

7. H. Falter, O. F. Hagena, W. Henkes, and H. von Wedel, "Einfluss der Elektronenenergie auf das Massenspektrum von Klustern in kondensierten Molekularstrahlen," Intern. J. Mass Spectrom. Ion. Phys., 4, No. 2 (1970).
8. N. V. Karelov, A. V. Kosov, A. K. Rebrov, and R. G. Sharafutdinov, "Study of low-density jet mixing zones," in: Rarefied Gas Dynamics [in Russian], Izd. Inst. Teplofiz. Sibirsk. Otd. Akad. Nauk SSSR, Novosibirsk (1976).
9. D. Golomb, R. E. Good, A. B. Bailey, and N. R. Busby, and Dawbarn, "Dimers, clusters, and condensation in free jets. II," Chem. Phys., 57, No. 9 (1972).
10. P. A. Skovorodko, "Influence of homogeneous condensation in a free jet on the molecular beam intensity," in: Some Hydrodynamic and Heat-Transfer Problems [in Russian], Izd. Inst. Teplofiz. Sibirsk. Otd. Akad. Nauk SSSR, Novosibirsk (1976).
11. O. F. Hagena and H. von Wedel, "Cluster beam from gas mixtures: effect of carried gas on cluster size and beam intensity," in: Rarefied Gas Dynamics. Proceedings of the Ninth International Symposium, Vol. 2, DFVLR-Press, Porz-Wahn (1974).
12. A. N. Vargin, N. A. Ganina, V. K. Konyukhov, and V. I. Selyakov, "Computation of the rotational transition probabilities of diatomic molecules for collisions with heavy particles," Zh. Prikl. Mekh. Tekh. Fiz., No. 2 (1975).
13. H. Rabitz and S. H. Lam, "Rotational energy relaxation in molecular hydrogen," Chem. Phys., 63, No. 8 (1975).
14. V. K. Konyukhov and V. N. Faizulaev, Kinetic Model of Supersaturated Gas Condensation [in Russian], Preprint No. 32, Physics Institute, Academy of Sciences of the USSR, (1976).

COMPUTATION OF THE ROTATIONAL TRANSITION
PROBABILITIES OF DIATOMIC MOLECULES WITH A MORSE
POTENTIAL

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This paper is a continuation of the computations of the excitation probabilities of the rotational degrees of freedom of diatomic molecules during collisions carried out in [1]. In connection with the enormous computational difficulties occurring in quantum-mechanical computations [2], a quasiclassical approach [3] is used which allows obtaining analytical dependence of the probability on both the number of the rotational level characterizing the transition and on the energy of the colliding particles. This last circumstance is a factor of no little importance in the application of the probabilities obtained in the description of the level kinetics of rotational relaxation under different conditions, for instance, under the efflux of gas mixtures from a slot of nozzle into a vacuum.

Analytic expressions are obtained in this paper for the rotational transition probabilities at which the quantum numbers of one (R-T transitions) or both (R-R transitions) molecules change by 1 or 2. A multiplicative integral is used in the solution of the system of equations for the probability amplitudes of the appropriate processes. In contrast to [1, 3], the change in energy in an inelastic collision is taken into account in the classical equation of motion, and the averaging of the probabilities with respect to the total energy is carried out more correctly. An experimental potential and a potential in the Morse form are used in computing the probabilities. The need for such computations is due, in particular, to the substantial influence of attraction on the magnitude of the probability for low energies of the colliding molecules.

Let us recall that according to the method described earlier, the molecule trajectory is considered classical with the use of the spherically symmetric part of the intermolecular potential, while the rotational motion is considered quantum mechanically. The anisotropic part of the potential hence governs the form of the perturbation operation.

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Let us examine a system consisting of two colliding molecules. The rotational motion of the system is determined by the Schroedinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = [\hat{H}_r^{(1)} + \hat{H}_r^{(2)} + \hat{H}_r + V_r] \Psi, \quad (1)$$

where \hat{H}_r is the Hamiltonian of relative rotation of the molecule, $H_r^{(i)}$ is the Hamiltonian of free rotation of the i -th molecule, Ψ is the angular part of the wave function of the system of two molecules, and V_r is the part of the intermolecular potential dependent on the molecule orientations.

The angular part of the wave function describing the state of the system of two molecules can be represented in the form of a product of angular parts of wave functions characterizing the free rotation of the molecules and the wave function governing the rotation of the system as a whole. Using the model of a rigid rotator to describe the rotation of the diatomic molecules, we can expand the angular part of the wave function in the spherical harmonic functions Y [1]:

$$\Psi = \sum_{\substack{j_1, j_2, J \\ m_1, m_2, m}} C(j_1 m_1 j_2 m_2 J m | t) \exp\left\{-\frac{it}{\hbar} [\varepsilon(j_1) + \varepsilon(j_2) + w(J)]\right\} \times \\ \times Y_{j_1 m_1}(\theta_1, \varphi_1) Y_{j_2 m_2}(\theta_2, \varphi_2) Y_{J m}(\theta, \varphi), \quad (2)$$

where j_i and m_i are quantum numbers characterizing the intrinsic rotational moment of the i -th molecule and its projection; j and m are quantum numbers characterizing the angular momentum of the relative rotation of the molecule and its projection; $\varepsilon(j_i)$ is the energy of free rotation of the i -th molecule; $w(J)$ is the energy of relative rotation of the two molecules; θ_i and φ_i are angles characterizing the rotation of the i -th molecule; θ and φ are angles describing the relative rotation of the molecules; and $C(j_1 m_1 j_2 m_2 J m | t)$ are expansion coefficients.

Let us note that $\varepsilon(j) = B_0 j(j+1)$, where B_0 is the rotational constant of the molecule.

Substituting the wave function (2) into (1) and taking account of the orthonormalized spherical harmonics, we obtain an equation for the coefficients $C(j_1 m_1 j_2 m_2 J m | t)$ which can be written in the matrix form [1, 3]

$$d\tilde{C}(t)/dt = \tilde{A}\tilde{C}(t),$$

where A is a Hermitian matrix with the elements

$$A(j_1 m_1 j_2 m_2 J m | t) = \langle j_1' m_1' j_2' m_2' J' m' | V_r | j_1 m_1 j_2 m_2 J m \rangle \exp\left\{-\frac{it}{\hbar} [\Delta\Sigma + \Delta w(J)]\right\}; \\ \Delta\Sigma = \varepsilon(j_1) - \varepsilon(j_1') + \varepsilon(j_2) - \varepsilon(j_2'); \\ \Delta w(J) = w(J) - w(J').$$

The solution of such a system with the initial condition

$$C(j_1 m_1 j_2 m_2 J m | t) \rightarrow \delta_{j_1, j_1'} \delta_{j_2, j_2'} \delta_{J, J'} \delta_{m_1, m_1'} \delta_{m_2, m_2'} \delta_{m, m'}$$

as $t \rightarrow -\infty$, where δ is the Kronecker delta, is expressed in terms of a Volterra multiplicative integral [5]:

$$\tilde{C}(t) = \tilde{C}(-\infty) \int_{-\infty}^t \tilde{A}(\tau) d\tau.$$

The transition probability of a system of states with the quantum numbers $j_1^0 m_1^0 j_2^0 m_2^0 J^0 m^0$ into a state $j_1' m_1' j_2' m_2' J' m'$ equals

$$P(j_1^0 \rightarrow j_1', j_2^0 \rightarrow j_2', J, E) = |C(j_1 m_1 j_2 m_2 J m | +\infty)|^2.$$

It is convenient to use the expression of the multiplicative integral obtained by Magnus in the form of an exponential of a matrix series [5] for the calculations:

$$\tilde{C}(+\infty) = \tilde{C}(-\infty) \exp\{\tilde{K}(+\infty)\}, \\ \tilde{K}(+\infty) = \int_{-\infty}^{+\infty} \tilde{A}(\tau) d\tau - \frac{1}{2} \int_{-\infty}^{+\infty} d\tau_1 \int_{\tau_1}^{+\infty} d\tau_2 [\tilde{A}(\tau_1) \tilde{A}(\tau_2)] + \\ + \frac{1}{6} \int_{-\infty}^{+\infty} d\tau_1 \int_{\tau_1}^{+\infty} d\tau_2 \int_{\tau_2}^{+\infty} d\tau_3 \{[\tilde{A}(\tau_1) [\tilde{A}(\tau_2) \tilde{A}(\tau_3)]] + [[\tilde{A}(\tau_1) \tilde{A}(\tau_2)] \tilde{A}(\tau_3)]\} + \dots, \quad (3)$$

where $[\hat{A}(\tau_1)\hat{A}(\tau_2)]$ is the commutator of the operators $\hat{A}(\tau_1)$ and $\hat{A}(\tau_2)$; $\exp\{\hat{K}(+\infty)\} = I + \hat{K} + (1/2)\hat{K}^2 + \dots$, I is the unit matrix.

The selection of the intermolecular potential V determines the magnitude of the rotational transition probabilities and the nature of their dependence on the energy and the quantum numbers. The magnitude of the transition probability determined for some one energy is due to the value of the potential at the greatest closure range [6]. Short ranges play the major part in the scattering of fast neutral particles by atoms or molecules, and the repulsion forces are governing. A fast change in the total potential with distance permits the influence of weak attraction forces near the initial and terminal sections of the trajectory to be neglected. However, as will be shown below, long-range attraction forces indirectly influence the rotational transition probability during collisions with low energies by accelerating the relative motion of the colliding particles. For collisions between polar molecules, the dipole-dipole part of the interaction is often taken into account as the component of the long-range forces, together with the usual components of the potential in the Morse or Lennard-Jones form [7]. It would be false (even for polar molecules) to limit oneself to just dipole-dipole interaction [8], which is valid only at remote ranges. A potential in the Morse form, which also takes attraction into account in contrast to the exponential potential, is used in this paper. For a pair of diatomic molecules, the potential is here expressed in the form of the sum of interaction potentials between separate atoms of the molecules:

$$V = \sum_{k=3,4} \sum_{i=1,2} \{D'_{ik} \exp(-\alpha_{ik}r_{ik}) - D''_{ik} \exp(-\alpha_{ik}r_{ik}/2)\}, \quad (4)$$

where D'_{ik} , D''_{ik} , and α_{ik} are intermolecular potential parameters; r_{ik} is the spacing between two atoms of the colliding molecules.

If the internuclear spacings ξ_i are small compared to the intermolecular spacing R , then (4) for the intermolecular potential can be expanded in a series of Legendre polynomials $P_i(\cos \chi)$ [3]. Assuming α_{ik} to be identical for all pairs of atoms, let us represent the interaction potentials between the two identical diatomic molecules, consisting of atoms with masses μ_1 and μ_2 , in the form

$$V = e^{-\alpha R} \left\{ B' + \sum_{i=1}^4 B'_{i0} [P_i(\cos \chi_1) + P_i(\cos \chi_2)] + \sum_{i=1}^2 B'_{ii} P_i(\cos \chi_1) \times \right. \\ \left. \times P_i(\cos \chi_2) + \dots \right\} - e^{-\frac{\alpha R}{2}} \left\{ B'' + \sum_{i=1}^4 B''_{i0} [P_i(\cos \chi_1) + P_i(\cos \chi_2)] + \right. \\ \left. + \sum_{i=1}^2 B''_{ii} P_i(\cos \chi_1) P_i(\cos \chi_2) + \dots \right\}, \quad (5)$$

where $B' = a_0^1 + 2/3 a_2^1$; $B'_{10} = a_1^1$; $B'_{20} = 2/3 a_2^1$; $B'_{30} = 2/5 a_3^1$; $B'_{40} = 8/35 a_4^1$; $B'_{11} = b_1^1$; $B'_{22} = 4/9 b_2^1$;

$$a_i = (\xi \alpha)^i \frac{\mu_1^i (D'_{12} + D'_{22}) + (-1)^i \mu_2^i (D'_{12} + D'_{11})}{i! (\mu_1 + \mu_2)^i}; \\ b_i = (\xi \alpha)^{2i} \frac{\mu_1^{2i} D'_{22} + (-1)^i 2\mu_1^i \mu_2^i D'_{12} + \mu_2^{2i} D'_{11}}{i^2 (\mu_1 + \mu_2)^{2i}},$$

and χ_i is the angle between the direction of the intermolecular vector and the axis of the i -th molecule.

The same relations can be obtained for the coefficients B''_{ik} as for the coefficients B'_{ik} by replacing D'_{ik} by D''_{ik} and α and $\alpha/2$. Let us note that the convergence of the series (5) is determined by the smallness of $\alpha \xi$.

The energy conservation equation for a system of two colliding molecules is written in the form

$$\frac{1}{2} M \left(\frac{dR}{dt} \right)^2 = E - V_0(R) - \frac{J^2 \hbar^2}{2MR^2}, \quad (6)$$

where E is total energy of the system of two molecules without taking account of the energy of the internal degrees of freedom, $V_0(R)$ is the spherical part of the intermolecular potential, $J\hbar$ is the angular momentum of the relative rotation of the molecules, and M is the reduced mass of the two particles.

The quantities E and J are changed when inelastic collisions occur, particularly rotational transitions. Hence, the right side of (6) for the times before and after collision differs by the small quantity ΔE , equal to the change in absolute value in the internal energy of the system during the collision. The change in J during

the collision can be neglected, since a change in several units is negligibly small for large J ($\approx 30-40$), and for small J the magnitude of the energy of relative molecule rotation is considerably less than the kinetic energy of the colliding molecules. To simplify (6), the variable quantity R was replaced by the constant R_c characterizing the range of effective molecule interaction [1] in the term describing the relative molecule rotation.

The solution of (6) by using the spherically symmetric part of the intermolecular potential $V_0(R) = B'e^{-\alpha R} - B''e^{-\alpha R/2}$ permits finding the motion trajectory of the colliding molecules and, therefore, also the time dependence of the perturbation operator characterizing the molecule interaction. In this case, the terms in the expression for the potential are written in the form

$$B'e^{-\alpha R} = \frac{4B'}{B''^2} \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right)^2 \left\{ \sqrt{1 + \frac{4B'}{B''^2} \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right)} \operatorname{ch} \sqrt{\frac{\alpha^2}{2M} \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right)} t - 1 \right\}^{-2},$$

$$B''e^{-\frac{\alpha R}{2}} = 2 \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right) \left\{ \sqrt{1 + \frac{4B'}{B''^2} \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right)} \operatorname{ch} \sqrt{\frac{\alpha^2}{2M} \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right)} t - 1 \right\}^{-1}.$$

If the commutator $\left[\hat{A}(t), \int_{t_0}^t \hat{A}(\tau) d\tau \right]$ tends to zero and the interaction is "weak" (i.e., the matrix elements

K are sufficiently small), only the first terms can be kept in the representation (3). In this case the rotational transition probability in the collision of two molecules will equal the square of the absolute value of the matrix element of the perturbation operator for this transition.

Evaluating the matrix element of the perturbation operator and averaging the probabilities with respect to the projections of the initial angular momentums m_1 , m_2 , and m , we obtain the following expression for the rotational transition probability during molecule collisions:

$$P(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2, J, E) =$$

$$= \frac{2\pi^2 M B''^2}{\hbar^2 \alpha^2 B'} \Phi(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) f(J) \times$$

$$\times \left| \frac{1}{\operatorname{sh} \beta} \left[\frac{1}{2} \frac{B'_{ih}}{B'} (\operatorname{sh} \gamma + \kappa \operatorname{ch} \gamma) - \frac{B''_{ih}}{B''} \operatorname{sh} \gamma \right] + \frac{1}{\operatorname{sh} \beta'} \left[\frac{1}{2} \frac{B'_{ih}}{B'} (\operatorname{sh} \gamma' + \kappa \operatorname{ch} \gamma') - \frac{B''_{ih}}{B''} \operatorname{sh} \gamma' \right] \right|^2,$$

where

$$\beta = \frac{\pi |\Delta \Sigma|}{\hbar \alpha} \sqrt{\frac{2M}{E - \frac{J^2 \hbar^2}{2MR_c^2}}}; \quad \kappa = \frac{|\Delta \Sigma|}{\hbar \alpha} \sqrt{\frac{2M}{B''^2}};$$

$$\gamma = \frac{\beta}{\pi} \arccos \left\{ - \left[1 + \frac{4B'}{B''^2} \left(E - \frac{J^2 \hbar^2}{2MR_c^2} \right) \right]^{-1/2} \right\}.$$

Let us note that β' and γ' are the same functions as β and γ , with respect to E' and J' , where $E' = E + \Delta \Sigma$. Moreover, in the case of deactivation of one of the molecules for one-quantum R-T transitions,

$$\Phi(j_1 \rightarrow j_1 - 1, j_2) = \frac{j_1}{2j_1 + 1}, \quad f(J) = 1;$$

for two-quantum R-T transitions,

$$\Phi(j_1 \rightarrow j_1 - 2, j_2) = \frac{9}{40} \frac{j_1(j_1 - 1)}{(2j_1 - 1)(2j_1 + 1)},$$

$$f(J) = 4 \frac{J^2 + J - 1}{(2J + 1)(2J + 3)};$$

and for one-quantum R-R transitions,

$$\Phi(j_1 \rightarrow j_1 - 1, j_2 \rightarrow j_2 - 1) = \frac{197}{405} \frac{j_1 j_2}{(2j_1 + 1)(2j_2 + 1)}, \quad f(J) = 1.$$

In the case of two-quantum R-R transitions, the averaging with respect to the projections is performed on an electronic computer, and the dependence obtained is approximated by functions convenient for the subsequent calculations. Consequently, for two-quantum R-R transitions,

$$\Phi(j_1 \rightarrow j_1 - 2, j_2 \rightarrow j_2 - 2) = \frac{81}{500} c \frac{j_1(j_1 - 1)j_2(j_2 - 1)}{(2j_1 - 1)(2j_1 + 1)(2j_2 - 1)(2j_2 + 1)},$$

$$f(J) = 1 + \frac{1}{c(aJ + b)},$$

where $a=5.42$, $b=7.82$, and $c=0.43$.

If one or both molecules are excited, in the expressions for Φ the rotational quantum number j should be replaced by $(j+1)$ everywhere except in the statistical weight $(2j+1)$ in the denominator.

Let us now determine the temperature dependence of the transition probability of a molecule with a j -th rotational level during the collision of two molecules. Under the assumption that the distribution of the total energy of the colliding molecules is subject to Gibbs law, and the distribution in the quantum number J is a Boltzmann distribution, the average probability is written as follows:

$$\begin{aligned}
 P(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) &= \frac{\pi^2}{\alpha^2 R_c^2 T} \frac{B''^2}{B'} \Phi(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) \times \\
 &\times e^{\frac{\Delta\Sigma - |\Delta\Sigma|}{2T}} \int_0^\infty (2J+1) j(J) e^{-\frac{J^2 \hbar^2}{MR_c^2 T}} dJ \times \\
 &\times \int_0^\infty \left[\frac{1}{\text{sh}\beta} \left[\frac{1}{2} \frac{B'_{ih}}{B'} (\text{sh}\gamma + \kappa \text{ch}\gamma) - \frac{B''_{ih}}{B''} \text{sh}\gamma \right] + \right. \\
 &\left. + \frac{1}{\text{sh}\beta'} \left[\frac{1}{2} \frac{B'_{ih}}{B''} (\text{sh}\gamma' + \kappa \text{ch}\gamma') - \frac{B''_{ih}}{B''} \text{sh}\gamma' \right] \right]^2 e^{-x} dx, \quad (7)
 \end{aligned}$$

where $x = (1/T) [E - (J^2 \hbar^2 / 2MR_c^2)]$ for $\Delta\Sigma > 0$; $x = (1/T) [E' - (J^2 \hbar^2 / 2MR_c^2)]$ for $\Delta\Sigma < 0$; and T is the temperature in energy units.

Using the saddle-point method to evaluate the integral in (7), the following expressions can be obtained for $P(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2)$:

$$P(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) = \frac{4\pi^2 M B''^2}{\hbar^2 \alpha^2 B'} \Phi(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) e^{\frac{\Delta\Sigma - |\Delta\Sigma|}{2T}} \times \quad (8)$$

$$\begin{aligned}
 &\times \left\{ (\xi_1 + \xi_2)^2 + \xi_2 (\xi_1 + \xi_2) \sqrt{\frac{\pi}{3}} \left(\frac{A}{1/T} \right)^{1/3} e^{-3 \left(\frac{A}{1/T} \right)^{2/3}} \left(1 + e^{\frac{|\Delta\Sigma|}{T}} \right) \right\}; \\
 P(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) &= \frac{2\pi^2 M B''^2}{\hbar^2 \alpha^2 B'} \Phi(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) \left\{ \frac{1}{2} \frac{B'_{ih}}{B'} (1 + \kappa) - \right. \\
 &\left. - \frac{B''_{ih}}{B''} \right\}^2 \sqrt{\frac{\pi}{3}} \left(\frac{A}{2/T} \right)^{1/3} e^{-3 \left(\frac{A}{2/T} \right)^{2/3}} \left(1 + e^{\frac{\Delta\Sigma}{2T}} \right)^2, \quad (9)
 \end{aligned}$$

where

$$\begin{aligned}
 \xi_1 &= \left(\frac{1}{2} \frac{B'_{ih}}{B'} - \frac{B''_{ih}}{B''} \right) \text{ch}\kappa - \frac{1}{2} \frac{B'_{ih}}{B'} \kappa \text{sh}\kappa; \quad \xi_2 = \frac{1}{2} \frac{B'_{ih}}{B'} \kappa \text{ch}\kappa - \left(\frac{1}{2} \frac{B'_{ih}}{B'} - \right. \\
 &\left. - \frac{B''_{ih}}{B''} \text{sh}(\kappa) \right); \quad A = \frac{\pi |\Delta\Sigma| \sqrt{2M}}{\hbar \alpha}.
 \end{aligned}$$

Because of the approximations used for the calculations, (8) is valid for $T < \kappa^2 \pi^2 \varepsilon_0$, if $\kappa\pi < 1$, and for

$T < \frac{1}{\kappa\pi} \varepsilon_0$, if $\kappa\pi > 1$, while (9) is valid for $\frac{2}{\pi\kappa} \varepsilon_0 < T < \frac{\pi^2 \kappa^2}{4} \varepsilon_0$, where $\varepsilon_0 = B''^2 / 4B'$ is the depth of the potential well.

If the role of attraction is small, it is possible to go from the Morse potential over to the potential of exponential form [3]:

$$\begin{aligned}
 P^{\text{exp}}(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) &= \frac{4\pi^2 M^2 |\Delta\Sigma|^2}{\hbar^4 \alpha^4} \times \\
 &\times \left(\frac{B'_{ih}}{B'} \right)^2 \Phi(j_1 \rightarrow j'_1, j_2 \rightarrow j'_2) \sqrt{\frac{\pi}{3}} \left(\frac{A}{2/T} \right)^{1/3} e^{-3 \left(\frac{A}{2/T} \right)^{2/3}} \left(1 + e^{\frac{\Delta\Sigma}{2T}} \right)^2, \quad (10)
 \end{aligned}$$

where $T < \pi^2 |\Delta\Sigma|^2 M / 2\hbar^2 \alpha^2$.

Analogous formulas [1] are obtained in computing the rotational transition probabilities during the collision between a molecule and an atom.

The formulas obtained are valid when the matrix elements \hat{K} , meaning the transition probabilities, are small. If this condition is not satisfied, then the contribution of the next terms in the expansion (3) to the probability should be taken into account. Such a computation can be performed by using an electronic computer.

The temperature ranges in which the expressions for the probabilities are applicable are determined by the value of the parameter $\kappa = \frac{|\Delta\Sigma|}{hc\alpha} \sqrt{\frac{2M}{\epsilon_0}}$. Formula (8) is valid at the temperatures $T < \epsilon_0$, while formula (9) is valid for $T > \epsilon_0$ (for the molecules HCl-HCl, for instance, for $T > 300^\circ\text{K}$).

The transition probability grows with the rise in temperature. For $\kappa < 1$, as well as for $\kappa > 1$ the probabilities at low levels increase with the rise in the number of the level j , and for $\kappa > 1$ they diminish exponentially at higher levels. Here the larger the rotational constant B_0 of the molecule, and the smaller the value of α , the more rapidly does the probability decrease.

Although exact relationships between the coefficients in the anisotropic part of the potential are unknown, it is interesting to compare the different transition probabilities on the basis of the results of this paper. Estimates show that the probabilities of one-quantum R-T and R-R transition are several times greater than the probabilities of two-quantum R-T and R-R transitions. Here the ratio between the probabilities of the one-quantum and two-quantum transitions increases with the increase in j . However, let us note that the probabilities of two-quantum transition can be commensurate to the probabilities of one-quantum transitions for small values of κ corresponding, particularly, to large α . But this is only observed for small j . Such a dependence of the rotational transition probabilities on the number of the level j can be explained by the fact that the spacing between the low levels is so small that the kinetic energy turns out to be sufficient to cause multiquantum transitions. The spacing between the levels increases for large quantum numbers j and one-quantum processes turn out to be more effective.

The probabilities of R-R processes are less than the probabilities of R-T processes when both colliding molecules are simultaneously excited or deactivated, but are commensurate and even greater if counter R-R transitions are considered (one molecule is excited while the other is deactivated).

Let us note that the exponential potential yields a different dependence of the probabilities on αj , and the other parameters at low temperatures than does the Morse potential. The probabilities (10) obtained by using the intermolecular potential in exponential form differ from the results in [1, 2]. This is related to the different method of taking the average with respect to the energy as well as to the more accurate solution of the classical equation of motion. The probabilities obtained in this paper satisfy the principle of detailed equilibrium.

LITERATURE CITED

1. A. N. Vargin, N. A. Ganina, V. K. Konyukhov, and V. I. Selyakov, "Computation of the rotational transition probabilities of diatomic molecules during collisions with heavy particles," *Zh. Prikl. Mekh. Tekh. Fiz.*, No. 2, 13-19 (1975).
2. T. Oka, "Collision-induced transitions between rotational levels," in: *Advances in Atomic and Molecular Physics*, Vol. 9, New York-London (1973), pp. 127-206.
3. K. Takayanagi, "Vibrational and rotational transitions in molecular collisions," *Progr. Theor. Phys.*, Suppl. No. 25, 1 (1963).
4. A. N. Vargin, N. A. Ganina, V. K. Konyukhov, A. I. Lukovnikov, and V. I. Selyakov, "Obtaining an inversion at the rotational levels of diatomic molecules during adiabatic gas expansion," *Kvant. Élektran.*, 2, No. 3, 599-602 (1975).
5. V. I. Rostokin and V. A. Kolkunov, "Asymptotic solutions of the problem of atom interaction with an external field," in: *Physics of a Gas-Discharge Plasma* [in Russian], No. 2, Atomizdat, Moscow (1969).
6. I. Amdur and J. Jordan, "Elastic scattering of high energy beams. Intermolecular repulsion forces," in: *Investigations with Molecular Beams* [Russian translation], Mir, Moscow (1969).
7. H. K. Shin, "Vibration-rotation-transition energy transfer in HF-HF and DF-DF," *Chem. Phys. Lett.*, 10, No. 1, 81-85 (1971).
8. P. W. Anderson, "Pressure broadening in the microwave and infrared regions," *Phys. Rev.*, 76, No. 5, 647-661 (1949); C. J. Tsao and B. Curnutte, "Line widths of pressure-broadened spectral lines," *J. Quant. Spectrosc. Radiat. Transfer*, 2, 41-91 (1962).