

Kinetic modelling of radiative reacting gas flow under strong nonequilibrium conditions

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Abstract

Radiative flows of reacting gas mixtures with strong vibrational and chemical nonequilibrium are studied on the basis of the kinetic theory. A closed system of macroscopic equations, taking into account the coupling of vibrational relaxation, chemical reactions and radiative transitions, is derived. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Recent experimental and theoretical results on nonequilibrium kinetics in high temperature and high enthalpy flows prove the existence of a strong coupling between the processes of vibrational relaxation and chemical reactions. This is the reason for rapid development of the state-to-state models of reacting gas flows, the peculiarity of these models is that they are not based on any quasi-stationary (Boltzmann or Treanor) distribution over vibrational energy. During the last decade, the state-to-state vibrational-chemical kinetics in various gas flows has been studied by many authors. One can cite here the results concerning high temperature flows in the relaxation zone behind shock waves [1–4], expanding flows in nozzles [5–8], flows in the boundary layer developing

around a vehicle during the re-entry phase [9,10], and flows near a blunt body [11]. The transport theory in the state-to-state approach has been developed in Refs. [4,12,13], and the results of Refs. [14–16] show a significant influence of the nonequilibrium vibrational distributions on the heat transfer. Nonequilibrium state-to-state reaction rates have been considered in Refs. [8,17,18], and a noticeable effect of nonequilibrium vibrational kinetics on the dissociation rate coefficients has been found.

It is well known that the vibrational relaxation and chemical reactions are usually accompanied by radiation. A wide variety of radiative transitions corresponding to different high temperature conditions is considered in Refs. [19,20]. Experimental aspects of radiative processes have been discussed by a great number of authors (see, for instance, Ref. [21]), one should mention an important role of radiative transitions for the laser technology, photochemistry, and shock tube measurements. A mutual effect of relaxation and radiation has to be studied experimentally as well

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as theoretically. Some analytical quasi-stationary vibrational distributions taking into account spontaneous radiative transitions have been obtained in Refs. [22–24]. The influence of laser radiation on the excitation of vibrational degrees of freedom and on the chemical reaction rates is considered in Ref. [25].

Another important problem is the estimation of the heat transfer caused by radiation for the calculation of thermal protection systems. The macroscopic equations of aerothermochemistry, taking into account the radiative effects, are given, for instance, in Refs. [26–28], using these equations, the contribution of the radiative flux to the total energy flux has been evaluated (see Ref. [27] for a review of results). However, equations given in Ref. [27] are based on the one-temperature model assuming the existence of thermal equilibrium Boltzmann distribution over vibrational energy.

The objective of the present paper is to generalize the state-to-state model elaborated in Refs. [4,13] in order to take into account the radiative processes. Our aim is to give a closed description of a nonequilibrium flow of gas mixture with coupled vibrational relaxation, dissociation, recombination, exchange reactions, absorption and emission of photons on the basis of the rigorous kinetic theory.

We suppose that the following relation between the characteristic times of different processes in a reacting mixture takes place:

$$\tau_{el} < \tau_{rot} \ll \tau_{vibr} < \tau_{react} \sim \tau_{rad} \sim \theta. \quad (1)$$

Here τ_{el} , τ_{rot} , τ_{vibr} , τ_{react} , τ_{rad} are, respectively, the mean times between the elastic collisions, those with change of rotational and vibrational energy, chemical reactive collisions, and the ones leading to absorption and emission of a photon; θ is the macroscopic time. Condition (1) is found to be valid in many experiments [21], it describes the rapid equilibration of translational and rotational modes of molecules and slow vibrational relaxation, chemical reactions and radiative processes. Moderate gas temperatures are considered when ionization and electronic excitation of atoms and molecules may be neglected.

2. Kinetic equations

The gas flow is simulated on the basis of the kinetic equations for distribution functions. The motion of particles is considered in a six-dimensional phase space, its coordinates are the three components of the position \mathbf{r} and three components of the momentum \mathbf{p} . According to the quantum theory, a radiation field may be regarded as being equivalent to a collection of particle-like entities called photons [20]. Photons may be characterized by the following properties: they all move with the speed of light c , their energy is determined by their frequency ν :

$$\varepsilon_\nu = h\nu, \quad (2)$$

where h is the Planck's constant, and they carry a momentum

$$\mathbf{p}_\nu = \frac{h\nu}{c} \boldsymbol{\Omega}_\nu, \quad (3)$$

where $\boldsymbol{\Omega}_\nu$ is the unit vector defining the direction of travel of the photon. One should recognize that the analogy between photons and material particles is not complete, and in some instances, essential differences exist.

The distribution functions $f_{cij}(\mathbf{r}, \mathbf{p}_c, t)$ are introduced for every chemical species c , vibrational i and rotational energy level j , and for photons $f_\nu(\mathbf{r}, \mathbf{p}_\nu, t)$. The kinetic equations for distribution functions have a form:

$$\frac{\partial f_{cij}}{\partial t} + \frac{\mathbf{p}_c}{m_c} \frac{\partial f_{cij}}{\partial \mathbf{r}} = J_{cij}, \quad (4)$$

$$\frac{\partial f_\nu}{\partial t} + c \boldsymbol{\Omega}_\nu \frac{\partial f_\nu}{\partial \mathbf{r}} = J_\nu, \quad (5)$$

where m_c is the mass of a material particle. The collision operators J_{cij} and J_ν describe all the collisions leading to the change of distribution function. They can be written as a sum of several terms corresponding to different processes:

$$J_{cij} = J_{cij}^{el} + J_{cij}^{inel} + J_{cij}^{react} + J_{cij}^{rad}. \quad (6)$$

The collision operators of elastic and inelastic collisions J_{cij}^{el} and J_{cij}^{inel} correspond to the collisions

of material particles, which do not result in the change of chemical species:

$$A_{cij} + A_{dkl} \leftrightarrow A_{cij} + A_{dkl}, \quad (7)$$

$$A_{cij} + A_{dkl} \leftrightarrow A_{c'i'j'} + A_{d'k'l'}. \quad (8)$$

Elastic collisions (7) lead to the change of only the particle velocities, and in collisions (8), the internal state of molecules also varies. Reaction (8) can describe the inelastic rotational–translational (RT) exchange, vibrational–translational (VT) and vibrational–vibrational (VV) exchange of vibrational quanta. Taking into account the detailed balance principle, the operator J_{cij}^{inel} may be written in the form [29,30]:

$$J_{cij}^{\text{inel}} = \sum_{dkl i' j' k' l'} \int \left(f_{c' i' j'} f_{d' k' l'} \frac{s_{ij}^c s_{kl}^d}{s_{i' j'}^c s_{k' l'}^d} - f_{cij} f_{dkl} \right) \times W_{cd,ijkl}^{cd, i' j' k' l'} \mathbf{dp}_d \mathbf{dp}'_c \mathbf{dp}'_d. \quad (9)$$

Here, $s_{i' j'}^c$ is the statistical weight, \mathbf{p}_c , \mathbf{p}_d are the momenta of colliding particles, \mathbf{p}'_c , \mathbf{p}'_d are their momenta after the collision, $W_{cd,ijkl}^{cd, i' j' k' l'}$ is the probability per unit time of the transition of particles at the internal states i, j and k, l and possessing the momenta \mathbf{p}_c and \mathbf{p}_d to particles at the internal states i', j' and k', l' with the momenta \mathbf{p}'_c , \mathbf{p}'_d . The expression for J_{cij}^{el} can be easily deduced from Eq. (9) if one assumes $i = i', j = j', k = k', l = l'$.

The collision operator of chemical reactive collisions J_{cij}^{react} describes exchange reactions:

$$A_{cij} + A_{dkl} \leftrightarrow A_{c' i' j'} + A_{d' k' l'} \quad (10)$$

and dissociation–recombination process in a mixture of diatomic molecules and atoms:

$$A_{cij} + A_{dkl} \leftrightarrow A_{d' k' l'} + A_{c'} + A_{f'}. \quad (11)$$

Therefore,

$$J_{cij}^{\text{react}} = J_{cij}^{\text{exch}} + J_{cij}^{\text{diss-rec}}. \quad (12)$$

The expressions of J_{cij}^{exch} and $J_{cij}^{\text{diss-rec}}$ are given in Refs. [30–34] and have the form:

$$J_{cij}^{\text{exch}} = \sum_{dc' d' k' l' j' k' l'} \int \left(f_{c' i' j'} f_{d' k' l'} \frac{s_{ij}^c s_{kl}^d}{s_{i' j'}^c s_{k' l'}^d} - f_{cij} f_{dkl} \right) \times W_{cd,ijkl}^{c' d', i' j' k' l'} \mathbf{dp}_d \mathbf{dp}'_c \mathbf{dp}'_d, \quad (13)$$

$$J_{cij}^{\text{diss-rec}} = \sum_{dkl k' l'} \int \left(f_{c'} f_{f'} f_{d' k' l'} h^3 \frac{s_{ij}^c s_{kl}^d}{s_{k' l'}^d} - f_{cij} f_{dkl} \right) \times W_{cd,ijkl}^{c' f' d, k' l'} \mathbf{dp}_c \mathbf{dp}_{f'} \mathbf{dp}'_d \mathbf{dp}_d, \quad (14)$$

$W_{cd,ijkl}^{c' d', i' j' k' l'}$ and $W_{cd,ijkl}^{c' f' d, k' l'}$ are the probabilities per unit time of the chemically active collision resulting in exchange reactions, and of the collision with dissociation of the molecule of c th species at the i th and j th vibrational and rotational levels interacting with the molecule d th species at k th and l th vibrational and rotational levels; c', f' are the atomic species product of dissociation, k' and l' are the vibrational and rotational levels of the partner after the collision.

Among the radiative collisions, the ones leading to absorption, emission and scattering of photons may be distinguished. In an absorption process, an entire photon is removed from the incident beam and the photon's energy is deposited in the material particle. The inverse process is an induced emission, in this case, photons of a particular frequency in the incident beam stimulate an excited particle to emit a photon in the same direction as the beam and at the same frequency. These two processes are described by the reaction,

$$A_{cij} + hv \leftrightarrow A_{c' i' j'} + 2hv. \quad (15)$$

An isolated excited particle is also capable of emitting a photon, even in the absence of stimulating radiation. This process is referred to as spontaneous emission and has no corresponding inverse process:

$$A_{cij} \rightarrow A_{c' i' j'} + hv. \quad (16)$$

Scattering of photons by a material particle occurs as a result of the following reaction:

$$A_{cij} + hv \leftrightarrow A_{c'i'j'} + hv'. \quad (17)$$

In this study, the gas flow at moderate temperature is simulated when the degree of ionization and electronic excitation is negligibly small ($T < 6000\text{--}8000$ K). In this case, one may take into account only the bound–bound radiative transitions between internal energy levels of molecules and neglect the transitions between electronic states and also bound–free and free–free radiative transitions. Under this condition, the collision operator of radiative processes is obtained in the form:

$$J_{cij}^{\text{rad}} = J_{cij}^{\text{em-abs}} + J_{cij}^{\text{scat}}. \quad (18)$$

The collision operator $J_{cij}^{\text{em-abs}}$ describing simultaneously processes (15) and (16) can be constructed in the following way:

$$J_{cij}^{\text{em-abs}} = \sum_{i'j'} \int \left(f_v f_{c'i'j'} W_{cv,i'j'}^{cv,i,j} - f_{cij} \left(f_v W_{cv,i,j}^{cv,i'j'} + W_{c,i,j}^{c,i'j'} \right) \right) d\mathbf{p}_v d\mathbf{p}'_c, \quad (19)$$

where $W_{cv,i'j'}^{cv,i,j}$, $W_{c,i,j}^{c,i'j'}$ are, correspondingly, the probabilities per unit time of induced and spontaneous emission of a photon with frequency ν by an excited particle of c chemical species at i th vibrational and j th rotational level, $W_{cv,i'j'}^{cv,i,j}$ is the probability of absorption of a photon resulting in excitation of a particle c from the initial state (i', j') to the more energetic state (i, j) .

The probabilities $W_{cv,i'j'}^{cv,i,j}$, $W_{c,i,j}^{c,i'j'}$ and $W_{cv,i'j'}^{c,i,j}$ are not independent and should be related by the principle of detailed balance. Under conditions of thermodynamic equilibrium, the differential reaction rates for each microscopic process and for the corresponding inverse process are equal, and therefore the following relation is satisfied:

$$f_v^{\text{eq}} \frac{f_{c'i'j'}^{\text{eq}}}{f_{cij}^{\text{eq}}} \frac{W_{cv,i'j'}^{cv,i,j}}{W_{cv,i,j}^{cv,i'j'}} = f_v^{\text{eq}} + \frac{W_{c,i,j}^{c,i'j'}}{W_{cv,i,j}^{c,i'j'}}. \quad (20)$$

The distribution functions of material particles under conditions of thermal and chemical equilibrium f_{cij}^{eq} are obtained in Ref. [30] and in the case considered their ratio is equal to

$$\frac{f_{c'i'j'}^{\text{eq}}}{f_{cij}^{\text{eq}}} = \frac{s_{i'j'}^c}{s_{ij}^c} \exp\left(\frac{\Delta \varepsilon_{ij'i'j'}}{kT}\right), \quad (21)$$

where k is the Boltzmann constant, T is the gas temperature, $\Delta \varepsilon_{ij'i'j'}^c = \varepsilon_{ij}^c - \varepsilon_{i'j'}^c$, ε_{ij}^c is the internal energy of a molecule c chemical species at i th vibrational and j th rotational level. For bound–bound radiative transitions, the frequency of a photon corresponds to the frequency of the transition between two discrete energy levels, and therefore $\nu = \nu_{ij'i'j'} = \Delta \varepsilon_{ij'i'j'}/h$. Thus, rearranging the terms in Eq. (20), one obtains

$$f_v^{\text{eq}} = \frac{W_{c,i,j}^{cv,i'j'}/W_{cv,i,j}^{cv,i'j'}}{\left(\frac{s_{i'j'}^c}{s_{ij}^c} \frac{W_{cv,i'j'}^{cv,i,j}}{W_{cv,i,j}^{cv,i'j'}} \exp\left(\frac{h\nu}{kT}\right) - 1\right)}. \quad (22)$$

The equilibrium distribution function of photons f_v^{eq} is connected with the Planck's function describing the specific intensity of equilibrium black body radiation [20], and may be found under the form:

$$f_v^{\text{eq}} = \frac{2/h^3}{\exp\left(\frac{h\nu}{kT}\right) - 1}. \quad (23)$$

Comparing Eqs. (22) and (23), one can conclude that the probabilities of absorption, induced and spontaneous emission are related to each other by the relations:

$$s_{i'j'}^c W_{cv,i'j'}^{cv,i,j} = s_{ij}^c W_{cv,i,j}^{c,i'j'}, \quad (24)$$

$$\frac{W_{c,i,j}^{cv,i'j'}}{W_{cv,i,j}^{c,i'j'}} = \frac{2}{h^3}. \quad (25)$$

These relations are similar to the ones connecting the spectral Einstein coefficients for absorption, induced and spontaneous emission.

Finally, the collision operator $J_{cij}^{\text{em-abs}}$ may be written in the next form:

$$J_{cij}^{\text{em-abs}} = \sum_{i'j'} \int \left(f_v f_{c'i'j'} \frac{s_{ij}^c}{s_{i'j'}^c} - f_{cij} \left(f_v + \frac{2}{h^3} \right) \right) \times W_{cv,i,j}^{cv,i'j'} d\mathbf{p}_v d\mathbf{p}'_c. \quad (26)$$

Similarly, the collision operator of photons scattering has been found:

$$J_{cij}^{\text{scat}} = \sum_{i'j'} \int \left(f_{\nu} f_{c'i'j'} \frac{S_{ij}^c}{S_{i'j'}^c} - f_{cij} f_{\nu} \right) W_{cv,ij}^{c\nu, i'j'} \mathbf{d}\mathbf{p}_\nu \mathbf{d}\mathbf{p}_{\nu'} \mathbf{d}\mathbf{p}'_c, \quad (27)$$

where $W_{cv,ij}^{c\nu, i'j'}$ is the probability of scattering of a photon with frequency ν by a particle of c species at i th vibrational and j th rotational level.

The probabilities $W_{cd,ijkl}^{c'd', i'j'k'l'}$ of different processes are defined by the expression [30]:

$$W_{cd,ijkl}^{c'd', i'j'k'l'} = \left| \frac{\mathbf{p}_c}{m_c} - \frac{\mathbf{p}_d}{m_d} \right| I_{cd,ijkl}^{c'd', i'j'k'l'}(\mathbf{p}_c, \mathbf{p}_d, \mathbf{p}_{c'}, \mathbf{p}_{d'}), \quad (28)$$

where $I_{cd,ijkl}^{c'd', i'j'k'l'}(\mathbf{p}_c, \mathbf{p}_d, \mathbf{p}_{c'}, \mathbf{p}_{d'})$ is the formal cross-section of the corresponding process. For further development, it is useful to introduce the differential cross-sections of various processes $\sigma_{cd,ijkl}^{c'd', i'j'k'l'}$. It is also conventional to determine the distribution functions of material particles in the phase space (\mathbf{r}, \mathbf{u}) , where \mathbf{u} is the microscopic velocity of a particle. It is obvious that

$$f_{cij}(\mathbf{r}, \mathbf{u}_c, t) = m_c^{-3} f_{cij}(\mathbf{r}, \mathbf{p}_c, t). \quad (29)$$

Hereafter, the same nomenclature for the distribution functions in different phase spaces is retained. Following the procedure described in Refs. [30,33], the collision operators may be rewritten in such a form:

$$J_{cij}^{\text{inel}} = \sum_{dkl'i'j'k'l'} \int \left(f_{c'i'j'} f_{dk'l'} \frac{S_{ij}^c S_{kl}^d}{S_{i'j'}^c S_{k'l'}^d} - f_{cij} f_{dkl} \right) \times g_{cd} \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega_{c'd'} \mathbf{d}\mathbf{u}_d, \quad (30)$$

$$J_{cij}^{\text{exch}} = \sum_{d'e'k'l'i'j'k'l'} \int \left(f_{c'e'j'} f_{d'k'l'} \frac{S_{ij}^c S_{kl}^d}{S_{i'j'}^c S_{k'l'}^d} \left(\frac{m_c m_d}{m_{c'} m_{d'}} \right)^3 - f_{cij} f_{dkl} \right) g_{cd} \sigma_{cd,ijkl}^{c'd', i'j'k'l'} d^2\Omega_{c'd'} \mathbf{d}\mathbf{u}_d, \quad (31)$$

$$J_{cij}^{\text{diss-rec}} = \sum_{dkl'k'l'} \int \left(f_{c'} f_{j'} f_{dk'l'} \hbar^3 \frac{S_{ij}^c S_{kl}^d}{S_{k'l'}^d} \left(\frac{m_c}{m_{c'} m_{j'}} \right)^3 - f_{cij} f_{dkl} \right) g_{cd} \sigma_{cd,ijkl}^{c'd', d, k'l'} \mathbf{d}\mathbf{u}_{c'} \mathbf{d}\mathbf{u}_{j'} \mathbf{d}\mathbf{u}_{d'} \mathbf{d}\mathbf{u}_d, \quad (32)$$

$$J_{cij}^{\text{em-abs}} = \sum_{i'j'} \int \left(f_{\nu} f_{c'i'j'} \frac{S_{ij}^c}{S_{i'j'}^c} - f_{cij} \left(f_{\nu} + \frac{2}{h^3} \right) \right) \times c \sigma_{cv,ij}^{c\nu, i'j'} \mathbf{d}\mathbf{p}_\nu \mathbf{d}\mathbf{u}'_c, \quad (33)$$

$$J_{cij}^{\text{scat}} = \sum_{i'j'} \int \left(f_{\nu} f_{c'i'j'} \frac{S_{ij}^c}{S_{i'j'}^c} - f_{cij} f_{\nu} \right) \times c \sigma_{cv,ij}^{c\nu, i'j'} \mathbf{d}\mathbf{p}_\nu \mathbf{d}\mathbf{p}_{\nu'} \mathbf{d}\mathbf{u}'_c. \quad (34)$$

Here, $\sigma_{cd,ijkl}^{c'd', i'j'k'l'}$, $\sigma_{cd,ijkl}^{c'd', d, k'l'}$, $\sigma_{cv,ij}^{c\nu, i'j'}$ are, respectively, the differential cross-sections of binary and triple collisions of material particles, and of the interaction of photons with material particles, g_{cd} is the relative velocity of colliding particles, $d\Omega_{c'd'}$ is the solid angle in which the relative velocity after the collision can appear. Strictly speaking, the relative velocity of the motion of a particle and a photon is $\mathbf{g}_{cv} = \mathbf{c} - \mathbf{u}_c$. However, one can neglect the magnitude of \mathbf{u}_c compared to the speed of light, and thus, c appears in Eqs. (33) and (34) instead of \mathbf{g}_{cv} . Note that in Eqs. (30)–(34), the distribution functions of material particles is defined in terms of the velocity, $f_{cij} = f_{cij}(\mathbf{r}, \mathbf{u}_c, t)$, whereas the distribution functions of photons are expressed in terms of the momentum, $f_{\nu} = f_{\nu}(\mathbf{r}, \mathbf{p}_{\nu}, t)$.

3. Zero-order solution and macroscopic equations

The dimensionless kinetic equations are given by

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \frac{\partial f_{cij}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{cij}^{\text{rap}} + J_{cij}^{\text{sl}}, \quad (35)$$

$$\frac{\partial f_{\nu}}{\partial t} + c \boldsymbol{\Omega}_{\nu} \frac{\partial f_{\nu}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{\nu}^{\text{rap}} + J_{\nu}^{\text{sl}}. \quad (36)$$

Here, J_{cij}^{rap} , J_v^{rap} and J_{cij}^{sl} , J_v^{sl} are the collision operators of rapid and slow processes, $\varepsilon = \tau_{\text{rap}}/\tau_{\text{sl}}$ is the small parameter, τ_{rap} , τ_{sl} are the average times between the frequent and rare collisions, respectively. For the solution of these kinetic equations, the Chapman–Enskog method generalized for rapid and slow processes [30,35] may be used. The solution is found as an expansion of the distribution functions in a power series of the parameter ε :

$$f_{cij} = \sum_n \varepsilon^n f_{cij}^{(n)}. \quad (37)$$

The zero-order approach gives the following relation:

$$J_{cij}^{\text{rap}}(f^{(0)}, f^{(0)}) = J_v^{\text{rap}}(f^{(0)}, f^{(0)}) = 0. \quad (38)$$

It is known that the zero-order distribution function is determined by the summational invariants of the most frequent collisions (eigenfunctions of the linearized collision operator of rapid processes J_{cij}^{rap}) [30]. The collision invariants are found under specific flow conditions.

Under condition (1), the operators of rapid and slow processes may be written in the form:

$$J_{cij}^{\text{rap}} = J_{cij}^{\text{el}} + J_{cij}^{\text{rot}}, \quad (39)$$

$$J_v^{\text{rap}} = 0, \quad (40)$$

$$J_{cij}^{\text{sl}} = J_{cij}^{\text{vibr}} + J_{cij}^{\text{react}} + J_{cij}^{\text{rad}}, \quad (41)$$

$$J_v^{\text{sl}} = J_v^{\text{rad}}. \quad (42)$$

One can observe that in the conditions of slow radiative processes equation (38) for the zero-order distribution function of photons, $f_v^{(0)}$ is satisfied identically. It means that the formalism of asymptotic methods of small parameter cannot be applied for determination of the photon distribution functions. Therefore, f_v are to be found directly from microscopic equations (36).

The collision invariants of any collision of material particles are $\psi_{cij}^{(1)} = 1$, $\psi_{cij}^{(\mu+1)} = m_c u_{c\mu}$ ($\mu = 1-3$ are the spatial indices), $\psi_{cij}^{(5)} = m_c u_c^2/2 + \varepsilon_{ij}^c$. For photons $\psi_v^{(\mu+1)} = p_{v\mu}$ ($\mu = 1-3$), $\psi_v^{(5)} = hv$. Besides that there exist additional invariants of the most frequent collisions. In conditions of slow vibrational relaxation and chemical

reactions, any variable a_{ci} independent of the velocity and the rotational energy level j and depending arbitrary on c and i is conserved: $\psi_{cij}^{(\lambda+5)} = a_{ci}$, ($\lambda = 1, \dots, N$, where $N = \sum_{ci} 1$).

The macroscopic parameters corresponding to the collision invariants are given by

$$\sum_j \int f_{cij} \mathbf{d}\mathbf{u}_c = \sum_j \int f_{cij}^{(0)} \mathbf{d}\mathbf{u}_c = n_{ci}, \quad (43)$$

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

$$\sum_{cij} m_c \int \mathbf{u}_c f_{cij} \mathbf{d}\mathbf{u}_c = \sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)} \mathbf{d}\mathbf{u}_c = \rho \mathbf{v}, \quad (44)$$

$$\begin{aligned} \sum_{cij} \int \left(\frac{m_c C_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon^c \right) f_{cij} \mathbf{d}\mathbf{u}_c \\ = \sum_{cij} \int \left(\frac{m_c C_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon^c \right) f_{cij}^{(0)} \mathbf{d}\mathbf{u}_c \\ = \frac{3}{2} nkT + \rho E_{\text{rot}} + \rho E_{\text{vibr}} + \rho E_f. \end{aligned} \quad (45)$$

Here, n_{ci} is the level population of i th level of chemical species c , L , the number of chemical species, L_c , the number of vibrational levels in c chemical species, \mathbf{v} , the macroscopic gas velocity, $\rho = \sum_c m_c n_c$, the gas density, $\mathbf{C}_c = \mathbf{u}_c - \mathbf{v}$, the peculiar velocity, $n = \sum_c n_c$, the total number density of particles, ε_j^{ci} , the rotational energy of a molecule c chemical species at i th vibrational level, ε_i^c , the vibrational energy, ε^c , the energy of formation of particles of c species, and E_{rot} , E_{vibr} and E_f are, respectively, the rotational energy, vibrational energy and energy of formation per unit mass.

One can introduce a mean momentum of photons per unit volume, π , and a mean radiative energy per unit volume, \mathcal{E}_{rad} :

$$\pi = \int \mathbf{p}_v f_v \mathbf{d}\mathbf{p}_v, \quad \mathcal{E}_{\text{rad}} = \int h\nu f_v \mathbf{d}\mathbf{p}_v. \quad (46)$$

Note that for these quantities, there are no normalizing conditions similar to Eqs. (43)–(45) for macroscopic parameters of material particles.

On the basis of the system of collision invariants and using the normalizing conditions (43)–(45), the zero-order distribution function of particles $f_{cij}^{(0)}$ is obtained in the form of the Maxwell–Boltzmann distribution over velocity and rotational energy depending on the nonequilibrium level populations of chemical species [35,13]:

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT} \right)^{3/2} \frac{n_{ci} s_j^{ci}}{Z_{rot}^{ci}} \exp \left(-\frac{m_c C_c^2}{2kT} - \frac{\epsilon_j^{ci}}{kT} \right), \quad (47)$$

s_j^{ci} is the rotational statistic weight, and Z_{rot}^{ci} , the rotational partition function. The distribution function (47) is expressed in terms of macroscopic parameters $n_{ci}(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$.

Following Ref. [20], it is conventional to define a specific intensity I_v of the radiation field in such a way

$$I_v d\mathbf{\Omega}_v d\mathbf{p}_v = ch\nu f_v d\mathbf{p}_v, \quad (48)$$

$d\mathbf{\Omega}_v$ denotes an element of solid angle defined by the unit vector $\mathbf{\Omega}_v$. Thus, taking into account relation (3),

$$I_v = \frac{h^4 \nu^3}{c^2} f_v. \quad (49)$$

The mean momentum of photons π and radiation energy \mathcal{E}_{rad} in terms of intensity have the form:

$$\begin{aligned} \pi &= \frac{1}{c^2} \int_0^\infty \int_{4\pi} I_v \mathbf{\Omega}_v d\nu d\mathbf{\Omega}_v, \\ \mathcal{E}_{rad} &= \frac{1}{c} \int_0^\infty \int_{4\pi} I_v d\nu d\mathbf{\Omega}_v. \end{aligned} \quad (50)$$

Consequently, Eq. (36) for f_v may be rewritten in terms of I_v :

$$\frac{1}{c} \frac{\partial I_v}{\partial t} + \mathbf{\Omega}_v \frac{\partial I_v}{\partial \mathbf{r}} = \frac{h^4 \nu^3}{c^3} J_v^{rad}, \quad v = \nu_1, \nu_2, \dots, \nu_R. \quad (51)$$

In the general case, there is an infinite set of frequencies ν at which a photon can appear. In practical calculations, the number of equations R corresponds to the number of characteristic frequencies in a flow. The equations for the specific intensity in form (51) are equivalent to the equations of radiative transfer [20].

Now, let us derive the macroscopic equations. For the vibrational level populations $n_{ci}(\mathbf{r}, t)$ similarly to Ref. [13], one can obtain

$$\begin{aligned} \frac{dn_{ci}}{dt} + n_{ci} \nabla \cdot \mathbf{v} + \nabla \cdot (n_{ci} \mathbf{V}_{ci}) &= R_{ci}, \\ c &= 1, \dots, L, \quad i = 0, \dots, L_c. \end{aligned} \quad (52)$$

Here, \mathbf{V}_{ci} is the diffusion velocity of c species at the i th vibrational level:

$$n_{ci} \mathbf{V}_{ci} = \sum_j \int \mathbf{C}_c f_{cij} d\mathbf{u}_c,$$

the right-hand side of the equations are defined as

$$R_{ci} = \sum_j \int J_{cij}^{sl} d\mathbf{u}_c = R_{ci}^{vibr} + R_{ci}^{react} + R_{ci}^{rad}. \quad (53)$$

Eq. (52) represent the equations of detailed vibrational-chemical kinetics taking into account radiative transitions.

The conservation of momentum in the general case may be expressed in the form:

$$\rho \frac{d\mathbf{v}}{dt} + \frac{\partial \pi}{\partial t} + \nabla \cdot \mathbf{P} + \nabla \cdot \mathbf{P}_{rad} = 0. \quad (54)$$

One can notice that only a partial derivative of π appears in Eq. (54), because there is no reason to write Eq. (36) in terms of peculiar velocity. In this equation, \mathbf{P} , \mathbf{P}_{rad} are the tensors of pressure for material particles and photons:

$$\mathbf{P} = \sum_{cij} \int m_c \mathbf{C}_c \mathbf{C}_c f_{cij} d\mathbf{u}_c,$$

$$\mathbf{P}_{rad} = \int \mathbf{p}_v c \mathbf{\Omega}_v f_v d\mathbf{p}_v = \frac{1}{c} \int_0^\infty \int_{4\pi} I_v \mathbf{\Omega}_v \mathbf{\Omega}_v d\nu d\mathbf{\Omega}_v.$$

It should be noted that the transfer of momentum in a photon–particle collision is very small, because usually the momentum carried by photons is much less compared to the momentum of material particles. Therefore, the contribution of π and \mathbf{P}_{rad} to the conservation equation of momentum may be neglected, and Eq. (54) takes the usual form:

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0. \quad (55)$$

On the contrary, the exchange of energy in the photon–particle collision is not negligible because the energy of a photon is of the same order of magnitude that the kinetic energy of a material particle. Therefore, the conservation of total energy is written as follows:

$$\rho \frac{dU}{dt} + \frac{\partial \mathcal{E}_{\text{rad}}}{\partial t} + \nabla \cdot \mathbf{q} + \nabla \cdot \mathbf{q}_{\text{rad}} + \mathbf{P} : \nabla \mathbf{v} = 0. \quad (56)$$

Here, U is the total energy of material particles per unit mass:

$$\rho U = \frac{3}{2}nkT + \rho E_{\text{rot}} + \rho E_{\text{vibr}} + \rho E_f,$$

\mathbf{q} is the heat flux for material particles:

$$\mathbf{q} = \sum_{cij} \int \left(\frac{m_c C_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon^c \right) \mathbf{C}_c f_{cij} \mathbf{d}\mathbf{u}_c,$$

and \mathbf{q}_{rad} is the radiative heat flux:

$$\mathbf{q}_{\text{rad}} = \int h\nu c \boldsymbol{\Omega}_v f_v \mathbf{d}\mathbf{p}_v = \int_0^\infty \int_{4\pi} I_\nu \boldsymbol{\Omega}_v \mathbf{d}\nu \mathbf{d}\boldsymbol{\Omega}_v.$$

The expressions for all transport terms of material particles have been derived in Refs. [4,13]. In particular, it has been shown that in this approach the heat flux is determined by the gradients of the gas temperature, number densities of atomic species and nonequilibrium populations of all vibrational levels of molecular species. The transport coefficients involved in the expressions for \mathbf{V}_{ci} , \mathbf{P} and \mathbf{q} are also obtained in Ref. [13]. Concerning the radiative flux, it can be found using the solution of equations of radiative transfer (51).

Eqs. (52), (55), (56) and (51) represent a closed system of equations describing the flow of a reacting and radiating gas mixture under strong nonequilibrium conditions. It is interesting to mention that in the zero-order approximation of the Chapman–Enskog method, the diffusion velocity and heat flux by material particles vanish as a result of the Maxwellian distribution over velocities ($\mathbf{V}_{ci} = 0$, $\mathbf{q} = 0$). However, the term containing radiative flux \mathbf{q}_{rad} should be kept in Eq. (56) in the Euler approximation, because it

depends on the specific intensity I_ν (distribution function of photons f_ν) that is not determined by the order of approximation of the Chapman–Enskog method.

4. Application to a flow of diatomic gas with VV, vibrational–translational vibrational energy exchange, dissociation and radiative transitions

In the Euler approximation for steady-state one-dimensional flow, Eq. (52) of detailed vibration–dissociation kinetics in diatomic gas taking into account radiative transitions between discrete vibrational levels are given by

$$\frac{d(vn_i)}{dx} = R_i^{\text{VT}} + R_i^{\text{VV}} + R_i^{\text{diss}} + R_i^{\text{rad}}, \quad (57)$$

$$i = 0, \dots, L,$$

$$\frac{d(vn_a)}{dx} = R_a^{\text{diss}}, \quad (58)$$

where v is the flow velocity in the x direction, n_i , the population of i th vibrational level, n_a the number density of atoms, R_i^{VT} , R_i^{VV} , R_i^{diss} , R_i^{rad} , the production terms due to VT, VV vibrational energy exchange, dissociation–recombination and radiative transitions, respectively. These production terms may be written using the expressions for the collision integrals derived in Section 2 substituting the zero-order distribution function (47). Thus, the production terms due to collisions of material particles are obtained in Refs. [1,17,18] in the next form:

$$R_i^{\text{VT}} = n_{\text{mol}} \sum_{k \neq i} (k_{ki}^{\text{mol}} n_k - k_{ik}^{\text{mol}} n_i) + n_a \sum_{k \neq i} (k_{ki}^{\text{at}} n_k - k_{ik}^{\text{at}} n_i), \quad (59)$$

$$R_i^{\text{VV}} = \sum_{\substack{k, k', i' \\ k' \neq k, i' \neq i}} (k_{i'i}^{k'k} n_{i'} n_{k'} - k_{i'i'}^{kk'} n_i n_k), \quad (60)$$

$$R_i^{\text{diss}} = n_{\text{mol}} (k_{\text{rec},i}^{\text{mol}} n_a^2 - k_{i,\text{diss}}^{\text{mol}} n_i) + n_a (k_{\text{rec},i}^{\text{at}} n_a^2 - k_{i,\text{diss}}^{\text{at}} n_i), \quad (61)$$

$$R_a = -2 \sum_i R_i^{\text{diss-rec}}. \quad (62)$$

Here, k_{ik}^{mol} , k_{ik}^{at} and $k_{i'i'}^{kk'}$ are the rate coefficients for the TV ($i \rightarrow k$) vibrational–translational energy transitions in a collision with a partner M (M is a molecule or an atom) and VV ($i, k \rightarrow i', k'$) vibrational energy exchange between two molecules; $k_{\text{rec},i}^{\text{mol}}$, $k_{\text{rec},i}^{\text{at}}$ are the state-to-state rate coefficients of recombination to the i th level, $k_{i,\text{diss}}^{\text{mol}}$, $k_{i,\text{diss}}^{\text{at}}$ are the rate coefficients of dissociation from the i th level. All the above introduced rate coefficients represent the cross-sections of corresponding processes averaged over velocities and rotational energies. The relations connecting the rate coefficients with the cross-sections are given in Ref. [17].

There exist different models for the calculation of the rate coefficients of vibrational energy exchange. One of the most popular analytical approach, based on the semi-classical first-order perturbation theory, a collinear collision model and an exponential repulsive potential, is the SSH theory [36]. Its generalization for anharmonic oscillators is given in Refs. [25,37]. However, for high-collision velocities and for high quantum numbers, the SSH theory does not have any theoretical basis. Exact quantum trajectory calculations of the rate coefficients for vibrational transitions have been performed by Billing [38,39]. Unfortunately, the direct use of these results in numerical calculations is hardly possible. As to experimental data for VV and VT energy transfer, up to now, at high vibrational quantum numbers, they have been obtained only for a few heteronuclear species, and only for low temperatures. An analytical nonperturbative semiclassical forced harmonic oscillator model has been elaborated in Ref. [3], it gives correct values for the probability of VV and VT transitions (including multi-quantum ones) at high temperature conditions. Besides that one should mention the model proposed in Ref. [40], this model is based on the information theory.

Taking into account only single-quantum transitions, the expression for R_i^{VT} and R_i^{VV} can be rather simplified [18,25,37]:

$$\begin{aligned} R_i^{\text{VT}} = & n_{i+1} \left(n_{\text{mol}} k_{i+1,i}^{\text{mol}} + n_{\text{at}} k_{i+1,i}^{\text{at}} \right) \\ & + n_{i-1} \left(n_{\text{mol}} k_{i-1,i}^{\text{mol}} + n_{\text{at}} k_{i-1,i}^{\text{at}} \right) \\ & - n_i \left(n_{\text{mol}} \left(k_{i,i+1}^{\text{mol}} + k_{i,i-1}^{\text{mol}} \right) \right. \\ & \left. + n_{\text{at}} \left(k_{i,i+1}^{\text{at}} + k_{i,i-1}^{\text{at}} \right) \right), \end{aligned} \quad (63)$$

$$\begin{aligned} R_i^{\text{VV}} = & n_{i+1} \sum_{k=0}^L k_{i+1,i}^{k,k+1} n_k + n_{i-1} \sum_{k=0}^L k_{i-1,i}^{k+1,k} n_{k+1} \\ & - n_i \sum_{k=0}^L \left(k_{i,i+1}^{k+1,k} n_{k+1} + k_{i,i-1}^{k,k+1} n_k \right). \end{aligned} \quad (64)$$

Dissociation–recombination reaction rates can also be simulated using different models. We will discuss two of them: the ladder climbing model [1,9,10,18] and the Treanor–Marrone one [2,18,41]. The ladder climbing model is based on the assumption that molecules dissociate only from the last level, and each molecule reaching 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 the lower-lying levels caused by VV and VT vibrational energy transitions.

In case, when dissociation may happen from any vibrational level, the expression for $k_{i,\text{diss}}^{(M)}$ can be derived using the results of Ref. [41]. Following this paper, the state-to-state rate coefficients may be connected with the thermal equilibrium rate coefficient $k_{\text{diss,eq}}^{(M)}$ by the expression [2,18]:

$$k_{i,\text{diss}}^{(M)} = Z_i(T, U) k_{\text{diss,eq}}^{(M)}, \quad (65)$$

with the nonequilibrium factor $Z_i(T, U)$ defined as

$$Z_i(T, U) = \frac{Z_{\text{vibr}}(T)}{Z_{\text{vibr}}(-U)} \exp \left(\frac{\varepsilon_i}{k} \left(\frac{1}{T} + \frac{1}{U} \right) \right). \quad (66)$$

Here, ε_i is the vibrational energy of i th level, s_i is the vibrational statistical weight ($s_i = 1$ for diatomic molecules), the vibrational partition

function at “temperature X ”, $Z_{\text{vibr}}(X)$, has the form:

$$Z_{\text{vibr}}(X) = \sum_i s_i \exp\left(-\frac{\varepsilon_i}{kX}\right). \quad (67)$$

The parameter of the model U has a dimension of temperature and describes how rapidly the dissociation probability decreases for low levels. The case $U = \infty$ corresponds to the equal probability of dissociation from any vibrational level. The thermal equilibrium rate coefficient $k_{\text{diss,eq}}^{(M)}$ can be computed using the generalized Arrhenius law. The parameters of the Arrhenius formula for various dissociation reactions are given in many sources [21,28,42].

Recombination rate coefficient $k_{\text{rec},i}^{(M)}$ is connected with $k_{i,\text{diss}}^{(M)}$ by the detailed balance principle [17,43]:

$$k_{\text{rec},i}^{(M)} = k_{i,\text{diss}}^{(M)} s_i h^3 \left(\frac{m_{\text{mol}}}{m_a m'_a}\right)^{3/2} (2\pi kT)^{-3/2} Z_{\text{rot}}^i \times \exp\left(-\frac{\varepsilon_i - D}{kT}\right), \quad (68)$$

m_{mol} is the mass of molecules, m_a , m'_a are the masses of atoms, which compose a molecule, D is the dissociation energy of a molecule.

The production rate due to radiative transitions R_i^{rad} neglecting scattering may be written on the basis of the collision integral (19). Let us introduce the spectral Einstein coefficients associated to the specific intensity I_ν :

$$\frac{1}{c} I_\nu b_{\nu,ijl'j'} d\Omega_\nu d\nu = f_\nu W_{\nu,ij}^{\nu,i'l'j'} dp_\nu, \quad (69)$$

$$\frac{h^3}{4\pi} a_{\nu,ijl'j'} d\Omega_\nu d\nu = W_{ij}^{\nu,i'l'j'} dp_\nu. \quad (70)$$

Coefficients $b_{i'l'j'ij}$, $b_{ijl'j'}$, $a_{ijl'j'}$ are the Einstein coefficients for absorption, induced and spontaneous emission, respectively. As well as the probabilities $W_{\nu,ij}^{\nu,i'l'j'}$, $W_{ij}^{\nu,i'l'j'}$, they are related by the detailed balance principle:

$$s_{i'l'j'} b_{\nu,i'l'j'ij} = s_{ij} b_{\nu,ijl'j'}, \quad \frac{a_{\nu,ijl'j'}}{b_{\nu,ijl'j'}} = \frac{8\pi h\nu^3}{c^2}. \quad (71)$$

The production term R_i^{rad} after substituting the zero order distribution function (47) takes the form:

$$R_i^{\text{rad}} = \sum_{i'<i} \sum_{j,j'<j} \left(n_{i'l'j'} \int_0^\infty \int_{4\pi} I_\nu b_{\nu,i'l'j'ij} d\nu d\Omega_\nu - n_{ij} \left(\int_0^\infty \int_{4\pi} I_\nu b_{\nu,ijl'j'} d\nu d\Omega_\nu + \frac{1}{4\pi} \int_0^\infty \int_{4\pi} a_{\nu,ijl'j'} d\nu d\Omega_\nu \right) \right). \quad (72)$$

Here, n_{ij} is the population of the internal energy level with vibrational and rotational quantum numbers i and j .

For bound-bound transitions the integral Einstein coefficients are usually defined in the form:

$$B_{ijl'j'} = \int_0^\infty b_{\nu,ijl'j'} d\nu, \quad (73)$$

$$A_{ijl'j'} = \int_0^\infty a_{\nu,ijl'j'} d\nu. \quad (74)$$

These coefficients describe probabilities of all radiative transitions, which contribute to the transition ($ij \rightarrow i'l'j'$). With the assumption that I_ν and $h\nu$ are slowly varying functions of frequency over the line width, the integral Einstein coefficients are related by the expressions similar to Eq. (71) with ν corresponding to the center of line. Under this assumption, one can put $I_\nu \sim I_{\nu,ijl'j'} = \text{const}$, where $I_{\nu,ijl'j'}$ is the mean specific intensity of the rotational-vibrational line. Then the expression for R_i^{rad} may be simplified:

$$R_i^{\text{rad}} = \sum_{i'<i} \sum_{j,j'<j} \left(n_{i'l'j'} I_{\nu,ijl'j'} B_{i'l'j'ij} - n_{ij} \left(I_{\nu,ijl'j'} B_{ijl'j'} + A_{ijl'j'} \right) \right). \quad (75)$$

Here, we have taken into account the isotropic character of spontaneous emission.

As there exists a quasi-stationary Boltzmann distribution over rotational energy, one can define

the averaged values of $I_{v,ij'i'j'}$, $I_{v,ij'i'j}$ and $A_{ij'i'j}$ over rotational spectrum:

$$I_{v,ii'} B_{ii'} = \sum_{j,j' < j} \frac{s_j^i I_{v,ij'i'j'} B_{ij'i'j'}}{Z_{\text{rot}}^i} \exp\left(-\frac{\epsilon_j^i}{kT}\right),$$

$$I_{v,ii'} B_{i'i} = \sum_{j,j' < j} \frac{s_j^i I_{v,ij'i'j} B_{i'j'ij}}{Z_{\text{rot}}^i} \exp\left(-\frac{\epsilon_j^i}{kT}\right),$$

$$A_{ii'} = \sum_{j,j' < j} \frac{s_j^i A_{ij'i'j'}}{Z_{\text{rot}}^i} \exp\left(-\frac{\epsilon_j^i}{kT}\right).$$

$I_{v,ii'}$ may be interpreted as a mean specific intensity of vibrational line, $B_{i'i}$, $B_{ii'}$, $A_{ii'}$ as the Einstein coefficients for the radiative transitions corresponding to the vibrational transition ($i \rightarrow i'$). In this case, the production rate R_i^{rad} is given by the expression similar to the one obtained in Ref. [25]:

$$R_i^{\text{rad}} = \sum_{i' < i} \left(n_{i'} I_{v,ii'} B_{i'i} - n_i (I_{v,ii'} B_{ii'} + A_{ii'}) \right). \quad (76)$$

The Einstein coefficients can be calculated using the method described, for instance, in Refs. [19,20].

Equations of detailed vibration–dissociation kinetics (57), with production terms (61)–(64), and (75) should be coupled with the conservation equations of momentum and total energy and equations of radiative transfer. In the Euler approximation for stationary one-dimensional flow conservation, Eqs. (55) and (56) are reduced to equations,

$$\rho v \frac{dv}{dx} + \frac{dp}{dx} = 0, \quad (77)$$

$$\rho v \frac{dU}{dx} + \frac{dq_{\text{rad}}}{dx} + p \frac{dv}{dx} = 0, \quad (78)$$

where $p = nkT$ is the pressure.

The equations of radiative transfer neglecting the scattering take the form:

$$\frac{dI_v}{dx} = R_v^{\text{rad}}, \quad v = v_1, v_2, \dots, v_R, \quad (79)$$

I_v describes the specific intensity of radiation propagating in the positive direction of the axis x . The right-hand sides of these equations are given by

$$R_v^{\text{rad}} = hv \sum_{ij'i'j'} \left(n_{ij'} \left(I_{v,b_{v,ij'i'j'}} + \frac{1}{4\pi} a_{v,ij'i'j'} \right) - n_{i'j'} I_{v,b_{v,i'j'ij}} \right), \quad (80)$$

or, after performing the averaging over rotational spectrum,

$$R_v^{\text{rad}} = hv \sum_{ii'} \left(n_i \left(I_{v,b_{v,ii'}} + \frac{1}{4\pi} a_{v,ii'} \right) - n_{i'} I_{v,b_{v,i'i}} \right). \quad (81)$$

It should be mentioned here that these expressions are obtained without usual assumption about local thermal equilibrium.

The infrared radiation intensity of N_2 first positive band has been calculated in a flow of dissociating nitrogen N_2 behind a strong shock wave (Fig. 1). The free stream conditions are as follows: $M_0 = 15$, $T_0 = 293$ K, $p_0 = 100$ Pa, initially gas supposed to be in equilibrium. Three different approaches have been used for the calculations: the model presented above, the multi-temperature model based on the quasi-stationary nonequilibrium Boltzmann distribution, and the one-temperature model based on the local thermal equilibrium assumption. One can see that both quasi-stationary approaches give an overestimation of the intensity. This fact can be explained by the different behaviour of the N_2 concentrations

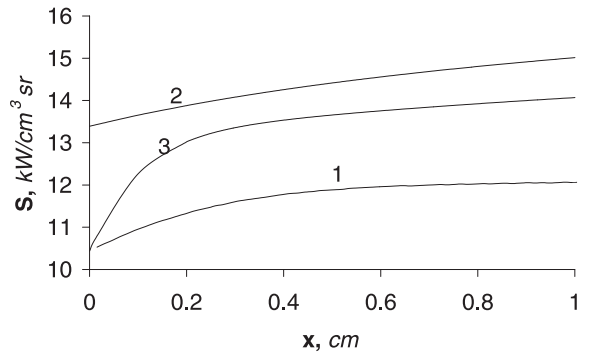


Fig. 1. Infrared radiation intensity of N_2 first positive band, S kW/cm² sr, as a function of x . Curve 1 represents present approach, curves 2, 3, the multi-temperature and one-temperature approaches, correspondingly.

computed using different models (see Refs. [4,13]) for a discussion of the macroscopic parameters behaviour).

5. Conclusions

A closed system of macroscopic equations describing the flow of a reacting and radiating gas mixture under strong nonequilibrium conditions is derived on the basis of the kinetic theory. This system consists of the equations of detailed vibration–dissociation kinetics coupled with the radiative transfer equations and conservation equations of the momentum and total energy. Solution of these equations is important for the investigation of radiation from the nonequilibrium regions of a gas flow with slow vibrational relaxation and chemical reactions. The model can be applied for the calculation of radiation intensity in different conditions, this is useful for the validation of various models for rate coefficients of chemical reactions and vibrational energy transitions. Another important application is the computation of the total energy and radiative fluxes in the regions of strong nonequilibrium near re-entering bodies.

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