

# Rotational Energy Relaxation Time for Vibrationally Excited Molecules

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**Abstract**—The effect of the vibrational level of a molecule on the relaxation time of its rotational energy is studied within the state-to-state kinetic theory approach. The rotational levels of molecules are described by the non-rigid rotator model, while the interaction between molecules is described by the variable soft sphere model. This model is used to calculate the  $N_2-N$ ,  $O_2-O$ , and  $NO-O$  collision cross sections for different vibrational and rotational levels of molecules. The rotational energy relaxation time is introduced for each vibrational level using the methods of the kinetic theory of nonequilibrium processes. The relaxation times are numerically calculated within a broad temperature range and compared with the relaxation time determined by the well-known Parker formula. The effect of various multi-quantum rotational transitions on the accuracy of the rotational relaxation time calculation is analyzed, and the convergence of the solution with an increase in the maximally possible number of quanta transmitted in the course of transition is demonstrated. It has been established that the vibrational state of a molecule has an appreciable effect on the rotational energy relaxation time in the state-to-state approach, and using the Parker formula may lead to a noticeable error in the calculation of state-to-state transport coefficients. The Parker formula provides a satisfactory agreement with the results obtained via the averaging of state-resolved relaxation times with a Boltzmann vibrational energy distribution in the one-temperature approximation at moderate temperatures.

**Keywords:** relaxation time, rotational energy, vibrationally excited state, state-to-state approach.

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## 1. INTRODUCTION

The modeling of non-equilibrium gas flows is important for aerospace applications, planetary atmosphere studies, and environmental problem solutions. The construction of a description for non-equilibrium flows necessitates the calculation of heat and diffusion fluxes and stress tensors, and the constitutive relationships between the flux terms contain the transport coefficients (heat conductivity, diffusion, and shear and bulk viscosity). In the kinetic theory of gases, transport coefficients are calculated within the generalized Chapman–Enskog method by solving the linear system of equations depending on the integral brackets, which are determined by the integral operator of fast processes [1]. To calculate the integral brackets, it is necessary to know the relaxation times of physicochemical processes, which are much faster than the change in the flow macroparameters.

This paper considers the flow of a gas mixture in the state-to-state approximation of the Chapman–Enskog method [1], in which elastic collisions and rotational energy transitions are classified among fast processes. In this case, the hierarchy of characteristic times has the form

$$\tau_{el} \lesssim \tau_{rot} \ll \tau_{vibr} < \tau_{react} \sim \theta. \quad (1)$$

Here,  $\tau_{el}$ ,  $\tau_{rot}$ ,  $\tau_{vibr}$ , and  $\tau_{react}$  are the relaxation times of translational, rotational, and vibrational degrees of freedom and the characteristic time of chemical reactions, respectively, and  $\theta$  is the characteristic time of change in the gas macroparameters. This relation between the times was confirmed by experiment [2].

When the rigorous methods of kinetic theory are used, the rotational energy relaxation time under condition (1) must be introduced for each vibrationally excited state of a molecule [1]. However, the experimental data for such relaxation times are currently unavailable. In practice, the rotational energy relaxation time is usually calculated using the Parker formula [3] derived under the assumption that  $\tau_{rot}$  is inde-

pendent of the vibrational spectrum of a molecule. This assumption appreciably simplifies the calculation of the relaxation time and, consequently, the transport coefficients in the state-to-state approximation.

The quantitative estimation of the effect produced by the account for the vibrational state of a molecule on the rotational energy relaxation time and the transport coefficients in the state-to-state approximation of the generalized Chapman–Enskog method has not been performed until now. The absence of such analysis does not allow us to estimate the accuracy of calculation for the transport coefficients, especially the bulk viscosity coefficient [4, 5]. The objective of this work was to study the rotational relaxation times for the collisions of molecules with atoms, taking into account the effect of vibrational excitation on the cross sections of the most probable elastic collisions, and to estimate the limits of applicability for the simplified models.

## 2. APPROXIMATION OF STATE-TO-STATE KINETICS

Let us introduce the macroparameters characterizing the flow of a non-equilibrium reacting mixture of gases in the state-to-state approximation [1], namely, the population of the  $i$ th vibrational level of molecules of the  $c$ th species  $n_{ci}(\mathbf{r}, t)$  ( $\mathbf{r}$  is the coordinate, and  $t$  is the time), the macroscopic gas velocity  $\mathbf{v}(\mathbf{r}, t)$ , and the temperature  $T(\mathbf{r}, t)$  (instead of which the total mixture energy per unit mass  $U(\mathbf{r}, t)$  may be considered). The mass density of a mixture of gases is  $\rho = \sum_{ci} m_c n_{ci}$ , where  $m_c$  is the mass of a particle of the  $c$ th species.

The system of equations for the macroparameters  $n_{ci}(\mathbf{r}, t)$ ,  $\mathbf{v}(\mathbf{r}, t)$ , and  $U(\mathbf{r}, t)$  can be written in the form [1]

$$\frac{dn_{ci}}{dt} + n_{ci} \nabla \cdot \mathbf{v} + \nabla \cdot (n_{ci} \mathbf{V}_{ci}) = R_{ci}, \quad c = 1, \dots, L, \quad i = 0, \dots, L_c, \quad (2)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (3)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0. \quad (4)$$

In this system,  $L$  is the number of chemical species in the mixture,  $L_c$  is the number of vibrationally excited states for molecules of the  $c$ th species,  $R_{ci}$  is the rate of change in the populations of vibrational levels due to slow processes (vibrational energy transfers and chemical reactions),  $\mathbf{P}$  is the stress tensor,  $\mathbf{V}_{ci}$  is the diffusion velocity for the  $c$ th-species molecules in the  $i$ th vibrational state, and  $\mathbf{q}$  is the total energy flux. The expressions for the flux terms in the state-to-state approximation are given in [1].

The flux terms in the first-order Chapman–Enskog method approximation corresponding to the model of a viscous heat conductive gas contain the transport coefficients, such as the heat conductivity, the viscosity, the bulk viscosity, and the diffusion and thermal diffusion coefficients. To perform the particular calculation of the transport coefficients, it is necessary to know the collision integrals and the rotational energy relaxation times, which are incorporated into the expression for the integral brackets [1]. In this work, the rotational relaxation time depending on the  $i$ th vibrational state is calculated.

## 3. ESTIMATION OF THE ROTATIONAL RELAXATION TIME

The departure from equilibrium in a system leads to the appearance of relaxation processes, which try to turn this system back to the total statistical equilibrium state. In the simplest theory of relaxation processes, it is usually assumed that the system is quiescent, and the gas with a non-equilibrium distribution over a degree of freedom represents a small admixture in a monoatomic gas, which is in equilibrium. In the case of such assumptions, the process of relaxation over the rotational degrees of freedom can be described by the equation [2]

$$\frac{dE_r(t)}{dt} = -\frac{E_r(t) - E_r^0}{\tau_{\text{rot}}}, \quad (5)$$

where  $E_r(t)$  is the energy of rotational degrees of freedom per unit volume, and  $E_r^0$  is the equilibrium value of this energy. Then the relaxation time  $\tau_{\text{rot}}$  can be written as

$$\tau_{\text{rot}} = \frac{E_r^0}{\left(\frac{dE_r(t)}{dt}\right)_{E_r=0}}. \quad (6)$$

The widely used Parker formula [3] was derived under the same assumptions as for Eq. (5). According to this formula, the number of collisions  $\zeta_c^{\text{rot}}$  required to attain equilibrium with respect to the rotational degrees of freedom for molecules of the  $c$ th species is

$$\zeta_c^{\text{rot}} = \frac{\zeta_c^\infty}{F_c(T)},$$

where the function  $F_c(T)$  has the form

$$F_c(T) = 1 + \frac{\pi^{3/2}}{2} \left(\frac{kT}{E_c^*}\right)^{-1/2} + \left(\frac{\pi^2}{4} + 2\right) \left(\frac{kT}{E_c^*}\right)^{-1} + \pi^{3/2} \left(\frac{kT}{E_c^*}\right).$$

Here,  $k$  is the Boltzmann constant,  $E_c^*$  is the interaction potential well depth, and the parameters  $\zeta_c^\infty$  are determined from the fitting of theoretical and experimental values. The formula for the rotational relaxation time  $\tau_c^{\text{rot}}$  for molecules of the  $c$ th species is as follows [1]:

$$\zeta_c^{\text{rot}} = \frac{4p\tau_c^{\text{rot}}}{\pi\eta_c}, \quad (7)$$

where  $\eta_c$  is the viscosity coefficient and  $p$  is the hydrostatic pressure. This relationship does not take into account the dependence of the relaxation time on the vibrational state of a molecule, so it is necessary to introduce a more rigorous definition.

Let us define the averaging operator in the state-to-state approximation as [1]

$$\langle F \rangle_{cidk} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2} \sum_{j'l', i'k'} \frac{s_j^{ci} s_l^{dk}}{Z_{ci}^{\text{rot}} Z_{dk}^{\text{rot}}} \int F_{cij} \gamma^3 \exp(-\gamma^2 - \mathcal{E}_j^{ci} - \mathcal{E}_l^{dk}) \sigma_{cd,ijkl}^{j'l'} d^2\Omega d\gamma. \quad (8)$$

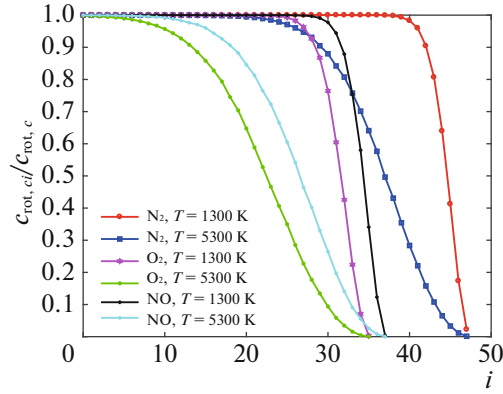
Here,  $j, l$  and  $j', l'$  are the rotational states of molecules of the  $c$ th and  $d$ th species before and after collision, respectively,  $Z_{ci}^{\text{rot}}$  is the partition function of rotational degrees of freedom for molecules of the  $c$ th species in the  $i$ th vibrational state,  $s_j^{ci} = 2j + 1$  is the statistical weight characterizing the degeneration of the state of a molecule with the rotational energy  $\epsilon_j^{ci}$ ,  $m_{cd} = m_c m_d / (m_c + m_d)$  is the reduced mass for particles of the  $c$ th and  $d$ th species,  $F_{cij}$  is a certain function depending on the velocity, the chemical species  $c$ , and the internal energy states  $i$  and  $j$ ,  $\gamma = (m_{cd}/(2kT))^{1/2} g$ ,  $\mathcal{E}_j^{ci} = \epsilon_j^{ci}/(kT)$  are the dimensionless relative velocity and rotational energy, respectively,  $\sigma_{cd,ijkl}^{j'l'}$  is the cross section of the most probable elastic collisions and the collisions with rotational energy transitions, and  $d^2\Omega$  is the solid angle, within which the relative velocity vector is located after collision.

The expression for the rotational energy  $\epsilon_j^{ci}$  has the form

$$\frac{\epsilon_j^{ci}}{hc} = B_i^c j(j+1) - D_i^c j^2(j+1)^2, \quad (9)$$

where  $h$  is the Planck constant,  $c$  is the light velocity, and the spectroscopic constants  $B_i^c$  and  $D_i^c$  are given in the work [6]. It can be seen that the rotational energy depends on the vibrational state of the  $i$ th molecule in the general case. For the rigid rotator model, the spectroscopic constants are equal to their equilibrium values  $B_i^c = B_c^c$  and  $D_i^c = D_c^c$ , and the rotational energy does not depend on the vibrational state.

Let us assume that the probability of collisions leading to the simultaneous change in the rotational and vibrational energies is small. This allows us to determine the rotational relaxation time  $\tau_{cidk}^{\text{rot}}$  for particles of



**Fig. 1.** Ratio of the specific rotational heat capacities  $c_{\text{rot}, ci}/c_{\text{rot}, c}$  as a function of the  $i$ th vibrational level at different temperatures.

the  $c$ th chemical species in the  $i$ th vibrational state upon the collision with particles of the  $d$ th species in the  $k$ th vibrational state as [1]

$$\frac{1}{\tau_{cidk}^{\text{rot}}} = \frac{4kn}{m_c c_{\text{rot}, ci}} \langle \Delta \mathcal{E}_{ci}^{\text{rot}} \Delta \mathcal{E}_{cidk}^{\text{rot}} \rangle_{cidk}. \quad (10)$$

Here,  $n = \sum_{c,i} n_{ci}$  is the number density of a gas mixture, and the dimensionless rotational energy variation upon collision  $\Delta \mathcal{E}_{cidk}^{\text{rot}}$  is determined as follows [1]:

$$\Delta \mathcal{E}_{cidk}^{\text{rot}} = \Delta \mathcal{E}_{ci}^{\text{rot}} + \tilde{\Delta} \mathcal{E}_{dk}^{\text{rot}},$$

$$\Delta \mathcal{E}_{ci}^{\text{rot}} = \frac{\epsilon_j^{ci} - \epsilon_j^{ci}}{kT}, \quad \tilde{\Delta} \mathcal{E}_{dk}^{\text{rot}} = \frac{\epsilon_l^{dk} - \epsilon_l^{dk}}{kT}.$$

The specific rotational heat capacity  $c_{\text{rot}, ci}$  of molecules of the  $c$ th species in the  $i$ th vibrational state is introduced in the state-to-state approximation [1]. In the rigid rotator model, the rotational energy does not depend on the vibrational state, so  $c_{\text{rot}, ci} = c_{\text{rot}, c}$  for any  $i$ . As a rule, the heat capacity of rotational degrees of freedom is assumed to be constant, i.e.,  $c_{\text{rot}, c} = k/m_c$ . For the more realistic non-rigid rotator model, the specific heat capacity of rotational degrees of freedom at a constant volume  $V$  depends on the temperature and the vibrational state, i.e.,

$$c_{\text{rot}, ci} = \left( \frac{\partial E_{\text{rot}, ci}}{\partial T} \right)_V,$$

and the specific rotational energy  $E_{\text{rot}, ci}$  of molecules of the  $c$ th species in the  $i$ th vibrational state is introduced by the expression

$$E_{\text{rot}, ci} = \frac{1}{m_c Z_{ci}^{\text{rot}}} \sum_j s_j^{ci} \epsilon_j^{ci} \exp\left(-\frac{\epsilon_j^{ci}}{kT}\right), \quad Z_{ci}^{\text{rot}} = \sum_j s_j^{ci} \exp\left(-\frac{\epsilon_j^{ci}}{kT}\right).$$

The ratios  $c_{\text{rot}, ci}/c_{\text{rot}, c}$  as functions of the vibrational state are plotted at fixed temperatures for air components in Fig. 1. It can be clearly seen that this ratio is close to unity for the lower states. However, the higher the temperature, the faster the decrease in the heat capacity with increasing vibrational level. To verify the calculation, the heat capacity  $c_{\text{rot}, c}$  found by averaging the heat capacity  $c_{\text{rot}, ci}$  with a Boltzmann distribution of populations  $n_{ci}$  over the vibrational energy was also estimated, and the result precisely coincided with  $c_{\text{rot}, c}$  determined by thermodynamics methods. When the distribution of  $n_{ci}$  deviates from the Boltzmann law, the rotator model may have an appreciable effect on the transport coefficients, and this fact is also mentioned in [4].

Writing the rotational relaxation time (Eq. (10)) in more details using the averaging operator (Eq. (8)) and substituting Eqs. (9) for the rotational energy change into it, results in the expression, in which all the parameters are specified except the collision cross section  $\sigma_{cd,ijkl}^{j'l'}$ . The form of the collision cross section

**Table 1.** Used constants

Collision	$\omega$	$c, \text{m}^2$	$\zeta_c^\infty$	$E_c^*, \text{J}$	$\theta_R, \text{K}$
N <sub>2</sub> –N	0.275	$240.3 \times 10^{-20}$	20.3898	$1.15127 \times 10^{-21}$	2.86256
O <sub>2</sub> –O	0.199	$114.7 \times 10^{-20}$	20.8478	$1.22331 \times 10^{-21}$	2.05706
NO–O	0.217	$135.4 \times 10^{-20}$	20.3898	$1.17846 \times 10^{-21}$	2.39326

depends on the intermolecular interaction model. The statistical model of an inelastic collision cross section is considered in this paper.

#### 4. STATISTICAL MODEL OF A NON-ELASTIC COLLISION CROSS SECTION

Realistic models of elastic and inelastic collision cross sections are necessary first of all for the modeling of rarefied gas flows by the direct statistical modeling (DSMC) method. The variable hard sphere (VHS) model based on the inverse power potential was proposed for elastic molecular collisions by G.A. Bird [7]. The VHS model is simple, but does not give correct values for the viscosity and diffusion coefficients at such a potential. To eliminate this restriction, K. Koura K. and H. Matsumoto [8] have introduced the variable soft sphere (VSS) model. Let us consider the VSS model in more details.

In the DSMC methods, molecular collisions are described by introducing the total cross sections  $\sigma_R(ij, \epsilon)$  of inelastic collisions as

$$\sigma_R = [\zeta(E) - \zeta_{j,l}(E)]\sigma_{el}(\epsilon). \quad (11)$$

Here,  $E$  is the total collision energy,  $\epsilon$  is the relative energy before collision, and  $\sigma_{el}(\epsilon)$  is the total elastic cross section. The functional form of  $\zeta_{j,l}(E)$  is determined as follows [9]:

$$\zeta_{j,l}(E) = C(E)c s_j^{ci} s_l^{dk} (E - \epsilon_j^{ci} - \epsilon_l^{dk})^{(1-\omega)}, \quad (12)$$

where  $\zeta(E)$  can be approximated at a good precision as

$$\zeta(E) = (4 - \omega)\Delta E_R(E)/E. \quad (13)$$

The function  $C(E)$  in Eq. (12) is specially determined for rotational inelastic collisions using the classic Parker energy function [3]. For each flux of molecules,  $C(E)$  takes the form

$$C(E) = 2\Delta E_R(E)/G_R(E). \quad (14)$$

The averaged rotational energy  $\overline{\Delta E_R}$  appearing upon the collision of molecules (with zero rotational energy) at a scattering angle  $\chi$  with the same approximation as introduced by Parker for the estimation of the number of rotational collisions gives the change in the rotational energy function as

$$\Delta E_R(\epsilon) = [\epsilon/2 + (2\pi/3)(\epsilon E_c^*)^{1/2} + (\pi^2/4 + 2)E_c^*]/\zeta_c^\infty. \quad (15)$$

The function  $G_R(E)$  determined by summing over a discrete rotational state may be approximated by means of integration over a continuous rotational state, as the characteristic rotational temperature  $\theta_R$  is small. For an elastic VSS cross section, the classic function  $G_R(E)$  takes the form

$$G_R(E) = \{c/[2(2 - \omega)(3 - \omega)(4 - \omega)(k\theta_R)^2]\}E^{4-\omega}. \quad (16)$$

For elastic collisions, the VSS model is used, i.e., the total elastic cross section is determined by the formula

$$\sigma_{el}(\epsilon) = c\epsilon^{-\omega}, \quad (17)$$

where the constants  $c$  and  $\omega$  are given in the table [10] for different gases.

The parameters of N<sub>2</sub>–N, O<sub>2</sub>–O, and NO–O collisions are also given in Table 1.

The dependence of the cross section calculated by the VSS model for the collision between a nitrogen molecule and a nitrogen atom on the rotational state at a fixed relative energy before collision in different vibrational states is plotted in Fig. 2. It can be seen that the cross section decreases with increasing rotational state by nearly 13% in the zero vibrational state and 3% in the 40th vibrational state. It can also be seen that the cross section decreases with increasing vibrational level. The change in the collision cross

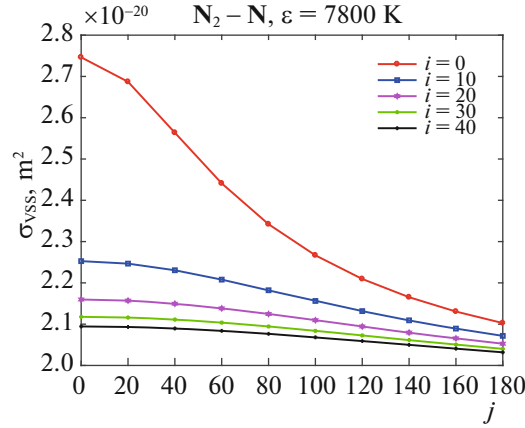


Fig. 2. Collision cross sections as functions of the  $j$ th rotational level at a fixed relative energy in different vibrational states.

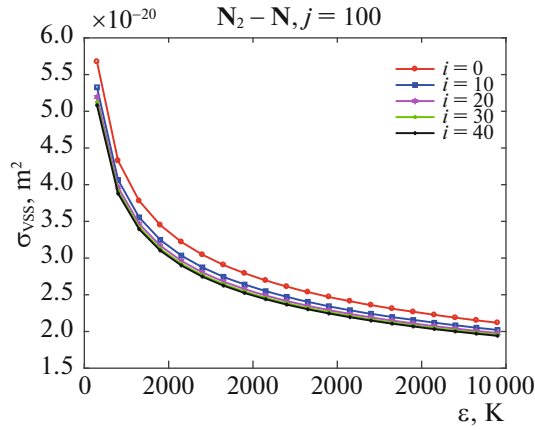


Fig. 3. Collision cross sections as functions of the relative energy at a fixed rotational level in different vibrational states.

section depending on the relative energy before collision (in Kelvins) in a fixed rotational state for different vibrational states is illustrated in Fig. 3. The cross section decreases with an increase in the relative energy.

## 5. CALCULATION OF THE ROTATIONAL ENERGY RELAXATION TIME

To simplify our calculations, we assume that the collision partner is an atom. Then Eq. (10) is reduced to the simpler expression

$$\frac{1}{\tau_{ci}^{\text{rot}}} = \frac{4kn}{m_c c_{\text{rot},ci}} \left\langle (\Delta \mathcal{E}_{ci}^{\text{rot}})^2 \right\rangle_{ci}. \quad (18)$$

In this case, the integral averaging operator (Eq. (8)) and the collision cross sections are independent of the internal energy states  $k, l$  of the collision partner. As a result,

$$\frac{1}{\tau_{ci}^{\text{rot}}} = \frac{4kn}{m_c c_{\text{rot},ci}} \left( \frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{j'} \frac{s_j^{ci}}{Z_{ci}^{\text{rot}}} \iiint (\mathcal{E}_{j'}^{ci} - \mathcal{E}_j^{ci})^2 \gamma^3 \exp(-\gamma^2 - \frac{\mathcal{E}_j^{ci}}{\epsilon}) \sigma_{cd,ij}^{j'}(\gamma, \chi, \epsilon) \sin \chi d\chi d\epsilon d\gamma. \quad (19)$$

The relationship used here is  $d^2\Omega = \sin \chi d\chi d\epsilon$ , where  $\chi$  is the scattering angle, and  $\epsilon$  is the azimuthal scattering angle. For the VSS model, the cross section does not depend on  $\epsilon$ , and the integration over this

angle gives  $2\pi$ . Moreover, the cross section determined by Eq. (11) has already been averaged over scattering angles, i.e.,

$$\sigma_R = 2\pi \int \sigma_{cd,ij}^{j'}(\gamma, \chi) \sin \chi d\chi.$$

This allows us to rewrite the relaxation time as

$$\frac{1}{\tau_{ci}^{\text{rot}}} = \frac{4kn}{m_c c_{\text{rot},ci}} \left( \frac{kT}{2\pi m_{cd}} \right)^{1/2} \sum_{jj'} \frac{s_j^{ci}}{Z_{ci}^{\text{rot}}} (\mathcal{E}_{j'}^{ci} - \mathcal{E}_j^{ci})^2 e^{-\mathcal{E}_j^{ci}} \int_{\gamma_{\min}}^{\infty} \gamma^3 e^{-\gamma^2} [\zeta(E) - \zeta_{j,j'}(E)] \sigma_{ei}(\epsilon) d\gamma. \quad (20)$$

Here, Eq. (11) is taken into account, and all the parameters independent of the velocity  $\gamma$  are placed outside the integral.

Let us consider the integral incorporated into this expression apart. Let us substitute Eqs. (13), (12), and (17) into this integral. In this case, the integral can be written as

$$\int_{\gamma_{\min}}^{\infty} \gamma^3 e^{-\gamma^2} \left[ (4 - \omega) \frac{\Delta E_R(E)}{E} - C(E) c s_j^{ci} (E - \mathcal{E}_j^{ci})^{(1-\omega)} \right] c \epsilon^{-\omega} d\gamma. \quad (21)$$

We take into account that the total collision energy has the form

$$E = \epsilon + \mathcal{E}_j^{ci} + \mathcal{E}_i^c$$

and also that  $\epsilon = (m_{cd} g^2)/2$  and  $\gamma = (m_{cd}/(2kT))^{1/2} g$ . We substitute these relationships into the expression for  $\Delta E_R(E)$ ,  $C(E)$ , and  $G_R(E)$  and, as a result, obtain the final expression for the rotational energy relaxation time for the VSS model.

Let multi-quantum rotational energy transitions  $j' = j \pm \Delta j$ , where  $\Delta j = 2, 4, 6, \dots$  for homonuclear molecules and  $\Delta j = 1, 2, 3, \dots$  for heteronuclear molecules, occur upon collision. Then the sum in Eq. (20) has the form

$$\sum_{jj'} = \sum_{j=0}^{N_{\text{rot},i}-1} \sum_{j-\Delta j \geq 0}^{j+\Delta j \leq N_{\text{rot},i}-1}, \quad (22)$$

where  $N_{\text{rot},i}$  is the number of rotational states for a molecule in the  $i$ th vibrational state.

The energy conservation law is written as follows:

$$\gamma^2 + \mathcal{E}_j^{ci} + \mathcal{E}_i^c = \gamma'^2 + \mathcal{E}_{j'}^{ci} + \mathcal{E}_i^c,$$

where  $\mathcal{E}_i^c$  is the dimensionless vibrational energy for molecules of the  $c$ th species in the  $i$ th state. The vibrational energy remains unchanged in the fast process (translational-rotational relaxation). Let  $\mathcal{E}_{j'}^{ci}$  be replaced to the left side

$$\gamma^2 + \mathcal{E}_j^{ci} - \mathcal{E}_{j'}^{ci} = \gamma'^2.$$

The right side of the equation is non-negative. Hence, its left side must also be non-negative. If  $j' < j$ ,  $\mathcal{E}_j^{ci} - \mathcal{E}_{j'}^{ci} > 0$ , i.e., the left side is always non-negative. Therefore, the relative velocity may have any value in this case, and then  $\gamma_{\min} = 0$ . If  $j' > j$ ,  $\mathcal{E}_j^{ci} - \mathcal{E}_{j'}^{ci} < 0$ , and there is the condition for  $\gamma$

$$\gamma \geq \sqrt{(\mathcal{E}_{j'}^{ci} - \mathcal{E}_j^{ci})}.$$

In this case,  $\gamma_{\min} = \sqrt{(\mathcal{E}_{j'}^{ci} - \mathcal{E}_j^{ci})}$ .

Since integral (21) cannot be analytically taken, it is calculated numerically using the method of Gauss–Kronrod quadratures for 15 points. It should also be noted that the calculation of sums (22) at great  $\Delta j$  require more essential computational efforts, as the number of rotational states in molecules is

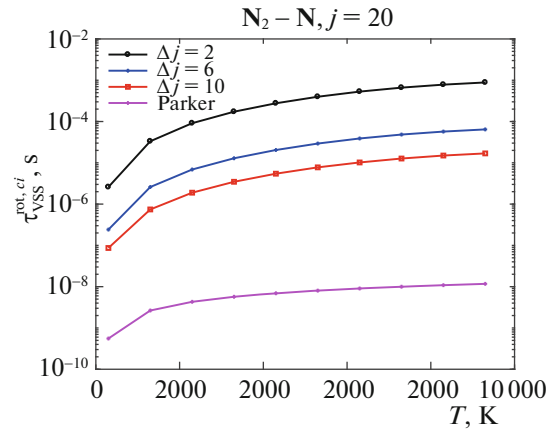


Fig. 4. Rotational energy relaxation time as a function of the temperature for different  $\Delta j$  at a fixed vibrational level.

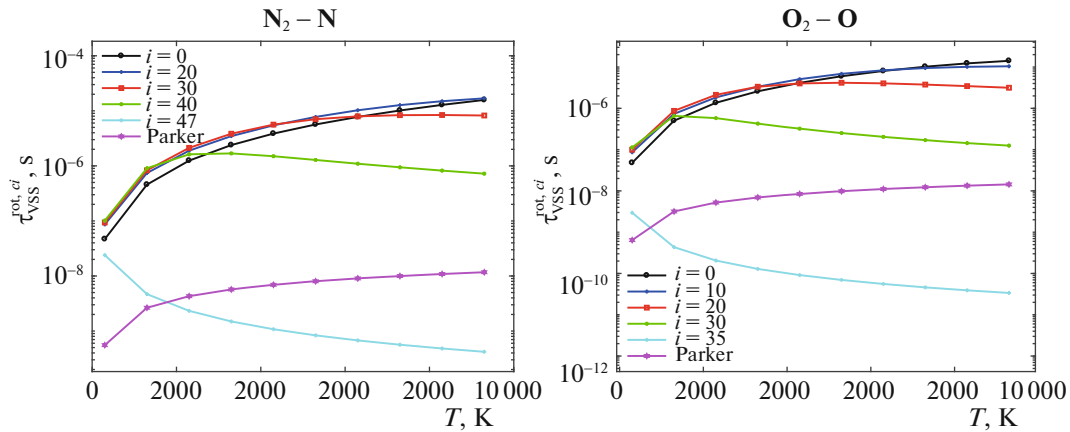


Fig. 5. Rotational energy relaxation time as a function of the temperature at different vibrational levels.

high. Thus, we have  $N_{\text{rot},0} = 197$  for  $\text{N}_2$ ,  $N_{\text{rot},0} = 168$  for  $\text{O}_2$ , and  $N_{\text{rot},0} = 176$  for  $\text{NO}$ . When the vibrational level grows, the number of possible rotational states decreases.

## 6. RESULTS

The results of calculating the rotational relaxation times depending on the vibrational state for the air components  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  are given below. Let us first estimate the effect of the number of possible multi-quantum transitions on the relaxation time. The relaxation times calculated numerically by Eq. (20) for the collision of a nitrogen molecule in the 20th vibrational state with a nitrogen atom are shown in Fig. 4. The maximum values of  $\Delta j$  were taken equal to 2, 6, and 10. It can be seen that the higher the number of rotational transitions taken into account, the closer our solution is to the Parker solution. The accuracy of calculation slightly grows with a further increase in  $\Delta j$ , but the solution requires more essential computational resources in this case. The further analysis is performed at  $\Delta j = 10$ .

The rotational energy relaxation times calculated for the  $\text{N}_2\text{-N}$  and  $\text{O}_2\text{-O}$  collisions and different vibrational states are compared with the relaxation time found by the Parker formula in Fig. 5. It can be seen that the relaxation time behaves in different ways at various vibrational levels. The temperature dependence may be non-monotonic for the upper levels. Such behavior is explained by the direct dependence of the relaxation time on the specific rotational heat capacity (see Fig. 1). At the lower levels, the heat capacity is nearly constant, but abruptly decreases with an increase in  $i$  and  $T$ . A decrease in the rotational relaxation time for the upper vibrational states is stipulated by a similar behavior of  $c_{\text{rot},ci}$ . The plot for the  $\text{NO-O}$  collision looks similar.



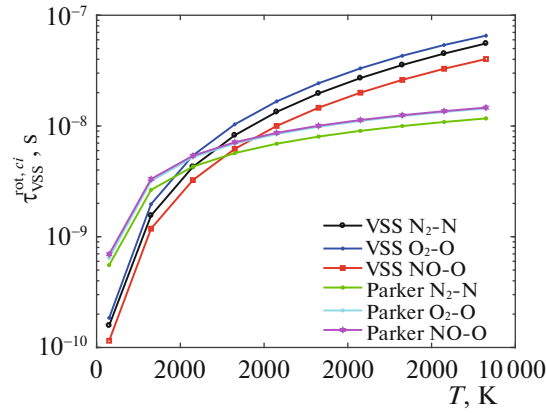


Fig. 6. Rotational energy relaxation time averaged over the vibrational levels as a function of the temperature.

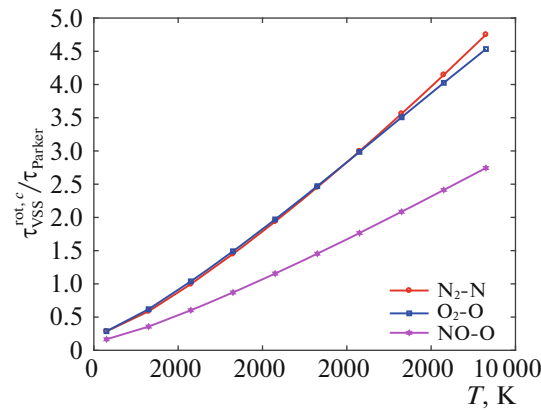


Fig. 7. Ratio of the averaged relaxation time to the Parker relaxation time as a function of the temperature.

It is of interest to compare the rotational energy relaxation time calculated by the Parker formula with  $\tau_c^{rot}$  found by averaging the state-resolved relaxation time (Eq. (18)) over the vibrational energy. To accomplish this, let us use the Boltzmann distribution with the gas temperature  $T$

$$\frac{c_{rot, c}}{\tau_c^{rot}} = \frac{1}{Z_c^{vibr}} \sum_i e^{-\mathcal{E}_i^c} \frac{c_{rot, ci}}{\tau_{ci}^{rot}}. \quad (23)$$

Here,  $Z_c^{vibr}$  is the partition function of vibrational degrees of freedom for a molecule of the  $c$ th species and  $\mathcal{E}_i^c$  is the dimensionless vibrational energy. From Figs. 6 and 7 it can be seen that the relaxation time averaged with the Boltzmann distribution over vibrational states at  $T < 10000$  K is rather close to the relaxation time calculated by the Parker formula. From Fig. 7 it can be seen that the ratio of relaxation times nearly linearly grows with temperature, and the calculations within a broader range of temperatures show that this ratio attains 17.6 at  $T = 30000$  K for the  $N_2-N$  collision, 14.1 for  $O_2-O$ , and 7.9 for  $NO-O$ . Since the Parker formula was derived for the one-temperature approximation and moderate temperatures, this result may be considered as the verification of this model for reliability under the condition of a weak deviation from thermal equilibrium. In the case of a strong deviation of distributions from the Boltzmann law, the averaged relaxation time may appreciably differ from the time calculated by the Parker formula.

The effect of the vibrational state of a molecule on the rotational energy relaxation time at different temperatures is illustrated in Fig. 8. To make the analysis more convenient, the ratio of  $\tau_{rot, ci}$  to the time  $\tau_{Parker}$  calculated by the Parker formula is given in the figures. It is obvious that the ratio of relaxation times strongly changes with an increase in the vibrational level. When the temperature increases, the application

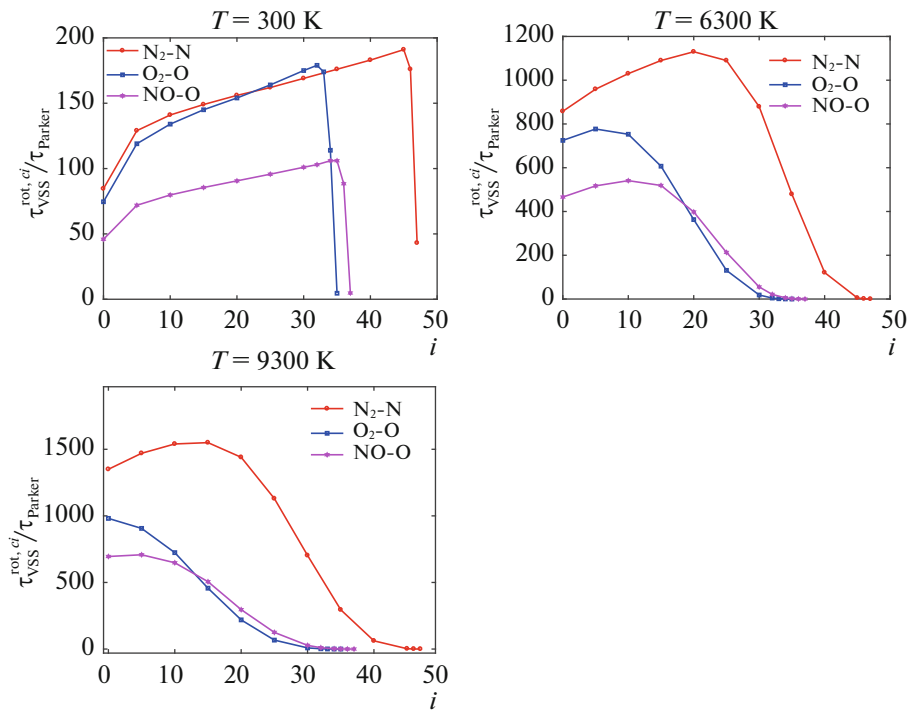


Fig. 8. Ratio of the rotational energy relaxation time to  $\tau_{\text{Parker}}$  as a function of the vibrational level at a fixed temperature.

of the Parker formula for the calculation of the rotational relaxation time at the lower and medium vibrational levels leads to an appreciable error. The best agreement was obtained for a NO molecule.

## 7. CONCLUSIONS

In this work, the rotational energy relaxation time has been calculated taking into account the vibrational state of a molecule. It has been established that the VSS interaction model gives more precise results, when a greater number of multi-quantum rotational transitions are taken into account. It has been established that the vibrational state of a molecule has an appreciable effect on the rotational energy relaxation time in the state-to-state approximation. Hence, the application of the Parker formula for the calculation of the state-resolved transport coefficients may lead to a noticeable error. Nevertheless, the Parker formula gives a satisfactory agreement with the results obtained by averaging the state-resolved relaxation times with the Boltzmann distribution over the vibrational energy in the one-temperature approximation at moderate temperatures.

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