

COMPARISON OF MODELS OF DISSOCIATION IN THE ABSENCE OF EQUILIBRIUM
 BETWEEN THE TRANSLATIONAL AND VIBRATIONAL DEGREES OF FREEDOM

V. G. Shcherbak

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In the one-temperature kinetic model diatomic molecules dissociate preferentially from the upper vibrational levels (within an energy kT of the dissociation limit) with the translational degrees of freedom in equilibrium. This model is based on the experimental fact that at low temperatures ($T \lesssim 8000$ K) the vibrational relaxation time is much smaller than the time required for dissociation.

In the case of reentry into the earth's atmosphere, dissociation in the shock wave occurs under conditions of incomplete vibrational relaxation over practically the entire thermally stressed part of the trajectory [1]. To calculate dissociation rates it is required to solve the dynamical problem of molecular collisions in order to determine the transition probabilities from the different vibrational levels and then the kinetic problem of determining the population densities [2]. However, for certain assumptions (the collision cross section does not depend on the vibrational levels of the colliding particles or on their relative velocity, chemical reactions do not disturb the Maxwellian velocity distribution, the population densities of the levels are quasi-Boltzmann) one can obtain corrections to the equilibrium dissociation rate constant.

Different models of dissociation have been used in the literature to interpret shock-tube experiments. In the present paper these models are used to determine heat transfer when a body reenters the earth's atmosphere.

1. Statement of the Problem. We consider the steady motion of an axisymmetric body in a viscous gas which is not in chemical or thermodynamic equilibrium. We will start from the model of a thin viscous shock layer. This model represents the asymptotic limit of the Navier-Stokes equations for large values of the Mach number, Reynolds number, and ratio of the densities behind and in front of the shock wave. These conditions are typical for the thermally stressed parts of reentry trajectories. Terms characterizing the boundary layer and inviscid shock layer in the hypersonic approximation are retained in the equations. In the altitude region $50 \lesssim H \lesssim 90$ km this model gives practically the same results near the body as the parabolic approximation to the Navier-Stokes equations, but are simpler and more convenient for numerical calculations [3]. The equations are written in the form (y is the distance from the body):

$$\begin{aligned} \rho u + \frac{\partial}{\partial y}(\rho v) &= 0, \quad \rho Du = -2p_1 + \frac{\partial}{\partial y} \left(\frac{\mu}{\text{Re}_\infty} \frac{\partial u}{\partial y} \right), \quad \frac{\partial p}{\partial y} = 0, \quad \frac{\partial p_1}{\partial y} = \rho u^2, \\ \rho c_p DT &= Dp + \rho \sum_{k=M} c_k D e_k^* + \frac{\partial}{\partial y} \left(\frac{\mu c_p}{\text{Re}_\infty \sigma} \frac{\partial T}{\partial y} - \frac{\rho}{\text{Re}_\infty} \sum_{k=M} c_k D_k \frac{\partial e_k^*}{\partial y} \right) - \\ &\quad - \sum_{i=1}^N h_i \dot{w}_i - \left(\sum_{i=1}^N c_{pi} I_i \right) \frac{\partial T}{\partial y} + \sum_{k=M} \left(\dot{w}_k e_k^* + I_k \frac{\partial e_k^*}{\partial y} \right), \\ \rho \left(\sum_{k=M} c_k e_k' \right) DT_v &+ \left(\sum_{k=M} I_k e_k' \right) \frac{\partial T_v}{\partial y} = \frac{\partial}{\partial y} \left[\frac{\rho}{\text{Re}_\infty} \left(\sum_{k=M} c_k D_k e_k' \right) \frac{\partial T_v}{\partial y} \right] + \sum_{k=M} \left(c_k \rho \frac{e_k^0 - e_k}{\tau_k} - \dot{w}_k e_k + R_k \right), \\ \rho Dc_i + \frac{\partial I_i}{\partial y} &= \dot{w}_i, \quad \frac{\mu}{\text{Re}_\infty} \frac{\partial m c_i}{\partial y} = \sum_{j=1}^N \frac{m^2}{m_j} S_{ij} (c_i I_j - c_j I_i), \\ p &= R_G \rho T \sum_{i=1}^N \frac{c_i}{m_i}, \quad \sum_{i=1}^N c_i = 1, \quad \sum_{i=1}^N I_i = 0, \end{aligned}$$

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$$D = v \frac{\partial}{\partial y}, \quad D_k = \frac{\mu}{\rho m} \sum_{i=1}^N \left(\frac{c_i}{m_i} S_{ik} \right)^{-1}, \quad e'_k = \frac{\partial e_k}{\partial T_v},$$

$$e_k^* = e_k^0 - e_k, \quad e_k = \frac{R_G}{m_k} \frac{\theta_k}{\exp(\theta_k/T_v) - 1}, \quad e_k^0 = e_k(T).$$

Here $V_{\infty x}$ and $V_{\infty y}$ are the physical components of the velocity vector; TT_0 and $T_v T_0$ are the translational and vibrational temperatures of the gas mixture of N components ($T_0 = V_{\infty}^2 / c_{p\infty}$); $\rho_{\infty} V_{\infty}^2$, ρ_{∞} , and $c_{p\infty} T_0 h$ are the pressure, density, and enthalpy of the gas mixture; μ_{∞} , $c_{p\infty}$, σ , m are the viscosity, specific heat, Prandtl number, and molecular mass of the mixture; c_i , m_i , $c_{p\infty} T_0 h_i$, $c_{p\infty} c_{p_i}$, $\rho_{\infty} V_{\infty} I_i$, $\rho_{\infty} V_{\infty} w_i / R$ are the mass concentration, molecular mass, specific enthalpy, heat capacity, normal component of the diffusion flux vector, and the rate of production of mass of the i -th component; $c_{p\infty} T_0 e_k$ and $T_0 \theta_k$ are the specific vibrational energy and the characteristic temperature of the k -th molecule; $V_{\infty} r_k / R$ is the relaxation time; $c_{p\infty} T_0 \rho_{\infty} V_{\infty} R_k / R$ is the source term; S_{ij} is the binary Schmidt number; R_G is the universal gas constant; V_{∞} is the magnitude of the velocity vector of the approach stream; all linear dimensions are measured in units of the radius of the blunt nose cone R ; $k = M$ implies a summation only over the molecules; the indices ∞ and w refer to parameters in the approach stream and on the surface of the body, respectively.

The boundary conditions on the surface of the body are derived from the condition that the fluid cannot penetrate the body, the no-slip condition, the assumption of heterogeneous recombination reactions, and the heat balance condition and have the form

$$u = v = 0, \quad I_i = -\rho k_{wi} c_i, \quad q = \frac{\varepsilon \sigma_B T_0^4}{\rho_{\infty} V_{\infty}^3} T_w^4,$$

$$q = \frac{\mu c_p}{\sigma R e_{\infty}} \frac{\partial T}{\partial y} - \sum_{i=1}^N h_i I_i + \sum_{k=M} \left(e_k^* I_k - \frac{\rho}{R e_{\infty}} c_k D_k \frac{\partial e_k^*}{\partial y} \right)$$

(ε is the emissivity of the surface, σ_B is the Stefan-Boltzmann constant, and T_w is the equilibrium temperature of the surface).

For the vibrational temperature on the surface we assume either the condition of equilibrium or that the wall is not a catalyst with respect to the internal degrees of freedom:

$$T_v = T_w; \quad (1.1)$$

$$\partial T_v / \partial y = 0. \quad (1.2)$$

We assume the generalized Rankine-Hugoniot boundary conditions in the shock wave.

We assume there are five components (N_2 , O_2 , NO , N , O) within the shock layer and dissociation, recombination, and exchange reactions occur between them.

2. Combined Effect of Vibrational Relaxation and Dissociation. The effect of vibrational relaxation on dissociation shows up in a change to the rate constant of dissociation

$$K^D(T, T_v) = K^D(T) V(T, T_v),$$

where $K^D(T)$ is the dissociation constant in thermodynamic equilibrium when $T_v = T$ and $V(T, T_v)$ is a function whose form depends on the assumed dissociation model. We put $V = 1$ in determining the rate of recombination. The effect of vibrational relaxation on the rate of exchange reactions was not taken into account.

The inverse effect of chemical reactions on vibrational relaxation was taken into account through the source term R_k [4]. As shown in [1], this effect is significant in the case of strong dissociation. We present the expression for the source term only for nitrogen molecules ($j = N_2$):

$$R_j = -m_j \left(\frac{\rho}{m} \right)^2 \left[\left(\sum_{i=1}^N K_{N-i}^R x_i \right) \left(e_{Dj} \frac{K_{pj}}{p} V_j x_j - e_{Rj} x_N^2 \right) + K_{N-NO}^R (e_{Dj} K_{px} x_j - e_{Rj} x_N x_{NO}) \right], \quad x_i = \frac{c_i m}{m_i}.$$

Here K_{N-i}^R , K_{N-NO}^R are the rate constants for recombination and exchange reactions; K_{pj} , K_p are the equilibrium constants; e_{Dj} , e_{Rj} are mean changes in the specific vibrational energy per dissociation and recombination. Assuming that the chemical reactions are independent of one another, we obtain $e_{Rj} = e_{Dj}$ in the case of complete thermodynamic equilibrium ($T_v = T$).

The vibrational relaxation time was calculated from the Millikan-White formula for a gas mixture with the correction for high temperature [5]. In the present paper the values of the reaction rates correspond to [6]. The method of numerical solution is analogous to [7].

3. Dissociation Models. Model 1. Dissociation occurs with a certain probability from any vibrational state and does not disturb the distribution of molecules over the vibrational levels. The probability distribution function is assumed to be exponential with a single adjustable parameter U having the dimensions of temperature and determining the degree of preferential dissociation from the upper levels in comparison with the lower levels [8]; $F(v) = \exp[-(T_D - E_v)/U]$ (T_D and E_v are the dissociation temperature and energy of level v in units of temperature).

Assuming a Boltzman distribution with temperature T_v , the function V has the form

$$V(T, T_v) = \frac{Q(T)Q(T_F)}{Q(T_v)Q(-U)}, \quad \frac{1}{T_F} = \frac{1}{T_v} - \frac{1}{T} - \frac{1}{U}$$

(Q is the partition function with respect to the vibrational degrees of freedom). For a harmonic oscillator it has the form

$$Q_h(T_v) = [1 - \exp(-\theta_h/T_v)]^{-1}.$$

We have for e_{Dk} and e_{Rk}

$$e_{Dk} = \frac{R_G}{m_R} \frac{\theta_k}{\exp(\theta_k/T_{Fk}) - 1}, \quad e_{Rk} = e_k(-U_k). \quad (3.1)$$

It was assumed in [8] that $U = T_D/g$. In the present paper we take $g = 2-6$.

Model 2. In [9] comparison with the solution of the classical dynamical problem for the reaction $O_2 + Ar \rightarrow 2O + Ar$ showed that $g \sim T^{-1}$ and it was assumed that $U = T/1.7$.

Model 3. The dissociations do not disturb the Boltzman distribution and occur when molecules suffer transitions from an effective vibrational level whose energy is a quantity βT below the dissociation limit [10]. Then

$$V(T, T_v) = \frac{Q(T)}{Q(T_v)} \exp\left[-(T_D - \beta T)\left(\frac{1}{T_v} - \frac{1}{T}\right)\right], \quad e_{Dk} = e_{Rk} = \frac{R_G}{m_R}(T_{Dk} - \beta T).$$

Experiments on nonequilibrium dissociation in shock tubes give $\beta = 3$ for N_2 and NO and $\beta = 1.5$ for O_2 .

Model 4. It was proposed in [11] that the rate of dissociation is given by the equations holding in thermodynamic equilibrium, but with the argument T_v instead of T . For example, if the rate constant is given by the Arrhenius formula then

$$K^D(T_v) = AT_v^n \exp(-E/T_v), \quad (3.2)$$

where A , n , and E are the preexponential factor, the power, and the activation energy (in degrees) calculated using chemical kinetics for $T_v = T$.

Model 5. In the formula for the rate constants of dissociation the argument T is replaced by the "average" temperature $T_a = \sqrt{TT_v}$, which to a certain degree takes into account the difference between T_v and T [12].

Models 4 and 5 are based only on general ideas about the role of vibrational excitation in the kinetics of chemical reactions. In these models e_D and e_R are calculated using the equations of model 1 with $U = T_D/6$.

4. Analysis of the Numerical Results. We consider a body moving along a trajectory reentering the earth's atmosphere. The conditions in the approach stream are assumed to correspond to the standard atmosphere. The emissivity of the surface is taken to be 0.8. The following characteristic temperatures and dissociation temperatures were assumed for N_2 , O_2 , and NO : $\theta_k = 3372, 2256, 2720$ K, $T_{Dk} = 113,000, 59,500, 75,500$ K. It was assumed that the surface of the body is not a catalyst with respect to heterogeneous recombination reactions.

Calculations were carried out for $R = 1$ and 0.25 m and for trajectories 1 and 2, which are quasisteady reentry trajectories with lift coefficients of 10^{-3} and $2 \cdot 10^{-4}$ m²/N, respectively [13]. They form a reentry corridor enclosing the possible quasisteady reentry trajectories.

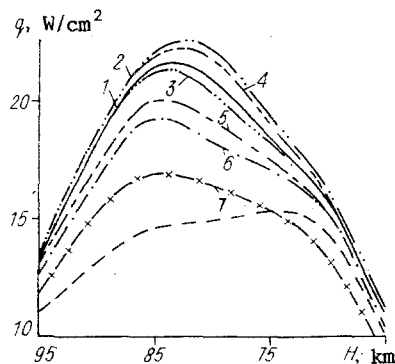


Fig. 1

In the figures curves 1-5 correspond to calculations using models 1-5 with the boundary conditions (1.1) for the vibrational temperatures and $g = 6$ in models 1, 4, 5; curve 6 corresponds to model 1 with $g = 2$, curve 7 corresponds to model 1 with $g = 2$ and the boundary condition (1.2), the dashed line corresponds to the assumption of thermodynamic equilibrium, i.e., all of the internal degrees of freedom are in equilibrium with one another and the vibrational temperature is equal to the translational temperature.

The altitude dependence of the heat flux is shown in Figs. 1 and 2 for trajectories 1 and 2 with $R = 1$ m and in Fig. 3 for trajectory 2 with $R = 0.25$ m. We consider the boundary condition (1.1). The different models of dissociation lead to differences of 20% in the heat flux and by 70-100°C in the equilibrium surface temperature. The differences between the results of models 2 and 3 do not exceed 10% in the heat flux and 30-50°C in the surface temperature, while for models 3 and 1 with $g = 6$ the corresponding differences are 5% and 10-20°C. Variation of g in model 1 between 2 and 6 changes the heat flux by up to 15% and the surface temperature by up to 50-70°C.

The assumption that the wall is not a catalyst with respect to the vibrational degrees of freedom [the boundary condition (1.2)] leads to a decrease in the heat flux. In the lower part of the trajectory, where there is strong recombination, the heat flux can turn out to be smaller than in calculations assuming equilibrium excitation of the internal degrees of freedom. Physically this is because internal energy accumulates as a result of recombination reactions and it is carried off with the flow. The boundary conditions considered here are limiting cases of the interaction between the surface of the body and the internal degrees of freedom of the molecules. The true values of the parameters for realistic surface properties should lie within the region defined by our results. This region depends on the conditions of flow and for the cases considered here extends up to 15% in the heat flux and up to 50°C in the surface temperature.

In the case of the boundary condition (1.2) the different models of dissociation lead to differences of ~15% in the heat flux and 50-80°C in the surface temperature. We note that at certain points of the trajectories the results obtained using models 2, 4, and 1 with $g = 6$ can exceed the values of the heat flux in the case of boundary condition (1.1) and models 5 and 1 with $g = 2$. The total uncertainty associated with the different boundary conditions and different models of dissociation is as large as 30-35% in the heat flux and 90-150°C in the equilibrium surface temperature.

The heat flux calculated using model 5 (curve 5) agrees with the results obtained using model 1 with $g = 3$. The heat flux drops in models 4 and 5 when e_p and e_r are calculated taking into account the effect of chemical reactions on the vibrational relaxation using (3.1) with $g = 3$ and 2. For example, in model 5 with $g = 3$ the heat flux lies somewhat above the results found using model 1 with $g = 2$ (curve 6), while for $g = 2$ the heat flux lies somewhat below these results. For model 4 with $g = 2$ the results lie above those obtained using model 3 (curve 3).

The translational and vibrational temperature profiles and the concentration of atomic oxygen are shown in Figs. 4 and 5 at $H = 85$ km (trajectory 2, $R = 1$ m). The relative positions of the profiles for the different models of dissociation remain the same for other points on the trajectory.

The translational temperature profiles calculated using models 2, 4 and 1 (with $g = 6$), and 3 are close. For the vibrational temperature profiles the results are close for models

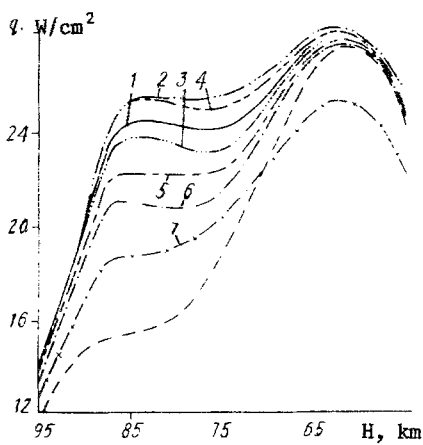


Fig. 2

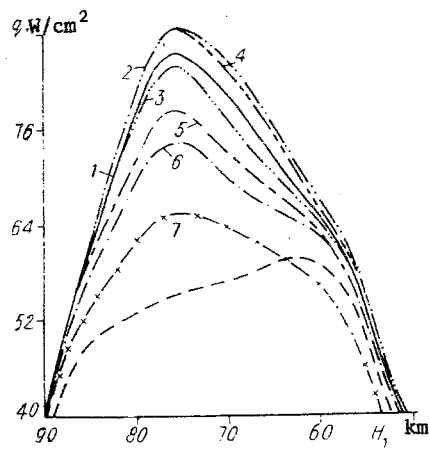


Fig. 3

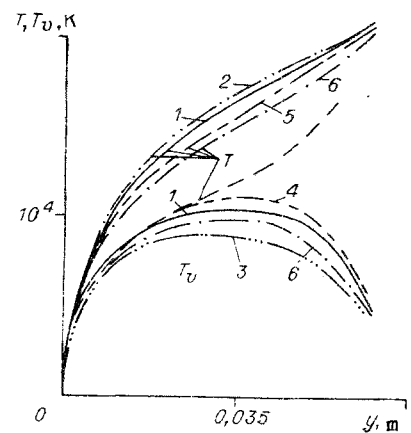


Fig. 4

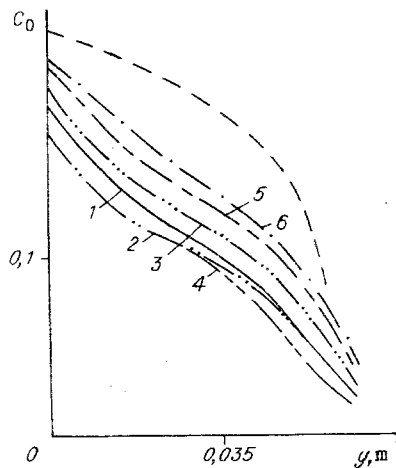


Fig. 5

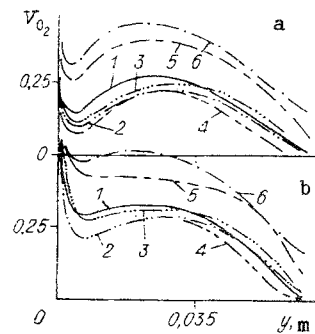


Fig. 6

1 (with $g = 6$), 2, 3, and 5. The differences in translational temperatures inside the shock layer reach $\sim 2000^\circ\text{C}$, while the differences in vibrational temperature reach $\sim 2500^\circ\text{C}$. The effect of the dissociation model on the departure of the shock wave is not significant. For models 1 ($g = 3$) and 5 the translational temperature profiles closely correspond with one another, but the vibrational temperature for model 1 ($g = 3$) is higher and lies between curves 1 and 6.

The degree of dissociation increases as the parameter g decreases in models 1, 4, and 5. Dissociation is most hindered in models 2 and 4. In the upper part of the trajectories the concentrations of atoms differ by several times for the different models.

It is interesting to note that if in models 4 and 5 we replace the argument in (3.2) for all reactions (including inverse and exchange reactions) and not only for dissociation reactions, then the heat flux and temperature profiles will be close to curves 4 and 5, respectively, except for the concentration profiles.

Figure 6 shows profiles of the function V for a dissociation constant of oxygen calculated for $R = 1$ m (a: trajectory 1, $H = 86$ km, $V_\infty = 7.5$ km/sec; b: trajectory 2, $H = 85$ km, $V_\infty = 7.8$ km/sec). We have $V = 1$ on the surface of the body.

We note that in model 4 the rate of dissociation decreases by several orders of magnitude when the vibrational temperature differs significantly from the translational temperature (near the shock wave and in the upper part of the trajectory).

Therefore use of the different models of dissociation with variable g (the parameter characterizing the probability of dissociation from the different vibrational levels) leads to larger uncertainties in the values of the heat flux than the limiting boundary conditions describing the interaction between the surface of the body and the internal degrees of freedom of the molecules. Putting $g = 6$ in correspondence with [14], the maximum difference in the heat flux for models 1-4 is less than 10%.

LITERATURE CITED

1. A. G. Tirsii and V. G. Shcherbak, "Combined effect of vibrational relaxation and dissociation on the supersonic motion of a blunt body through a viscous gas," *Prikl. Mekh. Tekh. Fiz.*, No. 6 (1990).
2. E. V. Stupochenko, S. A. Losev, and A. I. Osipov, *Relaxation Processes in Shock Waves* [in Russian], Nauka, Moscow (1965).
3. V. G. Shcherbak, "Calculation of the nonequilibrium flow around blunt bodies using simplified models," in: *Simulation in Mechanics* [in Russian], Vol. 2, No. 4, Novosibirsk (1988).
4. C. E. Treanor and P. V. Marrone, "Effects of dissociation on the rate of vibrational relaxation," *Phys. Fluids*, 5, No. 9 (1962).
5. C. Park, "Problems of rate chemistry in the flight regimes of aeroassisted orbital transfer vehicles," AIAA paper No. 1730, New York (1984).
6. S. W. Kang and M. J. Dunn, "Hypersonic viscous shock layer with chemical nonequilibrium for spherically blunted cones," *AIAA J.*, 10, No. 10 (1972).
7. V. G. Shcherbak, "On the boundary conditions on the shock wave for supersonic flow around a body," *Prikl. Mekh. Tekh. Fiz.*, No. 1 (1989).
8. P. V. Marrone and C. E. Treanor, "Chemical relaxation with preferential dissociation from excited vibrational levels," *Phys. Fluids*, 6, No. 10 (1963).
9. B. V. Kuksenko and S. A. Losev, "Vibrational excitation and dissociation of diatomic molecules induced by atom-molecule collisions in a gas at high temperature," *Dokl. Akad. Nauk SSSR*, 185, No. 1 (1969).
10. S. A. Losev and N. A. Generalov, "Vibrational excitation and dissociation of oxygen molecules at high temperature," *Dokl. Akad. Nauk SSSR*, 141, No. 5 (1961).
11. K. L. Wray, E. V. Feldman, and P. F. Lewis, "Shock tube study of the effect of vibrational energy of N_2 on the kinetics of the $O + N_2 \rightarrow NO + N$ reaction," *J. Chem. Phys.*, 53, No. 11 (1970).
12. C. Park, "Assessment of two-temperature kinetic model for describing dissociating and weakly-ionizing nitrogen," AIAA paper, No. 1347, New York (1986).
13. L. M. Shkadov, R. S. Bukhanova, V. F. Illarionov, and V. P. Plokhikh, *Mechanics of Optimum Spatial Motion of Aircraft in the Atmosphere* [in Russian], Mashinostroenie, Moscow (1972).
14. M. Camac and A. Vaughan, " O_2 dissociation rates in $O_2 + Ar$ mixtures," *J. Chem. Phys.*, 34, No. 2 (1961).

FORMATION OF A NONEQUILIBRIUM ENERGY DISTRIBUTION OVER VIBRATIONAL DEGREES OF FREEDOM OF THE H_2O MOLECULE AS WATER VAPOR EXPANDS IN A SUPERSONIC NOZZLE

A. B. Britan, V. A. Levin,
A. M. Starik, and A. N. Khmelevskii

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The study of the kinetics of inelastic collisions and the construction of models of vibrational energy transfer in mixtures containing water vapor are needed not only because of interest in the possibility of obtaining emission in the far-infrared and submillimeter ranges using a (H_2O-H_2-He) mixture as the active medium [1-7] and modeling the characteristics of such lasers, but also for the analysis of nonequilibrium processes in chemically reactive gases ($H_2 + O_2$) with excited vibrational degrees of freedom and in the passage of strong IR radiation through the atmosphere [8, 9]. Moreover, water vapor is always present in the products of combustion of hydrocarbons in air, which are used in CO_2 gas-dynamic lasers (GDLs) [10].

A small number of experimental papers have been devoted to the kinetics of vibrational energy transfer in mixtures based on water vapor. The excitation and subsequent relaxation

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