Vibration–electronic and chemical kinetics of non-equilibrium radiative diatomic gas flows

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Abstract

The Letter presents a generalization of the kinetic model for radiative flows of reacting gas mixtures with strong vibrational and chemical non-equilibrium. The new model takes into account the vibration–electronic (VE) transitions and radiative transitions from the electronically excited states. A closed set of macroscopic equations taking into account the coupling of vibrational relaxation, chemical reactions and radiative transitions is derived. The peculiarities of non-equilibrium kinetics of CO in different conditions are discussed. © 2001 Published by Elsevier Science B.V.

1. Introduction

Non-equilibrium state-to-state vibrational–chemical kinetics of diatomic molecules is widely discussed in the recent papers on molecular lasers, atmosphere chemistry and various gas dynamic applications. A short review of the results obtained for different flows by means of solution of master equations for the vibrational level populations together with conservation equations is given, for instance, in [1,2]; the kinetic theory of state-specific transport properties and reaction rates is developed in [2,3].

An extension of the state-to-state model which permits to treat properly radiative transitions is of importance for laser technology, photochemistry, shock tube measurements as well as for estimation of the heat transfer caused by radiation. A self-consistent model which allows one to describe a non-equilibrium gas mixture flow with coupled vibrational relaxation, chemical reactions, absorption and emission of photons based on the rigorous kinetic theory is proposed in [1]. This approach has been elaborated for the conditions when excitation of electronic molecular states can be neglected, i.e., for moderate gas temperatures or for the case of low storage of vibrational energy. Such a model can fail to describe optically pumped systems or some high temperature and high enthalpy flows.

In the present Letter the state-to-state model given in [1] is generalized by including in the kinetic scheme the vibration–electronic (VE) transitions and emission from the electronically excited states. As in the previous paper, the approach is based on the assumption of rapid equilibration of translational and rotational modes compared to the remaining processes. In this case the distributions over velocities and rotational energies follow

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the Maxwell–Boltzmann form, while no quasi-stationary distributions over vibrational energies (Boltzmann or Treanor) is established in the system. A closed set of macroscopic equations taking into account coupled vibrational and electronic relaxation, chemical reactions and radiative transitions is derived. The detailed non-equilibrium kinetics of carbon monoxide is considered as an example of possible application of the proposed model.

2. Kinetic theory approach

The gas flow is described on the basis of the kinetic equations for distribution functions. The distribution functions $f_{c\alpha ij}(\mathbf{r}, \mathbf{p}_c, t)$ are introduced for every chemical species c, electronic state α, vibrational and rotational energy levels i and j, respectively, and for photons $f_v(\mathbf{r}, \mathbf{p}_v, t)$ (t is the time, $\mathbf{r}$ and $\mathbf{p}$ are the spatial co-ordinates and momentum). For the convenience of notations one can designate the set of internal states by a unique number: $q = (\alpha, i, j)$. The kinetic equations for distribution functions of material particles can be expressed in terms of microscopic particle velocity $\mathbf{u}_c$:

$$\frac{\partial f_{cq}}{\partial t} + \mathbf{u}_c \frac{\partial f_{cq}}{\partial \mathbf{r}} = J_{cq}, \tag{1}$$

whereas for the distribution function of photons the equations are written in terms of momentum

$$\frac{\partial f_v}{\partial t} + c\mathbf{\Omega}_v \frac{\partial f_v}{\partial \mathbf{r}} = J_v, \tag{2}$$

where $\mathbf{\Omega}_v$ is the unit vector defining the direction of travel of the photon, c is the speed of light. The collision operators J_{cq} and J_v describe all the collisions leading to the change of distribution functions. They represent a sum of several terms corresponding to different processes

$$J_{cq} = J_{cq}^{\text{el}} + J_{cq}^{\text{inel}} + J_{cq}^{\text{react}} + J_{cq}^{\text{rad}}.$$

The integral operators of elastic and inelastic collisions J_{cq}^{el} and J_{cq}^{inel} correspond to the collisions of material particles which do not result in the change of chemical species:

$$A_{cq} + A_{dr} \rightleftharpoons A_{cq} + A_{dr}, \tag{3}$$

$$A_{cq} + A_{dr} \rightleftharpoons A_{cq'} + A_{dr'}. \tag{4}$$

Elastic collisions (3) lead to the change of only the particle velocities, and in collisions (4) the internal state of molecules varies also. Reaction (4) can describe the inelastic rotation–translation (RT) exchange (in this case only rotational quantum numbers j change during the collision); vibration–translation (VT) transitions, intramode vibration–vibration (VV) exchange, intermode VV′ transfer of vibrational quanta between unlike molecules (in all these cases both rotational and vibrational states i and j change); and, finally, VE transitions (this process leads to change of all internal states i, j, α). Consequently, the integral operator J_{cq}^{inel} can be presented in the next form

$$J_{cq}^{\text{inel}} = J_{cq}^{\text{RT}} + J_{cq}^{\text{VT}} + J_{cq}^{\text{VV}} + J_{cq}^{\text{VV}'} + J_{cq}^{\text{VE}}.$$

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

$$A_{cq} + A_{dr} \rightleftharpoons A_{c'q'} + A_{d'r'} \tag{5}$$

and dissociation–recombination process

$$A_{cq} + A_{dr} \rightleftharpoons A_{dr'} + A_{c'q'} + A_{f'p'}. \tag{6}$$

Therefore, $J_{cq}^{\text{react}} = J_{cq}^{\text{exch}} + J_{cq}^{\text{diss–rec}}$.

The collision operators for processes (3)–(6), except for the VE transitions, since the papers of Wang Chang and Uhlenbeck [4] and Ludwig and Heil [5] are obtained by many authors and summarized in [6,1]. The integral operator for VE transitions represents an extension of that for inelastic collisions without change of the electronic state

$$J_{cq}^{\text{VE}} = \sum_{d,r,q',r'} \int \left(f_{cq'} f_{dr'} \frac{s_q^c s_r^d}{s_{q'}^c s_{r'}^d} - f_{cq} f_{dr} \right) \\ \times g_{cd} \sigma_{cd, qr}^{q'r'} \, \mathrm{d}^2 \mathbf{\Omega}_{c'd'} \, \mathrm{d}\mathbf{u}_d, \tag{7}$$

where s_q^c is the statistical weight of corresponding state q; $\sigma_{cd, qr}^{q'r'}$ is the differential cross-section of the transition of particles at the internal states $q = (\alpha, i, j)$ and $r = (\beta, k, l)$ and possessing the velocities $\mathbf{u}_c$ and $\mathbf{u}_d$ to particles at the internal states $q' = (\alpha', i', j')$ and $r' = (\beta', k', l')$ with the velocities $\mathbf{u}'_c$, $\mathbf{u}'_d$; $\mathbf{g}_{cd}$ is the relative velocity of col-

liding particles; $d\Omega_{c'd'}$ is the solid angle in which the relative velocity after the collision can appear. Note, that the integral operator of inelastic collisions within the same electronic state can be easily deduced from (7) by keeping constant α, β and omitting the summation over β, α', β'.

Among the radiative collisions the ones leading to absorption, emission and scattering of photons may be distinguished. The following transitions correspond to absorption and induced emission processes

$$A_{cq} + h\nu \rightleftharpoons A_{cq'} + 2h\nu, \tag{8}$$

(h is the Planck constant, ν is the frequency), while spontaneous emission is described by the transition

$$A_{cq} \rightarrow A_{cq'} + h\nu \tag{9}$$

and has no corresponding inverse process. Another possible process is scattering of photons by a material particle. In the present study we neglect scattering as a much less probable process compared to (8) and (9) (see [1] for the definition of corresponding integral operator). Moreover, we consider the conditions when the degree of ionization is negligibly small. In this case one may take into account only the bound–bound radiative transitions between rotational, vibrational and electronic states of molecules and neglect the bound–free and free–free radiative transitions. Under this condition and neglecting scattering $J_{cq}^{\text{rad}} = J_{cq}^{\text{em–abs}}$.

The integral operators for processes (8) and (9) neglecting electronic excitation have been derived in [1]. The generalized operator $J_{cq}^{\text{em–abs}}$ taking into account electronic states can be written in the form

$$J_{cq}^{\text{em–abs}} = \sum_{q'} \int \left(f_\nu f_{cq'} \frac{s_q^c}{s_{q'}^c} - f_{cq} \left(f_\nu + \frac{2}{h^3} \right) \right)$$
$$\times c\sigma_{cv,q}^{cv,q'} \, d\mathbf{p}_\nu \, d\mathbf{u}_c'. \tag{10}$$

Here $\sigma_{cv,q}^{cv,q'}$ is the differential cross-section of induced emission of a photon with frequency ν by an excited particle of c chemical species at the internal state $q = (\alpha, i, j)$ with a consequent deactivation of a particle to the lower state $q' = (\alpha', i', j')$.

The integral operator J_ν which describes the change of the distribution functions of photons contains two terms: $J_\nu = J_\nu^{\text{rad}} = J_\nu^{\text{v}} + J_\nu^{\text{e}}$, the first term corresponds to the radiative transitions between vibrational levels within the same electronic state, and the second one is for the transitions between electronic states. The expression for J_ν^{v} is given in [1], it can be easily generalized for J_ν^{e} by performing the summation over electronic states.

For the solution of kinetic Eqs. (1) and (2) the Chapman–Enskog method generalized for rapid and slow processes [6,7] can be used. The zero-order distribution function is determined by the eigenfunctions of the linearized collision operator of rapid processes J_{cq}^{rap}. Under conditions considered in the Letter the operators of rapid and slow processes may be written in the form:

$$J_{cq}^{\text{rap}} = J_{cq}^{\text{el}} + J_{cq}^{\text{RT}}, \quad J_\nu^{\text{rap}} = 0, \tag{11}$$

$$J_{cq}^{sl} = J_{cq}^{\text{VV}} + J_{cq}^{\text{VV}'} + J_{cq}^{\text{VT}} + J_{cq}^{\text{VE}} + J_{cq}^{\text{react}} + J_{cq}^{\text{rad}},$$
$$J_\nu^{sl} = J_\nu^{\text{rad}}. \tag{12}$$

The zero-order distribution function of material particles $f_{cq}^{(0)}$ is obtained in the form of the Maxwell–Boltzmann distribution over velocity and rotational energy depending on the non-equilibrium level populations of chemical species [1,6]

$$f_{c\alpha ij}^{(0)} = \left(\frac{m_c}{2\pi kT} \right)^{3/2} \frac{n_{c\alpha i} s_j^{c\alpha i}}{Z_{\text{rot}}^{c\alpha i}} \exp\left(-\frac{m_c C_c^2}{2kT} - \frac{\varepsilon_j^{c\alpha i}}{kT} \right), \tag{13}$$

where m_c is the molecular mass, k is the Boltzmann constant, T is the gas temperature, $n_{c\alpha i}$ is the number density of molecules of c species at the internal state (α, i), $\mathbf{C}_c = \mathbf{u}_c - \mathbf{v}$ is the peculiar velocity ($\mathbf{v}$ is the macroscopic gas velocity), $s_j^{c\alpha i}$ and $\varepsilon_j^{c\alpha i}$ are, respectively, the rotational statistic weight and rotational energy at the corresponding electronic and vibrational state, $Z_{\text{rot}}^{c\alpha i}$ is the rotational partition function. Distribution function (13) is expressed in terms of macroscopic parameters $n_{c\alpha i}(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$. On the contrary, as it is shown in [1], the distribution functions of photons f_ν are to be found directly from microscopic equations (2).

The generalized Chapman–Enskog method allows one to derive a closed system of equations for the macroscopic parameters [1,6]. This system consists of the master equations for $n_{c\alpha i}$, conservation of momentum and total energy and equations of radiative transfer [1]

$$\frac{dn_{c\alpha i}}{dt} + n_{c\alpha i}\nabla \cdot \mathbf{v} + \nabla \cdot (n_{c\alpha i}\mathbf{V}_{c\alpha i}) = R_{c\alpha i},$$
$$c = 1,\ldots,L, \ \alpha = 1,\ldots,L_{ce}, \ i = 0,\ldots,L_{c\alpha v}, \tag{14}$$

$$\rho\frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \tag{15}$$

$$\rho\frac{dU}{dt} + \frac{\partial E_{\mathrm{rad}}}{\partial t} + \nabla \cdot \mathbf{q} + \nabla \cdot \mathbf{q}_{\mathrm{rad}} + \mathbf{P} : \nabla\mathbf{v} = 0, \tag{16}$$

$$\frac{1}{c}\frac{\partial I_v}{\partial t} + \mathbf{\Omega}_v\frac{\partial I_v}{\partial \mathbf{r}} = \frac{h^4 v^3}{c^3}J_v^{\mathrm{rad}}, \quad v$$
$$= v_1, v_2, \ldots, v_R. \tag{17}$$

Here L is the total number of chemical species, L_{ce} is the number of considered electronic states for this species, $L_{c\alpha v}$ is the number of excited vibrational levels for the corresponding electronic state, R corresponds to the number of characteristic frequencies in a flow, ρ is the density, U is the total energy of material particles per unit mass (U depends on the temperature and all $n_{c\alpha i}$), $\mathbf{V}_{c\alpha i}$ is the diffusion velocity of c species at the VE state (α, i), $\mathbf{P}$ and $\mathbf{q}$ are the tensor of pressure and heat flux for material particles, I_v is the specific intensity of the radiation field

$$I_v\, dv\, d\mathbf{\Omega}_v = chvf_v\, d\mathbf{p}_v, \tag{18}$$

E_{rad} and q_{rad} are the radiation energy and radiative heat flux

$$E_{\mathrm{rad}} = \frac{1}{c}\int_0^\infty \int_{4\pi} I_v\, dv\, d\mathbf{\Omega}_v, \qquad \mathbf{q}_{\mathrm{rad}}$$
$$= \int_0^\infty \int_{4\pi} I_v\mathbf{\Omega}_v\, dv\, d\mathbf{\Omega}_v. \tag{19}$$

Eqs. (14)–(17), represent a set of macroscopic equations describing a flow of a reacting and radiating gas mixture under strong non-equilibrium conditions. In order to close the system it is necessary to define all transport and production terms.

First, the radiative flux can be found directly using the solution of equations of radiative transfer (17) [1]. Note, 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 ($\mathbf{V}_{c\alpha i}^{(0)} = 0$, $\mathbf{q}^{(0)} = 0$). However, the radiative flux $\mathbf{q}_{\mathrm{rad}}$ cannot be removed from Eq. (16) in the Euler approximation, because it is determined by the microscopic distribution function of photons which does not depend on the order of approximation of the asymptotic method.

The expressions for the first-order state-specific transport terms of material particles at the ground electronic state have been derived in [2]. Taking into account electronic excitation these expressions can be generalized. Thus, the tensor of pressure is given by

$$\mathbf{P} = (p - p_{\mathrm{rel}})\mathbf{I} - 2\mu\mathbf{S} - \eta\nabla \cdot \mathbf{v}\mathbf{I}. \tag{20}$$

Here $\mathbf{I}$ is the unit tensor, $\mathbf{S}$ is the tensor of deformation velocities, μ, η are the shear and bulk viscosity coefficients, p_{rel} is the relaxation pressure. Strictly speaking [1], Eq. (15) should contain the terms responsible for the transfer of momentum in a photon–particle interaction (mean momentum of photons and tensor of pressure for photons). However, the contribution of these terms to the conservation of momentum is usually negligibly small. 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 as the kinetic energy of a material particle, and therefore the radiative heat flux cannot be neglected in Eq. (16).

The diffusion velocity takes the form

$$\mathbf{V}_{c\alpha i} = -\sum_{d,\beta,k} D_{c\alpha i}^{d\beta k}\mathbf{d}_{d\beta k} - D_{Tc\alpha i}\nabla\ln T, \tag{21}$$

where $D_{c\alpha i}^{d\beta k}$ and $D_{Tc\alpha i}$ are the diffusion and thermal diffusion coefficients for every chemical species and VE state. The diffusion velocity is expressed in terms of non-equilibrium distributions through the diffusion driving forces

$$\mathbf{d}_{c\alpha i} = \nabla\left(\frac{n_{c\alpha i}}{n}\right) + \left(\frac{n_{c\alpha i}}{n} - \frac{\rho_{c\alpha i}}{\rho}\right)\nabla\ln p,$$

where $\rho_{c\alpha i}$ is the mass fraction of the species c at the state (α, i).

The total energy flux is given by the following expression:

$$\mathbf{q} = -\lambda \nabla T - p \sum_{c,\alpha,i} D_{Tc\alpha i} \mathbf{d}_{c\alpha i}$$
$$+ \sum_{c,\alpha,i} \left(\frac{5}{2} kT + \overline{\varepsilon}_j^{c\alpha i} + \varepsilon_i^{c\alpha} + \varepsilon^c \right) n_{c\alpha i} \mathbf{V}_{c\alpha i}, \qquad (22)$$

where $\overline{\varepsilon}_j^{c\alpha i}$ is the averaged rotational energy, λ is the coefficient of thermal conductivity connected with elastic and inelastic translational–rotational TR energy transfers. The transfer of vibrational and electronic energy is described by introducing the diffusion coefficients for every VE state.

The transport coefficients involved in the expressions for $\mathbf{V}_{c\alpha i}$, $\mathbf{P}$ and $\mathbf{q}$ depend on the cross-sections of rapid processes (elastic collisions and RT transfers) and can be calculated following the method proposed in [2]. Finally they are expressed in terms of gas temperature, state-to-state level populations and elastic collision integrals. One should mention that in this approach the heat flux is determined by gradients of temperature and non-equilibrium populations $n_{c\alpha i}$, and thus depends essentially on the state-to-state vibrational distributions.

The production terms due to slow processes in Eq. (14)

$$R_{c\alpha i} = \sum_j \int J_{c\alpha i j}^{sl} \, \mathrm{d}\mathbf{u}_c$$
$$= R_{c\alpha i}^{VV} + R_{c\alpha i}^{VV'} + R_{c\alpha i}^{VT} + R_{c\alpha i}^{VE} + R_{c\alpha i}^{react} + R_{c\alpha i}^{rad} \qquad (23)$$

represent the functions of VE level populations, number densities of atoms and non-equilibrium rate coefficients of corresponding reactions. The kinetic theory of the state-specific rate coefficients is developed in [3]. The zero-order state-to-state rate coefficients correspond to the Maxwell–Boltzmann distribution over velocities and rotational energies and depend only on the gas temperature. On the contrary, the first-order rate coefficients depend on all level populations and atomic number densities. Moreover, the first-order rate coefficients in a moving gas contain the terms

proportional to $\nabla \cdot \mathbf{v}$. These terms are equal to zero if there is no any rapid inelastic process and only the elastic collisions determine the rapid process.

3. Non-equilibrium CO kinetics

The kinetic model presented above can be applied for investigation of any flow of a diatomic neutral gas mixture. A molecule of carbon monoxide is chosen because of its importance for many applications: molecular lasers, environmental problems, planetary atmospheres exploration. CO kinetics has been widely discussed in the literature for many years, the peculiarities of shock-heated CO flows have been studied experimentally in [8,9], the kinetics of electrical discharges and optically pumped CO remains the focus of attention for the last two decades [10–18]. The aim of this section is to give a short summary of recent results in this field and to list the main processes which have to be taken into account for the simulation of CO flow using the model described in the previous sections.

3.1. Radiative transitions

Two kinds of radiative transitions are distinguished: (1) IR radiation due to the transitions between vibrational states, and, (2) UV and visible radiation caused by the transitions between electronic states. The most intensive bands observed in the UV and visible range are: CO fourth positive band (the responsible transition is $A^1\Pi \rightarrow X^1\Sigma$); CO Cameron band ($a^3\Pi \rightarrow X^1\Sigma$), which is about 10^3 times less intensive than the fourth positive one [8]; C_2 Swan band ($d^3\Pi \rightarrow a^3\Pi$). Actually, several additional bands can be detected in the system (like CO third positive, C_2 Deslandres-d'Azambuja, Fox-Herzberg and Mulliken, and some O_2 bands) but they appear to be rather weak [17]. Finally, we take into account only three electronically excited states: the lowest singlet and triplet CO states: $CO(A^1\Pi)$, $CO(a^3\Pi)$, and also $C_2(d^3\Pi)$. The production terms due to radiation can be calculated using the Einstein coefficients [19] for the radiative transitions between vibrational levels

within the same electronic state, and using the formulas given in [15] for the transitions between electronic states.
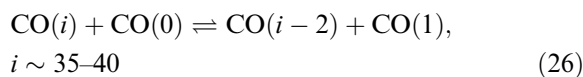
3.2. Vibrational energy exchange

Among the vibrational energy transfers we distinguish the VV exchange between the same molecules

$$CO(i) + CO(k) \rightleftharpoons CO(i') + CO(k'), \tag{24}$$
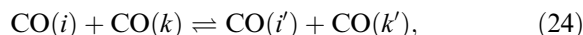
VV′ exchange between different vibrational modes, an example is the near-resonance exchange between CO and O_2 [20]

$$CO(i) + O_2(0) \rightleftharpoons CO(i-1) + O_2(1),$$
$$i \sim 25, \tag{25}$$
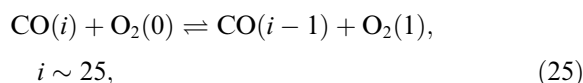
asymmetric one-by-two quanta near-resonance VV exchange [18]

$$CO(i) + CO(0) \rightleftharpoons CO(i-2) + CO(1),$$
$$i \sim 35\text{–}40 \tag{26}$$

and VT transfer

$$CO(i) + M \rightleftharpoons CO(i') + M. \tag{27}$$
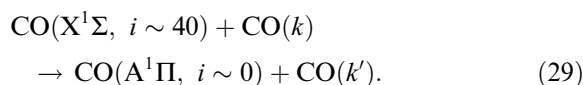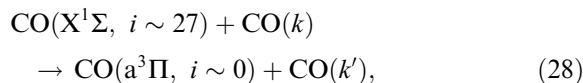
The state-specific rate coefficients for processes (24)–(27) are given by [21,15,22]. One should mention that processes (25) and (26) involving transitions between highly excited states do not contribute significantly to the formation of vibrational distributions in shock-heated CO. However, they can influence noticeably the level populations in optically pumped systems and expanding flows with high storage of vibrational energy.

3.3. Vibration–electronic transitions

In VV pumped systems the VE transitions from high vibrational levels to the approximately isoenergetic excited electronic states are found to be important [14,15,17,18]:

$$CO(X^1\Sigma, \ i \sim 27) + CO(k)$$
$$\rightarrow CO(a^3\Pi, \ i \sim 0) + CO(k'), \tag{28}$$

$$CO(X^1\Sigma, \ i \sim 40) + CO(k)$$
$$\rightarrow CO(A^1\Pi, \ i \sim 0) + CO(k'). \tag{29}$$

In particular, transition (29) is the main reason for the persistent termination of the VV up-pumping to the levels above $i \sim 40$ observed in many experiments [14,15,17,18]. On the contrary, process (28) does not stop the VV up-pump. Nevertheless, perturbation of the ground electronic state vibrational populations due to this transfer has been observed by Farrenq et al. [14].

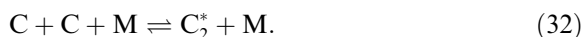## 3.4. C_2 formation and other chemical reactions

We propose two different mechanisms of C_2 formation. The first one can take place in high temperature gas. It comes through the thermal decomposition of CO

$$CO + M \rightleftharpoons C + O + M \tag{30}$$

and consequent C_2^* formation in the exchange reaction [8]:

$$C + CO \rightleftharpoons C_2^* + O, \tag{31}$$

or recombination of carbon atoms [8,17]:

$$C + C + M \rightleftharpoons C_2^* + M. \tag{32}$$

In both reactions (31) and (32) C_2 forms at the electronically excited state C_2^* [8,17] which comes to the ground state by spontaneous radiation decay.

The activation energy of reaction (30) is about 11 eV and therefore it cannot be the main source of carbon atoms in the low temperature gas. In this case the preferable mechanism is the following [10,17]: the initial formation of carbon proceeds through the reaction

$$CO(i) + CO(k) \rightleftharpoons CO_2 + C. \tag{33}$$
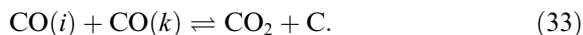
This reaction might become exothermic at high vibrational excitation of reactants (at $\varepsilon_i + \varepsilon_k \geqslant 5.7$ eV) [17]. Exchange reaction (31) is endothermic and cannot play any important role under the low temperature conditions. Therefore formation of C_2^* in this case proceeds either through recombination of carbon atoms (32) or by means of the scheme proposed in [16,17]

$$C + CO(k) + M \rightleftharpoons C_2O + C + M, \tag{34}$$
$$C + C_2O \rightleftharpoons C_2^* + CO. \tag{35}$$
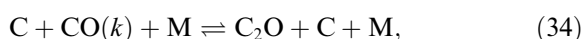
The reactions leading to formation of molecular oxygen in both ground and excited electronic states are the following:

$$O + CO \rightleftharpoons O_2 + C, \tag{36}$$

$$O + O + M \rightleftharpoons O_2 + M. \tag{37}$$

It is shown in [8,17] that reactions (36) and (37) contribute very weakly in the CO kinetics in shock tube experiments as well as in the VV pumped systems. However, the role of these processes is important in discharges [11].

Some carbon line radiation has been also observed by [8,17] in both low- and high-temperature conditions. Formation of electronically excited carbon atoms C^* can proceed through dissociation of CO: $CO(i) + CO(k) \rightleftharpoons C^* + O + CO$ if vibrational excitation of reactants is high.

The state-dependent rate coefficients for reactions (30)–(37), similarly to [23], can be represented as a production of thermal equilibrium rate coefficient $k(T)$ and non-equilibrium factor depending on the vibrational state of reagents. The data on the thermal equilibrium rate coefficients for the reactions listed in this section are given in [24,25].

3.5. Application to a flow behind shock wave

The kinetic model presented above has been applied for the investigation of non-equilibrium CO flow behind the shock wave. The free-stream conditions are the following: $M_0 = 8$, $T_0 = 293$ K, $p_0 = 540$ Pa, the initial vibrational distributions of CO molecules are supposed to in equilibrium at temperature T_0. Eqs. (14)–(17) have been solved in the stationary one-dimensional Euler approximation. VV, VT, VE exchanges (24) and (27)–(29) as well as dissociation–recombination reaction (30) and radiative transitions (8) and (9) have been taken into account for the simulation of production terms in Eq. (14); rate coefficients for these processes are summarized in [26,15]. Reactions (31), (32), (36), (37) leading to C_2 and O_2 formation have been neglected because of low dissociation degree in the considered conditions, and therefore low concentration of C and O atoms. Reaction mechanism (33)–(35) requires very high

vibrational excitation of the reactants and cannot be responsible for C_2 formation in a post shock flow.

It is well known that in electrical discharges and in optically pumped systems, where the stock of vibrational energy is high compared to that of translational energy, the shape of vibrational distributions of CO molecules is often essentially non-Boltzmann (see [12,15,18] and many other papers). However, in a shock-heated gas, the vibrational distributions are usually supposed to be close to the Boltzmann ones except some rather slight depletion of high states population due to dissociation. In Fig. 1 the vibrational distributions at different distances x from the shock front are given. For a comparison, at $x = 0.01$ cm the corresponding Boltzmann distribution with the temperature T_1 calculated from the first vibrational level energy storage ($T_1 = \varepsilon_1/k \ln(n_0/n_1)$) is given. One can see a noticeable deviation of the state-to-state distribution from the Boltzmann one. This can be explained by the peculiarities of VV and VE exchanges in CO molecules.

The mass fractions of atoms and electronic states $CO(a^3\Pi)$ and $CO(A^1\Pi)$ are plotted in Fig. 2 as functions of x. Under the present conditions the degree of dissociation is found to be weak. The concentrations of excited electronic states are also rather low. This is the reason for a weak contribution of UV radiation to the total radiation in-
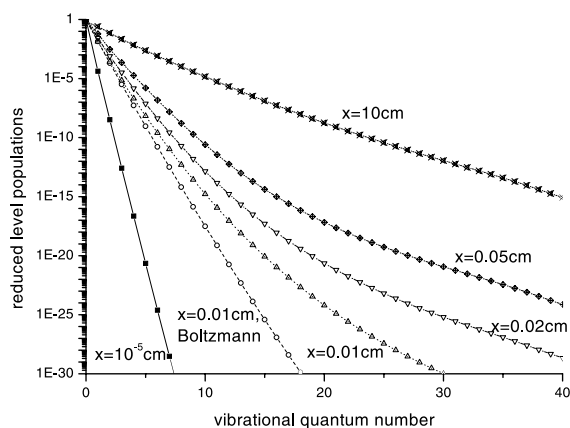

Fig. 1. Vibrational distributions of CO molecules at various distances x behind a shock.
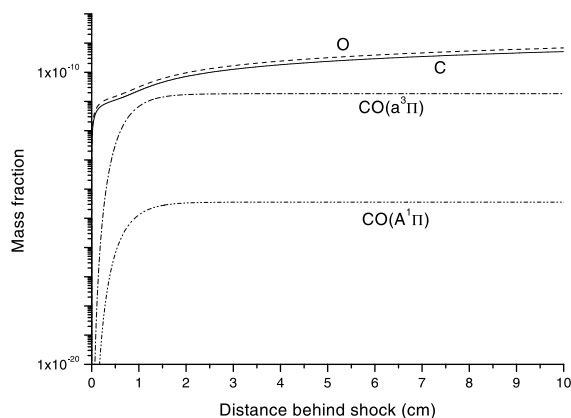
Fig. 2. Mass fractions of C, O, CO($a^3\Pi$) and CO($A^1\Pi$) as functions of *x*.
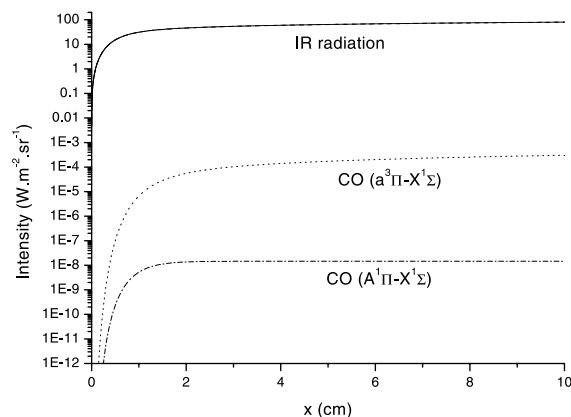

Fig. 3. Total IR radiation intensity and intensities of UV radiation from CO($a^3\Pi$) and CO($A^1\Pi$) states (W m^{-2} sr^{-1}) as functions of *x*.

tensity. It can be seen from Fig. 3 where a comparison of total IR radiation intensity and intensities of UV radiation from CO($a^3\Pi$) and CO($A^1\Pi$) electronic states is presented. At higher temperature conditions the role of electronic states in radiative processes is expected to be more important.

4. Conclusions

The kinetic model of a non-equilibrium gas mixture flow with coupled VV, VT, VE exchanges,

radiative transitions and chemical reactions is presented. The carbon monoxide kinetics is discussed in details, and the flow of CO behind a shock wave is studied using the state-to-state approach. The non-Boltzmann shape of vibrational distributions in a shock-heated gas has been obtained. The influence of electronic excitation on the total radiation intensity is found to be weak under conditions considered in the Letter.

References

[1] E. Kustova, A. Chikhaoui, Chem. Phys. 255 (2000) 59.
[2] E. Kustova, E. Nagnibeda, Chem. Phys. 233 (1998) 57.
[3] E. Kustova, E. Nagnibeda, A. Chauvin, Chem. Phys. 248 (2–3) (1999) 221.
[4] C.S. Wang Chang, G. Uhlenbeck, Transport phenomena in polyatomic gases, Cm-681, University of Michigan Research Report, 1951.
[5] G. Ludwig, M. Heil, Advances in Applied Mechanics, vol. VI, Academic Press, New York, 1960.
[6] A. Chikhaoui, J. Dudon, E. Kustova, E. Nagnibeda, J. Phys. A 247 (1–4) (1997) 526.
[7] S. Vallander, E. Nagnibeda, M. Rydalevskaya, Some Questions of the Kinetic Theory of the Chemical Reacting Gas Mixture, Leningrad University Press, Leningrad, 1977, (in Russian) Translation: US AirForce FASTC–ID (RS) TO–0608–93.
[8] A. Fairbairn, Proc. Roy. Soc. A 312 (1969) 207.
[9] O. Brandt, P. Roth, Phys. Fluids 30 (5) (1987) 1294.
[10] J.W. Rich, R. Bergman, Chem. Phys. 44 (1979) 53.
[11] S. De Benidictis, F. Cramarossa, R. D'Agostino, Chem. Phys. 82 (1983) 395.
[12] S. De Benidictis, M. Capitelli, F. Cramarossa, R. D'Agostino, C. Gorse, Chem. Phys. Lett. 112 (1) (1984) 54.
[13] C. Gorse, M. Cacciatore, M. Capitelli, Chem. Phys. 85 (2) (1984) 165.
[14] R. Farrenq, C. Rosetti, G. Guelachvili, W. Urban, Chem. Phys. 92 (1985) 389.
[15] C. Flament, T. George, K. Meister, J.W. Tufts, J.W. Rich, V. Subramanian, J.-P. Martin, B. Piar, M.-Y. Perrin, Chem. Phys. 163 (1992) 241.
[16] Y. Ionikh, I. Kostyukevich, N. Chernysheva, Opt. Spectrosc. 76 (1994) 361.
[17] H. Wallaart, B. Piar, M.-Y. Perrin, J.-P. Martin, Chem. Phys. 196 (1995) 149.
[18] E. Plönjes, P. Palm, A. Chernukho, I. Adamovich, J.W. Rich, Chem. Phys. 256 (2000) 315.
[19] H. Heaps, G. Herzberg, Z. Phys. 133 (1953) 49.
[20] E. Plönjes, P. Palm, W. Lee, M. Chidley, I. Adamovich, W. Lempert, J.W. Rich, Chem. Phys. 260 (2000) 353.
[21] M. Cacciatore, G. Billing, Chem. Phys. 58 (1981) 395.
[22] I. Adamovich, S. Macheret, J.W. Rich, C. Treanor, J. Thermophys. Heat Transfer 12 (1998) 57.

[23] E. Kustova, E. Nagnibeda, in: G. Ball, R. Hillier, G. Roberts (Eds.), Proceedings of the 22nd International Symposium on Shock Waves, vol. 1, University of Southampton, Southampton, UK, 2000, p. 783.

[24] W. Gardiner (Ed.), Combustion Chemistry, Springer, Berlin, 1984.

[25] W. Mallard, F. Westley, J. Herron, R. Hampson, NIST Chemical Kinetics Database – Ver. 6.0, NIST Standard Reference Data, Gaithersburg, MD, 1994.

[26] R. Deleon, J.W. Rich, Chem. Phys. 107 (1986) 283.