is small. A more detailed allowance of the dissipation is not a simple task, since the geometrical-optics equations used here (which are connected with Eqs. (7) and (6a) are essentially based on the assumption that the tensor $\hat{\varepsilon}$ is Hermitian. On the other hand, the quasi-isotropic approximation [formulas (4) and (6)], although not using this assumption, likewise do not guarantee a correct description of the effect (see Sec. 2).

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Radiative transitions in collisions of atoms and the photodissociation of vibrationally excited molecules

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We have developed in the quasiclassical approximation a theory which permits determination of the probability of radiative electronic transitions in the case when the extremum of the difference in the potential energies occurs close to the turning points on the potential curves. This theory contains previous results as limiting cases and, together with them, solves the problem of determining the spectral characteristics of the considered transitions over the entire frequency region.

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Radiation and absorption of photons in collisions of atoms is due mainly to transitions between the electronic terms of the quasimolecule formed in the collision process. The basis of the classical and quasiclassical theory of processes of this type was set forth in the work of Kramers and ter-Haar,[1] Bates,[2] and Jablonski.[3] Subsequently this theory was extended to the photodissociation of molecules with high vibrational levels.[4,5] The classical approach, which assumes that the nuclei are moving along classical trajectories, leads to a dependence of the cross sections for these processes on the difference of the potentials of the two electronic states. This approach is not valid, however, in the region of internuclear distances where the potential difference has an extremum, and for determination of the cross sections it is already impossible to use the concept of a classical trajectory of the motion of the nuclei. In this case an applicable method is that which uses quasiclassical wave functions of the nuclear motion for calculation of the probability of an electronic radiative transition. Both approaches are incorrect if the radiative transitions occur near the turning points on the potential curves. Use of quantum-mechanical nuclear wave functions[6] in this region of distances permits the transition probability to be obtained if the difference of the slopes of the potential curves near the turning points is sufficiently great.[1)]

In the present work we have developed a quantum-mechanical theory which permits determination of the radiative transition probability even in the case when the extremum of the difference of the potential curves occurs close to the turning points (the slopes of the potential curves at the turning points differ insignificantly). This theory contains the previous results as limiting cases. By combining this theory with existing the-

ories[1-9] we can solve the problem of finding the spectral characteristics of the considered processes over the entire frequency region.

1. The cross sections for the radiative processes under study are determined by well known formulas (see for example Refs. 10 and 11). The matrix element of the dipole moment in the Born-Oppenheimer approximation, which enters into these formulas, reduces to the form

$$D_{12}=\int \chi_1(R)\,d(R)\,\chi_2(R)\,dR.$$

Here R is the internuclear distance; $\chi_1(R)$ and $\chi_2(R)$ are the wave functions of radial motion of the nuclei in the lower and upper electronic states. The dipole moment of the electronic radiative transition $d(R)$ is a smooth function of the internuclear distance in comparison with $\chi_1(R)$ and $\chi_2(R)$. In addition, the relative variation in the dipole moment in the region of distances responsible for the principal contribution to D_{12} is usually small. Therefore the dipole moment $d(R)$ affects mainly the absolute value of the cross section. The dependence of the cross section on the frequency of the absorbed or emitted photon is determined by the shape of the potential curves of the electronic terms, in terms of the square of the overlap integral

$$S_{12}=\int \chi_1(R)\,\chi_2(R)\,dR. \tag{1}$$

The structure of the potential curves shown in Fig. 1 occurs rather frequently. In this case there is a point R_0 at which the difference of the potentials has an extremum. We shall obtain formulas which determine the frequency dependence of the cross sections for a photon energy close to the value $\hbar\omega_0=U_2(R_0)-U_1(R_0)$, when the radiative transitions occur mainly in the vicinity of the point R_0 [$U_1(R)$ and $U_2(R)$ are the potential curves of the lower and upper electronic terms]. If $U_1(R_0)<0$ and $U_2(R_0)>0$, quantum-mechanical effects associated with the closeness of the point R_0 to the turning points on the potential curves R_1 and R_2 (see Fig. 1) appear in the photodissociation and photorecombination processes. We shall assume that the bound states of the molecule correspond to high vibrational levels, and far from the turning points in the classical region we shall determine the wave functions of radial motion of the nuclei on the basis of the quasiclassical approximation:

$$\chi_1(R)=\left(\frac{2\mu}{\pi\hbar g(E_1)P_1(R)}\right)^{1/2}\sin\left(\frac{1}{\hbar}\int_{R_1}^{R}P_1(R')\,dR'+\frac{\pi}{4}\right),$$
$$\chi_2(R)=\left(\frac{2\mu}{\pi\hbar P_2(R)}\right)^{1/2}\sin\left(\frac{1}{\hbar}\int_{R_2}^{R}P_2(R')\,dR'+\frac{\pi}{4}\right). \tag{2}$$

Here $P(R)$ is the classical momentum of relative motion of the nuclei, μ is the reduced mass of the atoms, and $g(E_1)$ is the density of bound states. The wave functions (2) have been normalized by the condition

$$\int \chi_{1E}^2(R)\,dR=1,\quad \int \chi_{2E}(R)\,\chi_{2E'}(R)\,dR=\delta(E-E').$$

The usual quasiclassical approach utilizes the stationary-phase approximation. It is assumed that the main contribution to the overlap integral S_{12} is from the vicinity of the stationary-phase point R_c determined from

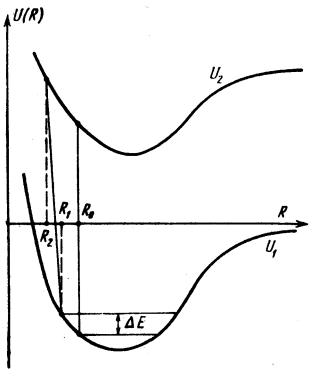

FIG. 1. Potential curves of electronic terms of the quasimolecule: R is the internuclear distance, $U_1(R)$ and $U_2(R)$ are the potential curves of the lower and upper electronic terms, and R_0 is the extremum point of the difference of the potentials.

the condition of equality to zero of the derivative of the difference of the arguments of the trigonometric functions (2) $[P_1(R_c)=P_2(R_c)]$. In the case considered here, in which radiative transitions occur at the region of distances $R\sim R_0$, the stationary-phase point, if it exists, also lies in this region. To take into account effects related to the closeness of the point R_0 to the turning points R_1 and R_2, we shall abandon the stationary-phase approximation and shall use the correct quasiclassical wave functions. The criterion of applicability of this approach will be given below.

Near the point R_0 we shall approximate the effective-potential-energy curves by the quadratic dependence

$$U(R)=U(R_0)+F(R_0)(R-R_0)+\tfrac{1}{2}F'(R_0)(R-R_0)^2, \tag{3}$$

where $F_1(R_0)=F_2(R_0)=F$ is the slope of the potential curves at the extremum point,

$$F'(R)=d^2U(R)/dR^2.$$

The structure of the potential curves, which is shown in Fig. 1, corresponds to the case

$$F_1'(R_0)>F_2'(R_0)>0,\quad F<0.$$

This approximation can be used in the problem under discussion if the period of the first oscillations of the wave functions $\chi_1(R)$ and $\chi_2(R)$ near the point R_0, which has a magnitude $\sim(\hbar/2\mu|F|)^{1/3}$, is significantly less than the characteristic distance $|F/F'|$ in which the slopes of the potential curves change. In the opposite case the potentials (3) with $F_1(R_0)=F_2(R_0)$ are applicable only in a very narrow region of distances $(R-R_0)$ which does not contribute substantially to the result. This leads to the condition

$$\gamma=\left(\frac{2\mu|F|}{\hbar^2}\right)^{1/2}\left|\frac{F}{F'_{1,2}}\right|\gg 1,\quad F'_{1,2}=F'_{1,2}(R_0). \tag{4}$$

Another restriction arises from the condition of smallness of the quadratic term in (3) in comparison with the linear term in the region of distances between the turning points and the extremum point R_0. It has the form

$$|F_{1,2}\Delta E_{1,2}|/F^2\ll 1, \tag{5}$$

where $\Delta E = E - U(R_0)$.

We shall find the overlap integral S_{12} by using the wave functions (2). The integrand in Eq. (1) is

$$\frac{\mu}{\pi\hbar}\frac{1}{[P_1(R)P_2(R)g(E_1)]^{1/2}}\Big[\cos\Big(\frac{1}{\hbar}\int_{R_1}^{R}P_1(R')dR' - \frac{1}{\hbar}\int_{R_2}^{R}P_2(R')dR'\Big) - \cos\Big(\frac{1}{\hbar}\int_{R_1}^{R}P_1(R')dR' + \frac{1}{\hbar}\int_{R_2}^{R}P_2(R')dR' + \frac{\pi}{2}\Big)\Big],$$

and here the main contribution to the integral is from the first term of this expression. In the region of distances $R - R_{1,2} \ll |F/F'_{1,2}|$, corresponding to the potential-curve approximation (3), we shall expand the arguments of the trigonometric functions (2) in powers of $R - R_1$ and $R - R_2$:

$$\frac{1}{\hbar}\int_{R_1}^{R}P_1(R')dR' = \frac{(2\mu|F|)^{1/2}}{\hbar}\Big\{\Big(\frac{2}{3}+\frac{1}{3}\frac{F_1'\Delta E_1}{F^2}\Big) \times (R-R_1)^{3/2} - \frac{1}{10}\frac{F_1'}{|F|}(R-R_1)^{5/2}\Big\}, \tag{6a}$$

$$\frac{1}{\hbar}\int_{R_2}^{R}P_2(R')dR' = \frac{(2\mu|F|)^{1/2}}{\hbar}\Big\{\Big(\frac{2}{3}+\frac{1}{3}\frac{F_2'\Delta E_2}{F^2}\Big) \times (R-R_2)^{3/2} - \frac{1}{10}\frac{F_2'}{|F|}(R-R_2)^{5/2}\Big\}. \tag{6b}$$

Assuming that $R - R_{1,2}$ is much greater than the distance between the turning points $|R_1 - R_2|$ and at the same time the following condition is satisfied,

$$|\hbar\Delta\omega/\Delta E_{1,2}| \ll 1, \quad \Delta\omega = \omega - \omega_0, \tag{7}$$

we also carry out the expansion of

$$\frac{1}{\hbar}\int_{R_2}^{R}P_2(R')dR'$$

in powers of $(R_1 - R_2)/(R - R_1)$. Confining ourselves to the first two terms of the expansion of the term $\frac{2}{3}(2\mu|F|)^{1/2}\hbar^{-1}(R-R_2)^{3/2}$, which has the greatest order of magnitude, and setting $R_2 = R_1$ in the remaining terms of (6b), we obtain

$$\frac{1}{\hbar}\int_{R_2}^{R}P_2(R')dR' = \frac{(2\mu|F|)^{1/2}}{\hbar}\Big\{\Big(\frac{2}{3}+\frac{R_1-R_2}{R-R_1}+\frac{1}{3}\frac{F_2'\Delta E_2}{F^2}\Big)(R-R_1)^{3/2} - \frac{1}{10}\frac{F_2'}{|F|}(R-R_1)^{5/2}\Big\} = \frac{(2\mu|F|)^{1/2}}{\hbar}\Big\{\Big(\frac{2}{3}+\frac{1}{3}\frac{F_2'\Delta F_1}{F^2}\Big)(R-R_1)^{3/2} + \Big(\frac{\hbar\Delta\omega}{|F|}+\frac{(\Delta E_1)^2\Delta F'}{2|F|^3}\Big)(R-R_1)^{1/2} - \frac{1}{10}\frac{F_2'}{|F|}(R-R_1)^{5/2}\Big\},$$

where $\Delta F' = F_1' - F_2'$. Here we have taken into account that in view of the quadratic dependence $U_{1,2}(R)$ of Eq. (3) the distance between the turning points is determined by the relation

$$R_1 - R_2 = \hbar\Delta\omega/|F| + \Delta F'(\Delta E_1)^2/2|F|^3.$$

From this we find

$$\frac{1}{\hbar}\int_{R_1}^{R}P_1(R')dR' - \frac{1}{\hbar}\int_{R_2}^{R}P_2(R')dR' = \frac{(2\mu|F|)^{1/2}}{\hbar}\Big\{\frac{1}{3}\frac{\Delta F'\Delta E_1}{F^2} - \Big(\frac{\hbar\Delta\omega}{|F|}+\frac{\Delta F'\Delta E_1^2}{2|F|^3}\Big)(R-R_1)^{1/2} - \frac{1}{10}\frac{\Delta F'}{|F|}(R-R_1)^{5/2}\Big\}. \tag{8}$$

We note that all terms of this expression can in principle be quantities of the same order. Utilizing it in integration in Eq. (1) and making the substitution of variables

$$y = (2\mu(\Delta F')^2/\hbar^2|F|)^{1/3}(R - R_1),$$

we obtain

$$S_{12} = \frac{1}{[\pi g(E_1)]^{1/2}}\Big(\frac{2\mu}{\hbar^2|F|}\Big)^{2/3}\frac{f(\alpha,\beta)}{|\Delta F'|^{1/3}}, \tag{9}$$

$$f(\alpha,\beta) = \frac{1}{\sqrt{\pi}}\int_0^\infty \cos\Big(\frac{\alpha y^3}{3} - \frac{1}{2}(\alpha^2+\beta)y - \frac{y^5}{10}\Big)dy. \tag{10}$$

The parameters α and β are determined by the expressions

$$\alpha = \Big(\frac{2\mu}{\hbar^2|F|}\Big)^{1/3}|\Delta F'|^{2/3}\frac{\Delta E_1}{|F|}, \quad \beta = 2\frac{\hbar\Delta\omega}{|F|}\Big|\frac{F}{\Delta F'}\Big|^{1/3}\Big(\frac{2\mu|F|}{\hbar^2}\Big)^{2/3}. \tag{11}$$

Equations (9) and (10) preserve their form on change of the sign of the slope of the potential curves at the extremum point. On change of sign of the quantity $\Delta F'$ in Eq. (10) it is necessary to make the substitution $\beta \to -\beta$.

In using Eq. (8) for calculation of the overlap integral S_{12} in Eq. (1), we have thereby assumed that the main contribution to this integral is associated with the region of internuclear distances in which the following condition is satisfied:

$$|R_1 - R_2| = \Big|\frac{\hbar\Delta\omega}{|F|}+\frac{\Delta F'(\Delta E_1)^2}{2|F|^3}\Big| \ll R - R_1 \ll \Big|\frac{F}{F'_{1,2}}\Big|. \tag{12}$$

If $|\alpha| \leq 1$ and $|\beta| \leq 1$, then the integral in Eq. (10) is accumulated mainly at values $y \sim 1$, which is equivalent to

$$R - R_1 \sim (\hbar^2|F|/2\mu(\Delta F')^2)^{1/3} \approx \gamma^{-2/3}|F/F_{1,2}| \tag{13}$$

(we assume that in order of magnitude $\Delta F' \sim F'_{1,2}$). It is evident from this that the upper bound in (12) follows automatically from the inequality (4). The lower bound is equivalent to the two inequalities:

$$R - R_1 \sim \gamma^{-2/3}\Big|\frac{F}{F'_{1,2}}\Big| \gg \Big|\frac{\hbar\Delta\omega}{F}\Big| \approx |\alpha|\gamma^{-2/3}\Big|\frac{\hbar\Delta\omega}{\Delta E}\frac{F}{F'_{1,2}}\Big|,$$

$$R - R_1 \sim \gamma^{-2/3}\Big|\frac{F}{F'_{1,2}}\Big| \gg \frac{\Delta E_1^2\Delta F'}{|F|^3} \approx \alpha^2\gamma^{-4/3}\Big|\frac{F}{F'_{1,2}}\Big|.$$

Both of these are satisfied in view of the conditions (4) and (7), and here in the region of small values of the parameter α the latter is not obligatory.

For large values of α it is sufficient to consider two limiting cases: $|\alpha| \gg \beta^2$ and $|\alpha| \ll \beta^2$ (the latter corresponds also to the region in which $|\alpha| \leq 1$, $|\beta| \gg 1$). In both cases the principal contribution to the integral (10) is from large values of y (respectively $y \sim |\alpha|^{1/2}$ and $y \sim |\beta|^{1/4}$). Thus, the inequality (4) again assures the upper bound in Eq. (12). For $|\alpha| \gg \beta^2$ the lower bound reduces to the following inequalities:

$$R - R_1 \sim \gamma^{-2/3}\Big|\frac{F}{F'_{1,2}}\Big||\alpha|^{1/2} \gg \Big|\frac{\hbar\Delta\omega}{F}\Big| \approx \beta\gamma^{-2/3}\Big|\frac{F}{F'_{1,2}}\Big|,$$

$$R - R_1 \sim \gamma^{-2/3}\Big|\frac{F}{F'_{1,2}}\Big||\alpha|^{1/2} \gg \frac{\Delta E_1^2\Delta F'}{|F|^3} \approx \Big|\frac{F_{1,2}\Delta E_1}{F^2}\Big|^{3/2}|\alpha|^{1/2}\gamma^{-3/10}\Big|\frac{F}{F'_{1,2}}\Big|.$$

The first of these inequalities is valid in view of the condition (4), and the second leads to appearance of an additional condition:

$$|F'_{1,2}\Delta E_1/F^2| \ll 1/\gamma^{1/2}. \tag{14a}$$

In the other limiting case ($|\alpha| \ll \beta^2$) the inequalities corresponding to the lower bound in (12) have the form

$$R-R_1\sim\gamma^{-1/5}\left|\frac{F}{F'_{1,2}}\right||\beta|^{1/4}\gg\left|\frac{\hbar\Delta\omega}{F}\right|$$

$$\approx|\beta|^{1/4}\left|\frac{\hbar\Delta\omega}{\Delta E_1}\frac{\Delta E_1F'_{1,2}}{F^2}\right|^{1/4}\gamma^{-1/10}\left|\frac{F}{F'_{1,2}}\right|,$$

$$R-R_1\sim\gamma^{-1/5}\left|\frac{F}{F'_{1,2}}\right||\beta|^{1/4}\gg\frac{\Delta E_1^2\Delta F'}{|F|^3}\approx\left|\frac{F'_{1,2}\Delta E_1}{F^2}\right|^{1/4}|\alpha|^{1/2}\gamma^{-1/10}\left|\frac{F}{F'_{1,2}}\right|$$

and are valid if the conditions (14a) are satisfied and

$$\left|\frac{\hbar\Delta\omega}{\Delta E_1}\frac{F'_{1,2}\Delta E_1}{F^2}\right|^{1/4}\ll\frac{1}{\gamma^{1/5}}. \tag{14b}$$

We note, however, that in a real situation the parameter γ never exceeds ~10^2. Therefore, the conditions (14a) and (14b) are essentially equivalent to (5) and (7).

The result [Eqs. (9) to (11)] takes into account the closeness of the point R_0 to the turning points on the potential curves in terms of the quasiclassical method. Therefore the criterion of applicability of the quasiclassical method is determined also by the legitimacy of use of the quasiclassical wave functions (2) in the region of distances which provide the principal contribution of the overlap integral S_{12}. The most unfavorable case here is the situation in which $|\alpha|\leq 1$, $|\beta|\leq 1$, and the size of this region is determined by Eq. (13). However, even in this case the condition of applicability of the quasiclassical approximation in the region indicated $(2\mu|F|/\hbar^2)^{1/3}(R-R_1)\gg 1$ is automatically satisfied in view of the inequality (4). Thus, as a whole the criterion of applicability of Eqs. (9) and (10) for the overlap integral S_{12} is determined by the inequalities (4), (5), and (7). It is necessary to mention that for small values of the parameter α the criterion becomes less strict: the necessity of the inequality (7) disappears.

We note that in principle the overlap integral S_{12} could be found by using the wave functions $\chi_1(R)$ and $\chi_2(R)$, which are exact solutions of the Schrödinger equation in the potentials (3). This approach, however, does not give new results, since by using in this problem the quadratic dependence (3) we are clearly assuming satisfaction of the criteria (4) and (5).

The position of the extremum point R_0, the slopes of the potential curves, and their derivatives at this point depend, generally speaking, on the rotational angular momentum of the quasimolecular j. However, in most cases this dependence is weak and the overlap integral S_{12} can be assumed to depend on j only through the parameter α.

2. We shall obtain analytical expressions for the function $f(\alpha,\beta)$ in a number of limiting cases. First consider the region of small values of the parameter α ($|\alpha|\ll 1$). For $|\beta|\ll 1$ the main contribution to the integral in Eq. (9) is due to the third term of the argument of the cosine and

$$f(\alpha,\beta)=\frac{\pi^{1/4}}{10^{1/4}\Gamma(^1/_5)\cos(2\pi/5)}=0.78. \tag{15}$$

However, if $|\beta|\gg 1$, we find on using the method of steepest descent[6,12] in the integration that

$$f(\alpha,\beta)=\frac{1}{|\beta|^{1/4}}\cos\left[\frac{\alpha|\beta|^{1/4}}{3}-\frac{(\alpha^2-|\beta|)}{2}|\beta|^{1/4}-\frac{|\beta|^{1/4}}{10}-\frac{\pi}{4}\right],\quad \beta<0;$$
$$f(\alpha,\beta)=\frac{1}{\beta^{1/4}}\cos\left\{\frac{1}{\sqrt{2}}\left[\frac{(\alpha^2+\beta)}{2}\beta^{1/4}+\frac{\alpha\beta^{1/4}}{3}-\frac{\beta^{1/4}}{10}\right]-\frac{\pi}{8}\right\}\times\exp\left\{-\frac{1}{\sqrt{2}}\left[\frac{(\alpha^2+\beta)}{2}\beta^{1/4}-\frac{\alpha\beta^{1/4}}{3}-\frac{\beta^{1/4}}{10}\right]\right\},\quad \beta>0. \tag{16}$$

Equation (16) is valid also for $|\alpha|\sim 1$.

Let us consider now the region of large positive values of the parameter α ($\alpha\gg 1$). We shall carry out the integration in (10) also on the basis of the method of steepest descent. In this case there are, generally speaking, two complex saddle points:

$$y_{1,2}=(\alpha\pm\sqrt{-\beta})^{1/2},$$

which for

$$|\beta|\ll\alpha^2 \tag{17}$$

lie near the point $y=\alpha^{1/2}$. Here there is an overlap of regions of values of y in the vicinity of these points which are responsible for the main contribution to the integral. Therefore in calculation of the integral we shall use the following procedure. In Eq. (10) we shall expand the argument of the cosine at the point $y=\alpha^{1/2}$ in powers of $y-\alpha^{1/2}$ with accuracy to the cubic term. Here the quadratic term of the expansion vanishes. As a result we find

$$f(\alpha,\beta)=\cos\left(\frac{4}{15}\alpha^{5/4}-\frac{1}{2}\beta\alpha^{1/2}\right)\left(\frac{4}{\alpha}\right)^{1/2}\Phi\left\{\frac{\beta}{2(2\alpha)^{1/2}}\right\}, \tag{18}$$

where $\Phi(x)$ is the Airy function. Equation (18) can be obtained also on the basis of a quasiclassical approach using an expansion of the arguments of the wave functions (2) at the extremum point with accuracy to the cubic term. In this connection we note that the result of Sando and Wormhoudt,[13] which was obtained for the case $\beta<0$ by just this method but with expansion not at the extremum point but at one of the stationary-phase points, is not completely correct, since it does not take into account the presence of a second stationary-phase point. According to Ref. 13, in the designations of the present work, $f(\alpha,\beta)$ is determined by Eq. (18) but with the argument of the Airy function equal to $\beta/2[2(\alpha-\sqrt{|\beta|})]^{1/2}$. It can be seen from this that the result of Ref. 13 agrees with Eq. (18) only when $\beta\ll\alpha^{8/9}$.

If the condition (17) is not satisfied, then the vicinities of the two saddle points contribute separately to the result. Let us analyze this case, when $-\alpha^2\leq\beta<0$ and

$$\alpha-\sqrt{|\beta|}\ll\alpha. \tag{19}$$

Under these conditions the main contribution to the result is due to the vicinity of the point $y_2=(\alpha-|\beta|)^{1/2}$. If $y_2\ll 1$, then the value of the integral in (10) is determined by the first and second terms of the argument of the cosine and

$$f(\alpha,\beta)=|\beta|^{-1/4}\Phi\{-(\alpha-\sqrt{|\beta|})|\beta|^{1/2}\}. \tag{20}$$

In the other limit ($y_2\gtrsim 1$), carrying out the integration in (10) by the method of steepest descent, we find

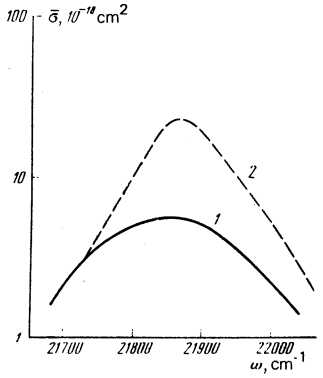

FIG. 2. Cross section for photodissociation $\bar{\sigma}(\omega)$ of the molecule Na_2 (the electronic transition $X^1\Sigma_g^+ \to B^1\Pi_u$) as a function of the frequency of the absorbed photon ω, obtained on the basis of the method developed in the present work (curve 1) and in terms of the ordinary quasiclassical approach (curve 2).

$$f(\alpha,\beta)=\frac{\cos(^2/_3|\beta|^{1/2}(\alpha-\sqrt{|\beta|})^{3/2}+^7/_{10}(\alpha-\sqrt{|\beta|})^{7/2}+\pi/4)}{|\beta|^{1/4}(\alpha-\sqrt{|\beta|})^{1/4}}. \quad (21)$$

With accuracy to the term $(\alpha-\sqrt{|\beta|})^{5/2}$ in the argument of the cosine, Eq. (21) coincides with the limit (20) for large values of the argument of the Airy function. We note that Eq. (20) actually is the result of Refs. 6–9, and Eq. (21) is the result of the classical approach.[1,2]

3. We shall use the results obtained above for calculation of the cross section for photodissociation of the Na_2 molecule as the result of the electronic transition $X^1\Sigma_g^+ \to B^1\Pi_u$, corresponding to resonance excitation of one of the atoms. In this case the photodissociation process occurs efficiently only from high vibrational levels of the ground-state term $X^1\Sigma_g^+$. At a gas temperature $T \gtrsim 300$ K these levels are heavily populated since the energy of a vibrational quantum of the molecule is less than the temperature of the gas. The photodissociation cross section averaged over the vibrational states of the ground-state term is determined by the expression

$$\bar{\sigma}(\omega)=\frac{4\pi^2\omega}{3cZ}d^2(R_0) \times g_2\int_{E_{min}}^{D} S_{12}^2(E_1,\omega)g(E_1)e^{-E_1/T}dE_1. \quad (22)$$

This formula assumes that the distribution function of the molecules over the vibrational levels is a Boltzmann function and that the difference in the energies of neighboring levels is significantly less than the temperature of the gas. The energy E_1 is measured from the bottom of the potential well, Z is the statistical sum of the vibrational states of the lower electronic term, and g_2 is the statistical weight of the upper electronic term. The lower limit of the integration E_{min} corresponds to the condition that photodissociation of the molecule is energetically possible only from levels whose energy is $E_1 \geq E_{min}$, and D is the dissociation energy of the molecule. The overlap integral S_{12} is determined by Eqs. (9) and (10) in which averaging over rotational sublevels has been carried out.

The photodissociation cross section $\bar{\sigma}(\omega)$ in the frequency region 21 700–22 000 cm^{-1} for $T = 500$ K obtained on the basis of the method developed in the present work[2)] and in terms of the ordinary quasiclassical method is shown in Fig. 2. The potential curves and the value of the dipole moment of the electronic transition have been taken from Refs. 14 and 15. As can be seen from Fig. 2, the results of the two approaches differ substantially, i.e., allowance for the influence of the turning points greatly changes the value of the photodissociation cross section.

[1)] The result given in the book by Landau and Lifshitz[6] utilizes a linear approximation of the potential curves near the turning points and is obtained in the problem of nonadiabatic radiationless transitions. In application to the problem of radiative transitions in collisions of atoms, a similar approach has been used in Refs. 7—9.

[2)] In addition to the analytic expressions obtained, we have utilized the results of a numerical calculation on the basis of Eqs. (9) and (10), which are not given here because of their cumbersome nature.

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