

# Multi-Temperature Kinetics and Transport Properties in CO<sub>2</sub>/N<sub>2</sub> Mixtures

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**Abstract.** Transport properties of vibrationally non-equilibrium CO<sub>2</sub>/N<sub>2</sub> mixtures are studied on the basis of the kinetic theory methods. Complex structure of CO<sub>2</sub> molecules, anharmonism of molecular vibrations, numerous channels of vibrational relaxation are taken into account. Multi-temperature transport algorithms are proposed, and transport coefficients are calculated in a wide range of non-equilibrium conditions. The model is applied for the investigation of heat transfer in a shock heated CO<sub>2</sub>/N<sub>2</sub>.

**Keywords:** Carbon dioxide, Transport properties, Non-equilibrium kinetics and heat transfer

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## INTRODUCTION

Correct prediction of the heat transfer in CO<sub>2</sub>/N<sub>2</sub> mixtures is of high priority for Mars re-entry problems and other areas of modern technologies. In particular, the influence of non-equilibrium excitation of several vibrational modes and different rates of energy exchanges within and between modes on the transport phenomena is not sufficiently investigated up to now.

In the present contribution, non-equilibrium vibrational kinetics and transport processes in CO<sub>2</sub>/N<sub>2</sub> mixtures are studied on the basis of the kinetic theory methods. Several multi-temperature models taking into account various rates of inter- and intra-mode vibrational energy exchanges were proposed in [1, 2]. The most detailed description among these models is the five-temperature one based on the following relation between the mean times of elementary processes:

$$\tau_{tr} < \tau_{rot} < \tau_{VV_m} \ll \tau_{VV'_{m-k}} \sim \tau_{VT_m} < \tau_{diss} \sim \theta, \quad m, k = 1, \dots, 4. \quad (1)$$

Here  $\tau_{tr}$ ,  $\tau_{rot}$ ,  $\tau_{VV_m}$ ,  $\tau_{VV'_{m-k}}$ ,  $\tau_{VT_m}$ ,  $\tau_{diss}$  are the characteristic times of translational, rotational relaxation; intra-mode VV exchanges within each mode ( $m = 1, 2, 3, 4$  correspond to CO<sub>2</sub> symmetric, bending, asymmetric modes and N<sub>2</sub>); inter-mode VV transitions; VT relaxation; chemical reactions;  $\theta$  is the mean time of gas dynamic parameters change. Under this relation, two stages of vibrational relaxation can be distinguished: during the rapid stage, some quasi-stationary distributions establish in each vibrational mode as a result of intra-mode VV transitions; during the slow stage, thermal equilibrium is attained due to inter-mode VV' and VT exchanges. For harmonic oscillators, one obtains non-equilibrium Boltzmann distributions with different vibrational temperatures of each mode; for anharmonic oscillators, more complicated Treanor-like distributions can be derived, depending on the gas temperature and temperatures of the first vibrational level of every mode [1].

It is known from experiments that Fermi resonance leads to the rapid VV'<sub>12</sub> exchange between symmetric and bending CO<sub>2</sub> modes and therefore to the following relation between characteristic times:

$$\tau_{tr} < \tau_{rot} < \tau_{VV_m} \sim \tau_{VV'_{1-2}} \ll \tau_{VV'_{1,2-3}} \sim \tau_{VV'_{2-3}} \sim \tau_{VV'_{3-4}} \sim \tau_{VT_m} < \tau_{diss} \sim \theta, \quad m = 1, \dots, 4. \quad (2)$$

This relation provides the basis for a four-temperature description of a CO<sub>2</sub>/N<sub>2</sub> flow. The temperatures of symmetric and bending modes equalize rapidly due to VV'<sub>12</sub> transitions, thus allowing for introducing a combined (coupled) mode with a single temperature  $T_{12}$  instead of two temperatures of the 1st and the 2d modes.

The objective of this study is to develop closed descriptions of non-equilibrium CO<sub>2</sub>/N<sub>2</sub> mixture flows based on relations (1) and (2) taking into account anharmonic effects. Transport algorithms are proposed for both five- and four-temperature models. The four-temperature model is then applied for the estimation of the heat transfer in shock heated CO<sub>2</sub>/N<sub>2</sub> flows.

## MACROSCOPIC EQUATIONS AND TRANSPORT TERMS

In the formalism of the Chapman-Enskog method modified for non-equilibrium gas flows with rapid and slow processes [3, 4], macroscopic flow equations are derived from the Boltzmann equation multiplying it by the invariants of the most frequent collisions, integrating over velocities and performing summation over internal states and chemical species. In the five-temperature approach, the collision invariants of rapid processes are: mass, momentum, total energy and numbers of vibrational quanta in each mode ( $i_m$ ,  $m = 1, 2, 3, 4$ ). For harmonic oscillators, these last invariants reduce to vibrational energies of each mode. On the basis of the set of collision invariants, the set of macroscopic parameters providing a closed flow description is introduced. For the five-temperature case, the set of macroscopic parameters consists of number densities of chemical species  $n_c$ , gas velocity  $\mathbf{v}$ , gas temperature  $T$  and mean numbers of vibrational quanta  $W_m$  ( $m = 1, 2, 3, 4$ ). Values  $W_m$  can be expressed in terms of the gas temperature  $T$  and temperatures of the first level of each vibrational mode  $T_m$  ( $m = 1, 2, 3, 4$ ).

Governing equations for macroscopic parameters are obtained in the following form

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{diss}, \quad (3)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (4)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0, \quad (5)$$

$$\rho_{CO_2} \frac{dW_m}{dt} + \nabla \cdot \mathbf{q}_w^m = R_m^w - m_{CO_2} W_m R_{CO_2}^{diss} + W_m \nabla \cdot (\rho_{CO_2} \mathbf{V}_{CO_2}), \quad m = 1, 2, 3, \quad (6)$$

$$\rho_{N_2} \frac{dW_4}{dt} + \nabla \cdot \mathbf{q}_w^4 = R_4^w - m_{N_2} W_4 R_{N_2}^{diss} + W_4 \nabla \cdot (\rho_{N_2} \mathbf{V}_{N_2}). \quad (7)$$

Here  $\rho$  is the mixture density,  $U$  is the total energy per unit mass,  $m_c$ ,  $\rho_c$  are the mass and density of species  $c$ ;  $R_c^{diss}$  is the production term due to dissociation,  $R_m^w$  are the production terms due to all slow processes: inter-mode  $VV^*_{m-k}$  exchange,  $VT_m$  transitions and dissociation;  $\mathbf{V}_c$  is the diffusion velocity,  $\mathbf{P}$  is the pressure tensor,  $\mathbf{q}$  is the heat flux,  $\mathbf{q}_w^m$  are the fluxes of vibrational quanta in the corresponding mode.

It should be noted that Eqs. (4)–(5) represent conservation equations of momentum and total energy, whereas the remaining equations describe variation of corresponding parameters as the result of relaxation processes and chemical reactions proceeding at the gas dynamic time scale: Eqs. (3) are the equations of five-temperature chemical kinetics; Eqs. (6)–(7) are the five-temperature relaxation equations.

In the zero-order approach of the modified Chapman-Enskog method, the distribution functions are obtained in the form of Maxwell-Boltzmann distributions over velocity and rotational energy and generalized Treanor distributions with temperatures  $T$ ,  $T_m$  in each vibrational mode [1]. One of the peculiarities of these distributions is that level populations of the  $m$ th mode depend significantly on the vibrational state of the remaining modes. In the case of harmonic oscillators, Treanor distributions reduce to non-equilibrium Boltzmann distributions with vibrational temperatures  $T_m$ . Therefore for harmonic oscillators, level populations of various modes are independent from the distributions in other modes. Equations (3)–(7) in the zero-order approximation take a form of Euler-like equations for an inviscid non-conductive non-equilibrium flow.

In order to get governing equations in the Navier-Stokes approximation, it is necessary to determine the first-order transport terms. Following the procedure of the modified Chapman-Enskog method, one can derive expressions for the pressure tensor, diffusion velocity and energy fluxes. Thus the pressure tensor takes the form

$$\mathbf{P} = (p - p_{rel}) \mathbf{I} - 2\mu \mathbf{S} - \eta \nabla \cdot \mathbf{v} \mathbf{I}, \quad (8)$$

where  $\mu$ ,  $\eta$  are the shear and bulk viscosity coefficients,  $p_{rel}$  is the relaxation pressure,  $\mathbf{S}$  is the deformation rate tensor,  $\mathbf{I}$  is the unit tensor.

The diffusion velocity is given by the expression

$$\mathbf{V}_c = - \sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T, \quad (9)$$

where  $D_{cd}$ ,  $D_{Tc}$  are the diffusion and thermal diffusion coefficients,  $\mathbf{d}_c$  is the diffusive driving force.

The total heat flux reads

$$\mathbf{q} = -\lambda \nabla T - \sum_{m=1}^4 \lambda_{v,m} \nabla T_m - p \sum_c D_{T_c} \mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c, \quad (10)$$

$\lambda$ ,  $\lambda_{v,m}$  are the thermal conductivity and vibrational thermal conductivity coefficients,  $p$  is the pressure,  $h_c$  is the specific enthalpy of species  $c$ .

Fluxes of vibrational quanta are obtained in the form

$$\varepsilon_1^m \mathbf{q}_w^m = -\lambda_{vt}^m \nabla T - \lambda_{vv}^m \nabla T_m, \quad m = 1, 2, 3, 4, \quad (11)$$

$\lambda_{vt}^m$ ,  $\lambda_{vv}^m$  represent some kind of additional thermal conductivity coefficients;  $\varepsilon_1^1 = \varepsilon_{100}$ ,  $\varepsilon_1^2 = \varepsilon_{010}$ ,  $\varepsilon_1^3 = \varepsilon_{001}$ ,  $\varepsilon_1^4 = \varepsilon_1^{N_2}$  are the vibrational energies of the first level in corresponding modes.

It is interesting to note that coefficients  $\lambda$ ,  $\lambda_{v,m}$  include contributions of various types of energy transfer:

$$\lambda = \lambda_{tr} + \lambda_{rot} + \lambda_{anh} + \sum_m \lambda_{vt}^m,$$

$$\lambda_{v,m} = \lambda_{tv}^m + \lambda_{vv}^m,$$

$\lambda_{tr}$ ,  $\lambda_{rot}$  are the contributions of translational and rotational degrees of freedom;  $\lambda_{anh}$  appears due to anharmonic effects;  $\lambda_{tv}^m$ ,  $\lambda_{vv}^m$  describe the energy transfer due to non-resonant character of intra-mode  $VV_m$  exchanges; coefficients  $\lambda_{vv}^m$  correspond to the transfer of vibrational quanta in the  $m$ th mode. One should keep in mind that for harmonic oscillators,

$$\lambda_{anh} = \lambda_{vt}^m = \lambda_{vv}^m = 0, \quad \lambda = \lambda_{tr} + \lambda_{rot}, \quad \lambda_{v,m} = \lambda_{vv}^m.$$

This leads to a simplification of the expressions for the heat flux and fluxes of vibrational quanta (which reduce to the fluxes of vibrational energy in corresponding modes).

## Four-temperature model

Under condition (2), collision invariants  $i_1$  and  $i_2$  are not independent as the result of rapid  $VV'_{1-2}$  exchange between symmetric and bending  $\text{CO}_2$  modes. One can introduce a single invariant  $2i_1 + i_2$  and therefore define the mean number of vibrational quanta  $W_{12}$  in the coupled (symmetric+bending) mode. It can be shown that temperatures  $T_1$  and  $T_2$  are also connected to each other [1], which allows one to reduce the number of independent macroscopic parameters introducing only one temperature  $T_{12}$  instead of  $T_1$  and  $T_2$ . In this case, two equations for  $W_1$ ,  $W_2$  in the system (3)–(7) should be replaced with the equation

$$\rho_{\text{CO}_2} \frac{dW_{12}}{dt} + \nabla \cdot \mathbf{q}_w^{12} = R_{12}^w - m_{\text{CO}_2} W_{12} R_{\text{CO}_2}^{\text{diss}} + W_{12} \nabla \cdot (\rho_{\text{CO}_2} \mathbf{V}_{\text{CO}_2}). \quad (12)$$

The production terms  $R_{12}^w$ ,  $R_3^w$  in relaxation equations in the four temperature approach do not include inter-mode  $VV'_{1-2}$  transitions which are now considered as rapid processes. The expressions for pressure tensor, diffusion velocity and fluxes  $\mathbf{q}_w^3$ ,  $\mathbf{q}_w^4$  formally remain unchanged (one should however be aware of the fact that transport coefficients in these expressions depend on the cross sections of other rapid processes); the total heat flux and the flux of vibrational quanta in the coupled mode take the form

$$\mathbf{q} = -\lambda \nabla T - \lambda_{v,12} \nabla T_{12} - \sum_{m=3,4} \lambda_{v,m} \nabla T_m - p \sum_c D_{T_c} \mathbf{d}_c + \sum_c \rho_c h_c \mathbf{V}_c, \quad (13)$$

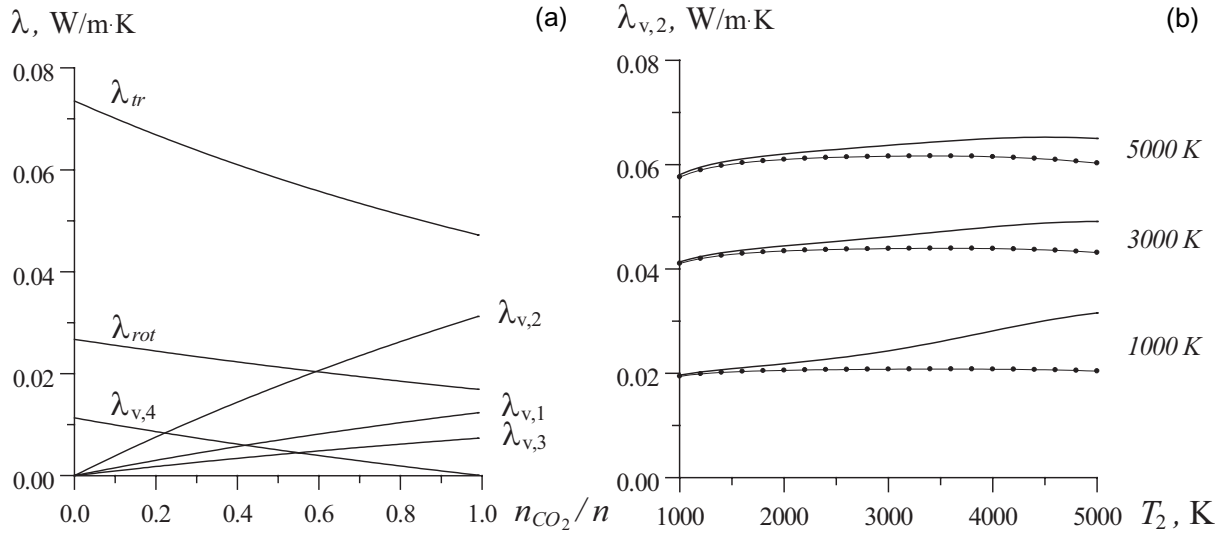
$$\varepsilon_1^1 \mathbf{q}_w^{12} = -\lambda_{vt}^{12} \nabla T - \lambda_{vv}^{12} \nabla T_{12}. \quad (14)$$

While the five-temperature model is the most detailed one among multi-temperature approaches, the four-temperature model appears to be more attractive for practical applications since the flow description is based on the reduced number of macroscopic parameters and the set of governing equations includes less relaxation equations.

## TRANSPORT COEFFICIENTS

Algorithms of transport coefficients calculation are similar for both five- and four-temperature models and consist of the following steps [4]:

1. Unknown functions are expanded in the series of Sonine and Waldmann-Trübenbacher polynomials; the trial functions are introduced accordingly to the right hand sides of integral equations for the first order correction to the distribution function;
2. Transport coefficients are expressed in terms of expansion coefficients;
3. Integral equations are reduced to the transport linear systems of algebraic equations involving bracket integrals as coefficients;
4. Bracket integrals are simplified on the basis of some assumptions about cross sections of rapid processes; finally they are expressed in terms of the standard  $\Omega_{cd}^{(l,r)}$ -integrals and relaxation times which can be measured experimentally. The  $\Omega_{cd}^{(l,r)}$ -integrals are calculated for particular models of inter-molecular interaction potentials. In the present study, the Lennard-Jones potential is used for low and moderate temperatures whereas in the high temperature interval, the repulsive potential is applied;
5. Transport coefficients are found as solutions of transport linear systems using some numerical algorithms (for instance, the Gauss method or new iterative procedures proposed in [5]).



**FIGURE 1.** Thermal conductivity coefficients for a binary CO<sub>2</sub>/N<sub>2</sub> mixture. (a): Various contributions to thermal conductivity as functions of CO<sub>2</sub> molar fraction.  $T = 2000$  K,  $T_m = 1000$  K. (b): Vibrational heat conductivity of CO<sub>2</sub> symmetric mode as a function of  $T_2$ . Pointed curves correspond to harmonic oscillators.

Transport coefficients have been calculated for a binary CO<sub>2</sub>/N<sub>2</sub> mixture in the temperature range 1000–5000 K using the five-temperature approach. Fig. 1a presents different contributions to the thermal conductivity coefficients as functions of CO<sub>2</sub> concentration at  $T = 2000$  K,  $T_m = 1000$  K. One can see that coefficients  $\lambda_{tr}$ ,  $\lambda_{rot}$ ,  $\lambda_{v,N_2}$  decrease with  $n_{CO_2}$  rising whereas vibrational heat conductivity coefficients of CO<sub>2</sub> modes increase. In Fig. 1b vibrational thermal conductivity of the bending CO<sub>2</sub> mode is plotted as a function of  $T_2$  at different  $T$ . A comparison with the harmonic oscillator model is also demonstrated. The role of anharmonicity becomes more important with rising the factor  $T_2/T$ ; for  $T_2/T < 1$  the harmonic oscillators model provides a satisfactory agreement. Similar conclusions are valid for all other vibrational modes.

Summarizing the results on transport coefficients, one can say that excitation of vibrational modes and anharmonicity influence essentially coefficients  $\lambda_{anh}$ ,  $\lambda_{v,m}$ ; on the contrary, coefficients  $\lambda_{tr}$ ,  $\lambda_{rot}$ ,  $D_{cd}$ ,  $D_{Tc}$ ,  $\mu$  are practically independent from the degree of vibrational excitation. Mixture composition influences weakly viscosity coefficient,

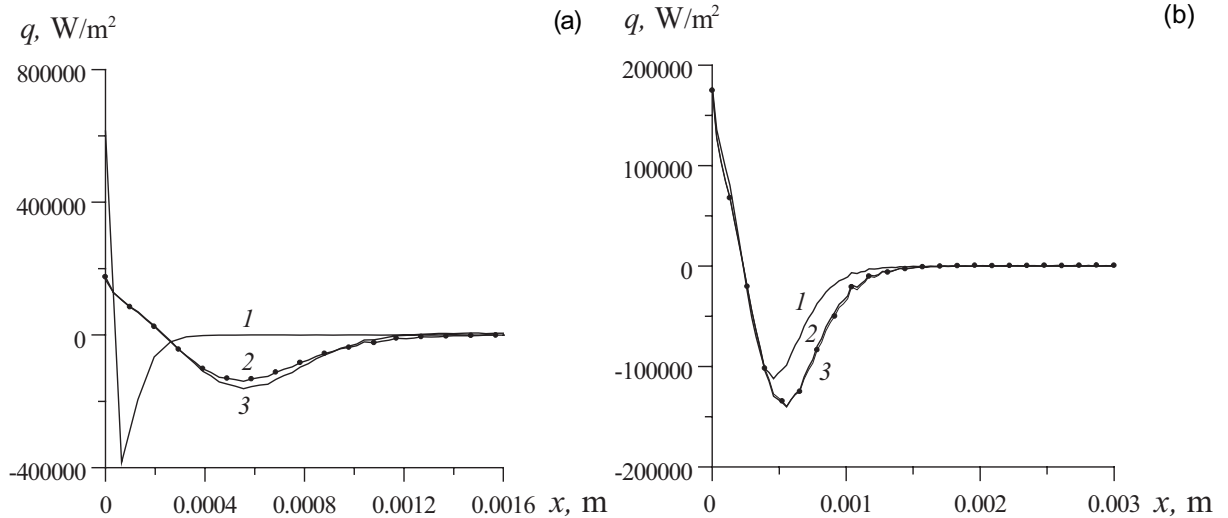
and affects significantly diffusion and thermal diffusion coefficients. Absolute values of all coefficients increase with temperature.

## HEAT TRANSFER BEHIND THE SHOCK WAVE

In order to estimate heat transfer in the shock heated  $\text{CO}_2/\text{N}_2$  mixture, an approximate method has been applied. At the first step, Eqs. (3)–(7) have been solved numerically for a one-dimensional quasi-stationary flow behind a shock wave. The equations have been written for an inviscid flow in the four-temperature approach. At the second step, transport coefficients and heat flux have been evaluated using the flow parameters obtained at the first step and transport algorithms developed above. This method allows one to understand the role of complex vibrational kinetics in the heat transfer.

The following conditions in the free stream have been considered:  $M_0 = 8$ ,  $T_0 = 293$  K,  $p_0 = 100$  Pa,  $n_{\text{CO}_2}/n = 0.8$ . Calculation of vibrational source terms have been performed using four-temperature vibrational distributions and different data for the rate coefficients of vibrational transitions: either analytical expressions of the first-order perturbation SSH theory [6] or experimental data [7, 8] on the transitions between low states. The part of the total heat flux depending on the gradients of  $T$ ,  $T_{12}$ ,  $T_3$ ,  $T_4$  is discussed below.

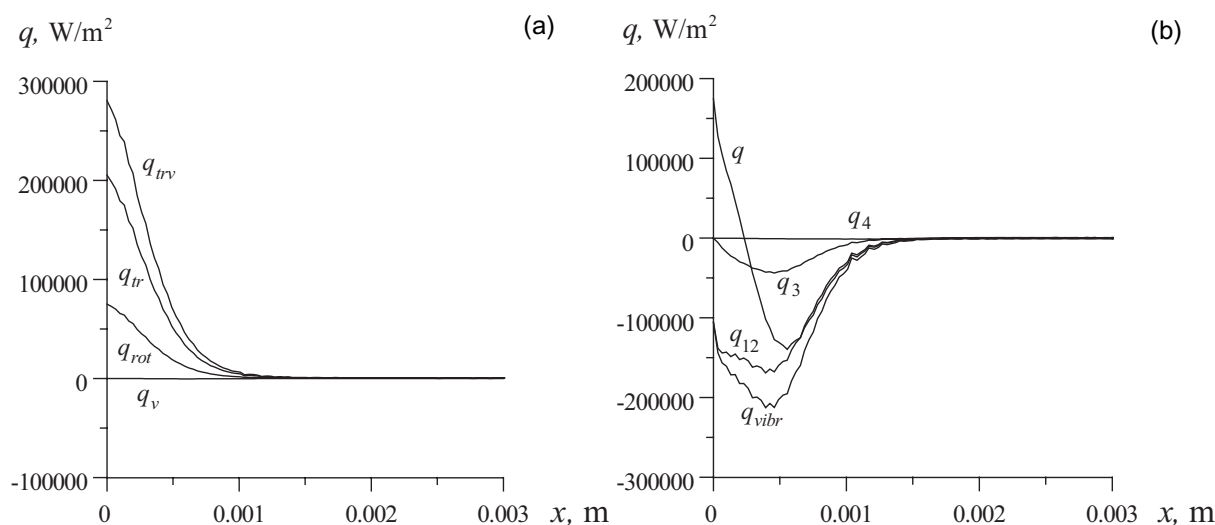
Fig. 2a presents a comparison of the results obtained using different sets of rate coefficients. Both experimental models provide rather close values of the heat flux whereas using the analytical SSH model leads to a significant discrepancy. Fig. 2b demonstrates the role of various vibrational transitions in the heat transfer. Curve 1 is obtained for the case, when only VT exchanges were taken into account in the kinetic scheme; curve 2 corresponds to adding inter-mode transitions  $\text{VV}'_{2-3}$  and  $\text{VV}'_{1-2-3}$ ; curve 3 represents the kinetic scheme involving all vibrational transitions including inter-molecular  $\text{VV}'_{3-4}$  exchange. One can see that taking into account VT and  $\text{VV}'_{2-3}$ ,  $\text{VV}'_{1-2-3}$  transitions is of importance for the correct prediction of the heat flux; the role of  $\text{VV}'_{3-4}$  transitions in the heat transfer is rather weak under conditions considered in the present study. The influence of anharmonicity on the heat flux is also found to be small in the test case studied here.



**FIGURE 2.** Heat flux as a function of a distance  $x$  from the shock front. (a) Different rates of vibrational transitions; 1 – SSH model, 2 – model [7], 3 – model [8]. (b) Different kinetic schemes, model [7]. 1 – VT transitions, 2 – VT +  $\text{VV}'_{2-3}$  +  $\text{VV}'_{1-2-3}$ , 3 – VT +  $\text{VV}'_{2-3}$  +  $\text{VV}'_{1-2-3}$  +  $\text{VV}'_{3-4}$

Fig. 3 shows contribution of different dissipative processes to the heat flux. In Fig. 3a, the heat flux determined by the temperature  $T$  gradient is given as well as its parts connected to the transfer of translational ( $q_{tr}$ ), rotational ( $q_{rot}$ ) and small part of vibrational energy ( $q_v$ ) associated to the coefficient  $\lambda_{anh} + \sum_m \lambda_{vt}^m$ . It is seen that the flux of translational energy exceeds the one of rotational energy; the flux  $q_v$  is small in the whole relaxation zone; this is explained by the weak influence of anharmonicity and therefore, negligible values of the coefficient  $\lambda_{anh} + \sum_m \lambda_{vt}^m$ . The parts of the heat flux associated to the gradients of vibrational temperatures are plotted in Fig. 3b. The main contribution belongs to

the energy transfer in the coupled CO<sub>2</sub> mode; the flux connected with the heat transfer in nitrogen is small because of low values of  $T_4$  gradient. Finally, one can notice that fluxes of translational-rotational and vibrational energies have different signs, and their absolute values are close to each other. Such a compensation effect diminishes the absolute value of the total heat flux in the relaxation zone.



**FIGURE 3.** Different contributions to the heat flux as functions of  $x$ . Model [7], full kinetic scheme. (a): Fluxes associated to  $\nabla T$ . (b): Total heat flux  $q$  and fluxes associated to  $\nabla T_m$

## CONCLUSIONS

Closed descriptions of five-temperature and four-temperature CO<sub>2</sub>/N<sub>2</sub> flows taking into account different rates of vibrational transitions and anharmonicity are proposed on the basis of the kinetic theory methods. Macroscopic equations and transport terms are derived, algorithms for the calculation of transport coefficients are developed. Transport coefficients are calculated in the temperature range 1000–5000 K, the influence of vibrational excitation, anharmonicity and mixture composition on transport properties is estimated. Heat transfer in the relaxation zone behind the shock wave is evaluated, contribution of various energy transitions to the total heat flux is discussed.

## ACKNOWLEDGMENTS

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