Mutual effect of vibrational relaxation and chemical reactions in viscous multitemperature flows

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We study coupling of vibrational relaxation and chemical reactions in nonequilibrium viscous multitemperature flows. A general theoretical model is proposed on the basis of the Chapman-Enskog method modified for strongly nonequilibrium reacting flows; the model differs from models commonly used in computational fluid dynamics since it is able to capture additional cross-coupling terms arising in viscous flow due to compressibility and mutual influence of all nonequilibrium processes occurring in a mixture. The set of fluid dynamic equations is derived starting from the Boltzmann equation; the relaxation terms in these equations are described using the kinetic transport theory formalism. Reaction and relaxation rates depend on the distribution function and thus differ in the zero-order and first-order approximations of the Chapman-Enskog method. An algorithm for the calculation of multitemperature reaction and relaxation rates in both inviscid and viscous flows is proposed for the harmonic oscillator model. This algorithm is applied to estimate the mutual effect of vibrational relaxation and dissociation in binary mixtures of N_2 and N, and O_2 and O, under various nonequilibrium conditions. It is shown that modification of the Landau-Teller expression for the VT relaxation term works rather well in nitrogen, whereas it fails to predict correctly the relaxation rate in oxygen at high temperatures. In oxygen (in contrast to nitrogen), the first-order cross effects of dissociation and VT relaxation are found to be significant. A method for calculation of vibrational relaxation time based on the kinetic theory definition is suggested. Two-temperature dissociation rate coefficients are calculated in the zero- and first-order approximations and compared to other models.

I. INTRODUCTION

Modeling of vibrational-chemical coupling in viscous high-temperature flows still remains a challenging task in modern nonequilibrium gas dynamics. Although dozens of papers are devoted to this subject, starting from the widely known works by Hammerling [1] and Treanor-Marrone [2] (see also Refs. [3–9] for multitemperature and [10–18] for state-to-state models), most of models are derived for the case of inviscid gas flows. Viscous effects in nonequilibrium chemical kinetics appear as cross-coupling terms between the rates of various reactions and velocity divergence resulting in the violation of the mass action law [19]. These coupling terms were discussed in Refs. [20–23] for one-temperature chemically reacting flows. However, the viscous effects and corresponding cross-coupling terms in vibrationally nonequilibrium flows have not been well studied up to the present time. There are only a few papers dealing with some aspects of vibrational-chemical coupling in viscous multitemperature [24–27] and state-to-state [28–30] flows. Nevertheless, taking into account the above-mentioned cross effects can be important in two-dimensional (2D) and 3D simulations of high-temperature flows.

In our recent paper [27], a self-consistent treatment of reaction rates in viscous multi-temperature flows was proposed and the methods described applied to study vibration-translation (VT) relaxation in a single-component molecular nitrogen flow. However, the complexity of the resulting equations in the general case makes it fairly nontrivial and computationally expensive to study first-order effects in viscous flows, especially in multicomponent mixtures, where numerous chemical reactions need to be accounted for. Thus, the objective of the present paper is to derive a simplified set of equations for the harmonic oscillator model and to study the cross influence of vibrational and chemical relaxation in binary mixture flows under various conditions.

The paper is organized as follows: First, we derive the closed set of fluid-dynamic equations for a nonequilibrium multitemperature gas mixture flow with vibrational relaxation and chemical reactions. Molecules are simulated by harmonic oscillators. Then we define the transport and relaxation terms. The relaxation terms are calculated in the zero-order (inviscid) and first-order (viscous) approximations of the Chapman-Enskog method [19]. In the zero-order approximation, we assess the limits of applicability of the commonly used Landau-Teller relaxation equation. For this purpose we introduce the vibrational relaxation time on the basis of a strict kinetic theory definition, as the integral of vibrational energy variation in VT transitions. We calculate this integral using advanced models of collisional cross sections and compare the obtained relaxation times to the commonly used theoretical values and experimental results. In the first-order approximation, we derive linear integral equations specifying the first-order (viscous) corrections to the reaction rates and develop the method for their solution. The rates of vibrational relaxation and dissociation are then calculated for N_2-N and O_2-O binary mixture flows under various thermal conditions and mixture compositions. The mutual influence of vibrational relaxation and dissociation in viscous flows is assessed, and some distinctive features of vibrational-chemical coupling in nitrogen and oxygen are discussed. Thermally nonequilibrium dissociation rate coefficients calculated using the zero- and first-order Chapman-Enskog solutions are compared to those commonly used in computational fluid dynamics.

II. GOVERNING EQUATIONS

We consider a nonequilibrium flow of gas mixtures taking into account vibrational and rotational energies of molecules and chemical reactions. Electronic excitation [31] and coupled rotational-vibrational nonequilibrium [15,16]

are not accounted for, since we limit our considerations to temperatures below 15 000 K.

In order to simplify the flow description we simulate molecular vibrations in the frame of a harmonic oscillator model. For harmonic oscillators, the vibrational energy ε_i^c (c is chemical species, i is the vibrational state) is given by

$$\varepsilon_i^c = h\nu_c\left(i + \tfrac{1}{2}\right) = \left(i + \tfrac{1}{2}\right)\varepsilon_1^c, \tag{1}$$

where h is the Planck constant and ν_c is the frequency.

For strongly nonequilibrium flows, when both rapid and slow processes occur in the gas, the Boltzmann equation for gas mixtures with internal degrees of freedom in the absence of external forces takes on the following form

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = \frac{1}{\varepsilon} J_{cij}^{\mathrm{rap}} + J_{cij}^{\mathrm{sl}}, \tag{2}$$

where f_{cij} is the distribution function of particles of species c at the i-th vibrational and j-th rotational levels, $\mathbf{u}_c$ is the velocity of particles of species c, J_{cij}^{rap} and J_{cij}^{sl} are the integral operators of rapid and slow processes, respectively, $\varepsilon = \tau_{\mathrm{rap}}/\tau_{\mathrm{sl}} \sim \tau_{\mathrm{rap}}/\vartheta$ is the small parameter in which the distribution function is expanded in the Chapman-Enskog framework, τ_{rap} and τ_{sl} are the characteristic times of rapid and slow processes, respectively, and ϑ is the gas-dynamic time.

We would like to emphasize that for our study we use a quasiclassical approach proposed by Wang Chang and Uhlenbeck in Ref. [32] treating the translational degrees of freedom classically and internal degrees of freedom in the frame of quantum mechanics. The expressions for collision integrals of chemical reactions in the quasiclassical approach are obtained, for instance, in Refs. [19,20]. More rigorous approach for writing the Boltzmann equation with chemical reactions based on purely quantum-mechanical approach is considered in Ref. [33]. However, implementation of this approach for derivation of fluid-dynamic equations for viscous flows appears to be too complicated.

In the present study, we take into account elastic and inelastic processes resulting in the exchange of internal energy and chemical reactions; each collisional process has its own characteristic time. Thus the following microscopic processes are considered: elastic collisions with the characteristic time τ_{tr}, rotational energy exchanges with the characteristic time τ_{rot}, VV exchanges of vibrational quanta between molecules of the same species (τ_{VV}), VV' exchanges of vibrational quanta between molecules of different species ($\tau_{\mathrm{VV'}}$), VT transitions of vibrational energy into translational (τ_{VT}), and chemical reactions (τ_{react}). We assume that the characteristic times satisfy the relation [19]

$$\tau_{\mathrm{tr}} < \tau_{\mathrm{rot}} < \tau_{\mathrm{VV}} \ll \tau_{\mathrm{VV'}} < \tau_{\mathrm{VT}} < \tau_{\mathrm{react}} \sim \vartheta. \tag{3}$$

Under this relation the small parameter in the Boltzmann equation is chosen as $\varepsilon = \tau_{\mathrm{VV}}/\vartheta$; this yields the basis for multitemperature flow modeling. During the rapid relaxation stage, quasistationary vibrational distributions establish depending on the model for molecular vibrations: the Treanor or Boltzmann distributions for anharmonic and harmonic vibrations respectively [19,34].

The set of macroscopic variables providing the closed description of a strongly nonequilibrium flow is introduced on the basis of the collision invariants of rapid processes [19,34]. Under condition (3) mass, momentum, and total energy are conserved in any collision; an additional invariant of the most frequent collisions is the vibrational energy ε_i^c (since it remains constant in VV collisions due to equidistant locations of vibrational levels).

The macroscopic parameters corresponding to quantities conserved during rapid processes are defined in terms of the distribution function as follows:

$$n_c = \sum_{ij} \int f_{cij}\, d\mathbf{u}_c, \quad c = 1, \ldots, L, \tag{4}$$

$$\rho \mathbf{v} = \sum_{cij} \int m_c \mathbf{u}_c f_{cij}\, d\mathbf{u}_c, \tag{5}$$

$$\rho U = \frac{3}{2}nkT + \sum_{c=1}^{L_m} \rho_c E_{\mathrm{rot},c} + \sum_{c=1}^{L_m} \rho_c E_{\mathrm{vibr},c} + \sum_{c=1}^{L} \rho_c E_{f,c}$$

$$= \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_{ij}^c + \varepsilon_c\right) f_{cij}\, d\mathbf{u}_c, \tag{6}$$

$$\rho_c E_{\mathrm{vibr},c} = \sum_{ij} \varepsilon_i^c \int f_{cij}\, d\mathbf{u}_c, \quad c = 1, \ldots, L_m, \tag{7}$$

where n_c, m_c are the number density and mass of particles of species c; $\mathbf{v}$ is the flow velocity; i and j are the vibrational and rotational levels of a molecule of species c; ρ is the mixture density; U is the total energy per unit of mass; ρ_c is the density of particles of species c; L is the number of chemical species in the mixture; L_m is the number of molecular species; $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$ is the peculiar velocity of a particle of species c; $\varepsilon_{ij}^c = \varepsilon_j^{ci} + \varepsilon_i^c$; ε_j^{ci} is the rotational energy of a molecule c in the vibrational state i and rotational state j; ε_c is the formation energy; and $E_{\mathrm{rot},c}$, $E_{\mathrm{vibr},c}$, and $E_{f,c}$ are the specific rotational, vibrational, and formation energies of molecular species c.

The governing flow equations for a multitemperature mixture of harmonic oscillators can be derived from the Boltzmann equation multiplying it by the collision invariants of rapid processes, integrating over velocities and summing over internal states and chemical species. The set of equations is obtained in the following form [7,19,34]:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{\mathrm{react}}, \quad c = 1, \ldots, L, \tag{8}$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla \cdot \mathbf{P}, \tag{9}$$

$$\rho \frac{dU}{dt} = -\nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v}, \tag{10}$$

$$\rho_c \frac{dE_{\mathrm{vibr},c}}{dt} + \nabla \cdot \mathbf{q}_{\mathrm{vibr},c} = R_c^{\mathrm{vibr}} - E_{\mathrm{vibr},c} m_c R_c^{\mathrm{react}}$$

$$+ E_{\mathrm{vibr},c} \nabla \cdot (\rho_c \mathbf{V}_c),$$

$$c = 1, \ldots, L_m, \tag{11}$$

Here $\mathbf{V}_c$ is the diffusion velocity of particles of species c, $\mathbf{P}$ is the stress tensor, $\mathbf{q}$ is the energy flux, and $\mathbf{q}_{\mathrm{vibr},c}$ is the flux of vibrational energy of molecules of species c. The set of governing Eqs. (8)–(11) includes conservation equations for the momentum and total energy (9) and (10) coupled to the equations of multitemperature chemical kinetics (8) and

relaxation equations for specific vibrational energies $E_{\text{vibr},c}$. Conservation of mass follows from Eqs. (8).

The transport terms in Eqs. (8)–(11) $\mathbf{V}_c$, $\mathbf{P}$, $\mathbf{q}$, $\mathbf{q}_{\text{vibr},c}$ are defined by the following expressions:

$$n_c \mathbf{V}_c = \sum_{ij} \int \mathbf{c}_c f_{cij} d\mathbf{u}_c, \tag{12}$$

$$\mathbf{P} = -\sum_{cij} \int m_c \mathbf{c}_c \mathbf{c}_c f_{cij} d\mathbf{u}_c, \tag{13}$$

$$\mathbf{q} = \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon_c \right) \mathbf{c}_c f_{cij} d\mathbf{u}_c, \tag{14}$$

$$\mathbf{q}_{\text{vibr},c} = \sum_{ij} \varepsilon_i^c \int \mathbf{c}_c f_{cij} d\mathbf{u}_c. \tag{15}$$

The relaxation terms are defined as follows [19]:

$$R_c^{\text{vibr}} = \sum_{ij} \varepsilon_i^c \int J_{cij}^{\text{sl}} d\mathbf{u}_c, \quad R_c^{\text{react}} = \sum_{ij} \int J_{cij}^{\text{react}} d\mathbf{u}_c, \tag{16}$$

where $J_{cij}^{\text{sl}} = J_{cij}^{VV'} + J_{cij}^{VT} + J_{cij}^{2 \rightleftarrows 2} + J_{cij}^{2 \rightleftarrows 3}$ is the integral operator of slow processes ($J_{cij}^{VV'}$, J_{cij}^{VT}, $J_{cij}^{2 \rightleftarrows 2}$, and $J_{cij}^{2 \rightleftarrows 3}$ being the operators corresponding to slow VV' exchanges, VT transitions, bimolecular exchange reactions, and dissociation-recombination reactions; correspondingly, [19,27]) and $J_{cij}^{\text{react}} = J_{cij}^{2 \rightleftarrows 2} + J_{cij}^{2 \rightleftarrows 3}$ is the collision operator for chemical reactions.

The integral operator of slow processes can be split into several terms in the form proposed in Refs. [22,27]:

$$J_{cij}^{\text{sl}} = \sum_{r=1}^{N_{VV'}} \nu_{r,ci} J_{cij}^{VV',r} + \sum_{r=1}^{N_{VT}} \nu_{r,ci} J_{cij}^{VT,r} + \sum_{r=1}^{N_{2 \rightleftarrows 2}} \nu_{r,ci} J_{cij}^{2 \rightleftarrows 2, r}$$
$$+ \sum_{r=1}^{N_{2 \rightleftarrows 3}} \nu_{r,ci} J_{cij}^{2 \rightleftarrows 3, r}. \tag{17}$$

Here $N_{VV'}$, N_{VT}, $N_{2 \rightleftarrows 2}$, $N_{2 \rightleftarrows 3}$ denote respectively the amount of VV' exchanges, VT transitions, chemical exchange reactions, and dissociation-recombination reactions occurring in the mixture; $J_{cij}^{VV',r}$, $J_{cij}^{VT,r}$, $J_{cij}^{2 \rightleftarrows 2, r}$, and $J_{cij}^{2 \rightleftarrows 3, r}$ are the operators for the r-th VV' exchange, VT transition, chemical exchange, and dissociation reactions, correspondingly. The expressions for these integral operators are given in Ref. [27]; $\nu_{r,ci}$ are the global stoichiometric coefficients for the r-th transition. It should be noted that when using such a representation, it is sufficient to explicitly consider reactions of only one kind ("forward" reactions), as the corresponding reverse processes are included via the stoichiometric coefficients.

Based on this representation, one can introduce the reaction rate for a specific reaction r [22]:

$$\dot{\xi}_r = \frac{1}{N_a} \sum_j \int J_{cij}^r d\mathbf{u}_c \tag{18}$$

and the corresponding reaction rate coefficient:

$$k_r = N_a \sum_{jlj'l'} \int \frac{f_{cij} f_{dkl}}{n_{ci} n_{dk}} g \widetilde{\sigma}_{f,r} d\mathbf{u}_d d\mathbf{u}_c, \tag{19}$$

where $\mathbf{g}$ is the colliding particles relative velocity; $\widetilde{\sigma}_{f,r} = \widetilde{\sigma}_{f,r}(g)$ is the integral cross section for the r-th process (i.e., the differential cross section integrated over velocities of particles after collisions [19]); N_a is the Avogadro number; and vibrational levels i, i', k, k' are fixed for each particular reaction r.

To simplify further notation, we denote the different sets of types of slow processes as follows:

$$\mathcal{V} = \{VV', VT\}, \quad \mathcal{R} = \{2 \rightleftarrows 2, 2 \rightleftarrows 3\},$$
$$\mathcal{VR} = \{VV', VT, 2 \rightleftarrows 2, 2 \rightleftarrows 3\}. \tag{20}$$

Then the relaxation terms R_c^{vibr}, R_c^{react} can be expressed in terms of reaction rates:

$$R_c^{\text{react}} = N_a \sum_i \sum_{\gamma \in \mathcal{R}} \sum_{r=1}^{N_\gamma} \nu_{r,ci} \dot{\xi}_{\gamma,r}, \tag{21}$$

$$R_c^{\text{vibr}} = N_a \sum_i \varepsilon_i^c \sum_{\gamma \in \mathcal{VR}} \sum_{r=1}^{N_\gamma} \nu_{r,ci} \dot{\xi}_{\gamma,r} = N_a \sum_i \sum_{\gamma \in \mathcal{VR}} \sum_{r=1}^{N_\gamma} \Delta \varepsilon_i^c \dot{\xi}_{\gamma,r}, \tag{22}$$

where $\Delta \varepsilon_i^c = \varepsilon_{i'}^c - \varepsilon_i^c$ and i' denotes the vibrational level after the inelastic collision.

The relaxation terms in case of a binary mixture with slow VT transitions and dissociation-recombination reactions can be simplified taking into account the fact that only single-quantum vibrational energy transitions are allowed for harmonic oscillators. Thus instead of energy variation $\Delta \varepsilon_i^c$, the constant value $h\nu_c$ appears in the reaction rates:

$$R_c^{\text{react}} = -N_a \sum_{r=1}^{N_{2 \rightleftarrows 3}} \dot{\xi}_{2 \rightleftarrows 3, r}, \tag{23}$$

$$N_a \sum_{r=1}^{N_{VT}} \Delta \varepsilon_i^c \dot{\xi}_{VT,r} = -h\nu_c N_a \sum_{r=1}^{N_{VT}} \dot{\xi}_{VT,r}, \tag{24}$$

$$N_a \sum_{r=1}^{N_{2 \rightleftarrows 3}} \Delta \varepsilon_i^c \dot{\xi}_{2 \rightleftarrows 3, r} = -h\nu_c N_a \sum_{r=1}^{N_{2 \rightleftarrows 3}} i \, \dot{\xi}_{2 \rightleftarrows 3, r}, \tag{25}$$

where in the last equation i is the vibrational level of the dissociating molecule (fixed for a specific reaction r). In the above expressions, only "forward" reactions appear, which in this case are VT deactivation transitions (with $i' = i - 1$) and dissociation reactions. As is mentioned before, "backward" transitions are taken into account in the integral operators via stoichiometric coefficients.

It is worth mentioning that in Eqs. (21) and (22), vibrational relaxation and chemical reactions are coupled naturally and self-consistently; the rate of vibrational energy production R_c^{vibr} depends on the rates of all slow processes including VT, VV' transitions, and chemical reactions. There is no need to introduce artificially some phenomenological coupling factors like in commonly used coupled vibration-dissociation-vibration (CVDV) and coupled vibration-chemistry-vibration (CVCV) models [2,6]. Note also that in the present model, the coupling factors depend on the order of the Chapman-Enskog expansion and therefore differ in the zero-order (inviscid) and first-order (viscous) approximations. The difference appears

in the expressions for the reaction rates $\dot{\xi}_r^{(0)}$ and $\dot{\xi}_r^{(1)}$ calculated on the basis of the zero- and first-order distribution functions.

III. ZERO-ORDER APPROXIMATION

In the zero-order approximation of the Chapman-Enskog method in the multitemperature case, the distribution function for a molecule with harmonic vibrations is a combination of Maxwell-Boltzmann distributions over velocity and internal energies with a vibrational temperature T_v^c differing from the temperature T:

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT} \right)^{3/2} \frac{n_c}{Z_c^{\text{int}}} s_{ij}^c \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT} - \frac{\varepsilon_i^c}{kT_v^c} \right), \tag{26}$$

where s_{ij}^c is the degeneracy of the molecular state with internal energy $\varepsilon_{ij}^c = \varepsilon_j^{ci} + \varepsilon_i^c$, k is the Boltzmann constant, and Z_c^{int} is the internal partition function defined as follows:

$$Z_c^{\text{int}} = \sum_{ij} s_{ij}^c \exp\left(-\frac{\varepsilon_j^{ci}}{kT} - \frac{\varepsilon_i^c}{kT_v^c} \right). \tag{27}$$

Considering the rotational energies to be independent of the vibrational states ($\varepsilon_j^{ci} = \varepsilon_j^c$, $s_{ij}^c = s_j^c$), we can rewrite Z_c^{int}:

$$Z_c^{\text{int}} = Z_c^{\text{rot}} Z_c^{\text{vibr}}, \tag{28}$$

where Z_c^{rot} and Z_c^{vibr} are the rotational and vibrational partition functions, correspondingly, defined as

$$Z_c^{\text{rot}} = \sum_j s_j^c \exp\left(-\frac{\varepsilon_j^c}{kT} \right), \tag{29}$$

$$Z_c^{\text{vibr}} = \sum_i \exp\left(-\frac{\varepsilon_i^c}{kT_v^c} \right). \tag{30}$$

Thus, the vibrational level population n_{ci} is given by the expression

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}} \exp\left(-\frac{\varepsilon_i^c}{kT_v^c} \right). \tag{31}$$

A. Zero-order reaction and relaxation rates

By substituting the zero-order distribution function into the integral reaction operators and applying microscopic laws of energy conservation during collisions, it is possible to obtain that

$$J_{cij}^{r(0)} = \Gamma^r \sum_{lj'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} g \widetilde{\sigma}_{f,r} d\mathbf{u}_d. \tag{32}$$

In the case of VT exchanges, one should omit summation over l' and in the case of dissociation reactions one should omit summation over $j'l'$. Here

$$\Gamma^r = 1 - \exp\left(\frac{A_r}{kT} \right), \tag{33}$$

A_r are quantities introduced by analogy with affinities of chemical reactions [25]. For the harmonic oscillator model,

these generalized affinities take on the following form:

$$A_{\text{VV}',r} = \Delta\varepsilon_i^c \left(1 - \frac{T}{T_v^c} \right) + \Delta\varepsilon_k^d \left(1 - \frac{T}{T_v^d} \right), \tag{34}$$

$$A_{\text{VT},r} = \Delta\varepsilon_i^c \left(1 - \frac{T}{T_v^c} \right), \tag{35}$$

$$\begin{aligned}
A_{2\rightleftarrows 2,r} = {} & \frac{3}{2}kT \ln \frac{m_c m_d}{m_{c'} m_{d'}} + kT \ln \frac{Z_c^{\text{int}} Z_d^{\text{int}}}{Z_{c'}^{\text{int}} Z_{d'}^{\text{int}}} \\
& - kT \ln \frac{n_c n_d}{n_{c'} n_{d'}} + \varepsilon_{c'} + \varepsilon_{d'} - \varepsilon_c - \varepsilon_d \\
& + \varepsilon_i^c \left(\frac{T}{T_v^c} - 1 \right) + \varepsilon_k^d \left(\frac{T}{T_v^d} - 1 \right) - \varepsilon_{i'}^{c'} \left(\frac{T}{T_v^{c'}} - 1 \right) \\
& - \varepsilon_{k'}^{d'} \left(\frac{T}{T_v^{d'}} - 1 \right), \tag{36}
\end{aligned}$$

$$\begin{aligned}
A_{2\rightleftarrows 3,r} = {} & \frac{3}{2}kT \ln \frac{m_c}{m_{c',a} m_{f',a}} - \frac{3}{2}kT \ln(2\pi kT) \\
& + 3kT \ln h + kT \ln Z_c^{\text{int}} - kT \ln \frac{n_c}{n_{c',a} n_{f',a}} \\
& + \varepsilon_{c',a} + \varepsilon_{f',a} - \varepsilon_c + \varepsilon_i^c \left(\frac{T}{T_v^c} - 1 \right), \tag{37}
\end{aligned}$$

where indices c',a and f',a denote the atomic products of the dissociation reaction. Note that for harmonic oscillators $\Delta\varepsilon_i^c$ does not depend on the vibrational state: $\Delta\varepsilon_i^c = \pm h\nu_c$. For a binary mixture of homonuclear molecules and atoms we need only the expressions for $A_{\text{VT},r}$, $A_{2\rightleftarrows 3,r}$; the latter takes a simplified form since $m_{c',a} = m_{f',a} = m_c/2$, $n_{c',a} n_{f',a} = n_a^2$, $\varepsilon_{c',a} + \varepsilon_{f',a} - \varepsilon_c = D_c$, D_c is the dissociation energy of a molecule of species c.

Substituting Eqs. (26) and (32) into Eq. (18), we find that reaction rates in the zero-order approximations are linear functions of Γ^r,

$$\dot{\xi}_r^{(0)} = \Gamma^r k_{f,r}^{(0)} \prod_{c=1}^{L} \prod_{i=1}^{L_c} \left(\frac{n_{ci}}{N_a} \right)^{\nu_{r,ci}^{(r)}}, \tag{38}$$

and involve zero-order reaction rate coefficients $k_{f,r}^{(0)}$ obtained substituting distribution function (26) into the definition (19). Here L_c denotes the number of vibrational levels in chemical species c and $\nu_{r,ci}^{(r)}$ is the reactant stoichiometric coefficient. It is evident that for the distribution function (26), Eq. (38) differs from the mass action law since the reaction rate depends on both temperatures T and T_v^c through the vibrational distributions. When the flow approaches thermal equilibrium, vibrational level populations follow the equilibrium Boltzmann distribution, and Eq. (38) reduces to the mass action law.

Using Eq. (38), one can easily calculate the relaxation terms (21) and (22) in the zero-order approximation. This gives the reaction rate and vibrational energy production rate in inviscid gas flows. Once again, we emphasize here that R_c^{vibr} takes into account all slow processes occurring in a flow and therefore provides a self-consistent coupling between vibrational relaxation and chemical reactions.

Macroscopic equations (8)–(11) can be written in terms of variables n_c, $\mathbf{v}$, T, and T_v^c instead of n_c, $\mathbf{v}$, U, and $E_{\text{vibr},c}$, which is useful for the derivation of the first-order distribution

function. The specific energies U and $E_{\mathrm{vibr},c}$ can be expressed using the zero-order distribution function

$$
\rho U = \frac{3}{2} nkT + \sum_{c=1}^{L_m} \rho_c E_{\mathrm{rot},c}(T) + \sum_{c=1}^{L_m} \rho_c E_{\mathrm{vibr},c}\big(T_v^c\big)
$$

$$
+ \sum_{c=1}^{L} \rho_c E_{f,c} = U\big(n_c, T, T_v^c\big), \qquad (39)
$$

$$
E_{\mathrm{vibr},c}\big(T, T_v^c\big) = \frac{1}{\rho_c} \sum_i \varepsilon_i^c n_{ci}
$$

$$
= \frac{1}{m_c Z_c^{\mathrm{vibr}}\big(T_v^c\big)} \sum_i \varepsilon_i^c \exp\left(-\frac{\varepsilon_i^c}{kT_v^c}\right). \quad (40)
$$

Then, introducing the specific heats

$$
c_u = \frac{\partial U}{\partial T} = c_{\mathrm{tr}} + c_{\mathrm{rot}} = \frac{3}{2}\frac{kn}{\rho} + \sum \frac{\rho_c}{\rho} \frac{\partial E_{\mathrm{rot},c}}{\partial T}, \qquad (41)
$$

$$
c_{v,c} = \frac{\partial E_{\mathrm{vibr},c}}{\partial T_v^c}, \qquad (42)
$$

one can obtain the expressions

$$
dU = \sum_{c=1}^{L} \frac{\partial U}{\partial n_c}\, dn_c + c_u dT + \sum_{c=1}^{L_m} \frac{\rho_c}{\rho} c_{v,c}\, dT_v^c, \qquad (43)
$$

$$
dE_{\mathrm{vibr},c} = c_{v,c}\, dT_v^c. \qquad (44)
$$

Calculation of the derivatives is straightforward and is omitted for the sake of brevity. Thus one can see that the sets of macroscopic variables $(n_c, \mathbf{v}, U, E_{\mathrm{vibr},c})$ and $(n_c, \mathbf{v}, T, T_v^c)$ are equivalent.

B. Landau-Teller equation and relaxation times

In nonequilibrium fluid dynamics, the rate of vibrational energy production caused by VT transitions is commonly calculated using the Landau-Teller expression [35]:

$$
R_c^{\mathrm{vibr,VT}} = \rho_c \frac{E_{\mathrm{vibr},c}^{\mathrm{eq}}(T) - E_{\mathrm{vibr},c}\big(T_v^c\big)}{\tau_c^{VT}}, \qquad (45)
$$

where $E_{\mathrm{vibr},c}^{\mathrm{eq}}(T)$ is the equilibrium vibrational energy per unit of mass and τ_c^{VT} is the VT relaxation time for species c. Derived initially [35] for the conditions of sound dispersion assuming weak deviations from equilibrium and harmonic vibrations, it became very popular in computational fluid dynamics due to its simplicity and now is commonly used for arbitrary deviations from equilibrium without justification.

In Ref. [27] it was shown that the Landau-Teller expression can be obtained from a strict kinetic-theory definition of the relaxation terms (by expanding the expressions in a power series and keeping only linear terms) under the following assumptions: (1) the vibrational spectrum of molecular species is harmonic, (2) deviations from vibrational equilibrium are weak ($T/T_v \approx 1$), and (3) vibrational specific heats are constant.

An intermediate version of the Landau-Teller expression was also obtained:

$$
R_c^{\mathrm{vibr,VT}} = \frac{T}{T_v^c}\big(T - T_v^c\big)\rho_c c_{v,c} \sum_d \frac{n_c}{n\tau_{cd}^{VT}}, \qquad (46)
$$

where τ_{cd}^{VT} is the VT relaxation time for collisions of molecules of species c with particles of chemical species d. It was shown that such an expression for the relaxation terms provides significantly better agreement with strict kinetic theory results for a harmonic oscillator case. Thus, it is of interest to compare results obtained using different versions of the Landau-Teller formula, since the modified expression can be considered an easy-to-implement and more accurate replacement of the classic Landau-Teller formula.

A model for calculation of vibrational relaxation times is also needed. The Millikan-White formula is commonly used (often with the high-temperature correction proposed by Park [4]), but, as shown in Ref. [8], it does not provide a satisfactory agreement with experimental data at high temperatures ($T > 6000$ K). VT relaxation times can be calculated using a rigorous kinetic-theory definition if the cross sections of various VT transitions are known. The strict kinetic-theory definition of the VT relaxation time τ_{cd}^{VT} for collisions between molecules of species c and particles of species d is as follows [19]:

$$
\frac{1}{\tau_{cd}^{VT}} = \frac{4kn}{m_c c_{v,c}}\big\langle\big(\Delta\mathcal{E}_c^{\mathrm{vibr}}\big)^2\big\rangle_{cd}^{VT}, \qquad (47)
$$

where $\Delta\mathcal{E}_c^{\mathrm{vibr}} = (\varepsilon_{i'}^c - \varepsilon_i^c)/kT$ and averaging is defined by:

$$
\langle F \rangle_{cd}^{\mathrm{VT}} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2} \sum_{iki'jlj'l'} \frac{s_{ij}^c s_{kl}^d}{Z_c^{\mathrm{int}} Z_d^{\mathrm{int}}} \int F_{cij} g_0^3 \exp
$$

$$
\times \left(-g_0^2 - \mathcal{E}_j^c - \mathcal{E}_l^d - \frac{\varepsilon_i^c}{kT_v^c} - \frac{\varepsilon_k^d}{kT_v^d}\right)
$$

$$
\times \sigma_{cd,ijkl}^{i'j'kl'} d^2\Omega dg_0, \qquad (48)
$$

where $m_{cd} = m_c m_d/(m_c + m_d)$ is the collision reduced mass, $g_0 = \sqrt{m_{cd}/2kT}\, g$ is the dimensionless relative velocity, $\mathcal{E}_j^c = \varepsilon_j^c/kT$ is the dimensionless rotational energy, and $\sigma_{cd,ijkl}^{i'j'kl'}$ is the cross section of a VT transition in which the vibrational level i and rotational level j of a molecule of species c change to i' and j' after colliding with a particles of species d with vibrational level k and rotational level l, the latter of which changes to l'. It is worth noting that this strict definition of relaxation times includes a dependence both on T and on T_v^c, while the Millikan-White formula does not. However, the calculation of relaxation times using formula (47) requires significant computational effort and is not very well suited for implementation in practical CFD solvers, but the results of calculations using formula (47) may be precomputed for the chemical species of interest and approximated numerically in a wide range of temperatures, and these approximations are used instead of the Millikan-White formula. The obtained formula for the VT relaxation time is similar to the general formula given in Ref. [36] for relaxation times of internal degrees of freedom.

To calculate the vibrational relaxation times using formula (47), the VT cross sections were calculated using the method
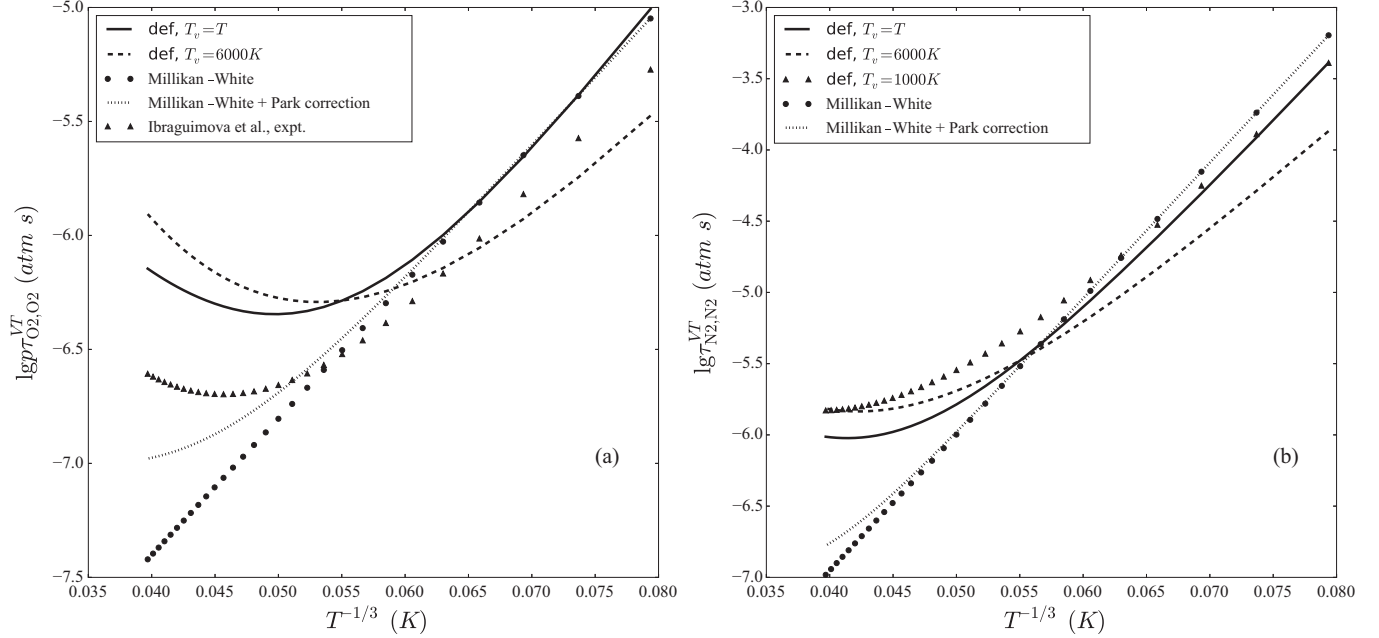
FIG. 1. VT relaxation times in molecular oxygen (a) and nitrogen (b) as a function of temperature; solid line, definition (47) with $T_v = T$; dashed line, definition (47) with $T_v = 6000$ K; dots, Millikan-White formula; dotted line, Millikan-White formula with Park's high-temperature correction; triangles, approximation of experimental results [8] for the case of oxygen (a) and relaxation times calculated using definition (47) with $T_v = 1000$ K for the case of nitrogen (b).

detailed in Ref. [27], using the forced harmonic oscillator (FHO) model [37] for VT transition probabilities and the variable soft sphere (VSS) model [38] for elastic cross sections.

Relaxation times calculated as a function of temperature using various models in molecular oxygen and nitrogen are shown on Fig. 1, along with an approximation of experimental data for oxygen VT relaxation times given in Ref. [8]. It can be seen that vibrational nonequilibrium has a noticeable effect on vibrational relaxation time which increases as the difference between T and T_v grows. At temperatures lower than 6000 K, relaxation times calculated using definition (47) with $T = T_v$ give a good agreement with the Millikan-White formula (the discrepancy between approximation [8] and the Millikan-White formula at temperatures lower than 6000 K can be neglected, since the approximation was made for temperatures between 6000 and 11 000 K), while at higher temperatures definition (47) shows a nonmonotonic behavior of the relaxation times, providing qualitative agreement with both the Park correction and experimental results, while the Millikan-White formula gives physically unrealistically low VT relaxation times. However, the values given by formula (47) are higher than those obtained using other models (in Ref. [39] it was also shown that accounting for vibrational anharmonicity when using formula (47) leads to higher values of vibrational relaxation times at high temperatures). The method of calculation of relaxation times using definition (47) can be expanded to other gas species if the VT transition cross sections (or probabilities) are known. In Ref. [9], precomputed values of vibrational relaxation times calculated using definition (47), depending on both the translational and vibrational temperatures, were used in conjunction with the modified Landau-Teller formula (46), and it was shown that

such a model provides good agreement with experimental data on temperatures behind shock waves [8].

Therefore, we can see that the Millikan-White formula, even with the Park corrections, significantly underestimates the vibrational relaxation times at high temperatures and is poorly suited for modeling of strongly nonequilibrium high-temperature flows (see also Ref. [9]).

For molecular-atom collisions in oxygen, relaxation times have recently been calculated using an accurate three-body potential surface [18], and it is shown that at high temperatures they are indeed nonlinear functions of temperature; however, there is a discrepancy between results obtained in Ref. [18] and other models, namely the fact that at lower temperatures, the vibrational relaxation times do not decrease as the temperature rises. Comparisons to vibrational times calculated in Ref. [18] are not presented in this paper, since we consider only VT relaxation via molecule-molecule collisions, for which there is experimental data and which is correctly described by the Millikan-White formula at low temperatures.

IV. FIRST-ORDER APPROXIMATION

The first-order correction to the distribution function can be written as $f_{cij}^{(1)} = f_{cij}^{(0)} \phi_{cij}$, where function ϕ_{cij} satisfies the integral equation,

$$-\sum_d n_c n_d I_{cijd}(\phi) = D f_{cij}^{(0)} - J_{cij}^{sl(0)}, \qquad (49)$$

where I_{cijd} is the linearized integral operator of rapid processes and $D f_{cij}^{(0)}$ is the streaming operator [19].

Calculating the streaming operator on the basis of the zero-order distribution function (26) and zero-order fluid dynamic equations, one can rewrite the first-order distribution function

in terms of the gradients of macroscopic variables:

$$f_{cij}^{(1)} = \frac{f_{cij}^{(0)}}{n} \left(-\mathbf{A}_{cij} \cdot \nabla \ln T - \sum_{d=1}^{L_m} \mathbf{A}_{cij}^{d(1)} \cdot \nabla \ln T_v^d \right.$$

$$- \sum_{d=1}^{L} \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \mathbf{B}_{cij} : \nabla \mathbf{v}$$

$$\left. - F_{cij} \nabla \cdot \mathbf{v} - \sum_{\gamma \in \mathcal{VR}} \sum_r G_{cij}^{\gamma,r} \Gamma^{\gamma,r} \right), \qquad (50)$$

where $\mathbf{d}_c$ are diffusive driving forces:

$$\mathbf{d}_c = \nabla \left(\frac{n_c}{n} \right) + \left(\frac{n_c}{n} - \frac{\rho_c}{\rho} \right) \nabla \ln p. \qquad (51)$$

$\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\mathbf{B}_{cij}$, $\mathbf{D}_{cij}^d$, F_{cij}, $G_{cij}^{\gamma,r}$, $\gamma \in \mathcal{VR}$ are unknown functions of the peculiar velocity and macroscopic variables. It must be noted that such a form for the first-order correction (50) differs from the usual one reported in Ref. [19] since instead of one term G_{cij} we have a combination of four sums, which explicitly include the generalized affinities $\Gamma^{VV',r}$, $\Gamma^{VT,r}$, $\Gamma^{2 \rightleftarrows 2,r}$, and $\Gamma^{2 \rightleftarrows 3,r}$.

A. Integral equations

Integral equations for functions $\mathbf{A}_{cij}$, $\mathbf{A}_{cij}^{d(1)}$, $\mathbf{B}_{cij}$, $\mathbf{D}_{cij}^d$, F_{cij}, $G_{cij}^{\gamma,r}$ are obtained by substituting representation (50) into (49) and equating corresponding terms in the right- and left-hand sides of the resulting equation. For F_{cij}, these terms are the ones appearing in front of $\nabla \cdot \mathbf{v}$, while for $G_{cij}^{\gamma,r}$ the terms appearing in the right-hand side of corresponding equations (49) are multipliers in front of the generalized thermodynamic forces $\Gamma^{\gamma,r}$.

The equations for F_{cij} can be found in Ref. [19], while the equations for $G_{cij}^{\gamma,r}$ are as follows:

$$\sum_d \frac{n_c n_d}{n^2} I_{cijd}(G^{\gamma,r}) = \frac{1}{n} f_{cij}^{(0)} \Phi_{cij}^{\gamma,r}, \quad r = 1, \ldots, N_\gamma, \ \gamma \in \mathcal{VR}, \qquad (52)$$

where $\Phi_{cij}^{\gamma,r}$ are defined as:

$$\Phi_{cij}^{\gamma,r} = -N_a \frac{H_{cj}}{c_u} \sum_{d=1}^{L_m} \frac{\Delta \varepsilon^d}{\rho_d} \dot{\xi}_{\gamma,r}^{(0)} + N_a \left[\frac{\varepsilon_i^c}{kT_v^c} \right]_{\mathrm{vibr}}'$$

$$\times \frac{1}{T_v^c} c_{v,c}^{-1} \frac{\Delta \varepsilon^c}{\rho_c} \dot{\xi}_{\gamma,r}^{(0)} - \widetilde{J}_{\gamma,rc}, \quad \gamma \in \mathcal{V}, \qquad (53)$$

$$\Phi_{cij}^{\gamma,r} = -N_a \frac{H_{cj}}{c_u} \sum_{d=1}^{L_m} \frac{\Delta \varepsilon^d - \nu_{r,d} E_{\mathrm{vibr},d} m_d}{\rho_d} \dot{\xi}_{\gamma,r}^{(0)}$$

$$- N_a \frac{H_{cj}}{c_u} \sum_{d=1}^{L} \nu_{r,d} \frac{\partial U}{\partial n_d} \dot{\xi}_{\gamma,r}^{(0)}$$

$$+ N_a \left[\frac{\varepsilon_i^c}{kT_v^c} \right]_{\mathrm{vibr}}' \frac{1}{T_v^c} c_{v,c}^{-1} \frac{\Delta \varepsilon^c - \nu_{r,c} E_{\mathrm{vibr},c} m_c}{\rho_c} \dot{\xi}_{\gamma,r}^{(0)}$$

$$+ \frac{N_a}{n_c} \nu_{r,c} \dot{\xi}_{\gamma,r}^{(0)} - \widetilde{J}_{\gamma,rc}, \quad \gamma \in \mathcal{R}. \qquad (54)$$

Here $\nu_{r,c} = \sum_i \nu_{r,ci}$, $\widetilde{J}_{\gamma,rc} = \nu_{r,ci} \sum_{lj'l'} \int f_{dkl}^{(0)} g \widetilde{\sigma}_{f,r}^\gamma d\mathbf{u}_d$ (for the case of $\gamma = 2 \rightleftarrows 3$ summation over j', l' is omitted), $[\zeta_j]_{\mathrm{rot}}' = \zeta_j - \langle \zeta_j \rangle_{\mathrm{rot}}$, and $[\zeta_i]_{\mathrm{vibr}}' = \zeta_i - \langle \zeta_i \rangle_{\mathrm{vibr}}$, where $\langle \zeta_j \rangle_{\mathrm{rot}}$ and $\langle \zeta_j \rangle_{\mathrm{vibr}}$ denote averaging over the rotational and vibrational energy spectrum, respectively:

$$\langle \zeta_j \rangle_{\mathrm{rot}} = \frac{1}{Z_c^{\mathrm{rot}}} \sum_j s_j^c \zeta_j \exp \left(-\frac{\varepsilon_j^c}{kT} \right), \qquad (55)$$

$$\langle \zeta_i \rangle_{\mathrm{vibr}} = \frac{1}{Z_c^{\mathrm{vibr}}} \sum_j s_i^c \zeta_i \exp \left(-\frac{\varepsilon_i^c}{kT_v^c} \right). \qquad (56)$$

The function H_{cj} is defined as follows:

$$H_{cj} = \frac{1}{T} \left(-\frac{3}{2} + \frac{m_c c_c^2}{2kT} + \left[\frac{\varepsilon_j^c}{kT} \right]_{\mathrm{rot}}' \right). \qquad (57)$$

It can be seen that the equations defining functions $G_{cij}^{\gamma,r}$ for a flow with molecules with harmonic vibrational spectra are less complicated than those in the general case, as given in Refs. [26,27]. This leads to a simplified set of equations for calculation of first-order corrections to normal mean stress and reaction rates.

For a binary mixture of molecules and atoms with slow single-quantum VT transitions and dissociation-recombination reactions, the definitions of functions $\Phi_{cij}^{\gamma,r}$:

$$\Phi_{Mij}^{\mathrm{VT},r} = -\frac{N_a}{\rho_M} h \nu_M \dot{\xi}_{\mathrm{VT},r}^{(0)} \left(\frac{H_{Mj}}{c_u} - \left[\frac{\varepsilon_i^M}{kT_v^M} \right]_{\mathrm{vibr}}' \frac{1}{T_v^M} c_{v,M}^{-1} \right) - \widetilde{J}_{\mathrm{VT},rM}, \qquad (58)$$

$$\Phi_A^{\mathrm{VT},r} = -\frac{N_a}{\rho_M} h \nu_M \dot{\xi}_{\mathrm{VT},r}^{(0)} \frac{H_A}{c_u}, \qquad (59)$$

$$\Phi_{Mij}^{2 \rightleftarrows 3,r} = -\frac{N_a}{\rho_M} \dot{\xi}_{\mathrm{VT},r}^{(0)} (\Delta \varepsilon^M + E_{\mathrm{vibr},M} m_M)$$

$$\times \left(\frac{H_{Mj}}{c_u} - \left[\frac{\varepsilon_i^M}{kT_v^M} \right]_{\mathrm{vibr}}' \frac{1}{T_v^M} c_{v,M}^{-1} \right) - \frac{N_a}{n_M} \dot{\xi}_{\gamma,r}^{(0)}$$

$$- N_a \frac{H_{Mj}}{c_u} \left(2 \frac{\partial U}{\partial n_A} - \frac{\partial U}{\partial n_M} \right) \xi_{\gamma,r}^{(0)} - \widetilde{J}_{\mathrm{VT},rM}, \quad (60)$$

$$\Phi_A^{2 \rightleftarrows 3,r} = -\frac{N_a}{\rho_M} \dot{\xi}_{\mathrm{VT},r}^{(0)} (\Delta \varepsilon^M + E_{\mathrm{vibr},M} m_M)$$

$$\times \frac{H_A}{c_u} + 2 \frac{N_a}{n_A} \dot{\xi}_{\gamma,r}^{(0)} - N_a \frac{H_A}{c_u} \left(2 \frac{\partial U}{\partial n_A} - \frac{\partial U}{\partial n_M} \right) \dot{\xi}_{\gamma,r}^{(0)}$$

$$- \widetilde{J}_{\mathrm{VT},rA}. \qquad (61)$$

Here M and A denote the molecular and atomic species, correspondingly.

Additional constraints for the functions $G_{cij}^{\gamma,r}$ follow from the normalization conditions imposed on the distribution function [27]:

$$\sum_{ij} \int f_{cij}^{(0)} G_{cij}^{\gamma,r} d\mathbf{u}_c = 0, \quad c = 1, \ldots, L,$$

$$r = 1, \ldots, N_\gamma, \ \gamma \in \mathcal{VR}, \qquad (62)$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_{ij}^c \right) G_{cij}^{\gamma,r} d\mathbf{u}_c = 0, \quad r = 1, \dots, N_\gamma,$$

$$\gamma \in \mathcal{VR}. \tag{63}$$

$$\sum_{ij} \varepsilon_i^c \int f_{cij}^{(0)} G_{cij}^{\gamma,r} d\mathbf{u}_c = 0, \quad c = 1, \dots, L_m,$$

$$r = 1, \dots, N_\gamma, \quad \gamma \in \mathcal{VR}. \tag{64}$$

The first-order correction to the reaction rates can be expressed in terms of integral brackets of functions F_{cij} and $G_{cij}^{\gamma,r}$:

$$N_a \dot{\xi}_{r,\gamma}^{(1)} = \sum_{\beta,s} [G^{\gamma,r}, G^{\beta,s}] \Gamma^{\beta,s} + [G^{\gamma,r}, F] \nabla \cdot \mathbf{v}. \tag{65}$$

The integral brackets are introduced similarly to Refs. [19,27] on the basis of the linearized integral operator of rapid processes.

One can see that in the first-order approximation, the rates of all nonequilibrium processes depend on the velocity divergence and affinities of other reactions; moreover, the normal mean stress is also expressed in terms of the same thermodynamic forces. Such a coupling has been reported before [20–22] for one-temperature flows and in our previous paper [27] for multitemperature flows. Therefore, in viscous flows, coupling of vibrational relaxation and chemical reactions is much more complex compared to the case of inviscid flows

corresponding to the zero-order approximation. That is why, commonly used in computational fluid dynamics, zero-order CVDV and CVCV models similar to the Treanor-Marrone one [2] are not able to capture these mutual effects of reactions, relaxation, and flow compressibility.

B. Numerical solution methods

The general approach to numerical computation of first-order corrections to the reaction rates is given in Refs. [19] and [27], and the reader is referred to Ref. [27] for a detailed description of the methods and quantities involved. However, compared to the expressions for the general multitemperature case [27], since we consider only harmonic vibrational spectra, some simplifications can be made. The unknown functions $G_{cij}^{\gamma,r}$ are expanded in terms of Sonine polynomials $S_{1/2}^{(q)}$ and Waldmann-Trubenbacher polynomials $P_{ij}^{(p)}$:

$$G_{cij}^{\gamma,r} = \sum_{qp} g_{c,qp}^{\gamma,r} S_{1/2}^{(q)} \left(\frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left(\frac{\varepsilon_j^c}{kT} + \frac{\varepsilon_i^c}{kT_v^c} \right), \gamma \in \mathcal{VR}. \tag{66}$$

System of linear equations for the expansion coefficients $g_{c,qp}^{\gamma,r}$ are obtained by multiplying equations (52) by the quantity

$$Q_{cij}^{qp} = S_{1/2}^{(q)} \left(\frac{m_c c_c^2}{2kT} \right) P_{ij}^{(p)} \left(\frac{\varepsilon_j^c}{kT} + \frac{\varepsilon_i^c}{kT_v^c} \right), \tag{67}$$

integrating over $\mathbf{u}_c$ and performing summation over i, j, which results in the following equations:

$$\sum_d \sum_{q'p'} \beta_{qq'pp'}^{cd,\gamma,r} g_{d,q'p'}^{\gamma,r} = \frac{n_c}{n} \left[\frac{3}{2} \delta_{q1} \delta_{p0} M_1^{\gamma,r} + \delta_{q0} \delta_{p1} \left(M_1^{\gamma,r} \frac{m_c}{k} c_{\text{rot},c} - M_{2,c}^{\gamma,r} \frac{m_c}{k} c_{v,c} \right) \right] - \frac{1}{n} \sum_{ij} \int Q_{cij}^{qp,\gamma,r} f_{cij}^{(0)} \widetilde{J}_{\gamma,rc} d\mathbf{u}_c, \quad \gamma \in \mathcal{V}, \tag{68}$$

$$\sum_d \sum_{q'p'} \beta_{qq'pp'}^{cd,\gamma,r} g_{d,q'p'}^{\gamma,r} = \frac{n_c}{n} \left[\frac{3}{2} \delta_{q1} \delta_{p0} M_1^{\gamma,r} + \delta_{q0} \delta_{p1} \left(M_1^{\gamma,r} \frac{m_c}{k} c_{\text{rot},c} - M_{2,c}^{\gamma,r} \frac{m_c}{k} c_{v,c} \right) \right]$$

$$+ \delta_{q0p0} \frac{N_a}{n_c} v_{r,c} \xi_{\gamma,r}^{(0)} - \frac{1}{n} \sum_{ij} \int Q_{cij}^{qp,\gamma,r} f_{cij}^{(0)} \widetilde{J}_{\gamma,rc} d\mathbf{u}_c, \gamma \in \mathcal{R}, \tag{69}$$

where the bracket integrals $\beta_{qq'pp'}^{cd,\gamma,r}$ are defined in the same manner as in Ref. [19], $c_{\text{rot},c}$ is the specific heat capacity of rotational degrees of freedom of species c, and the quantities $M_1^{\gamma,r}$, $M_{2,c}^{\gamma,r}$ are given by the following expressions:

$$M_1^{\gamma,r} = \frac{N_a}{T c_u} \sum_{d=1}^{L_m} \frac{\Delta \varepsilon^d}{\rho_d} \xi_{\gamma,r}^{(0)}, \quad \gamma \in \mathcal{V}, \tag{70}$$

$$M_1^{\gamma,r} = \frac{N_a}{T c_u} \sum_{d=1}^{L_m} \frac{\Delta \varepsilon^d - v_{r,d} E_{\text{vibr},d} m_d}{\rho_d} \xi_{\gamma,r}^{(0)}$$

$$+ \frac{N_a}{T c_u} \sum_{d=1}^{L} v_{r,d} \frac{\partial U}{\partial n_d} \xi_{\gamma,r}^{(0)},$$

$$\gamma \in \mathcal{R}, \tag{71}$$

$$M_{2,c}^{\gamma,r} = \frac{N_a}{T_v^c} c_{v,c}^{-1} \frac{\Delta \varepsilon^c}{\rho_c} \xi_{\gamma,r}^{(0)}, \quad \gamma \in \mathcal{V}, \tag{72}$$

$$M_{2,c}^{\gamma,r} = \frac{N_a}{T_v^c} c_{v,c}^{-1} \frac{\Delta \varepsilon^c - v_{r,d} E_{\text{vibr},c} m_c}{\rho_c} \xi_{\gamma,r}^{(0)}, \quad \gamma \in \mathcal{R}. \tag{73}$$

Equations (68) and (69) have to be completed by constraints arising from the normalization conditions (62)–(64):

$$g_{c,00}^{\gamma,r} = 0, \quad r = 1, \dots, N_\gamma, \quad \gamma \in \mathcal{VR}, \tag{74}$$

$$\sum_c \frac{n_c}{n} \left(\frac{3}{2} g_{c,10}^{\gamma,r} + \frac{m_c}{k} c_{\text{rot},c} g_{c,01}^{\gamma,r} + \frac{m_c}{k} c_{v,c} g_{c,01}^{\gamma,r} \right) = 0,$$

$$r = 1, \dots, N_\gamma, \quad \gamma \in \mathcal{VR}. \tag{75}$$

Introducing the generalized averaging operators [19,27]

$$
\langle F \rangle_{cd}^{\gamma,r} = \left(\frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{jlj'l'} \frac{s_{ij}^c s_{kl}^d}{Z_c^{\mathrm{int}} Z_d^{\mathrm{int}}} \int F g_0^3 \exp
$$

$$
\times \left(-g_0^2 - \mathcal{E}_j^c - \mathcal{E}_l^d - \frac{\varepsilon_i^c}{kT_v^c} - \frac{\varepsilon_k^d}{kT_v^d} \right) \sigma_{f,r} d^2\Omega dg_0,
$$

$$
\gamma = \mathrm{VV}', \mathrm{VT}, 2 \rightleftarrows 2, \tag{76}
$$

$$
\langle F \rangle_{cd}^{2\rightleftarrows 3,r} = \left(\frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{jl} \frac{s_{ij}^c s_{kl}^d}{Z_c^{\mathrm{int}} Z_d^{\mathrm{int}}} \int F g_0^3 \exp
$$

$$
\times \left(-g_0^2 - \mathcal{E}_j^c - \mathcal{E}_l^d - \frac{\varepsilon_i^c}{kT_v^c} - \frac{\varepsilon_k^d}{kT_v^d} \right) \sigma_{f,r} dg_0,
$$

$$
\tag{77}
$$

and the generalized collision integrals

$$
\Omega_{c,v}^{\gamma,r(l,m)'} = \left\langle v_{r,ci} g_0^{2l} \left(P_{ij}^{(1)} \left(\frac{\varepsilon_j^c}{kT} + \frac{\varepsilon_i^c}{kT_v^c} \right) \right)^m \right\rangle_c^{\gamma,r}, \tag{78}
$$

we can write out the expressions for the bracket integrals $[F, G^{\gamma,r}]$ and $[G^{\gamma,r}, G^{\beta,s}]$ in terms of expansion coefficients of functions $G_{cij}^{\gamma,r}$ (considering only the zero-order and first-order expansion coefficients):

$$
[F, G^{\gamma,r}] = \sum_c \frac{n_c}{n} \left(-g_{c,10}^{\gamma,r} - \frac{p}{\rho T c_u} g_{c,01}^{\gamma,r} \frac{m_c}{k} c_{v,c} \right), \tag{79}
$$

$$
[G^{\gamma,r}, G^{\beta,s}] = \sum_c \frac{n_c}{n} \left\{ -g_{c,01}^{\beta,s} \frac{m_c}{k} c_{v,c} \left(M_{1,r}^{\gamma,h} + M_{2,cr}^{\gamma,h} \right) \right.
$$

$$
- n_d \left[12 g_{c,10}^{\beta,s} \frac{m_{cd}}{m_c} \left(\Omega_{c,v}^{\gamma,r(0,0)'} - \frac{2}{3} \Omega_{c,v}^{\gamma,r(1,0)'} \right) \right.
$$

$$
\left. \left. + 8 g_{c,01}^{\beta,s} \left\langle v_{r,ci} P_{ij}^{(1)} \left(\frac{\varepsilon_j^c}{kT} + \frac{\varepsilon_i^c}{kT_v^c} \right) \right\rangle_c^{\gamma,r} \right] \right\}. \tag{80}
$$

Solving the linear systems (68)–(69), we can find the expansion coefficients $g_{c,qp}^{\gamma,r}$, substitute them into expressions (79) and (80), and thus calculate the first-order corrections to the reaction rates (65).

The computational costs for solving the given linear systems are similar to those required for the calculation of transport coefficients. The number of equations in the linear systems is the same as in the systems for the calculation of bulk viscosity. However, calculation of the right-hand sides of the systems requires evaluation of integrals over the magnitude of the relative velocity of the colliding particles, which, coupled with the large number of processes (for each of which a linear system needs to be solved), leads to increased computational costs.

V. NUMERICAL RESULTS

We applied the model developed above to binary mixture flows of nitrogen (N_2-N) and oxygen (O_2-O) under various conditions (translational and vibrational temperatures, mixture composition) to study the influence of first-order effects on vibrational relaxation rates and the influence of cross-coupling between dissociation-recombination reactions and VT transitions on the vibrational relaxation rates. We also studied the influence of first-order effects and coupling between vibrational relaxation and chemical reactions on chemical relaxation rates.

For numerical modeling, VT transition cross section were calculated using the FHO and VSS models, while dissociation cross sections and dissociation rate coefficients were computed using the rigid sphere model, accounting for the vibrational energy of the dissociating molecule. While such a model for dissociation cross sections gives less precise values of the rate coefficients compared to other dissociation models, it allows us to calculate higher-order generalized collision integrals (78) [whereas other models, such as the Treanor-Marrone [2] or Park [40] models, give only expressions for the dissociation rate coefficients and do not provide a way to compute higher-order integrals which appear in Eqs. (69)].

It should be mentioned that while expression (65) includes a term depending on the velocity divergence, its influence on nonequilibrium rates is found negligibly small (for the case of a pure gas see also Ref. [27]). Therefore, this term is not included in the following discussion.

Figures 2–5 give the ratio of vibrational relaxation terms $R_c^{\mathrm{vibr,VT}}$ due to VT transitions in nitrogen and oxygen flows to the Landau-Teller vibrational energy production term (45) as functions of temperature T for various fixed values of the vibrational temperature T_v and various mixture compositions. It can be seen that under strongly nonequilibrium conditions, such as those in Fig. 2, the modified Landau-Teller expression does not provide accurate values for the vibrational energy production terms. In nitrogen, first-order effects are significant (a correction of up to 50%) at high temperatures and low vibrational temperatures (strong vibrational nonequilibrium); as the vibrational temperature increases, the influence of these first-order effects diminishes. In addition, in nitrogen flows, the influence of dissociation on VT transition rates (through first-order coupling effects) is insignificant. In oxygen, at low vibrational temperatures and high temperatures, the influence of first-order corrections is even more significant (a contribution of up to 300%). Moreover, as the vibrational temperature increases, cross-coupling between dissociation and VT transitions starts to play an important role. This can be attributed to the low dissociation energy of oxygen and the increase of numeric density of oxygen molecules at higher vibrational levels (which leads to increased dissociation due to preferential dissociation from levels with higher internal energy). Therefore, while in nitrogen flows the modified Landau-Teller formula provides a good approximation of vibrational energy production due to VT transitions under a wide range of conditions, in oxygen, strict kinetic theory results which account for cross-coupling effects show that variations on the Landau-Teller formula do not work, since they do not account for the influence of dissociation on VT transition rates.

Figure 6 shows the ratio of vibrational relaxation terms $R_c^{\mathrm{vibr,VT}}$ due to VT transitions in nitrogen and oxygen flows to the full vibrational energy production rate defined as

$$
\rho_c \dot{E}_{\mathrm{vibr},c} = R_c^{\mathrm{vibr}} - E_{\mathrm{vibr},c} m_c R_c^{\mathrm{react}}. \tag{81}
$$

Near the point of vibrational equilibrium $T = T_v$ chemical reactions provide the main contribution to the vibrational energy production, while at high temperatures and low vibrational
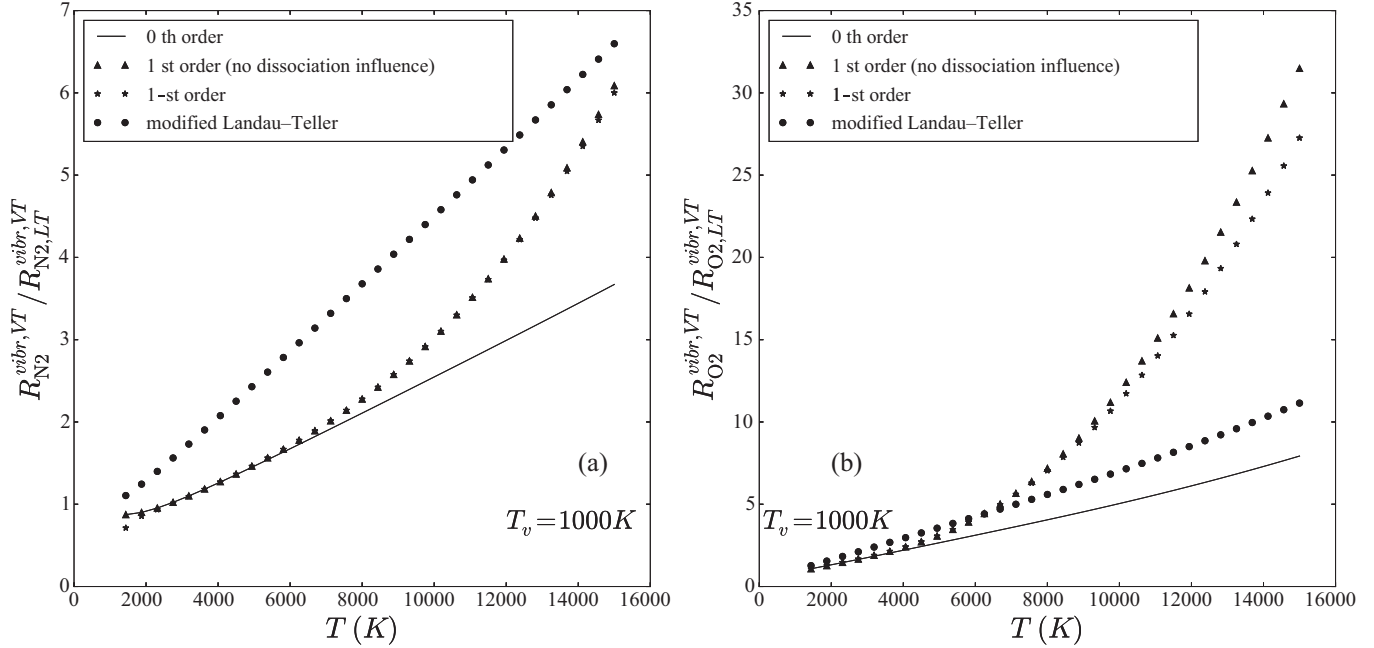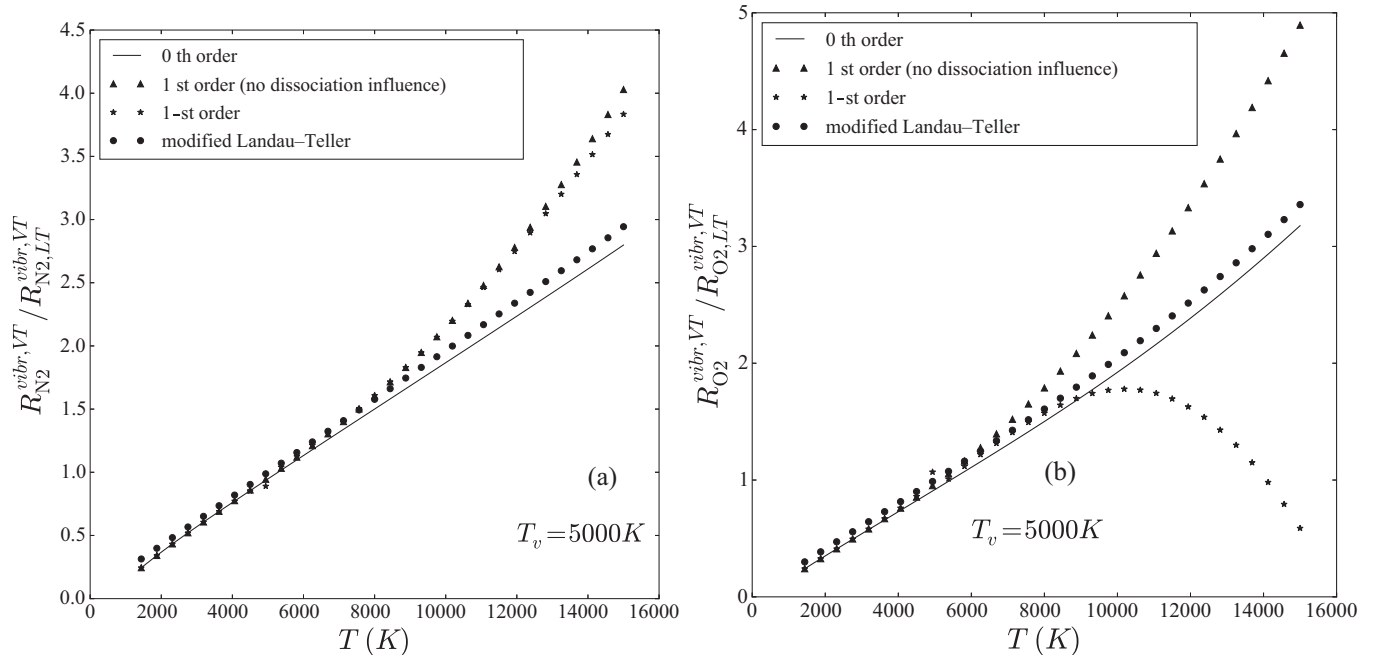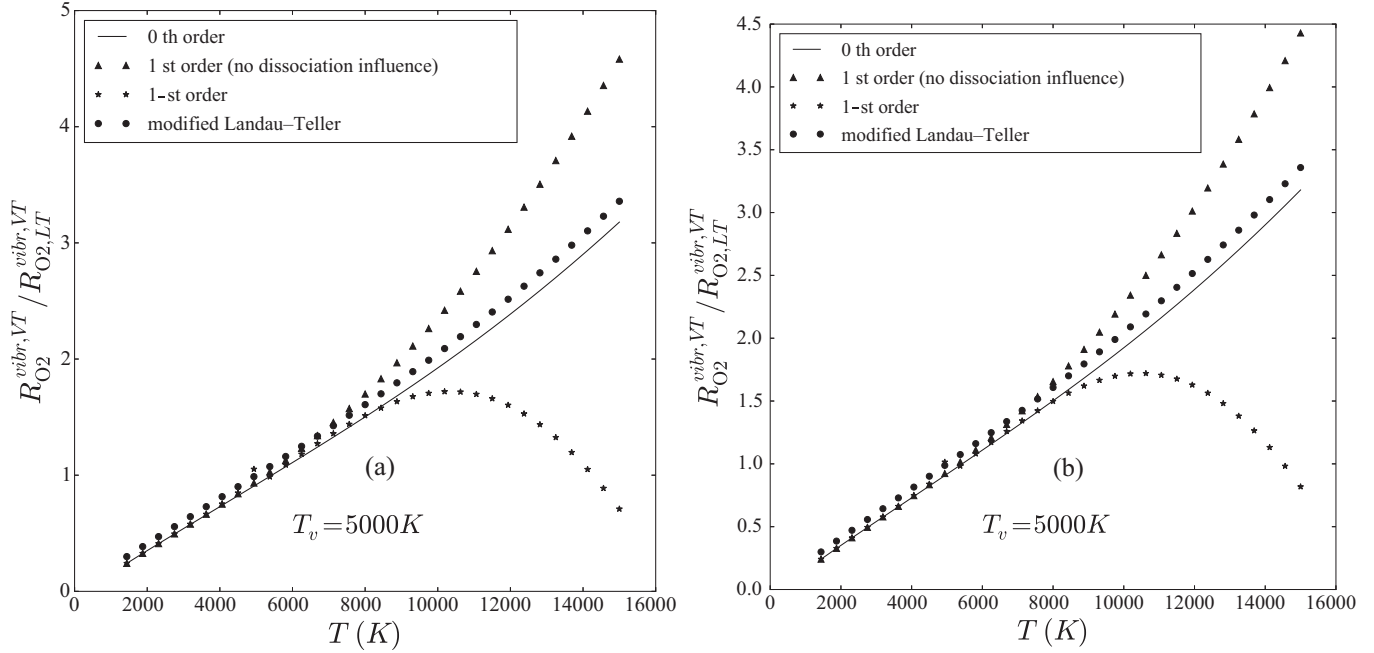
FIG. 2. The ratio of relaxation terms due to slow VT transitions calculated using various models to the VT relaxation terms as given by the Landau-Teller formula (45) as a function of temperature in N_2-N (a) and O_2-O (b) flows. $T_v = 1000$ K, $x_N = x_O = 0.5$.

temperatures, VT transitions play the more important role, while the effect of chemical reactions is negligible. Combined with the fact that for nitrogen the Landau-Teller formula works in a wide range of flow conditions, these facts may be utilized to simplify calculation of vibrational energy relaxation rates. By contrast, in oxygen, when first-order effects are taken into account, the relative contribution of VT transitions declines at high temperatures due to strong cross-coupling effects, as described earlier.

Figure 7 shows the ratio of $R_c^{\mathrm{vibr,VT}}$ due to VT transitions in nitrogen and oxygen flows to the full vibrational energy production rate $\rho_c \dot{E}_{\mathrm{vibr},c}$ under conditions of vibrational equilibrium ($T = T_v$) for various mixture compositions. Due to chemical nonequilibrium, first-order VT transition rates

FIG. 3. The ratio of relaxation terms due to slow VT transitions calculated using various models to the VT relaxation terms as given by the Landau-Teller formula (45) as a function of temperature in N_2-N (a) and O_2-O (b) flows. $T_v = 5000$ K, $x_N = x_O = 0.5$.

FIG. 4. The ratio of relaxation terms due to slow VT transitions calculated using various models to the VT relaxation terms as given by the Landau-Teller formula (45) as a function of temperature in a O_2-O flow with $x_O = 0.25$ (a) and $x_O = 0.1$ (b). $T_v = 5000$ K.

are nonzero; however, their contribution to vibrational energy production rates does not exceed 5%.

Figure 8 shows the ratio of the chemical relaxation terms in the first-order approximation to the chemical relaxation terms in the zero-order approximation $(R_c^{react,(0)} + R_c^{react,(1)})/R_c^{react,(0)}$ in nitrogen and oxygen flows in vibrational equilibrium. In nitrogen, even at high temperatures, the first-order correction to the dissociation rates does not exceed 10%, while in oxygen, where the effects of dissociation are more signifi-

cant, the first-order correction exceeds 200%. However, when the number of atoms in the flow decreases, the first-order corrections also become less significant (for oxygen the first-order correction is less than 20% when $x_O = 0.1$). This decrease is due to the larger dissociation cross section for molecule-atom collisions compared to molecule-molecule collisions.

To compare the dissociation rate coefficients obtained in the zero- and first-order approximations of the Chapman-Enskog method to other models [2,40], we first computed effective
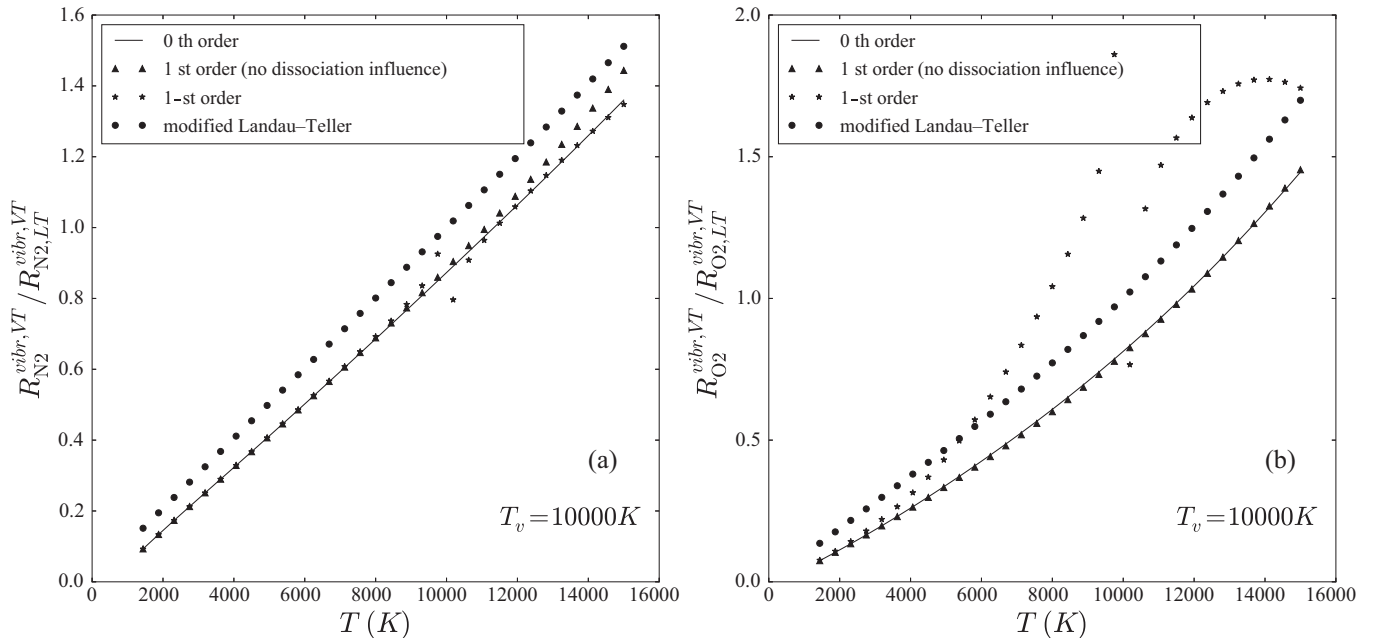

FIG. 5. The ratio of relaxation terms due to slow VT transitions calculated using various models to the VT relaxation terms as given by the Landau-Teller formula (45) as a function of temperature in N_2-N (a) and O_2-O (b) flows. $T_v = 10\,000$ K, $x_N = x_O = 0.5$.
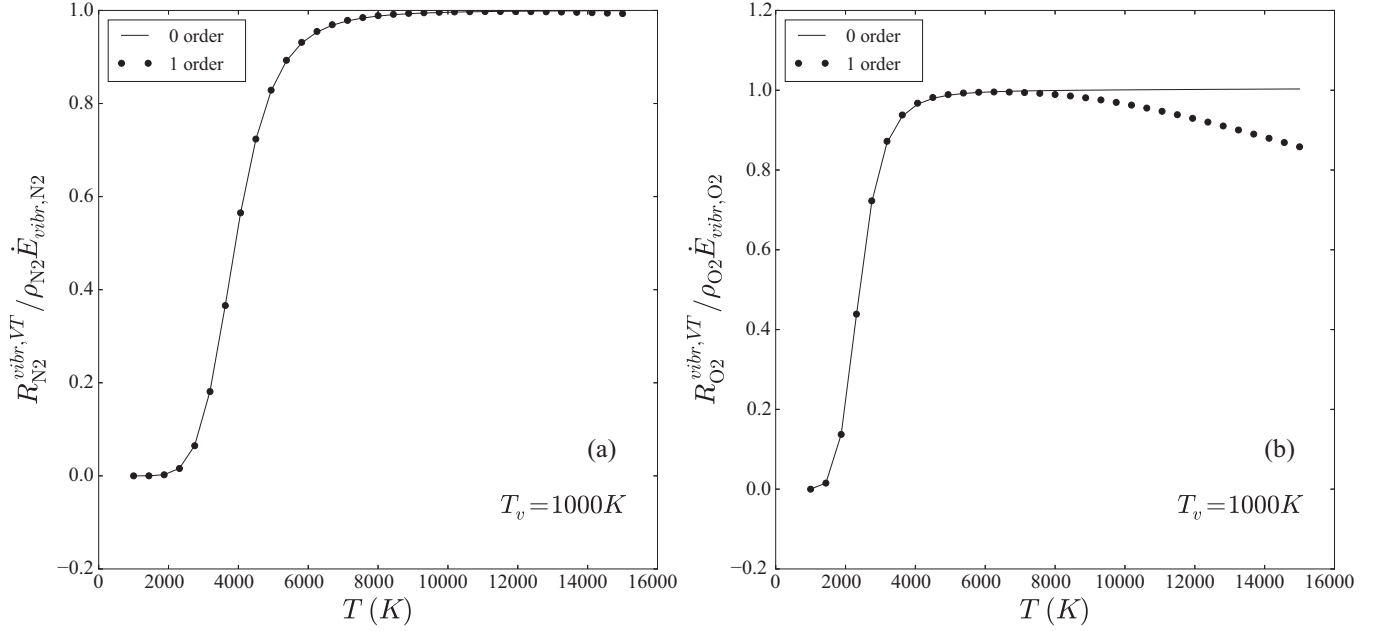
FIG. 6. The ratio of relaxation terms due to slow VT transitions in the zero- and first-order approximation of the Chapman-Enskog method to the full vibrational relaxation term $\rho_c \dot{E}_{\text{vibr},c}$ (which takes into account the dissociation and recombination of molecules and the associated change in specific vibrational energy) as a function of temperature in N_2-N (a) and O_2-O (b) flows. $T_v = 1000$ K, $x_N = x_O = 0.5$.

dissociation rate coefficients, based on expression (38):

$$k_{\text{diss},r}^{\text{eff}} = \frac{1}{\Gamma^r} \dot{\xi}_{r,2 \rightleftarrows 3} \prod_{c=1}^{L} \prod_{i=1}^{L_c} \left(\frac{n_{ci}}{N_a} \right)^{-\nu_{r,ci}^{(r)}}, \qquad (82)$$

and then calculated an effective multitemperature rate coefficient by averaging the state-specific effective rate coefficients over the nonequilibrium Boltzmann distribution (the vibra-

tional level i is a function of the specific reaction r, therefore, summation over all the vibrational levels is interchangeable with summation over all possible dissociation reactions):

$$k_{\text{diss}}^{\text{eff}} = \sum_r \frac{1}{Z_c^{\text{vibr}}} k_{\text{diss},r}^{\text{eff}} \exp \left(-\frac{\varepsilon_i^c}{k T_v^c} \right), \qquad (83)$$

where c denotes the chemical species of the dissociating molecule.
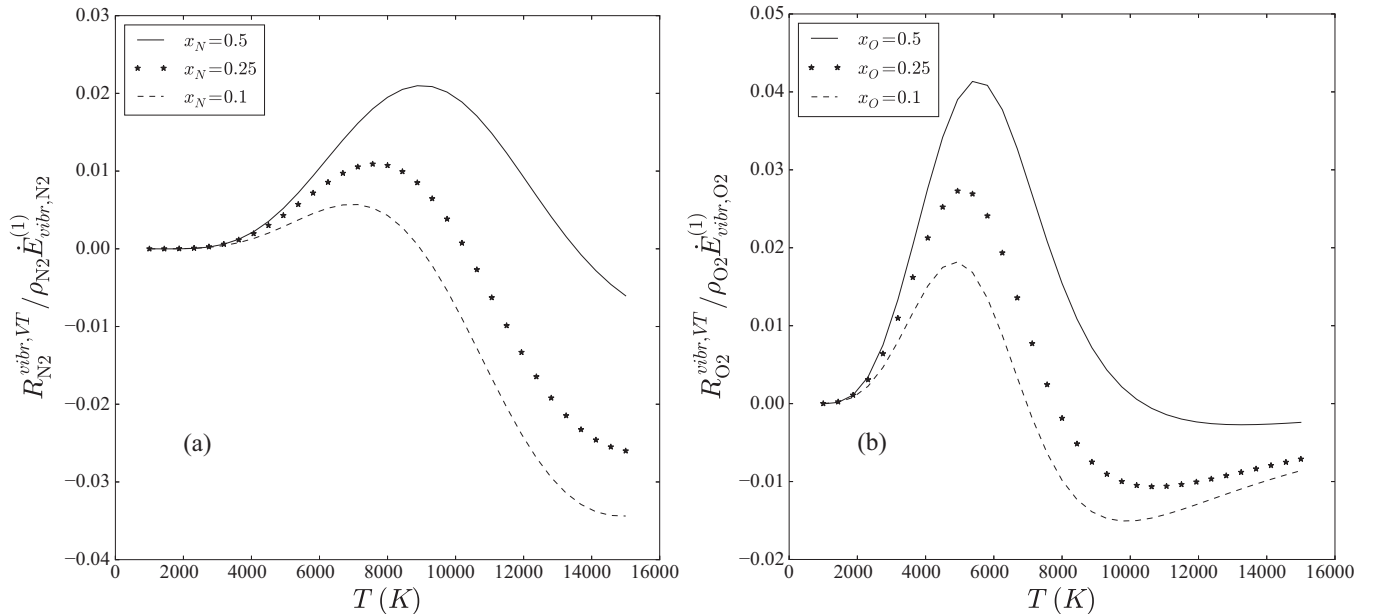

FIG. 7. The ratio of relaxation terms due to slow VT transitions in the first-order approximation of the Chapman-Enskog method to the full vibrational relaxation term $\rho_c \dot{E}_{\text{vibr},c}$ (which takes into account the dissociation and recombination of molecules and the associated change in specific vibrational energy) as a function of temperature in N_2-N (a) and O_2-O (b) flows in a state of vibrational equilibrium for various values of the atom molar fractions.
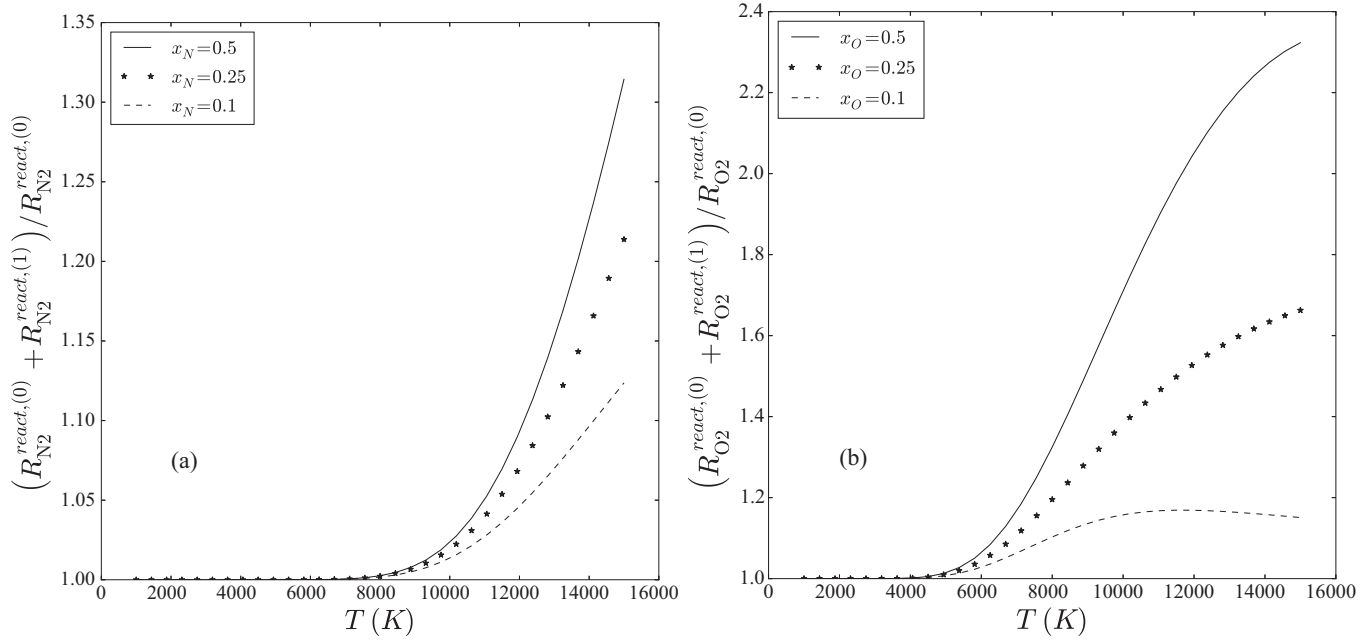
FIG. 8. The ratio of the chemical relaxation rates in the first-order approximation to the corresponding zero-order chemical relaxation term as a function of temperature in N_2-N (a) and O_2-O (b) flows in a state of vibrational equilibrium for various values of the atom molar fractions.

Figures 9 and 10 show a comparison between the effective multitemperature rate coefficients obtained using the approach presented in the paper in both the zero- and first-order approximations and Treanor-Marrone [2] and Park [40] models for dissociation reactions of nitrogen and oxygen with different collision partners (atoms and molecules). The Park model underestimates the dissociation rate at lower temperatures, but the discrepancy becomes lower at higher temperatures. A comparison with the Macheret-Fridman model [5] was also

made, and the results given by it are very similar to our calculations; however, so as not to complicate the plots, they are not presented. It can be seen that for both oxygen and nitrogen for temperatures lower than 10 000 K, the zero-order and first-order dissociation rate coefficients are close to the values given by the Treanor-Marrone model; the contribution of viscous coupling terms becomes more important at high temperatures and high ratio T/T_v (conditions specific for strong shock waves). Thus, in shock-heated gases, taking into
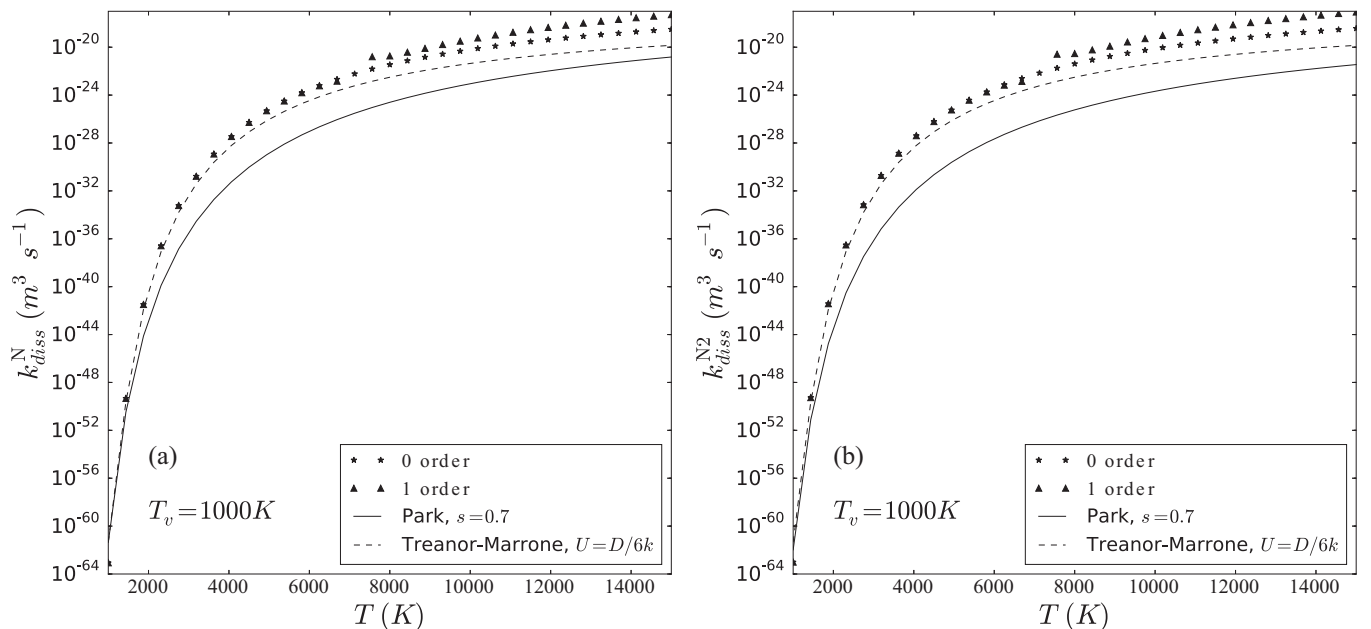

FIG. 9. A comparison between effective multitemperature dissociation rate coefficients computed using the approach present in the paper and the Treanor-Marrone and Park's models for dissociation of nitrogen, where the collision partners are N (a) and N_2 (b) as a function of temperature T. $T_v = 1000$ K, $x_N = 0.5$.
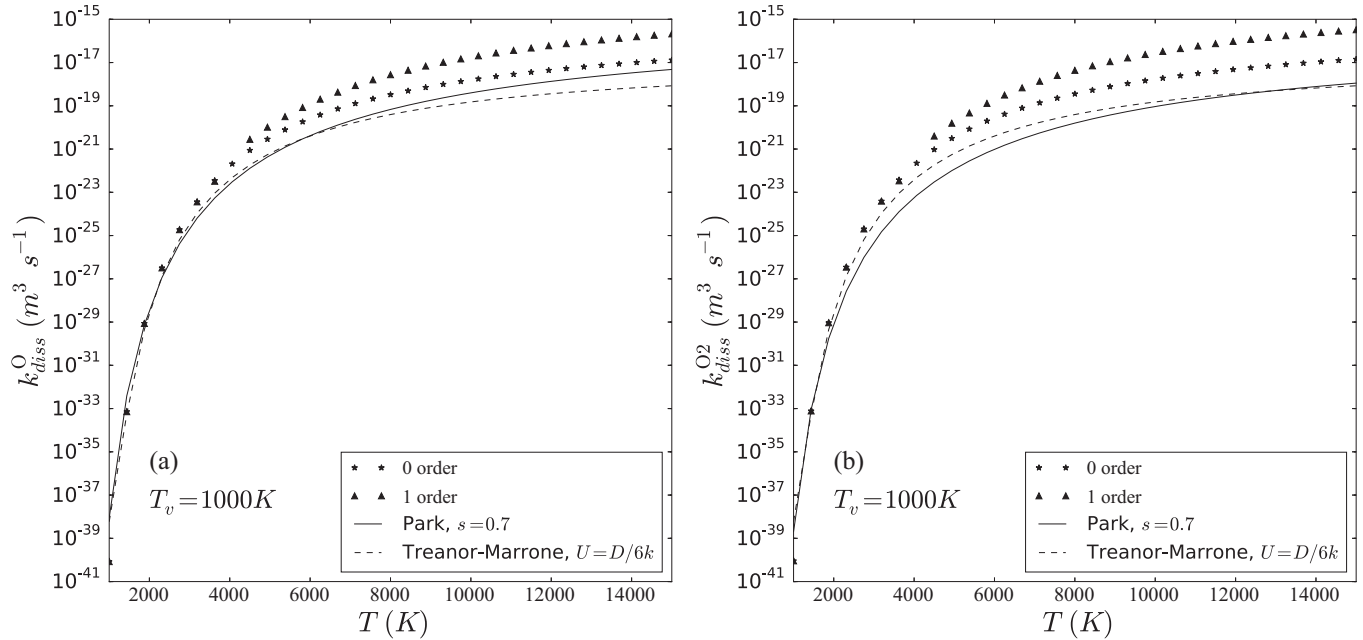
FIG. 10. A comparison between effective multitemperature dissociation rate coefficients computed using the approach present in the paper and the Treanor-Marrone and Park's models for dissociation of oxygen, where the collision partners are O (a) and O_2 (b) as a function of temperature T. $T_v = 1000$ K, $x_O = 0.5$.

account first-order effects may result in higher dissociation rates close to the shock front.

VI. CONCLUSIONS

Coupling of vibrational relaxation and chemical reactions in nonequilibrium viscous multitemperature flows is studied in this paper. The developed general theoretical model differs from the well-known CVDV and CVCV models commonly used in computational fluid dynamics since it is able to capture additional cross-coupling terms arising in the first-order approximation of the Chapman-Enskog method. The set of fluid dynamic equations for reacting thermal nonequilibrium flow is derived starting from the Boltzmann equation; the relaxation terms in these equations are described using the kinetic theory formalism similar to the procedures applied for the calculation of the transport terms (heat flux, stress tensor, etc.) and transport coefficients. It is shown that reaction and relaxation rates depend on the distribution function and thus differ in the zero-order and first-order approximations of the Chapman-Enskog method. In viscous flows corresponding to the first-order approximation, the rates of nonequilibrium processes depend on the velocity divergence and affinities of all reactions and energy transitions occurring in a flow.

An algorithm for the calculation of multitemperature reaction and relaxation rates in both inviscid and viscous flows is proposed for the harmonic oscillator model. This algorithm is applied to estimate the mutual effect of vibrational relaxation and dissociation in binary mixtures of N_2 and N as well as O_2 and O under various nonequilibrium conditions. The results are compared to those obtained using other models. It is shown that modification of the Landau-Teller expression for the VT relaxation term works rather well in nitrogen, whereas it fails to predict correctly the relaxation rate in oxygen at high

temperatures. This is explained by the fact that in oxygen (in contrast to nitrogen), the first-order cross effects of dissociation and VT relaxation are found to be significant.

A method for calculation of vibrational relaxation time based on the kinetic theory definition is suggested. The strict definition does not involve any empirical parameters and depends only on the cross sections of VT transitions. In multitemperature flows, the relaxation time depends on both translational and vibrational temperatures, and its temperature dependence is nonmonotonic, which is in line with the recent experimental studies. It is demonstrated that the Millikan-White formula, even with the Park's correction, cannot be applied for temperatures higher than 10 000 K.

Two-temperature dissociation rate coefficients are calculated in the zero- and first-order approximations and compared to other models. Our results are in agreement with the Macheret-Fridman and Treanor-Marrone model; the Park model underestimates the rate coefficients; the first-order effects become noticeable at $T > 10\,000$ K. It is interesting to note that the first-order cross effects give a more important contribution to the reaction rates than to the rate coefficients. Accounting for the cross-coupling can be important in viscous shock heated flows, when the temperature is high and $T_v < T$.

As we see, coupling of vibrational relaxation and dissociation manifests in different ways in oxygen and nitrogen. Including exchange reactions into consideration may considerably change the rates of other processes. In future work we plan to study the cross-coupling of relaxation, dissociation, and exchange reactions in viscous air flows.

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