AD-A131 069 CALCULATING THE PROBABILITY OF RADIATION FROM THE DISSOCIATED STATES OF DIATOMIC MOLECULES(U) FOREIGN TECHNOLOGY DIV WRIGHT-PATTERSON AFB OH V A KOCHELAP 06 JUL 83 FTD-ID(RS)T-0571-83 1/1

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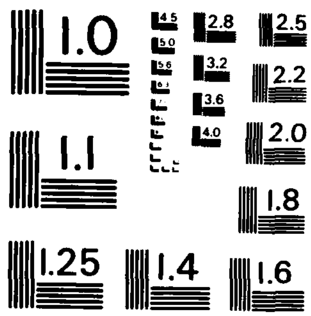

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CALCULATING THE PROBABILITY OF RADIATION FROM THE DISSOCIATED STATES OF DIATOMIC MOLECULES

by

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FOREIGN TECHNOLOGY DIVISION

FTD-ID(RS)T-0571-83

EDITED TRANSLATION

FTD-ID(RS)T-0571-83 6 July 1983

MICROFICHE NR: FTD-83-C-000818

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English pages: 16

Source: Ukrainskiy Fizicheskiy Zhurnal, Vol. 15, Nr. 6, June 1980, pp. 1000-1013

Country of origin: USSR
Translated by: Victor Messenzeff
Requester: FTD/TQTD
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В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
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К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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CALCULATING THE PROBABILITY OF RADIATION FROM THE DISSOCIATED STATES OF DIATOMIC MOLECULES

V. A. Kochelap

The probability of electronic phototransition accompanying the collision of two atoms, i.e., photctransition from the dissociated states of a diatomic molecule, was calculated. The main problem is a correct consideration of the relative motion of atoms, which constitutes the specific nature of the phototransition under consideration. The electron motion is assumed to be given (in an adiabatic approximation). The relative motion of electrons is being examined with the aid of the approximate solutions of the Shroedinger equation. The velocity distribution of the colliding atoms is taken into account by means of the density operator. The results obtained are more general than those of the clssical theory. In instances where the classical theory yields a result that is different from zero, the criteria of validity of classical examination are written out. This article investigates the spectral dependence of the probability of radiation during a collision of two atoms.

Introduction

In the work done by Pekar [1], a qualitatively new possibility of using chemical processes in lasers is shown. His approach is to stimulate the radiative transitions occurring immediately during the elementary chemical events.

In order to estimate the capabilities of the laser proposed in [1], it is necessary to know quantitatively the probabilities of phototransitions accompanying the elementary chemical processes. The special feature of such transitions is the fact that the light is emitted by the atoms which have not formed a molecule at the moment of their collision, i.e., from the dissociated states of atoms.

This work is devoted to the study of phototransitions from the dissociated states of atoms and develops some of the results obtained in [2].

It is convenient to conduct this examination in an adiabatic approximation. Then the wave function of an atom pair $\psi_{gs}(\varrho, r)$ can be presented in the form $\psi_{gs}(\varrho, r) = \Psi_g(\varrho, r)\varphi_{gs}(r)$, where $\Psi_g(\varrho, r)$ is the electron wave function, $\varphi_{gs}(r)$ - wave function of nuclear motion, ϱ - set of electron coordinates, r - relative distance between nuclei, s - set quantum numbers characterizing nuclear motion, and g - electron quantum number. The $\Psi_g(\varrho, r)$ depends on r as on the parameter, $\varphi_{gs}(r)$ is the eigenfunction of the Hamiltonian of the nuclear subsystem $H_g(r) = -\frac{\hbar^2\Delta_r}{2\mu} + u_g(r)$, here μ is the reduced mass of the atom pair and $u_g(r)$ - potential energy of the nuclei, which is determined by the electron motion.

Since $u_g(r)$ is a centally symmetrical potential, $\varphi_{gs}(r) = \frac{1}{r}\chi_{gs}(r)Y_{lm}(\vartheta, \varphi)$, $s \equiv (n, l, m)$, $Y_{lm}(\vartheta, \varphi)$ are spherical functions and n is a vibrational quantum number for the bound states and simply energy for the dissociated states. The $\chi_{gs}(r)$ satisfies the Shroedinger equation with the potential $u_{gl}(r) = u_g(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}$, the eigenvalue of this equation is the total energy of the system in the state with the quantum numbers (g, s). The energy of the dissociated states is independent of l and m.

According to [2], the probability of the phototransition from the electron state g to the state g' can be presented as

$$w_{gg'} = \frac{2\pi e^2}{\hbar\omega}\int_{-\infty}^{+\infty} dt e^{-i\omega t}\,\mathrm{Sp}\left[|U_{xgg'}(r)|^2 R_g e^{-i\frac{H_{g'}t}{\hbar}} e^{i\frac{H_g t}{\hbar}}\right], \qquad (1)$$

where $U_{xgg'}(r)$ is the matrix element of the electron-velocity operator calculated on the wave functions $\Psi_g(\varrho, r)$ and $\Psi_{g'}(\varrho, r)$, ω - frequency of light, and R_g - density operator determining the population of the energy levels of the atom pair, when the electrons are in the g state. In expression (1) it is necessary to take into account only the relative motion of atoms. This motion is the one which constitutes the specific nature of these phototransitions, and to calculate it is the main objective of this work. We will assume that such electron characteristics as $u_g(r)$, $u_{g'}(r)$, and $u_{xgg'}(r)$ are given.

In order to calculate the probability of a phototransition during a collision, we will differentiate between cases A and B.

Case A is realized if the centrifugal energy of the relative rotation of the atoms does not prevent the atoms from moving towards one another reaching distances at which an effective phototransition occurs, i.e., if $u_g(r)$ diminishes slower than r^{-2} with $r \to \infty$.

Case B, on the other hand, occurs in the presence of a centrifugal barrier in the function $u_{gl}(r)$ with $r>0$, i.e., when $u_g(r)$ diminishes faster than r^{-2}.

Case A was examined in work [2] with a quasiclassical motion of the nuclei. In this work this case will be examined without the indicated limitation and we will obtain the applicability criteria for a quasi-classical investigation of motion of the nuclei. We will also conduct a thorough analysis of case B.

1. Calculation of Matrix Elements

1. In a number of cases, it is convenient to calculate the expression for the probability of phototransition (1) with the aid of the matrix elements. If we assume that a dissociated diatomic molecule is in the electron state g and during radiation it passes to the g' state, the following form of matrix elements should be calculated:

$$\langle gEl\,|U_x|\,g'nl\rangle = \int_0^\infty dr\,\chi^*_{gEl}(r)\,U_{xgg'}(r)\,\chi_{g'nl}(r), \qquad (2)$$

where the energy of the initial E and final $E_{g's}$ states are coupled by the law of conservation $E - E_{g's} = \hbar\omega$.

For the dissociated states everywhere, with the exception of the stopping point r_1, the wave function $\chi_{gEl}(r)$ can be calculated in the quasiclassic approximation[1]:

$$\chi_{gEl}(r) = \begin{cases} \dfrac{A}{2\sqrt{|P(r)|}}\exp\left[-\dfrac{1}{\hbar}\displaystyle\int_r^{r_1} dr\,|P(r)|\right], & r < r_1, \qquad (3) \\ \dfrac{A}{\sqrt{P(r)}}\sin\left[\dfrac{1}{\hbar}\displaystyle\int_{r_1}^{r} dr P(r) + \dfrac{\pi}{4}\right], & r > r_1, \qquad (4) \end{cases}$$

here $P(r) = P_{gEl}(r) = \sqrt{2\mu(E - u_{gl}(r))}$, A is a normalized constant. We will assume that in the vicinity $r_1 (P(r_1) = 0)$, $u_{gl}(r) \approx -(r - r_1)F_g(r_1)$; then, in this region, $\chi_{gEl}(r)$ is given by the Airy function [3]:

[1] For the sake of brevity we omit the indices g, E, and l in the values $P_{gEl}(r), r_{1l}, r_{0l}$ and other. The values pertaining to the g' state we denote by dashes, for example, $P'(r) = P_{g'nl}(r)$ etc.

$$\chi_{gEl}(r) = \frac{A}{\sqrt[6]{2\mu\hbar F_g(r_1)}} A\left[(r_1 - r)\sqrt[3]{\frac{2\mu F_g(r_1)}{\hbar^2}}\right], \qquad (5)$$

where

$$A[x] = \frac{1}{\sqrt{\pi}}\int_0^\infty dy \cos\left(\frac{y^3}{3} + xy\right).$$

For the lowest bound states it is possible to restrict oneself to the quadratic expansion of $u_{g'l}(r)$ in the vicinity of its minimum r_0, i.e., having assumed that $u_{g'l}(r) \approx u_{g'l}(r_0) + \frac{\mu\omega_0^2}{2}(r - r_0)^2$. Then the wave function of the rotational sublevels of the principal vibrational state, for example, is presented as

$$\chi_{g'0l}(r) = \frac{1}{\sqrt{2x_0\sqrt{\pi}}} e^{-\frac{(r-r_0)^2}{2x_0^2}}, \quad x_0 = \sqrt{\frac{\hbar}{\mu\omega_0}}. \qquad (6)$$

The energy of these sublevels $E_{0l} = E_{00} + \frac{\hbar^2 l(l+1)}{2\mu r_0^2}$.

We can use the following quasiclassical expression for the strongly excited states:

$$\chi_{g'nl}(r) = \begin{cases} \frac{A'}{\sqrt{P'(r)}} \sin\left[\frac{1}{\hbar}\int_{r_1'}^{r} dr P'(r) + \frac{\pi}{4}\right], & r_1' < r < r_2', \qquad (7) \\ \frac{A'}{2\sqrt{|P'(r)|}} e^{-\int_{r_2'}^{r} dr |P'(r)|}, & r > r_2'. \qquad (8) \end{cases}$$

Here $P'(r) \equiv P_{g'nl}(r)$, $A' = \sqrt{\frac{2\mu\omega_n}{\pi}}$, ω_n is the frequency of vibrations, r_1' and r_2' are the stopping points ($P'(r_1') = P'(r_2') = 0$). In the vicinity of these points it is possible to write, analogously to (5), the function $\chi_{g'nl}(r)$; for example, in the vicinity of r_1'

$$\chi_{g'nl}(r) = \frac{A}{\sqrt[6]{2\mu|F_{g'}(r_1')|}} A'\left[(r_1' - r)\sqrt[3]{\frac{2\mu|F_{g'}(r_1')|}{\hbar^2}}\right], \qquad (9)$$

$F_{g'} = -\frac{\partial u_{g'l}}{\partial r}$, here $F_{g'}(r_1') > 0$, $F_{g'}(r_2') < 0$.

2. The matrix element (2) is calculated easily with the aid of functions (3)–(6), when $n = 0, l > 0$. The analytical expressions for (2) differ in such cases: $r_0 < r_1$, $r_0 \approx r_1$, $r_0 > r_1$.

In the first case one should use expression (3) as the wave function of the dissociated state. Considering the $U_{xgg}(r)$ a smooth function, we take it out from under the integral sign at the maximum point of the expression r_m under the integral sign whose vicinity is determined by (2), as a result we obtain

$$\langle gEl|U_x|g'nl\rangle = \frac{A\sqrt[4]{\pi}\,U_{xgg'}(r_m)}{a\sqrt{2x_0|P(r_m)|}}\,e^{-\varphi(r_m)},$$

$$a^2 = \frac{\hbar^2 x_0^2 + 2\mu F_g(r_m)|P(r_m)|}{2\mu x_0 F_g(r_m)|P(r_m)|}, \quad r_0 < r_1, \qquad (10)$$

where r_m is determined from the condition $\frac{d\varphi}{dr}(r) = 0,\ \varphi(r) = -\frac{(r-r_0)^2}{2x_0^2} + \int_{r_1}^{r} dr\,|P(r)|$.

With $r_0 \approx r_1$ we will use $\chi_{gEl}(r)$ from (5); then, after carrying out $U_{xgg'}$ at point r_1, we write

$$\langle gEl|U_x|g'nl\rangle = \frac{A\sqrt{2x_0\sqrt{\pi}}\,U_{xgg'}(r_1)}{\sqrt[6]{2\mu\hbar F_g(r_1)}}\,e^{\eta\frac{b^6}{2}+\frac{b^6}{6}}\,A\left[b\eta + \frac{b^4}{4}\right], \qquad (11)$$

here $b = x_0\sqrt[3]{\frac{2\mu F_g(r_1)}{\hbar^2}},\ \eta = \frac{r_1 - r_0}{\chi_0}$.

Finally, for the third case $(r_0 > r_1)$, we find the following from (4) and (6):

$$\langle gEl|U_x|g'nl\rangle = \frac{A\sqrt{2x_0}\,U_{xgg'}(r_0)}{\sqrt{\pi P(r_0)}}\,\sin\varphi(r_0)\,e^{-\frac{2(E-u_g(r_0))}{\hbar\omega_0}}, \qquad (12)$$

where $\varphi(r) = \frac{\pi}{4} + \int_{r_1}^{r} dr P(r)$.

We note that expressions (10)-(12) change into one another, just as functions (3)-(5), at the limits of their applicability regions. Thus, these formulas determine the matrix element of transition to the lowest excited states with any relative disposition of the curves $u_{gl}(r)$ and $u_{g'l}(r)$.

3. When n>>1, we will use functions (3)-(5) and (7)-(9) for calculating (2). As is known (see, for example, [3] and also [2], when n>>1, the main contribution to the matrix element is due to the

neighborhoods of the transition points r_j determined from the equation

$$\hbar\Omega_{gg'}(r) = u_g(r) - u_{g'}(r) = \hbar\omega. \qquad (13)$$

Here we will calculate the contribution made by points r_j to (2), when $\left.\frac{d\Omega_{gg'}}{dr}\right|_{r\to r_j} \neq 0$. The contribution of these points depends substantially on the form of the potential-energy curves. In particular, it is easy to check that the contribution of points r_j to (2) is small, when $r_j<\max(r_1, r_1)$ and $r_j>\max(r_2, r_2)$.

With $r_2'<r<r_1$, after substituting expressions (3) and (8) in (2) and carrying out $U_{xgg'}(r)$ at point r_j, we obtain the following exponentially small expression for the matrix element:

$$\langle gEl|U_x|g'nl\rangle = \frac{AA'\sqrt{2\pi\hbar}\,U_{xgg'}(r_j)}{4\sqrt{P(r_j)\mu(F_g(r_j)+|F_{g'}(r_j)|)}}\, e^{-\frac{1}{\hbar}\int_{r_2'}^{r_j} dr|P'(r)| - \frac{1}{\hbar}\int_{r_j}^{r_2} dr|P(r)|}. \qquad (14)$$

With r_1, $r_1'<r<r_2'$, a similar calculation with the aid of functions (4) and (7) results in the following:

$$\langle gEl|U_x|g'nl\rangle = \frac{AA'\sqrt{\pi\hbar}\,U_{xgg'}(r_j)}{\sqrt{\mu P(r_j)\left|\frac{d\Omega_{gg'}}{dr}\right|_{r_j}}}\cos\varphi(r_j). \qquad (15)$$

$$\varphi(r_j) = \frac{1}{\hbar}\int_{r_1}^{r_j} drP(r) - \frac{1}{\hbar}\int_{r_2'}^{r_j} drP'(r).$$

In the cases $r_1\approx r_1'\approx r_j$ and $r_1\approx r_2'\approx r_j$ one should use formulas (5) and (9); thus, we obtain

$$\langle gEl|U_x|g'nl\rangle = \frac{AA'U_{xgg'}(r_j)\sqrt{\pi}\,A\left[(E-u_{gl}(r_j))\sqrt[3]{\frac{2\mu|F_g(r_j)-F_{g'}(r_j)|}{\hbar^2(F_g(r_j)\cdot F_{g'}(r_j))^2}}\right]}{\sqrt[3]{\frac{2\mu}{\hbar}\left|\frac{d\Omega_{gg'}}{dr}\right|_{r_j}}\sqrt{F_g(r_j)|F_{g'}(r_j)|}}. \qquad (16)$$

We note that with a change in r_j, expressions (14)-(16) change into one another.

Expressions (15) and (16), also some of those presented below, are oscillating functions r_j, E, l etc. This is connected with the fact that the phototransition is realized from a state (or between states), which is of the standing-wave type (4) and (7). The matrix element vanishes when the point r_j coincides with the node of this wave; since the contribution of other points $r \neq r_j$ to (2) is small, in reality, the vanishing of the matrix element corresponds to very small probabilities of phototransitions.

4. Since in the general case the difference $\Omega_{gg'}(r)$ is limited from above and below, then there is an upper or a lower boundary of the frequency region, in which equation (13) has a solution and in which expressions (14)–(16) are valid.

Let us calculate (2) close to any of the indicated boundaries. Let the value of the threshold frequency be $\omega=\omega^0$ and r_j^0 is the root of equation (13), when $\omega=\omega^0$. It is possible to show that r_j^0 is a multiple root, while $\left.\frac{d\Omega_{gg'}}{dr}\right|_{r_j^0}=0$. As before, the main contribution to the matrix element is made by the neighborhood of the point r_j^0, where $\Omega_{gg'}(r)$ – does not have to be zero, but always small. For definiteness, let ω^0 correspond to the maximum $\Omega_{gg'}(r)$, then, in the neighborhood $r_j^0 \left(\left.\frac{d^2\Omega_{gg'}}{dr^2}\right|_{r_j^0}<0\right)$, it is possible to write

$$\Omega_{gg'}(r) \approx \begin{cases} \omega^0 + \frac{1}{2}\left(r-r_j^0\right)\left.\frac{d^2\Omega_{gg'}}{dr^2}\right|_{r_j^0}, & \omega>\omega^0; \\ \omega+(r-r_j)\left.\frac{d\Omega_{gg'}}{dr}\right|_{r_j}+\frac{1}{2}(r-r_j)^2\left.\frac{d^2\Omega_{gg'}}{dr^2}\right|_{r_j}, & \omega<\omega^0. \end{cases} \tag{17}$$

Taking into account (17), with the aid of (4) and (7) we calculate the matrix element, assuming that the main contribution is due to the neighborhood of the point r_j^0, as a result we obtain the following: with $\omega>\omega^0$

$$\langle gEl|U_x|g'nl\rangle = \frac{AA'\sqrt{\pi}\,U_{xgg'}(r_j^0)\cos\varphi(r_j^0)}{\left[4\mu P^2(r_j^0)\left.\frac{d^2\Omega_{gg'}}{dr^2}\right|_{r_j^0}\right]^{\frac{1}{3}}} A\left[\frac{\omega^0-\omega}{\sqrt[3]{\frac{P^2(r_j^0)}{2\mu^2}\frac{d^2\Omega_{gg'}(r_j^0)}{dr^2}}}\right]; \tag{18}$$

with $\omega<\omega^0$

$$\langle gEl|U_x|g'nl\rangle = \frac{AA'\sqrt{\pi}\,U_{xgg'}(r_j)\cos\Psi(r_j)}{\left[4\mu P^2(r_j)\left.\frac{d^2\Omega_{gg'}}{dr^2}\right|_{r_j}\right]^{1/3}} A(-C^2), \tag{19}$$

$$C = \left.\frac{d\Omega_{gg'}}{dr}\right|_{r_j}\mu^{1/3}\left(4P(r_j)\frac{d^2\Omega_{gg'}(r_j^0)}{dr^2}\right)^{-1/3},$$

where $\varphi(r)$ should be taken from (15) and $\Psi(r)=\varphi(r)-\frac{2C^2}{3}$.

Expression (19) describes the behavior of the matrix element in the region, where (15) ceases to be valid due to the tendency towards zero $\left.\frac{d\Omega_{gg'}}{dr}\right|_{r_j}$. Hence the applicability criterion of formula (15):

$$\left|\left.\frac{d\Omega_{gg'}}{dr}\right|_{r_j}\right| \gg \left(\frac{4P(r_j)}{\mu}\right)^{1/3}\left(\left|\left.\frac{d^2\Omega_{gg'}}{dr^2}\right|_{r_j}\right|\right)^{2/3}. \qquad (20)$$

We note that the applicability criteria of formulas (14) and (16) have an analogous form.

Generally speaking, the edge of the frequency region, in which (13) has a solution, can wind up at such a point r_j^0, where $r_j^0 \approx r_1 \approx r_1'$. However, this is a rare case for us, since it requires the fulfillment of two conditions simultaneously: $r_j^0 \approx r_1 \approx r_1'$ and $\left.\frac{d\Omega_{gg'}}{dr}\right|_{r_j^0}=0$ with the same parameter ω. A simple geometrical examination shows that there can be no other relations between r_j^0, r_1, r_1', and r_2 with the exception of those calculated.

2. Calculating the Probabilities of Phototransitions with the Aid of Matrix Elements

1. Expression (1) can be written in the following form for the phototransitions from the dissociated states:

$$w_{gg'}=\frac{4\pi^2e^2}{\omega}\int_0^\infty dE\sum_{n,l}(2l+1)R_{gEl}|\langle gEl|U_x|g'nl\rangle|^2\delta(E-E_{nl}-\hbar\omega), \qquad (21)$$

where R_{gEl} are matrix elements of the diagonal density operator R_g.

In the case A we will use the Gibbs distribution for R_g with an explicit account of the fact that only the dissociated states[2]

$$R_g=c\Theta(H_g)\times\exp\left(-\frac{H_g}{T}\right),\ \mathrm{Sp}R_g=1,\ \text{and}\ \Theta(x)=\begin{cases}1 & \text{with } x\geq 0,\\ 0 & \text{with } x<0\end{cases} \qquad (22)$$

are populated. The last equality defines the normalized constant c which, when calculating with the aid of functions (3)-(5), equals

---

[2] In (22), and later in (38), we introduced the Θ function for the the purpose of exclusion of the bound states [2] from the consideration. We note that population of these states, occurring in the process of the usual chemical reactions, can lead to a case, which corresponds to an ordinary chemical laser (see, for example, [4 and 5].

$\frac{8\sqrt{\pi}\hbar^3}{T^{3/2}A^2(2\mu)^{3/2}V}$, when standardizing these functions for the δ function from energy $c=\frac{(2\pi\hbar^2)^{3/2}}{V(\mu T)^{3/2}}$ (V is the space where the atom pair is).

In the general case, the expressions obtained in section 1 fully determine the probabilities of phototransitions in the case A together with (21) and (22).

Below we will examine the characteristic extreme cases, in which assumes a simple analytical form.

2. Let us analyze the probability of a phototransition when one of the lowest bound states $(n=0, l\geqslant 0)$ is the final one.

First of all, we can see from the analytical expressions (10)-(12), defining the matrix element in this case, that the probability of a phototransition is not small only when $r_1 \approx r_0$; otherwise it diminishes exponentially. When $r_1 < r_0$, this occurs because the kinetic energy of the atoms in the $r \approx r_0$ region is high and its loss is unlikely (according to the Franck-Condon principle). When $r_1 > r_0$, the probability of their getting close to one another for the phototransition to occur is exponentially small.

It is easy to calculate expression (21) when $\frac{\hbar^2}{2\mu r_0^2} \ll T \ll E_{10}-E_{00}$, then in (21) it is possible to bring out the matrix element from under the l sum, when $l=0$, and replace the remaining sum with an integral. The criterion of such an approximation $r_0F_g(r_0) \gg T$ is always satisfied. As a result, we find

$$w_{gg'}=\frac{64\pi^3e^2x_0r_0^2|U_{xgg'}(r_0)|^2}{\omega T^{1/2}\sqrt[3]{\hbar F_g(r_0)}V}e^{\eta b^2+\frac{b^6}{3}}A^2\left[b\eta+\frac{b^4}{4}\right]. \qquad (23)$$

We will use the following values of the parameters for a quantitative estimate of expression (23):

$$U_{xgg'}(r_0)=\omega\cdot 10^{-8}\ см,\ \omega=3\cdot 10^{15}\ сек^{-1},\ r_0=2\cdot 10^{-8}\ см,\ T= \\ =0{,}025\ эв,\ n_1=n_2=10^{19}\ см^{-3}, \qquad (24)$$

and also $F_g(r_0)=1.6\cdot 10^{-4}$ erg$\cdot$cm^{-1}. At these values of the parameters, the maximum of expression (23) is realized when $r_0=r_1$ and equals $w_{gg'}=9.3\cdot 10^{-30}$ cm^{-3}/V. According to [2], the amplification factor α of the light wave is connected with $w_{gg'}$ and the concentration of atoms n_1 and n_2 by the simple relation $\alpha=\frac{V}{c}w_{gg'}n_1n_2$, with the values of n_1 and n_2 from (24) $\alpha=0.031$ cm^{-1}.

According to [2], the probability of photon absorption by the dissociated states at the same frequency ω, significant only when $u_g(\infty) = u_{g'}(\infty)$, is given by the formula

$$w_{g'g} = \frac{32\pi^{5/2} e^2 |U_{xgg'}(r_j)|^2 r_j^2}{\omega |F_g(r_j) - F_{g'}(r_j)| V} \sqrt{\frac{|u_{g'}(r_j)|}{T}}, \quad |u_{g'}(r_j)| \gg T, \qquad (25)$$

here r_j is the root of equation (13), for our case $r_j \approx r_0$. We can see from the comparison of (23) and (25) that $\frac{w_{gg'}}{w_{g'g}} \ll \sqrt{\frac{\hbar\omega_0}{|u_{g'}(r_j)|}} < 1$, i.e., the probability of absorptoin is always greater than the probability of radiation. This means that in order for the negative absorption to exist in the recombination reactions, it is necessary that $u_g(\infty) < u_{g'}(\infty)$ in the case A.

3. The probabilities of phototransitions to highly excited levels will be examined in the following section; here, we will estimate the probability of a phototransition at the frequency $\omega = \omega^0$. As is noted in [2], this case is of particular interest since the classical calculation corresponding to it yields $w_{gg'} \to \infty$, and conversely, it is possible to obtain the final result with the aid of the matrix elements (18) and (19). We will presented it for $\omega = \omega^0$, $|u_g(r_j)| \gg T$. In calculating (21) we will use integration instead of the summation over n and l; in this case, we will sum over l to those values at which $E > u_{gl}(r_j)$, because, when $E < u_{gl}(r_j)$, the probability of the particles closing towards one another to within $\sim r_j$ is exponentially small, i.e., such l do not make a significant contribution to the probability of a phototransition. As a result

$$w_{gg'} = \frac{48\pi^{5/2} (8\mu)^{1/6} (r_j^0)^2 e^2 |U_{xgg'}(r_j^0)|^2}{\hbar\omega \cdot T^{1/2} \left(\frac{d^2\Omega_{gg'}}{dr^2}\right)_{r_j^0}^{2/3} V} |u_g(r_j^0)|^{1/3} A^2(0). \qquad (26)$$

It can be seen from (26) that the probability of transition also with $\omega = \omega^0$ remains to be a gradually increasing one with the $|u_g(r_j)|$ function, just as expression (25).

In addition to the parameters in (24), we will also use $\mu = 10^{-23}$ g, $|u_g(r_j^0)| = 1$ eV, $(d^2\Omega_{gg'}/dr^2)_{r_j^0} = 2 \cdot 10^{31}$ $s^{-1} \cdot cm^{-2}$ [2] for a numerical estimate. As a result, $w_{gg'} \approx 3{,}2 \cdot 10^{-28}$ cm^{-3}/V, $\alpha = 3.2$ cm^{-1}.

We note that the estimate of the probability of phototransition in [2] in the case of $\omega = \omega^0$ was performed based on other considerations.

In its order of magnitude the result proved to coincide with the one presented above.

3. The Probabilities of Phototransitions to Quasiclassical Levels

1. In this case the calculation of $w_{gg'}$ with the aid of (21) is difficult because the transitions taking place are to the many nearby vibration-rotational levels. A direct calculation of expression (1) seems convenient to us with the aid of the known operator methods [4].

Just as above, we will assume that the main contribution is due to the neighborhoods of points r_j defined by equation (13). We will calculate the contribution made by one of such points, assuming, for the sake of simplicity, that equation (13) has only one solution. We will assume that $u_g(r) \approx u_g(r_j) - (r-r_j)F_g + \frac{(r-r_j)^2}{2}\frac{\partial^2 u_g}{\partial r^2} + \ldots$ in the neighborhood of this point and, considering the $u_g(r)$ a relatively smooth function, we make use of the following approximation [4]:

$$e^{\tau H_g} \approx \left(1 + \frac{\hbar^2\tau^2}{4\mu}\frac{\partial^2 u_g}{\partial r^2}\bigg|_{r_j} + \ldots\right) e^{\tau u_g(r_j)} e^{-\tau\left[\frac{\hbar^2\Delta_r}{2\mu} + F_g(r-r_j)\right]}, \qquad (27)$$

below we will also assume that

$$\frac{\hbar^2\tau^2}{4\mu}\left|\frac{\partial^2 u_g}{\partial r^2}\right|_{r_j} \ll 1. \qquad (28)$$

We will make use of an integral representation of the Θ function for the following transformation ($\tau>0$):

$$\Theta(x)e^{-\tau x} = e^{-\tau x}\frac{i}{\pi}\lim_{\eta\to 0}\int_{-\infty}^{+\infty} dy\,\frac{e^{-ixy}}{y+i\eta} = \frac{i}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-ixy}}{y+i\tau}\,dy. \qquad (29)$$

Then taking into account (29), we can write (22) as

$$R_g(H_g) = c\Theta(H_g)e^{-\frac{H_g}{T}} = \frac{ic}{\pi}\int_{-\infty}^{+\infty} dy\,\frac{e^{-iyH_g}}{y+i\tau}, \qquad (30)$$

which makes it possible to obtain a convenient form for expression (1):

$$w_{gg'} = i\,\frac{2^{5/2}\pi^{3/2}\hbar^3 e^2 |U_{xgg'}(r_j)|^2}{\omega(\mu T)^{3/2} V} \times$$
$$\times \int_{-\infty}^{+\infty}\int d\tau_1 d\tau_2\,\frac{e^{-i\hbar\omega\tau_2}}{\tau_1+\tau_2+\frac{i}{T}}\,\mathrm{Sp}\left[e^{-i\tau_1 H_g}e^{-i\tau_2 H_g}\right]. \qquad (31)$$

It is simple to rewrite the exponent in (27) as follows [4]:

$$e^{-\tau\left[\frac{\hbar^2\Delta_r}{2\mu}+F_g(r-r_j)\right]}=e^{-\tau F_g(r-r_j)-\frac{\hbar^2F_g^2}{6\mu}\tau^3}e^{\frac{\hbar^2\tau}{2\mu}\left[\frac{\tau}{r}F_g+\tau F_g\frac{\partial}{\partial r}-\Delta_r\right]}\approx$$

$$\approx\exp\left[-\tau F_g(r-r_j)-\frac{\hbar^2F_g^2}{6\mu}\tau^3+\frac{\hbar^2\tau^2}{2\mu r_j}F_g\right]\exp\left[\frac{\hbar^2\tau^2}{2\mu}F_g\frac{\partial}{\partial r}-\frac{\hbar^2\tau}{2\mu}\Delta_r\right]. \qquad (32)$$

Here we disregarded the noncommutativity $\frac{1}{r}$ with the operators of the type $\frac{\partial}{\partial r}$ and assumed that $\frac{1}{r}=\frac{1}{r_j}$. It is possible to show that such an approximation does not introduce a significant error.

Omitting further details in the calculation of (31) using the complete system of Fourier functions $\frac{1}{(2\pi)^{3/2}}e^{ikr}$ [2], we present the final result:

$$w_{gg'}=\frac{16\pi^3r_j^2e^2|U_{xgg'}(r_j)|^2}{\omega|F_g(r_j)-F_{g'}(r_j)|}P(r_j), \qquad (33)$$

where the value of $P(r_j)$ is determined by the integral

$$P(r)=\frac{1}{\pi^{3/2}V}\lim_{\delta\to 0}\int_{-\infty}^{+\infty}\int_{-\infty}^{\infty}d\eta d\tau\frac{e^{-i\tau(\eta^2+u)-i\frac{a_1\tau^3}{3}-\frac{a_2\tau^2}{2}}}{(\tau+i)(\tau-i\delta)}.$$

$$u=\frac{u_g(r)}{T},\ a_1=\frac{\hbar^2F_g^2(r_j)F_{g'}^2(r_j)}{8\mu T^3(F_g-F_{g'})^2_{r_j}};\ a_2=\frac{\hbar^2F_g(r_j)F_{g'}(r_j)(F_g(r_j)+F_{g'}(r_j))}{\mu r_jT^2(F_g(r_j)-F_{g'}(r_j))^2}. \qquad (34)$$

Formula (34) was obtained by us for the case $a_2\geqslant 0$, other cases can be investigated analogously, but this leads to long expressions. The integral over η is easily calculated in (34); however, for further deductions, this type of expressions (34) is sufficient for us.

2. From the standpoint of accuracy, expression (33) coincides with the classic expression obtained in work [2]; however, (34) differs from the corresponding formulas of work [2]. A classical case is obtained from (33) and (34) when $\hbar\to 0$, which corresponds to $a_1=0$, $a_2=0$. In reality, however, the last equalities never occur; however, using the expansion of expression (34) in values of a_1 and a_2, it is easy to show that a classical result is obtained when

$$\frac{a_1}{8|u|^3}\ll 1,\ \frac{a_2}{8|u|^2}\ll 1,\ u<0,\ \text{if } |u|\gg 1, \qquad (35)$$

and

$$\frac{a_1}{3}\ll 1,\ \frac{a_2}{3}\ll 1,\ u<0 \text{ or } u>0,\ \text{if } |u|\sim 1. \qquad (36)$$

When criterion (36) is violated, $w_{gg'}$ as a function of the quantity u changes as follows: with $|u|>>1$ in places where criterion (35) is satisfied, $w_{gg'}$ is close to its quasiclassical value, which corresponds to the phototransition passing from the state with high energy $\sim T|u|$, i.e., from a quasiclassical state; with a decrease in $|u|$ the value of $w_{gg'}$ also decreases, exceeding the classical expression predicted in work [2]. This is connected with the stopping point when $u\approx 0$, increasing the probability of phototransition. When $u>0$, $w_{gg'}$ diminishes exponentially with an increase in u; thus, when $u>>1$, the following can be obtained from (34):

$$P(r)\approx\frac{1}{V}\exp\left[-u(r_j)+\frac{a_1}{3}+\frac{a_2}{2}\right],\ u(r_j)>a_1+a_2. \qquad (37)$$

Thus, as before, the probability of phototransition $w_{gg'}$ remains a steadily increasing function with a change in the value of $|u_g(r_j)|$.

Let us estimate a_1, and a_2, and also criterion (28), with the following values of the parameters: $F_g=2F_{g'}=1.6\cdot10^{-4}$ erg·cm^{-1}, $\mu=10^{-23}$ g, $r_j=2\cdot10^{-8}$ cm, $\frac{\hbar d^2\Omega_{gg'}}{dr^2}$ = 10^4 erg·cm^{-2}. Then $a_1=0.6\left(\frac{10^3}{T^0}\right)^2$, and $a_2=0.7\left(\frac{10^3}{T^0}\right)^2$, where T^0 should be in degrees Kelvin. For estimating (28), we note that, analogously to criteria (35) and (36), significant are such τ which are proportional to T^{-1} when $u>0$ and $|u|\sim 1$ and proportional to $\frac{u}{T}$ when $u<0$ and $|u|>>1$. For the above-given values of the parameters and $T=600^0$K $\frac{\hbar^2\tau^2}{4\mu}\left|\frac{\partial^2\Omega_{gg'}}{\partial r^2}\right|\lesssim 0.1$.

4. The probabilities of Phototransitions in the Presence of a Centrifugal Barrier (case B)

1. In this case the potential energy $u_{gl}(r)$ $(l>0)$ is characterized by a centrifugal barrier, whose maximum is situated with $r=r_l$, and the height equals $u_{gl}(r_l)$. These parameters are found easily from the following conditions:

$$\frac{\partial u_{gl}(r_l)}{\partial r}=0,\ \frac{\partial^2 u_{gl}(r_l)}{\partial r^2}<0,\ l>0. \qquad (38)$$

Disregarding the tunneling of atoms through this barrier, we will use the following expression for the density operator in the re- gion:

$$R_{gEl}=c\Theta[E-u_{gl}(r_l)]e^{-\frac{E}{T}}. \qquad (39$$

Such a form of the operator R_g corresponds to the fact that out of the number of colliding atoms, whose relative rotation is characterized by the quantum number l, only the atoms, whose energy of translational motion exceeds the height of the barrier $u_{gl}(r_l)$, are able to penetrate to the distances $\leq r_l$.

The constant c in expression (39) is determined as before and equals $\frac{1}{V}\left(\frac{2\pi\hbar^2}{\mu T}\right)^{3/2}$.

2. The simplest way to calcul-t the probability of phototransition is by means of a quasiclassical approximation. This calculation is performed conveniently with the use of the complete system of functions $\varphi_{k\,m} = \sqrt{\frac{2}{\pi}}\frac{\cos kr}{r} Y_{lm}(\vartheta, \varphi)$. Omitting the details, we present the final result (the calculation is performed similarly to the way it was done in work [2]

$$w_{gg'} = \frac{4\pi e^2}{\hbar\omega}\sum_j \frac{P_g(r_j)\,|U_{xgg'}(r_j)|^2}{\left|\frac{\partial\Omega_{gg'}}{\partial r}\right|_{r_j}}, \quad (40)$$

where

$$P_g(r) = \sum_l (2l+1) P_{gl}(r) = \sum_l (2l+1)\int_0^\infty dk R_{gEl}\left(\frac{\hbar^2 k^2}{2\mu} + u_{gl}(r)\right), \quad (41)$$

$$P_{gl}(r_j) = \frac{2\pi^2\hbar^2}{\mu T V} e^{-\frac{u_{gl}(r_j)}{T}} \begin{cases} 1 & \text{with } u_{gl}(r_j) > u_{gl}(r_l), \\ 1 - \Phi\left[\sqrt{\frac{u_{gl}(r_l) - u_{gl}(r_j)}{T}}\right] & \text{with } u_{gl}(r_j) < u_{gl}(r_l). \end{cases} \quad (42)$$

r_j is the root of equation (13), $\Phi(x) = \frac{2}{\pi}\int_0^x dy e^{-y^2}$.

The following extreme cases are easily obtained from (40)-(42). With $u_{gl}(r_j) > 0$ we find the exact formula

$$w_{gg'} = \frac{16\pi^3 e^2}{\hbar\omega V}\sum_j \frac{r_j^2 |U_{xgg'}(r_j)|^2}{\left|\frac{d\Omega_{gg'}(r_j)}{dr}\right|} e^{-\frac{u_{gl}(r_j)}{T}}. \quad (43)$$

With $u_g(r_j) < 0$, $|u_g(r_j)| \gg u_{gl}(r_j) \sim T$, we find approximately

$$w_{gg'} = \frac{8\pi^{7/2} e^2\hbar}{\omega\mu T^{1/2} V}\sum_j \frac{|U_{xgg'}(r_j)|^2 \sigma_g}{\sqrt{|u_g(r_j)|}\left|\frac{d\Omega_{gg'}}{dr}\right|_{r_j}}. \quad (44)$$

where

$$\sigma_g = \sum_l (2l+1) e^{-\frac{u_{gl}(r_l)}{T}} . \qquad (45)$$

3. In the case $\omega \approx \omega^0$ we employ formulas (18) and (19), from which, with $u_g(r_j) < 0$, $|u_g(r_j)| \gg u_{gl}(r_l) \sim T$, follows the

$$w_{gg'} = \frac{2^{\frac{17}{6}} \pi^{\frac{5}{2}} e^2 \hbar |U_{xgg'}(r_j^0)|^2 \sigma_g}{\omega T^{1/2} \mu^{1/6} \left| \frac{d^2\Omega_{gg'}(r_j^0)}{dr^2} \right|^{2/3} |u_g(r_j^0)|^{2/3} V} \times$$

$$\times A^2 \left[\frac{\omega^0 - \omega}{\sqrt[3]{\frac{P^2(r_j^0)}{2\mu} \frac{d^2\Omega_{gg'}(r_j^0)}{dr^2}}} \right], \text{ if } \omega > \omega^0; \qquad (46)$$

$$w_{gg'} = \frac{2^{17/6} \pi^{5/2} e^2 \hbar |U_{xgg'}(r_j)|^2 \sigma_g A^2 |-C^2|}{\omega T^{1/2} \mu^{1/6} \left| \frac{d^2\Omega_{gg'}(r_j)}{dr^2} \right|^{2/3} |u_g(r_j^0)|^{2/3} V}, \qquad (47)$$

$$C = \frac{d\Omega_{gg'}}{dr}\Big|_{r_j} \left(\frac{\mu}{4P(r_j)} \right)^{2/3} \left(\frac{d^2\Omega_{gg'}}{dr^2} \right)_{r_j}^{-2/3}, \text{ if } \omega < \omega^0.$$

For definiteness, it is assumed in (46) and (47) that ω^0 is the upper limit of the region, in which equation (13) has a solution. On the basis of (46) and (47) it is possible to observe a spectral dependence of the probability of the phototransition $w_{gg'}(\omega)$. First of all, it can be seen that ω^0 determines the edge of the luminescence line, since with $\omega > \omega^0$ the probability of phototransition decreases exponentially:

$$w_{gg} \sim \exp\left[- \frac{2^{5/2} \mu^{1/2} (\omega - \omega^0)^{3/2}}{3P(r_j^0) \left| \frac{d^2\Omega_{gg'}}{dr^2} \right|_{r_j^0}^{1/2}} \right].$$

To determine the frequency dependence of the phototransition probability when $\omega < \omega^0$, we have to determine $r_j = r_j(\omega)$ from (13). Close to r_j^0 $r_j - r_j^0 \approx \sqrt{2(\omega^0 - \omega)} \left(\frac{d^2\Omega_{gg'}}{dr^2} \right)_{r_j}^{-1}$, $\frac{d\Omega_{gg'}}{dr}\Big|_{r_j} \approx \left| 2(\omega^0 - \omega) \left| \frac{d^2\Omega_{gg'}}{dr^2} \right|_{r_j^0} \right|^{1/2}$; substituting these values in (47), we find that formula (46) describes approximately the spectral dependence $w_{gg'}(\omega)$ also when $\omega < \omega^0$. Now we can see that the maximum $w_{gg'}(\omega)$ is realized with $\omega^0 - \omega = \left| \frac{u_g(r_j^0)}{\mu} \left(\frac{d^2\Omega_{gg'}}{dr^2} \right)_{r_j^0} \right|^{1/3}$ and equals

$$\max w_{gg'}(\omega) = \frac{5{,}2 \pi^{5/2} \hbar e^2 |U_{xgg'}(r_j^0)|^2 \sigma_g}{\omega T^{1/2} \mu^{5/6} \left| u_g(r_j^0) \left(\frac{d^2\Omega_{gg'}}{dr^2} \right)_{r_j^0} \right|^{2/3}}. \qquad (48)$$

The half-width of the chemiluminescence "line," determined by the conventional method from (46) and (47), proves to be equal to

$$\Delta\omega \approx 0.8 \sqrt[3]{\frac{u_g(r_i^0)}{\mu}\left(\frac{d^2\Omega_{gg'}}{dr^2}\right)_{r_i^0}}. \qquad (49)$$

Let us estimate expressions (48) and (49), using the following values of the parameters in addition to (24): $\mu = 10^{-23}$ g, $|u_g(r_i^0)| = 1$ eV, $(d^2\Omega_{gg'}(r_i^0)/dr^2) = 2\cdot 10^{31}\ s^{-1}\cdot cm^{-2}$ (concerning the estimation of the last parameter, see work [2]). We estimate the quantity σ_g using the usual parameters of curves $u_g(r)$ (see, for example, [7]), as a result we find $\sigma_g \approx 50-100$. The substitution of these values in (48) and (49) yields $\Delta\omega = 1\cdot 10^{14}\ s^{-1}$, $\max w_{gg'}(\omega) \approx (3-6)\cdot 10^{-29}\ cm^{-1}/V$, $\alpha \approx (0.1-0.2)\ cm^{-1}$.

The author is very grateful to S. I. Pekar, academician of the AS UkrSSR, for the numerous discussions of this work.

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Received
9/9/1969.

CALCULATION OF PROBABILITY OF RADIATION FROM BIATOMIC MOLECULE DISSOCIATION STATES

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Summary

To estimate possibilities of a laser, where a photostimulated chemical reaction is used, calculation was carried out of probabilities of radiation from biatomic molecule dissociation states. Quantum consideration made it possible to investigate in detail those cases when the classical theory is not applicable and to find out the applicability criteria of the quasi-classical results obtained earlier. Numerical estimations substantiate the possibility to realize the laser where the photostimulated chemical reaction is used.

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