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# On the influence of state-resolved rates of Zeldovich reactions on shock heated air flow parameters

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**Abstract.** In this paper, the impact of non-equilibrium rates of Zeldovich reactions  $N_2 + O \leftrightarrow NO + N$ ,  $O_2 + N \leftrightarrow NO + O$  on shock heated air flows parameters are studied on the basis of state-to-state approach. The comparison of computed macroscopic parameters using different state-specific rate coefficients models for exchange reactions is presented. The influence of NO molecules vibrational excitation on total relaxation process behind a shock wave is shown.

## 1. Introduction

The important task for investigations of hypersonic flows behind the shock waves appearing near space crafts, in nozzles, in high enthalpy facilities are the accurate description of the non-equilibrium chemistry and vibrational energy relaxation and the prediction of gas parameters. Until the recent time upon modeling of five-component air mixture  $N_2/O_2/NO/N/O$  flows within the frame of state-to-state approach the main problem was the lack of models and data for the state-dependent rate coefficients of Zeldovich reactions



that take into account a vibrational state of product molecules NO. Therefore, the assumption that nitrogen oxide molecules remain at the ground vibrational state whereas only the vibrational state of the reactant molecules ( $N_2$  or  $O_2$ ) is taking into account was often accepted. So the number of works [1, 2, 3, 4, 5] focused on the study of different air flows and did not consider the process of vibrational relaxation of NO molecules. For such assumption there are enough models from which we can distinguish:

- Model [6] based on the theory of reactive hard spheres.
- Given in [7] expression for the state-specific rate coefficients is the approximation of numerical solutions of dynamic problems for reactive molecular collisions.
- The expressions for state-resolved rate coefficients of bimolecular exchange reactions suggested by Bose and Candler [8, 9] on the basis of quasiclassical trajectory calculations.

Until recently the only model that describes the state-dependend rates of exchange chemical reactions in consideration of vibrational levels of both included molecules was model proposed by Starikovskii [10] and based on the model of vibronic terms [11]. Recently, the STELLAR



database [12] has been compiled on the basis of results of Lino da Silva *et al.* The database includes the rate coefficients of all possible processes in the vibrational non-equilibrium air. There are present the Zeldovich reaction state-specific rate coefficients for a wide range of temperatures. These data were obtained on the basis of expressions of [8, 9] by expanding the model to a full range of molecule vibrational energies and the extrapolation of rate coefficients for temperature range from 100 K to  $10^5$  K.

In the present paper we consider the flow of five-component air mixture in the relaxation zone behind a shock wave taking into account the full kinetic mechanism. The influence of the models [10] and [12] for Zeldovich reaction rates, exchange chemical reactions themselves and vibrational relaxation of NO molecules on the gas flow parameters behind a shock wave is studied.

## 2. State-to-state description of shock heated air flows

The complete scheme of kinetic processes in five-component air mixture  $N_2(i)/O_2(i)/NO(i)/N/O$  in the relaxation zone behind shock waves includes

- $VT(TV)$  exchanges between vibrational and translational energies

$$A_{ci} + M \leftrightarrow A_{ci'} + M, \quad (3)$$

- $VV$  vibration energy exchanges at the collisions of the same molecular species

$$A_{ci} + A_{ck} \leftrightarrow A_{ci'} + A_{ck'}, \quad (4)$$

- $VV'$  exchanges between different species

$$A_{ci} + A_{dk} \leftrightarrow A_{ci'} + A_{dk'}, \quad (5)$$

- dissociation and recombination reactions

$$A_{ci} + M \leftrightarrow A_{c'} + A_{f'} + M, \quad (6)$$

- and Zeldovich exchange reactions (1) and (2) in general form

$$A_{ci} + A_{dk} \leftrightarrow A_{c'i'} + A_{d'k'}. \quad (7)$$

Here  $A_{ci}$  and  $A_{dk}$  indicate the different species of molecules  $c$  and  $d$ , the symbol "prime" denotes the new species after reaction,  $i$ ,  $k$  and  $i'$ ,  $k'$  are vibrational states of molecules before and after the collision,  $M$  is a partner in a collision (it can be a particle of an either mixture species).

In the present paper we consider the temperature range corresponding the conditions when the influence of electronic excitation, ionization and radiation remains weaker than that of vibration and chemical relaxation. Therefore in our work these processes are not taken into account.

### 2.1. Governing equations

The non-equilibrium air flow under the considered conditions is described by the equations for non-equilibrium kinetics coupled to the conservation equations for impulse and total energy.

The system of equations for the considered reacting air mixture includes the kinetic equations for the vibrational level populations of molecular species and number densities of atoms

complemented by conservation equations for impulse and total energy. In the zero-order (Euler) approximation of stationary one-dimensional inviscid flow of the considered mixture we obtain:

$$\frac{d(vn_{ci})}{dx} = R_{ci}^{VT} + R_{ci}^{VV} + R_{ci}^{VV'} + R_{ci}^{DR} + R_{ci}^{ZR}, \quad (8)$$

$$i = 0, 1, \dots, l_c - 1, \quad c = \text{N}_2, \text{O}_2, \text{NO},$$

$$\frac{d(vn_c)}{dx} = R_c^{DR} + R_c^{ZR}, \quad c = \text{N}, \text{O}, \quad (9)$$

$$\rho v \frac{dv}{dx} + \frac{dp}{dx} = 0, \quad (10)$$

$$v \frac{dE}{dx} + (p + E) \frac{dv}{dx} = 0. \quad (11)$$

Here  $\rho$  is the gas density,  $p$  is the pressure,  $v$  is the velocity,  $E$  is the total energy per unit volume presented as a sum of translational, rotational, vibrational and formation energies:

$$E = \frac{3}{2}nk_B T + E_{rot} + \sum_{c,i} \varepsilon_i^c n_{ci} + \sum_c \varepsilon_c n_c, \quad (12)$$

$n$  is the number mixture density,  $k_B$  is the Boltzmann constant,  $\varepsilon_i^c$  is the vibrational energy of a molecule  $c$  species at the  $i$ -th vibrational level,  $E_{rot}$  is the rotational mixture energy,  $\varepsilon_c$  is the formation energy of a particle  $c$  species,  $n_c$ ,  $n_{ci}$  are the number density and vibrational population of  $i$ -th level for species  $c$ ,  $l_c$  are the numbers of vibrational levels  $i$  of molecules ( $l_{\text{N}_2} = 61$ ,  $l_{\text{O}_2} = 46$  and  $l_{\text{NO}} = 48$ ).

The terms  $R_{ci}^{VT}$ ,  $R_{ci}^{VV}$ ,  $R_{ci}^{VV'}$  describe vibrational energy transitions (3)–(5):

$$R_{ci}^{VT} = \sum_M \sum_{i'=0}^{l_c-1} n_M \left( n_{ci'} k_{c,i'i}^M - n_{ci} k_{c,i'i'}^M \right), \quad c = \text{N}_2, \text{O}_2, \text{NO}, \quad (13)$$

$$R_{ci}^{VV} = \sum_{k=0}^{l_c-1} \sum_{i'=0}^{l_c-1} \sum_{k'=0}^{l_c-1} \left( n_{ci'} n_{ck'} k_{c,i'i}^{c,k'k} - n_{ci} n_{ck} k_{c,i'i'}^{c,kk'} \right), \quad (14)$$

$$R_{ci}^{VV'} = \sum_d \sum_{k=0}^{l_d-1} \sum_{i'=0}^{l_c-1} \sum_{k'=0}^{l_d-1} \left( n_{ci'} n_{dk'} k_{c,i'i}^{d,k'k} - n_{ci} n_{dk} k_{c,i'i'}^{d,kk'} \right), \quad (15)$$

$$d = \text{N}_2, \text{O}_2, \text{NO}, \quad d \neq c,$$

where  $k_{c,i'i}^M$ ,  $k_{c,i'i'}^{c,k'k}$  and  $k_{c,i'i'}^{d,kk'}$  are the state-dependent rate coefficients for  $VT(TV)$ ,  $VV$  and  $VV'$  transitions, respectively.

The term  $R_{ci}^{DR}$  describes dissociation and recombination (6):

$$R_{ci}^{DR} = \sum_M n_M (n_{c'} n_f k_{rec,ci}^M - n_{ci} k_{ci,diss}^M). \quad (16)$$

Here  $k_{ci,diss}^M$  is the dissociation rate coefficient in result of a collision with a particle  $M$ ,  $k_{rec,ci}^M$  is the recombination rate coefficient.

The source term  $R_{ci}^{ZR}$  describes Zeldovich exchange reaction (7):

$$R_{ci}^{ZR} = \sum_{i'=0}^{l_{c'}} (n_{c'i'} n_{d'k'} k_{c'i',ci}^{d',k',dk} - n_{ci} n_{dk} k_{ci,c'i'}^{dk,d'k'}), \quad (17)$$

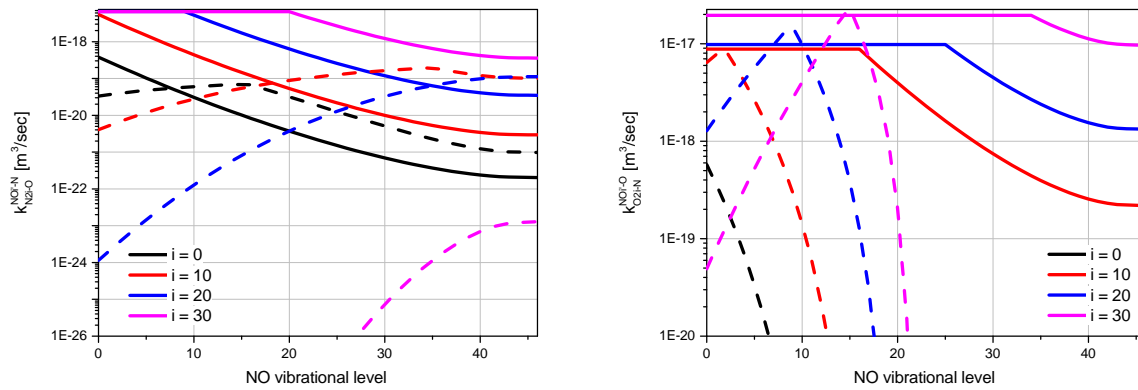
where  $k_{ci,c'i'}^{dk,d'k'}$  is the rate coefficient of the forward reaction, the coefficient  $k_{c'i',ci}^{d'k',dk}$  corresponds to the backward reaction.

## 2.2. State-resolved rate coefficients

The relaxation terms in equations (13)–(17) contain state-specific rate coefficients for energy transitions and chemical reactions. So the important problem for modeling of multicomponent reacting mixture flows is the choice of adequate models for the state-dependent rate coefficients of kinetic processes.

In present work the rate coefficients for vibrational energy transitions are calculated using the forced harmonic oscillator model [13]. For dissociation rate coefficients the Treanor-Marrone model [14] modified in [15] for the state-to-state approximation is used.

The state-specific rate coefficients of exchange reactions (1) and (2) are taken from the STELLAR database [12] and computing with using formula proposed in [10]. The state-specific rate coefficients  $k_{N_2 i, O}^{NO i', N}$  and  $k_{O_2 i, N}^{NO i', O}$  of Zeldovich reactions in dependence of a product molecule vibrational state  $i'$  for the considered models is shown in figure 1 for  $T = 10,000$  K.



**Figure 1.** The rate coefficients  $k_{N_2 i, O}^{NO i', N}$  (left) and  $k_{O_2 i, N}^{NO i', O}$  (right) of reactions (1) and (2) as functions of the NO vibrational level  $i'$  for temperature  $T = 10,000$  K and different vibrational state  $i$  of  $N_2$  and  $O_2$  molecules. STELLAR database: —; model [10]: - - -.

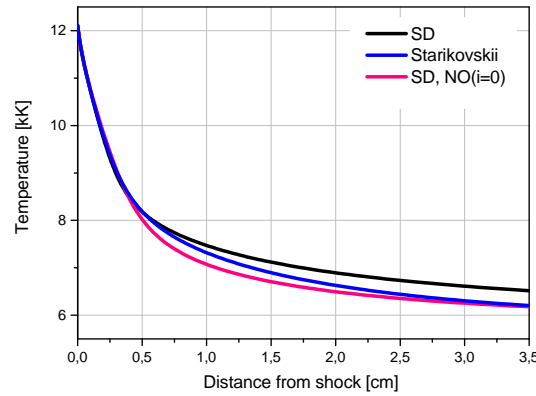
Calculations show absolutely different behavior of the reaction rate coefficients with rising of NO vibrational level number. The data obtained from the generalization of quasi trajectory calculations [8, 9] take into account the reduction of the probability of forward reactions on the upper levels of the product molecules. At the same time the analytical model shows similar behaviour of reaction rate coefficients for  $i < 10$  of  $N_2$  molecules for the reaction (1), and does not describe this decrease for probabilities of reactions from higher levels of reagent molecules. In the case of reaction (2) model [10] gives a rapid non-monotonic variation of reaction rates for  $i > 0$ , meanwhile the maximum of  $k_{O_2 i, N}^{NO i', O}$  increases with the number  $i$  and shifts towards increasing  $i'$ .

## 3. Results and discussion

Below we present the results of numerical solution of equations (8)–(11) for the following conditions in the free stream:  $T_\infty = 271$  K,  $p_\infty = 100$  Pa,  $M_\infty = 15$ , the mixture composition includes 79% of  $N_2$  and 21% of  $O_2$  molecules. The distributions over vibrational states in the free stream are assumed to be the Boltzmann ones with the temperature  $T_\infty$ .

Calculations have been made with using the STELLAR database (SD) and Starikovskii model [10] for rate coefficients of reactions (1) and (2). Also we consider the case without NO excitation assuming that NO molecules form and remain on the zero-th vibrational level.

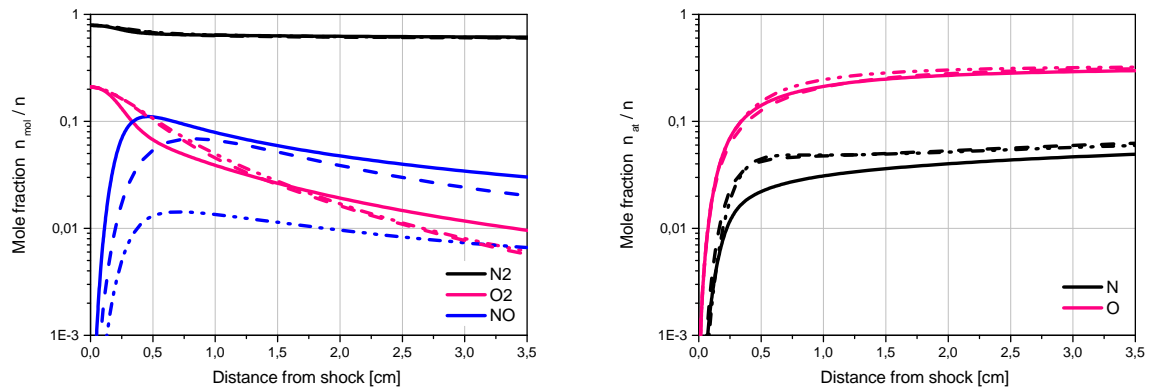
Figure 2 presents the comparison of the air temperature values as functions of the distance from a shock front. The gas temperature behind a shock decreases due to the vibrational and



**Figure 2.** The temperature  $T$  as a function of  $x$ .

chemical relaxation. At the beginning of the relaxation zone the different models give practically the same temperature values, with  $x$  rising these values diverge a little and converge again approaching to the thermal and chemical equilibrium. The maximum temperature discrepancy obtained for three cases does not exceed 6 %.

The air mixture composition is presented in figure 3. Due to the dissociation reactions the number of nitrogen and oxygen molecules reduces with distance from the shock, while the number of free atoms increases. The non-monotonous variation of NO molar fractions is

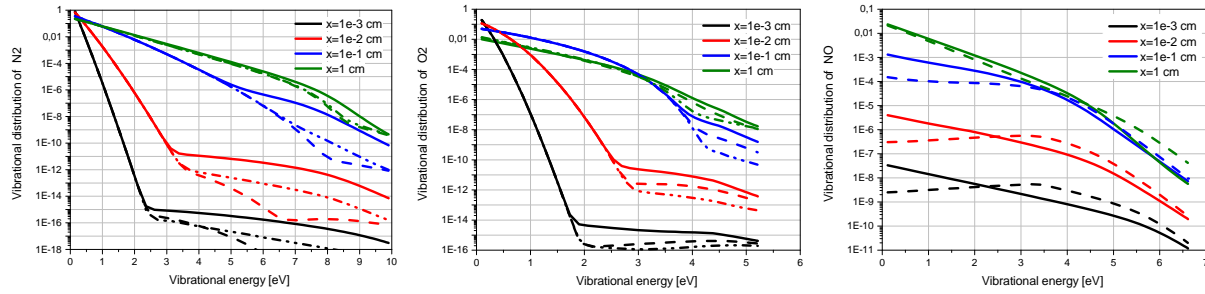


**Figure 3.** The molecular (left) and atomic (right) molar fractions behind the shock front as functions of  $x$ . SD: —; model [10]: - - -; SD, NO on  $i' = 0$ : — · · —.

connected with influence of Zeldovich reactions: first,  $n_{\text{NO}}/n$  increases due to forward reactions (1) and (2), then decreases in result of the backward reactions and dissociation. Calculations show nonessential impact of the models for the rate coefficients of exchange reactions (1) and (2) on the number density of  $\text{N}_2$  molecules (the difference is 3.5%), as well as the influence of NO molecules excitation on  $n_{\text{N}_2}/n$  (4.5%). At the same time variation of the number densities of oxygen molecules and atoms show a more noticeable distinction between the cases of two Zeldovich reaction models with excited NO molecules and the case when  $i' = 0$ . The difference reaches 15% and 50% for atoms and molecules, respectively. The number density of nitrogen atoms, obtained using model [10] and in case where  $i' = 0$ , is two-times higher than the number density  $n_{\text{N}}/n$  for the case of using the STELLAR database. The greatest impact of a choice of the reaction rate models is found on the number of nitrogen oxide molecules. The value  $n_{\text{NO}}/n$

obtained using the database [12] exceed in 4.5 times the data calculated with the use [10] and in 16 times the values found neglecting NO vibrational excitation.

Figure 4 represents the vibrational distributions of air molecules in four positions behind the shock. For molecules of nitrogen and oxygen the excitation process can be seen in the figure, also the deactivation of the lower vibrational levels is noticeable. We can see that all three considered cases give the same values of the  $N_2$  and  $O_2$  level populations for low and intermediate vibrational energies with rising of distance from a shock front. The main difference



**Figure 4.** The vibrational distributions  $n_{N_2 i}/n$  (left),  $n_{O_2 i}/n$  (center) and  $n_{NO i}/n$  (right) for different values of  $x$ . SD: —; model [10]: - -; SD, NO on  $i = 0$ : — · · —.

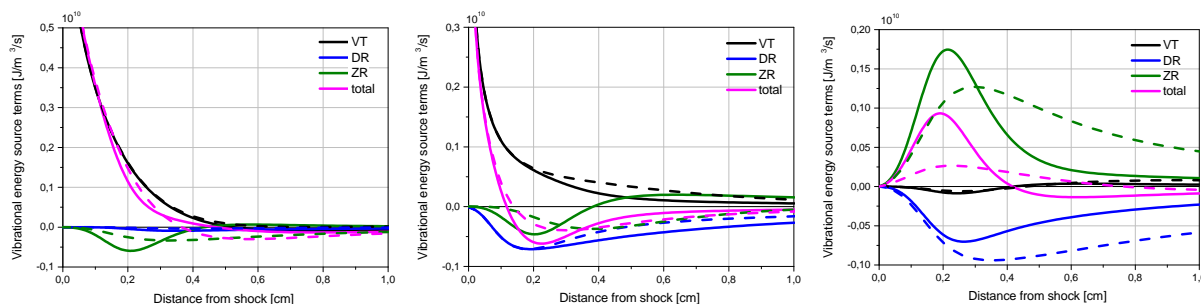
between the populations of molecules is found on the upper vibrational levels. The distinctions in the state-resolved rate coefficients of reactions (1) and (2) provide difference in number densities in 4 orders of magnitude for the nitrogen molecules and 1.5 for the oxygen molecules. In the case  $i' = 0$  upper  $O_2$  levels are underpopulated, upper  $N_2$  level populations lie between the ones obtained with using database [12] and model [10].

Variation of NO level populations is the most interesting. Calculations show that  $VT$ ,  $VV$  and  $VV'$  processes do not affect significantly on NO populations, while the chemical reactions play a major role. Using the STELLAR database for rates of Zeldovich reactions we obtain more populated low levels and less populated upper levels of NO molecules. At the same time the model [10] predicts more populated middle levels in the beginning of relaxation zone. This behavior corresponds to the form of the state-specific rate coefficients of reactions (1) and (2) (see figure. 1).

On the basis of the models considered above we calculated changing of vibrational energies of various species due to different kinetic processes which is described by the source terms:

$$\Omega_c^r = \sum_{i=0}^{l_c-1} R_i^r \varepsilon_i^c, \quad c = N_2, O_2, NO, \quad r = VT, VV, VV', DR, ZR.$$

Figure 5 presents the vibrational energy source terms. The results made it possible to estimate the vibrational energy gain or loss accounting for different processes as well as the sum of all these contributions. Calculations showed insignificant contribution of  $VV$  and  $VV'$  exchanges for considered conditions, so they are not presented in figure 5. For molecules of nitrogen and oxygen the process of  $TV$ -excitation at the beginning of the relaxation zone plays a dominant role, leading to an increase of the middle and upper vibrational level populations of  $N_2$  and  $O_2$  molecules and a decrease of translational temperature. Then with  $x$  rising the second phase begins where the chemical reactions prevail: for  $N_2$  molecules it is Zeldovich exchange reaction (1), the dissociation process is not active; for  $O_2$  molecules the greatest loss of vibrational energy is due to the dissociation reaction. We can see that accumulation of a large number of free atoms N and O switches Zeldovich reactions (1) and (2) in the opposite direction.



**Figure 5.** Vibrational energy source terms for  $N_2$  (left),  $O_2$  (center) and  $NO$  (right) as functions of  $x$ . SD: —; model [10]: - - -.

In the case of  $NO$  molecules (figure 5 (right)) one can notice a delay of all chemical processes in the excitation region in the absence of a sufficient number of free atoms to start the formation of  $NO$  molecules. Then on the short distance the forward Zeldovich reactions are the main contributors to  $NO$  vibrational energy. With  $x$  rising the contributions of exchange reactions and dissociation reaction become of the same order of magnitude and the sum of all energetic contributions tends to zero. As noted above vibrational energy transfers have a small effect on variation of  $NO$  number density and their contribution to vibrational energy is about 1.5 order of magnitude lower than including of chemical reactions.

Comparing the  $\Omega_c^{VT}$  and  $\Omega_c^{DR}$  obtained using two models for exchange reactions a qualitatively similar behavior may be noted. For model [10] contribution of direct Zeldovich reactions to the vibrational energy of all molecular species is dominant.

#### 4. Conclusion

In the present paper non-equilibrium flows of the reacting five-component air mixture in the relaxation zone behind shock waves are studied using two models for state-resolved rate coefficients of Zeldovich reactions. The results were compared with those obtained solving governing equations with an incomplete scheme of kinetic processes (under the assumption that  $NO$  molecules form and remain at the ground vibrational state).

It has been shown that a choice of description of exchange reaction rates and accounting excitation of  $NO$  molecules have a substantial effect on the number density of  $NO$  molecules. The essential difference between the vibrational level populations of  $NO$  molecules derived with using Zeldovich reactions rates from STELLAR database and model proposed by Starikovskii was shown. Neglecting vibrational excitation of  $NO$  molecules results in noticeable underestimated  $NO$  number densities. This may be important for higher temperatures, when  $NO$  molecules may be an essential source of radiation.

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