

State-to-state nonequilibrium reaction rates

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Abstract

The paper studies the strongly nonequilibrium vibrational and chemical kinetics in a reacting gas flow in the state-to-state approach. Considered are exchange reactions, dissociation and recombination. The algorithms for calculation of reaction rate coefficients, depending on vibrational levels of components are developed on the basis of the kinetic theory. Formulas for reaction rate coefficients are obtained taking into account non-maxwellian velocity distributions. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The influence of chemical reactions on the molecular distributions and gas flow parameters is of great importance in many problems of aerothermodynamics, chemical technology and other fields of science and applications. This subject has been investigated on the basis of the kinetic theory by many authors starting from Refs. [1,2]. The nonequilibrium contributions to the rates of chemical reactions were studied in Refs. [3,4], later this problem was considered by several authors using different models for vibrational distributions. The majority of the models are based on the weakly nonequilibrium one-temperature distribution or on the quasi-stationary multi-temperature distributions over vibrational levels. In recent years the necessity of the detailed multi-level modelling of strongly nonequilibrium flows has been understood. The approximate solution of the Boltzmann equation in the state-to-state approach has been obtained in Ref. [5] with generalized Chapman-Enskog method and was used for the investigation of strongly nonequilibrium transport

properties in various gas flows: behind shock waves [6,7], in a hypersonic boundary layer [8,9], in a nozzle expansion [10]. The nonequilibrium non-Arrhenius dissociation rates have been found in Refs. [11,12], using the state-to-state vibrational level populations with the Maxwell distributions over velocities. These rates correspond to the zero order generalized Chapman-Enskog solution. However the development of the Navier-Stokes computing codes for viscous heat conductive gas flows with strong vibrational and chemical nonequilibrium requires the simulation of the state-to-state rates of vibrational and chemical transitions in the first order non-maxwellian approximation. The first steps in this direction were done in Refs. [13,14], for a one-component vibrationally excited gas. Non-maxwellian effects on dissociation rates were considered in Ref. [15] in the case of a weak deviation from the equilibrium over vibrational energy.

The present paper deals with the simulation of the state-to-state reaction rates under the conditions of strong both vibrational and chemical nonequilibrium. The Navier-Stokes equations are coupled with the

equations for the vibrational level populations for molecular species. These equations contain the first order rates of vibrational energy transitions and chemical reactions depending on the vibrational levels of colliding molecules which, as well as the transport terms, can be found using the distribution functions over velocities and internal energies. We use the distribution functions derived in Ref. [5] in the state-to-state approximation and develop the algorithms for the calculation of the zero order and first order rates of vibrational energy transitions, exchange reactions and dissociation.

2. Macroscopic equations

We consider a nonequilibrium reactive flow of a gas mixture with internal modes and chemical reactions. In the state-to-state approximation the closed set of the equations for the nonequilibrium flow parameters are the equations for the vibrational level populations of molecular species and number densities of atomic species, coupled with the conservation equations for the momentum and total energy:

$$\frac{dn_{ci}}{dt} + n_{ci} \nabla \cdot \mathbf{v} + \nabla \cdot (n_{ci} \mathbf{V}_{ci}) = R_{ci},$$

$$c = 1, \dots, L, i = 0, 1, \dots, L_c \quad (1)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (2)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0. \quad (3)$$

Here n_{ci} is the population of the i th level of c species (for atomic species $n_{ci} = n_c$), ρ , \mathbf{v} are the gas density and macroscopic velocity, L is the number of chemical species, L_c is the number of excited vibrational levels of species c , U is the total energy per unit mass:

$$\rho U = \frac{3}{2} n k T + \rho E_r + \rho E_v + \rho E_f.$$

Here $n = \sum_{ci} n_{ci}$ is the total number of particles, k is the Boltzmann constant, T is the gas temperature,

$$\rho E_r(T) = \sum_{cij} \int \varepsilon_j^{ci} f_{cij} d\mathbf{u}_c, \quad \rho E_v = \sum_{ci} \varepsilon_i^c n_{ci},$$

$$\rho E_f = \sum_c \varepsilon^c n_c,$$

E_r and E_v are, respectively, the rotational and vibra-

tional energy per unit mass. Here ε_j^{ci} is the rotational energy of a molecule of species c at the i th vibrational level, $f_{cij} = f_{cij}(\mathbf{r}, \mathbf{u}_c, t)$ is the distribution function for every chemical species c , vibrational i and rotational energy level j over the velocities \mathbf{u}_c , the spatial and temporal co-ordinates, ε_i^c is the vibrational energy of a molecule of species c , counted from the minimum of its potential curve, $\varepsilon^c = -D_c$, D_c is the energy of dissociation of molecular species c , $n_c = \sum_i n_{ci}$.

Eqs. (1)–(3) contain the transport terms: the diffusion velocities of c species at the i th level \mathbf{V}_{ci} , the pressure tensor \mathbf{P} and the total energy flux \mathbf{q} , and the production terms R_{ci} . The expressions for the transport properties are given in Ref. [5]. The right hand sides of Eqs. (1) R_{ci} describe the change of molecules of c species at i th level due to the collisions and are expressed in terms of the collision integrals for slow processes:

$$R_{ci} = \sum_j \int J_{cij}^{sl} d\mathbf{u}_c = \sum_j \int (J_{cij}^{vibr} + J_{cij}^{react}) d\mathbf{u}_c$$

$$= R_{ci}^{vibr} + R_{ci}^{react}, \quad (4)$$

The collision integrals J_{cij}^{vibr} and J_{cij}^{react} corresponding to the collisions with vibrational energy transitions and chemical reactions can be found in Refs. [2,16–18]. For diatomic molecules J_{cij}^{vibr} has the following form:

$$J_{cij}^{vibr} = \sum_{dkl'i'j'k'l'} \int \left(f_{ci'i'j'} f_{dk'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'j'}^c s_{k'l'}^d} - f_{cij} f_{dkl} \right)$$

$$\times g \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d, \quad (5)$$

where s_{ij}^c and s_{kl}^d are the statistical weight factors and $\sigma_{cd,ijkl}^{i'j'k'l'}$ is the cross section of the collision leading to the vibrational energy change for the molecules of chemical species c and d , respectively at the i th and k th vibrational levels and j th and l th rotational ones; i' , j' , k' , l' are the labels of the energy levels after collision; $\mathbf{g} = \mathbf{u}_c - \mathbf{u}_d$ is the relative velocity, and $d^2\Omega$ is the solid angle referring to the relative velocity after collision. The integral J_{cij}^{react} may be split into parts corresponding to collisions

with chemical exchange reactions and collisions with dissociation and recombination:

$$J_{cij}^{\text{react}} = J_{cij}^{2 \leftrightarrow 2} + J_{cij}^{2 \leftrightarrow 3}, \quad (6)$$

$$J_{cij}^{2 \leftrightarrow 2} = \sum_{d'c'd'kl'j'k'l'} \int \left(f_{c'i'j'} f_{d'k'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'j'}^{c'} s_{k'l'}^{d'}} \left(\frac{m_c m_d}{m_{c'} m_{d'}} \right)^3 - f_{cij} f_{dkl} \right) g \sigma_{cd,ijkl}^{c'd',i'j'k'l'} d^2\Omega d\mathbf{u}_d, \quad (7)$$

where $\sigma_{cd,ijkl}^{c'd',i'j'k'l'}$ is the cross section of the collision with a bimolecular reaction. The expression for $J_{cij}^{2 \leftrightarrow 3}$ in a mixture of diatomic molecules and atoms can be written in the form:

$$J_{cij}^{2 \leftrightarrow 3} = \sum_{dkl} \int f_{dkl} \left(f_{c'} f_{f'} h^3 s_{ij}^c \left(\frac{m_c}{m_{c'} m_{f'}} \right)^3 - f_{cij} \right) \times g \sigma_{cij,d}^{\text{diss}} d\mathbf{u}_d d\mathbf{u}_{c'} d\mathbf{u}_{f'} d\mathbf{u}'_d, \quad (8)$$

where $\sigma_{cij,d}^{\text{diss}}$ is the cross section for dissociation of the molecule of c th species at the i th and j th vibrational and rotational levels in a collision with the molecule of d th species; c' , f' are the atomic species of dissociation products, \mathbf{u}_c , \mathbf{u}_d and $\mathbf{u}_{c'}$, $\mathbf{u}_{f'}$, \mathbf{u}'_d are the velocities of particles before and after collision respectively. Usually it is supposed that the dissociation cross section does not depend on the internal energy levels of the partner and that these levels do not change in the result of reaction. Hereafter we use this assumption.

The transport and production terms in Eqs. (1)–(3) are defined by the distribution functions. Previously we investigated the transport terms in these equations using the distribution functions found by the generalized Chapman-Enskog method in the state-to-state approach [5]. In the present paper we use this method and consider the production terms in Eqs. (1) in the zero and first order approximation.

The distribution functions in the generalized Chapman-Enskog method [5] are found as a power series over a small parameter ε equal to the ratio of the mean times of rapid and slow processes:

$$f_{cij} = f_{cij}^{(0)} + \varepsilon f_{cij}^{(1)} + \dots \quad (9)$$

The zero order distribution functions are given by:

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT} \right)^{3/2} s_j^{ci} \frac{n_{ci}}{Z_{ci}^{\text{rot}}(T)} \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT} \right) \quad (10)$$

where m_c is the molecular mass, Z_{ci}^{rot} is the rotational partition function, $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$ is the peculiar velocity. The first order distribution functions take the form $f_{cij} = f_{cij}^{(0)} + \varepsilon f_{cij}^{(1)}$, where

$$f_{cij}^{(1)} = f_{cij}^{(0)} \phi_{cij} = f_{cij}^{(0)} \left(-\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_{dk} \mathbf{D}_{cij}^{dk} \cdot \mathbf{d}_{dk} - \frac{1}{n} \mathbf{B}_{cij} \cdot \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right), \quad (11)$$

\mathbf{d}_{dk} are the diffusion driving forces. The functions \mathbf{A}_{cij} , \mathbf{B}_{cij} , \mathbf{D}_{cij}^{dk} , F_{cij} and G_{cij} are found from the linear integral equations given in Ref. [5]. These equations contain the linearized operator of rapid processes: elastic collisions and the ones leading to the RT exchange. For the unity of solution of the integral equations the additional constraints on the functions \mathbf{A}_{cij} , \mathbf{B}_{cij} , \mathbf{D}_{cij}^{dk} , F_{cij} and G_{cij} are derived from normalization conditions for the distribution functions. These constraints are obtained in Ref. [5].

3. Production terms

The expressions for the production terms R_{ci} in Eqs. (1) are obtained substituting Eq. (9) into Eq. (4). Restricting our consideration to the first order terms we obtain:

$$R_{ci}^{\text{vibr}} = \sum_{dkl'k'} (n_{c'i} n_{dk'} P_{cd'i'k'}^{ik} - n_{ci} n_{dk} P_{cdik}^{i'k'}), \quad (12)$$

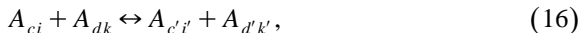
$$R_{ci}^{2 \leftrightarrow 2} = \sum_{dkc'd'j'k'} (n_{c'i} n_{d'k'} P_{c'd'i'k'}^{cdik} - n_{ci} n_{dk} P_{cdik}^{c'd'j'k'}), \quad (13)$$

$$R_{ci}^{2 \leftrightarrow 3} = \sum_{dk} n_{dk} (n_{c'} n_{f'} P_{rec,dk}^{ci} - n_{ci} P_{ci,dk}^{\text{diss}}), \quad (14)$$

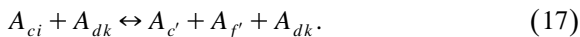
where the rate coefficients $P_{cdik}^{i'k'}$, $P_{cdik}^{c'd'i'k'}$, $P_{rec,dk}^{ci}$, $P_{ci,dk}^{diss}$ correspond to the vibrational energy transfers:



exchange reactions:



and dissociation–recombination reactions:



We would like to note that Eq. (15) describes VT(TV) exchanges when $k' = k$ or when the particle A_d is an atom, if $c = d$ Eq. (15) corresponds to the VV exchange between the molecules of the same chemical species, and for $c \neq d$ Eq. (15) describes the VV' exchange between different chemical species. Also, in reaction Eq. (16) the partner A_d may be molecule or atom. In the last case



For the vibrational energy transitions we have:

$$P_{cdik}^{i'k'} = \sum_{j'l'j''} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (1 + \varepsilon(\phi_{cij} + \phi_{dkl})) \times g \sigma_{cdijk'l}^{i'j'k'l''} d^2\Omega du_d du_c. \quad (19)$$

Substituting Eq. (11) to Eq. (19) and taking into account the vanishing integrals from the odd function, one can see that $P_{cdik}^{i'k'}$ depend only on the functions F_{cij} and G_{cij} involved in ϕ_{cij} , and may be written in the following form [13,17]:

$$P_{cdik}^{i'k'} = P_{cdik}^{i'k'(0)}(T) + \varepsilon(P_{cdik}^{i'k'(1)}(n_{ci}, T) + \nabla \cdot \mathbf{v} P_{cdik}^{i'k'(2)}(n_{ci}, T)). \quad (20)$$

In this expression

$$P_{cdik}^{i'k'(0)} = \frac{4\pi}{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}} \left(\frac{m_{cd}}{2\pi kT} \right)^{3/2} \sum_{j'l'j''} \int \exp\left(-\frac{m_{cd} g^2}{2kT}\right) \times s_j^{ci} s_l^{dk} \exp\left(-\frac{\varepsilon_j^{ci} + \varepsilon_l^{dk}}{kT}\right) g^3 \tilde{\sigma}_{cdijk'l}^{i'j'k'l''} dg, \quad (21)$$

where m_{cd} is the reduced mass, $\tilde{\sigma}_{cdijk'l}^{i'j'k'l''}$ is the integral cross section of the inelastic collisions:

$$\tilde{\sigma}_{cdijk'l}^{i'j'k'l''}(g) = \frac{1}{4\pi} \int \sigma_{cdijk'l}^{i'j'k'l''}(g, \Omega) d^2\Omega d^2\Omega'.$$

The terms $P_{cdik}^{i'k'(1)}$, $P_{cdik}^{i'k'(2)}$ are given by:

$$P_{cdik}^{i'k'(1)} = \sum_{j'l'j''} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (G_{cij} + G_{dkl}) \times g \sigma_{cdijk'l}^{i'j'k'l''} d^2\Omega du_d du_c, \quad (22)$$

$$P_{cdik}^{i'k'(2)} = \sum_{j'l'j''} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (F_{cij} + F_{dkl}) \times g \sigma_{cdijk'l}^{i'j'k'l''} d^2\Omega du_d du_c. \quad (23)$$

The rate coefficients $P_{cdik}^{i'k'(0)}$ are defined by the Maxwell-Boltzmann distribution over velocities and rotational energies whereas $P_{cdik}^{i'k'(1)}$ and $P_{cdik}^{i'k'(2)}$ are determined by the weak deviations from this distribution.

Similarly one can obtain the expressions for the remaining rate coefficients:

$$P_{(\gamma)} = P_{(\gamma)}^{(0)}(T) + \varepsilon(P_{(\gamma)}^{(1)}(n_{ci}, T) + \nabla \cdot \mathbf{v} P_{(\gamma)}^{(2)}(n_{ci}, T)), \quad (24)$$

where $P_{(\gamma)}$ at $\gamma = 1, 2, 3$ denote $P_{cdik}^{c'd'i'k'}$, $P_{rec,dk}^{ci}$ and $P_{ci,dk}^{diss}$ respectively.

In so doing we can write for exchange reactions:

$$P_{cdik}^{c'd'i'k'(0)} = \frac{4\pi}{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}} \left(\frac{m_{cd}}{2\pi kT} \right)^{3/2} \times \sum_{j'l'j''} \int \exp\left(-\frac{m_{cd} g^2}{2kT}\right) s_j^{ci} s_l^{dk} \times \exp\left(-\frac{\varepsilon_j^{ci} + \varepsilon_l^{dk}}{kT}\right) g^3 \tilde{\sigma}_{cdijk'l}^{c'd'i'j'k'l''} dg, \quad (25)$$

$$P_{cdik}^{c'd'i'k'(1)} = \sum_{j'l'j''} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (G_{cij} + G_{dkl}) \times g \sigma_{cdijk'l}^{c'd'i'j'k'l''} d^2\Omega du_d du_c, \quad (26)$$

$$P_{cdik}^{c'd'i'k'(2)} = \sum_{j'l'j''} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (F_{cij} + F_{dkl}) \times g \sigma_{cdijk'l}^{c'd'i'j'k'l''} d^2\Omega du_d du_c, \quad (27)$$

and for recombination-dissociation:

$$P_{\text{rec}, dk}^{ci(0)} = P_{\text{rec}, d}^{ci(0)} = \frac{(m_c m_{d'} m_d)^{3/2}}{(2\pi kT)^{9/2}} \times \sum_j \int \exp\left(-\frac{m_c u_c^2 + m_{d'} u_{d'}^2 + m_d u_d^2}{2kT}\right) \times \tilde{\sigma}_{\text{rec}, d}^{cij}(\mathbf{u}_c, \mathbf{u}_{d'}, \mathbf{u}_d) d\mathbf{u}_c d\mathbf{u}_{d'} d\mathbf{u}_d, \quad (28)$$

$$\tilde{\sigma}_{\text{rec}, d}^{cij} = \int \sigma_{\text{rec}, d}^{cij}(\mathbf{u}_c, \mathbf{u}_{d'}, \mathbf{u}_d, \mathbf{u}_c, \mathbf{u}_d) d\mathbf{u}_c d\mathbf{u}_d, \\ P_{\text{rec}, dk}^{ci(1)} = \sum_{jl} \int \frac{f_c^{(0)} f_{d'}^{(0)} f_{dk}^{(0)}}{n_c n_{d'} n_{dk}} (G_c + G_{d'} + G_{dk}) \times \sigma_{\text{rec}, d}^{cij} d\mathbf{u}_c d\mathbf{u}_{d'} d\mathbf{u}_d d\mathbf{u}_c d\mathbf{u}_d, \quad (29)$$

$$P_{\text{rec}, dk}^{ci(2)} = \sum_{jl} \int \frac{f_c^{(0)} f_{d'}^{(0)} f_{dk}^{(0)}}{n_c n_{d'} n_{dk}} (F_c + F_{d'} + G_{dk}) \times \sigma_{\text{rec}, d}^{cij} d\mathbf{u}_c d\mathbf{u}_{d'} d\mathbf{u}_d d\mathbf{u}_c d\mathbf{u}_d, \quad (30)$$

$$P_{ci, dk}^{\text{diss}(0)} = P_{ci, d}^{\text{diss}(0)} = \frac{4\pi}{Z_{ci}^{\text{rot}}} \left(\frac{m_{cd}}{2\pi kT}\right)^{3/2} \times \sum_j \int \exp\left(-\frac{m_{cd} g^2}{2kT}\right) s_j^{ci} \exp\left(-\frac{\varepsilon_j^{ci}}{kT}\right) \times g^3 \tilde{\sigma}_{cij, d}^{\text{diss}} dg, \quad (31)$$

$$\tilde{\sigma}_{cij, d}^{\text{diss}} = \int \sigma_{cij, d}^{\text{diss}}(\mathbf{u}_c, \mathbf{u}_{d'}, \mathbf{u}_d, \mathbf{u}_c, \mathbf{u}_d) d\mathbf{u}_c d\mathbf{u}_{d'} d\mathbf{u}_d, \\ P_{ci, dk}^{\text{diss}(1)} = \sum_{jl} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (G_{cij} + G_{dkl}) \times \sigma_{cij, d}^{\text{diss}} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{d'} d\mathbf{u}_d, \quad (32)$$

$$P_{ci, dk}^{\text{diss}(2)} = \sum_{jl} \int \frac{f_{cij}^{(0)} f_{dkl}^{(0)}}{n_{ci} n_{dk}} (F_{cij} + F_{dkl}) \times \sigma_{cij, d}^{\text{diss}} d\mathbf{u}_c d\mathbf{u}_d d\mathbf{u}_{d'} d\mathbf{u}_d. \quad (33)$$

Here $\sigma_{\text{rec}, d}^{cij}$ is the cross section of the collision leading to the formation of c th molecule at the i th and j th vibrational and rotational levels due to recombination.

The formulas for all rate coefficients $P_{(\gamma)}^{(0)}$, $P_{(\gamma)}^{(1)}$, $P_{(\gamma)}^{(2)}$ contain the cross sections of the corresponding

slow process. The zero order rate coefficients $P_{(\gamma)}^{(0)}$ depend only on the gas temperature. On the contrary, the first order rate coefficients $P_{(\gamma)}^{(1)}$ and $P_{(\gamma)}^{(2)}$ depend on all level populations and atomic number densities. Moreover, the first order rate coefficients in a moving gas contain the terms proportional to $\nabla \cdot \mathbf{v}$. It can be noticed that this term is equal to zero if there is no any rapid inelastic process and only the elastic collisions determine the rapid process. It takes place in a mixture of light molecules where the rotational relaxation is much slower than the translational one or in the case when the rotational degrees of freedom are neglected.

It can be noticed that the equations connecting the zero order rate coefficients of forward and backward reactions follow from the detailed balance principle for the inelastic cross sections [2,19], after averaging over the Maxwell-Boltzmann distributions over velocities and rotational energies [20,21]. For vibrational energy transitions (15) one can write

$$P_{cdi'k'}^{ik(0)} = P_{cdik}^{i'k'(0)} \frac{s_i^c s_k^d}{s_{i'}^c s_{k'}^d} \frac{Z_{ci}^{\text{rot}} Z_{ck}^{\text{rot}}}{Z_{ci'}^{\text{rot}} Z_{dk'}^{\text{rot}}} \times \exp\left(\frac{\varepsilon_i^c + \varepsilon_k^d - \varepsilon_{i'}^c - \varepsilon_{k'}^d}{kT}\right) \quad (34)$$

Similarly for reactive collisions (16) and (17):

$$P_{cdi'k'}^{cdi'k'(0)} = P_{cdik}^{c'd'i'k'(0)} \frac{s_i^c s_k^d}{s_{i'}^c s_{k'}^d} \left(\frac{m_c m_d}{m_{c'} m_{d'}}\right)^{3/2} \frac{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}}{Z_{ci'}^{\text{rot}} Z_{dk'}^{\text{rot}}} \times \exp\left(\frac{\varepsilon_i^c + \varepsilon_k^d - \varepsilon_{i'}^c - \varepsilon_{k'}^d}{kT}\right) \times \exp\left(\frac{D_c + D_d - D_{c'} - D_{d'}}{kT}\right) \quad (35)$$

$$P_{\text{rec}, dk}^{ci(0)} = P_{ci, dk}^{\text{diss}(0)} s_i^c \left(\frac{m_c}{m_c m_{d'}}\right)^{3/2} h^3 (2\pi kT)^{-3/2} Z_{ci}^{\text{rot}} \times \exp\left(-\frac{\varepsilon_i^c - D_c}{kT}\right) \quad (36)$$

Here $m_c = m_{c'} + m_{d'}$, h is the Planck constant.

For diatomic molecules usually $s_i^c = 1$. If the vibrational and rotational energies of a molecule can be considered independently (like for the rigid rota-

tor model), the rotational partition function does not depend on the vibrational level i : $Z_{ci}^{\text{rot}} = Z_c^{\text{rot}}$ [22]. Then

$$P_{cdi'k'}^{ik(0)} = P_{cdik}^{i'k'(0)} \exp\left(\frac{\varepsilon_i^c + \varepsilon_{k'}^d - \varepsilon_i^c - \varepsilon_k^d}{kT}\right) \quad (37)$$

$$P_{cdi'k'}^{cdik(0)} = P_{cdik}^{c'd'i'k'(0)} \left(\frac{m_c m_d}{m_{c'} m_{d'}}\right)^{3/2} \frac{Z_c^{\text{rot}} Z_d^{\text{rot}}}{Z_{c'}^{\text{rot}} Z_{d'}^{\text{rot}}} \\ \times \exp\left(\frac{\varepsilon_{i'}^{c'} + \varepsilon_{k'}^{d'} - \varepsilon_i^c - \varepsilon_k^d}{kT}\right) \\ \times \exp\left(\frac{D_c + D_d - D_{c'} - D_{d'}}{kT}\right) \quad (38)$$

$$P_{rec,dk}^{ci(0)} = P_{ci,dk}^{\text{diss}(0)} \left(\frac{m_c}{m_{c'} m_{d'}}\right)^{3/2} h^3 (2\pi kT)^{-3/2} Z_c^{\text{rot}} \\ \times \exp\left(-\frac{\varepsilon_i^c - D_c}{kT}\right) \quad (39)$$

4. Zero order rate coefficients

The zero order rates of vibrational energy transitions have been widely studied by many authors both theoretically and experimentally. Theoretical models based on different methods of the calculation of inelastic cross sections can be found in Refs. [23,24], and in other works, some results are given in Refs. [25,26]. The cross sections of chemically reactive collisions with dissociation, recombination and exchange reactions are not sufficiently elaborated. Therefore the phenomenological approximate models are often used for the calculation of the reaction rates. A review of the different models of the dissociation rates is given in Ref. [27]. One of the first simple models for the cross sections of reactive collisions was proposed by Prigogine [1]. This model takes into account the threshold character of chemical reaction and represents the dependence of the cross sections on the translational energy of colliding particles, but does not reflect the dependence of the cross sections on the internal energy of reagents. The most often used models are ladder-climbing one and the Treanor-Marrone model for dissociation–recombination processes [28], the generalization of the Treanor-Marrone model for exchange reactions is

given in Ref. [29]. These models simulate the dependence of the microscopic reaction rates on the vibrational energy of the molecules participating in a reaction but do not describe the cross sections of the reactive collisions and their dependence on the relative velocity. The ladder-climbing model is based on the assumption that molecules dissociate only from the last level and each molecule reached this level dissociates immediately with the probability equal to unit. Thus the dissociation rate is determined by the stream of molecules to the last level from lower levels due to VV and VT vibrational energy exchange (see for example Refs. [11,30]). The Treanor-Marrone model permits dissociation not only from the last level supposing the preferential dissociation from high levels. The probability of dissociation is expressed in terms of the arbitrary parameters which should be found from the fitting of the experimental data.

5. First order rate coefficients

For the calculation of the first order rate coefficients the linear integral equations for the functions G_{cij} and F_{cij} have to be solved. These equations are obtained in Ref. [5] in the following form:

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(F) \\ = \frac{1}{n} f_{cij}^{(0)} \left(\frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T (c_{tr} + c_{rot})} \right. \\ \left. \times \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]_r \right) \right), \quad (40)$$

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(G) \\ = -J_{cij}^{sl(0)} + \frac{1}{n} f_{cij}^{(0)} \left(\frac{R_{ci}^{(0)}}{n_{ci}} \right. \\ \left. - \frac{\sum_{ci} R_{ci}^{(0)} (\langle \varepsilon_j^{ci} \rangle_r + \varepsilon_i^c + \varepsilon^c)}{\rho T (c_{tr} + c_{rot})} \right) \\ \times \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]_r \right). \quad (41)$$

In this equation c_{tr} and c_{rot} are the translational and rotational specific heats, $[\varepsilon_j^{ci}]_r = \varepsilon_j^{ci} - m_c E_r^{ci}$, E_r^{ci} is the rotational energy of c species at the i th vibrational level, averaged over rotational spectrum:

$$\rho_{ci} E_r^{ci} = \sum_j \int \varepsilon_j^{ci} f_{cij} d\mathbf{u}_c = \langle \varepsilon_j^{ci} \rangle_r n_{ci},$$

I_{cijdk} is the linearized operator of rapid processes:

$$I_{cijdk}(\phi) = \frac{1}{n_{ci} n_{dk}} \sum_{j'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (\phi_{cij} + \phi_{dkl} - \phi_{cij'} - \phi_{dkl'}) g \sigma_{cidk, j'l'}^j d^2\Omega d\mathbf{u}_d, \quad (42)$$

$\sigma_{cidk, j'l}^{j'l'}$ is the cross section of the elastic collisions and collisions resulting in the RT exchange (for the elastic collisions $j' = j$, $l' = l$). In Ref. [5] it is shown that the functions F_{cij} and G_{cij} define the nonequilibrium terms in the diagonal elements of the pressure tensor such as bulk viscosity and relaxation pressure. These terms appear because of the inelastic rapid RT energy exchange.

Now, the solutions of Eqs. (40), (41) are expanded in the series of the Sonine and Waldmann-Trübenbacher [31] orthogonal polynomials over reduced translational and rotational energy:

$$F_{cij} = \sum_{rp} f_{ci,rp} S_{1/2}^{(r)} \left(\frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left(\frac{\varepsilon_j^{ci}}{kT} \right), \quad (43)$$

$$G_{cij} = \sum_{rp} g_{ci,rp} S_{1/2}^{(r)} \left(\frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left(\frac{\varepsilon_j^{ci}}{kT} \right). \quad (44)$$

Following [5], in order to obtain the algebraic equations for the coefficients f_{cij} and g_{cij} , we substitute expansions (43), (44) into Eqs. (40), (41) and multiply them by the corresponding polynomial. Then, we integrate these equations over the velocity and make a summation over the rotational levels. Thus the algebraic equations for the expansion coefficients $f_{ci,rp}$ are obtained in the form:

$$\begin{aligned} & \sum_{dk} \sum_{r'p'} \beta_{rr'pp'}^{cidk} f_{dk,r'p'} \\ &= \frac{n_{ci}}{n} \frac{1}{\tilde{c}_{tr} + \tilde{c}_{rot}} \left(-\tilde{c}_{rot} \delta_{r1} \delta_{p0} + c_{rot,ci} \delta_{r0} \delta_{p1} \right), \\ & c = 1, \dots, L, i = 0, 1, \dots, L_c, r, p = 0, 1, \dots \end{aligned} \quad (45)$$

Here \tilde{c}_{tr} and \tilde{c}_{rot} are the dimensionless (divided by the gas constant R) translational and rotational specific heats, the dimensionless rotational specific heat of c species at the i th vibrational level $c_{rot,ci}$ is defined as:

$$c_{rot,ci} = \frac{m_c}{k} \frac{\partial E_r^{ci}}{\partial T}.$$

In the case when the rotational and vibrational energy of a molecule are considered independently (in particular, for the rigid rotator model), $c_{rot,ci} = c_{rot,c}$.

The coefficients of system (45) are expressed in terms of bracket integrals and level populations:

$$\begin{aligned} \beta_{rr'pp'}^{cidk} &= \sqrt{m_c m_d} \left(\delta_{cd} \delta_{ik} \sum_{bl} \frac{n_{ci} n_{bl}}{n^2} [Q^{rp}, Q^{r'p'}]_{cibl} \right. \\ &\quad \left. + \frac{n_{ci} n_{dk}}{n^2} [Q^{rp}, Q^{r'p'}]_{cidk}' \right), \end{aligned} \quad (46)$$

and

$$Q_{cij}^{rp} = S_{1/2}^{(r)} \left(\frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left(\frac{\varepsilon_j^{ci}}{kT} \right).$$

The partial bracket integrals are introduced as follows [5,32]:

$$\begin{aligned} [A, B]_{cidk} &= \frac{1}{2n_{ci} n_{dk}} \sum_{j'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (B_{cij} - B_{cij'}) \\ &\quad \times (A_{cij} - A_{cij'}) g \sigma_{cidk, j'l}^j d^2\Omega d\mathbf{u}_c d\mathbf{u}_d, \end{aligned}$$

$$\begin{aligned} [A, B]_{cidk}' &= \frac{1}{2n_{ci} n_{dk}} \sum_{j'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (B_{cij} - B_{cij'}) \\ &\quad \times (A_{dkl} - A_{dkl'}) g \sigma_{cidk, j'l}^j d^2\Omega d\mathbf{u}_c d\mathbf{u}_d. \end{aligned}$$

For $r = p = 0$, system (45) is not linearly independent. In that case it should be supplemented by the constraints derived from normalization conditions for the distribution functions [5]:

$$f_{ci,00} = 0, \quad c = 1, \dots, L, \quad i = 0, 1, \dots, L_c \quad (47)$$

$$\sum_{ci} \frac{n_{ci}}{n} (\tilde{c}_{tr} f_{ci,10} + c_{rot,ci} f_{ci,01}) = 0. \quad (48)$$

Eqs. (45), (47)–(48) for the coefficients $f_{ci,rp}$ of expansion (43) have a unique solution in any approximation.

The equations for the coefficients $g_{ci,rp}$ of expansions (44) are obtained using the similar procedure. The system of algebraic equations takes the form:

$$\begin{aligned} & \sum_{dk} \sum_{r'p'} \beta_{rr'pp'}^{cldk} g_{dk,r'p'} \\ &= \frac{n_{ci}}{n} \frac{\sum_{ci} R_{ci}^{(0)} (\langle \epsilon_j^{ci} \rangle_r + \epsilon_i^c + \epsilon^c)}{\rho T (c_u + c_{rot})} \\ & \times \left(\frac{3}{2} \delta_{r1} \delta_{p0} + c_{rot,ci} \delta_{r0} \delta_{p1} \right) + \frac{R_{ci}^{(0)}}{n} \delta_{r0} \delta_{p0} \\ & - \sum_j \int S_{1/2}^{(r)} P_j^{(p)} J_{cij}^{sl(0)} d\mathbf{u}_c, \end{aligned} \quad (49)$$

and the constraints, providing the unique solution, are given by

$$g_{ci,00} = 0, \quad c = 1, \dots, L, \quad i = 0, 1, \dots, L_c \quad (50)$$

$$\sum_{ci} \frac{n_{ci}}{n} (\tilde{c}_u g_{ci,10} + c_{rot,ci} g_{ci,01}) = 0 \quad (51)$$

Substituting expansions (43), (44) into expressions (22), (23), (26), (27), (29), (30), (32), (33) we obtain the formulas for the first-order rate coefficients $P_{(\gamma)}^{(1)}$ and $P_{(\gamma)}^{(2)}$. These coefficients are expressed in terms of $f_{ci,rp}$, $g_{ci,rp}$ and the integrals containing the cross sections of the collisions in the inelastic slow processes. Actually, the expressions for $P_{cdik}^{i'k'(1)}$ have the form [13,17]

$$\begin{aligned} P_{cdik}^{i'k'(1)} &= \sum_{rp} g_{ci,rp} \sum_{jl'l'} \int \frac{f_{cij}^{(0)}}{n_{ci}} \frac{f_{dkl}^{(0)}}{n_{kl}} \\ & \times Q_{cij}^{rp} g \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_c d\mathbf{u}_d + \sum_{rp} g_{dk,rp} \\ & \times \sum_{jl'l'} \int \frac{f_{cij}^{(0)}}{n_{ci}} \frac{f_{dkl}^{(0)}}{n_{kl}} Q_{dkl}^{rp} g \sigma_{cd,ijkl}^{i'j'k'l'} \\ & \times d^2\Omega d\mathbf{u}_c d\mathbf{u}_d. \end{aligned} \quad (52)$$

These expressions can be simplified. Let us introduce the averaging operator for any function F connected to the process α (α stands for any processes considered: elastic collisions, RT exchange, vibrational energy transitions and chemical reactions)

$$\begin{aligned} \langle F \rangle_{cdik}^{(\alpha)} &= \left(\frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{jl'l'} \frac{s_j^{ci} s_l^{dk}}{Z_{ci}^{rot} Z_{dk}^{rot}} \int F g_0^3 \\ & \times \exp(-g_0^2 - \epsilon_j^{ci} - \epsilon_l^{dk}) \sigma^{(\alpha)} d^2\Omega d\mathbf{g}_0. \end{aligned} \quad (53)$$

Here $g_0 = (m_{cd}/2kT)^{1/2} g$ is the dimensionless value of the relative velocity. $\epsilon_j^{ci} = \epsilon_j^{ci}/kT$ is the dimensionless rotational energy. The cross section $\sigma^{(\alpha)}$ in Eq. (53) should be replaced by the cross section of the corresponding process. Thus, for the most frequent collisions ($\alpha = \text{'rap'}$), $\sigma^{(\alpha)} = \sigma_{cdik,jl}^{i'j'}$, for the vibrational energy transitions ($\alpha = \text{'vibr'}$), $\sigma^{(\alpha)} = \sigma_{cd,ijkl}^{i'j'k'l'}$. In so doing the integrals in (52) can be reduced to the average values of the relative velocity and rotational energy of the type:

$$\tilde{\Omega}_{cdik}^{vibr(r,p)} = \langle g^{2r} (\epsilon_j^{ci})^p \rangle_{cdik}^{(vibr)}.$$

It can be noticed that $\tilde{\Omega}_{cdik}^{vibr(0,0)}$ is proportional to $P_{cdik}^{i'k'(0)}$.

The expressions for the remaining rate coefficients are written similarly and expressed in terms of the inelastic collision integrals with the corresponding cross sections for exchange reactions and dissociation–recombination. However one should take into account that the averaging operators for recombination and dissociation differ from (53) and are derived from expressions (28) and (31), respectively.

Finally, we can conclude that the calculation of $P_{(\gamma)}^{(1)}$ and $P_{(\gamma)}^{(2)}$ reduces to the solution of the linear algebraic equations and to the computing of the collision integrals containing the cross sections of corresponding slow inelastic process (vibrational and chemical transitions). In the next section some simplifications of the linear systems and integral brackets are proposed.

6. Simplified formulas for the rate coefficients

The systems of algebraic equations for the expansion coefficients $f_{ci,rp}$ and $g_{ci,rp}$ (45) and (49) can be simplified if one keeps only the first non-vanishing terms of the expansions ($r = 1$, $p = 0$ and $r = 0$, $p = 1$). In this case systems (45) and (49) take the form:

$$\sum_{dk} (\beta_{1100}^{cidd} f_{dk,10} + \beta_{1001}^{cidd} f_{dk,01}) = -\frac{n_{ci}}{n} \frac{\tilde{c}_{rot}}{\tilde{c}_{tr} + \tilde{c}_{rot}},$$

$$\sum_{dk} (\beta_{0110}^{cidd} f_{dk,10} + \beta_{0011}^{cidd} f_{dk,01}) = \frac{n_{ci}}{n} \frac{c_{rot,ci}}{\tilde{c}_{tr} + \tilde{c}_{rot}}. \quad (54)$$

$$\sum_{dk} (\beta_{1100}^{cidd} g_{dk,10} + \beta_{1001}^{cidd} g_{dk,01})$$

$$= \frac{3}{2} \frac{n_{ci}}{n} \Phi - \sum_j \int \left(\frac{3}{2} - \frac{m_c c_c^2}{2kT} \right) J_{cij}^{sl(0)} d\mathbf{u}_c,$$

$$\sum_{dk} (\beta_{0110}^{cidd} g_{dk,10} + \beta_{0011}^{cidd} g_{dk,01})$$

$$= c_{rot,ci} \frac{n_{ci}}{n} \Phi + \sum_j \int \left[\frac{\varepsilon_j^{ci}}{kT} \right]' J_{cij}^{sl(0)} d\mathbf{u}_c. \quad (55)$$

$$\Phi = \frac{\sum_{ci} R_{ci}^{(0)} (\langle \varepsilon_j^{ci} \rangle_r + \varepsilon_i^c + \varepsilon^c)}{\rho T (c_{tr} + c_{rot})}$$

The integral brackets in the left hand sides of these systems may be calculated using the assumptions discussed in Refs. [5,33–35]. First, all complex collisions are assumed to be rare and are neglected, i.e. we neglect the collisions in which the internal states of both colliding molecules change, or in which both internal modes of one of the molecules change in one collision. Furthermore like in Ref. [34] we consider the internal and translational motions as the uncorrelated ones. Then, following [5] we suppose that in the most frequent collisions the collision diameter and deflection angle do not depend on the vibrational level of a molecule. Therefore the cross sections of the elastic collisions and the collisions

leading to the RT exchange are independent from the vibrational state. Finally, the simplified expressions for the bracket integrals are obtained:

$$\beta_{1100}^{cici} = kT \sum_{\substack{b \neq c \\ n \neq i}} \left[5 \frac{x_{ci} x_{bn}}{A_{cb}^* \mu_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} + \frac{4T}{\pi} \frac{x_{ci} x_{bn}}{\mu_{cb}} \frac{m_b^2}{(m_c + m_b)^2} \right. \\ \left. \times \left(\frac{c_{rot,ci}}{\zeta_{cibn}} + \frac{c_{rot,bn}}{\zeta_{bnci}} \right) \right] + \frac{4T}{\pi} \frac{x_{ci}^2}{\mu_c} \frac{c_{rot,ci}}{\zeta_{cici}}, \quad (56)$$

$$\beta_{1100}^{cidd} = -5kT \frac{x_{ci} x_{dk}}{A_{cd}^* \mu_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \\ + \frac{4T}{\pi} \frac{x_{ci} x_{dk}}{\mu_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \\ \times \left(\frac{c_{rot,ci}}{\zeta_{cidk}} + \frac{c_{rot,dk}}{\zeta_{dkci}} \right), \quad (c \neq d \text{ or } i \neq k), \quad (57)$$

$$\beta_{1001}^{cici} = -\frac{4T}{\pi} \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci} x_{bn}}{\mu_{cb}} \frac{m_b}{(m_c + m_b)} \\ \times \frac{c_{rot,ci}}{\zeta_{cibn}} - \frac{4T}{\pi} \frac{x_{ci}^2}{\mu_c} \frac{c_{rot,ci}}{\zeta_{cici}}, \quad (58)$$

$$\beta_{1001}^{cidd} = -\frac{4T}{\pi} \frac{x_{ci} x_{dk}}{\mu_{cidk}} \frac{m_d}{(m_c + m_d)} \frac{c_{rot,dk}}{\zeta_{dkci}}, \\ (c \neq d \text{ or } i \neq k), \quad (59)$$

$$\beta_{0011}^{cici} = \frac{4T}{\pi} \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci} x_{bn}}{\mu_{cb}} \frac{c_{rot,ci}}{\zeta_{cibn}} + \frac{4T}{\pi} \frac{x_{ci}^2}{\mu_c} \frac{c_{rot,ci}}{\zeta_{cici}}, \quad (60)$$

$$\beta_{0011}^{cidd} = 0, \quad (c \neq d \text{ or } i \neq k), \quad (61)$$

$$\beta_{0110}^{cidd} = \beta_{1001}^{dkci} \quad (62)$$

Here the following notations are introduced: $x_{ci} = n_{ci}/n$ is the dimensionless number density of molecules of c chemical species at the i th vibra-

tional level, ζ_{cjdk} are the rotational collision numbers, μ_c and μ_{cd} are the fictitious viscosity coefficients:

$$\mu_c = \frac{5}{16} \frac{(2\pi m_c kT)^{1/2}}{\pi \bar{\sigma}_c^2 \Omega_c^{(2,2)*}},$$

$$\mu_{cd} = \frac{5}{16} \frac{(2\pi m_{cd} kT)^{1/2}}{\pi \bar{\sigma}_{cd}^2 \Omega_{cd}^{(2,2)*}}, \quad (63)$$

$\bar{\sigma}_{cd}$ is the collision diameter.

The collision integrals $\Omega_{cd}^{(l,r)}$ are introduced as follows:

$$\Omega_{cd}^{(l,r)} = \left(\frac{kT}{2\pi m_{cd}} \right)^{1/2} \int_0^\infty \exp(-g_0^2) g_0^{2r+3} \mathcal{Q}_{cd}^{(l)} dg_0, \quad (64)$$

$$\mathcal{Q}_{cd}^{(l)} = 2\pi \int (1 - \cos^l \chi_{cd}(b, g)) b db.$$

Here $\chi_{cd}(b, g)$ is the deflection angle, b is the impact parameter. The reduced collision integrals $\Omega_{cd}^{(l,r)*}$ have such a form:

$$\Omega_{cd}^{(l,r)*} = \frac{\Omega_{cd}^{(l,r)}}{(\Omega_{cd}^{(l,r)})_{\text{h.s.}}} \quad (65)$$

where the collision integrals $(\Omega_{cd}^{(l,r)})_{\text{h.s.}}$ are calculated for the hard spheres model. The function A_{cd}^* is given by:

$$A_{cd}^* = \frac{\Omega_{cd}^{(2,2)*}}{\Omega_{cd}^{(1,1)*}}. \quad (66)$$

We would like to note here that in the general case all the quantities A_{cd}^* , $\Omega_{cd}^{(l,r)}$, μ_{cd} should depend on the vibrational state of the particles. In the present paper we use the assumption about the independence of the collision diameter and deflection angle on the vibrational level: $\bar{\sigma}_{cjdk} = \bar{\sigma}_{cd}$, $\chi_{cjdk}(b, g) = \chi_{cd}(b, g)$.

The rotational collision numbers ζ_{cjdk} related to the rotational relaxation times τ_{cjdk}^{rot} are introduced by analogy to Refs. [34,35]:

$$\zeta_{cjdk} = \frac{4}{\pi} \frac{p \tau_{cjdk}^{\text{rot}}}{\mu_{cjdk}}, \quad (67)$$

p is the pressure. The relaxation time τ_{cjdk} means the rotational relaxation time for the c species at the i th vibrational level at the collisions with the molecules of d species at the k th vibrational level. These relaxation times are connected with the resonance defect in the inelastic RT exchange and are given by the expressions similar to those introduced in Refs. [34,35]:

$$\frac{1}{\tau_{cici}^{\text{rot}}} = \frac{2n}{c_{\text{rot},ci}} \langle (\Delta \epsilon_{cici})^2 \rangle_{cici}^{(\text{rap})},$$

$$\frac{1}{\tau_{cjdk}^{\text{rot}}} = \frac{4n}{c_{\text{rot},ci}} \langle \Delta \epsilon_{ci} \Delta \epsilon_{cjdk} \rangle_{cjdk}^{(\text{rap})} \quad (68)$$

Here the averaging (53) is performed in respect to the cross sections of rapid processes: elastic collisions and RT exchange, the resonance defects at the collisions are introduced as

$$\Delta \epsilon_{cjdk} = \epsilon_j^{ci} + \epsilon_l^{dk} - \epsilon_j^{ci} - \epsilon_l^{dk}, \quad \Delta \epsilon_{ci} = \epsilon_j^{ci} - \epsilon_j^{ci} \quad (69)$$

The computation or experimental measurement of the relaxation times τ_{cjdk}^{rot} depending on the partner in the collision remains a very complicated task. Usually, all the relaxation times and therefore the collision numbers ζ_{cjdk} are approximated by the times τ_{ci}^{rot} (collision numbers ζ_{ci}) independent on the chemical and vibrational species d, k of the partner. Furthermore, if one assumes the rotational relaxation time to be independent of the vibrational state, then τ_{ci}^{rot} may be approximated by the relaxation time τ_c^{rot} of chemical species, its value can be measured experimentally (see, for instance, Refs. [36]) or calculated using the Parker model [37]. The elastic collision integrals, that appear in expressions for the bracket integrals (56)–(62) have been computed and tabulated by many authors (see Refs. [38,39]). The analysis of the transport coefficients calculated on the basis of different sources for the elastic collision integrals is presented in Ref. [40], and we can recommend the results of Refs. [41] and [39] for a practical use. These data were used in Ref. [42].

Finally, the simplified systems (54), (55) with coefficients (56)–(62) have been derived for the calculation of the expansion coefficients $f_{ci,10}$, $f_{ci,01}$ and $g_{ci,10}$, $g_{ci,01}$. Keeping only these terms in ex-

pression (52), one can obtain the simplified expression for the rate coefficient of vibrational energy exchange $P_{cdik}^{i'k'(1)}$ in the form:

$$\begin{aligned}
 P_{cdik}^{i'k'(1)} = & \frac{m_d g_{ci,10} + m_c g_{dk,10}}{m_c + m_d} \left(\frac{3}{2} P_{cdik}^{i'k'(0)} \right. \\
 & \left. - \frac{m_{cd}}{2kT} \langle g^2 \rangle_{cdik}^{(\text{vibr})} \right) \\
 & - \frac{g_{dk,01} m_c E_r^{ci} + g_{ci,01} m_d E_r^{dk}}{kT} \\
 & \times P_{cdik}^{i'k'(0)} + g_{ci,01} \langle \epsilon_j^{ci} \rangle_{cdik}^{(\text{vibr})} \\
 & + g_{dk,01} \langle \epsilon_i^{dk} \rangle_{dkci}^{(\text{vibr})}. \quad (70)
 \end{aligned}$$

The remaining rate coefficients $P_{(\gamma)}^{(1)}$ and $P_{(\gamma)}^{(2)}$ may be written similarly using the corresponding averaging operator.

It should be noted that systems of algebraic equations (54), (55) coincide with the systems for the calculation of the bulk viscosity coefficients and relaxation pressure [5], and therefore the algorithm proposed in the present paper may be used for the calculation of these transport coefficients.

7. Conclusions

In this paper the multi-level kinetic theory approach is used for the modelling of the nonequilibrium rates of vibrational energy transitions, dissociation, recombination and exchange reactions in a reacting gas mixture flow. The zero and first order approximations of the generalized Chapman-Enskog method are considered, and the algorithms for the calculation of the state-to-state transition rates are presented. The zero order rate constants correspond to the Maxwell-Boltzmann distribution over velocities and rotational energies. The first order approximation takes into account weak deviations from the Maxwell-Boltzmann distribution over translational and rotational energies and strong nonequilibrium over vibrational energies. The first order rates of the vibrational energy transitions and chemical reactions for different vibrational levels depend not only on the gas temperature but also on all vibrational level populations and atomic number densities and include the term proportional to $\nabla \cdot \nu$. The formulas obtained

express the first order rate coefficients in terms of the solutions of the linear algebraic equations, collision integrals containing the cross sections for slow processes (vibrational energy transitions and chemical reactions), elastic collision integrals and the inelastic ones for the rapid process (translational-rotational energy exchange). The last integrals are connected with the rotational relaxation times that can be measured experimentally. The formulas derived in the paper can be inserted to the Navier-Stokes computational codes for the rigorous calculation of the strong nonequilibrium gas flow parameters.

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