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ROTATIONAL EXCITATION OF DIATOMIC MOLECULES IN COLLISIONS

WITH ATOMS

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The rate constants for rotational excitation, the coefficient of RT diffusion for the Ar-N₂ system, and the rotational relaxation time in N₂ are calculated using the quasiclassical approximation.

The growing interest in analytical methods for calculating the rotational excitation of molecules has been aroused by research on the possibilities of creating lasers based on rotational transitions, experiments with expanding jets, studies of the contribution of rotational degrees of freedom to the transport properties of a gas and the behavior of a molecular gas in a magnetic field, research in molecular acoustics, spectroscopy, etc. In [1, 2], a method based on a rigorous quasiclassical approximation to the T scattering operator in terms of action-angle variables was proposed for calculating the vibrational-rotational interaction of particles. In our opinion, this method is more accurate and efficient than previously proposed methods (see, for example, the review in [3]), if we are talking about three-dimensional collisions of complicated objects (polyatomic molecules, clusters) with one another or with a surface. The good accuracy of a simplified variant of this theory (eikonal approximation) achieved in calculations of the differential cross sections of electronic [1] as well as vibrational-rotational [2] excitations with small changes in quantum numbers was demonstrated.

In this work, we continue the investigation of the theory and we perform specific calculations of the rotational excitation of diatomic molecules by atoms using the proposed method for typical gasdynamic conditions. We show that for the model of a plane rotator the increment to the classical action of the atom + rotator system, which determines the transition amplitude, contains only terms that are quadratic with respect to the potential. We include approximately the spatial configurations of the rotator. The cross sections obtained

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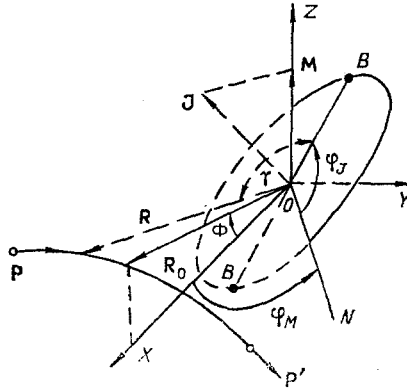


Fig. 1. Collision of an atom with a diatomic molecule: φ_J, φ_M) angular variables of the target in a fixed system of coordinates XYZ; γ) angle between the radius vector of the relative position of the colliding particles R and the axis of the molecule BB.

are used to calculate the rate constants of RT processes, the diffusion coefficients in the Fokker-Planck relaxation equations, and the rotational relaxation time τ_R in N_2 . The latter permits calculating the coefficient of bulk viscosity, as well as other transport coefficients in rotationally excited nitrogen, using the Mason-Monchik approximation.

1. General Expressions for the Rotational Excitation Profile for a Rigid Rotator. We start from the following expression for the amplitude of rotational excitation $j_m \rightarrow j'm'$ in the eikonal approximation [2]:

$$f_{jm}^{j'm'}(p \rightarrow p') = -\frac{ik}{2\pi} \int dR_0 \exp\left(\frac{i}{\hbar} \Delta \cdot R_0\right) \Gamma_{jm}^{j'm'}(R_0) \quad (1)$$

$$\Gamma_{jm}^{j'm'}(R_0) = \int_0^{2\pi} \frac{d\varphi_{0J}}{2\pi} \int_0^{2\pi} \frac{d\varphi_{0M}}{2\pi} \exp(i\Delta j\varphi_{0J} + i\Delta m\varphi_{0M}) \left\{ \exp\left[\frac{i}{\hbar} \Delta S(R_0, \varphi_{0J}, \varphi_{0M})\right] - \delta_{jj'} \delta_{mm'} \right\} \quad (2)$$

In these equations j, m are the orbital and magnetic quantum numbers, respectively; $\Delta j = j - j'$, $\Delta m = m - m'$; $\varphi_{0J} = \varphi_J(t=0)$, $\varphi_{0M} = \varphi_M(t=0)$ are the angular variables of the rotator at the moment of greatest approach of the particle; $R_0 = R(t=0)$ (see Fig. 1); $\Delta = p - p'$ is the momentum transferred; $\Delta S = S - S_0$ is the increment to the classical action; $\delta_{jj'}$ is Kronecker's symbol; and k is the modulus of the wave vector.

We are examining a gas at room and higher temperatures (Fig. 1) when the solution of the Hamilton-Jacobi equation is sought in the form [4]

$$S = \sum_{p=0}^{\infty} S_p(\varphi, J_i; R, p_i),$$

$$J = \hbar(n + \delta), \quad J = (J, M), \quad n = (j, m),$$

where J_L, p_L are the generalized momenta on a section of the eikonal trajectory L ; $R(t), \varphi(t)$ are its conjugate coordinates; $\varphi = (\varphi_J, \varphi_M)$. We write the system of equations for S_p :

$$\begin{aligned} \frac{\partial \mathcal{H}_0(J_i)}{\partial J_i} \cdot \frac{\partial S_p}{\partial \varphi} + v_i \cdot \frac{\partial S_p}{\partial R} &= \mathcal{H}^p(\varphi, J_i; R, p_i), \\ S_0 &= p_i \cdot R + J_i \cdot \varphi, \\ \mathcal{H}^1(\xi, z) &= V(\xi, z), \end{aligned} \quad (3)$$

$$\mathcal{H}^2(\xi, z) = \{S_1, V\} + \frac{1}{2} \{S_1, \{S_1, \mathcal{H}_0\}\}, \dots$$

In Eqs. (3), $\xi = (R, \varphi)$; $z = (p, J)$; \mathcal{H}_0 is the Hamiltonian of the rotating molecule; V is the interaction potential of the colliding particles; the symbol $\{X, Y\}$ indicates the clas-

sical Poisson bracket with respect to the variables ξ, z and, in addition, after these brackets are calculated, we must set $z = \mathbf{z}_L = (\rho_L, J_L)$. Below, we assume that the trajectory of relative motion lies in a plane parallel to the XY plane and the point of closest approach lies in the XZ plane. The equation for S_1 is integrated simply as

$$\Delta S_1 = - \int_{-\infty}^{+\infty} d\tau V[\mathbf{R}(\tau), \varphi(\tau)] \quad (4)$$

and, in addition, for $\mathbf{R}(\tau), \varphi(\tau)$ we use the eikonal approximation

$$\mathbf{R}(\tau) = \mathbf{R}_0 + \mathbf{v}_{i,j}\tau, \quad \varphi(\tau) = \varphi_0 + \nu_{i,j}\tau, \quad \nu = \frac{\partial \mathcal{H}_0(\mathbf{J})}{\partial \mathbf{J}} \quad (5)$$

In the next higher orders, we shall include only the flat configurations of the rotator, when in the course of a collision the plane of rotation of the rotator coincides with the plane of relative motion of the colliding particles, i.e., $\varphi = (0, \varphi), \mathbf{J} = (0, J)$.

Using the relations $\partial S_1 / \partial \mathbf{J} = \partial V / \partial \mathbf{J} = 0, \mathcal{H}_0(\mathbf{J}) = (B_e / \hbar^2) J^2$, we obtain the following expression for \mathcal{H}^2 :

$$\mathcal{H}^2 = -\frac{1}{2} \left(\frac{\partial S_1}{\partial \varphi} \right)^2 \frac{\partial^2 \mathcal{H}_0}{\partial J^2} = \frac{B_e}{\hbar^2} \left(\frac{\partial S_1}{\partial \varphi} \right)^2$$

It is clear that all subsequent \mathcal{H}^p ($p > 2$) vanish by virtue of the quadratic dependence of \mathcal{H}_0 on J . For this reason, we obtain the following expression for the increment to the classical action of a plane rigid rotator on the incoming branch of the trajectory:

$$\Delta S_2^i(t) = -\frac{B_e}{\hbar^2} \lim_{T_0 \rightarrow \infty} \int_{-T_0}^t d\tau \left[\frac{\partial}{\partial \varphi_i} \int_{-T_0}^{\tau} d\tau' V(\mathbf{R}_i(\tau'), \varphi_i(\tau')) \right]^2$$

$$\mathbf{R}_i(\tau') = \mathbf{R}_0 + \mathbf{v}_i \tau', \quad \varphi_i(\tau') = \varphi_0 + \nu_i \tau', \quad \varphi_i(\tau) \equiv \varphi_i$$

Making the substitution $\varphi_0 = \varphi_0 + \nu_i \tau'$ and differentiating with respect to the upper limit $\varphi_i = \varphi_i(\tau)$ in the inner integral, we obtain

$$\Delta S_2^i(t) = -\frac{B_e}{\nu_i^2 \hbar^2} \lim_{T_0 \rightarrow \infty} \int_{-T_0}^t d\tau V^2[\mathbf{R}_i(\tau), \varphi_i(\tau)]$$

If we introduce instead of ν_i and ν_f the average rotational frequency of the rotator $\nu_s = (\nu_i + \nu_f)/2$, then the increment to the action is written in the form

$$\Delta S = \Delta S_1 + \Delta S_2 \quad (6)$$

$$\Delta S_2 = -\frac{B_e}{\nu_s^2 \hbar^2} \int_{-\infty}^{+\infty} d\tau V^2[\mathbf{R}(\tau), \varphi(\tau)] \quad (7)$$

In expressions (4) and (7) we can substitute the more accurate smooth approximations $\mathbf{R}(\tau), \varphi(\tau)$ for the eikonal trajectories (5) with a "break".

Next, we shall examine the system $A + B_2$ and we shall select the interaction potential in the form

$$V(R, \gamma) = W_0(R) + V_1(R, \gamma), \quad V_1(R, \gamma) = W_2(R) \cos^2 \gamma \quad (8)$$

where γ is the angle between the radius vector \mathbf{R} and the axis of the rotator (Fig. 1). Instead of the complicated formula (1), we shall use below its simplified variant [2]:

$$f_{jm}^{i'm'}(p \rightarrow p') = f_0(E, \Theta) \Gamma_{1,j'm'}^{i'm'}[R_0(\Theta), \Theta = 0] \quad (9)$$

where $f_0(E, \Theta)$ is the elastic scattering amplitude for the potential $W_0(R)$ as a function of the scattering angle Θ and the energy E of relative motion of the colliding particles in the initial channel; $\Gamma_{1,j'm'}^{i'm'}$ is the inelastic scattering profile, which is defined by Eq. (2), if for ΔS we use expressions (6), (4), and (7), in which we must substitute V_1 for V . In this case, the dependence of the point of closest approach R_0 on the scattering angle Θ is determined from the solution of the trajectory equation for the potential $W_0(R)$.

In analyzing the effect of different factors on the analytic expression for the cross section, below we shall restrict our attention to first-order perturbation theory in calculating ΔS . As shown in [2], for $\Gamma_{1j'm'jm}$ in the case of potentials of the type (8), the following representation is valid:

$$\Gamma_{1j'm'}^{j'm'}(R_0) = \int_0^{2\pi} \frac{d\varphi_{0M}}{2\pi} \exp \left(i\Delta m\varphi_{0M} + \frac{i}{\hbar} C_0 + \frac{i\zeta_0\Delta j}{2} \right) J_{\frac{\Delta j}{2}} \left(\frac{F}{\hbar} \right),$$

where $J_q(x)$ is a Bessel function, C_0 , ζ_0 , F are some functions of φ_{0M} , which are easily calculated, if in the required variables we substitute for $\cos \gamma$ with the help of the relations

$$\begin{aligned} \cos \gamma &= \left[-\frac{X(t)}{R(t)} \sin \varphi_{0M} - \frac{Y(t)}{R(t)} \cos \varphi_{0M} \right] \sin(\varphi_{0J} + v_s t) - \\ & \left[\frac{X(t)}{R(t)} \lambda \cos \varphi_{0M} + \frac{Y(t)}{R(t)} \lambda \sin \varphi_{0M} + \frac{Z(t)}{R(t)} \sqrt{1-\lambda^2} \right] \cos(\varphi_{0J} + v_s t), \\ \lambda &= M/J, \quad R(t) = (X(t), Y(t), Z(t)), \end{aligned}$$

and carry out the integrals over time. These functions are represented in the form

$$\begin{aligned} F &= (A^2 + B^2)^{1/2}, \quad \zeta_0 = \arctg B/A, \quad C_0 = c_1 \cos 2\varphi_{0M} + c_2 \cos \varphi_{0M} + c_3, \\ A &= a_1 \sin 2\varphi_{0M} + a_2 \cos \varphi_{0M}, \quad B = b_1 \cos 2\varphi_{0M} + b_2 \cos \varphi_{0M} + b_3, \end{aligned}$$

where the coefficients a_1 , b_1 , c_1 are expressed in terms of an integral of the type (\bar{F} is the algebraic sum of the quantities indicated)

$$Q = - \int_{-\infty}^{+\infty} dt \frac{W_2 |R(t)|}{2R^2(t)} \bar{F} |\sin v_s t, \cos v_s t, \lambda, X(t), Y(t), Z(t)|. \quad (10)$$

In particular, for the model of a plane rotator ($\lambda = 1$), we obtain:

$$\begin{aligned} C_0 &= \text{const}, \quad \zeta_0 = \pi - 2\varphi_{0M}, \\ F &= \left| \int_{-\infty}^{+\infty} dt \frac{W_2 |R(t)|}{2R^2(t)} [Y^2(t) \cos 2v_s t - X^2(t) \cos 2v_s t - 2X(t)Y(t) \sin 2v_s t] \right|, \end{aligned} \quad (11)$$

$$\Gamma_{1j'm'}^{j'm'}(R_0) = \exp \left(\frac{i}{\hbar} C_0 \right) \delta_{\Delta m + \Delta j, 0} J_{\frac{\Delta j}{2}} \left(\frac{F}{\hbar} \right).$$

2. Expressions for the Rotational Excitation Cross Sections. We shall calculate the differential cross section of rotational excitation using the equation

$$\sigma_{jj'}(E, \Theta) = \frac{1}{2j+1} \frac{k'}{k} \sum_{m, m'} |f_{jm'}^{j'm'}(E, \Theta)|^2. \quad (12)$$

We substitute here the product $(f_{jm'}^{j'm'})^* \cdot f_{jm'}^{j'm'}$, using Eq. (9), and replace the sum over m, m' by summation over $m, \Delta m$. We note further that the increment to the action ΔS is virtually independent of Δm , which gives

$$\sum_{\Delta m = -M_0}^{M_0} \exp(i\Delta m \Delta \varphi_{0M}) = \frac{\sin \left(M_0 + \frac{1}{2} \right) \Delta \varphi_{0M}}{\sin(\Delta \varphi_{0M}/2)} \equiv U(\Delta \varphi_{0M}),$$

where $M_0 = j + j' + 1$, $\Delta \varphi_{0M} = \varphi_{0M} - \varphi'_{0M}$.

Under the assumption that M_0 is very large (for small M_0 we can use different approximations, which are related to the determining contribution of large impact parameters), we shall use the approximate equality

$$\int_0^{2\pi} \frac{d\varphi_{0M}}{2\pi} \int_0^{2\pi} \frac{d\varphi'_{0M}}{2\pi} U(\Delta \varphi_{0M}) \approx \int_0^{2\pi} \frac{d\varphi_{0M}}{2\pi}$$

Making the substitutions $M = J\lambda$, $\lambda = \cos \beta$, $m = (j + 1/2)\lambda$ and replacing the sum over m by the corresponding integral, we have

$$\frac{1}{2j+1} \sum_{m=-j-\frac{1}{2}}^{j+\frac{1}{2}} \rightarrow \frac{1}{2j+1} \int_{-j-1/2}^{j+1/2} dm \rightarrow \frac{1}{2} \int_{-1}^1 d\lambda \rightarrow \frac{1}{2} \int_0^\pi d\beta \sin \beta$$

Thus, for large j and j' we can use the following representation for the differential cross section, which takes into account approximately the spatial configurations of the rotator:

$$\begin{aligned} \sigma_{jj'}(E, \Theta) &= \sigma_0(E, \Theta) \mathcal{P}_{jj'}[E, R_0(\Theta), \Phi = 0], \\ \mathcal{P}_{jj'} &= \frac{1}{2} \frac{k'}{k} \int_0^\pi d\beta \sin \beta \int_0^{2\pi} \frac{d\varphi_{0M}}{2\pi} |\Gamma'_{1,j}(\varphi_{0M}, \beta, R_0)|^2, \\ \Gamma'_{1,j} &= \int_0^{2\pi} \frac{d\varphi_{0J}}{2\pi} \exp \left[i\Delta j \varphi_{0J} + \frac{i}{\hbar} \Delta S_1(R_0, \varphi_{0M}, \varphi_{0J}, \beta) \right]. \end{aligned} \quad (13)$$

In first-order perturbation theory, for the planar configuration of the rotator

$$|\Gamma'_{1,j}(\varphi_{0M}, \beta, R_0)| = \left| J \frac{\Delta j}{2} \left(\frac{F}{\hbar} \right) \right|.$$

As far as the exact cross sections (12) are concerned, they must satisfy the principle of detailed balance [5]:

$$E(2j-1)\sigma_{jj'}(E, \Theta) = E'(2j'+1)\sigma_{j'j}(E', \Theta).$$

In order that expression (13) satisfy this principle, we introduce, following [5], the modified cross section

$$\sigma_{jj'}^M(E, \Theta) = \left(\frac{2j'+1}{2j+1} \right)^{1/2} \sigma_{jj'}(E, \Theta),$$

by integrating which over the scattering angle Θ , we obtain the following representation of the total cross section in the form of an integral over the impact parameter ρ :

$$\sigma_{jj'}^M(E) = 2\pi \left(\frac{2j'+1}{2j+1} \right)^{1/2} \int_0^\infty d\rho \rho \mathcal{P}_{jj'}[E, R_0(\rho), \Phi = 0]$$

We note that in order to obtain the dependence $R_0(\rho)$ we use the relation $\rho^2 = R_0^2[1 - W_0(R_0)/E_s]$, where $E_s = (E + E')/2$ is the average energy of relative motion.

For the model of a plane rotator, summation over m , m' in (12) is performed simply and gives

$$\sigma_{jj'}^M(E) = 2\pi \frac{2j+1}{2j+1} \frac{k'}{k} \int_0^\infty d\rho \rho J_{\frac{\Delta j}{2}}^2 \left[\frac{F(R_0(\rho))}{\hbar} \right] \quad (14)$$

where $F(R_0)$ has the form (11), and $\hat{j} = \min(j, j')$.

3. Trajectory Problem. In view of the approximate condition $\Phi = 0$, the trajectory of relative motion lies in the XY plane (Fig. 1) and is found from the equations

$$\frac{\mu}{2} \left(\frac{dR}{dt} \right)^2 = E_s(1 - \rho^2/R^2) - W_0(R), \quad R(0) = R_0, \quad (15)$$

$$\frac{dX_0}{dt} = \frac{\rho}{R^2} \left(\frac{2E_s}{\mu} \right)^{1/2}, \quad X_0(0) = 0, \quad (16)$$

where X_0 is the polar angle; μ is the reduced mass of the colliding particles. The integration of the system (15), (16) and calculation of the integrals Q (10) permit finding quite

TABLE 1. Rate Constants $K_{0j}(T) \cdot 10^{16}$ (m^3/sec) for the system Ar-N₂

T, K		j'				
		2	4	6	8	10
A	300	1,3 (1,6)	0,79 (0,21)	0,36 (0,014)	0,13	
	450	1,46	1,05	0,62	0,31	0,13
	618	1,60	1,23	0,85	0,50	0,26
	768	1,68	1,35	1,00	0,66	0,38
B	300	0,77	0,45	0,12	0,017	
	450	0,85	0,69	0,27	0,063	0,015
	618	0,90	0,88	0,46	0,14	0,030
	768	0,94	0,90	0,61	0,23	0,061

Note. A corresponds to the calculation with the argument of the Bessel function in the form (19), while for B the form (20) was used. The experimental data in [9] are shown in the parentheses.

accurately F (11) or all quantities entering into the more general expressions for the scattering profile.

To obtain the explicit form of the Q integrals we shall use the approximate trajectory of relative motion, obtained by the effective quantum number method [6], according to which in (15) the radial term $1/R^2$ is replaced by $1/R_0^2$. The problem (15) then has an exact solution for an exponential potential

$$W_0(R) = C \exp(-\alpha R) \quad (17)$$

and for the Morse potential

$$W_0^M(R) = \varepsilon [1 - \exp(-\alpha_0(R - a_0))]^2 - 1, \quad (18)$$

which has the following form, respectively,

$$\exp[-\alpha R(t)] = \exp(-\alpha R_0) \operatorname{sech}^2 \left[\frac{\alpha}{2} \sqrt{\frac{2}{\mu}} W_0(R_0) t \right],$$

$$\exp\{-\alpha_0[R(t) - a_0]\} = \sqrt{W_0^M(R_0)/\varepsilon} \sin \psi / (\operatorname{ch} qt - \cos \psi),$$

where

$$q = \alpha_0 \sqrt{\frac{2}{\mu} W_0^M(R_0)}, \quad \sin \psi = \sqrt{\frac{W_0^M(R_0)/\varepsilon}{1 + W_0^M(R_0)/\varepsilon}}.$$

4. Calculation of the Argument F (11) of the Bessel Function. We shall calculate the quantity F (11) in the approximation $Y(t) = 0$ and under the assumption that the potential $W_2(R)$ is related to the potential $W_0(R)$ via the anisotropy parameter γ_0 ($W_2(R) = \gamma_0 W_0(R)$), which depends on R much more weakly than $W_0(R)$ and was assumed to be constant in the calculations. In this case, for the potentials (17) and (18) we obtain, respectively,

$$F(R_0) = -\gamma_0 \frac{2\pi\mu v_s}{\alpha^2} \operatorname{cosech} \left\{ \frac{2\pi v_s}{\alpha} \left[\frac{2}{\mu} W_0(R_0) \right]^{-1/2} \right\}. \quad (19)$$

$$F(R_0) = F^+(R_0) - F^-(R_0), \quad (20)$$

where

$$F^+(R_0) = \gamma_0 \frac{[W_0^M(R_0)]^2}{\varepsilon} \cos^2 \psi \frac{2\pi v_s}{q^2} \frac{\operatorname{ch}(-2v_s\psi/q)}{\sin^2 \psi \operatorname{sh}(2\pi v_s/q)},$$

$$F^-(R_0) = \gamma_0 \frac{2\pi}{q} \sqrt{\varepsilon W_0^M(R_0)} \operatorname{cosech} \frac{2\pi v_s}{a} \operatorname{sh}(-2v_s\psi/q).$$

TABLE 2. Coefficient of RT Diffusion $\mathcal{D}^{RT}(T, j) \cdot 10^{16} \text{ m}^2/\text{sec}$ for the System Ar-N₂. The Orders of Magnitude are Shown in Parentheses

T, K	j						
	2	4	6	8	10	12	14
100	0,30	0,48	0,52	0,62	0,76	0,61(-3)	0,26(-6)
200	0,72	0,95	1,2	1,76	3,2	0,24(-1)	0,18(-3)
300	0,99	1,3	1,7	2,3	4,5	0,85(-1)	0,21(-2)
400	1,2	1,6	2,1	2,7	5,1	0,16	0,77(-2)
500	1,4	1,9	2,4	2,8	5,2	0,24	0,16(-1)
600	1,6	2,1	2,7	2,8	5,2	0,31	0,29(-1)
700	1,7	2,3	2,9	2,8	5,1	0,36	0,42(-1)
800	1,7	2,4	3,0	2,9	4,9	0,41	0,56(-1)
900	1,8	2,5	3,1	2,7	4,8	0,44	0,68(-1)
1000	1,8	2,5	3,2	2,7	4,6	0,47	0,81(-1)

5. Rate Constants of RT Processes. The total cross section (14) was used to calculate the rate constants of rotational excitation in the system Ar-N₂

$$K_{jj'}(T) = 4 \left(\frac{2k_b T}{\pi \mu} \right)^{1/2} \int_{\sqrt{\epsilon_* X(\epsilon_*)}}^{\infty} dq q^3 \exp(-q^2) \sigma_{jj'}^i [E \rightarrow k_b T q^2], \quad (21)$$

where k_b is Boltzmann's constant; T, temperature; $\epsilon_* = E_*/(k_b T)$; $E_* = B_e [j'(j'+1) - j(j+1)]$, resonance defect; and X, Heaviside function.

In performing the calculations, we used the representation of the interaction potential in the form (8). The spherically symmetrical functions W_r ($r = 0; 2$) were determined in one case using the method in [7] and in the other by analyzing the numerical calculations [8]. As a result we obtain the approximations (17) and (18) with the parameters (atomic units): 1) $C = 1.85 \cdot 10^5$, $\alpha = 2.936$, $\gamma_0 = 1$; 2) $\epsilon = 0.51 \cdot 10^{-3}$, $\alpha_0 = 0.98$, $\alpha_0 = 6.51$, $\gamma_0 = 0.2$.

The results of the calculation of the constants $K_{0j'}(T)$ (21) for the arguments (19) and (20) are presented in Table 1. Good agreement is observed with the experimental data [9] at $T = 300^\circ\text{K}$. The difference in the arguments has little effect in the range of temperatures and quantum numbers studied.

6. Coefficient of RT Diffusion. In the approximation of a small rotational quantum relative to $k_b T$, the system of relaxation equations can be replaced by a single Fokker-Planck equation with the RT collision integral in the form [10]

$$\mathcal{D}^{RT}(j) = -n \frac{\partial \Pi^{RT}(j)}{\partial j}, \quad \Pi^{RT}(j) = -\mathcal{D}^{RT}(T, j) \frac{\partial z(j)}{\partial j},$$

where n is the number density of structureless particles participating in the collisions; $z(j)$ is the relative population density; $\mathcal{D}^{RT}(T, j)$ is the coefficient of RT diffusion over quantum numbers, which is calculated in terms of the rate constants as follows:

$$\mathcal{D}^{RT}(T, j) = \frac{1}{2} \sum_{\Delta j=0}^{\infty} (\Delta j)^2 [K_{jj+\Delta j}(T) + K_{jj-\Delta j}(T)]. \quad (22)$$

The calculation of the coefficient \mathcal{D}^{RT} was performed for the system Ar-N₂ using the equation

$$\begin{aligned} \mathcal{D}^{RT}(T, j) = & \frac{s(j)}{2Q(T)} \exp[-\epsilon(j)] \sum_{\Delta j=0}^{\infty} (\Delta j)^2 [s(j-\Delta j) X(j-\Delta j)] \cdot \\ & \times \sum_{\kappa=\Delta j}^{2j-\Delta j} \begin{pmatrix} j-\Delta j & \kappa & j \\ 0 & 0 & 0 \end{pmatrix}^2 K_{0\kappa}(T) + s(j+\Delta j) \sum_{\kappa=\Delta j}^{2j+\Delta j} \begin{pmatrix} j+\Delta j & \kappa & j \\ 0 & 0 & 0 \end{pmatrix}^2 K_{0\kappa}(T), \end{aligned} \quad (23)$$

where $s(j) = 2j + 1$; $Q(T)$ is the partition function; $\epsilon(j) = (B_e/k_b T)j(j+1)$; $\begin{pmatrix} a & b & c \\ 0 & 0 & 0 \end{pmatrix}$ are the Clebsh-Gordon coefficients; and $X(j') \equiv \exp(\Delta\epsilon(j', j))$.

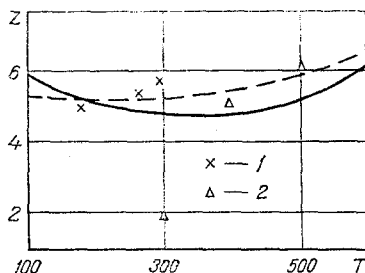


Fig. 2. Behavior of the ratio of the rotational relaxation time to the translational relaxation time as a function of temperature: 1) experiment [13], 2) experiment [14], the continuous curve shows the results of this work, and the dashed curve shows the trajectory calculations [15], T, °K.

Equation (23) was obtained from (22) using the principle of detailed balance for rotational constants and the relationship between the RT constants of an arbitrary transition and the constants of a transition out of the ground state with the help of the Clebsch-Gordon coefficients [11]. The results of the calculation are presented in Table 2.

7. Average Rotational Relaxation Time. The cross sections obtained permit calculating the rotational relaxation time τ_R , which is expressed in terms of the integral bracket I_{33} of the Van-Chang-Uhlenbeck equation

$$\tau_R = \frac{3}{2} \frac{C_V^R}{C_V^T} (I_{33})^{-1} \quad (24)$$

where C_V^T , C_V^R are the constant-volume heat capacities for the translational and rotational degrees of freedom, respectively. In the case of a diatomic gas, the integral bracket I_{33} is expressed in terms of the total cross section as follows:

$$I_{33} = \frac{4}{3} \frac{n}{Q^2(T)} \left(\frac{k_b T}{\pi m_0} \right)^{1/2} \sum_{\substack{j_1, j_2 \\ j_1', j_2'}} s(j_1) s(j_2) \exp[-\varepsilon(j_1) - \varepsilon(j_2)] \int_0^\infty dq q^3 \exp(-q)^2 \varepsilon_*^2 \sigma_{j_1 j_2}^{j_1' j_2'}(E \rightarrow k_b T q^2),$$

where n is the number density and m_0 is the mass of the molecules.

The RT collision cross section for diatomic molecules was represented in the form [2]

$$\sigma_{j_1 j_2}^{j_1' j_2'}(E) = 2\pi \frac{(2\hat{j}_1 + 1)(2\hat{j}_2 + 1)}{(2j_1 + 1)(2j_2 + 1)} \left(\frac{E - E_*}{E} \right)^{1/2} \int_0^\infty d\rho \rho J_{\Delta j_1}^2 \left[\frac{F_1(R_0(\rho))}{\hbar} \right] J_{\Delta j_2}^2 \left[\frac{F_2(R_0(\rho))}{\hbar} \right],$$

where $\Delta j_r = j_r - j_r'$.

In order to describe RT processes in the homonuclear diatomic gas, we select the interaction potential in the following form:

$$W(R, \gamma_1, \gamma_2) = W_0(R) + W_2(R) [\cos^2 \gamma_1 + \cos^2 \gamma_2]. \quad (26)$$

In particular, in calculating the quantity τ_R (24) in N_2 the parameters of the interaction potential (26) are determined from calculations of the potential surface [12] and have the form $C = 98.8$, $\alpha = 1.8$, $\gamma_0 = 0.54$.

In the case under study, the arguments of the Bessel functions in (25) have the form (19), where the substitution $\nu_s \rightarrow \nu_{sr} = B_e(j_r + j_r' + 1)$ must be made in order to obtain F_r ($r = 1, 2$).

The results of the calculation of the quantity τ_R are shown in Fig. 2, which shows the quantity $Z(T) = \tau_R(T)/\tau_t(T)$; $\tau_t(T)$ is the average relaxation time of the translational degrees of freedom.

A comparison of the calculations with the experimental data [13, 14], as well as with the calculation in [15], shows that the model used for the collision gives satisfactory agreement. For $T < 200^\circ K$, the calculation deviates from the experimental data. As preliminary calcula-

tions show, this is related to the neglect of RR processes in this temperature range in the calculation of the integral bracket as well as the attractive forces in the elastic part of the intermolecular interaction potential.

NOTATION

$f_{jm}^{j'm'}$, amplitude of rotational excitation; \mathbf{p} , momentum of the oncoming particle before the collision; h , Planck's constant; $i = \nu(-1)$; $\pi = 3.14, \dots$; \mathbf{R}_0 , radius vector of the point of closest approach; $\Gamma_{jm}^{j'm'}$, scattering profile; φ_i, φ_M , angular variables which are conjugate to the orbital J and magnetic M moments, respectively; $\varphi_{0J}, \varphi_{0M}$, initial values of the angular variables φ_i and φ_M ; S , classical action; τ, t , time variables; $\mathbf{R}(t) = (X(t), Y(t), Z(t))$, radius vector of the particle along the trajectory of relative motion; φ , set of angular variables; \mathbf{J} , set of action variables; \mathbf{n} , set of quantum numbers; δ , vector of constants in the Bohr-Sommerfeld quantization condition; S_p , successive approximation of order p to the classical motion; \mathbf{J}_l , set of action variables on the section l (initial or final) of the eikonal trajectory; \mathbf{p}_l , momentum on the section l of the eikonal trajectory; \mathcal{H}^p , right side of the equation for S_p ; $\Phi(\tau)$, time dependence of the angular variable; $\mathbf{v}_{i,f}$, relative velocity of the colliding particles in the initial ($l = i$) and final ($l = f$) channels; $\mathbf{v}_{i,f}$, vector of frequencies in the initial ($l = i$) and final ($l = f$) channels; ΔS_k , increment to the classical action in the k -th order; B_e , rotational constant of the molecule; T_0 , limit of integration over time; $W_0(R)$, elastic interaction potential; $V_1(R, \gamma)$, inelastic interaction potential; $W_2(R)$, elastic part of the potential in the inelastic potential $V_1(R, \gamma)$; $J_{\Delta j/2}$, a Bessel function of order $\Delta j/2$; F/ν , argument of the Bessel function; λ , ratio of the magnetic and orbital moments; β , angle between the orbital and magnetic moments; \mathcal{P}_{ij} , value of the inelastic scattering profile averaged over the angular variables; Φ , azimuthal angle in the dynamic plane of impact parameters; γ_r ($r = 1; 2$), angle between the axis connecting the centers of mass of the molecules and the axis of the r -th rotator.

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INVESTIGATION OF A HIGH-ENTHALPY SUBMERGED JET DISCHARGING FROM
THE CHANNEL OF AN ARC PLASMOTRON

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The variation of the main parameters over the length and cross section of the jet is determined experimentally and is compared with theoretical data.

To organize the efficient mixing of plasma jets with the initial products in multiarc plasmachemical reactors [1, 2] one must know, first of all, the distribution of the velocity head and specific heat flux (temperature) over the length and cross section of the jet, as well as the diameter of the jet at any distance from its orifice.

The exact analytic determination of these quantities is hindered by the considerable variation of the gas density along the jet axis, the intense swirling of the stream in the discharge channel of the plasmotron, and the action of external electromagnetic forces on the conducting section of the jet.

A submerged high-enthalpy air jet discharging from the channel of an arc plasmotron, with the average length of the arc fixed by a step, was investigated experimentally. A comparatively small section of the jet of about five diameters was studied. This was due to the requirement of compactness of the mixing devices of plasmachemical reactors. In addition, at a large distance from the nozzle cut the values of the parameters of the jet decay and the jet loses its individuality as a result of mixing of the working body of the jet with the entrained stream [3], so that prediction of its behavior in a confined space (the reactor) becomes problematical.

Test conditions: gas flow rate $(1.1-2.76) \cdot 10^{-3}$ kg/sec, specific enthalpy of air (5300-8400) kJ/kg, diameter of discharge channel of the plasmotron $8 \cdot 10^{-3}$ and $9.5 \cdot 10^{-3}$ m, step diameter $(15 \text{ and } 17.5) \cdot 10^{-3}$ m, respectively, step length $4 \cdot 10^{-2}$ m, number of ampere turns of the solenoid $(0-24) \cdot 10^3$.

First we found the value of the specific heat flux from the jet to the calorimetric probe of enhanced sensitivity. The construction of the probe and the measurement procedure are described in detail in [4]. The dynamic head was determined with a water-cooled Pitot tube, structurally combined with the calorimetric probe. The pressure was converted into an electrical signal by a measurement complex of the IKD6TDF type. The probe allows one to make a simultaneous continuous recording of the specific heat flux and the excess pressure in a cross section of the jet. The total error in determining the specific values of the heat fluxes was 9.5% [5] and the accuracy in measuring the excess pressure was ± 2.5 rel. %.

The gasdynamic and thermal radii of the jet were determined from the corresponding oscillograms and were compared with Töpler photographs. The temperature was calculated through the value of q by the method of [6]. To reduce the number of tests and formalize the statistical treatment of the results obtained, we used a central, composite, rotatable plan for the experiment [7].

The results of the measurements are presented in Table 1. To treat the test data we obtained interpolation equations describing distributions of velocity head, specific heat flux, and temperature along the jet axis as functions of the gas flow rate and the number

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