ROTATIONAL TRANSITION PROBABILITIES FOR A WATER
MOLECULE COLLIDING WITH AN ATOM

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A quasiclassical method of calculating the collisional rotational transition probabilities (CRTP) for diatomic molecules interacting with an impinging heavy particle was developed in [1, 2]. The CRTP obtained by this method were then used to calculate the kinetics of the populations of the rotational levels, which showed that it was possible in principle to obtain an inverse population on the rotational levels of diatomic molecules in an adiabatically expanding gas [3]. In this connection it is of interest to investigate the rotational transitions of a water molecule colliding with an atom. This gives rise to the need for calculation of the CRTP of triatomic molecules of the asymmetric-top type.

In this paper we calculate the CRTP of triatomic molecules, exemplified by the H_2O molecule, which interacts with an atom in three-dimensional space. For the calculation we use a quasiclassical method similar to that used in [1]. The essence of the method is as follows. We calculate the trajectory of motion of the atom and molecule by the classical method and obtain the time dependence of the perturbation operator, by averaging which over the rotational wave functions of the initial and final states of the molecule we find the collisional transition probability in the first approximation of perturbation theory. To calculate the trajectory we use the spherically symmetric part of the potential. The anisotropic part of the latter determines the selection rules and the probability. The conditions for applicability of the quasiclassical method of calculating CRTP were discussed in [1] and reduce to the fulfillment of two conditions: $\Delta E/E \ll 1$, $|K| < 1/2$, where ΔE and K are, respectively, the energy and modulus of the matrix element of the rotational transition; E is the kinetic energy of the impinging particle. The first requirement determines the condition for classical calculation of the trajectory, and the second requirement is connected with the applicability of the first approximation of perturbation theory. In principle, when the velocities of the colliding particles are high enough and the second requirement is not fulfilled, higher-order perturbation theory can be used, as was suggested in [2].

1. **Wave Functions of Molecule–Atom System.** The wave functions characterizing the states of the molecule–atom system are found from a solution of the Schrödinger equation [4]

$$\hat{H}\Psi = i/\hbar \partial \Psi/\partial t,$$

$$\hat{H} = \hbar^2/2 \left[(I_\xi)^{-1} \hat{L}_\xi^2 + (I_\eta)^{-1} \hat{L}_\eta^2 + (I_\zeta)^{-1} \hat{L}_\zeta^2 \right] + V(R, \theta, \Phi, \alpha, \beta, \gamma) - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2}, \qquad (1.1)$$

where $\hat{L}_\xi$, $\hat{L}_\eta$, $\hat{L}_\zeta$ are the operators of projection of the angular momentum on the ξ, η, and ζ axes, directed along the principal axes of the ellipsoid of inertia of the molecule (Fig. 1); I_ξ, I_η, and I_ζ are the principal moments of inertia of the molecule; $V(R, \theta, \Phi, \alpha, \beta, \gamma)$ is the molecule–atom interaction potential; R is the distance between the atom and the center of mass of the molecule; α, β, and γ are the Eulerian angles, characterizing the position of the system of coordinates ξ, η, and ζ, rigidly attached to the molecule, relative to the laboratory system of coordinates x, y, and z (Fig. 2); the angles θ, Φ characterize the direction of the impinging atom relative to the laboratory system (Fig. 3); μ is the reduced mass of the molecule and atom.

The wave function characterizing the state of the atom–molecule system can be represented in the form of a superposition of products of the wave functions characterizing the spin of the molecule, and the wave function of a particle moving in direction θ, Φ (Fig. 3) relative to a molecule situated at the center of the laboratory system:

$$\Psi = \sum_{j,m,J,M}' C(j, m, k_1, k_{-1}, M, J \mid t) \Psi_{j,m,k_1,k_{-1}} \exp \left[i \left(E_{j,k_1,k_{-1}} + E_J \right) t/\hbar \right] \Psi_1,$$

where j, m, k_1, k_{-1} are the quantum numbers characterizing the rotational state of the molecule in accordance with conventional notation [5]; J is the quantum number characterizing the angular momentum $J\hbar$ of the molecule–particle system; $\Psi_{j,m,k_1,k_{-1}}$ is a function characterizing the spin of the molecule; $E_{j,k_1,k_{-1}}$ is the rotational energy of the molecule in a state determined by quantum numbers j, k_1 and k_{-1}; E_J is the energy of relative rotation of the system; Ψ_1 is a wave function representing the relative motion of the particles as the movement of a particle of mass μ in a centrally symmetric field V(R). This function characterizes the probability of finding a particle with mass μ in a state with particular J in the case where its kinetic energy is E. According to [6], it has the form

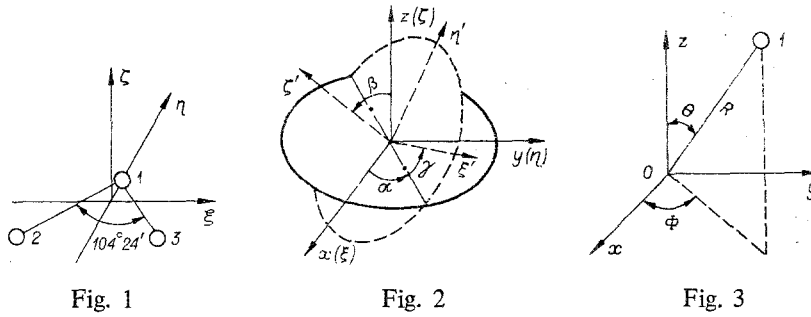$$\Psi_1 = \sqrt{\mu/k_0\hbar} \exp (ik_0 R \cos \theta), \qquad (1.2)$$

Fig. 1   Fig. 2   Fig. 3

where $k_0 = \sqrt{2\mu E/\hbar}$ is the wave vector. The plane wave (1.2) can be expanded in terms of functions

$$\Psi^{\pm}_{k_0 JM} = R^{\pm}_{k_0 J}(R)\, Y_{JM}(\theta, \Phi) \quad [6]:$$

$$\sqrt{\mu/k_0\hbar}\, \exp\left(ik_0 R \cos\theta\right) = \sum_{J=0}^{\infty} \sqrt{\pi\,(2J+1)}\, \frac{1}{ik_0}\left(\Psi^{+}_{k_0, J, 0} - \Psi^{-}_{k_0, J, 0}\right).$$

Here the square of the modulus of the coefficient of $\Psi^{-}_{k_0, J, 0}$ in this expression determines, according to general rules, the probability that a particle will have moment $J\hbar$. The angular dependence of the wave function of a particle with fixed angular momentum $J\hbar$ and its projection $M\hbar$ on the axis is described by the spherical function $Y_{JM}(\theta, \Phi)$. The fundamental asymmetric-top wave functions satisfy the equation

$$\widehat{H}_r \Psi_{j,m,k_1,k_{-1}} = E\Psi_{j,m,k_1,k_{-1}}, \quad \widehat{H}_r = \frac{\hbar^2}{2}\left[(I_\xi)^{-1}\widehat{L}_\xi^2 + (I_\eta)^{-1}\widehat{L}_\eta^2 + (I_\zeta)^{-1}\widehat{L}_\zeta^2\right] \tag{1.3}$$

and are usually represented as a linear combination of symmetric-top wave functions $|jk\rangle$, which can be expressed in terms of generalized spherical functions [7]

$$|jk\rangle = \sqrt{\frac{2j+1}{8\pi^2}}\, D^j_{mk}(\alpha, \beta, \gamma). \tag{1.4}$$

The Hamiltonian $\widehat{H}_r$ and the commutation rules for operators $\widehat{L}_\xi$, $\widehat{L}_\eta$, $\widehat{L}_\zeta$ are invariant to transformations of symmetry group $D2$ [6]. Hence, there are four types of nondegenerate levels corresponding to representations A, B_1, B_2, B_3, and it is convenient to expand the asymmetric-top wave function not in terms of functions $|jk\rangle$, but by using functions Ψ_{jk} [6]:

$$\Psi^{+}_{jk} = \frac{1}{\sqrt{2}}\left(|j, k\rangle + |j, -k\rangle\right), \quad \Psi^{-}_{jk} = \frac{1}{\sqrt{2}}\left(|j, k\rangle - |j, -k\rangle\right), \quad \Psi^{+}_{j0} = \sqrt{\frac{2j+1}{8\pi^2}}\, D^j_{m,0}.$$

The types of representations corresponding to functions Ψ_{jk} are given in Table 1.

Thus, using Table 1, we can construct the linear combination corresponding to the particular type of level:

$$\Psi_{j,m,k_1,k_{-1}} = \sum_k g_k \Psi_{jk}, \tag{1.5}$$

by substituting which in Eq. (3), we obtain the system of equations

$$\sum_{k'}\left\{\langle\Psi_{jk}|\widehat{H}|\Psi_{jk'}\rangle - E\delta_{kk'}\right\}g_{k'} = 0. \tag{1.6}$$

The condition for solvability of this system reduces to a power equation for E. The roots of the obtained equation give $E_{j,k_1,k_{-1}}$ – the asymmetric-top energy levels corresponding to momentum j. Substituting $E_{j,k_1,k_{-1}}$ in (1.6) and using the conditions $\sum_{k'}|g_{k'}|^2 = 1$, we can find the coefficients of the expansion in (1.5). There is no need in principle to calculate the asymmetric-top energy levels, since they are tabulated in [5]. Some water molecule wave functions calculated in explicit form are given in Table 2. The system of rotational levels of water is shown in Fig. 4.

2. Potential of Interaction of H_2O Molecule and Atom. The water molecule, as is known, has symmetry characterized by the group C_{2v} [7]. Owing to the identity of the hydrogen atoms the interaction potential is not altered by rotation of the molecule through an angle π around the η axis and reflection in the $\zeta\eta$ plane (Fig. 1). Hence, the angular part of the potential will be represented by combinations of generalized spherical functions invariant to these transformations. Reflection in the $\zeta\eta$ plane can be represented as the result of rotation through angle π around the η axis followed by reflection in the $\xi\zeta$ plane. The first operation multiplies Ψ_{jk} by $(-1)^k$, while the second is equivalent to a change in the sign of k. Taking

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TABLE 1

	j	k	Type		j	k	Type
Ψ_{jk}^{+}	even	even	A	Ψ_{jk}^{-}	even	even	B_1
	even	odd	B_3		even	odd	B_2
	odd	even	B_1		odd	even	A
	odd	odd	B_2		odd	odd	B_3

TABLE 2

$$J=1 \begin{cases} B_1: \Psi_{10}=|10\rangle, \\[2mm] B_2: \Psi_{00}=\dfrac{1}{\sqrt{2}}(|11\rangle+|1-1\rangle), \\[2mm] B_3: \Psi_{01}=\dfrac{1}{\sqrt{2}}(|11\rangle-|1-1\rangle) \end{cases}$$

$$J=2 \begin{cases} A: \Psi_{20}=0{,}374\dfrac{1}{\sqrt{2}}(|22\rangle+|2-2\rangle)+0{,}928|20\rangle, \\[2mm] B_3: \Psi_{21}=\dfrac{1}{\sqrt{2}}(|21\rangle+|2-1\rangle), \\[2mm] B_2: \Psi_{11}=\dfrac{1}{\sqrt{2}}(|21\rangle-|2-1\rangle), \\[2mm] B_1: \Psi_{12}=\dfrac{1}{\sqrt{2}}(|22\rangle-|2-2\rangle), \\[2mm] A: \Psi_{02}=-0{,}93\dfrac{1}{\sqrt{2}}(|22\rangle+|2-2\rangle)+0{,}3688|20\rangle \end{cases}$$

TABLE 3

$\varkappa r$	c_0^0	c_1^1	c_0^2	c_2^2	c_1^3	c_3^3
1	8,3323	1,9665	0,566	−0,1676	−1,2773	0,0966
3	23,675	11,989	8,691	−2,5717	−2,733	−3,973

into account the definition of functions Ψ_{jk}, we obtain $\sigma_{\zeta\eta}: \Psi_{jk} \rightarrow \Psi_{j,-k}$. Whence it follows that the potential should be expressed in terms of functions Ψ_{jk}^{+} invariant to this transformation. Rotation through angle π around the η axis (symmetry $C_2^{(\eta)}$ operation) leads to multiplication of Ψ_{jk} by $(-1)^{n+k}$ [6]:

$$\Psi_{n,k} \rightarrow \Psi_{n,-k}(-1)^{n+k}.$$

Hence, in the expansion of the potential only terms for which condition $n + k$ is an even number is fulfilled are nonzero. When n and k are even, the term of the expansion corresponds to the type A representation, and if n and k are odd it corresponds to the type B_2 representation.

To calculate the CRTP we need to assign a specific kind of potential. To calculate the CRTP in this work we use a potential in the form of a sum of repulsive exponential potentials. We assume here that the center of gravity of the molecule coincides with the oxygen atom. We conduct the treatment in the Eulerian system of coordinates in the case where the impinging atom moves along the z axis (Fig. 5).

Using the formulas for conversion between the systems of coordinates (x, y, z) and (ξ, η, ζ) we find the distances between the impinging atom and the asymmetric-top atoms, whose principal moments coincide with the ξ, η, and ζ axes. In the case of the water molecule these distances, accurate to $\sim(r/R)^2$ are: $r_{12} = R$, $r_{11} \approx R + r \sin\beta \sin(\gamma + 52°)$, $r_{13} \approx R + r \sin\beta \sin(\gamma - 52°)$, where r is the distance between the hydrogen and oxygen atoms in the molecule. The interaction potential is written accordingly in the form

$$V(R, \gamma, \beta) = e^{-\varkappa R} \{A_{12} + A_{11}[\exp(-\varkappa r \sin\beta \sin(\gamma + 52°)) + \exp(-\varkappa r \sin\beta \sin(\gamma - 52°))]\}, \qquad (2.1)$$

where A_{12} and A_{11} are the pre-exponential factors of the potentials of interaction of the impinging atom with the molecule atoms. The potential (2.1), as was to be expected, depends only on the two angles β and γ, since rotation around the ξ axis through angle α does not alter the values of r_{13} and r_{11}. In accordance with the above, the expansion of the potential in terms of generalized spherical functions has the form
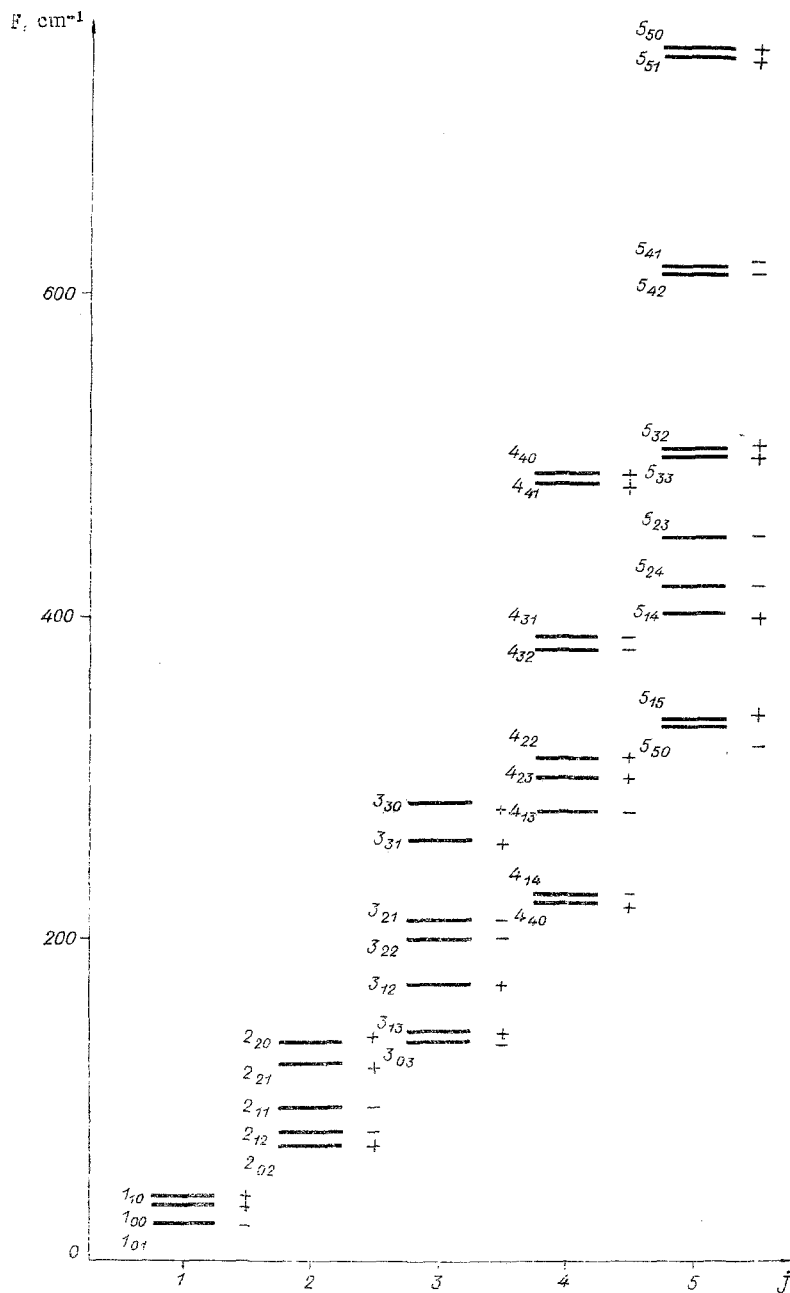
Fig. 4

$$V\left(R,\,\gamma,\,\beta\right)=\mathrm{e}^{-\varkappa R}\left\{A_{12}+A_{11}\sum_{n=0}^{\infty}\sum_{p=0}^{n}\left(-1\right)^{p}C_{p}^{n}\sqrt{\frac{2n+1}{4\pi}}\left[D_{0,p}^{n}\left(0,\,\beta,\,\gamma\right)+D_{0,-p}^{n}\left(0,\,\beta,\,\gamma\right)\right]\right\}.$$

(2.2)

The coefficients of the expansion are found from the formula

$$C_{p}^{n}=\int_{0}^{2\pi}\int_{0}^{\pi}\left\{\exp\left[-\varkappa r\sin\beta\sin\left(\gamma+52°\right)\right]+\exp\left[-\varkappa r\sin\beta\sin\left(\gamma-52°\right)\right]\right\}Y_{p}^{n}\left(\beta,\,\gamma\right)\sin\beta d\beta d\gamma,$$

(2.3)

where $Y_{p}^{n}(\beta,\,\gamma)$ are normalized spherical functions. For $\varkappa r = 1$ and 3 the nonzero coefficients were calculated from Eq. (2.3) on a computer and are given in Table 3.

Thus, in the case where the impinging atom moves along the z axis the interaction potential is given by Eq. (2.2). If the atom moves relative to the laboratory system in a direction determined by angles θ, Φ (Fig. 3), the interaction potential can be found from expression (2.2), by using the known relation

$$D_{0p}^{n}\left(0,\,\beta',\,\gamma'\right)=\sum_{l}D_{0l}^{n}\left(0,\,-\theta,\,-\Phi\right)D_{lp}^{n}\left(\alpha,\,\beta,\,\gamma\right).$$
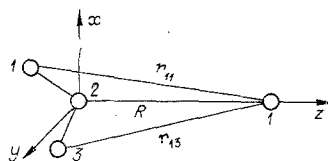
Fig. 5

Taking into account $D_{0l}^n(0,-\theta,-\Phi) = Y_l^n(\theta, \Phi) \sqrt{\frac{4\pi}{2n+1}}$, we obtain an expansion of the potential in terms of functions characterizing the orientation of the atom and molecule relative to the laboratory system:

$$
\begin{aligned}
V(R, \theta, \Phi, \alpha, \beta, \gamma) \approx e^{-\varkappa R} \{A_{12} + A_{11} \{C_0^0 - C_1^1 [Y_{1,-1}(D_{1,1}^1 + \\
+ D_{1,-1}^1) + Y_{1,0}(D_{0,1}^1 + D_{0,-1}^1) + Y_{1,1}(D_{-1,1}^1 + D_{-1,1}^1)] + \\
+ C_0^2 [Y_{2,-2}D_{2,0}^2 + Y_{2,-1}D_{1,0}^2 + Y_{2,0}D_{-1,0}^2 + Y_{2,2}D_{-2,0}^2] + \ldots \}\}.
\end{aligned}
$$

3. Matrix Elements of CRTP.

The CRTP matrix element, found from Eq. (1.1) by using the expression for the wave function Ψ of the system, in the first approximation of perturbation theory has the form

$$
K = -\frac{i}{\hbar} \int_{-\infty}^{\infty} \langle \Psi^* | V(R(t), \theta, \Phi, \alpha, \beta, \gamma) | \Psi \rangle \, dt. \tag{3.1}
$$

As mentioned at the beginning of this paper, the time dependence of the radical part of the wave function of the molecule — atom systems can be found by using the classical equation of motion in the center-of-mass system

$$
\frac{1}{2}\mu(dR/dt)^2 = E - V(R, \theta, \Phi, \alpha, \beta, \gamma) - J^2\hbar^2/2\mu R^2, \tag{3.2}
$$

where E is the total energy; $J\hbar$ is the angular momentum of the relative motion. According to [4], we can obtain an analytical solution of this equation if in Eq. (3.2) we substitute the principal spherically symmetric term of the expansion of potential (2.4), and replace the value of R in the third term of the right-hand side of (3.2) by the effective value R_c. As a result we obtain

$$
(A_{12} + C_0^0 A_{11}) e^{-\varkappa R(t)} = \text{ch}^{-2}\left\{\varkappa\left[\frac{E - J^2\hbar^2/2\mu R_c^2}{2\mu}\right]^{1/2}\right\}[E - J^2\hbar^2/2\mu R_c^2]. \tag{3.3}
$$

Since the interaction potential is divided by the product of the radial and angular parts, we take expression (3.3) into account and find, accurate to the phase factor,

$$
K = -\frac{i}{\hbar} \sum_{\substack{n=0 \\ j,m,k_1,k_{-1},J,M \to j',m',k_1',k_{-1}',J',M'}}^{\infty} \sum_{p=0}^{n} C_p^n(-1)^p (n, j', l, m'|j, m) \, S_{JM}S_j \frac{2\sqrt{2\mu(E - J^2\hbar^2/2\mu R_c^2)}}{\varkappa \, \text{sh} \, \Lambda} \Lambda, \tag{3.4}
$$

where

$$
S_{JM} = \int_0^{2\pi} \int_0^{\pi} Y_{JM}^* Y_{n,-l} Y_{J'M'} \sin\theta d\theta d\varphi;
$$

$$
S_j = \frac{1}{A_{12} + C_0^0 A_{11}} \sqrt{\frac{2j'+1}{2j+1}} \sum_k \sum_{k'} g_k g_{k'} (n, j', p, k'|j, k) \sqrt{1 + (\delta_{k,0} - \delta_{k',0})^2};
$$

$$
\Lambda = \frac{\pi \left(E_{j',m',k_1',k_{-1}',J',M'} - E_{j,m,k_1,k_{-1},J,M}\right)}{2\hbar\varkappa \sqrt{\frac{1}{2\mu}(E - J^2\hbar^2/2\mu R_c^2)}}.
$$

Here g_k and $g_{k'}$ are the coefficients of the expansion in (1.5) of the fundamental asymmetric-top wave functions for the upper and lower levels, respectively; $(n, j', p, k'|j, k)$ and $(n, j', l, m'|j, m)$ are the Clebsch—Gordan coefficients [7], which appear when the anisotropic part of the potential is averaged. The coefficients are nonzero only on condition that: k = k' + p; m = m' + l; J = J' + n.

The expression containing the Kronecker deltas $\delta_{k,0}$ and $\delta_{k';0}$ takes into account the normalized coefficients of functions Ψ_{jk} and Ψ_{j0}. The factor S_{JM} appears when the interaction potential is averaged over the wave functions characterizing the relative rotation of the molecule and atom; the presence of factors S_j and $(n, j', l, m'|j, m)$ is due, respectively, to the change in the angular momentum of the molecule and its projection.

The matrix element K corresponds to the rotational transition of the molecule from the state characterized by quantum numbers j, m, k_1, k_{-1} to the state with quantum numbers j', m', k_1', k_{-1}'. In view of the law of conservation of angular momentum the relative rotation of the molecule and atom is simultaneously altered, which corresponds to a transition from the state with quantum numbers J and M to the state with quantum numbers J' and M'.

Averaging the anisotropic part of the potential over the wave functions determines the selection rules and the value of the angular part of the matrix element.

As mentioned above, the terms of the potential expansion, which depend on angles α, β, γ, belong to symmetry types A and B_2. Since the potential terms corresponding to symmetry type A are fully symmetric, then on averaging them over the fundamental wave functions of the molecule the matrix elements are nonzero only for transitions $A \leftrightarrow A$, $B_1 \leftrightarrow B_1$, $B_2 \leftrightarrow B_2$, $B_3 \leftrightarrow B_3$. Expansions of the direct products of B_2 with other irreducible representations of group D_2 will be: $B_1 \times B_1 = B_3$, $B_3 \times B_2 = B_1$, $A \times B_2 = B_2$. Hence, for potential terms possessing symmetry type B_2 the matrix elements for transitions $B_1 \leftrightarrow B_3$, $A \leftrightarrow B_2$ are nonzero. Moreover, additional prohibitions on the transitions are imposed by the law of conservation of parity. It follows from the law of conservation of parity of a closed system that the numbers $\Delta j = j' - j$ and $\Delta J = J' - J$, which characterize the change in state of the molecule−atom system, must have the same parity.

When the potential is averaged over the spherical functions $Y_{JM}(\theta, \Phi)$ a nonzero result is obtained when condition [4] is fulfilled: J + J' + n is an even number. This means that terms of the potential expansion with odd (even) n determine transitions with odd (even) ΔJ. Hence, the type A potential terms determine the transitions between levels of the same parity with $\Delta j = 0, \pm 2, \pm 4 ...$, and the type B_2 terms determine transitions with $\Delta j = \pm 1, \pm 3, \pm 5, ...$ between levels with different parity. Whence, in view of the selection rules obtained above, it follows that the positive levels do not combine with negative levels.

4. **Collisional Rotational Transition Probabilities.** The CRTP can be found in a first approximation from expression (3.4) by leaving in it for the particular transition the principal terms of the expansion, which make the main contribution to the modulus of the matrix element of this transition. After averaging over the quantum numbers m and M we obtain the CRTP for the transitions $j \to j - \Delta j$:

$$P(j, k_1, k_{-1}, J) = \frac{1}{\hbar^2} S_{jJ}^{\Delta j} R_j^{\Delta j} \frac{8\mu \left(E - J^2 \hbar^2 / 2\mu R_c^2\right)}{\varkappa^2} \frac{\Lambda^2}{\mathrm{sh}^2 \Lambda},$$

where

$$S_{jJ}^{\Delta j} = \frac{1}{(2j+1)(2J+1)} \sum_m \sum_M S_{JM}^2 (n, j', -l, m' \mid j, m)^2.$$

The expressions for $R_j^{\Delta j}$ and $S_{jJ}^{\Delta j}$, and also the selection rules in the case $\Delta j = 0, 1, 2$ are given below

$$\Delta j = 0: \quad \Delta m = \Delta M = 0, \quad S_{jJ}^0 = 1, \quad R_j^0 = \left[\sum_k g_k g_{k'}\right]^2,$$

$$(+) \leftrightarrow (+), (-) \leftrightarrow (-), \text{ even} \leftrightarrow \text{even}, \text{ odd} \leftrightarrow \text{odd}; \quad ;$$

$$\Delta j = 1: \begin{matrix} j+1 \to j, \\ k+1 \to k, \end{matrix} \quad R_j^1 = \left(\frac{C_1^1 A_{11}}{A_{12} + C_0^0 A_{11}}\right)^2 \frac{2j+1}{2j+3} (S_j^1)^2,$$

$$S_j^1 = \sum_{k>0} g_k g_{k'} \sqrt{\frac{(j+k+1)(j+k+2)}{(2j+1)(2j+2)}} \, \sqrt{1 + (\delta_{k,0} - \delta_{k',0}^2)};$$

$$S_{jJ}^1 \approx 1.45 \cdot 10^{-1}; \quad \Delta m = -\Delta M = 0, \quad \pm 1;$$

$$(+) \leftrightarrow (+); (-) \leftrightarrow (-); \text{ even} \leftrightarrow \text{odd};$$

$$\Delta j = 2: \begin{matrix} j+2 \to j, \\ k+2 \to k, \\ k \to k, \end{matrix} \quad R_j^2 = \frac{(2j+1)}{(2j+5)} \left[C_0^2 S_{j,k \to k}^2 + C_2^2 S_{j,k \to k-2}^2\right]^2,$$

where

$$S_{j,k \to k}^2 = \sum_{k>0} g_k g_{k'} \left[\frac{6(j+k+2)(j+k+1)(j-k+2)(j-k+1)}{(2j+1)(2j+2)(2j+3)(2j+4)}\right]^{1/2};$$

$$S_{j,k \to k-2}^2 = \sum_{k>0} g_k g_{k'} \left\{\frac{(j-k+1)(j-k)(j-k+1)(j-k+2)[1 + (\delta_{k,0} - \delta_{k',0})^2]}{(2j+1)(2j+2)(2j+3)(2j+4)}\right\}^{1/2};$$

$$S_{jJ}^2 \approx 3.1 \cdot 10^{-2}; \quad \Delta m = -\Delta M = 0, \pm 1, \pm 2; (+) \leftrightarrow (+); (-) \leftrightarrow (-);$$

even $\leftrightarrow$ even; odd $\leftrightarrow$ odd. Here g_k and $g_{k'}$ are the coefficients in the wave-function expansions. The values of R_j^0, S_j^1, and S_j^2 for some transitions are given in Table 4.

To calculate the kinetics of the populations of the rotational levels we need to know the temperature dependences of the cross sections of collisional transitions from the j-th level of the molecule. In the case where the particles have a Maxwellian velocity distribution the transition cross section can be found by averaging over the velocities and the quantum

TABLE 4

Transitions	$2_{20}\to2_{12}$	$3_{30}\to3_{12}$	$3_{22}\to3_{03}$	$4_{40}\to4_{22}$	$4_{22}\to4_{04}$	$5_{50}\to5_{32}$	$6_{60}\to6_{42}$
R_j^0	0,14	$5,3\cdot10^{-3}$	$1,21\cdot10^{-2}$	0,925	$1,6\cdot10^{-3}$	$8,2\cdot10^{-2}$	$2,88\cdot10^{-4}$

	$6_{42}\to6_{24}$	$7_{70}\to7_{52}$	$7_{52}\to7_{34}$	$7_{34}\to7_{16}$	$7_{61}\to7_{43}$
R_j^0	$3,24\cdot10^{-4}$	$4,35\cdot10^{-3}$	$2,1\cdot10^{-2}$	0,425	$2,5\cdot10^{-3}$

	$3_{30}\to2_{21}$	$4_{40}\to3_{31}$	$4_{22}\to4_{31}$	$5_{51}\to4_{40}$	$5_{42}\to4_{31}$	$6_{16}\to5_{05}$
S_j^1	0,58	0,62	0,335	0,4	0,65	0,54

	$5_{50}\to3_{30}$	$5_{51}\to3_{31}$	$5_{50}\to3_{12}$
S_j^2	0,042	0,033	0,2

number J. The probability of collision of a molecule with an atom possessing quantum number J is given by relation (1.2) [4]. Neglecting partial-wave interference and replacing summation over J by integration, we can find the temperature dependence of the cross section from the formula

$$Q(j\to j',\,T)\approx\pi\int_0^\infty\frac{\hbar^2}{2\mu E}Z(E,\,T)\int_0^\infty P_{j\to j'}(2J+1)\,dJ\,dE,$$

where $Z(E,\,T)\,dE=N_0d_0^2\sqrt{\dfrac{8\pi}{qT}}\exp\left(-\dfrac{E}{qT}\right)dE$ is the number of collisions in unit time between the gas particles possessing energy of relative motion in the interval E to E + dE; N_0 is the concentration of atoms; d_0 is the gas-kinetic diameter of the molecule; q is the Boltzmann constant.

Using the method of steepest descents [8] for averaging over E, we obtain the following expression for the cross section of the transition with Δj = 0, 1, 2:

$$Q(j,\,k_1,\,k_{-1},\,T)=\frac{8\pi R_c^2}{\hbar^2}\sqrt{\frac{8}{3\mu}}N_0d_0^2(A_0qT)^{1/3}S_{jj}^{\Delta j}R_j^{\Delta j}\exp\left[-3A_0^{2/3}/(qT)^{1/3}\right],$$

where

$$A_0=\pi\left(E_{j,k_1,k_{-1}}-E_{j',k_1',k_{-1}'}\right)\big/2\hbar\varkappa.$$

Discussion of Results. We have obtained selection rules for collisional rotational transitions of the water molecule and have calculated the CRTP in the case of interaction of the molecule with an impinging heavy particle. The most remarkable fact is the absence of rotational transitions between the (+) and (−) levels. This is due to the symmetry of the molecule, whose potential is not altered by interchange of the hydrogen atoms, nor by the prohibitions imposed by the law of conservation of parity. Thus, in conditions where the probability of radiative transitions is much less than the CRTP, rotational relaxation proceeds independently at the (+) and (−) levels.

It should be noted that, irrespective of the kind of interaction potential, the allowed transitions in the zeroth approximation are those with Δj = 0, determined by the main spherically symmetric term of the potential. In the first approximation transitions with Δj = ±1 are allowed, in the second approximation transitions with Δj = ±2, etc. In this case the rotational transition cross sections, as Eq. (3.4) indicates, are determined by two factors: the spherical factor and the energy of the rotational quantum ΔE_j corresponding to the particular transition. The relation between the cross sections in this case has the form

$$\frac{Q_{j\to j-\Delta j}}{Q_{j\to j}}\frac{R_j^{\Delta j}S_{jj}^{\Delta j}}{R_j^0}\left(\frac{A_0^{\Delta j}}{A_0}\right)^{1/3}\exp\left\{-3\left[(A_0^{\Delta j})^{2/3}-A_0^{2/3}\right]/(qT)^{1/3}\right\},$$

where $A_0^{\Delta j}=\pi\Delta E^{\Delta j}/2\hbar\varkappa$; $\Delta E^{\Delta j}$ is the energy of the rotational quantum corresponding to the transition with Δj = 0, 1, 2.

In addition, the relation depends on $\varkappa r$, which in principle must be determined from experiment. As estimates show, the value of $\varkappa r$ lies in the interval 1 to 3. In the case of interaction of the water molecule with the He atom the preexponential factors are [1]

$$\mathrm{H-He:}\ A_{11}=1,4\cdot10^{-11}\ \mathrm{erg},\quad \mathrm{O-He:}\ A_{12}=10^{-9}\ \mathrm{erg}.$$

In this case

$$\frac{R_j^1 S_{jJ}^1}{R_j^0} \approx \begin{cases} 3.3 \cdot 10^{-3} \left(S_j^1\right)^2 / R_j^0 & \text{for } \varkappa r = 1, \\ 3.54 \cdot 10^{-2} \left(S_j^1\right)^2 / R_j^0 & \varkappa r = 3, \end{cases}$$

$$\frac{R_j^2 S_{jJ}^2}{R_j^0} \approx \begin{cases} 5.7 \cdot 10^{-5} \left(S_{j,k\to k}^2\right)^2 / R_j^0 & \text{for } \varkappa r = 1, \\ 4 \cdot 10^{-3} \left(S_{j,k\to k}^2\right)^2 / R_j^0 & \varkappa r = 3. \end{cases} \tag{5.1}$$

Substituting in (5.1) the values given in Table 4 we can see that the cross sections of multiquantum transitions can be comparable with the cross sections of transitions with $\Delta j = 0$. Hence, the picture of rotational relaxation of the water molecules is very complex and a detailed analysis is required for determination of the main relaxation channels.

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RESONANCE ABSORPTION OF EMISSION (10.6 μm) IN $CO_2 - N_2$ MIXTURES BEHIND A SHOCK FRONT

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An important parameter affecting the shape of the absorption (amplification) line is the collisional width of the spectral line. In application to flows of $CO_2 - N_2 - H_2O$ (He) mixtures the accuracy of its assignment throughout the range of the translational temperature of the flow as the gas cools in a nozzle significantly affects the correctness of calculation of the amplification factor of the medium. The question of the temperature dependence of the CO_2 molecule spectral line width is of particular importance in the construction of mathematical models of vibrational energy transfer, if the criterion of their correctness in the comparison of theory and experiment is the amplification factor.

The value of the collisional width b_c of the spectral line for the CO_2 molecule is known sufficiently accurately at T = 300°K for $CO_2 - N_2 -$ He mixtures [1]. Yet, despite the fairly large number of investigations of the temperature dependence $b_c(T)$ [2-5], this question still remains open. Different forms of $b_c = f(T)$ have been proposed to improve the agreement between the theoretical and experimental temperature dependences of the absorption coefficient in CO_2. For instance, in [2] the best agreement between theory and experiment at T = 360-400°K was obtained on the assumption that $b_c \sim T^{-3/2}$, whereas in [4] the relation $b_c \sim 1/T$ was used to explain the experimental results up to T = 1600°K and the contribution of the "hot" transitions $R23(01^11 \to 11^10)$ and $R4(02^0 1 \to 12^00)$ was taken into account. At the same time, in [3, 5] the charge in absorption coefficient k_ν with temperature could be explained on the assumption that $b_c \sim T^{-1/2}$, including a consideration of the contribution of additional transitions and the overlap of the rotational bands at p > 1 atm and T > 1000°K. It should also be noted that these investigations were mainly concerned with the relation $k_\nu(T)$ in pure CO_2, and there are hardly any data for $CO_2 - NO_2$ mixtures.

To determine the temperature dependence of the collisional width of the collision line in $CO_2 - N_2$ mixtures in the present investigations we considered the behavior of the absorption coefficient on the P20 $(00^0 1 \to 10^0 0)$ transition of the CO_2 molecule behind a straight shock front for temperatures in the range 700-1250°K and N_2 content of the mixture 0-95%.