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Rate Coefficients of Exchange Reactions Accounting for Vibrational Excitation of Reagents and Products

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Abstract. Theoretical models for the vibrational state-resolved Zeldovich reaction are assessed by comparison with the results of quasi-classical trajectory (QCT) calculations. An error in the model of Aliat is corrected; the model is generalized taking into account NO vibrational states. The proposed model is fairly simple and can be easily implemented to the software for non-equilibrium flow modeling. It provides a good agreement with the QCT rate coefficients in the whole range of temperatures and reagent/product vibrational states. The developed models are tested in simulations of vibrational and chemical relaxation of air mixture behind a shock wave. The importance of accounting for excited NO vibrational states and accurate prediction of Zeldovich reactions rates is shown.

INTRODUCTION

Theoretical simulations of high-temperature non-equilibrium flows typical in planetary entry problems require detailed models for collisional processes in gases under consideration. Molecular dynamics provides accurate data for the cross sections and rate coefficients of physical and chemical processes. However these data cannot be directly applied in the computational fluid dynamics (CFD) due to considerable computational efforts required for their implementation. Moreover existing approximations obtained on the basis of trajectory calculations have a limited range of applicability and are closely associated with the used vibrational ladder and therefore cannot be easily transferred to other models. At the same time, for the description of state-to-state kinetics, a fairly simple model for the reaction rate coefficients based on the Treanor–Marrone model [1] can be applied.

Previously, we have developed simple but accurate models for the state-resolved dissociation rate coefficients [2, 3, 4] based on the comparison with quasi-classical trajectory (QCT) calculations [5, 6, 7, 8]. Piecewise continuous functions for the Treanor–Marrone model parameter U in O_2/O and N_2/N mixtures depending on the temperature and the vibrational energy state have been obtained by fitting the rate coefficients to those given by the QCT calculations. One of the significant advantages of the proposed model is its independence of the vibrational ladder. The results obtained using these models demonstrate a very good agreement with the QCT calculations. The models were used to simulate binary O_2 and N_2 mixture flows as well as air flows behind the shock wave [3].

At the same time, the exchange reaction rate coefficients are not very well studied up to now. There are only a few theoretical models depending on the vibrational state, among them the models of Rusanov and Fridman [9], Polak [10] and Warnatz [11]; approximations of trajectory calculations for the first 30 levels of N_2 and 15 levels of O_2 [12, 13]; and a theoretical generalization of the Treanor–Marrone model [14]. Some QCT data are available in the STELLAR database [15]. Recent *ab initio* results taking into account rotational states are presented in [16].

The main idea of this work is to provide a range of parameters for the generalised Treanor–Marrone-like model for the state-resolved exchange reaction rate coefficients. In particular, we study the Zeldovich reactions



where i and k are the vibrational states of corresponding molecules. A method similar to that described in [4] allows us to obtain the sought parameters as functions of temperature and vibrational energy of both the reaction reagents and products and thus to get the state-specific exchange reaction rate coefficients close to those given by QCT calculations. The resulting model with variable parameters retains the simplicity and structure of the original model but provides much better accuracy.

The developed models are used in simulations of strongly thermochemically non-equilibrium flows. As a test case we study a reacting air mixture flow behind the shock wave. The effect of NO excited states populated as a result of the Zeldovich reaction on the flow parameters is discussed. The contribution of various kinetic processes to the vibrational energy source terms is evaluated.

MODELS FOR STATE-RESOLVED EXCHANGE REACTION RATE COEFFICIENTS

First we examine the existing theoretical models of the rate coefficients for non-equilibrium exchange reactions and compare them with those obtained by means of QCT calculations. Several theoretical models are considered, among them the Rusanov–Fridman [9], the Polak [10] and Warnatz [11] models. The rate coefficients introduced in these models depend on the N_2 vibrational state but do not account for the final vibrational state of the reaction product NO. For the detailed description of the above models see Ref. [17].

An approach based on the generalization of the Treanor–Marrone method with allowance for electronic excitation was proposed by A. Aliat [18, 14]. In the particular case of the ground electronic state it turns into the model that depends only on the vibrational level. Then the exchange reaction rate coefficients are calculated as follows [14]:

$$k_{ci,d}^{\text{exch}}(T, U) = \begin{cases} C(T, U) k_{\text{eq}}^{\text{exch}} \exp\left(-\frac{E_a}{kU}\right) \exp\left[\frac{\varepsilon_i^c}{k} \left(\frac{1}{T} + \frac{1}{U}\right)\right], & \varepsilon_i^c < E_a \\ C(T, U) k_{\text{eq}}^{\text{exch}} \exp\left(\frac{E_a}{kT}\right), & \varepsilon_i^c > E_a, \end{cases} \quad (3)$$

where T is the temperature, U is the Treanor–Marrone model parameter, k is the Boltzmann constant, $k_{\text{eq}}^{\text{exch}}$ is the Arrhenius thermal equilibrium rate coefficient of the exchange reaction:

$$k_{\text{eq}}^{\text{exch}} = AT^b \exp\left(-\frac{E_a}{kT}\right), \quad (4)$$

A , b are the parameters found by fitting experimental data, E_a is the reaction activation energy, ε_i^c is the vibrational energy of the molecule c at the i -th vibrational level, and the normalizing coefficient $C(T, U)$ is given by:

$$C(T, U) = Z_c^{\text{vibr}}(T) \left[\sum_{i=0}^{i^*} \exp\left(-\frac{E_a - \varepsilon_i^c}{kU}\right) + \sum_{i=i^*+1}^{l_c} \exp\left(-\frac{E_a - \varepsilon_i^c}{kT}\right) \right]^{-1}, \quad (5)$$

where $Z_c^{\text{vibr}}(T)$ is the equilibrium vibrational partition function, i^* corresponds to the last vibrational level below the activation energy, $\varepsilon_{i^*}^c \leq E_a$, $\varepsilon_{i^*+1}^c > E_a$, whereas l_c is the last vibrational level below the dissociation energy of species c . Calculations for this model are performed using two classical parameter U values: $U = 3T$ and $U = D/6k$. For reaction (1), $E_a = 5.175 \cdot 10^{-19}$ J or 3.23 eV, $A = 0.8 \cdot 10^{-16}$ m³/s, $b = 0$.

The exchange reaction rate coefficients were calculated for all presented models using the anharmonic oscillator model for the vibrational energy spectrum of the reacting molecule in the temperature range from 2000 K to 20,000 K with the increment of 1000 K. The results are compared with the data from the Stellar database [15], which presents the results of QCT calculations for chemical reactions in air (using its own ladder of vibrational levels). As far as we know, the Stellar database uses data based on *ab initio* $^3A''$ and $^3A'$ potential energy surfaces from Ref. [12]. It is worth mentioning that all above theoretical models do not take into account the vibrational state of the reaction product, namely, the NO molecule. Therefore for the comparison with the QCT data, the rate coefficients corresponding to the case of NO formation at the ground state ($k = 0$) are chosen from the database. The rate coefficients as functions of the N_2 vibrational energy for fixed temperatures are shown in Fig. 1, and in Fig. 2 they are given as functions of temperature at fixed vibrational levels.

It is seen from the Fig. 1 that the coefficients obtained using the Rusanov–Fridman, Polak, and Aliat models show the following feature: starting from a certain vibrational level (determined by the combination of the activation energy

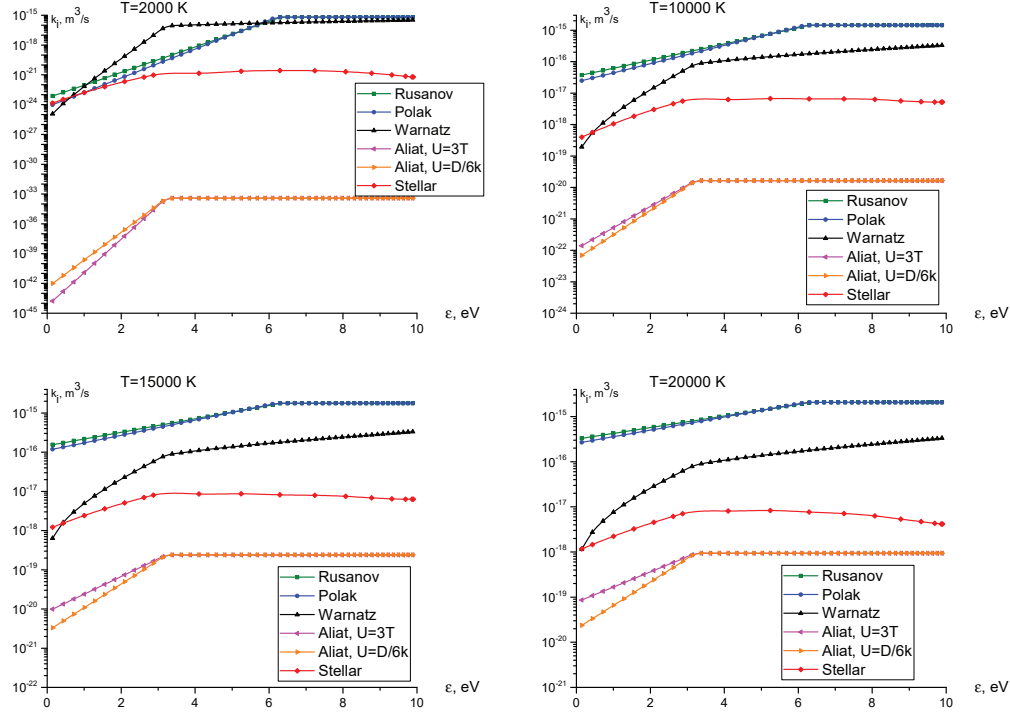


FIGURE 1. Exchange reaction rate coefficients for N_2+O reaction as functions of the N_2 vibrational energy with fixed temperature for different models.

and parameters which characterize the contributions of translational and vibrational energies into the reaction), the growth of the coefficients at a given temperature ceases, and they attain the constant value. Contrarily, the use of the Warnatz formula provides a slow but steady increase in the coefficients in the whole range of vibrational levels. At the same time, the coefficients from the Stellar database show a tendency to some decrease in the values with increasing vibrational energy after reaching a certain maximum value. One can notice that for low temperatures, the models of Rusanov–Fridman, Polak, and Warnatz demonstrate fairly close agreement with the Stellar data, whereas the results obtained using the Aliat model are lower by 10–12 orders of magnitude.

With increasing temperature, one can see qualitative changes: the results of calculations based on the Rusanov–Fridman and Polack models strongly overestimate the exchange reactions rate coefficients as compared to the QCT data, whereas the results based on the Warnatz model continue showing good agreement with the QCT data for the low energy states, but they accumulate the error with increasing the vibrational energy, although less than the first two models. An interesting point is that the results of calculations based on the Aliat model demonstrate a gradual qualitative improvement with increasing temperature and at 20,000 K they give the smallest error among all the considered models in comparison with the QCT data from Stellar database.

A similar situation can be observed while comparing the results for the selected levels (Fig. 2). For the 0-th vibrational level, in the entire temperature range the Warnatz model provides the best match with the QCT data, whereas the Rusanov–Fridman and Polak models are not much inferior, and the Aliat model is quite poor at low temperatures. With increasing the energy level, the temperature range where the Rusanov–Fridman and Polak models show the results close to the QCT data is reducing.

As one can see, in the whole range of parameters, the results obtained in the frame of the Rusanov–Fridman and Polak models are very close. Hereafter to simplify the analysis, we keep only the Polak model while comparing the rate coefficients.

It is worth noting that we expected much better results from using the Aliat model and were rather disappointed by the obtained discrepancy. For this reason, we decided to check the formulae and following the methodology proposed in the paper by Aliat [14] we thoroughly re-derived the expressions for the rate coefficients starting from the original Treanor–Marrone model. As a result, the next expression was obtained for the normalizing factor $C(T, U)$ instead of

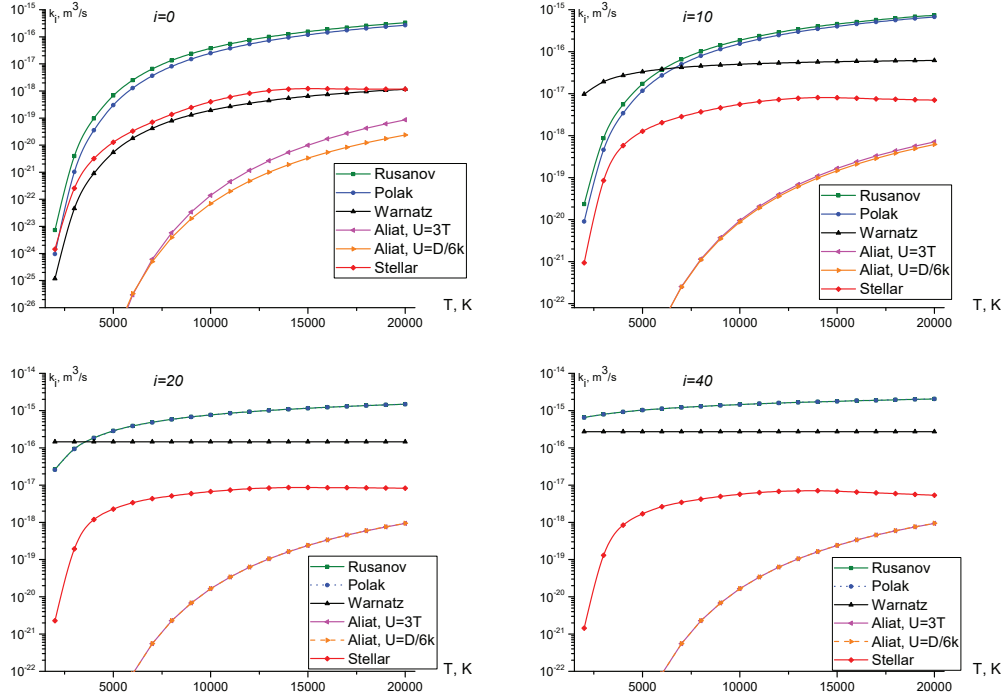


FIGURE 2. Exchange reaction rate coefficients for N_2+O reaction as functions of the temperature with fixed N_2 vibrational level for different models.

the expression (5):

$$C(T, U) = Z_c^{\text{vibr}}(T) \left[\sum_{i=0}^{i^*} \exp\left(-\frac{E_a - \varepsilon_i^c}{kU}\right) + \sum_{i=i^*+1}^{l_c} \exp\left(\frac{E_a - \varepsilon_i^c}{kT}\right) \right]^{-1}. \quad (6)$$

The difference between the original expression (5) and the new one (6) is the absence of a "minus" sign under the exponent in the second sum. After this correction, the results based on the Aliat model demonstrate a significant qualitative improvement in behavior and the best match with the QCT data over the entire range of temperature and vibrational levels as we can see in Fig. 3. We also compared the data obtained by the corrected model with those presented in [16] for the 0-th rotation level (QCT data based on the $1^3A''$ and $1^3A'$ *ab initio* potential energy surface by Gamallo *et al.* [19]). The obtained results show a good qualitative coincidence; some quantitative discrepancy is due to the choice of parameters in Eq. (4). The only drawback of the present model is that it does not predict some decrease in the rate coefficients for the very high energy states. However this decrease does not make a significant contribution to the fluid-dynamic variables.

Finally we strongly recommend using the corrected formula (6) instead of the original one (5) while applying the Aliat model for the exchange reaction rate coefficients.

GENERALIZATION OF THE ALIAT MODEL

As is emphasized in the previous section, all the described theoretical models can be used to calculate the exchange reactions rate coefficients only for the NO ground vibrational energy state $k = 0$. At the same time, the coefficients for all vibrational states of the reaction product are available in the database [15] and are also required for the correct state-to-state flow simulations. Based on this arguments we decided to further generalize and improve the model of Aliat. The objective is to introduce some corrections to the original model that would allow us for taking into account not only the vibrational state of the reacting molecule, but also the vibrational state of the reaction product. For carrying out such a refinement, reliable reference data are needed. Until recently, the only source of such data available to

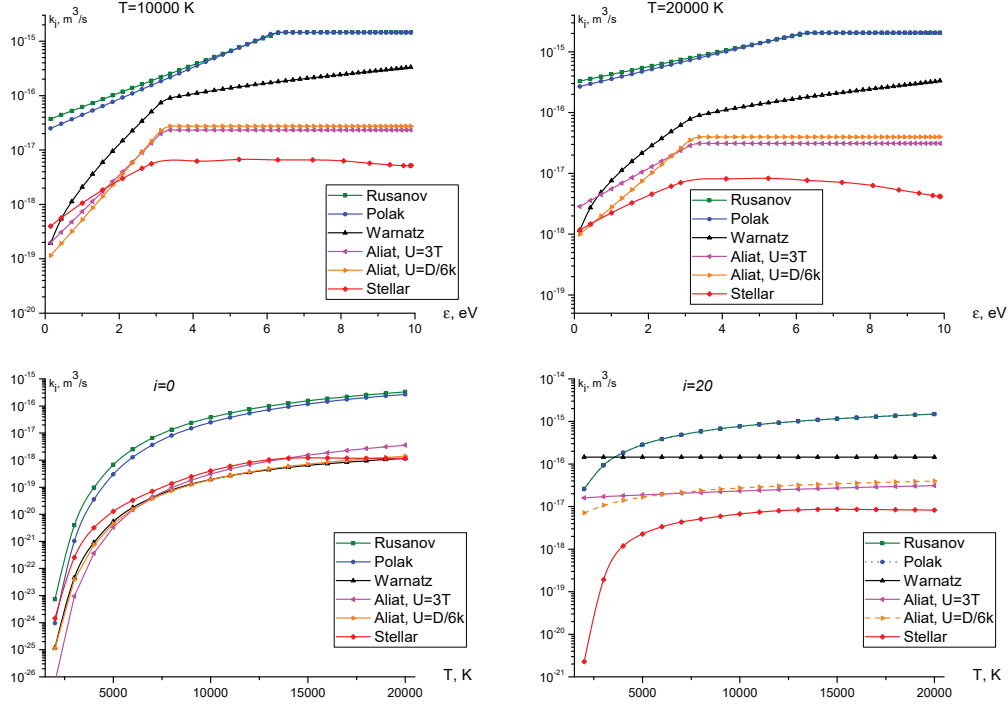


FIGURE 3. Exchange reaction rate coefficients for N_2+O reaction for different models with corrected Aliat model.

us was the data from Stellar database [15]. Recently in the paper [20], the new data set has been published; the QCT calculations for the rate coefficients of reaction (1) depending on both i and k have been performed on the two PESs ($^3A''$ ground state, $^3A'$ first excited state, asymptotically degenerated). First we assessed the data comparing the new rate coefficients with those from the Stellar database. Thorough analysis demonstrates that both models show qualitatively identical behavior, however they yield certain discrepancies in the absolute values of rate coefficients and also in the description of high energy states. Nevertheless, both models provide the dependence of the rate coefficients on the reagent vibrational state as a combination of an exponentially growing part and a plateau. While the length of these parts depends on the NO vibrational state, the plateau starting points are very close for both models.

This general agreement between the QCT results of two independent groups makes it possible to use their results as a basis in the construction of our updated model. One of the fundamental observations is the coincidence of points of termination of the coefficients growth for both models. Further analysis shows that this displacement exactly coincides with the energy value of the corresponding vibrational level of the NO molecule. This gives us an idea how to modify the Aliat model: for each selected NO vibrational state we shift the reaction activation energy adding to its value the corresponding NO vibrational energy. More accurate investigation shows that we can use a linear function of the corresponding NO energy state. Moreover, for a better coincidence of our rate coefficients with those from the Stellar database [15], we need to introduce some correction for the equilibrium rate coefficients. The new expression for the rate coefficients taking into account the vibrational level of the reaction product suitable for both reactions (1) and (2) is obtained in the form:

$$k_{M_2(i),NO(k)}^{\text{exch}}(T, U) = \begin{cases} C_k(T, U) k_{\text{eq},k}^{\text{exch}} \exp\left(-\frac{E_{a,k}}{kU}\right) \exp\left[\frac{\varepsilon_i^{M_2}}{k} \left(\frac{1}{T} + \frac{1}{U}\right)\right], & \varepsilon_i^{M_2} < E_{a,k}, \\ C_k(T, U) k_{\text{eq},k}^{\text{exch}} \exp\left(\frac{E_{a,k}}{kT}\right), & \varepsilon_i^{M_2} > E_{a,k}, \end{cases} \quad (7)$$

$$C_k(T, U) = Z_{M_2}^{\text{vibr}}(T) \left[\sum_{i=0}^{i^*} \exp\left(-\frac{E_{a,k} - \varepsilon_i^{M_2}}{kU}\right) + \sum_{i^*+1}^{l_c} \exp\left(\frac{E_{a,k} - \varepsilon_i^{M_2}}{kT}\right) \right]^{-1}, \quad (8)$$

$$k_{\text{eq},k}^{\text{exch}} = AP_k T^b \exp\left(-\frac{E_{a,k}}{kT}\right), \quad (9)$$

where M_2 stands for N_2 or O_2 in (1) and (2) respectively, $E_{a,k}$ is the shifted activation energy, P_k is a function of NO vibrational state, $\varepsilon_i^{M_2}$ is the vibrational energy of molecule M_2 at the corresponding level. It should be noted that for the generalized model, the equilibrium rate coefficient, the activation energy and the normalizing constant are introduced for each vibrational state of NO molecule.

Based on the comparison with the Stellar database [15] we recommend to use in Eqs. (7)–(9) the parameters given in Table 1. Note that in the Table, the energies are given in eV and that is why we use the tilde sign to denote them. In order to use the modified activation energies in Eqs. (7)–(9) one has to multiply $\tilde{E}_{a,k}$ by the factor $1.60218 \cdot 10^{-19}$ J/eV.

TABLE 1. Coefficients in Eqs. (7)–(9)

Reaction	A, m ³ /s	b	U	P _k	$\tilde{E}_{a,k}$, eV
O ₂ +N	$3 \cdot 10^{-17}$	0	∞	$1 + \tilde{\varepsilon}_k^{NO}/3$	$2.8793 + 1.0223 \cdot \tilde{\varepsilon}_k^{NO}$
N ₂ +O	$4 \cdot 10^{-16}$	-0.39	∞	$\tilde{E}_{a,k} + 0.8$	$0.098, \quad \tilde{\varepsilon}_k^{NO} < 1.3706 \text{ eV},$ $-0.6521 + 0.5474 \cdot \tilde{\varepsilon}_k^{NO}, \quad 1.3706 \text{ eV} < \tilde{\varepsilon}_k^{NO} < 2.4121 \text{ eV},$ $-1.8451 + 1.04189 \cdot \tilde{\varepsilon}_k^{NO}, \quad 2.4121 \text{ eV} < \tilde{\varepsilon}_k^{NO}$

The results are shown in Fig. 4. If we compare the results presented in Figs. 3 and 4, we can easily see that the corrected Aliat model still yields an error up to the one and a half order of magnitude in the entire temperature range and N_2 vibrational levels. At the same time, the generalized model not only reduces this difference by a factor of 5 to 10 for the NO ground energy state, but also ensures the same accuracy for all NO vibrational states over a wide range of temperatures. The most significant discrepancies are observed for the low N_2 levels, which requires some additional investigation, as well as further comparisons with the results of Esposito et al. [20]

Finally, we can see that the new model provides a very good agreement with the data presented by QCT calculations in a wide range of temperature and vibrational states of both reagents (N_2 and O_2) and products (NO molecules). At the same time, it keeps the simplicity of the original Treanor–Marrone model and thus can be easily implemented to the CFD simulations of high-temperature flows.

It is interesting to emphasize that for the state-specific dissociation rate coefficients, the choice of the parameter U is extremely important; to obtain the best fit to the QCT data, U is found as a function of temperature and vibrational level [3, 4]. Contrarily to this, in the case of exchange reactions (1) and (2), the main effect is due to the choice of parameters in the Arrhenius law (A , b , $E_{a,k}$, and P_k depending on the vibrational state of NO). The choice of the parameter U is not so important, and the optimal value for the parameter in our case is $U = \infty$. In this case, equations (7)–(8) can be simplified:

$$k_{M_2(i),NO(k)}^{\text{exch}}(T) = \begin{cases} C_k(T) k_{\text{eq},k}^{\text{exch}} \exp\left(\frac{\varepsilon_i^{M_2}}{kT}\right), & \varepsilon_i^{M_2} < E_{a,k}, \\ C_k(T) k_{\text{eq},k}^{\text{exch}} \exp\left(\frac{E_{a,k}}{kT}\right), & \varepsilon_i^{M_2} > E_{a,k}, \end{cases} \quad C_k(T) = Z_{M_2}^{\text{vibr}}(T) \left[i^* + 1 + \sum_{i^*=1}^{l_c} \exp\left(\frac{E_{a,k} - \varepsilon_i^{M_2}}{kT}\right) \right]^{-1}. \quad (10)$$

Implementation of these expressions is more straightforward than Eqs. (7)–(8) and requires less computational efforts.

MODEL ASSESSMENT

This section presents the results of testing of the developed models for exchange reaction rate coefficients by modeling inviscid air mixture flows behind the front of a plane shock wave. For this purpose we solve a set of ordinary differential equations including the conservation equations of momentum and total energy of the mixture coupled to the master equations for vibrational level populations of molecules and atomic number densities. The source terms in these equations describe the following kinetic processes: single-quantum energy exchanges between translational and vibrational degrees of freedom (VT exchanges); vibrational energy exchanges between molecules of the same species (VV exchanges) and different species (VV' exchanges), with the exception of VV' interactions with NO molecules,

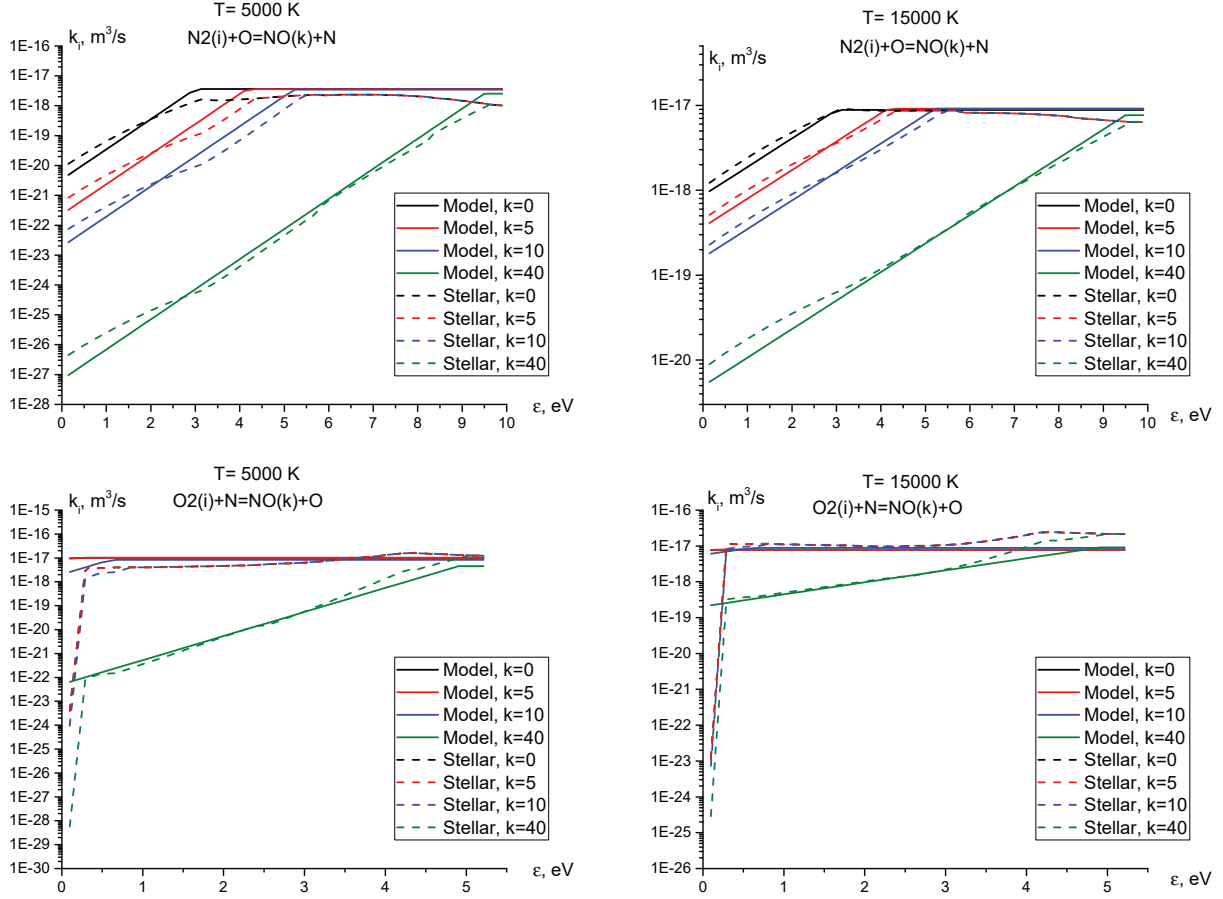


FIGURE 4. State-specific rate coefficients of reaction (1) as functions of N_2 vibrational energy (upper plots) and reaction (2) as functions of O_2 vibrational energy (lower plots) for different NO vibrational levels. Comparison of the Stellar and present models.

in view of the smallness of their number; state-specific dissociation and recombination reactions (*DR*), and Zeldovich exchange reactions (*ZR*). As the initial conditions, the temperature ($T_\infty = 271$ K), pressure ($p_\infty = 100$ Pa), and Mach number (M_∞) of the free stream are set. It is supposed that air in the free stream consists of 79% of nitrogen and 21% of oxygen molecules with the Boltzmann vibrational distributions. A detailed mathematical formulation of this problem and the method for its solving are given in [17].

As was shown earlier (see for instance [17]), for the high shock wave intensity the number of NO molecules changes non-monotonically (increasing, then decreasing) with the distance from the shock as a result of the competition of different kinetic processes. In Fig. 5 (left) the maximum of the NO number density as a function of the Mach number in the free stream is presented for two cases: 1) the complete kinetic scheme taking into account NO excitation; 2) the reduced scheme assuming that in the exchange reactions, NO always appears in the ground vibrational state and then remains unexcited during the relaxation process. This assumption is commonly used in the state-to-state simulations of air flows (see, for example, [21, 22, 23]). For both cases, the largest value of n_{NO}/n is obtained for the "medium" Mach numbers, in the range where the Zeldovich reactions prevail. With increasing the Mach number and, correspondingly, the mixture temperature, the dissociation reactions of NO molecules become more efficient. Following the above analysis, we choose the free stream Mach number $M_\infty = 13$ which yields the largest value of n_{NO}/n , to evaluate the effect of the proposed rate coefficient models on the mixture parameters in the relaxation zone behind the shock wave.

Figs. 5 (center, right) present a variation of mixture temperature, number densities of atoms and nitrogen oxide molecules with the distance from the shock front obtained using expression (7) for the rate coefficients of exchange

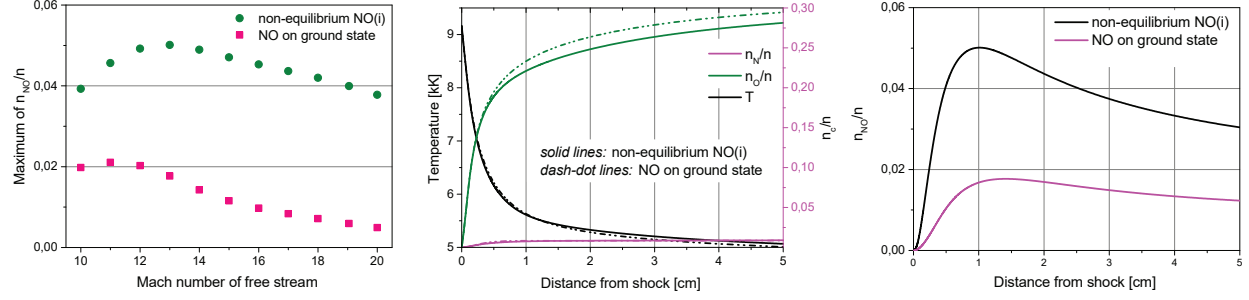


FIGURE 5. The maximum of n_{NO}/n versus the free stream velocity (left). The temperature T , the atomic (center) and NO (right) molar fractions behind the shock front as functions of x .

reactions. It can be seen that neglecting the excitation of nitrogen oxide molecules yields underpredicted gas temperature at $x > 1.2$ cm and considerably overpredicted atomic number densities. At the same time, the number of NO molecules is 6 times smaller than in the case with excitation of nitric oxide molecules.

To estimate the contribution of various processes, the vibrational energy gain or loss due to those processes was calculated: $\Omega_c^r = \sum_{i=0}^{l_c-1} R_i^r \epsilon_i^c$, $c = \text{N}_2, \text{O}_2, \text{NO}$, $r = VT, VV, VV', DR, ZR$, where R_i^r is the source term describing the r -th process. In Fig. 6, the vibrational energy source terms are given. We do not plot the contributions of VV exchanges since they are small compared to other processes. While VT exchanges play the main role in the change

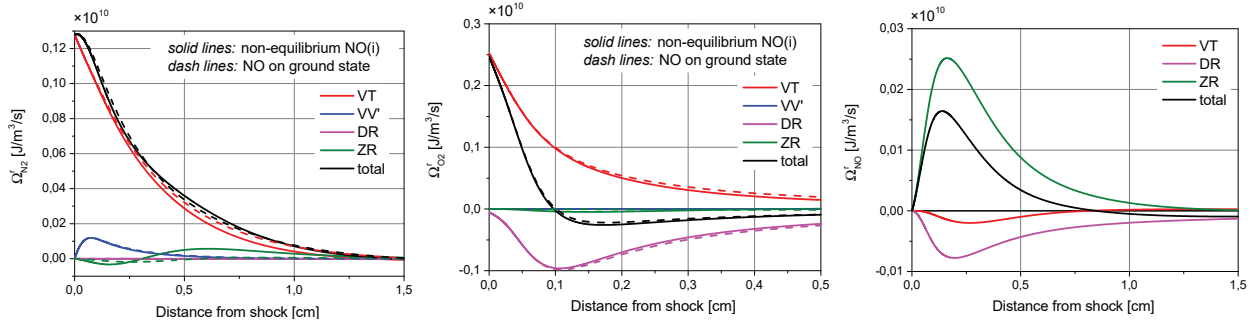


FIGURE 6. Vibrational energy source terms for N_2 (left), O_2 (center) and NO (right) as functions of x .

of vibrational energy of N_2 , both VT transitions and dissociation are dominating in the O_2 vibrational relaxation. However competition of these processes leads to a decrease in the total O_2 vibrational energy production. With x rising the values of $\Omega_{\text{N}_2}^{\text{ZR}}$ and $\Omega_{\text{O}_2}^{\text{ZR}}$ change their sign from negative to positive; at the beginning of the relaxation zone, the forward Zeldovich reactions are more efficient than the backward ones. Under the considered conditions, oxygen and NO molecules dissociate actively, whereas N_2 dissociates weakly. Calculations show that vibrational energy transfers have a small effect on the variation of NO number density (difference from the data obtained without VT and VV exchanges does not exceed 0.02%) and on the NO specific vibrational energy compared to the contributions of chemical reactions (contribution of VT exchanges to the vibrational energy is about one order of magnitude lower than that of Zeldovich reactions). Obviously, the main role in the change of NO vibrational energy and NO number density belongs to the Zeldovich reactions. Therefore, accurate prediction of their rates is of vital importance for high-temperature non-equilibrium flow simulations.

CONCLUSIONS

Existing state-resolved theoretical models of the Zeldovich exchange reaction rate coefficients are assessed using the QCT calculations. The discrepancies between quasi-classical trajectory and theoretical models are clearly demonstrated. An error has been discovered and corrected in the original Aliat model; the corrected expressions provide much better agreement with the QCT data than other theoretical models. Generalization of the corrected Aliat model

is proposed allowing to take into account the vibrational level of the reaction product. With the optimal choice of the Arrhenius law parameters and the Aliat model parameter, the theoretical state-specific rate coefficients are very close to the QCT ones. The resulting model is quite simple and accurate and can be easily implemented to CFD solvers.

It is shown that accounting for excited vibrational states of NO molecules is necessary for air flows modeling behind the front of a shock wave. Neglecting NO vibrational excitation leads to appreciably underestimated values of the number density of nitrogen oxide molecules.

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