



## Research paper

## Generalized Treanor–Marrone model for state-specific dissociation rate coefficients



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## ABSTRACT

We propose a simple and accurate model for state-specific dissociation rate coefficients based on the widely used Treanor–Marrone model. It takes into account the dependence of its parameter on temperature and vibrational level and can be used with arbitrary vibrational ladder. The model is validated by comparisons with state-specific dissociation rate coefficients of  $O_2$  and  $N_2$  obtained using molecular dynamics, and its good accuracy is demonstrated. Non-equilibrium kinetics of  $O_2/O$  and  $N_2/N$  mixtures under heat bath conditions is studied; applying the optimized Treanor–Marrone model leads to more efficient dissociation and vibrational relaxation.

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## 1. Introduction

State-to-state vibrational-chemical kinetics is widely used in modern high-temperature and high-enthalpy fluid dynamics for simulation of strongly non-equilibrium flows. In the beginning, it was used mainly for 1D inviscid flows [1–5] and simple 2D flows [6] due to its high computational cost and lack of models for the state-specific transport coefficients. Increasing capacity of computational tools allowed applying the state-to-state model for simulation of more complex mixtures [7,8], coupled rotational-vibrational [9,10] and vibration-electronic-radiation [11] kinetics. In the meanwhile, the kinetic transport theory for the state-to-state approach was developed [12,13] which gives a possibility to study the effect of non-equilibrium kinetics on heat and mass transfer in different flows [14–19].

The accuracy of gas-dynamic parameters predicted in state-to-state flow simulations depends essentially on the rate coefficients of energy transitions and chemical reactions. In the present study we are interested in the state-specific dissociation rate coefficients. Experimental measurement of thermally non-equilibrium dissociation rate coefficients is quite challenging, and at the present time the only experimental data available in the literature are those for multi-temperature dissociation rate coefficients [20]. Molecular dynamics provides a powerful tool for the calculation of state dependent dissociation rate coefficients [21–24], however its direct application in computational fluid dynamics (CFD) is not possible. Approximate formulas obtained on the basis of quasi-classical trajectory (QCT) calculations [25]

have a good accuracy only in the limited range of temperatures and vibrational states and cannot be applied at temperatures higher than 10,000 K. Therefore there is a need in reliable, accurate and easy-to-implement models of state-specific dissociation rate coefficients.

The simplest analytical model of coupled vibrational relaxation and dissociation is the ladder climbing model allowing dissociation from the last vibrational state [3], however its accuracy is low, and it can be used for rough estimates only. A better model of preferential dissociation from any vibrational state was proposed by Treanor and Marrone [26] for two-temperature flows of harmonic oscillators. Later it was generalized for multi-temperature flows of anharmonic oscillators [27] and for the state-to-state approach [1,28] including the case of vibration-electronic-dissociation coupling [29,30]. This simple model can be easily implemented for non-equilibrium flow simulations and it is indeed widely used in CFD. The Treanor–Marrone model involves one adjustable parameter  $U$  which can be varied to fit the results to experimental data. This parameter is basically set to constant,  $U = \infty$  (which corresponds to equiprobable dissociation from each vibrational level),  $U = D/(6k)$  ( $D$  is the dissociation energy,  $k$  is the Boltzmann constant), or defined as a linear function of temperature, for example,  $U = 3T$ . The latter two cases describe preferential dissociation from high vibrational levels. Thorough analysis performed in [28,31] shows that neither constant values of  $U$  nor linear function of  $T$  can provide satisfactory agreement of the state-specific dissociation rate coefficients with those obtained by quasi-classical trajectory calculations in the whole range of temperature and vibrational states.

Several attempts to modify the Treanor–Marrone model have been performed recently in [31,32,34] to account for different

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behavior of the parameter  $U$  for various vibrational levels. In particular, a modification proposed in [34] for multi-temperature approach gives  $U$  as a piecewise function of vibrational energy. The objective of the present paper is to adapt the model described in [34] to the state-to-state approach, to validate it using the state-specific dissociation rate coefficients obtained by QCT simulations [21–23] and to assess the generalized model solving the problem of space-homogeneous vibrational-chemical relaxation of  $O_2/O$  and  $N_2/N$  mixtures under strongly non-equilibrium heat bath conditions.

## 2. Generalized Treanor-Marrone model

In the frame of original Treanor-Marrone model for the state-specific dissociation, the rate coefficient  $k_{i,diss}^M$  of dissociation from the vibrational state  $i$  after a collision with a partner  $M$  is introduced in the form:

$$k_{i,diss}^M = Z_i^M k_{i,diss,eq}^M(T), \quad (1)$$

where  $k_{i,diss,eq}^M(T)$  is the thermal equilibrium dissociation rate coefficient,  $Z_i^M$  is the non-equilibrium factor determined as:

$$Z_i^M = Z_i(T, U) = \frac{Z_{vibr}(T)}{Z_{vibr}(-U)} \exp\left(\frac{\varepsilon_i}{k} \left(\frac{1}{T} + \frac{1}{U}\right)\right), \quad (2)$$

$\varepsilon_i$  is the vibrational energy of the  $i$ th state,  $Z_{vibr}(T)$  is the equilibrium vibrational partition function

$$Z_{vibr}(T) = \sum_i \exp\left(-\frac{\varepsilon_i}{kT}\right). \quad (3)$$

The thermal equilibrium dissociation rate coefficient can be calculated on the basis of the Arrhenius law:

$$k_{i,diss,eq}^M = AT^b \exp\left(-\frac{E}{T}\right), \quad (4)$$

$A, b, E$  are the parameters found by fitting experimental data.

Eq. (2) for the non-equilibrium factor has been obtained originally assuming  $U$  independent of the vibrational state (see for instance [28]). If we apply this procedure to the state-dependent parameter  $U = U(i, T)$ , we obtain a modified formula:

$$Z_i^M = Z_i(T, U) = \frac{Z_{vibr}(T) \exp\left(-\frac{D}{kU_i}\right)}{\sum_j \exp\left(-\frac{D-\varepsilon_j}{kU_j}\right)} \exp\left(\frac{\varepsilon_i}{k} \left(\frac{1}{T} + \frac{1}{U_i}\right)\right). \quad (5)$$

One can see that this expression includes explicitly the dissociation energy  $D$ . It is evident also that Eq. (2) can be derived from Eq. (5) as the limit case corresponding to  $U$  independent of  $i$ .

As it is shown in [28,31], the accuracy of the Treanor-Marrone model and its generalizations depends on two factors: the choice of the Arrhenius law parameters and the choice of the parameter  $U$ . For the reactions considered in the present study, recommended parameters for the Arrhenius law are the following [34]: for  $O_2 + O$  dissociation reaction,  $A = 6.1953 \cdot 10^{-12} \text{ m}^3/\text{s}$ ,  $b = -0.55724$ , and  $E = 60,496 \text{ K}$ ; for  $N_2 + N$ ,  $A = 1.0 \cdot 10^{-11} \text{ m}^3/\text{s}$ ,  $b = -0.68$ , and  $E = 113,500 \text{ K}$ . Concerning the parameter  $U$ , recently in Ref. [34] we have found a piecewise continuous polynomial function providing its optimal choice and depending on  $T$  and  $\tilde{\varepsilon}_i$  ( $\tilde{\varepsilon}_i$  is the vibrational energy in eV):

$$U(i, T) = \sum_{n=0}^N a_n \tilde{\varepsilon}_i^n \exp\left(T \sum_{k=0}^K b_k \tilde{\varepsilon}_i^k\right). \quad (6)$$

Coefficients  $a_n, b_k$  in the formula (6) reported originally in [34] provide a very good accuracy in multi-temperature flow simulations. However using these coefficients in the state-to-state approach yields physically inadequate behavior of the state-specific dissociation rate coefficients at the upper vibrational levels and even their decreasing with  $i$ . Therefore, in the present study we had to work on improving the model [34]. Upgraded values of coefficients  $a_n, b_k$  are given in Table 1.

Another modification for the parameter  $U$  for  $O_2/O$  mixture was introduced in [32] as a weighted linear combination of  $U = D/(6k)$  and  $U = 3T$ . The hybrid value of the parameter  $U$  proposed in [32]

**Table 1**  
Coefficients in Eq. (6) for  $O_2 + O$  and  $N_2 + N$  reactions.

O <sub>2</sub> + O					
n, k	$\tilde{\varepsilon}_i < 0.67 \text{ eV}$		0.67 eV < $\tilde{\varepsilon}_i < 2.237 \text{ eV}$		$\tilde{\varepsilon}_i > 2.237 \text{ eV}$
	$a_n$	$b_k$	$a_n$	$b_k$	
		$\tilde{\varepsilon}_i < 0.67 \text{ eV}$		$\tilde{\varepsilon}_i > 0.67 \text{ eV}$	
0	$2.9177 \cdot 10^4$	$1.0034 \cdot 10^{-4}$	$2.9177 \cdot 10^4$	$1.2267 \cdot 10^{-4}$	$U(\tilde{\varepsilon}_i = 2.237, T)$
1	$-5.7075 \cdot 10^4$	$-1.3047 \cdot 10^{-5}$	$-5.7075 \cdot 10^4$	$-3.0141 \cdot 10^{-5}$	
2	$2.7321 \cdot 10^5$	$2.4290 \cdot 10^{-5}$	$2.7321 \cdot 10^5$	–	
3	$-6.6291 \cdot 10^5$	–	$-6.6291 \cdot 10^5$	–	
4	$8.8254 \cdot 10^5$	–	$8.8254 \cdot 10^5$	–	
5	$-6.8447 \cdot 10^5$	–	$-6.8447 \cdot 10^5$	–	
6	$3.2435 \cdot 10^5$	–	$3.2435 \cdot 10^5$	–	
7	$-9.5511 \cdot 10^4$	–	$-9.5511 \cdot 10^4$	–	
8	$1.7081 \cdot 10^4$	–	$1.7081 \cdot 10^4$	–	
9	$-1.7002 \cdot 10^3$	–	$-1.7002 \cdot 10^3$	–	
10	$7.2293 \cdot 10^1$	–	$7.2293 \cdot 10^1$	–	
N <sub>2</sub> + N					
n, k	$\tilde{\varepsilon}_i < 2.85 \text{ eV}$		2.85 eV < $\tilde{\varepsilon}_i < 8.31 \text{ eV}$		$\tilde{\varepsilon}_i > 8.31 \text{ eV}$
	$a_n$	$b_k$	$a_n$	$b_k$	
0	$1.8586 \cdot 10^4$	$5.4119 \cdot 10^{-5}$	$1.5970 \cdot 10^4$	$1.7421 \cdot 10^{-4}$	$U(\tilde{\varepsilon}_i = 8.31, T)$
1	$-1.2897 \cdot 10^3$	$7.3290 \cdot 10^{-6}$	$8.4580 \cdot 10^2$	$-8.9603 \cdot 10^{-5}$	
2	–	–	$-6.9535 \cdot 10^2$	$2.7691 \cdot 10^{-5}$	
3	–	–	$1.1342 \cdot 10^2$	$-3.3879 \cdot 10^{-6}$	
4	–	–	$-6.9833 \cdot 10^0$	$1.3575 \cdot 10^{-7}$	

is based on the  $O_2$ -O QCT data. The state-specific dissociation rates in  $O_2$ - $O_2$  collisions were obtained by scaling the state-resolved  $O_2$ -O dissociation rates with the ratio of the global dissociation rate for diatom-atom and diatom-diatom collisions as a scale factor. Dissociation rate coefficients calculated on the basis of the formula proposed above and using the model of [32] are compared in the next section.

### 3. Validation of the model

To assess the choice of the parameter  $U$  we have calculated the state-specific dissociation rate coefficients using Eqs. (1) and (5) with different  $U$  values:  $U = D/(6k)$ ,  $U = 3T$ , weighted linear combination from [32] and our piecewise continuous polynomial function (6). The results are compared with those obtained by QCT calculations [21–23,25] and approximation formula from [25].

First let us consider dissociation reaction  $O_2(i) + O = 3O$ . State-specific dissociation rate coefficients for different vibrational levels and temperatures are presented in Figs. 1 and 2. As we can see, the original approximation of [25] works very well for temperatures below 10,000 K and especially good for high vibrational levels. This formula has however a disadvantage since it depends on the vibrational quantum number and thus is associated with the specific vibrational ladder. As to our model (6), it depends on the vibrational energy and therefore can be used for any model of vibrational spectrum. One can notice that our model gives an excellent agreement to the QCT calculations in the whole range of temperature and vibrational energy.

It is worth mentioning that using the constant parameter  $U = D/(6k)$  for oxygen results in a significant error in the whole temperature and vibrational energy range whereas  $U = 3T$  gives a satisfactory agreement for high temperature and intermediate and high states in the low-temperature range. Modification proposed in [32] gives better results than  $U = D/(6k)$  or  $U = 3T$  for intermediate vibrational states, but it does not describe

correctly the low states since for this levels it is very close to the model with  $U = D/(6k)$ .

It should be noted that the results reported in [22,23] are limited to the energy range of 0.001–3 eV. However the values given in [25] are assumed to be valid for energies 0.001–5.21 eV, and correspondingly the temperatures of 500–20,000 K. We compared the results for  $O_2/O$  state-specific dissociation rate coefficients from [25] with those reported in [33] and we have got a good qualitative and quantitative agreement in the whole temperature range.

Next let us discuss  $N_2(i) + N = 3N$  reaction. For this reaction we have no model similar to [32] for oxygen, that is why we compare our model (6) only with the traditional values, approximation and data from [25]. Results for different vibrational states and temperatures are presented in Figs. 3 and 4. As we can see, for nitrogen approximation formula of [25] is incorrect for temperatures exceeding 10,000 K. At the same time, as in the oxygen case, our function for  $U$  demonstrates the best agreement with trajectory calculations in the whole temperature and energy state range. Another important observation is that for temperatures greater than 8000 K and vibrational states with energy less than 7 eV, using values  $U = 3T$  and our formula yields practically identical results for dissociation rate coefficients. However  $U = 3T$  gives a significant error for low temperatures and for high energy states.

As we can see, for both  $O_2/O$  and  $N_2/N$  mixtures in the whole temperature range our function for  $U$  demonstrates the best agreement with results from [25] except the narrow energy interval close to the dissociation threshold where dissociation rate coefficients obtained by QCT calculations show exponential growing.

### 4. Heat bath calculations

In this section, the proposed model is applied to study vibrational–chemical relaxation of  $O_2/O$  and  $N_2/N$  mixtures under thermochemically non-equilibrium heat bath conditions. Taking

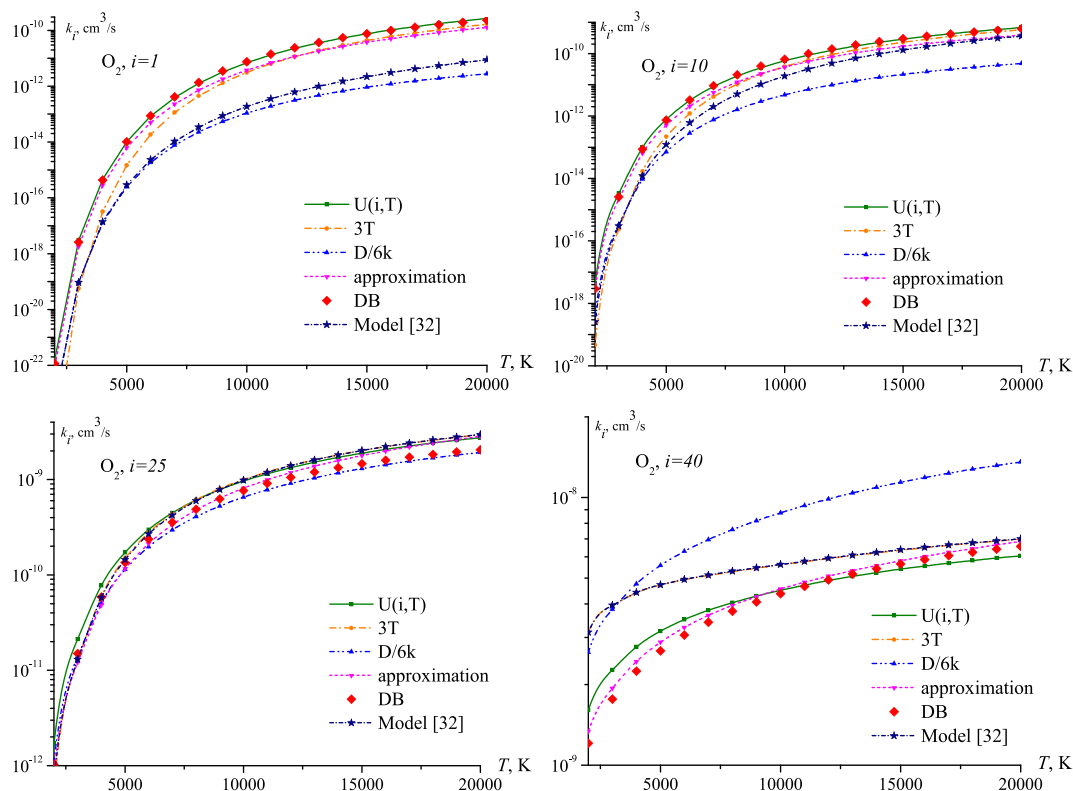


Fig. 1. Dissociation rate coefficients for fixed vibrational states in  $O_2$  as functions of temperature for different parameter  $U$ .

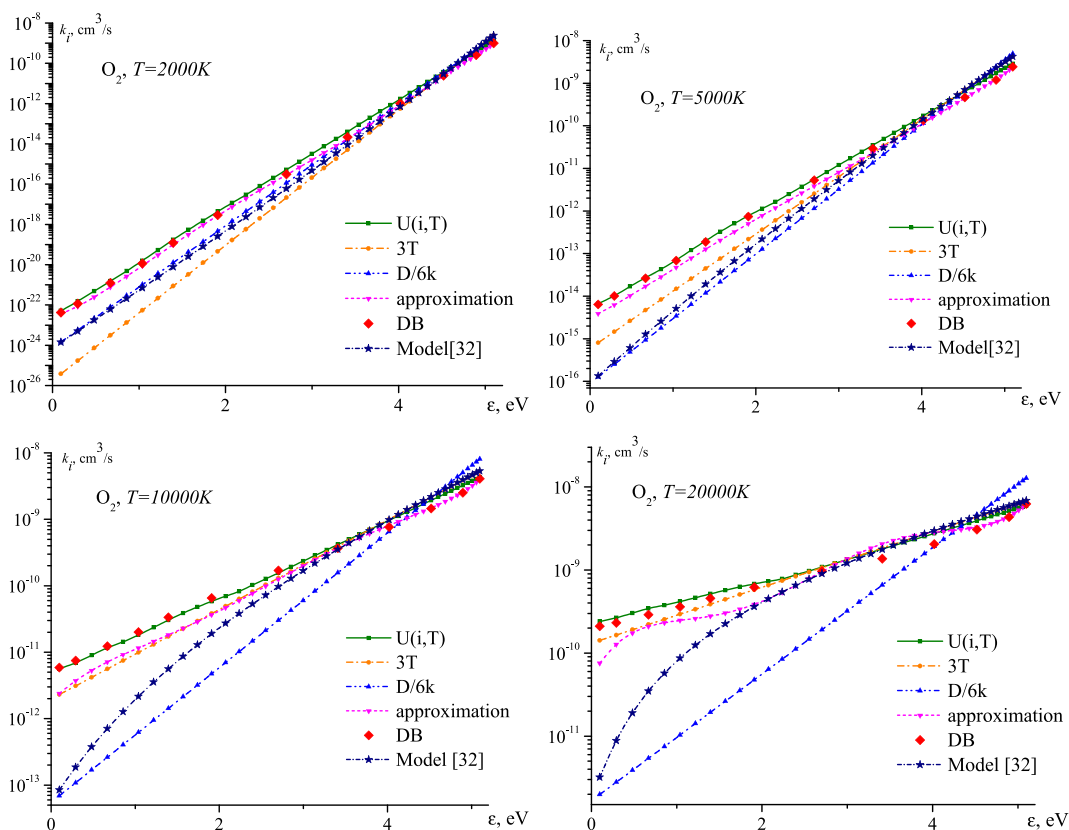


Fig. 2. Dissociation rate coefficients for fixed temperatures in  $\text{O}_2$  as functions of vibrational energy for different parameter  $U$ .

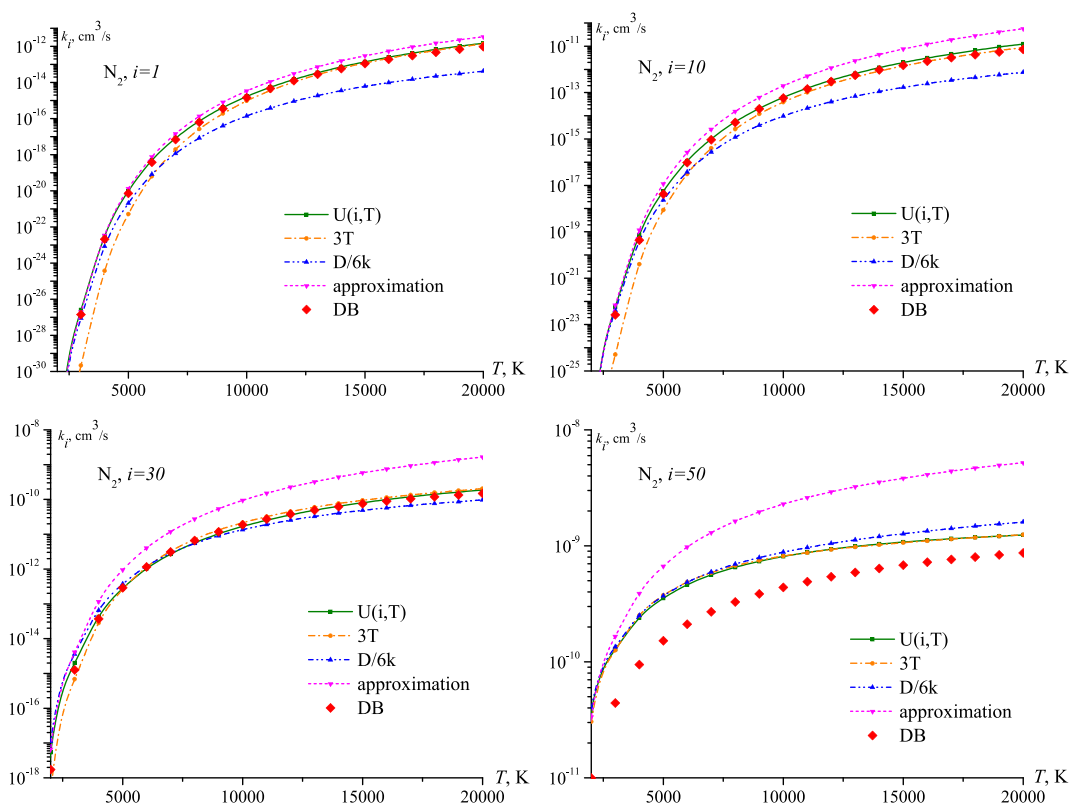


Fig. 3. Dissociation rate coefficients for fixed vibrational states in  $\text{N}_2$  as functions of temperature for different parameter  $U$ .

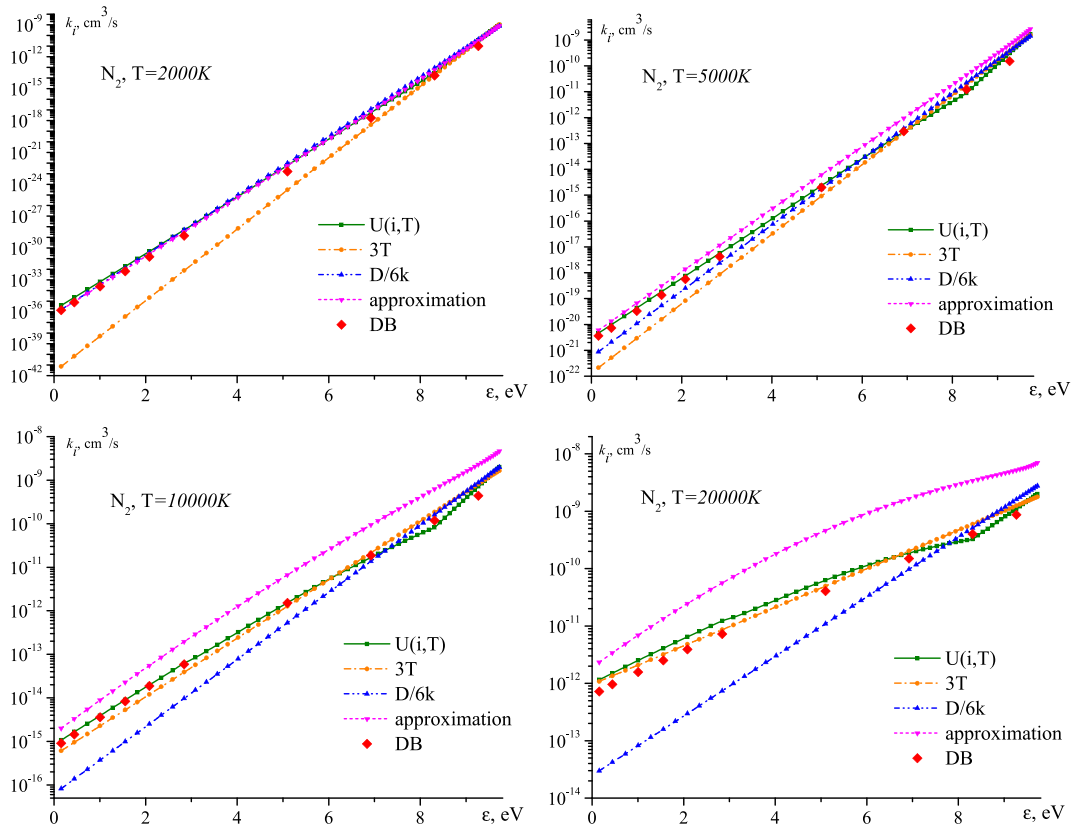


Fig. 4. Dissociation rate coefficients for fixed temperatures in  $N_2$  as functions of vibrational energy for different parameter  $U$ .

into account the kinetic processes of dissociation and recombination, VV vibrational energy transitions and VT(TV) exchanges between vibrational and translational energies, we investigate the evolution of the initial non-equilibrium vibrational distributions and gas parameters. The rate coefficients for vibrational energy transitions are calculated using the forced harmonic oscillator model (FHO) [2], dissociation rate coefficients are found with the use of the various parameter  $U$  of the Treanor-Marrone model considered above. For dissociation reactions in a collision with a molecule we use the following recommended parameters for the Arrhenius law [34]: for  $O_2 + O_2$  dissociation reaction,  $A = 5.33 \cdot 10^{-11} \text{ m}^3/\text{s}$ ,  $b = -1$ , and  $E = 59,370 \text{ K}$ ; for  $N_2 + N_2$ ,  $A = 4.1 \cdot 10^{-12} \text{ m}^3/\text{s}$ ,  $b = -0.62$ , and  $E = 113,500 \text{ K}$ . It is necessary to emphasize that in order to take into account molecule-molecule collisions, similarly to [34,32] we propose to adjust the parameters

in the Arrhenius law. To assess this assumption, we compare the state-specific  $O_2$ - $O_2$  dissociation rate coefficients calculated using the Arrhenius parameters proposed in [23,20] and variable parameter  $U(i, T)$  with the QCT data recently reported in [35] for the selected vibrational states and temperatures (see Fig. 5). One can see a rather good agreement, especially for the middle and high levels where dissociation is more efficient; the Arrhenius parameters given in [23] provide better agreement.

Simulations have been performed for the following test cases corresponding to strong initial heating of the gas:

1.  $O_2/O$ :  $p_0 = 1 \text{ atm}$ ,  $T_0 = 10^4 \text{ K}$ ,  $T_{v0} = 5 \cdot 10^3 \text{ K}$ ,  $n_{mol}(0) = n_{at}(0) = 0.5n_0$ ;
2.  $N_2/N$ :  $p_0 = 1 \text{ atm}$ ,  $T_0 = 1.5 \cdot 10^4 \text{ K}$ ,  $T_{v0} = 5 \cdot 10^3 \text{ K}$ ,  $n_{mol}(0) = n_{at}(0) = 0.5n_0$ .

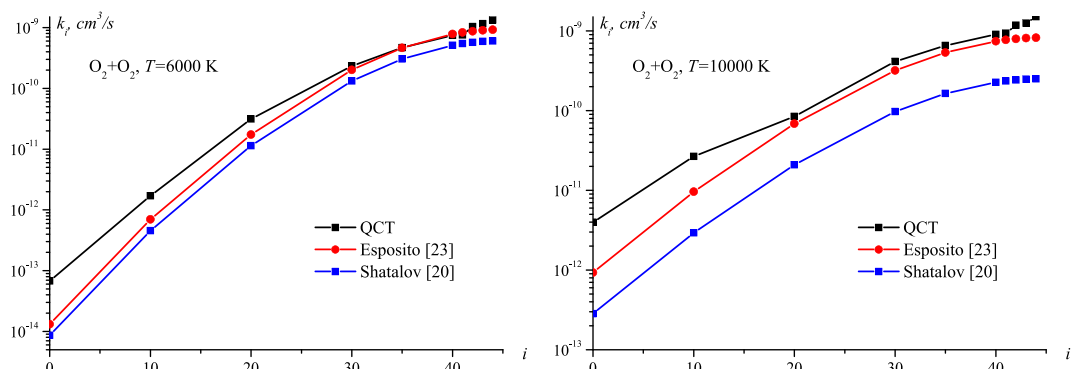
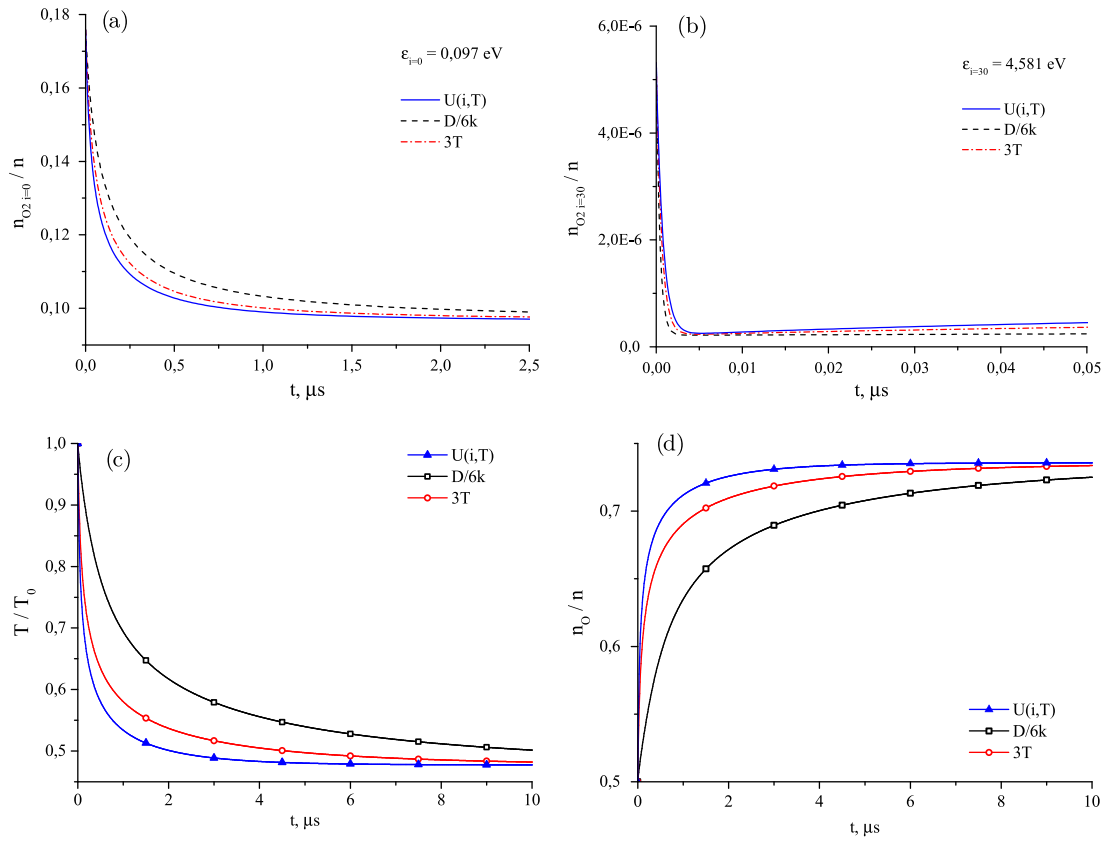
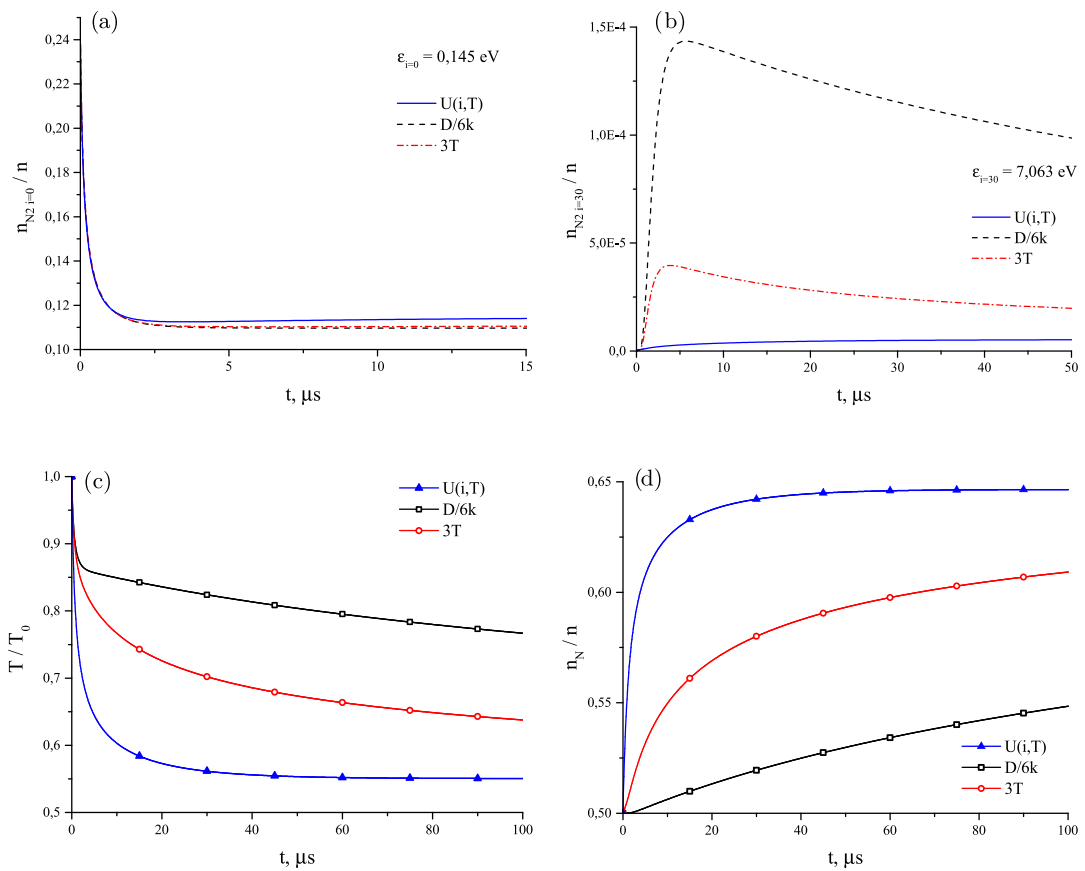


Fig. 5. Dissociation rate coefficients for fixed temperatures in  $O_2$ - $O_2$  collisions as functions of vibrational states. Comparison with QCT results.



**Fig. 6.** The vibrational level populations  $n_{O_2, i} / n$  (a–b), temperature  $T / T_0$  (c) and atomic molar fraction  $n_O / n$  (d) as functions of  $t$ .



**Fig. 7.** The vibrational level populations  $n_{N_2, i} / n$  (a – b), temperature  $T / T_0$  (c) and atomic molar fraction  $n_N / n$  (d) as functions of  $t$ .



At  $t = 0$  we assume that the vibrational level populations  $n_i(0)$  have the form of non-equilibrium Boltzmann distribution with the vibrational temperature  $T_{v0}$  different from  $T_0$ .

Level populations of oxygen and nitrogen molecules as functions of time are given in Figs. 6(a and b) and 7(a and b) for  $i = 0$  and  $i = 30$  and different  $U$ . Monotonic decrease of populations for zero levels is found for both  $O_2$  and  $N_2$  molecules as a result of dissociation and, in a greater degree, VT deactivation. Calculations show that for  $\epsilon_i^{O_2} > 0,849$  eV dissociation of molecules gives the main contribution to the reduction of the oxygen vibrational level populations. Populations  $n_{0,i}$  of levels with  $i > 0$  increase slightly with time due to TV and VV processes (Fig. 6(b)). In the case of nitrogen we can see following behavior of the level populations with  $i > 0$  (Fig. 7(b)): the rapid increase caused by TV vibrational excitation and then the decrease as a result of dissociation and deactivation of excited molecules. The choice of dissociation model has different effects on the population of various vibrational states: for oxygen molecules, using the modified model with  $U = U(i, T)$  leads to a less populated lower and middle levels, and more populated upper-levels compared to the other two parameters  $U = D/6k$  and  $U = 3T$ ; for nitrogen, the use of the proposed model yields a smaller number of molecules in all excited states ( $i > 0$ ).

The variation of gas temperature and number densities of oxygen and nitrogen atoms in  $O_2/O$  and  $N_2/N$  mixtures found for different parameter  $U$  is presented in Figs. 6(c and d) and 7(c and d) as a function of time. The comparisons of  $T/T_0$  and  $n_{at}/n$  for different  $U$  demonstrate that dissociation and vibrational relaxation proceed more efficiently for the proposed modification of parameter  $U$ . It is explained by higher values of state-specific dissociation rate coefficients for considered temperatures almost in the whole vibrational energy range except a few upper energy levels. However these top levels are weakly populated and do not make a great contribution to the total number of free atoms. Also it can be seen that using  $U = D/6k$  yields the slowest relaxation rate in both  $O_2/O$  and  $N_2/N$  mixtures. Linear function of temperature,  $U = 3T$ , gives better approximation to the results obtained with the new model but still under-predicts the rate of dissociation under high temperature conditions.

## 5. Conclusions

A generalization of the widely known Treanor–Marrone model suitable for the state-to-state flow simulations is proposed in the paper. The main peculiarity of the model is that we take into account possible dependence of its parameter  $U$  on the vibrational state of a dissociating molecule. This yields a correction to the traditional formula for the non-equilibrium factor. The function  $U(i, T)$  for  $N_2$  and  $O_2$  is obtained by fitting the state-specific dissociation rate coefficients calculated using the molecular dynamic methods. Rate coefficients computed on the basis of the proposed model are compared with those given by QCT simulations and also calculated with commonly used values of the parameter  $U$  in a wide range of energy states and temperatures. For both  $O_2$  and  $N_2$  dissociation reactions it is shown that conventional parameter values ( $U = D/6k, U = 3T$ ) and their simple modifications do not provide a satisfactory agreement with the QCT results. The most important difference is found for the low energy states. The generalized Treanor–Marrone model with the function  $U(i, T)$  provides a good agreement with QCT rate coefficients in the whole range of  $i$  and  $T$ . Moreover, this model can be applied for any vibrational ladder and does not require rescaling while switching from harmonic/anharmonic oscillator vibrational levels to those obtained by more rigorous models.

The developed model is assessed for the problem of space-homogeneous vibrational-chemical relaxation of  $O_2/O$  and  $N_2/N$

mixtures under strongly non-equilibrium heat bath conditions. Applying our model yields more efficient dissociation process compared to the commonly used parameter values  $U = D/6k$  or  $U = 3T$ . It is worth noting that  $U = 3T$  presents better accuracy for calculations than  $U = D/6k$  for the majority of temperatures, but still gives a discrepancy to the proposed generalized model, especially under high temperature conditions.

The implementation of the generalized Treanor–Marrone model to existing CFD solvers does not present any difficulty. Thus the proposed model can be efficiently used for simulations of strongly non-equilibrium flows such as shock waves, nozzle expansions and boundary layers.

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