Quasiclassical description of rotational transitions in molecules of asymmetric-top type

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The rotational Hamiltonian in action-angle variables is written down for the water molecule considered as a rigid asymmetric top. A method for parametrizing multidimensional potential surfaces is proposed. Quasiclassical quantization of the Hamiltonian, based on the Bohr-Sommerfeld principle, is carried out. Analytic formulas for the cross sections for excitation of rotational levels of the H_2O molecule in collisions with atoms are derived by the quasiclassical Dubrovskiĭ-Bogdanov T-matrix method. The rotational excitation constants for a number of rotational levels in the H_2O + He system are calculated over a broad temperature range. The results are compared with those of calculations based on the close-coupling method.

1. INTRODUCTION

The rapid development of both high and superhigh resolution molecular spectroscopy,[1] the appearance of sensitive experiments measuring the rotational distributions of the reaction products of photodissociation[2] and monomolecular dissociation,[3] the search for a means of obtaining population inversions of rotational levels in gaseous flows,[4,5] the problem of cosmic masers,[6] and a number of other problems have necessitated a deep study of the rotational dynamics of polyatomic molecules. The goal of the present article is a consideration of collisional rotational transitions within the framework of the quasiclassical Boganov-Dubrovskiĭ T-matrix method,[7] which uses a representation of the scattering amplitude in action-angle variables, and the generalized eikonal approximation based on it.[8,9] It may be noted that such an approach has a number of advantages over the sudden-perturbation approximation, presently in wide use, or "exact" calculations based on the close-coupling method, since the latter involve uncontrollable approximations (such as, e.g., the choice of the basis in the close-coupling method) and do not enable one to obtain analytic approximations for the cross sections or the rate constants of the rotational transitions.

The generalized eikonal method has been previously used for the description of the rotational excitation of asymmetric-top molecules in Ref. 10, but the method used there of introducing the action-angle variables[11] did not permit the calculation of the quasiclassical spectrum of the molecule, thereby creating definite difficulties of the calculation of the cross sections of the rotational transitions.

For this reason we introduce (in Sec. 2) the action-angle variables for the asymmetric top, following the technique in Ref. 12. In Sec. 3 we discuss questions of the quasiclassical quantization of the rotational degrees of freedom of the H_2O molecule, and in Sec. 4 we consider the probability of the rotational excitation of this molecule by a helium atom.

2. ACTION-ANGLE VARIABLES FOR AN ASYMMETRIC TOP

The classical Hamiltonian of the asymmetric top has the form

$$H = AJ_\xi^2 + BJ_\eta^2 + CJ_\zeta^2, \qquad (2.1)$$

where J_ξ, J_η, and J_ζ are the projections of the angular momentum vector on the ξ, η, and ζ axes of the moving molecular coordinate system and are aligned with the major axes of the ellipsoid of inertia of the molecule, and A, B, and C are rotational constants of the molecule, inversely proportional to its principal moments of inertia. We will assume for definiteness that $A > B > C$. For the water molecule this condition leads to a choice of the moving system shown in Fig. 1. Rotation of the molecule is described with the help of the Euler angles α, β, and γ, which characterize the orientation of the molecular system with respect to the fixed laboratory coordinate system x, y, z (Fig. 2).

To transform Eq. (2.1) to action-angle variables we first write this expression in the canonical conjugate coordinates of Deprit[12] $L = J_\xi$, $I_2 = J$, and $I_3 = J_z$,

$$H = (I_2^2 - L^2)(A \sin^2 l + B \cos^2 l) + CL^2. \qquad (2.2)$$

The angle l as well as the angles φ_2 and φ_3, which will be used below, are indicated in Fig. 2 and defined in its caption.

From Eq. (2.2) it can be seen that the variables I_2 and I_3 are integrals of the motion, from which it follows that the energy of rotational motion is degenerate. Thus, for a given value of I_2 the problem of rotation of an asymmetric rotator reduces to determining the motion of a conservative system with one degree of freedom

$$\chi = \frac{2B - A - C}{A - C}, \quad \varkappa^2 = \frac{1 - \chi}{1 + \chi}, \quad r^2 = \varkappa^2 \frac{CI_2^2 - H}{H - AI_2^2}, \quad r'^2 = 1 - r^2. \qquad (2.3)$$

Solving Eq. (2.2) for L^2, we obtain

$$L^2 = I_2^2 \frac{\varkappa^2}{\varkappa^2 + r^2} \frac{r'^2 + (\varkappa^2 + r^2)\sin^2 l}{1 + \varkappa^2 \sin^2 l}. \qquad (2.4)$$

For a fixed value of the momentum I_2 the phase space (L,l) of the Hamiltonian (2.2), filled with the trajectories of one-dimensional motion, is a sphere of radius I_2. The trajectories $L(l)$ on this sphere, which are determined by the value of the energy $E = H$, are closed. The separatrix $r = 1$ divides the phase space into four invariant regions (see Fig. 3), in each of which one can introduce the action-angle variables[1] I_1 and q_1 (Ref. 12):
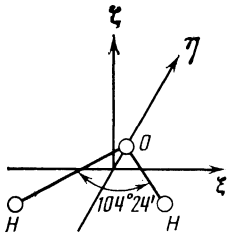
$$I_1 = \frac{1}{2\pi} \oint L \, dl. \qquad (2.5a)$$

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FIG. 1. Choice of the molecular coordinate system for the water molecule.

FIG. 3. Phase space of the system with Hamiltonian (2.2) (scan of the sphere of radius I_2).

Substituting expression (2.4) into the integrand and taking into account the periodicity of the trajectory, we write this integral in the form

$$I_1 = \frac{2I_2\varkappa}{\pi(\varkappa^2+r^2)^{1/2}} \int\limits_{l_0}^{l_0+l_1} \left[\frac{r'^{\,2}+(\varkappa^2+r^2)\sin^2 l}{1+\varkappa^2\sin^2 l} \right]^{1/2} dl, \quad (2.5b)$$

where the choice of l_0 and l_1 for regions I–IV is made as shown in Table I.

For $r < 1$, the integral (2.5b) with the help of the substitution

$$\mathrm{ctg}\, l = -(1+\varkappa^2)^{1/2}\,\mathrm{tg}\,\xi \quad (2.6a)$$

reduces to complete elliptic integrals of the first $K(r)$ and third $\Pi(\varkappa^2,r)$ kinds:

$$I_1 = \frac{2I_2}{\pi\varkappa}\left(\frac{1+\varkappa^2}{r^2+\varkappa^2}\right)^{1/2} [(r^2+\varkappa^2)\Pi(\varkappa^2,r) - r^2 K(r)]. \quad (2.7a)$$

It can be shown[12] that I_1 is monotonically decreasing with increasing r, therefore Eq. (2.7a) determines r as a function of the action variables

$$r=\Phi_1(I_1/I_2). \quad (2.8a)$$

Recalling the definition of the parameter r (Eq. 2.3), we solve it for H, which, taking Eq. (2.8a) into account, gives the Hamiltonian function in action-angle variables

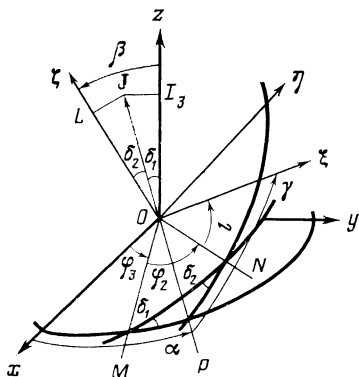$$H=AI_2^2\left(1 - \frac{A-C}{A}\frac{\varkappa^2}{\varkappa^2+r^2}\right). \quad (2.9)$$

FIG. 2. Mutual placement of the laboratory (x,y,z) and the molecular (ξ,η,ζ) coordinate systems: α, β, γ are the Euler angles, and l, φ_2, φ_3 are the Deprit angle variables (OP is the line of nodes, $OM \perp J$, $OM \perp J$).

For $r > 1$ integral (2.5b) reduces to elliptical functions with the help of the substitution

$$\cos l = -\frac{(1+\varkappa^2)^{1/2}}{r}\frac{\sin\xi}{(1+(\varkappa^2/r^2)\sin^2\xi)^{1/2}}. \quad (2.6b)$$

After some transformation we obtain in this case in place of Eq. (2.7a)

$$I_1 = \frac{2I_2}{\pi\varkappa r}\left(\frac{1+\varkappa^2}{r^2+\varkappa^2}\right)^{1/2}\left[(r^2+\varkappa^2)\Pi\left(\frac{\varkappa^2}{r^2},\frac{1}{r}\right) - r^2 K\left(\frac{1}{r}\right)\right]. \quad (2.7b)$$

Like Eq. (2.7a) expression (2.7b) determines the dependence of r on the action variables:

$$r=\Phi_2(I_1/I_2). \quad (2.8b)$$

The Hamiltonian in action-angle variables in regions III and IV, as before, has the form (2.9), but the r defined by Eqs. (2.8b) and (2.7b).

The angle variables $\mathbf{q} = (q_1,q_2,q_3)$, canonically conjugate to the action variables $\mathbf{I} = (I_1,I_2,I_3)$, are calculated with the help of the generator $G(I_1,I_2,I_3;l,\varphi_2,\varphi_3)$ of the canonical transformation

$$G=I_3\varphi_3+I_2\varphi_2 \pm \int\limits_{l_0}^{l} dx\, L(x;\mathbf{I}), \quad (2.10)$$

where the minus sign is chosen in region II and $L(l,\mathbf{I})$ is defined by Eqs. (2.4) and (2.8). Differentiating G with respect to the corresponding action variables, we find ($\Phi = \Phi_1$ or Φ_2 for $r < 1$ or $r > 1$)

$$q_1 = \pm\frac{\partial\Phi}{\partial I_1}\int\limits_{l_0}^{l} dx\,\frac{\partial L}{\partial r},$$

$$q_2=\varphi_2 \pm \frac{1}{I_2}\int\limits_{l_0}^{l} dx\, L \pm \frac{\partial\Phi}{\partial I_2}\int\limits_{l_0}^{l} dx\,\frac{\partial L}{\partial r},$$

$$q_3=\varphi_3.$$

With the help of substitutions (2.6) the integrals in these expressions reduce to elliptical functions

TABLE I. Choice of the initial point of the integration (L_0, l_0) in the integral (2.5) for the various regions of phase space.

Region	I	II	III	IV
r	$0 \leqslant r < 1$		$1 < r < +\infty$	
sign L_0	$+$	$-$	$+$	$-$
l_0	$\dfrac{\pi}{2}$	$\dfrac{3\pi}{2}$	$\dfrac{\pi}{2}$	$\dfrac{3\pi}{2}$
l_1	$\dfrac{\pi}{2}$	$-\dfrac{\pi}{2}$	$\arccos\left(\dfrac{r^2-1}{r^2+\varkappa^2}\right)^{1/2}$	$-\arccos\left(\dfrac{r^2-1}{r^2+\varkappa^2}\right)^{1/2}$

$$q_1 = \pm\frac{\pi}{2}\left[\frac{F(\xi,\lambda)}{K(\lambda)}\right],$$

$$q_2 = \varphi_2 \pm \frac{1}{\mu}\left[(1+\mu^2)(\lambda^2+\mu^2)\right]^{1/2}\Big\{\Pi(\xi,\mu^2,\lambda)$$

$$-\Pi(\mu^2,\lambda)\frac{F(\xi,\lambda)}{K(\lambda)}\Big\},$$

$$q_3 = \varphi_3. \tag{2.11}$$

For the sake of brevity the following notation has been introduced in Eq. (2.11):

$$\lambda = r, \quad \mu = \varkappa \quad \text{for} \quad r < 1,$$

$$\lambda = 1/r, \quad \mu = \varkappa/r \quad \text{for} \quad r > 1. \tag{2.12}$$

To complete the description of the free rotation of the asymmetric rotator in the variables $(\mathbf{I}, \mathbf{q})$ we express in these variables the elements of the direction-cosine $A(\alpha,\beta,\gamma)$ matrix of the system $\xi\eta\zeta$ in the system xyz. From Fig. 2 it can be seen that a rotation about the angles α, β, γ can be represented in the form of two successive rotations: $\varphi_3, \delta_1, 0$ and φ_2, δ_2, l,

$$A(\alpha,\beta,\gamma) = A(\varphi_2,\delta_2,l)A(\varphi_3,\delta_1,0). \tag{2.13}$$

Since $\varphi_3 = q_3$ and $\cos\delta_1 = I_3/I_2$, the second factor in Eq. (2.13) is already written in terms of action-angle variables. To write the first factor in terms of these variables it is necessary to invert relation (2.11), taking into account Eqs. (2.4) and (2.6) and the definition of the angle δ_2: $\cos\delta_2 = L/I_2$. The result of this inversion can be written in the form[11]

$$A(\mathbf{I},\mathbf{q}) = A(\Delta,\delta_2,l(\xi))A(q_2,0,0)A(q_3,\delta_1,0), \tag{2.14}$$

where

$$\Delta = \frac{i}{2}\ln\left[\frac{\theta_4(q_1+ia)}{\theta_4(q_1-ia)}\right], \quad a = \frac{\pi}{2}\frac{F(\text{arctg}\,\mu/\lambda,(1-\lambda^2)^{1/2})}{K(\lambda)},$$

$$\xi = \pm\,\text{am}\left[\frac{2K(\lambda)}{\pi}q_1,\lambda\right].$$

In these formulas the notation (2.12) is used again. The quantity L is expressed in terms of $I_1, I_2,$ and q_1 in the following way:

$$L = \pm\frac{\varkappa I_2}{(\varkappa^2+r^2)^{1/2}}\left\{\begin{matrix}\text{dn}\\\text{cn}\end{matrix}\right\}\left[\frac{2K(\lambda)}{\pi}q_1,\lambda\right], \quad r \lessgtr 1,$$

θ, am, dn, and cn are elliptical functions. Simplification of (2.14) can be realized by expanding the elements of the first factor in series in the Jacobi parameter[2]:

$$g = \exp[-\pi K((1-\lambda^2)^{1/2})/K(\lambda)].$$

Note that the action variable I_1 can be introduced in an analogous way by averaging the projection $L' = J_\xi$ of the angular momentum along the ξ axis. The choice of one of the projections (which for us means a choice of the quantization axis) is connected with the peculiarities of the motion of the top for different values of the parameters r and $\varkappa$ will be discussed in the next section.

3. QUASICLASSICAL QUANTIZATION OF THE ROTATIONAL DEGREES OF FREEDOM OF AN ASYMMETRIC TOP

Applying the Bohr-Sommerfeld principle, the action variables above can be expressed in terms of the corresponding quantum numbers:

$$I_3 = m\hbar, \quad I_2 = (j+^1/_2)\hbar, \quad I_1 = (k+\gamma)\hbar, \tag{3.1}$$

where γ is a number of the order of unity. To determine γ, let us consider in more detail the character of the rotational motion of an asymmetric rotator. This can be most easily visualized with the help of an analog of the potential energy surface—the rotational-energy surface, which was introduced in Ref. 13. The form of the rotational-energy surface and the trajectories on it are shown in Fig. 4 for an asymmetric top.

As can be seen from the figure, for $J_\xi \sim J(r \ll 1)$ the vector $\mathbf{J}$ precesses rapidly about the ζ axis, completing small librational oscillations with respect to the two other axes. For $J_\xi \sim J(r \gg 1)$ the vector $\mathbf{J}$ precesses about the ξ axis. These two types of trajectories are separated by the separatrix, which is defined by the equality $r = 1$. The trajectories close to the separatrix are characterized by nonuniform rates of motion: the vector $\mathbf{J}$, slowing down, approaches the η axis, remains close to it for some time, and then with accelerating motion migrates to its opposite end. It can be seen from Eqs. (2.3) that on the separatrix the energy of rotational motion is equal to

$$E = BI_2^2. \tag{3.2}$$

Since the quantization rule (3.1) with $\gamma = 0$ is most appropriate for prescessional motions, it is reasonable to take the ζ axis as the axis of quantization for $r < 1$ $(CI_2^2 < E < BI_2^2)$, in which case[3] $k = k_+$, and to take the ξ
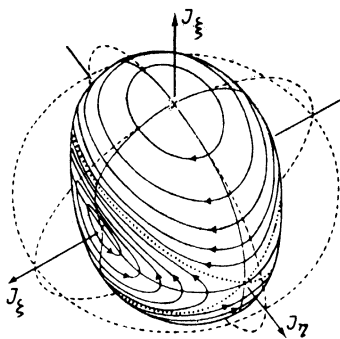
FIG. 4. Rotational energy surface for an asymmetric-top molecule: the solid lines with the arrow are the trajectories of the vector $\mathbf{J}$; the dashed lines show the constant energy sphere for $E = E_{max} = AI_2^2$; the dotted lines show the separatrix, defined by the intersection of the rotational energy surface with the sphere $E = BI_2^2$.

axis for $r > 1$ $(BI_2^2 < E < AI_2^2)$, in which case $k = k_-$. Passage across the separatrix is accompanied by a changeover from rotational precession to oscillatory libration for which, due to the existence of two turning points, $|\gamma|$ equals $1/2$. Such a choice of γ is in agreement with the results of the calculation of the quantity I_1 according to Eq. (2.7) based on experimental data[14] on the rotational spectrum of the water molecule. In the region of small values of the projection J_ζ these quantities with good accuracy take half-integer values, and in the region of large values of the projection, close to the value of the total angular momentum J, these quantities take on integer values with the same accuracy. Results of calculation of the spectrum of the H_2O molecule within the framework of this approach are displayed in Table II, where they are compared with experimental data.[14] It

can be seen that quasiclassical quantization works well in the region $|\tau| \geqslant 2$, where $\tau = k_- k_+$ is the "number" of the level. The so-obtained quasiclassical spectrum turns out to be degenerate: for each level with energy less (greater) than BI_2^2, to each value of k_+ (k_-) there correspond two values of k_- (k_+), equal to

$$k_\mp = j + {}^1/_2 - k_\pm \pm {}^1/_2. \tag{3.3}$$

This degeneracy is lifted when one allows for the finite value of the probability of transition from a rotational state with given $\mathbf{J}$ to a state with angular momentum $-\mathbf{J}$ (Ref. 15).

In conjunction with the assumed quantization rule for the calculation of the transition probabilities it is convenient to have available the possibility of a unified description of the rotational levels. This can be achieved with the help of the relation

$$I_{1(\zeta)} + I_{1(\xi)} = I_2, \tag{3.4}$$

where $I_{1(\alpha)}$ denotes the action variable (2.5a) quantized along the α axis (i.e., $L = J_\alpha$). To prove (3.4) we differentiate (2.7a) with respect to r:

$$\frac{dI_{1(\zeta)}}{dr} = -\frac{2I_2}{\pi} \frac{\varkappa r(1+\varkappa^2)^{1/2}}{(\varkappa^2 + r^2)^{3/2}} K(r). \tag{3.5}$$

The choice of ξ as the axis of quantization corresponds to exchanging A and C in Eqs. (2.2) and (2.3). Here formulas (2.7a) and (2.7b) remain valid if in them one makes the substitutions $r \to r_\xi = r^{-1}$ and $\varkappa \to \varkappa_\xi = \varkappa^{-1}$. We obtain then for (2.7b) $(r_\xi > 1$ for $r < 1)$

$$\frac{dI_{1(\xi)}}{dr_\xi} = -\frac{2I_2}{\pi} \frac{\varkappa_\xi(1+\varkappa_\xi^2)^{1/2}}{(r_\xi^2 + \varkappa_\xi^2)^{3/2}} K(r_\xi^{-1}). \tag{3.6}$$

From Eqs. (3.5) and (3.6) it follows that $d(I_{1(\zeta)} + I_{1(\xi)})/$

TABLE II. Rotational spectrum of the water molecule (in cm^{-1}): Upper row (which takes into account degeneracy, see text)—calculation according to equation (3.1), Lower row—experimental spectrum.[14]

$I_1 = 1$			$I_2 = 2$				
1_{01}	1_{11}	1_{10}	2_{02}	2_{12}	2_{11}	2_{21}	2_{20}
28.8	38.0	54.1	76.1	76.1	89.6	131	131
23.8	37.1	42.4	70	79.2	95.1	134.9	136.16

$I_2 = 4$

4_{04}	4_{14}	4_{13}	4_{23}	4_{22}	4_{32}	4_{31}	4_{41}	4_{40}
224.3	224.3	287.8	308.3	308.3	380.1	380.1	484.2	484.2
222	224.8	275.5	300.4	315.8	382.5	383.8	488.1	488.1

$I_2 = 6$

6_{06}	6_{16}	6_{15}	6_{25}	6_{24}	6_{34}	6_{33}	6_{43}	6_{42}	6_{52}	6_{51}	6_{61}	6_{60}
444	444	552	552	593	593	661	757	757	891	891	1056	1056
447	447	543	553	603	643	656	757	758	889	889	1045.1	1045

$dr = 0$, and since $I_{1(\zeta)} (r = 0) = I_2$ and $I_{1(\xi)} (r = 0) = 0$, we obtain the result (3.4). Quantization of relation (3.4) with the help of Eqs. (3.1) for $\gamma = \pm 1/2$ leads to Eq. (3.3).

4. CALCULATION OF THE PROBABILITY OF EXCITATION BY AN ATOM OF THE ROTATIONAL STATES OF AN ASYMMETRIC-TOP MOLECULE

To approximate the true potential-energy surfaces of the interaction of an atom with an asymmetric-top molecule one commonly uses an expansion of these surfaces in spherical harmonics. Thus, to describe the interaction of a water molecule with a helium atom S. Green[16] has proposed a potential of the form

$$V(R, \vartheta, \varphi) = \sum_{\alpha \geqslant \beta \geqslant 0}' \frac{V_{\alpha\beta}(R)}{1+\delta_{\beta,0}} [Y_{\alpha\beta}(\vartheta, \varphi) + Y_{\alpha-\beta}(\vartheta, \varphi)],$$

(4.1)

where $\mathbf{R}$ is the radius vector directed from the center of mass of the molecule to the atom, and ϑ and φ are the angle corresponding to the direction $\mathbf{R}$ in the spherical coordinate system associated with the molecule (with major axis directed along the η axis, see Fig. 1). The prime in Eq. (4.1) signifies that the sum is to be taken only over even β, as dictated by the symmetry of the H_2O molecule. The radial dependence of the coefficients $V_{\alpha\beta}$, calculated within the framework of the electron-gas model, is given in Ref. 16 in tabular form.

In the construction of the analytic approximations of the partial coefficients $V_{\alpha\beta}$ we take the spherically symmetric part of the potential V_{00} in the form of a sum of a repulsive $V_{00}^{(r)}$ and an attractive $V_{00}^{(a)}$ part, and we represent the remaining coefficients in the form

$$V_{\alpha\beta}(R) = a_{\alpha\beta}^{(r)} V_0^{(r)}(R) + a_{\alpha\beta}^{(a)} V_{00}^{(a)}(R),$$

(4.2)

where $a_{\alpha\beta}^{(r,a)}$ are the coupling constants for the repulsive and attractive parts of the potential and are indepenent of R. Use of two coupling constants in place of one permits a more accurate account of the dependence of the coefficients $V_{\alpha\beta}$ on the intermolecular distance. The necessity of such an approximation, reflecting the different degree of anisotropy of the long- and short-range parts of the potential, follows from the strong and nonmonotonic dependence of the cross sections of the inelastic transition on these parameters.[17] We will approximate the functions $V_{00}^{(r,a)}$ by either an exponential or an inverse-power law dependence. In this case one can recover both the parameters of the spherically symmetric part and the coupling constants $a_{\alpha\beta}^{(r,a)}$ from the data in Ref. 16.

The scheme of calculation of the scattering cross section within the framework of the generalized eikonal method[8,9] reduces to the following. The potential (4.1) is written in action-angle variables with the help of the transition matrix (2.14) (see Appendix A). The problem of finding the trajectory in multidimensional phase space is then solved (usually within the framework of one of the variants of perturbation theory, making use of a separation into fast and slow motion). The increment of the classical action along the trajectory is then calculated, followed by the scattering profile, the square of the modulus of which determines the probability of the inelastic transition.

As was shown in Refs. 8 and 9, the quasiclassical scattering amplitude T (Ref. 7) can be represented in the form of a product of the elastic scattering amplitude T_0 and the inelastic scattering profile Γ:

$$T_{if} = T_0 \Gamma_{if} = T_0 \int_{[0]}^{[2\pi]} \frac{d\mathbf{q}_0}{(2\pi)^3} \exp\left\{ \frac{i}{\hbar} (\Delta \mathbf{I} \mathbf{q}_0 - S_{in}) \right\},$$

(4.3)

$$S_{in}(\mathbf{I}_i, \Delta \mathbf{I}) = \int_0^\infty \tilde{V}(\rho_0 + \mathbf{v}t, \mathbf{q}_0 + \omega t) dt, \quad \tilde{V} = V - V_{00},$$

$$\Delta \mathbf{I} = \mathbf{I}_i - \mathbf{I}_f, \quad \omega = \partial H / \partial \mathbf{I}.$$

(4.4)

The integration in Eq. (4.3) is carried out over the three-dimensional cube with side equal to 2π; ω is the vector of the frequencies of the rotational motions (see Appendix A), and H is the Hamiltonian of the unperturbed motion (2.9). The integration in the calculation of S_{in} is carried out along the multidimensional classical trajectory[9] consisting of two branches with fixed values of the action variables $\mathbf{I} = \mathbf{I}_{i(f)}$ at $t = -\infty (+\infty)$ and angle variables $\mathbf{q} = \mathbf{q}_0$ at $t = 0$. Such a statement of the problem of finding the trajectory in multidimensional phase space provides a more effective application of perturbation theory, for even in the zeroth approximation the boundary conditions are satisfied for the trajectories at $t = \pm \infty$. The perturbation theory is based on a separation of the cases of fast ($\Lambda_\alpha \ll 1$) and slow ($\Lambda_\alpha \gg 1$) motions, where $\Lambda_\alpha = \omega_\alpha d / v$ is the classical Massey parameter, d is the radius of the interaction region, and ω_α is the frequency of the αth internal degree of freedom, where in estimating the frequency one commonly chooses its value in the corresponding channel $k = i, f$.

A perturbation theory for slow collisions was developed in Refs. 18 and 19. Its main result is that in this case the increment of the action is mainly a result of motion in the direction perpendicular to the bisectrix of the scattering angle. This permits one to reduce the problem of the translational motion to a one-dimensional problem and to obtain analytic expressions for the increment of the classical action S_{in}.

For fast collisions, one treats the increment of the action S_{in} by neglecting the intramolecular motion ($\omega_\alpha = 0$) or by using interpolation procedures based on the approximation of average frequencies ($\omega = (\omega_i + \omega_f)/2$) and aveage translational energies ($E = (E_i + E_f)/2$) (Refs. 8 and 20).

We include in our scheme one more simplification, which has to do with the degeneracy of the Hamiltonian H with respect to the action variable $I_3 = m\hbar$. The probability of a transition between two states with different energies is determined by the square of the modulus of the scattering profile averaged over the initial values of the quantum number and summed over all of its values:

$$P = P_0 \frac{1}{2j_i + 1} \sum_{m_i=-j_i}^{j_i} \sum_{m_f=-j_f}^{j_f} |\Gamma_{m_i m_f}|^2, \quad P_0 = |T_0|^2.$$

(4.5)

Since the transitions between states with different m do not interest us, we use in what follows a potential averaged over the angle variable q_3 conjugate to I_3 (Ref. 10):

$$\bar{V}(q_1, q_2) = \int_0^{2\pi} \frac{dq_3}{2\pi} V(\mathbf{q}). \qquad (4.6)$$

Using the explicit form of the transition matrix (2.14) given in Appendix A, we obtain ($\mathbf{R} = (\rho, \psi, z)$ where ρ, ψ, and z are the coordinates of the atom in a cylindrical coordinate system with major axis aligned with the z axis of the laboratory system)

$$\mathbf{A}(q_3, \delta_1, 0)\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \mathbf{A}_3 \begin{pmatrix} \rho \cos \psi \\ \rho \sin \psi \\ z \end{pmatrix}$$

$$= \begin{pmatrix} \rho \cos (q_3 - \psi) \\ \rho \cos \delta_1 \sin (\psi - q_3) + z \sin \delta_1 \\ \rho \sin \delta_1 \sin (q_3 - \psi) + z \cos \delta_1 \end{pmatrix}.$$

After averaging over q_3, those terms drop out which are proportional to ρ. It can be shown that in the case of fast collisions ($\Lambda \ll 1$), where Λ is determiend by the rotational frequencies corresonding to the transition under consideration, the discarded terms are proportional to Λ, and in the case of slow collisions they are proportional to Λ^{-1}, i.e., in both limiting cases the difference of the increments of the action, calculated in the potentials V and $\bar{V}$, are small, which argues strongly in favor of using potential (4.6).

After averaging the potential [Eq. (4.6)] it is possible to integrate over q_3 in the expression for the scattering profile (4.3). Indeed, since S_{in} is already independent of q_3, we obtain

$$\Gamma_{ij} = \Gamma_{1ij}\delta_{m_i\, m_j}, \qquad (4.7)$$

where δ_{mn} is the Kronecker symbol.

Relation (4.7) shows that with the given accuracy the projection of the angular momentum on the axis of the fixed coordinate system is conserved. Here it is fitting to say a few words about the consequences of this fact which are connected with the collisional selection rules for polyatomic molecules. If one considers the state of a molecule with fixed m, then one can choose the fixed coordinate system to be such that the projection of $\mathbf{J}$ on a chosen axis is zero. This makes it possible to write the rotational wave function of an asymmetric-top molecule in terms of the spherical functions Y. Then, as follows from the analysis in Ref. 21, additional collisional selection rules appear which follow from the symmetry of the specific choice of the coordinate system. However, the summation in Eq. (4.5) lifts these exclusions (they are manifested only in the vanishing of the term $\Gamma_{m_i = 0, m_j = 0}$). Thus, to describe the collisional transitions it is necessary either to write the rotational wave functions in terms of Wigner's D-functions or, if one wishes to remain within the framework of the Y-description, to take into account the necessity of carrying out the average indicated in Eq. (4.5), meaning in this case an average over the ensemble of chosen coordinate systems.

Let us now go directly to the calculation of the cross sections of the rotational transitions in the collision of a water molecule with a helium atom, choosing as an example the transition $1_{01} \to 1_{10}$. Using the set of quantum numbers introduced in Eqs. (3.1), we can write this transition as $j_i = 1$, $k_i = 0 \to j_f = 1$, $k_f = 1$. The first term of series (4.1) which

gives a nontrivial contribution to the amplitude of this transition is the one associated with the harmonic $Y_{10} = (3/4\pi)^{1/2}\cos\vartheta$, where ϑ is the angle between the symmetry axis of the molecule (η) and the direction vector to the atom. The connection of this function with the angular variables and the coordinates of the radius vector of the atom in the fixed coordinate system $\mathbf{R} = (x,y,z)$ is made with the help of the transition matrix (2.14), whose explicit form is given in Appendix A:

$$\cos \vartheta = (0,\, 1,\, 0)\,\mathbf{A}\begin{pmatrix} x/R \\ y/R \\ z/R \end{pmatrix}. \qquad (4.8)$$

After averaging over q_3, we obtain

$$Y_{10} = 2\left(\frac{3}{4\pi}\right)^{1/2}\frac{z}{R}\cos\delta_1\Theta(g(1+\varkappa^2))^{1/2}\sin q_1, \qquad (4.9)$$

where Θ and g are parameters of the transition matrix. Hence it is clear [see the definition of $\cos\delta_1$ following Eq. (2.13) and Fig. 2] that only for $m_z = 0$ does expression (4.9) indentically vanish, leading to the exclusion of the corresponding transition.

We will dwell briefly on the solution of the problem of finding the trajectory in multidimensional phase space. For high enough collision energies $E_i > D$ (D is the well depth of the potential V_{00}) in the case of fast collisions ($\Lambda \ll 1$) a quite accurate solution of the equations of motion is given by a rectilinear trajectory with constant velocity and $\Lambda = 0$ (i.e., $\mathbf{q} = \mathbf{q}_0$). It is possible to account for slow collisions with the help of an interpolation procedure which reduces to the substitution $\mathbf{q}_0 \to \mathbf{q}_0 + \omega t$ (Ref. 8), and in the case $|\Lambda_i' - \Lambda_f'| \lesssim 1$ we will use the average frequency approximation, while in the opposite case we will set $\omega_\alpha = \min_{k = i,f}\{\omega_{\alpha k}\}$. In order that this approximation may be introduced on a par in the high-energy ($E_i > D$) and the low-energy cases, the generalized adiabaticity parameters $\Lambda' = \omega\mu d/(2\mu E')^{1/2}$ were used above, where $E' = E$ for $E > D$ and $E' = D$ for $E \leqslant D$. As a result we obtain a single formula for the scattering profile for both fast and slow collisions. Calculation of the profile for slow collisions using canonical perturbation theory leads to the same dependence on the parameters of the problem and to close values for the scattering cross sections. It is therefore more convenient in obtaining analytic approximations of the rate constants to use formulas derived in the framework of the interpolation approach. In this case we obtain for the increment of the action (see Eq. 4.3)

$$\Delta S_{in} = \hbar G \sin q_{10}$$

$$= \hbar F \frac{\rho_0}{d}\cos\delta_1\left[a_{10}^{(r)}\exp\left(\frac{2r_0}{d}\right)K_0\left(\frac{\rho_0}{d}(\Lambda_1^2 + 4)^{1/2}\right)\right.$$

$$\left. - 2a_{10}^{(a)}\exp\left(\frac{r_0}{d}\right)K_0\left(\frac{\rho_0}{d}(\Lambda_1^2 + 1)^{1/2}\right)\right]\sin q_{10},$$

$$\Lambda_1 = \frac{\omega_1 d}{v}, \qquad F = 4\hbar^{-1}D\Theta\frac{d}{v}\left(\frac{3}{4\pi}g(1+\varkappa^2)\right)^{1/2}, \qquad (4.10)$$

where D, d, and r_0 are the parameters of the Morse potenital which approximates V_{00} and V_{10}, and ρ_0 is the distance of closest approach (the impact parameter). For not too high collision energies ($E_i \lesssim 500$ K) the condition $\rho_0/d \gg 1$ is sat-

isfied, by virtue of which it is possible to use the asymptotic representation of the Macdonald function K_0 in Eq. (4.10) for large values of the argument. As a result we obtain for the profile Γ_1 the Bessel approximation[8] $\Gamma_1 = e^{i\varphi'} J_1(G)$, where φ' is the phase and is of no significance in what follows. The quantity G, which characterizes the increment of the action "accumulated" in the potential V_{10}, turns out to be quite small ($G < 1$), which makes it possible to use the asymptotic limit of the Bessel function for small arguments. After doing this and taking into account the equality $\cos\delta_1 = m/(j + 1/2) \approx m/((j(j+1))^{1/2})$, the averaging (4.5) can be carried out explicitly ($j_i = j_f = j$):

$$P = P_0 \frac{1}{2j_i+1} \sum_{m_i m_f} \left(\frac{G}{2}\right)^2 \delta_{m_i\,m_f} = P_0 \left(\frac{G}{2\cos\delta_1}\right)^2$$

$$\times \frac{1}{2j_i+1} \sum_m \frac{m^2}{j(j+1)} = \frac{P_0}{3}\left(\frac{G}{2\cos\delta_1}\right)^2. \qquad (4.11)$$

We remark that by virtue of Eq. (4.10) the ratio $G/\cos\delta_1$ is independent of m.

In the case when it is determined by rectilinear trajectories, it is convenient to write the total scattering cross section in the form of an integral over the impact parameter[17]:

$$\sigma_{if} = 2\pi B \int_{\rho_0^\bullet}^{\infty} \rho_0\, d\rho_0 \left[1 - \left(V_{00}(\rho_0) + \frac{3}{2}V_{00}'(\rho_0)\right)\Big/E_i\right] P(\rho_0),$$

$$(4.12)$$

where $B = p_f/p_i$ for activation processes and $B = 1$ for deactivation processes.

To obtain analytic approximations it is convenient to model V_{00} by the Lennard-Jones potential

$$V_{00} = 4D\left[(\rho^0/\rho)^{12} - (\rho^0/\rho)^6\right],$$

making use of the fact that the parameters of the Morse and Lennard-Jones models can be revaluated by using the relations $\rho^0 = r_0 - d\ln2$ and $r_0 = 2^{1/6}\rho^0$ for equal well depths. Then

$$\rho_0^\bullet = \rho^0(2/(1 + (1 + E_i/D)^{1/2}))^{1/6}.$$

The integral in Eq. (4.12) can be calculated by the Laplace method, taking into account the fact that the main contribution to it comes from the lower integration limit.

As a result we obtain an analytic, albeit somewhat complicated, expression

$$\sigma_{if} = 2\pi(\rho_0^\bullet)^2 B \frac{\pi F^2}{24} \sum_{k=1}^{3} \frac{A_k}{s_k} \exp[((k+1)r_0 - s_k\rho_0^\bullet)/d]$$

$$\times \left\{\frac{s_k}{s_k - 2d/\rho_0^\bullet} + \frac{4D}{E}\left(\frac{\rho^0}{\rho_0^\bullet}\right)^6\left[\frac{5s_k}{s_k + 10d/\rho_0^\bullet} - \frac{2s_k}{s_k + 4d/\rho_0^\bullet}\right]\right\},$$

$$(4.13)$$

where

$$A_1 = 4(a_{01}^{(a)})^2/(\Lambda_1^2 + 1)^{1/2},$$

$$A_2 = -4a_{01}^{(a)}a_{01}^{(r)}/((\Lambda_1^2 + 1)(\Lambda_1^2 + 4))^{1/2},$$

$$A_3 = 2(a_{01}^{(r)})^2/(\Lambda_1^2 + 4)^{1/2},$$

$$s_1 = 2(\Lambda_1^2 + 1)^{1/2}, \quad s_2 = (\Lambda_1^2 + 1)^{1/2} + (\Lambda_1^2 + 4)^{1/2}, \quad s_3 = 2(\Lambda_1^2 + 4)^{1/2}.$$

Calculation of the cross section according to this formula for the transition $1_{01} \to 1_{10}$ for the energy $E = 300$ K gives the value $\sigma = 2.6$ (a.u.)^2, which is in good agreement with the data in Ref. 16 $\sigma = 3.1$ (a.u.)^2. Here the values of the parameters $D = 0.52 \cdot 10^{-3}$ a.u. and $\rho^0 = 5.18$ a.u. of the Lennard-Jones potential V_{00}, with anisotropy coefficients $a_{01}^{(r)} = 0.30$ and $a_{01}^{(a)} = 0.15$ were used, which were recovered by the method of least squares from the potential surface in Ref. 16.

In the low-energy region $E \lesssim D$ it is necessary to change the form of our scheme for calculating the cross section somewhat because of the onset of the rotational barrier (at $E < 4D/5$ for the Lennard-Jones potential) and the appearance of the classically forbidden region of closest-approach distances (ρ_{01}, ρ_{02}), which should be included in the integral in Eq. (4.12). For the Lennard-Jones potential

$$\rho_{01,\,2} = {}^1\!/_5\rho^0(1 \pm (1 - 5E_i/4D)^{1/2})^{-1/6}.$$

In addition, it is necessary to refine the approximation of the solutions of the problem of finding the trajectory in multidimensional phase space. Estimates show that the main contribution to the integral in Eq. (4.12) comes from the region of distances $\rho_0 < \rho_{01}$ associated with trajectories close to head-on. The region $\rho_0 > \rho_{02}$ corresponds to scattering from trajectoires which are close to rectilinear, and contributes insignificantly to the cross section under the considered conditions.

Using the explicit form of the transition matrix for the increment of the action in the case of the transfer of one quantum, it is possible to obtain the representation

$$\Delta S_{in} = \int_{-\infty}^{\infty} V_{10}(R(t))2\left(\frac{3}{4\pi}\right)^{1/2}\Theta(g(1 + \varkappa^2))^{1/2}$$

$$\times \cos\delta_1 \frac{z(t)}{R(t)}\sin q_1(t)\,dt. \qquad (4.14)$$

For trajectories which are close to head-on, we have $z/R \sim 1$, and

$$R(t) = R_0 + d\ln\left[\frac{D}{E_z}\left(1 + \frac{E_z}{D}\right)^{-1/2}\mathrm{ch}\,\frac{p_z t}{\mu d} - 1\right],$$

$$E_z = \frac{p_z^2}{2\mu} = E\sin^2\frac{\vartheta_s}{2},$$

where ϑ_s is the scattering angle. If, as before, we use the generalized eikonal approximation $q_1(t) = q_{10} + \omega_1 t$ for $q_1(t)$, we obtain

$$\Delta S_{in} = (3\pi)^{1/2}d\cos\delta_1\Theta(2\mu Dg(1 + \varkappa^2))^{1/2}$$

$$\times \exp\left(-\Lambda_{1z}\,\mathrm{arctg}\left(\frac{E_z}{D}\right)^{1/2}\right)$$

$$\times [a_{01}^{(r)}\,\omega_1\mu d/(2\mu D)^{1/2} - (2a_{01}^{(a)} - a_{01}^{(r)})]\sin q_{10}, \quad \Lambda_{1z} = \omega_1\mu d/p_z.$$

$$(4.15)$$

In the small-energy region this function depends weakly on ϑ_s, wherefore in the calculation of the total cross section the inelastic scattering profile Γ_1, defined by ΔS_{in}, can be taken out from under the integral over the scattering angle, calculating it at some fixed value of ϑ_s (e.g., $\vartheta_s = \pi$), and in the rest of the expression transform to an integral over the impact parameter. Then for the low-energy cross section we obtain the approximate expression

$$\sigma_{ij} = 2\pi B \int_0^{b_1} \overline{|\Gamma_1(\Delta S_{in}(\vartheta_s))|^2} b\, db = 2\pi B b_1{}^2 \overline{|\Gamma_1(\vartheta_s = \pi)|^2},$$

$$\overline{|\Gamma_1(\pi)|^2} = \frac{\pi}{2}(d\Theta/\hbar)^2 g(1+\varkappa^2)\mu D \exp(-2\Lambda_{12}\,\mathrm{arctg}\,(E_z/D)^{1/2})$$

$$\times [\,a_{01}^{(r)}\omega_1\mu d/(2\mu D)^{1/2} - (2a_{01}^{(a)} - a_{01}^{(r)})\,]^2. \qquad (4.16)$$

The bar denotes averaging over the projections of the angular momentum of the form (4.5), and b_1 is the impact parameter corresponding to ρ_{01} (for the Lennard-Jones potential $b_1^2 = \rho_{01}^2(1 - V_{00}(\rho_{01})/E_i)$).

Let us now consider the peculiarities associated with the calculation of the cross sections of other transitions. The scheme of such a calculation for diatomic molecules, based on the form of the interaction potential written in action-angle variables and represented in the form of a Fourier series over the angular variables, was developed in Refs. 8 and 19. It is based on singling out in the potential the one term corresponding to the given transition. An analog of this scheme can also be proposed for the general case under consideration. Thus, for example, the transition in which the quantum number k changes to the value Δk for fixed j corresponds to a term in the potential which is proportional to $\sin(\Delta k q_1 + q')$ (see Appendix A). The transition with simultaneous change of both quantum numbers to the values Δj and $\pm \Delta k$ correspond to two terms, proportional to

$\sin(\pm\Delta k q_1 + \Delta j q_2 + q'')$, where q' and q'' are some constants. For the cross section of single-quantum transitions formulas of the form (4.13) and (4.16) were used, and for multiquantum transitions more complicated expressions were used. However, the potential surface is usually given in the form of an expansion in spherical harmonics. It is possible to somewhat simplify the cumbersome procedure of transforming to action-angle variables with the help of perturbation theory, within the framework of which contributions from the harmonics $Y_{\alpha\beta}$ with different values of the index α do not interfere (see Appendix B). This makes it possible to recover the individual parts of the potential surface generated by the partial sums $\Sigma V_{\alpha\beta} Y_{\alpha\beta}$, to calculate the corresponding probabilities, and after this to carry out the summation over α.

In conclusion we present the results of the calculation of the rate constants of a number of rotational transitions which were determined according to the formula (for the activation process)

$$K_{ij} = \frac{8\pi\mu}{(2\pi\mu k_B T)^{3/2}} \int_{\Delta E}^{\infty} E_i \sigma_{ij} \exp\left(-\frac{E_i}{k_B T}\right) dE_i. \qquad (4.17)$$

In the recovery of the parameters of the potential $V(\mathbf{I},\mathbf{q})$ the contributions from the three harmonics Y_{10}, Y_{30}, and Y_{32} were taken into account. Data on the corresponding coefficients $V_{\alpha\beta}$ were taken from Ref. 16. To simplify the integration in Eq. (4.17), which was carried out numerically, we made use of the circumstance that the quantity b_1 from Eq. (4.16) depends weakly on the energy and for the investigated energy region varies within the limits $b_1^2 = (3.5-4.5)(\rho^0)^2$. This latter circumstance permitted us to set $b_1^2 = 4(\rho^0)^2$.

In Table III the values which we obtained for the constants in the temperature region 50–500 K are compared with the results of an exact quantum-mechanical calculation

TABLE III. Rate constants of the rotational transitions. $K(j_{ik_{i},k_{i}} \to j_{jk_{i},k_{j}}) \cdot 10^{11}$ cm^3/s in the system He + H$_2$O. The upper row gives the calculation according to equation (4.17) and the lower row gives the calculation based on the close-coupling method.[16]

T, K						
50	80	100	200	300	400	500
Transition $1_{01} \to 1_{10}$						
1.6(−1)	3.2(−1)	4.0(−1)	6.7(−1)	8.4(−1)	1.0	1.1
0.9(−1)	2.4(−1)	3.4(−1)	7.2(−1)	9.7(−1)	1.2	1.3
Transition $1_{01} \to 2_{12}$						
5.3(−1)	11.6(−1)	1.5	2.5	3.2	3.7	4.2
2.7(−1)	7.7(−1)	1.1	2.2	3.0	3.6	4.0
Transition $1_{01} \to 2_{21}$						
1.8(−2)	6.3(−2)	10(−2)	2.7(−1)	4.1(−1)	5.3(−1)	6.4(−1)
1.6(−2)	5.9(−2)	9.3(−2)	2.7(−1)	4.2(−1)	5.3(−1)	6.3(−1)
Transition $2_{12} \to 2_{21}$						
1.1(−1)	2.4(−1)	3.1(−1)	5.3(−1)	6.7(−1)	7.9(−1)	8.9(−1)
1.3(−1)	2.4(−1)	3.1(−1)	5.3(−1)	6.7(−1)	7.7(−1)	8.5(−1)
Transition $7_{43} \to 7_{34}$						
4.5(−1)	0.72	0.92	1.6	2.1	2.4	2.8
7.4(−1)	1.1	1.2	1.7	2.0	2.4	2.8

carried out within the framework of the close coupling method.[16] From the displayed data it can be seen that the proposed method accurately reproduces both the temperature dependence of the constants (especially for temperatures $\gtrsim 80$ K) and their dependences on the quantum numbers.

Thus, the quasiclassical method which we have developed here for calculating the probabilities of collision-induced intramolecular transitions has enabled a major advance in the direction of obtaining analytic expressions for the scattering cross sections and has made it possible to calculate quite accurately the constants of rotational transitions in polyatomic molecules with incomparably smaller requirements of computer time in comparison with quantum-mechanical methods.

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APPENDIX A

Retaining the first terms of the expansion of the matrix of direction cosines in a series in the Jacobi parameters, we obtain the following expressions for the matrix $A(\Delta, \delta_2, l) A(q_2, 0, 0)$ [see Eq. (2.14)], given here line-by-line, for $r < 1$:

$$\Theta g''(-\Xi_- sq_{12}^+ - e^{-\sigma} sq_{12}^-, \ \Xi_- cq_{12}^+ - e^{-\sigma} cq_{12}^-, \ 2cq_1)$$
$$\Theta g''(-\Xi_+ cq_{12}^+ - e^{-\sigma} cq_{12}^-, \ -\Xi_+ sq_{12}^+ + e^{-\sigma} sq_{12}^-, \ -2sq_1)$$
$$\Theta x \left(\frac{sq_2}{2 \, \mathrm{sh} \, \sigma}, \ -\frac{cq_2}{2 \, \mathrm{sh} \, \sigma}, \ \frac{1}{2} \right),$$

and for $r > 1$:

$$\Theta g'' \left(-\Xi_- sq_{12}^+ - e^{-\sigma} sq_{12}^-, \ \Xi_- cq_{12}^+ - e^{-\sigma} cq_{12}^-, \ \frac{g^{-1/2}}{2} \right)$$
$$\Theta (1+x^2)^{1/2} (-cq_2/2 \, \mathrm{ch} \, \sigma, \ -sq_2/2 \, \mathrm{ch} \, \sigma, \ -2g^{1/2} sq_1)$$
$$\Theta x (sq_2/2 \, \mathrm{sh} \, \sigma, \ -cq_2/2 \, \mathrm{sh} \, \sigma, \ 2g^{1/2} cq_1),$$

where

$$sq_{12}^{\pm} = \sin(q_1 \pm q_2), \quad sq_k = \sin q_k, \quad cq_{12}^{\pm} = \cos(q_1 \pm q_2),$$
$$cq_k = \cos q_k, \ k = 1, 2; \ \Xi_{\pm} = e^{\sigma}/(1 \pm g e^{2\sigma}),$$
$$\Theta = \frac{\pi x}{\mu K(\lambda)(r^2 + x^2)^{1/2}}, \quad \sigma = \frac{\pi}{2K(\lambda)} F(\mathrm{arctg} \, \mu/\lambda, \ (1-\lambda^2)^{1/2}).$$

The difference between the matrix forms is connected with the different character of the rotational motion of the asymmetric top, which is shown graphically in Fig. 4. Using formulas (2.7) and (4.4), we obtain the following formulas for the frequencies

$$\omega_1 = \frac{\pi I_2 (A-C) x^2}{K(\lambda)\mu((1+x^2)(r^2+x^2))^{1/2}},$$

$$\omega_2 = A I_2 \left[1 - \left(1 - \frac{C}{A} \right) \frac{\Pi(\mu^2, \lambda)}{K(\lambda)} \right], \quad \omega_3 = 0.$$

The matrix $A(q_3, \delta_1, 0) = A_3$ has the usual form

$$\begin{pmatrix} \cos q_3 & \sin q_3 & 0 \\ -\cos \delta_1 \sin q_3 & \cos \delta_1 \cos q_3 & \sin \delta_1 \\ \sin \delta_1 \sin q_3 & -\sin \delta_1 \cos q_3 & \cos \delta_1 \end{pmatrix}.$$

APPENDIX B

Within the framework of perturbation theory, applied to the case $\Delta S_{in}/\hbar \ll 1$ where ΔS_{in} is the increment of the action accumulated in the anisotropic part of the potential $V = \Sigma_{\alpha\beta} V_{\alpha\beta} Y_{\alpha\beta}$, it is possible to show that the contributions to the transition probabilities from the harmonics $Y_{\alpha\beta}$ with different values of the index α do not interfere. Consider the transition amplitude W:

$$W = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \, e^{i\Delta Et/\hbar} \langle f | V | i \rangle$$

$$= -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \, e^{i\Delta Et/\hbar} \sum_{\alpha\beta\gamma} V_{\alpha\beta}(R(t)) Y_{\alpha\beta}(\theta, \psi) \langle f | D_{\gamma\beta}^{\alpha*} | i \rangle$$

$$\equiv \sum_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \langle f | D_{\gamma\beta}^{\alpha*} | i \rangle \equiv \sum_{\alpha\beta\gamma} B_{\alpha\beta\gamma} \begin{pmatrix} \alpha & j_i & j_f \\ -\gamma & m_i & m_j \end{pmatrix} \langle f \| D_{\beta}^{\alpha*} \| i \rangle,$$

where

$$V = \sum_{\alpha\beta} V_{\alpha\beta} Y_{\alpha\beta} = \sum_{\alpha\beta\gamma} V_{\alpha\beta}(R) D_{\gamma\beta}^{\alpha*} Y_{\alpha\gamma}(\theta, \psi).$$

The asterisk denotes the complex conjugate. Using the orthogonality properties of the Clebsch-Gordon coefficients

$$\sum_{m_i m_j} \begin{pmatrix} k & j_i & j_f \\ -l & m_i & m_j \end{pmatrix} \begin{pmatrix} k_1 & j_i & j_f \\ -l_1 & m_i & m_j \end{pmatrix} = \frac{1}{2k+1} \delta_{kk_1} \delta_{ll_1}$$

for the average transition probability P, we obtain

$$P = \frac{1}{2j_i+1} \sum_{m_i m_j} |W|^2 = \frac{1}{2j_i+1} \sum_{\alpha\beta\beta_1\gamma} \frac{B_{\alpha\beta\gamma} B_{\alpha\beta_1\gamma}^*}{2\alpha+1}$$

$$\times \langle f \| D_{\beta}^{\alpha*} \| i \rangle \langle f \| D_{\beta_1}^{\alpha} \| i \rangle$$

$$= \frac{1}{2j_i+1} \sum_{\alpha\gamma} \frac{1}{2\alpha+1} \left| \sum_{\beta} B_{\alpha\beta\gamma} \langle f \| D_{\beta}^{\alpha*} \| i \rangle \right|^2,$$

which completes the proof.

[1] Equation (2.5a) can be rewritten in the form $I_1 = (1/2\pi) \oint l \, dL$, whereupon it becomes equivalent to the formula in Ref. 15.

[2] The matrix of direction cosines, calculated by the indicated technique, is given in Appendix A.

[3] k_+ and k_- are pseudoquantum numbers which are used in the spectroscopy of the asymmetric top and which characterize the rotational energy levels.

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