model supposes that transitions between N₂ and CO₂ asymmetric mode also proceed fast, thus providing a single vibrational temperature of these modes T_{34} . A two temperature model assumes slow relaxation of CO₂ asymmetric mode and nitrogen with the single vibrational temperature while all the remaining modes are in thermal equilibrium due to rapid vibrational energy exchanges within and between these modes. And, finally, if only dissociation-recombination reactions proceed in the gasdynamic time scale whereas all vibrational energy transitions occur faster than chemical reactions, a thermally equilibrium one-temperature model of strongly non-equilibrium chemical kinetics is appropriate for a flow description.

In the next sections we consider the four temperature kinetic model which is based on the experimentally justified assumption of rapid VV' ₁₂ exchange caused by the Fermi-resonance, and at the same time provides an accurate description of all other vibrational energy transitions.

GOVERNING EQUATIONS

In the four-temperature approximation, when anharmonism of vibrations is taken into account, level populations of CO₂ have the form of the generalized Treanor distribution [7] and are defined by the temperatures T_{12} , T_3 , T . N₂ level populations are described by the Treanor distribution depending on T_4 and T . The set of equations for the mixture containing dissociating CO₂ molecules, products of dissociation CO and O, non-dissociating N₂ in the Euler approximation has the form:

$$\frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0, \quad (1)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla p, \quad (2)$$

$$\rho \frac{du}{dt} + p \nabla \cdot \mathbf{v} = 0, \quad (3)$$

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} = R_c^{diss}, \quad c = \text{CO}_2, \text{CO}, \text{O}, \quad (4)$$

$$\rho_{CO_2} \frac{dW_{12}}{dt} = R_{12} - m_{CO_2} W_{12} R_{CO_2}^{diss}, \quad (5)$$

$$\rho_{CO_2} \frac{dW_3}{dt} = R_3 - m_{CO_2} W_3 R_{CO_2}^{diss}, \quad (6)$$

$$\rho_{N_2} \frac{dW_4}{dt} = R_4. \quad (7)$$

Here ρ is the mixture density, p is the pressure, u is the total energy per unit mass, n_c and ρ_c are the number and mass densities of species c , W_{12} , W_3 , W_4 are the mean numbers of vibrational quanta in the combined (symmetric+bending), asymmetric CO_2 modes and N_2 respectively. The production term due to dissociation in equation (4) is given by the following expression:

$$R_{CO_2}^{diss} = \sum_M n_M (k_{rec,CO_2}^M(T) n_{CO} n_O - k_{CO_2,diss}^M(T, T_{12}, T_3) n_{CO_2}) \quad (8)$$

$k_{CO_2,diss}^M(T, T_{12}, T_3)$ is the three-temperature dissociation rate coefficient for a reaction involving a partner M ($M=CO_2$, CO , O , N_2); $k_{rec,CO_2}^M(T)$ is the recombination rate coefficient. The multi-temperature dissociation rate coefficient can be calculated using the state-to-state rate coefficient $k_{i_1 i_2 i_3, diss}^M(T)$

$$k_{CO_2,diss}^M = \frac{1}{n_{CO_2}} \sum_{i_1, i_2, i_3} n_{i_1 i_2 i_3} k_{i_1 i_2 i_3, diss}^M(T), \quad (9)$$

where vibrational level populations $n_{i_1 i_2 i_3}$ can be described by various quasi-stationary distributions accordingly to the chosen model. The state-to-state rate coefficients of dissociation from each CO_2 vibrational level are found using the Treanor-Marrone model [9] extended for three-atomic molecules. Thus the state-to-state dissociation rate coefficient $k_{i_1 i_2 i_3, diss}^M(T)$ can be connected with the thermal equilibrium dissociation rate coefficient $k_{eq, diss}^M$ by the expression:

$$k_{i_1 i_2 i_3, diss}^M(T) = \frac{Z_{vibr}(T)}{Z_{vibr}(-U)} \exp\left(\frac{\epsilon_{i_1 i_2 i_3}}{k} \left(\frac{1}{T} + \frac{1}{U}\right)\right) k_{eq, diss}^M \quad (10)$$

where $\epsilon_{i_1 i_2 i_3}$ is the vibrational energy of a CO_2 molecule, Z_{vibr} is the equilibrium vibrational partition function, U is the parameter of the model. The recombination rate coefficients are connected to $k_{CO_2, diss}^M$ by the detailed balance principle.

The source terms in Eqs. (5)–(7) describe variation of the mean numbers of vibrational quanta due to different slow VV' and VT_m energy transitions, dissociation and recombination:

$$R_{12} = \sum_{i_1, i_2, i_3} (i_1 \epsilon_{100} + i_2 \epsilon_{010}) \left(R_{i_1 i_2 i_3}^{VV'_{2-3}} + R_{i_1 i_2 i_3}^{VV'_{1-2-3}} + R_{i_1 i_2 i_3}^{VV'_{3-4}} + R_{i_1 i_2 i_3}^{VT_2} + R_{i_1 i_2 i_3}^{diss} \right), \quad (11)$$

$$R_3 = \sum_{i_1, i_2, i_3} i_3 \epsilon_{001} \left(R_{i_1 i_2 i_3}^{VV'_{2-3}} + R_{i_1 i_2 i_3}^{VV'_{1-2-3}} + R_{i_1 i_2 i_3}^{VV'_{3-4}} + R_{i_1 i_2 i_3}^{VT_2} + R_{i_1 i_2 i_3}^{diss} \right), \quad (12)$$

$$R_4 = \sum_{i_4} i_4 \epsilon_1^{N_2} \left(R_{i_4}^{VV'_{3-4}} + R_{i_4}^{VT_4} \right), \quad (13)$$

where ϵ_{100} , ϵ_{010} , ϵ_{001} , $\epsilon_1^{N_2}$ are the vibrational energies of the first levels in corresponding CO_2 modes and N_2 , $R_{i_1 i_2 i_3}^{(\gamma)}$ are the state-to-state production terms connected to the collision process γ . These production terms are determined by the state-dependent rate coefficients of processes γ . It should be noted that VT_1 and VT_3 processes are neglected here because VT relaxation of CO_2 proceeds mainly through the VT_2 channel.

RESULTS

Eqs. (1)–(7) have been solved numerically for a one-dimensional quasi-stationary flow behind a shock wave at the following conditions in the free stream: $M_0 = 8$, $T_0 = 293$ K, $p_0 = 100$ Pa, $n_{CO_2}/n = 0.8$. Calculation of vibrational and dissociation source terms have been performed using four temperature vibrational distributions as well as experimental and theoretical data for the state-dependent rate coefficients of vibrational transitions. Thus, the state-dependent

vibrational rate coefficients for the transitions between low levels have been calculated using either experimental data [10, 11] or analytical expressions of the first-order perturbation SSH theory [12]. The transitions between higher states are described by the generalized SSH theory. Dissociation source terms contain multi-temperature reaction rate coefficients. For the calculation of dissociation rate coefficients, expressions (9)–(10) have been used. The results obtained for the relaxation zone behind a shock are discussed below.

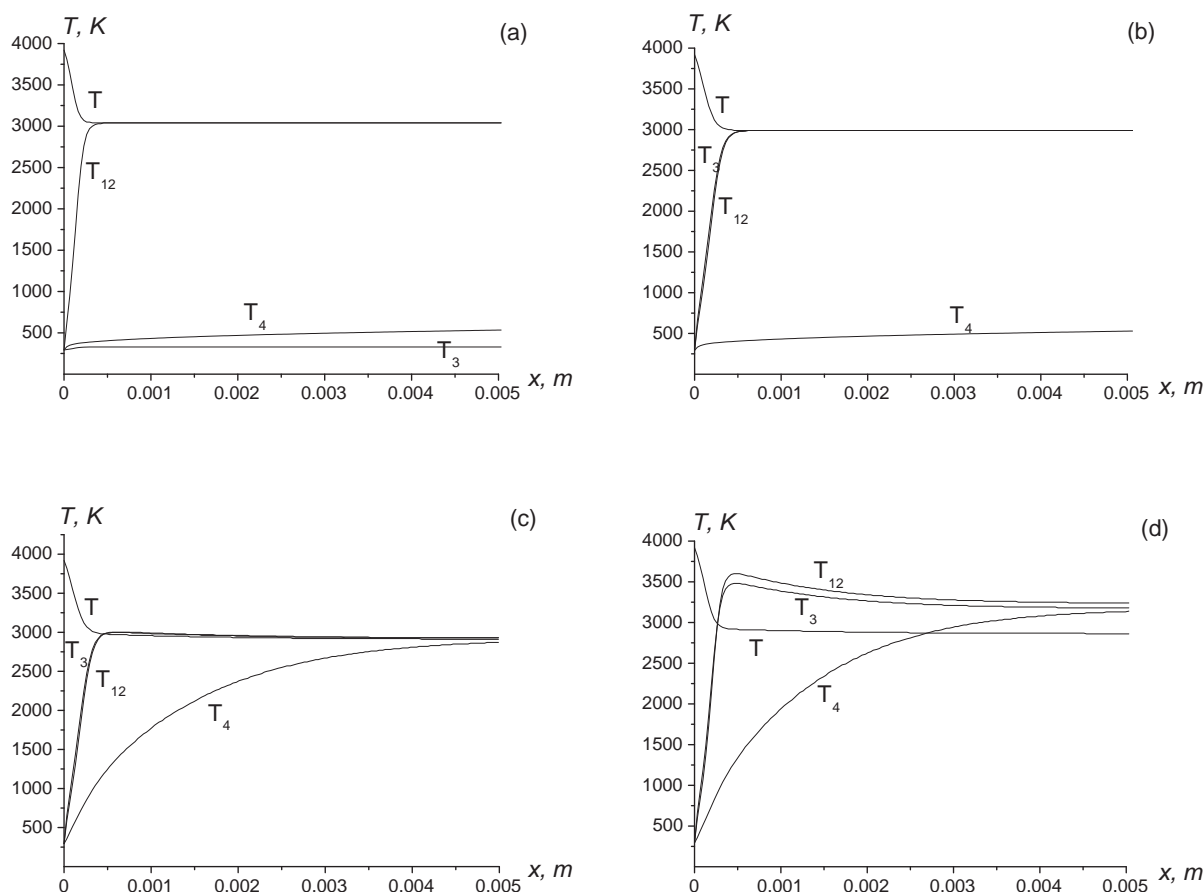


FIGURE 1. Temperature distribution for different schemes. Model [10]. (a): VT_2+VT_4 ; (b): $VT_2+VT_4+VV'_{2-3}+VV'_{1-2-3}$; (c): $VT_2+VT_4+VV'_{2-3}+VV'_{1-2-3}+VV'_{3-4}$; (d): $VT_2+VT_4+VV'_{2-3}+VV'_{1-2-3}+VV'_{3-4}+diss$

Fig. 1 presents vibrational and gas temperatures as functions of a distance from the shock front. Rate coefficients of vibrational transitions are calculated using [10]. Four kinetics schemes of slow processes are considered involving successively following transitions:

1. Only VT transitions are taken into account: VT_2+VT_4 ;
2. Inter-mode exchanges in CO_2 are included: $VT_2+VT_4+VV'_{2-3}+VV'_{1-2-3}$;
3. Exchange between N_2 and CO_2 asymmetric mode is added: $VT_2+VT_4+VV'_{2-3}+VV'_{1-2-3}+VV'_{3-4}$;
4. Finally, dissociation is also included to the kinetic scheme: $VT_2+VT_4+VV'_{2-3}+VV'_{1-2-3}+VV'_{3-4}+diss$.

In all schemes VT_1 and VT_3 transitions are neglected because in CO_2 the preferential channel of VT relaxation corresponds to the bending mode. The results show the role of different strongly non-equilibrium processes in the relaxation zone. Thus one can conclude that the main channel of relaxation in the asymmetric mode is inter-mode exchange VV'_{2-3} and VV'_{1-2-3} ; nitrogen attains equilibrium mainly through inter-molecular VV'_{3-4} transitions, whereas the

coupled (symmetric+bending) CO_2 mode goes to equilibrium through VT_2 relaxation mechanism. Including dissociation changes noticeably the behaviour of vibrational temperatures. Furthermore, it is found that for shock heated gases, the role of anharmonicity in gas dynamics appears to be weak (its contribution to temperatures does not exceed 5%).

Fig. 2 plots gas temperature and all vibrational temperatures versus x calculated for the kinetic scheme 3 using three models for rate coefficients of vibrational transitions: (1): analytical SSH model [12] for all vibrational states, and (2), (3): semi empirical models [10] and [11] based on different experimental data for the transitions between low levels and using the SSH theory for computing the transitions between higher states.

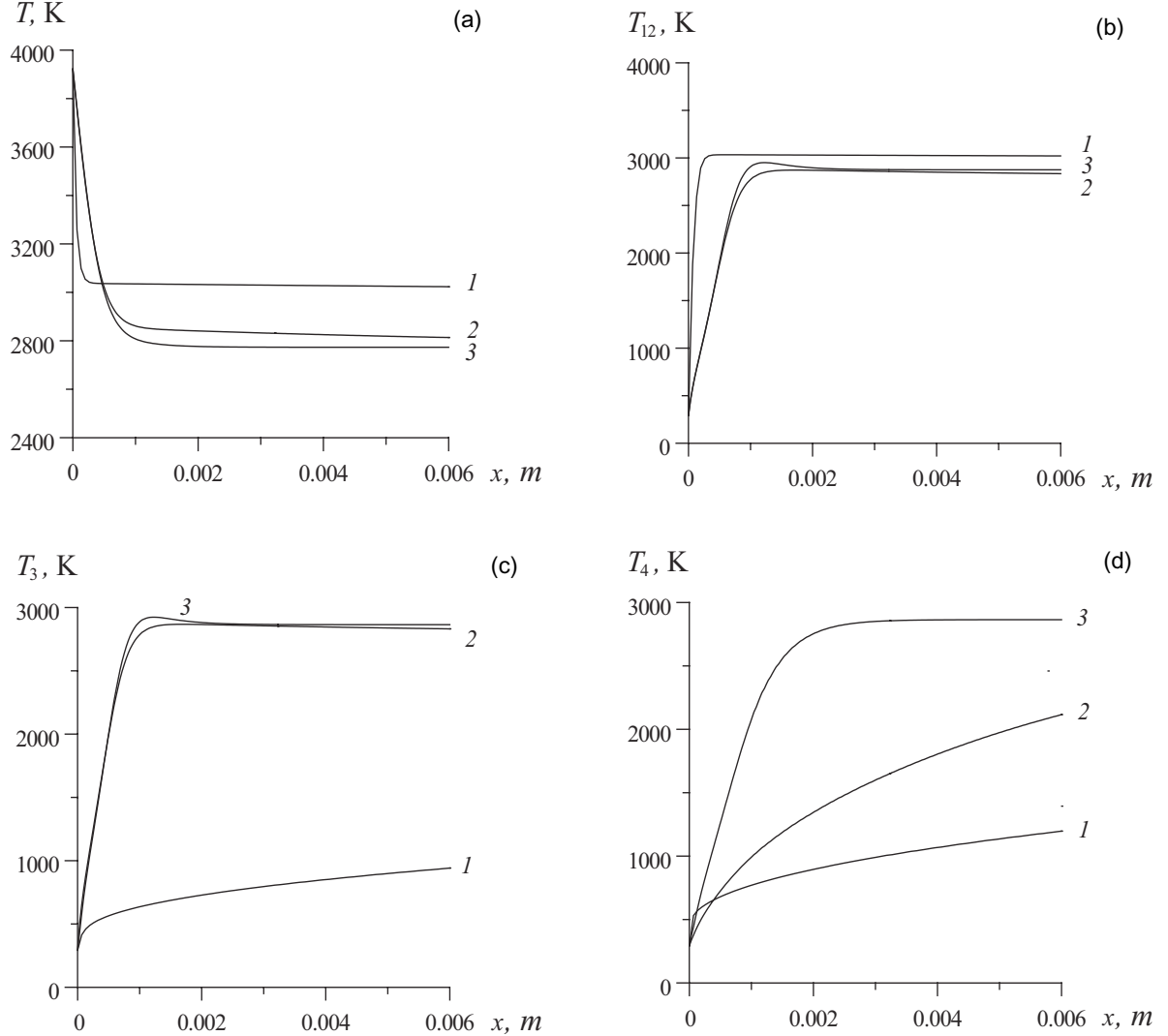


FIGURE 2. Gas temperature T (a), vibrational temperatures of the combined and asymmetric modes CO_2 (b), (c), and of N_2 (d). Curves 1 — SSH model; 2 — model [10]; 3 — model [11]

One can observe that semi empirical models provide rather close results for the gas temperature and temperatures T_{12} , T_3 whereas there is a noticeable discrepancy in the temperature T_4 , which is explained by a considerable difference in the rates of VV'_{3-4} transitions. On the other hand, the analytical SSH model gives essentially different results compared to the experimental models. Since the rates of inter-mode exchanges given by models [10] and [11] are significantly higher, temperatures T_{12} and T_3 equalize rapidly for these models; for the SSH model, temperature T_3 remains low for a long time due to the weak contribution of inter-mode VV'_{2-3} and VV'_{1-2-3} to the vibrational

kinetics. The rate of VT₂ exchange obtained using the SSH theory exceeds the one given by empirical models, therefore, for the SSH model, temperatures T and T_{12} come to local equilibrium much faster.

It should be taken into account that experimental measurements of rate coefficients [10, 11] have been performed under low temperature conditions appropriate for laser applications. Using these data for the investigation of shock heated gases should be additionally justified. On the contrary, the SSH theory has been developed for moderate and high temperature conditions. However, analytical expressions for probabilities of vibrational transitions in CO₂ contain some parameters which require a correct definition. Therefore the present analysis of theoretical and experimental models has a qualitative character. In order to give some recommendations on the choice of a model, the gas flow parameters calculated numerically should be validated against corresponding experimentally measured values.

CONCLUSIONS

In the present paper, non-equilibrium vibration-dissociation kinetics in a CO₂/N₂ mixture is studied on the basis of the four-temperature approximation of the kinetic theory. Gas dynamic equations are coupled to the equations of four-temperature vibrational-chemical kinetics and applied to a flow behind a shock wave. For the rates of vibrational transitions and dissociation, available data on the state-to-state rate coefficients for corresponding processes are used. The analysis shows that for a correct prediction of gas flow parameters, an accurate choice of a kinetic model as well as a model for the elementary processes is of crucial importance.

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