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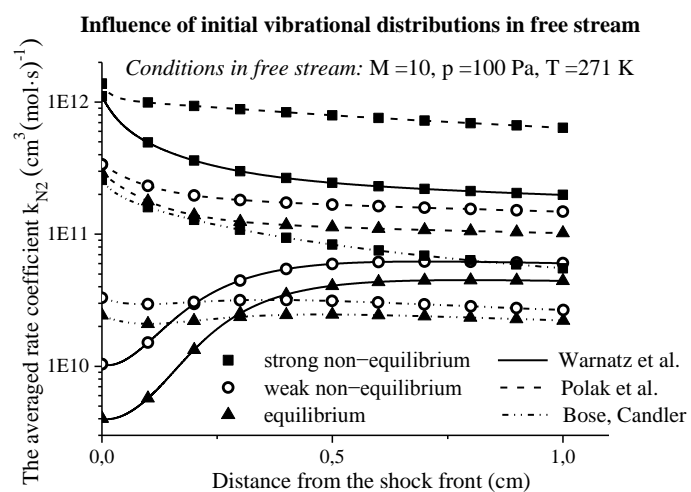
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Global rates of Zeldovich reactions in shock heated air flows are studied.

The results are obtained for different state-specific models of exchange reactions.

Dramatic impact of free stream vibrational excitation on reaction rates is shown.

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On the Influence of State-to-state Distributions on Exchange Reaction Rates in Shock Heated Air Flows

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Abstract

In this Letter, non-equilibrium rates of Zeldovich reactions $N_2(i) + O \rightleftharpoons NO + N$, $O_2(i) + N \rightleftharpoons NO + O$ in shock heated air flows are studied on the basis of state-to-state vibrational distributions. The comparison of reaction rate coefficients computed using state-to-state and thermally equilibrium vibrational distributions behind shock waves and different state-specific models for exchange reactions is presented. Reaction rates are calculated for various conditions before a shock front including a particular case of vibrationally excited free stream molecules. An essential influence of initial vibrational excitation of reactants on reaction rates behind a shock wave is shown.

Key words: exchange chemical reactions, vibrational distributions, state-to-state approach, reaction rate coefficients

1 Introduction

Chemical reaction rates in high temperature atmospheric gases have been studied theoretically and experimentally by many authors during several last decades. In thermally equilibrium gases rate coefficients depend only on the gas temperature and are often described by the generalized Arrhenius law. Expressions for one-temperature rate coefficients for different reactions in air components under various temperature conditions may be found for example in [1, 2, 3, 4]. In high temperature air flows, molecular distributions deviate from thermally equilibrium ones and should be taken into account for accurate calculations of chemical reaction rates. At present time, experimental estimates for non-equilibrium reaction rates are available mainly for dissociation processes (see [5], and References therein). Theoretical models for non-equilibrium rates of chemical reactions are based on different molecular distributions over velocities and internal energies. General kinetic theory algorithms for calculations of reaction rates [6, 7] include averaging of differential cross-sections for reactive collisions with distribution functions over velocities and internal energies of reactants in different approaches. In vibrationally non-equilibrium gases a simple expression for two-temperature reaction rates was proposed by Park [8]. The Treanor-Marrone dissociation model [9] is often used as well as its modifications for endothermic bimolecular reactions of molecules with atoms [10, 11] and for state-dependent dissociation rates [12, 13, 7]. Contributions to one-temperature, two-temperature and state-dependent reaction rates due to non-Maxwell velocity distributions are studied in [14, 15, 16, 17, 18, 19, 20].

Numerical simulations of the state-to-state vibrational and chemical kinetics make it possible to study reaction rates under strongly non-equilibrium conditions when vibrational distributions deviate noticeably from the one-temperature or two-temperature ones. The impact of state-dependent vibrational level populations on global dissociation rates is studied in the flows of

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binary mixtures N_2/N or O_2/O behind shock waves [21], in nozzles [22, 23], in a boundary layer [24, 25]. Comparison of trajectory calculations and the Treanor-Marrone model for dissociation rates is discussed in [26], verification of exchange reaction models on the basis of trajectory calculations is given in [27].

In multi-component mixtures exchange reactions play an important role, however, the effect of detailed vibrational kinetics for global reaction rates has not been studied yet. The aim of this Letter is to show an impact of state-dependent vibrational distributions in shock heated air flows on global rate coefficients of Zeldovich exchange reactions. Besides that, two another new effects are studied in the Letter. Thus, along with a traditionally equilibrium flow before a shock front, we consider the case of vibrationally excited free stream molecules and show the influence of initial vibrational excitation on global reaction rates in a relaxation zone behind a shock wave. We also present the comparison of reaction rates calculated using several models for state-dependent rate coefficients and discuss a role of choosing of a state-specific reaction model for prediction of global reaction rates in high-temperature air flows.

2 State-dependent and thermal equilibrium rate coefficients

We consider shock heated flows of the mixture $N_2(i)/O_2(i)/NO/N/O$ with the following kinetic processes:

- dissociation-recombination



- Zeldovich exchange reactions of NO formation



- TV(VT) vibrational-translational energy transitions, VV exchanges of vibrational energies at the collisions of molecules of the same species, VV' vibrational energy exchanges at the collisions of different molecules (i is a vibrational level number, $M = N_2, O_2, NO, N, O$).

In high-temperature air components, the translational and rotational degrees of freedom equilibrate much faster than the vibrational and chemical relaxation proceeds [3, 28], therefore distributions over translational and rotational energies are supposed to be thermally equilibrium ones. We study the influence of the state-to-state vibrational kinetics on averaged rate coefficients of forward exchange reactions (4)-(5) which are defined as [7]:

$$k_c = \frac{1}{n_c} \sum_i n_{ci} k_{ci}(T), \quad c = N_2, O_2, \quad (6)$$

where n_{ci} are populations of the i -th vibrational level of N_2 and O_2 molecules, n_c are molecular number densities, k_{ci} are vibrational state-specific rate coefficients of forward reactions (4), (5), T is the gas temperature. Taking into account participation of rotational energies in reaction (4), (5) and the equilibrium rotational energy distributions we can write

$$k_{ci}(T) = \sum_j s_j^{ci} \exp\left(-\frac{\varepsilon_j^{ci}}{kT}\right) \frac{1}{Z_{ci}^{rot}(T)} k_{cij}(T), \quad (7)$$

where ε_j^{ci} is the rotational energy of a molecule at the i -th vibrational and j -th rotational levels, $k_{cij}(T)$ are rate coefficients depending on rotational and vibrational states, s_j^{ci} is the rotational statistical weight, Z_c^{rot} is the rotational partition function.

For rigid rotator [29] $\varepsilon_j^{ci} = \varepsilon_j^c$, $s_j^{ci} = s_j^c$, $Z_c^{rot} = Z_c^{rot}$ and equation (7) takes the form

$$k_{ci}(T) = \frac{1}{Z_c^{rot}(T)} \sum_j s_j^c \exp\left(-\frac{\varepsilon_j^c}{kT}\right) k_{cij}(T). \quad (8)$$

For evaluation of coefficients k_c using Eqs. (6) one needs level populations of nitrogen and oxygen molecules n_{ci} and analytical expressions for $k_{ci}(T)$. Detailed models for exchange reactions are proposed in a number of papers on the basis of different ideas such as fitting for results of accurate quantum-mechanical or quasi-classical trajectory calculations [30, 31, 32, 33], extending the Treanor-Marrone dissociation model [9] for binary reactions [10, 34], or using empirical expressions [35]. In the frame of the most existing models contribution of rotational energy to overcoming of the activation energy is not taking into account and analytical expressions are given for $k_{cij}(T) = k_{ci}(T)$. In this Letter, we consider global reaction rates for the reactions (4), (5) calculated with the use of three models for coefficients k_{N_2i} and k_{O_2i} proposed in [30, 33, 31, 32] and presented also in [3].

The expressions for state-specific rate coefficients k_{ci} suggested by Warnatz et al. [30] and Polak et al. [33] take into account a different efficiency of the vibrational energy of reactants in overcoming the activation energy E_a . According to [30]

$$k_{ci}(T) = C(i+1)T^\beta \exp\left(-\frac{E_a - \varepsilon_i^c}{kT} \tilde{\Theta}(E_a - \varepsilon_i^c)\right), \quad (9)$$

and following to [33]

$$k_{ci}(T) = A(T) \exp\left(-\frac{E_a - \alpha \varepsilon_i^c}{\gamma kT} \tilde{\Theta}(E_a - \alpha \varepsilon_i^c)\right). \quad (10)$$

In these expressions $\tilde{\Theta}$ is the Heaviside function, k is the Boltzmann constant, $C = 4.17 \cdot 10^{12}$, $\beta = 0$, $\alpha = 0.52$, $\gamma = 0.90$ for the reaction (4) and $C = 1.15 \cdot 10^9$, $\beta = 1$, $\alpha = 0.12$, $\gamma = 0.46$ for the reaction (5), $A(T)$ is close to the collision frequency per unit time $A \approx \pi r_0^2 (8kT/\pi\bar{\mu})^{1/2}$ (r_0 is the collision diameter, $\bar{\mu}$ is the reduced mass of colliding particles). Vibrational energies ε_i^c of molecules c at the i -th level are counted from the zero-th level energy using the anharmonic oscillator model.

The results of quasi-classical trajectory calculations of coefficients k_{ci} [31, 32] are approximated by the following expressions for the reaction (4)

$$\log_{10} k_{N_2i} = b_0 + b_1 \varepsilon_i^{N_2} + b_2 (\varepsilon_i^{N_2})^2 + b_3 (\varepsilon_i^{N_2})^3, \quad (11)$$

and for the reaction (5)

$$\log_{10} k_{O_2i}(T) = \sum_{m,k} a_{m,k} T^m (\varepsilon_i^{O_2})^k, \quad (12)$$

where adjusting coefficients are given in Table 1(A, B). In Eqs. (9)-(12) the rate coefficients are in $\text{mol}^{-1}\text{cm}^3\text{s}^{-1}$, in Eqs. (9), (10) the vibrational energy ε_i^c is in J, in Eqs. (11), (12) it is in eV.

The temperature dependence of coefficients k_{N_2i} , k_{O_2i} for the considered models is shown in Figs. 1 for $i = 10$. Calculations show an increase of the reaction rate coefficients with rising of the gas temperature and vibrational level number. The exception is the model of Warnatz et al. which gives the temperature-independent rate coefficients of the reaction (4) for $i \geq 13$.

Table 1: The coefficients in Eqs. (11)-(12).

A				
Temperature, K	b_0	b_1	b_2	b_3
7000	10.99	$7.809 \cdot 10^{-1}$	$-6.605 \cdot 10^{-2}$	$1.672 \cdot 10^{-3}$
10000	11.93	$5.496 \cdot 10^{-1}$	$-4.512 \cdot 10^{-2}$	$1.257 \cdot 10^{-3}$
14000	12.58	$3.919 \cdot 10^{-1}$	$-2.978 \cdot 10^{-2}$	$7.670 \cdot 10^{-4}$

B		
$a_{00} = 10.97$	$a_{10} = 9.313 \cdot 10^{-4}$	$a_{21} = 4.651 \cdot 10^{-9}$
$a_{01} = 7.947 \cdot 10^{-2}$	$a_{11} = -1.735 \cdot 10^{-5}$	$a_{22} = 1.252 \cdot 10^{-9}$
$a_{02} = 2.709 \cdot 10^{-1}$	$a_{12} = -3.118 \cdot 10^{-5}$	$a_{30} = 8.162 \cdot 10^{-12}$
$a_{03} = -7.159 \cdot 10^{-2}$	$a_{13} = 1.280 \cdot 10^{-6}$	$a_{31} = -2.503 \cdot 10^{-13}$
$a_{04} = 1.052 \cdot 10^{-2}$	$a_{20} = -1.268 \cdot 10^{-7}$	$a_{40} = -1.964 \cdot 10^{-16}$

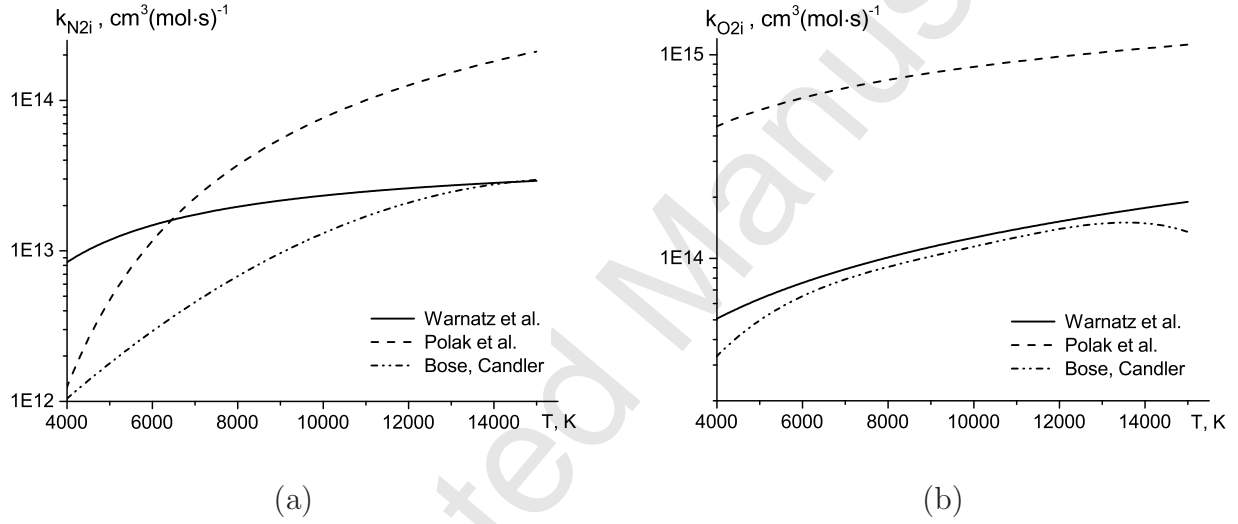


Figure 1: The rate coefficients k_{N_2i} (a) and k_{O_2i} (b) of reactions (4), (5) as functions of the temperature for $i = 10$.

Averaging state-specific coefficients (9)-(12) over Boltzmann vibrational distributions we obtain thermally equilibrium coefficients $k_c^B(T)$ [7]:

$$k_c^B(T) = \frac{1}{Z_c^{vibr}(T)} \sum_i \exp\left(-\frac{\varepsilon_i^c}{kT}\right) k_{ci}, \quad c = N_2, O_2, \quad (13)$$

$Z_c^{vibr}(T) = \sum_i \exp\left(-\frac{\varepsilon_i^c}{kT}\right)$ is the vibrational partition function.

Figs. 2 depict the comparison of temperature dependence for thermally equilibrium coefficients $k_{N_2}^B(T)$, $k_{O_2}^B(T)$ calculated using the expressions (13) and the Arrhenius law:

$$k_c^A = AT^b \exp\left(-\frac{E_a}{kT}\right), \quad (14)$$

where parameters A , b are recommended in [4, 36].

The models of Warnatz et al. and Bose et al. give rather close values of averaged coefficients k_c^B for both reaction (4) and (5). As for state-dependent coefficients (see Figs. 1), the difference

between the values of k_c^B obtained for these two models decreases with the gas temperature rising. In the frame of these models, the averaged coefficients $k_{N_2}^B$ are found in a satisfactory agreement with $k_{N_2}^A$ with parameters taken from [4] for the temperature values $4000 < T < 9000$ K whereas for higher temperatures $T > 9000$ K a better consistency with $k_{N_2}^A$ is reached using the parameters taken from [36]. Coefficients $k_{O_2}^B$ occur noticeably higher than the Arrhenius ones with considered parameters. For both reactions the model suggested by Polak et al. gives considerably higher values for k_c^B than two other models and Eq. (14).

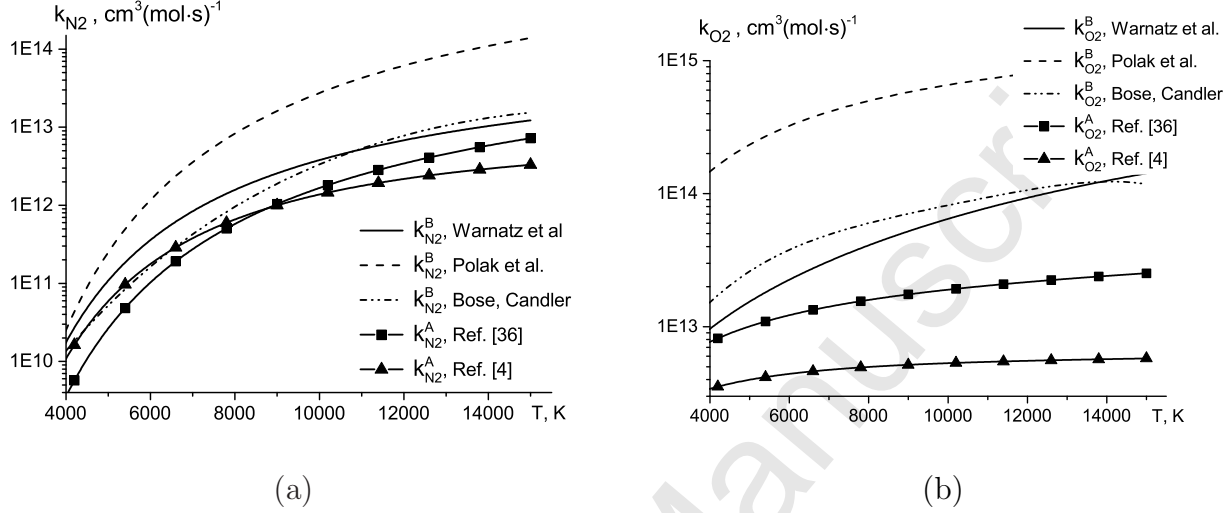


Figure 2: The averaged rate coefficients $k_{N_2}^B$ (a) and $k_{O_2}^B$ (b) as functions of the temperature.

In the next section, we show global rate coefficients $k_{N_2}(T)$ and $k_{O_2}(T)$ obtained by averaging of state-specific coefficients k_{ci} with non-equilibrium vibrational distributions behind shock waves.

We would like to note that in Zeldovich scheme for air reactions and in the frame of the most models for state-dependent rate coefficients for the reactions (4), (5), vibrational excitation of NO molecules is not taken into account. In our calculations vibrationally excited NO molecules are also not included to the kinetic scheme. To consider formation of excited NO molecules in the reactions (4), (5), reliable data on rate coefficients depending on vibrational states of both reactants and products are needed. Unfortunately, up to present time, such data are lacking in the available literature except the very recent paper [37] where QCT method is used to calculate rate coefficients for reaction (4), (5), resulting in formation of $\text{NO}(i)$ molecules, however analytical expressions for these coefficients are not given yet.

3 Rate coefficients in shock heated air flows

3.1 Equilibrium free stream conditions

Now we study the impact of non-equilibrium vibrational distributions on global rate coefficients for Zeldovich reactions in shock heated air flows. In this section we consider the case of equilibrium free stream conditions with Mach number $M_0 = 15$, the gas temperature and pressure $T_0 = 271$ K, $p_0 = 100$ Pa, mixture composition $n_{N_2}(0) = 0.79n_0$, $n_{O_2}(0) = 0.21n_0$, n_0 is the total number density, $n_{NO}(0) = n_N(0) = n_O(0) = 0$ and the Boltzmann equilibrium distributions of N_2 and O_2 molecules with the gas temperature T_0 . These conditions correspond to the Earth re-entry parameters for flight altitudes $H = 48$ km.

As input data for the expressions (6) for global rate coefficients k_c , we use the vibrational distributions n_{N_2i} , n_{O_2i} and the gas temperature T found in numerical simulations of air flows in

the relaxation zone behind shock waves in the state-to-state and one-temperature approximations [38, 39]. Within the state-to-state approach, equations for vibrational level populations n_{N_2i} , n_{O_2i} and number densities n_N , n_O , n_{NO} are coupled to the conservation equations for the momentum and total energy. State-specific rate coefficients for non-equilibrium processes entering into the equations of vibrational-chemical kinetics are computed using the generalized formulas of Schwartz, Slawsky, Herzfeld [3] for energy transitions, the modified Treanor-Marrone dissociation model [9, 7] and the expressions (9)-(12) for the reactions (4), (5). Rate coefficients of forward and backward processes (1)-(5) are connected by the detailed balance principle [7]. Thermally equilibrium flows are computed using the system of equations for species number densities, the gas temperature and velocity.

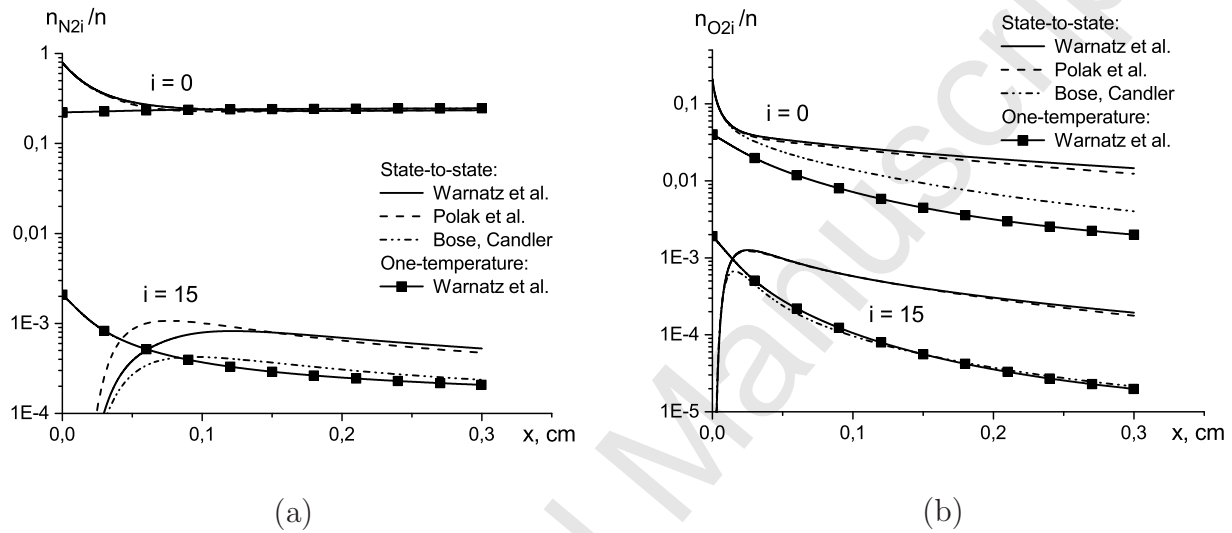


Figure 3: Reduced level populations n_{N_2i}/n (a) and n_{O_2i}/n (b) versus x .

Figs. 3 present dimensionless populations for the vibrational levels $i = 0, 15$ of N_2 and O_2 molecules in dependence of the distance x from a shock front obtained in the state-to-state and one-temperature (thermally equilibrium) approaches with the use of three state-specific reaction models considered in the previous section. All three models show rapid excitation of levels $i > 0$ close to the shock and then a decrease of all level populations due to dissociation and exchange reactions which proceed more intensively for O_2 molecules. Thermally equilibrium level populations are given for the model [30]. The one-temperature approach does not take into account a stage of vibrational excitation. That is why in a thin region close to the shock front the thermally equilibrium model overestimates level populations, then, after vibrational excitation, the state-to-state model shows more populated vibrational levels than the one-temperature approach. We can notice a considerable distinction between non-equilibrium vibrational distributions calculated using different state-specific reaction models whereas this discrepancy becomes negligible for thermally equilibrium level populations. Along the whole relaxation zone, populations of low levels occur higher than those for upper levels.

State-dependent coefficients k_{N_2i} , k_{O_2i} found using the considered models behind the shock wave are shown in Figs. 4 in dependence of x for $i = 0, 15$. Calculations show, on the one hand, more active reactions from upper levels and, on the other hand, a decrease of coefficients k_{N_2i} , k_{O_2i} with x rising due to the gas temperature diminishing along a relaxation zone.

Level populations n_{N_2i} , n_{O_2i} , the gas temperature T and state-specific coefficients k_{N_2i} , k_{O_2i} have been incorporated to the relations (6) for global rate coefficients k_{N_2} , k_{O_2} . In the one-temperature approach, the gas temperature values found from the thermally equilibrium flow equations has been substituted to the expressions (13) for k_c^B . Results of calculations are

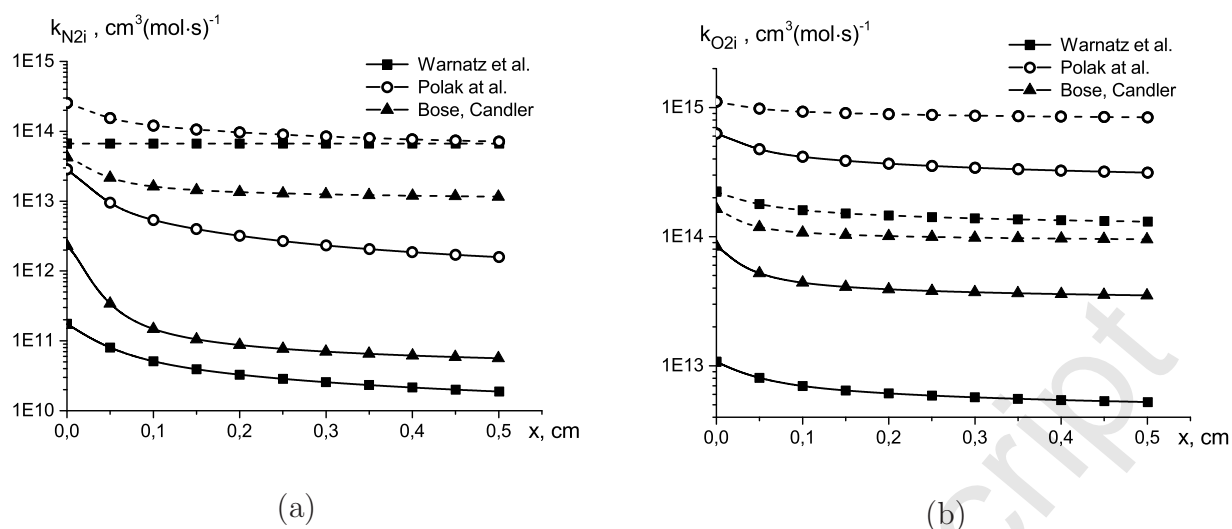


Figure 4: The rate coefficients k_{N_2i} (a) and k_{O_2i} (b) as functions of x . Solid and dash lines correspond to $i = 0$ and $i = 15$, respectively.

given in Figs. 5. The curves for non-equilibrium rate coefficients illustrate a compensation of

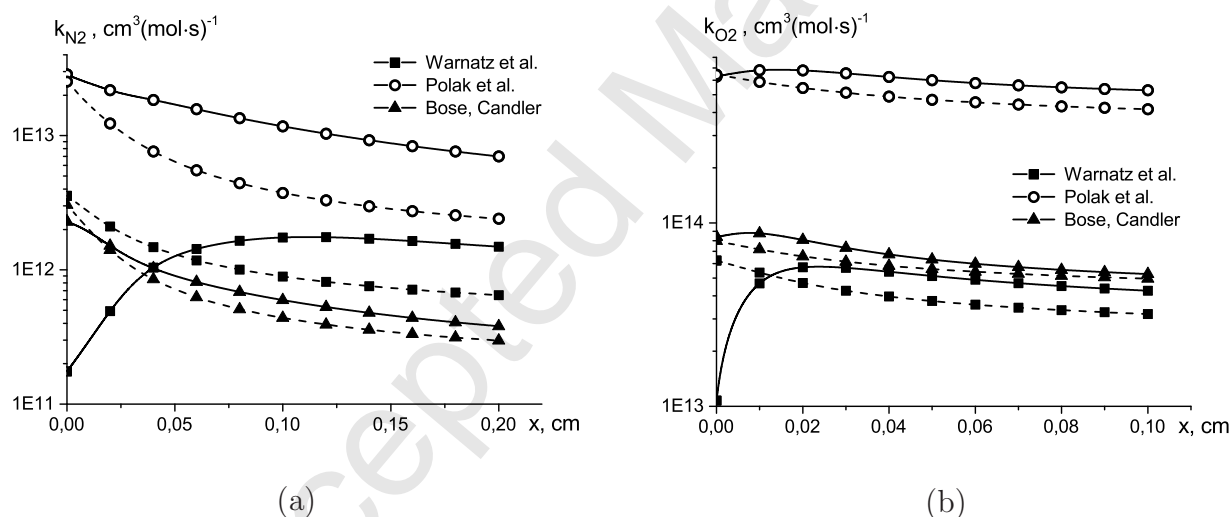


Figure 5: The averaged rate coefficients k_{N_2} (a) and k_{O_2} (b) as functions of x . Solid and dash lines represent the state-to-state and one-temperature approaches, respectively.

variations of level populations and state-dependent rate coefficients along the relaxation zone. As it is mentioned above (see Figs. 4), rate coefficients for reactions from upper levels are much higher than for low levels. However, upper levels are practically not populated just behind a shock because molecules are not excited yet (see Figs. 3). Rapid vibrational excitation close to the shock front and then chemical reactions cause non-monotonous variation of level populations with x rising whereas coefficients k_{ci} decrease monotonously along a relaxation zone with the gas temperature diminishing. Superposition of these effects explains a character of changing for averaged coefficients k_{N_2} , k_{O_2} .

We would like to emphasize a quite different character of non-equilibrium rate coefficients k_c (solid lines) and thermally equilibrium ones k_c^B (dash lines) for both reactions (4) and (5) which is particularly noticeable in the beginning of the relaxation zone. As for level populations, the one-temperature approach overestimates rate coefficients k_c in the very beginning of the

relaxation zone, this is seen for coefficients k_{N_2} (Fig. 4a) for the models of Warnatz et al. and Bose et al. as well as for coefficients k_{O_2} (Fig. 4b) for the model of Warnatz et al. Non-monotonous variation along the relaxation zone is seen for non-equilibrium coefficients k_{O_2} in the frame of the all three considered models. First, the coefficients rise rapidly due to excitation of vibrational levels in a thin region close to the shock front and then decrease with diminishing of the gas temperature and level populations, remaining, however, higher than the one-temperature rate coefficients. A similar effect for dissociation rates in N_2/N and O_2/O flows is found in [21]. At the same time, coefficients k_{N_2} for the models of Polak et al. and Bose et al. decrease monotonously with x rising. It is due to a large contribution of populations of the zeroth level of nitrogen molecules to the values k_{N_2} and a very high sensitivity of coefficients k_{N_2i} to reduction in the gas temperature.

The model of Polak et al. shows global rate coefficients much higher compared to models of Warnatz et al. and Bose et al. Within the framework of this model, non-equilibrium coefficients exceed thermally equilibrium ones just from the beginning of the relaxation zone. The difference between the global coefficients averaged over the state-to-state and one-temperature distributions decreases with x rising and approaching to the thermal equilibrium in a flow.

3.2 Vibrationally excited free stream molecules

Now we consider rate coefficients of the reactions (4), (5) behind shock waves forming in a vibrationally excited flows. Such conditions may occur in experimental facilities, for example in a flow after its freezing in a shock tube nozzle [40] and also in problems of conducting by chemical reactions in shock heated gases due to vibrational energy pumping before a shock. A deformation of a relaxation zone structure is found in [41] for N_2/N mixture for the case of vibrationally excited N_2 molecules before a shock. Qualitative analysis of vibrational relaxation behind a shock wave occurring in an initially excited flow is given in [42, 1]. In our previous paper [38], this problem is studied numerically for reacting air flows and a dramatic impact of free stream non-equilibrium conditions on the gas temperature and level populations of air components behind a shock is found. Now we study this effect for global rates of the exchange reactions (4), (5).

In the present case, vibrational distributions before a shock front are described by the non-equilibrium Boltzmann distributions with vibrational temperatures $T_v^{N_2}(0)$, $T_v^{O_2}(0)$ which are much higher than the gas temperature. Three cases are studied: 1) $T_v^{N_2}(0) = 8000$ K, $T_v^{O_2}(0) = 4000$ K; 2) $T_v^{N_2}(0) = 2400$ K, $T_v^{O_2}(0) = 1150$ K and 3) $T_v^{N_2}(0) = T_v^{O_2}(0) = T(0) = 271$ K (thermal equilibrium free stream); the mixture composition before a shock front is considered the same as in the section 3.1, $M_0 = 10$, $p_0 = 100$ Pa. The second case corresponds to a nozzle expansion before a shock whereas the first one represents more strong initial vibrational energy pumping. Profiles of the gas temperature along the relaxation zone calculated in [38] are presented in Fig. 6a for three considered reaction models and in Fig. 6b for various conditions in the free stream. Fig. 6b shows also variation of vibrational temperatures $T_1^{N_2}$, $T_1^{O_2}$ found in [38, 39].

Vibrational level populations and the gas temperature computed for the cases 1, 2 and 3 are substituted to the expressions (6) for coefficients k_c with the use of the three state-specific models [31, 32, 30, 33]. In Figs. 7 we compare coefficients k_{N_2} and k_{O_2} along the relaxation zone found in the cases 1, 2 of vibrationally excited free stream molecules (curves with square and circle markers, correspondingly) and for the case 3 (curves with trigonal markers) along the relaxation zone.

An essential difference between rate coefficients computed for three considered cases can be seen in Figs. 7 for an each reaction model. Vibrational excitation of free stream molecules causes more active chemical reactions behind a shock than in the case of the equilibrium free

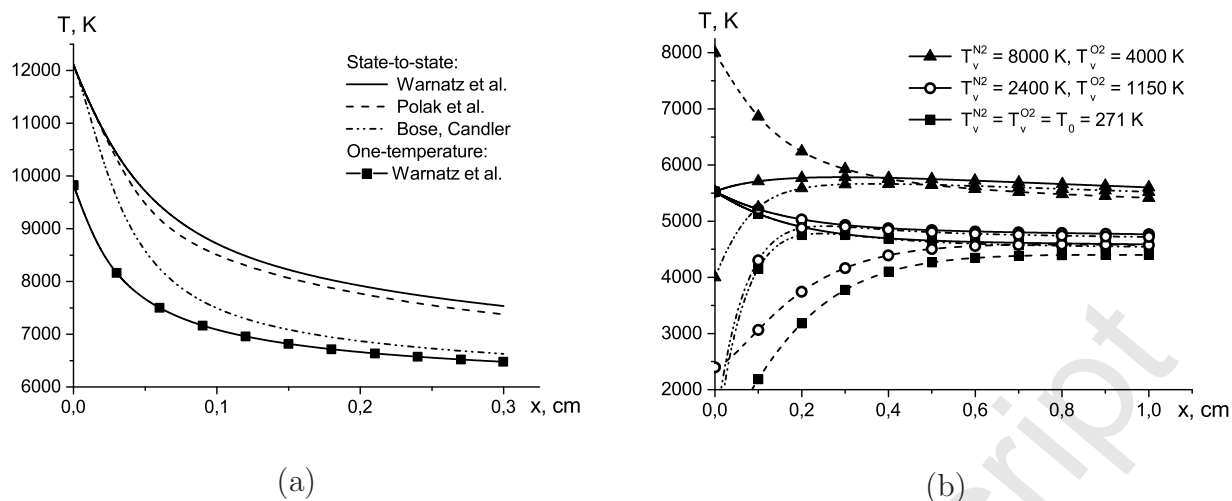


Figure 6: The gas temperature T and vibrational temperatures $T_1^{N_2}$, $T_1^{O_2}$ as functions of x . (a): $M_0 = 15$, equilibrium free stream; (b): $M_0 = 10$, solid, dash and dash-dot lines correspond to T , $T_1^{N_2}$ and $T_1^{O_2}$, respectively, Warnatz et al. model.

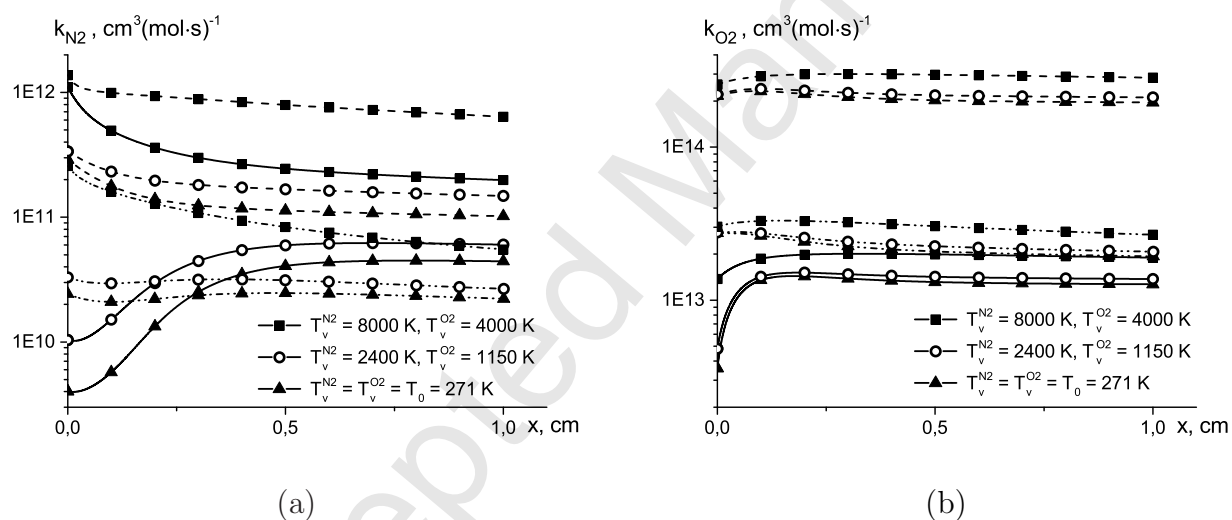


Figure 7: The averaged rate coefficients k_{N_2} (a) and k_{O_2} (b) as functions of x . Solid, dash and dash-dot lines correspond to Warnatz et al. model, Polak et al. model and Bose et al. model, respectively.

stream. From the very beginning of the relaxation zone, coefficients k_{N_2} and k_{O_2} obtained in the cases 1, 2 exceed those found for the equilibrium free stream conditions (case 3). This effect shows up most noticeably in the first case for the reaction $N_2(i) + O \rightleftharpoons NO + N$ (see Fig. 7a). A difference between the coefficients k_{N_2} obtained for the first and third cases reaches two orders of magnitude for the model of Warnatz et al. and about an order of magnitude for the model of Polak et al. and Bose et al. The difference between coefficients k_{N_2} found for the cases 2 and 3 is not so strong and remains within an order of magnitude, for the reaction (5) a discrepancy in coefficients k_{O_2} found for the cases 1, 3 and 2, 3 does not exceed 74% and 25%, correspondingly.

In the first case, the temperature $T_v^{N_2}$ occurs higher than the gas temperature T_1 immediately behind a shock [38] ($T_v^{N_2} > T_1 > T_v^{O_2} > T_0$). Because of highly excited N_2 molecules before a shock in the case 1, the character of vibrational relaxation and chemical reactions behind a shock front differs dramatically from the cases 2 and 3. The reactions (4) start just from

the beginning of the relaxation zone, vibrational levels of nitrogen molecules deactivate and coefficients k_{N_2} decrease monotonically with x rising. In the second case, initial vibrational excitation is weaker ($T_1 > T_v^{N_2} > T_v^{O_2} > T_0$) than in the case 1, therefore non-monotonous variation of the coefficients k_{N_2} , k_{O_2} can be noticed. Similarly to the case 3 ($T_1 > T_v^{N_2} = T_v^{O_2} = T_0$), coefficients increase in a thin region close to the shock front due to energy transfer from translational to vibrational degrees of freedom. Then, after sufficient vibrational excitation of reactants, the reactions (4), (5) start and rate coefficients k_{N_2} , k_{O_2} decrease along the relaxation zone.

4 Conclusions

Global rate coefficients for Zeldovich reactions of NO formation in air flows behind shock waves are studied for different conditions in a free stream using the state-to-state and thermal equilibrium vibrational distributions of N_2 and O_2 molecules. The following three effects are emphasized in the Letter: an essential difference between non-equilibrium rate coefficients and thermally equilibrium ones, a dramatic impact of vibrational excitation of free stream molecules on global reaction rates behind a shock wave and a considerable discrepancy between rate coefficients obtained for various state-specific reaction models. All these effects are found to be important at high temperatures in the beginning of the relaxation zone and decrease with x rising and approaching to the thermal equilibrium conditions in a flow.

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