Nonadiabatic electron transitions during collisions between atoms and ions in an electromagnetic field

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(Submitted 19 December 1978)
Zh. Eksp. Teor. Fiz. **76**, 1969–1976 (June 1979)

Inelastic collisions (charge transfer) between atoms and ions in an electromagnetic field are considered. An expression for the probability for a field-induced transition at the point of quasi-intersection of the terms (the case of positive- and negative-ion neutralization) is derived which is a generalization of the adiabatic Landau-Zener formula. The possibility of the existence of a field-induced nonadiabaticity region whose position depends on the field intensity is demonstrated in the particular case of ion-atom collisions. The cross sections for specific processes are estimated.

PACS numbers: 34.70.+e

The investigation of the interaction of electromagnetic waves with atomic and molecular systems has received quite a great deal of attention (see, for example, the monographs by Kondrat'ev and Nikitin[1] and Hasted[2] and the review article by Yakovlenko[3]). There are, apparently, two main problems connected with the use of an electromagnetic field (EMF) in atomic and molecular collisions: the investigation of the mechanisms underlying the elementary processes and the controlled variation of the reaction channel. Recently, a number of cases of the effect of an EMF on the probabilities for nonresonance electron transitions between two states, occurring as a result of the absorption or emission of a light-energy quantum, $\hbar\omega$, in the course of a collision between two particles, have been discussed in the literature.[3] A characteristic feature of the processes considered in these papers is that the EMF dependence is contained only in the off-diagonal interaction matrix element (in the basis of atomic functions or other functions not depending parametrically on the internuclear distance R), which has the form $H_{12}=H_{12}^0\cos\omega t$. In this case, by setting $\tilde{H}_2-\tilde{H}_1=H_2-H_1\pm\hbar\omega$, $\tilde{H}_{12}=H_{12}^0$, we can reduce the problem to a problem of the two-level models well-known in the theory of atomic collisions (see, for example, Ref. 4)—basically, to a problem of the linear Landau–Zener model.[3]

It is to be expected that, in order to obtain results that exhibit specific distinctive features of the effect of an EMF on inelastic collisions, we should take into account the field dependence of the diagonal matrix elements H_1 and H_2. This situation is realized, in particular, in a charge-transfer process, i.e., in the process involving the transition of an electron from one particle to another. In the present investigation (some preliminary results of which are given in Ref. 5), we first consider charge transfer between a positive and a negative ion, i.e., the process

$$A^++B^-\pm\hbar\omega\to A+B. \tag{1}$$

Using this process as an example, we shall investigate the effect of an EMF on the transition probability for the system as it passes through the localized nonadiabaticity region that exists in zero field, and generalize the adiabatic Landau–Zener formula to the case when an EMF is present. Secondly, we study the mechanism underlying the nonadiabatic transition that occurs between quasimolecular states as a result of a multiphoton absorption, i.e., underlying the process

$$A^{+(-)}+B\pm n\hbar\omega\to A+B^{+(-)}, \tag{2}$$

and show that a new nonadiabaticity region (which exists only in an EMF) is responsible for this process. The cross-section estimates obtained for (1) and (2) indicate that these cross sections can have quite large values (~ 1 Å^2) in EMF of presently attainable strengths ε.

1. A schematic representation of the behavior of the electronic terms of the ionic, H_1, and covalent, H_2, states of the quasimolecule AB for the process (1) is shown in Fig. 1. To these states correspond wave functions, Ψ_1 and Ψ_2, that are responsible for the localization of the valence electron on the individual particles. Let us denote the interaction between these states by H_{12}. Let us consider the behavior of the system in the region, $R\sim R_0$, $H_1(R_0)=H_2(R_0)$, of quasi-intersection of the indicated terms, using in this case the approximations and the corresponding parameters of the Landau–Zener model: $\Delta H\equiv H_1-H_2=Fx$, $x=R-R_0=vt$, $H_{12}(R_0)=a$, where v is the relative radial velocity and t is the time. Then the adiabatic functions assume the form

$$\Psi'=\cos(\chi/2)\,\Psi_1+\sin(\chi/2)\,\Psi_2,\ \Psi''=-\sin(\chi/2)\,\Psi_1+\cos(\chi/2)\,\Psi_2,$$
$$\operatorname{tg}\chi=2a/Fx,$$

while the splitting between the adiabatic terms $\Delta U=[(Fx)^2+4a^2]^{1/2}$. We shall also assume that the collision process is adiabatic in the absence of an EMF, i.e., that the Landau–Zener parameter $\delta=4a^2/Fv\gg 1$, and, consequently, that the probability, $p_{12}=\exp(-\pi\delta/2)$, of the transition between the adiabatic terms is exponentially small. Notice that this "adiabatic" formula cannot be obtained with the aid of perturbation theory in terms of the nonadiabaticity operator $\partial/\partial t$ because of the singularities of the system of equations for the amplitudes at the complex point $\bar{t}=i2a/Fv$, where $\Delta U(\bar{t})=0$.[4]

Upon the application of an EMF, there appears in the electron Hamiltonian a new term $H_\varepsilon=\mathbf{r}\cdot\boldsymbol{\varepsilon}\cos(\omega t+\varphi)$, which describes the interaction of the valence electron with the field. In this case

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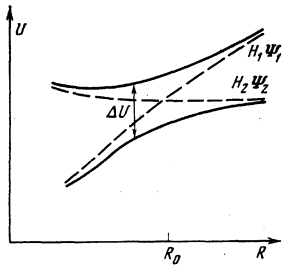

FIG. 1. Electronic terms of the quasimolecule AB for the process (1): the dashed curves are the ionic and covalent terms; the solid curves, the adiabatic terms.

$$\Delta H_\varepsilon=\Delta H+\langle 1|\hat{H}_\varepsilon|1\rangle-\langle 2|\hat{H}_\varepsilon|2\rangle=Fx+\varepsilon R\cos(\omega t+\varphi).$$

Applying the traditional—in the two-level model—transformations, we obtain in first-order perturbation theory in terms of ε the following expression for the probability of transition between the adiabatic terms in an EMF,

$$P_\varepsilon=\left|\int_{-\infty}^{\infty}\frac{\sin\chi}{4}\varepsilon R\exp\left\{i\int^{t}[\Delta U(t')-\omega]dt'\right\}dt\right|^2. \tag{3}$$

The locations of the stationary-phase points are given by the expression

$$t_\varepsilon^2=\tilde{t}^2(1-\lambda),\ \lambda=\omega/2a. \tag{4}$$

It can be seen that $\mathrm{Im}\,t_\varepsilon<\mathrm{Im}\,\tilde{t}$, i.e., as ω is increased, the point t_ε moves towards the real axis. In the process, the degree of adiabaticity of the transition decreases, and when $\lambda\gtrsim 1$, the process becomes nonadiabatic. In the case when $|1-\lambda|\gg 1/\delta$, the integration in (3) is performed by the stationary-phase method. We obtain for $\lambda<1$:

$$P_\varepsilon=\frac{1}{3}C\exp(-\delta_\varepsilon),\quad C=\frac{\pi}{8}\frac{(R_0\varepsilon)^2}{Fv\lambda(1-\lambda^2)^{1/2}},\quad \delta_\varepsilon=\delta f(\lambda). \tag{5}$$

$C\ll 1$ is the applicability condition for the perturbation theory, $f(\lambda)=\arcsin(1-\lambda^2)^{1/2}-\lambda(1-\lambda^2)^{1/2}$, and the factor 1/3 is due to the averaging over the angle between $\boldsymbol{\varepsilon}$ and $\mathbf{R}$. Notice that the parameter δ_ε can be regarded as a generalized Landau–Zener parameter characterising the degree of adiabaticity of the process as a function not only of the behavior of the electronic terms, but also of the EMF frequency. If, on the other hand, $\lambda>1$, then the expression

$$P_\varepsilon=^2/_3C \tag{6}$$

gives the probability for a transition to occur during the crossing of the two neighboring nonadiabaticity regions, whose positions are given by (4) (we can neglect the interference between them because of the large advance in phase). In the case when $|1-\lambda|\ll 1$, the integration in (3) can be carried out by expanding $\Delta U(t)$ in a series in the vicinity of $t=0$. Then

$$P_\varepsilon=\frac{\pi}{12}\left(\frac{R\varepsilon}{\omega}\right)^{2/3}\gamma^{4/3}\Phi^2[(1-\lambda)\gamma^{2/3}], \tag{7}$$

where $\gamma=2^{1/2}\delta$ and Φ is the Airy function. As can be seen from the applicability conditions for the obtained expressions, the regions where the formulas (5) and (6), as well as the regions where (6) and (7), are applicable overlap. This can also be easily verified by using the asymptotic representation for the Airy functions. Notice that the expression (7) takes the interference effect into account in the $\lambda>1$ case. Using the characteristic values of the parameters[1)] of the process (1), $\omega\approx 2a=10^{-2}$, $v=10^{-3}$, $R_0=10$, and $F\approx R^{-2}$ (Ref. 6), we obtain the cross section $\sigma\approx 1$ Å^2 for $\varepsilon\approx 10^5$ V/cm.

In conclusion of this section, let us note the following circumstance. Since the expressions (5)–(7) were derived in first-order perturbation theory in terms of ε, they describe the line shape of the radiation emitted during the photoneutralization of positive and negative ions, i.e., emitted in the process

$$A^+ + B^- \begin{matrix} \nearrow A + B + \hbar\omega \\ \searrow AB + \hbar\omega \end{matrix}. \tag{8}$$

It follows from the properties of the Airy function[7] that this line has it peaks in the vicinity of $\omega_m\approx(1+1.02\gamma^{-2/3})2a$ and decays rapidly into the long-wave region. The shape of this line is similar to the shape of satellites of spectral lines.[8] To determine the cross section, σ_0, for photoneutralization in crossing the region ($R\approx R_0$, $\Delta R\approx 2a/F\approx 2aR_0^2$) of strong coupling between the ionic and covalent states, let us use the following expression for the emission probability per unit time[9]:

$$W(R)=\frac{4\omega^3}{3c^3}|d_{12}(R)|^2, \tag{9}$$

where $\omega=\Delta U(R)$, c is the velocity of light, and we have set the statistical weights of the upper and lower adiabatic terms equal to unity. In the region under consideration $\omega\approx 2a$, $|d_{12}|=R/2$, and the time taken to cross it $\Delta t=\Delta R/v$. As a result, we obtain

$$\sigma_0=\frac{32\pi}{3}\frac{R_0^6a^4}{vc^3}. \tag{10}$$

The substitution of the above-used values for the individual parameters into this expression yields the estimate $\sigma_0\approx 2\times 10^{-6}$ Å^2. The purely "collision" (i.e., radiationless) cross section σ_s is in this case of the order of 10^{-5} Å^2. Thus, upon further increase of the parameter δ, the cross section σ_0 exceeds σ_s, and the photoneutralization process becomes the decisive process. The use of an external EMF source enables us to effectively change the channel in which the reaction occurs. Investigating then the frequency dependence of the cross section, we can determine the quantity $\Delta U(R\approx R_0)$.

2. Let us now consider the process, (2), of nonresonance (the Massey parameter is large: $\zeta\equiv\Delta E/\alpha v\gg 1$) charge transfer without a change in the ionic character of the states of the quasimolecule. Here ΔE is the energy defect for $R\to\infty$, i.e., the difference between the ionization potentials or between the electron affinity energies of the colliding particles, $1/\alpha$ is the characteristic dimension of the region of variation of the inter-

action potential, and v is the relative velocity of the particles. The probability of such a process in the absence of EMF is exponentially small ($\sim \exp(-\zeta)$; see Ref. 1). In a strong EMF the charge-transfer cross section can significantly increase. This can be achieved, for example, by choosing a frequency $\omega \approx \Delta E$.[3] Another case is investigated below. It is connected with the appearance of a new, field-induced, nonadiabaticity region at large values of R.[5] Indeed, the difference between the diagonal elements of the Hamiltonian is given by the expression

$$H_1 - H_2 = \Delta E - \varepsilon R \cos(\omega t + \varphi). \tag{11}$$

It can be seen from this expression that multiple "intersection" of the terms occurs at $R \gtrsim R_\varepsilon \equiv \Delta E/\varepsilon$. We shall further assume that $\alpha R_\varepsilon \gg 1$.

The off-diagonal matrix element of the interaction has the form

$$H_{12} = R^{-1} A(R) \exp(-\alpha R). \tag{12}$$

For charge transfer by a negative ion $A \approx \text{const}$, while in the case of a positive ion $A \sim R^s$, where $s \approx 1/\alpha$.[10] At large distances H_{12} is exponentially small, and we can use perturbation theory to determine the transition amplitude a_2 and the probability $P_{12} = |a_2|^2$:

$$a_2 = \int_{-\infty}^{\infty} H_{12}(t) \exp\left[i \int^{t} (H_1 - H_2)\, dt' \right] dt. \tag{13}$$

In analyzing this expression we shall distinguish two limiting cases.

Case A. The field frequency is low, and the EMF does not change over the transition time Δt ($\omega \Delta t \ll 1$; the expression for Δt will be derived below). Then from (11) and (13), for a rectilinear trajectory, $\mathbf{R} = \mathbf{b} + \mathbf{v}t$ ($\mathbf{b}$ is the impact parameter), of the relative motion we have

$$a_2 = \int_{-\infty}^{\infty} H_{12}(t) \exp[i(\Delta E - \varepsilon_0 \mathbf{b})t - i\varepsilon_0 \mathbf{v} t^2/2]\, dt, \tag{14}$$

where $\varepsilon_0 = \varepsilon \cos\varphi_0$; φ_0 is the EMF phase at the moment when the transition occurs. The stationary-phase point in (14) is $t_0 = (\Delta E - \boldsymbol{\varepsilon}_0 \cdot \mathbf{b})/\boldsymbol{\varepsilon}_0 \cdot \mathbf{v}$, while the transition time $\Delta t \approx (\boldsymbol{\varepsilon} \cdot \mathbf{v})^{-1/2}$. If H_{12} changes little during this time, i.e., if $\alpha v/(\boldsymbol{\varepsilon} \cdot \mathbf{v})^{-1/2} \ll 1$, and the dimension of the nonadiabaticity region is small, i.e., $\Delta R/R_\varepsilon = v\Delta t/R_\varepsilon \ll 1$, then, computing the integral (14) by the method of steepest descent, we obtain for the charge-transfer cross section, the following formula:

$$\sigma = \pi R_{t_0}^2 \frac{2\pi |H_{12}(R_{t_0})|^2}{\alpha v \Delta E}. \tag{15}$$

As can be seen from the conditions of its applicability, the expression (15) is valid for sufficiently large values of the quantity $\boldsymbol{\varepsilon} \cdot \mathbf{v}$, a condition which is violated at small values of $\cos\vartheta$ (ϑ is the angle between $\boldsymbol{\varepsilon}$ and $\mathbf{v}$). However, this expression does not itself depend on ϑ, and, as will be shown below, is valid for any ϑ. Let us also note that the inequality $\alpha R_\varepsilon \ll \zeta$ follows from the conditions given above. Thus, although the index $(2\alpha R_\varepsilon)$ of the exponential function in (15) is large, it is much smaller than the Massey parameter, so that the application of a strong EMF does indeed lead to the increase of the charge-transfer cross section.

For a constant field ($\omega = 0$) we should set $\varphi_0 = 0$. If, on the other hand, the advance in phase of the EMF over the relaxation time of the process ($\tau_r^{-1} = N\langle v\sigma \rangle$, where N is the concentration of the particles to which charge is transferred and σ is the cross section for the process) is large (i.e., if $\omega \tau_r \gg 1$), then the expression (15) should be averaged over φ_0. Because of the large values of R_ε, the contribution is made by small values of φ_0, so that we have as a result the expression

$$\bar{\sigma} = \pi R_\varepsilon^2 \frac{2\pi^{1/2} |H_{12}(R_\varepsilon)|^2}{\alpha v \Delta E (\alpha R_\varepsilon)^{1/2}}. \tag{16}$$

Case B. The field frequency is high ($|\boldsymbol{\varepsilon} \cdot \mathbf{v}|/\omega^2 \ll 1$). Then from Eqs. (11) and (13) for the probability amplitude we obtain the expression

$$a_2 = \sum_n e^{in\varphi} \int_{-\infty}^{\infty} dt\, H_{12}(t) J_n\left(\frac{\varepsilon R}{\omega}\right) \exp[i(\Delta E - n\omega)t] = \sum_n e^{in\varphi} c_n, \tag{17}$$

where J_n is a Bessel function. As can be seen from (17), the coefficient c_n has the meaning of an amplitude for a transition involving the absorption of n light quanta. Owing to the randomness of the phase φ, the cross section for the process also has the form of a sum of multiphoton-transition cross sections, σ_n, for whose computation it is convenient to go over to the Fourier components, c_n, of the amplitudes:

$$c_n = \frac{1}{2\pi} \int f_n(\boldsymbol{\varkappa}) e^{-i\mathbf{b}\boldsymbol{\varkappa}} d\boldsymbol{\varkappa}, \quad f_n = \frac{1}{2\pi} \int H_{12}(R) J_n\left(\frac{\varepsilon R}{\omega}\right) e^{i\mathbf{q}\mathbf{R}} \frac{d\mathbf{R}}{v}, \tag{18}$$

$$\sigma_n = \int |c_n|^2 d\mathbf{b} = \int |f_n|^2 d\boldsymbol{\varkappa}, \tag{19}$$

the vector $\mathbf{q}$ coinciding with the vector $\boldsymbol{\varkappa}$ in the plane perpendicular to $\mathbf{v}$, and having a component along the direction of $\mathbf{v}$ equal to $(\Delta E - n\omega)/v$. The quantity f_n determines the inelastic-scattering amplitude in the Born approximation in the presence of an EMF.

As can be seen from (18), charge transfer occurs at large distances when $n \gg 1$. In this case $R \sim R_\varepsilon$ (in a strong EMF), or $R \sim n/\alpha$ (in a weak EMF), in the integration domain determining the quantity f_n; the corresponding criterion will be formulated below. Indeed, let us, for the purpose of the integration, choose the z axis along the vector $\boldsymbol{\varepsilon}$, denote the components of the vector $\mathbf{q}$ along, and perpendicular to, $\boldsymbol{\varepsilon}$ by $q_\parallel$ and $q_\perp$ respectively, and direct the x axis along $\mathbf{q}_\perp$. We perform the integration in the (x, y) plane with allowance for the condition that $\alpha |z| \gg 1$. The largest contribution to the integral is made by the region of small y and $x \approx i|z| q_\perp/(\alpha^2 + q_\perp^2)^{1/2}$, i.e., by the region where $R = |z| \alpha/(\alpha^2 + q_\perp^2)^{1/2}$. Carrying out direct computations, we obtain

$$f_n = \frac{2}{v(\alpha^2 + q_\perp^2)^{1/2}} \int_0^{\infty} A\left(\frac{\alpha z}{(\alpha^2 + q_\perp^2)^{1/2}}\right) J_n\left(\frac{\varepsilon z}{\omega}\right) \times \exp\left(-\frac{\varepsilon z}{\omega} \operatorname{sh} \xi\right) dz, \tag{20}$$

where $\sinh\xi = \omega((\alpha^2+q_\perp^2)^{1/2} - iq_\parallel)/\varepsilon$, it being necessary to take the real part of the integral when n is even and the imaginary part when n is odd. For $n \gg 1$, the integral in (20) can be evaluated by the method of steepest descent. Replacing the Bessel function by the asymptotic expression[11]

$$J_n(x) \approx [2\pi n(1-(x/n)^2)^{1/2}]^{-1/2} \exp\{n[1-(x/n)^2]^{1/2} - n \operatorname{Arch}(n/x)\}, \tag{21}$$

we find that the saddle point is located at $z_0 = n\omega/\varepsilon\cosh\xi$, while the integration range $\Delta z/z = (\tanh\xi/n)^{1/2} \ll 1$. Then from (20) we obtain

$$f_n \approx \frac{2\omega}{\varepsilon v(\alpha^2+q_\perp^2)^{1/2}} A\left(\frac{\alpha z_0}{(\alpha^2+q_\perp^2)^{1/2}}\right)\frac{\exp(-n\xi)}{\operatorname{ch}\xi}, \tag{22}$$

where again the real or imaginary part is taken, depending on the parity of n.

To compute σ_n, we go over to new integration variables ξ' and ξ'' defined by the relation $\xi = \xi' - i\xi''$, and discard the rapidly oscillating terms (i.e., the term proportional to $\cos 2n\xi''$ and $\sin 2n\xi''$). We then obtain for the cross section an expression that is the same for any n:

$$\sigma_n = \frac{2\omega^2}{\varepsilon^2 v^2}\iint \frac{|A(pz_0/\operatorname{sh}\xi'\cos\xi'')|^2 \exp(-2n\xi')\,d\xi'\,d\xi''}{\operatorname{sh}\xi'|\cos\xi''|[(a_1-\sin\xi'')(\sin\xi''-a_2)(\operatorname{sh}^2\xi'+\cos^2\vartheta)]^{1/2}} \tag{23}$$

where $a_{1,2}$ are the roots of the equation

$$(\operatorname{sh}^2\xi'+\cos^2\vartheta)a^2 - 2p_n \operatorname{ch}\xi'\cos\vartheta a + p_n^2 + p^2\sin^2\vartheta - \operatorname{sh}^2\xi'\sin^2\vartheta = 0, \tag{24}$$

and $p = \alpha\omega/\varepsilon$, $p_n = \zeta_n p$, $\zeta_n = (\Delta E - n\omega)/\alpha v$. The integration in (23) over ξ'' is performed for $a_1 > \sin\xi'' > a_2$, while the integration over ξ' is carried out for $\xi' > \xi_0$, where

$$2\operatorname{sh}^2\xi_0 = p^2 + p_n^2 - \cos^2\vartheta + [(p^2+p_n^2-\cos^2\vartheta)^2 + 4p^2\cos^2\vartheta]^{1/2}. \tag{25}$$

Notice that $2n\xi_0 \gg 1$. Setting everywhere in (23), except in the exponent, $\xi' = \xi_0$, as a result of which $a_1 \to a_2 \to a_0 = p_n\cosh\xi_0\cos\vartheta/(\sinh^2\xi_0 + \cos^2\vartheta)$, we obtain

$$\sigma_n \approx \frac{2\pi\omega^2}{n\varepsilon^2 v^2}|A(R^*)|^2 \frac{\exp(-2n\xi_0)}{\operatorname{sh}\xi_0(1-a_0^2)(\operatorname{sh}^2\xi_0+\cos^2\vartheta)^{1/2}}, \tag{26}$$

where $R^* = n\omega p/\varepsilon \sinh\xi_0[(\cosh^2\xi_0 - a_0^2)(1-a_0^2)]^{1/2}$. The formula (26) describes the line shape for n-photon absorption in an electron transition from one atom to another. In particular, for $\cos\vartheta = 0$.

$$\sigma_n = \frac{2\pi A^2(R^*)\exp[-2n \operatorname{Arsh}(p(1+\zeta_n^2)^{1/2})]}{n(\alpha v)^2(1+\zeta_n^2)}. \tag{27}$$

The expression (27) gives the cross section for charge transfer in intersecting atomic beams if the light beam is directed along the relative velocity. Notice also that, for $\cos\vartheta = 0$, the formula (27) is valid for all frequencies, including the case when $\omega \to 0$. In this case many σ_n terms for $n \sim \Delta E/\omega$ make a contribution to the total cross section. By replacing the sum by an integral, we can obtain the expression (16), which is thus valid for all angles between ε and v.

As can be seen from (27), the cross section decreases rapidly with increasing detuning. The width of the n-photon resonance is of the order of $v(\alpha/R_0)^{1/2}$, while at a sufficiently exact resonance, i.e., for $|\zeta_n| \ll 1$, we have from (26) (after averaging over ϑ) the expression

$$\sigma_n = \frac{2\pi A^2(R_0)}{n\alpha^2 v^2} p \operatorname{Arsh}\left(\frac{1}{p}\right)\exp(-2n \operatorname{Arsh} p), \tag{28}$$

where $R_0 = R_\varepsilon/(1+p^2)^{1/2}$. Thus, the EMF in the charge-transfer process can be considered to be strong when $p \lesssim 1$. Then the location, $R_0 \approx R_\varepsilon$, of the transition region is determined by the field intensity. In the other case, when $p \gg 1$, the value of R_0 is determined by the quantum nature of the process, and is estimated by the relation $R_0 \approx n/\alpha$.

TABLE I. Charge-transfer cross sections σ_n (in Å^2) in an electromagnetic field.

Process No.	Colliding partners	n	ε, V/cm			
			$2{,}5\cdot10^6$	$5\cdot10^6$	$1\cdot10^7$	$2\cdot10^7$
I	O$^-$+H	6	$3\cdot10^{-3}$	3,8	264 *	
II	K$^+$+Na	7	$1\cdot10^{-3}$	8,5	81 *	
III	K$^+$+Li	9	$4\cdot10^{-7}$	$4\cdot10^{-2}$	135 *	
IV	Cs$^+$+Na	11	$9\cdot10^{-11}$	$2\cdot10^{-4}$	31	95 *
V	Cs$^+$+Li	13	$2\cdot10^{-14}$	$5\cdot10^{-7}$	1	132 *

Footnote. The asterisks indicate the values of σ_m.

In Table I we present the computed charge-transfer cross sections for certain systems in a CO_2-laser field. For the process I, $A \approx 0.28$; for the processes II – V, $A \approx 0.07R^{3,4}$. It can be seen that the cross section at first increases very sharply with increasing ε, and attains the value $\sigma_m = \pi R_0^2$. The quantity σ_m gives the order of magnitude of the greatest possible cross section for the process. As ε increases further, the cross section varies very slowly. This can be verified by computing P_{12} for very large impact parameters (i.e., for $b\varepsilon/\omega > 1$).

[1)] Atomic units with $\hbar = 1$ are used everywhere, except where it is otherwise indicated specifically.

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Translated by A. K. Agyei

Self-induced transparency in two-photon resonance on an inhomogeneously broadened line

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(Submitted 2 January 1979)
Zh. Eksp. Teor. Fiz. 76, 1977–1985 (June 1979)

Results are presented of an experimental and theoretical investigation of the interaction of ultrashort laser pulses with an inhomogeneously broadened two-photon resonance transition. The experiments were performed on neodymium glass. At low temperature the interaction is coherent, as manifest by a partial bleaching of the sample and by a decrease of the pulse propagation velocity; in some cases the pulse broke up into two subpulses on leaving the sample. With rising temperature, these phenomena disappeared. The results of a numerical analysis have shown that the evolution of the laser pulse as it propagates in the sample depends substantially on the Stark shift of the levels and on the width of the resonance line. The experimental results agree qualitatively with the calculations.

PACS numbers: 42.65.Gv, 42.70.Ce

1. INTRODUCTION

Processes of coherent interaction of radiation with matter, such as optical nutation, photon echo, and self-induced transparency, have been intensively investigated in the last few years (see, e.g., Ref. 1). For the interaction to be coherent it is necessary that the duration of the radiation pulse τ_p be shorter than the time or irreversible relaxation of the polarization T_2' of the medium. These processes were customarily investigated under conditions of single-photon resonance. However, the development of two-photon resonance spectroscopy[2] raises the natural question of how the coherent interaction is changed under these conditions.

If the interaction is coherent, then when a pulse passes through a resonant medium self-induced transparency (SIT) sets in. This phenomenon was first predicted and experimentally investigated for one-photon resonance by McCall and Hahn.[3] The possibility of observing such an effect in two-photon resonance is not self-evident. Nonetheless, if the scatter of the levels of the resonant atoms can be neglected (i.e., if the time T_2^* of reversible relaxation of the polarization is infinitely long), and if the doubled frequency of the radiation field coincides exactly with the frequency of the resonant atoms, then the effect of self-induced transparency in two-photon absorption (TPSIT) is possible, as was theoretically shown by Belenev and Poluéktov.[4] It turned out that the additional nonlinearity introduced by the two-photon interaction leads to new consequences, such as narrowing and peak enhancement of high-energy pulses.[5,6]

In a real experimental situation one encounters more frequently a line with inhomogeneous broadening. In contrast to homogeneous broadening, this situation has been investigated in less detail. The particular case when the homogeneous broadenings are equal ($T_2' = T_2^* < \infty$) was considered theoretically.[7] Under these conditions the coherent interaction can take place only when the spectral line width is less than the spectrum of the pulse (narrow line).

TPSIT was experimentally observed in media in which the excited levels were inhomogeneously broadened: in semiconductors (on interband transitions)[7,8] and in potassium vapor (the resonance was produced here by a sum of two photons of unequal energy).[9]

Anomalously weak absorption of the pulse energy and a decrease in its propagation velocity were reported in Refs. 7 and 8. The impossibility of resolving the pulse time structure prevented the authors of these papers from investigating this phenomenon fully.

In the present paper we present the results of an experimental and theoretical investigation of TPSIT on an inhomogeneously broadened line. We investigated experimentally a sample of neodymium glass, where it is easy to realize the case of a broad line, i.e., to satisfy the condition $T_2^* < \tau_p$. Allowance for the inhomogeneous broadening greatly complicates the theoretical analysis. In this case there are no analytic solutions and computer calculations are necessary, but we did not perform them. The influence of inhomogeneous broadening manifests itself noticably in the case of a broad line. Under these conditions, owing to the high-frequency Stark effect, the excited atoms are those whose frequency scatter exceeds the spectrum of the pulse. The damping of the induced polarization by the dephasing of the atomic radiators is accelerated, thereby significantly influencing the evolution of the pulse.

 0038-5646/79/061002-05$02.40 © 1979 American Institute of Physics