Dissociative recombination of electrons and molecular ions in monochromatic IR light

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The interaction of slow electrons with XY^+ molecular ions in monochromatic IR laser light is studied. At the field levels considered here, the mechanism by which the field acts on the $e^- + XY^+$ system is manifested in the stage in which an intermediate Rydberg complex XY^{**} forms. This mechanism is basically a change in the characteristics of spontaneous decay and the formation of compound resonances in the field-induced interaction of closely spaced quasistationary states of the complex. The cross sections for dissociative recombination are studied as a function of the angle θ between the direction of the electron beam and the field vector of the light (for linearly polarized light). The relationship between these characteristics of the process and the type of molecular orbital of the Rydberg states in XY^{**} is found. Various physical situations which arise when resonances of the Rydberg complex accidentally overlap are analyzed. The particular system $e^- + H_2^+$ is used as an example to study how the field-induced mixing of p, d, and f states affects the reaction rate. Criteria for predicting a significant acceleration of the dissociative recombination are formulated.

1. INTRODUCTION

Research on the dissociative recombination

$$e^- + XY^+ \rightarrow X + Y \tag{1}$$

of electrons e^- and molecular ions XY^+ in an external electromagnetic field is important to the theory of radiative collisions and also in connection with the development of laser methods for stimulating elementary processes involving atoms and molecules. There is particular interest in the case of monochromatic IR light under limitations on the frequency ω_f and amplitude f of the external field such that this field affects the $e^- + XY^+$ system only in the stage in which intermediate Rydberg complexes XY^{**} form (such complexes are known[1] to play an important role in the dynamics of dissociative recombination). A necessary condition here is that the laser radiation not cause any resonant intramolecular transitions in the isolated XY^+ ion. The next limitation is the inequality ($\hbar = m_e = e = 1$)

$$f\omega_f^{-5/3} \ll 1, \tag{2}$$

which means that transitions between continuum states in the Coulomb potential (in which the corresponding transition dipole moment satisfies[2] $D \propto \omega_f^{-5/3}$) are improbable. Under these conditions, the field-induced broadening of the Rydberg levels, $\Gamma_q^f \propto (f\omega_f^{-5/3})^2/n_q^3$ (n_q is the main quantum number of the q series of Rydberg resonances; the index q incorporates the angular momentum l of the electron; its projection Λ onto the molecular axis; and the internal state of the ion), is a measure of the effect on the XY^{**} complex. This broadening must be compared with the natural half-width $\Gamma_q^e \propto \gamma/n_q^3$, where the decay rate satisfies $\gamma \ll 1$ according to the concept of an intermediate complex. Consequently, one of the conditions for the field to strongly affect the intermediate complex takes the form

$$\gamma \lesssim (f\omega_f^{-5/3})^2 \ll 1. \tag{3}$$

The field can also affect the XY^{**} complex even at much lower field amplitudes f, if resonances of different Rydberg series (e.g., n_q and $n'_{q'}$) overlap or are accidentally close together. In this case, the field-induced interaction of resonance states [$V^f_{n_q n'_{q'}} \propto f\omega_f^{-5/3}(n_q n'_{q'})^{-3/2}$ for a dipole-allowed transition] must be compared with either the half-width of these states or with the distance between levels $\Delta_{n_q n'_{q'}} = |E_{nq} - E_{n'q'}|$:

$$V^f_{n_q n'_{q'}} \propto \begin{cases} \Gamma^e_{n_q}, \Gamma^e_{n'_{q'}}, & \Gamma \gtrsim \Delta, \\ \Delta_{n_q n'_{q'}}, & \Delta \gtrsim \Gamma. \end{cases} \tag{4}$$

Although the basic mechanisms for the effect of monochromatic laser radiation on the intermediate spontaneous-decay complexes described above are well known, and general mathematical approaches have been developed for describing them (see, for example, Refs. 3–9), many aspects of the theory for processes which go in accordance with the continuum-complex-continuum scheme have yet to be resolved. From the general theoretical standpoint, this problem is quite different from the problems which are being solved in the theory of the interaction of laser radiation with atoms and molecules. There is also a distinction from the problems treated in the standard theory of radiative collisions,[10,11] in which the most successful approach is the semiclassical approximation. This approximation has proved successful in research on the collisions of atoms in a radiation field. It is more difficult to analyze the quantum conditions of the relative motion of particles in the conventional theory of radiative collisions, particularly for reactions with reactive channels, in which case there is a restructuring of particles [in particular, reaction (1) falls in this category]. It is apparently for this reason that electron-ion radiative collisions involving Rydberg states

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have become the subject of an independent field of research, which has begun to develop systematically only in the past few years.

The behavior of Rydberg atoms in a laser radiation field was studied in Refs. 12–15. Rydberg molecular complexes XY** and processes involving them were studied in Refs. 16 and 17, where attention was focused on the resonant ($\omega_f \approx \omega$) situation, in which the field is tuned to the frequency ω of vibrational transitions in XY**.

In the present paper we are interested in the dynamics of the dissociative-recombination reaction (1) in the field of linearly polarized IR radiation under nonresonant conditions, $\omega_f \neq \omega$. We examine in detail the dependence of the cross section for reaction (1) on the relative orientation of the electron and laser beams (Sec. 3). We also analyze situations which arise when resonances of different Rydberg series accidentally overlap. We study (in Sec. 5) the corresponding manifestations in the cross sections and corresponding reaction rate constants, averaged over the electron energy. The results are illustrated in the particular case of the $e^- + \mathrm{H}_2^+$ system.

In Sec. 2, before we get into the basic material of this study, we write operator equations for the matrix of radiative multichannel scattering, which we derived in some earlier papers. The novel aspect of this section of the paper is the derivation of Eq. (19), which relates the scattering **T**-matrix to the submatrices of open and closed channels. This equation makes the subsequent analysis more compact and physically clearer. Equation (19) is a generalization of Seaton's matrix equations[18] for the **S**- and **R**-matrices. Those equations were derived without consideration of reactive channels or the effect of resonances which do not conform to the systematics of Rydberg levels.

2. MATRIX OF RADIATIVE MULTICHANNEL SCATTERING

If we describe the interaction of the $e^- + \mathrm{XY}^+$ system with the external field by a dependence which is periodic in the time,

$$\mathbf{u}_f = 2\mathbf{V}^f \cos \omega_f t, \quad \mathbf{V}^f = \frac{\mathbf{Df}}{2} \tag{5}$$

(**D** is the dipole moment operator), the analysis can be conducted in the steady-state theory of the multichannel quantum defect, in which the field is taken into account by introducing quasienergy states and some new channels of motion associated with these states.[15–17] The entire analysis is based on information on adiabatic terms of the Rydberg complex XY**, which are assumed known. The most important aspects of this picture of the terms are shown in Fig. 1. Among them are the Rydberg terms $U^{**}(R)$, the dissociation terms $U_\beta(R) = U_{\mathrm{X+Y}}(R)$, and also the terms $U_{\widetilde{\mathrm{XY}}}(R)$, which represent the $\widetilde{\mathrm{XY}}$ valence configuration which is interacting with them. The latter configuration is characterized by a quasifinite motion of nuclei (R is the interatomic distance). Note that the number of electronic configurations taken into account in this system can also be large. After we have presented the general calculation method, it will become clear that the incorporation of these configurations in the theory poses no major difficulty.

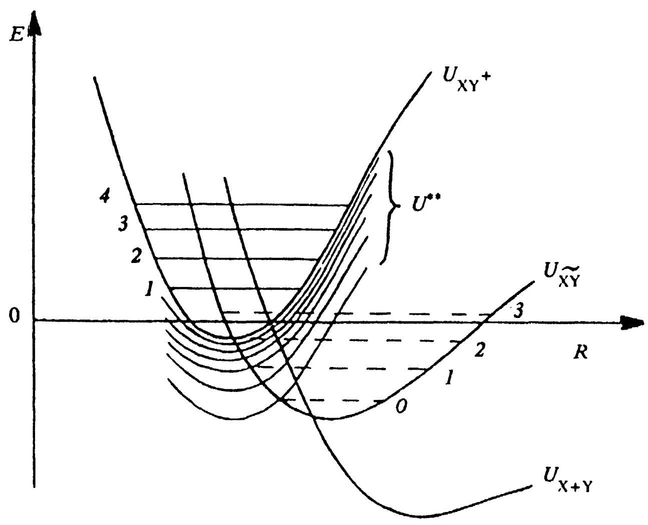

FIG. 1. Schematic diagram of the terms of the XY molecule which lie near the ion term (the numbers and lines specify the vibrational levels of the ion and valence potentials).

The electron terms shown in Fig. 1 are, strictly speaking diabatic, since they are written without consideration of the configurational interaction $\mathbf{V}^{ci}$, which causes term splitting in local regions of a quasicrossing of terms, and which is also assumed known.

In outlining the theory of the multichannel quantum defect, we restrict the discussion to the case in which the angular momentum l of the electron is a "good" quantum number. We will also be focusing on the spectral region which is adiabatic with respect to rotation, $Bn^3 \ll 1$ (B is the rotational constant of the ion), for which the molecular axis is assumed to remain fixed in the course of the collision, and the analysis is conducted in the coordinate system of the XY molecule. The null Hamiltonian $\mathbf{H}_0$ is chosen in such a way that all the interactions in the isolated (diabatic) configurations X+Y and $\widetilde{\mathrm{XY}}$ are taken into account exactly, while in the Rydberg states the Coulomb potential $V_c = -1/r$ (r is the coordinate of the weakly bound electron) and the non-Coulomb part of the interaction with the ion core, $\mathbf{V}_{nc}(R_e^+)$, are taken into account for the equilibrium position of the R_e^+ atoms. In the complete Hamiltonian of the system, $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$, the operator1)

$$\mathbf{V} = \mathbf{V}_{nc}(\mathbf{R}) - \mathbf{V}_{nc}(R_e^+) + \mathbf{V}^{ci} + \mathbf{V}^f$$

then includes the interaction with the core, the configurational interaction $\mathbf{V}^{ci}$ (which couples the configurations $e^- + \mathrm{XY}^+$, X+Y, and $\widetilde{\mathrm{XY}}$, which we denote by the indices q, β, and s, respectively), and the interaction with the external field $\mathbf{V}^f$. We also require that the basis wave functions $|q_m\rangle$, $|\beta_m\rangle$, and $|s_m\rangle$ (the index m specifies the change in the number of photons in the system) be normalized in accordance with

$$\langle q_m(E)\,|\,q_{m'}(E')\rangle = \langle \beta_m(E)\,|\,\beta_{m'}(E')\rangle$$

$$= \pi\delta(E-E')\delta_{mm'},$$

$$\langle S_m\,|\,S'_{m'}\rangle = \delta_{ss'}\delta_{mm'}.$$

A distinctive feature of the wave functions $|q_m\rangle$ is that at values of r on the order of atomic distances ($r\sim 1$) these functions describe a fast electron and a slow nuclear subsystem; i.e., they are adiabatic. Consequently, $|q_m\rangle$, $|\beta_m\rangle$, and $|s_m\rangle$ can be calculated in the Born–Oppenheimer approximation by the standard methods of quantum chemistry.

For a given choice of $\mathbf{H}_0$, the basis functions of the Rydberg configuration $e^- + \mathrm{XY}^+$ can be written

$$|q_m\rangle = \pi^{1/2}\phi_{\nu_{vm},l}(r)\chi_v(R)Y_{l\Lambda}(\hat{r})\,|m\rangle, \tag{6}$$

where $\chi_v(R)$ is the vibrational wave function of the XY^+ ion (v is the vibrational quantum number), $Y_{l\Lambda}(\hat{r})$ is the spherical harmonic ($\hat{r}$ is the set of spherical coordinates of the electron), and $|m\rangle$ is the phonon part of wave function (6). The function $\phi_{\nu_{vm},l}$ is the radial wave function of an electron with an angular momentum l, distorted at short range by the interaction $\mathbf{V}_{nc}(R_e^+)$. This wave function is regular at the origin (as $r\to 0$). Under the conditions $(l+1/2)^2 \ll r \ll |E|^{-1}$, this wave function takes the form

$$\phi_{\nu_{vm},l} \approx \left(\frac{2}{\pi^2 r^3}\right)^{1/4} \sin\left(\sigma_l(r) - \pi l - \frac{\pi}{4} + \pi\mu_{l\Lambda}^0\right),$$

where $\sigma_l(r)$ is a semiclassical phase shift. Under the condition $l \ll |\varepsilon_{vm}|^{-1/3}$, and in first order in the small parameter $r|\varepsilon_{vm}|$, this shift is given by $\sigma_l = (8r)^{1/2} + \frac{1}{3}(2r^3)^{1/2}|\varepsilon_{vm}|$. In addition, $\mu_{l\Lambda}^0 = \mu_{l\Lambda}(R_e^+)$ is the diabatic quantum defect of the $l\Lambda$ Rydberg level, determined at $V^{ci} = V^f = 0$, and $\nu_{vm} = (-2\varepsilon_{vm})^{-1/2}$ is the effective principal quantum number, which corresponds to an energy $\varepsilon_{vm} = E - v\omega_v - m\omega_f$. By analogy with (6), we also define the wave functions $|\beta_m\rangle$ and $|s_m\rangle$ of the valence (non-Rydberg) configurations of $\mathrm{X+Y}$ and $\widetilde{\mathrm{XY}}$.

Multichannel quantum defect theory leads to the following fundamental equation for the T-matrix of radiative multichannel scattering (Refs. 16 and 17, for example):

$$\mathbf{T} = \mathbf{t} + \mathbf{t}\sum_{q,m} |q_m\rangle\langle q_m|\,\mathrm{ctg}[\pi(\nu_{vm} + \mu_{l\Lambda}^0)]\mathbf{T} - i\mathbf{t}\sum_{\beta,m}|\beta_m\rangle$$

$$\times \langle\beta_m|\mathbf{T} + \mathbf{t}\sum_{s,m}\frac{|s_m\rangle\langle s_m|}{E - E_{sm}}\mathbf{T}. \tag{7}$$

Here $E_{sm} = E_s + m\omega_f$ are the energy eigenvalues of an isolated $\widetilde{\mathrm{XY}}$ valence configuration in the quasienergy state representation, and the index q is $q = \{l\Lambda, v\}$. The operator $\mathbf{T}$ describes the interaction of the electron with the ion core in the presence of an electromagnetic field and obeys the equation

$$\mathbf{t} = \mathbf{V} + \mathbf{V}\mathbf{G}\mathbf{t}, \tag{8}$$

where the Green's operator $\mathbf{G}$ is a smooth function of the energy E and is represented by the contributions of the $e^- + \mathrm{XY}^+$ Rydberg states (minus the hole singularities which arise from the discrete level structure of the Coulomb center) and the $\mathrm{X+Y}$ dissociation:

$$\mathbf{G} = \frac{1}{\pi}\sum_{q,m} P\int \frac{|q_m\rangle\langle q_m|}{\varepsilon_{vm} - \varepsilon}\,d\varepsilon$$

$$+ \frac{1}{\pi}\sum_{\beta,m} P\int \frac{|\beta_m\langle\beta_m|}{E - m\omega_f - \varepsilon_\beta}\,d\varepsilon_\beta \tag{9}$$

(P means the principal value of the integral), without consideration of the $\mathbf{V}$ interaction. In writing the contributions from the $e^- + \mathrm{XY}^+$ states we used the similarity factor of the wave functions of the continuous and discrete spectra at $|E| \ll 1$.

The operator $\mathbf{V}$ consist of two parts: an electrostatic interaction $\mathbf{V}^e$ and an electromagnetic interaction $\mathbf{V}^f$. The matrix elements of the operator $\mathbf{V}^e$ are diagonal in m. The quantities

$$\langle q_m|\mathbf{V}^e|\beta_m\rangle,\quad \langle q_m|\mathbf{V}^e|s_m\rangle,\quad \langle\beta_m|\mathbf{V}^e|s_m\rangle \tag{10}$$

describe the configuration interaction of the $e^- + \mathrm{XY}^+$ and $\mathrm{X+Y}$, $e^- + \mathrm{XY}^+$ and $\widetilde{\mathrm{XY}}$, and $\mathrm{X+Y}$ and $\widetilde{\mathrm{XY}}$ states, respectively. The matrix elements $\langle q_m|\mathbf{V}^e|q'_m\rangle$ are responsible for vibron transitions in the $e^- + \mathrm{XY}^+$ system. The elements of the operator $\mathbf{V}^f$ couple the states with m and $m' = m \pm 1$. Under conditions (2)–(4), which we are assuming here, these elements should be regarded as small on the scale of the changes in Green's function (9).

Equation (7) has a structure which makes it possible to use an algebraic method to construct the unitary scattering S-matrix without regard to the number of channels of motion taken into account. The elements $T_{q_m q'_{m'}}$ and $T_{q_m \beta_{m'}}$ with open-channel indices {where $E > v\omega_v + m\omega_f$ and $\cot[\pi(\nu_{vm} + \mu_{l\Lambda}^0)] = -i$} characterize the amplitudes for inelastic scattering and for dissociative recombination (1). Since the configurational coupling is small, and since we have the small parameter $a_0/R_e^+ \ll 1$ (α_0 is the amplitude of the zero-point vibrations), we can restrict (7) to a finite number of states. That the configurational coupling is small is not as obvious, since the configurational interaction is determined by the particular features of the electronic structure of the molecules. However, the examples of the (well-studied) systems $e^- + \mathrm{XY}^+$ ($\mathrm{XY}^+ = \mathrm{H}_2^+$, N_2^+, NO^+, 0_2^+, etc.) show that this interaction is indeed small [in the sense that the quantities written in (10) are small in comparison with unity]. As a result, in determining the matrix elements of the operator $\mathbf{t}$ we use an iterative procedure, in which $\mathbf{t}$ on the right side of (8) is replaced by $\mathbf{V}$. After some straightforward manipulations we find

$$\mathbf{t} = \mathbf{t}^e + \mathbf{t}^f, \tag{11}$$

where the elements are given by

$$t^e_{q_m q'_m}=t^{(0)}_{q_m q'_m}+\frac{1}{\pi}\sum_\beta P\int\frac{V^e_{q_m\beta_m}V^e_{\beta_m q'_m}}{E-m\omega_f-\varepsilon_\beta}d\varepsilon_\beta,$$

$$t^e_{q_m\beta_m}=V^e_{q_m\beta_m}+\frac{1}{\pi}\sum_{q'} P\int\frac{t^{(0)}_{q_m q'_m}V^e_{q'_m\beta_m}}{\varepsilon_{vm}-\varepsilon}d\varepsilon,$$

$$t^{(0)}_{q_m q'_{m'}}=-\langle\chi_v|\mathrm{tg}[\pi(\mu_{l\Lambda}-\mu^0_{l\Lambda})]\,|\chi_{v'}\rangle\delta_{mm'} \tag{12}$$

(there are corresponding expressions for the elements $t^e_{\beta_m s_m}$, $t^e_{q_m s_m}$, and $t^e_{\beta_m\beta_m}$) and the second term in (11), which is responsible for the effective interaction with the external field, can be written as follows, to within terms quadratic in $\mathbf{V}^f$:

$$\mathbf{t}^f=[1+\mathbf{V}^e\mathbf{G}(E)][\mathbf{V}^f+\mathbf{V}^f\mathbf{G}(E)\mathbf{V}^f][1+\mathbf{G}(E)\mathbf{V}^e]. \tag{13}$$

Under condition (2) it is sufficient to use the linear approximation for the matrix elements of operator (13):

$$t^f_{q_m q'_{m\pm1}}=\tfrac{1}{2}fr(l'\Lambda'\to l\Lambda)S^{l'\Lambda',l\Lambda}\delta_{vv'}, \tag{14}$$

where the radial elements are[19]

$$r(l'\Lambda'\to l\Lambda)$$
$$=\frac{\sqrt{2}}{\pi^2}\Gamma\left(\frac{2}{3}\right)\left(\frac{4}{3}\right)^{1/3}\omega_f^{-5/3}$$
$$\times\cos\left[\pi\left(\Delta\mu_{l\Lambda,l'\Lambda'}+\frac{1}{6}\right)\right] \tag{15}$$

[$\Gamma(x)$ is the gamma function, and $\Delta\mu_{l\Lambda,l\Lambda}=\mu^0_{l\Lambda}-\mu^0_{l'\Lambda'}$ is the difference between the corresponding quantum defects]. The angular elements are given by[3)]

$$S^{l'\Lambda',l\Lambda}=\frac{4\pi}{3}\sum_k Y^*_{1k}\left(\frac{\mathbf{f}}{f}\right)\langle Y_{l\Lambda}Y_{1k}|Y_{l'\Lambda'}\rangle$$
$$=\sqrt{\frac{4\pi(2l+1)}{3(2l'+1)}}(l100|l0)(l1\Lambda\Lambda'$$
$$-\Lambda|l'\Lambda')Y^*_{1\Lambda'-\Lambda}\left(\frac{\mathbf{f}}{f}\right). \tag{16}$$

We now wish to discuss some general properties of Eq. (7). The matrix **T** can be determined directly from this equation. Its rank is equal to the sum (N) of the number of physically open channels of motion (N_o), the number of closed Rydberg channels (N^R_c), and the number of states of the $\mathcal{XY}$ valence configuration taken into account (N^V_c):

$$N=N_o+N^R_c+N^V_c.$$

Here N_0 includes the continuum states of the $e^-+\mathrm{XY}^+$ system and dissociative channels of X+Y.

Below we show that the solution of the operator equation (7) can also be written formally as a general relation in which the matrix of interest, $\mathbf{T}_{oo}$, is expressed in terms of the submatrices $\mathbf{T}'_{oo}$ (of rank $N_o\times N_o$), $\mathbf{T}'_{cc}$ ($N_c\times N_c$), and the submatrices $\mathbf{T}'_{oc}$, $\mathbf{T}'_{co}$ ($N_o\times N_c$). Each of these submatrices can be found from a simpler operator equation (of the Heitler type[21]) defined on the basis of physically open channels, i.e.,

$$\mathbf{T}'=\mathbf{t}-i\mathbf{t}\sum_{p=1}^{N_o}|p\rangle\langle p|\mathbf{T}' \tag{17}$$

(the index p represents open channels). Using (17), we can put the operator equation (7) in the form

$$\mathbf{T}=\mathbf{T}'+\mathbf{T}'\sum_{c=1}^{N_c}|c\rangle\langle c|\frac{1}{\mathbf{E}}\mathbf{T}'. \tag{18}$$

Here the diagonal matrix **E** specifies the spectrum of energy eigenvalues in the closed Rydberg channels and the discrete levels of the isolated $\mathcal{XY}$ configuration, $\mathbf{E}_{cc}=\tan[\pi(\nu_c+\mu^0)]$ for Rydberg channels (with energy normalization of the wave functions) and $\mathbf{E}_{cc}=\mathbf{E}-\mathbf{E}_c$ (with the wave functions $|c\rangle$ normalized to unity; i.e., $\langle c|c'\rangle=\delta_{cc'}$). Constructing a chain of equations for $\mathbf{T}'_{oo}$, $\mathbf{T}'_{co}$, and $\mathbf{T}'_{cc}$, we find

$$\mathbf{T}_{oo}=\mathbf{T}'_{oo}+\mathbf{T}'_{oc}\frac{1}{\mathbf{E}-\mathbf{T}'_{cc}}\mathbf{T}'_{co}, \tag{19}$$

where

$$\mathbf{T}'_{cc}=\mathbf{t}_{cc}-i\mathbf{t}_{co}\mathbf{T}'_{oc}.$$

Relation (19), like the Seaton relation[18] for the multichannel scattering **S**-matrix in the absence of a field (when there is an attractive Coulomb field in all channels of motion), is written for physically observable characteristics. It brings out the resonant structure of the transition in a more graphic way: The zeros of the determinant

$$\det|\mathbf{E}-\mathbf{t}_{cc}+i\mathbf{t}_{co}\mathbf{T}'_{oc}|=0$$

characterize the positions of the levels which are interacting with the continua of discrete states. In the case of an isolated resonance ($N^R_c=0, N^V_c=1$) we find from (19) the general Breit–Wigner formula (here we have a direct method for determining the phase relations between the contributions of the background and resonant mechanisms). In addition, the equation derived here is more general, since its derivation incorporated the reactive channels and the interacting quasistationary states of a closed channel of an arbitrary type. This relation also makes it possible to describe such processes when there is an external field which is periodic in the time.[4)]

Qualitatively, the consequences of the application of the laser radiation to the $e^-+\mathrm{XY}^+$ system can be understood even on the basis of (19). The consequences evidently stem from the resonant contribution of the second term, namely, 1) the change in the spontaneous-decay characteristics of those resonances which are also important in the absence of a field (the terms with $m=0$), 2) the appearance in induced resonances {in spectral intervals in which the condition $\tan[\pi(\nu_{vm}+\mu^0)]=0$ holds for $m\neq0$}, and 3) the superposition of resonances of different Rydberg series and the manifestation of their field-induced mixing (hybrid states).

3. CROSS SECTION FOR DISSOCIATIVE RECOMBINATION IN THE FIELD OF LINEARLY POLARIZED IR RADIATION

Dissociative recombination (1), i.e., the production of neutral fragments in the interaction of an electron with a molecular ion, occurs either because of a direct transition to the dissociation continuum β or through the production of an intermediate complex XY** and its subsequent decay to a dissociation state. The amplitudes corresponding to these transitions interfere with each other, making the cross section for dissociative recombination a rather complicated function of the energy E. If the molecular ion XY^+ is in the vibrational ground state ($v=0$), the closest closed channel, $v=1$, plays the most important role in shaping the resonant structure of the spectrum at energies below the threshold for the vibrational excitation of the vibrational ground state. The states of this channel give rise to an infinite set of Fano-Feshbach resonances:

$$\sigma(E)=\sigma_0(E)\,\frac{(x+q)^2}{1+x^2},\quad x=\frac{E-E_n^{(r)}}{\Gamma_n}$$

(near the nth resonance $E_n^{(r)}$). Here Γ_n is the half-width of this resonance, and q is a profile index. [Corresponding expressions for $\sigma_0(E)$, Γ_n, and q can be found from those written below when the external field is turned off, i.e., in the case $f=0$.] In the series of resonances we find an obvious pattern: The same factor n^3 characterizes the decrease in the half-widths Γ_n, in the intensities $I_n=\pi q^2\sigma_0(E_n^{(r)})\Gamma_n$, and in the distances between resonances with increasing index (n) of the level of the closed channel. This regularity can be disrupted only by resonances of other Rydberg series (with $v>1$) or quasidiscrete states of valence (non-Rydberg) configurations of XY. Below we examine effects stemming from the influence of the external field on the e^-+XY^+ system, so we restrict the discussion to the part of the spectrum in which these disruptions are negligible.

We would first like to determine which conditions are most favorable for laser stimulation of reaction (1) when the stimulation is applied to states of isolated resonance series. Here we assume that the molecular ion XY^+ is in the vibrational ground state ($v=0$). It can be shown that these conditions hold in the spectral region $E<\min(\omega,\omega_f)$, in which the field-induced level broadening is comparable to the natural linewidths, i.e., in which condition (3) holds. Radiationless transitions involving the formation of Rydberg complexes of XY** in ($v=1$, $m=0$) states and transitions to ($v=0$, $m=1$) states accompanied by the emission of a field photon make the greatest contribution here. In the coordinate system tied to the axis of the molecule, the amplitudes of these transitions are as follows, where we are making use of the small values of elements (12) and (14) (in the two-channel approximation in terms of the vibron coupling):

$$T_{\beta_0 0_0}(l\Lambda\to l\Lambda)=\frac{t^e_{\beta_0 0_0}(z_{10}+i\gamma^f_{1_0})+t^e_{\beta_0 1_0}t^e_{1_0 0_0}}{z_{10}+i\gamma_{1_0}},\qquad(20)$$

$$T_{\beta_1 0_0}(l'\Lambda'\to l\Lambda)=\frac{t^e_{\beta_1 0_1}t^f_{0_1 0_0}(l'\Lambda'\to l\Lambda)}{z_{01}+i\gamma_{0_1}}.\qquad(21)$$

Here

$$z_{vm}(E)=\tan\,[\pi(\nu_{vm}(E)+\mu^0_{l\Lambda})]-t^e_{v_m v_m}.$$

The elements $t^e_{v_m v'_m}$ and $t^e_{\beta_m v_m}$, which are responsible for the electrostatic interaction, are defined for $l\Lambda$ states of the XY** complex, which we have omitted for simplicity.

In our formulation of the problem, the diagonal elements of the operator $\mathbf{t}^e$ are written as the sum of two terms in accordance with (12). The first term stems from the interaction with the ion core, while the second describes mixing of the Rydberg series with the dissociation continuum. To find an explicit expression for this term, we use the semiclassical approximation. We also make use of the circumstance that for the rather "steep" term $U_\beta(R)$ near the classical turning point R^*_m, at which we have $\varepsilon_m = E - m\omega_f = U_\beta(R^*_m)$ we can use the Vinans-Stückelberg approximation for the nuclear wave function under the condition $U'_\beta a_0\gg\omega$:

$$\chi_{\beta_m}(R)=|U'_\beta(R)|^{-1/2}\delta[R-R^*_m(\varepsilon_m)].$$

For the elements $t^e_{v_m v_m}$ we can then write

$$t^e_{v_m v_m}=t^{(0)}_{v_m v_m}+\pi\sum_\beta P\int\frac{V^2_\beta(R)\chi^2_v(R)dR}{\varepsilon_m-U_\beta(R)}$$

[$V_\beta(R)$ is the electron part of the configuration interaction, which is related to the splitting of the $l\Lambda$ Rydberg term and the β dissociative term by $\Delta_n=2V_\beta/(\pi n^3)^{1/2}$]. We can also introduce the adiabatic quantum defect of the $l\Lambda$ Rydberg levels, which is determined from the relation

$$\tan[\pi(\boldsymbol{\nu}+\boldsymbol{\mu}^0)]=\mathbf{t}^e.$$

Specifically, this defect is

$$\tilde{\mu}_{l\Lambda}(R)=\mu^0_{l\Lambda}-\frac{1}{\pi}\,\mathrm{arctg}\langle l\Lambda m|\mathbf{t}^e(\varepsilon_m,R)|l\Lambda m\rangle$$

[$|l\Lambda m\rangle$ is the electron-photon part of wave function (6)]. Far from the turning point R^*_m, this defect becomes

$$\tilde{\mu}_{l\Lambda}(R)=\mu_{l\Lambda}(R)+\frac{1}{\pi}\,\mathrm{arctg}\left[\pi\sum_\beta\frac{V^{2(l\Lambda)}_\beta(R)}{U_\beta(R)-\varepsilon_m}\right].\qquad(22)$$

The total rates of decay from the $l\Lambda$ state, which appear in (20) and (21), i.e.,

$$\gamma_{1_0}=\gamma^i_{1_0}+\gamma^\beta_{1_0}+\gamma^f_{1_0},\quad\gamma_{0_1}=\gamma^\beta_{0_1}+\gamma^f_{0_1},\qquad(23)$$

include partial rates of autoionization (γ^i), predissociation (γ^β), and field-induced decay (γ^f). These partial rates can be expressed in terms of matrix elements:

$$\gamma^i_{v_m}=|t^e_{v_m,v-1_m}|^2,\quad\gamma^\beta_{v_m}=|t^e_{\beta_m v_m}|^2,$$

$$\gamma^f_{v_m}=\sum_{l'\Lambda'}|t^f_{v_m v_{m-1}}(l'\Lambda'\to l\Lambda)|^2\qquad(24)$$

($l'\Lambda'$ are states allowed by the selection rules during the radiative decay of the predissociation Rydberg $l\Lambda$ state). The relationship with the natural (Γ^e) and field-induced (Γ^f) half-widths is given by

$$\Gamma^e=(\gamma^i+\gamma^\beta)/\pi n^3,\quad \Gamma^f=\gamma^f/\pi n^3.$$

The total cross section for dissociative recombination for the transition to dissociation channel β with fixed quantum numbers $l\Lambda$ is

$$\sigma_{\beta 0}(\theta)=\frac{8\pi^2}{E}g\sum_m\left\langle\left|\sum_{l'\Lambda'}i^{l'}\exp(i\delta_{l'\Lambda'})Y^*_{l'\Lambda'}(\mathbf{n})\right.\right.$$
$$\left.\left.\times T_{\beta_m 0_0}(l'\Lambda'\to l\Lambda)\right|^2\right\rangle,$$
$$\delta_{l\Lambda}=\arg[\Gamma(l+1-i/k)]+\pi\mu^0_{l\Lambda},\quad k=(2E)^{1/2},\qquad (25)$$

where g is a spin factor, m takes on the values 0 and 1, the vector n specifies the direction of the incident electron beam with respect to the axis of the XY molecule, θ is the angle between the vectors **n** and **f**, and the angle brackets $\langle\ldots\rangle$ mean an average over all possible orientations of the molecules.

Substituting (20) and (21) into (25), we can write

$$\sigma_{\beta 0}=\sigma_{\beta_0 0_0}+\sigma_{\beta_1 0_0},\qquad (26)$$

where the first term,

$$\sigma_{\beta_0 0_0}=\frac{8\pi^2}{E}g\langle|Y^*_{l\Lambda}(\mathbf{n})T_{\beta_0 0_0}(l\Lambda\to l\Lambda)|^2\rangle,\qquad (26')$$

describes a transition not accompanied by an exchange of energy with the field, while the second term,

$$\sigma_{\beta_1 0_0}=\frac{8\pi^2}{E}g\left\langle\left(\frac{\gamma^\beta_{0_1}\tilde{\gamma}_{0_1}(\mathbf{n},\mathbf{f})}{z^2_{01}+\gamma^2_{0_1}}\right)\right\rangle,\qquad (26'')$$

is responsible for a transition accompanied by the emission of a field quantum. Expression (26″) is written so as to display the interference structure in the course of the field-induced filling of the $l\Lambda$ predissociation state of the XY** complex due to the contribution of $l'\Lambda'$ electron states (with $l'=l\pm 1$). The quantity $\tilde{\gamma}_{0_1}$ is given by

$$\tilde{\gamma}_{0_1}(\mathbf{n},\mathbf{f})=\frac{f^2}{4}\left|\sum_{l'\Lambda'}r(l'\Lambda'\right.$$
$$\left.\to l\Lambda)S^{(l'\Lambda',l\Lambda)}\left(\frac{\mathbf{f}}{f}\right)Y^*_{l'\Lambda'}(\mathbf{n})\exp(i\pi\mu^0_{l'\Lambda'})\right|^2\qquad (27)$$

[$r(l'\Lambda'\to l\Lambda)$ and $S^{(l'\Lambda',l\Lambda)}$ are given by (15) and (16)]. characterizes the dependence of the cross section on the angle θ between **n** and **f**. In incorporating the Coulomb phase shifts δ^c_l in (27), we make use of the circumstance that the following relation holds under the condition $kl\ll 1$, according to the selection rules:

$$\delta^c_{l+1}-\delta^c_{l-1}=-2\ \mathrm{arctg}\frac{1}{kl}\approx-\pi.$$

Let us first analyze the most general aspects of the energy dependence of the cross section (26). This dependence has a resonance structure, formed by a superposition of two Rydberg series of different origins. The first corresponds to a series of vibron resonances which converge on the threshold $E=\omega$ of the first vibrational excitation of the XY$^+$ ion. It is determined by a nonadiabatic vibron coupling in the XY** molecule. The second series incorporates a series of field-induced Breit–Wigner resonances, which converge on the threshold $E=\omega_f$. The resulting picture must therefore depend on the relation between ω and ω_f. If $\omega_f>\omega$, for example, we should see some fairly widely spaced field-induced resonances of a Breit–Wigner type against the background of the Rydberg resonances of the first series. In the opposite case, $\omega_f<\omega$, these series trade roles.

How does the cross section in (26) depend on the field intensity f? It is not difficult to see that the main factor in the influence of the field in the first term (26′), which is responsible for the radiationless transition, reduces to a broadening of the resonance lines at small values of f. This broadening is important under the condition $\Gamma^f\gtrsim\Gamma^e$ (this condition corresponds to fields $f\gtrsim 10^{-5}$–10^{-4}). In stronger fields ($f\sim 10^{-3}$), the partial cross section $\sigma_{\beta_0 0_0}$ becomes a weak function of x and tends toward the value

$$\sigma^{(d)}_{\beta_0 0_0}=\frac{2\pi}{E}g\gamma^\beta_{0_0},$$

which is partial cross section for the direct (background) dissociative recombination in the absence of external radiation.

In the second term (26″), this dependence is considerably more complicated, because of the angular anisotropy in $\tilde{\gamma}_{0_1}$. At small values of $f(\sim 10^{-7}$–$10^{-6})$, the behavior can take different forms. For example, the total cross section (26), may in fact decrease with increasing f at certain values of θ and at certain energies $E_n=\omega-1/2(n-\tilde{\mu}^0_{l\Lambda})^2$. On the other hand, the height of the field-induced Breit-Wigner peaks should increase as f^2. For sufficiently strong external electromagnetic fields ($\sim 10^{-4}$–10^{-3}), the picture changes significantly since the angular distribution becomes a weak function of f in this case. On the other hand, the height of the peaks superposed on the gently sloping plateau should decrease in proportion to $1/f^2$.

Let us illustrate these features in a specific example ($g=1/4$):

$$e^-+\mathrm{H}_2^+(v=0)+N_0\omega_f\to\mathrm{H}_2^{**}\to\mathrm{H}^*+\mathrm{H}+N\omega_f\qquad (28)$$

(N is the number of photons in the system, which differs from from the initial number N_0 by an amount $m=N-N_0$). In the H_2^{**} quasimolecule, we know that the Rydberg series $nd\sigma_g(^1\Sigma_g^+)$ undergoes predissociation. In this series, the angular momentum of the electron, $l=2$, is a "good" quantum number.[22] Consequently, the main contribution to (28) for a process not accompanied by a change in the number of photons ($m=0$) is made by the state with angular momentum $l=2$ (the d wave), while for

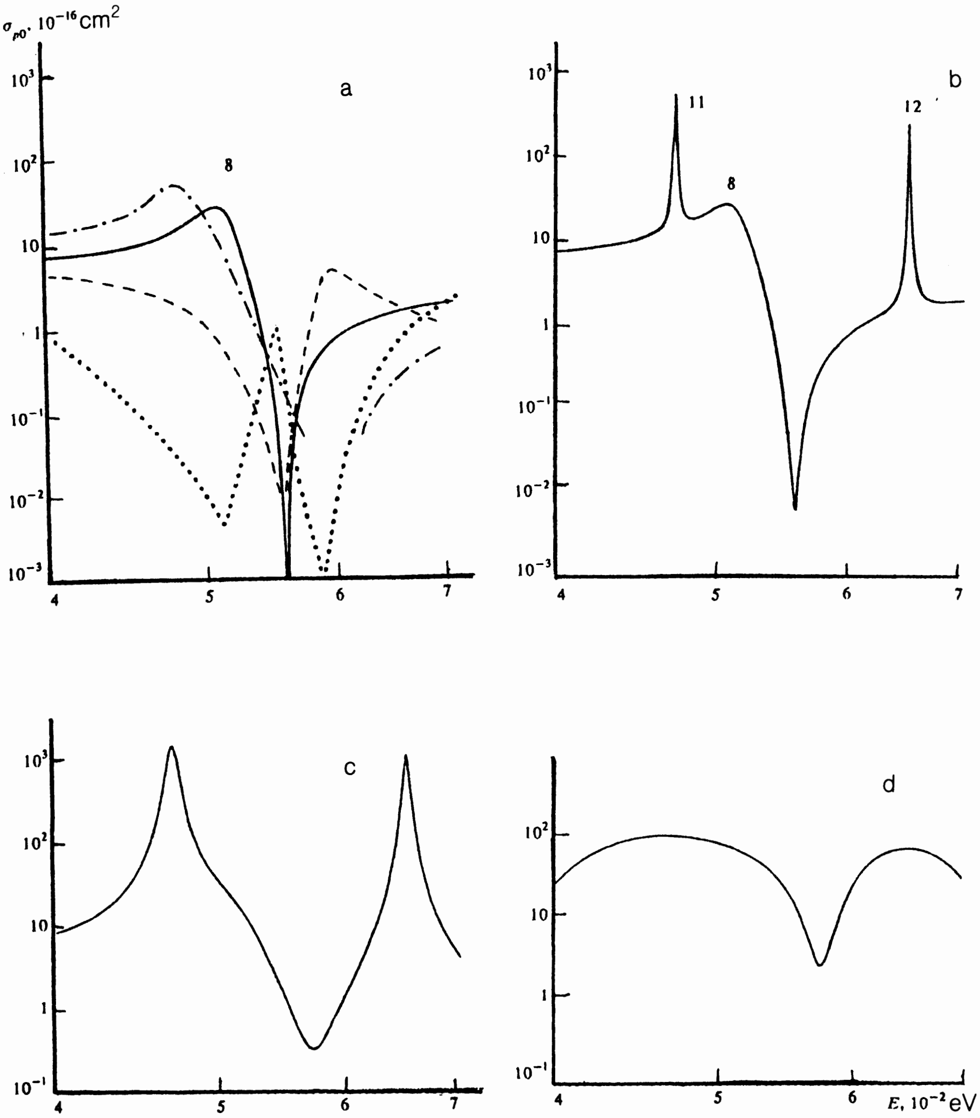

FIG. 2. Cross section for reaction (28) versus the electron energy. a—$f=0$ (solid curve; see the text proper for an explanation); b—$f=10^{-4}$; c—$f=10^{-3}$; d—$f=5\cdot10^{-3}$.

a process which is accompanied by the emission of a photon ($m=1$) the angular momenta $l=1$ and 3 (p and f waves) are important. In this case the partial decay rates (24) of the intermediate complex are

$$\gamma^{i}_{1_0}=\frac{\pi^2}{2M\omega}\left(\frac{d}{dR}\tilde{\mu}_{d\sigma}\right)^2_{R_e^+},\quad \gamma^{\beta}_{v_m}=\pi\alpha_{v_m\beta}V^2_\beta(R^*_m),$$

$$\gamma^{f}_{1_0}=\gamma^{f}_{0_1}=\frac{f^2}{4}\left|\sum_{l\Lambda}a_{l\Lambda}Y_{1\Lambda}(\theta_f,0)\right|^2. \qquad (29)$$

Here M is the reduced mass of the molecule; $\alpha_{v_m\beta}$ is the Franck–Condon factor, which is a measure of the efficiency of the transition from an ionic term to a dissociative term with the energy $\varepsilon_m=E-m^0\omega_f$; and R^*_m is the ε_m-dependent classical turning point [$\varepsilon_m = U_\beta(R^*_m)$]. The rate of the field-induced decay (27), can be written in the following form according to (14)–(16):

$$\tilde{\gamma}_{0_1}(\theta)=\frac{f^2}{4}\left|\sum_{l\Lambda,k}\exp(i\pi\mu^0_{l\Lambda})a_{l\Lambda}D^{*l}_{\Lambda k}(0,\theta_f,\pi-\phi_f)\right.$$
$$\left.\times Y_{1\Lambda}(\theta_f,0)Y^*_{lk}(\theta,\phi)\right|^2. \qquad (30)$$

Here $D^l_{\Lambda k}(\alpha,\beta,\gamma)$ is the Wigner function,[20] θ_f and φ_f are the spherical angles which specify the direction of the axis of the molecule with respect to the vector **f**, and the coefficients are given by

$$a_{1\Lambda}=\frac{2}{3}\sqrt{\frac{\pi}{5}}(2-3\Lambda^2)r(1\Lambda\to20),$$

$$a_{3\Lambda}=\sqrt{\frac{\pi(9-\Lambda^2)(4-\Lambda^2)}{3\cdot5\cdot7}}r(3\Lambda\to20) \qquad (31)$$

($\Lambda=0,\pm1$). The subsequent averaging of cross section (26) is carried out over the angle θ_f and the angular difference $\phi-\phi_f$.

Figures 2–5 shows results calculated for the cross section for reaction (28) from Eqs. (26) and (29)-(31) with the help of data on $\mu_{l\Lambda}(R)$, $U_\beta(R)$, and $V_\beta(R)$ from Refs. 22 and 23. The matrix elements for the vibron coupling for the $d\sigma$ series, allowing for transitions through the dissociation continuum, are

$$t^e_{0_1 0_1}=-0.17, \quad t^e_{1_0 1_0}=-0.21, \quad t^e_{1_0 0_0}=-0.11.$$

The Franck–Condon factors which appear in the definition of the predissociation rate $\gamma^\beta_{v_m}$ were calculated in the semiclassical approximation with the help of Morse vibrational functions $\chi_v(R)$ (with the parameter value $x=D_e/\omega=9.31$, where D_e is the dissociation energy of the H_2^+ ion). Figure 2 shows the total cross section for reaction (28) as a function of the energy E for an external-field frequency $\omega_f=0.6\omega$. The curve for the dissociative recombination in the absence of a field ($f=0$; Fig. 2a) is drawn for comparison with the results of previous calculations[22,24] for the spectral region adjacent to the isolated vibron resonance $n_{01}=8(v=1)$. The dot-dashed curve here reproduces the result derived in Bardsley's theory,[24] which of course ignores the interaction of closed channels. In the version of the theory of the multichannel quantum defect proposed in Ref. 24, this interaction is taken into account (for example, in Refs. 22 and 24, nine closed channels are taken into account), but virtual transitions through the dissociation continuum are ignored (in contrast with Bardsley's theory[24] and our own). For this reason, the dotted[22] and dashed[24] curves in Fig. 2a have a clearly expressed "antiresonance" structure. In our version of the theory of the multichannel quantum defect, vibron transitions through the dissociative continuum are taken into account systematically. However, for simplicity in describing dissociative recombination in an external field, we restricted the discussion to a single closed channel ($v=1$) and to the energy region in which this description was valid. For this reason, the results derived in this paper are close to those found by Bardsley.[24] The only explanation for the difference is that we are using more-accurate data on the parameters of the $e^-+H_2^+$ system[22] (for example, in Ref. 24 the derivative of the diabatic quantum defect $d\mu/dR$ was taken to be 0.1, while according to recent data[22] the value is 0.008).

Figure 2, b–d, clearly demonstrates the dependence of the cross section for reaction (28) on the field intensity f. The curves are drawn for the case $\theta=0$, in which the electron beam and the light beam are mutually perpendicular. The curve labels (Fig. 2, a and b) specify the positions of the vibron level ($n_{10}=8$) and of the field-induced resonant levels ($n_{01}=11$ and 12).

Let us analyze the angular dependence of the cross section for reaction (1), which is shown in Figs. 3 and 4 for the ratio $\sigma_{\beta 0}(E,f,\theta)/\sigma_{\beta 0}(E,f,0)$. For weak external fields ($f\sim 10^{-5}$), the θ dependence is weak. Using representations (26) and (30) (and ignoring the small contributions of the $f\Lambda$ harmonics), we can put this ratio in the form

$$\frac{\sigma_{\beta 0}(E,f,\theta)}{\sigma_{\beta 0}(E,f,0)}=1-w(E,f)\sin^2\theta, \qquad (32)$$

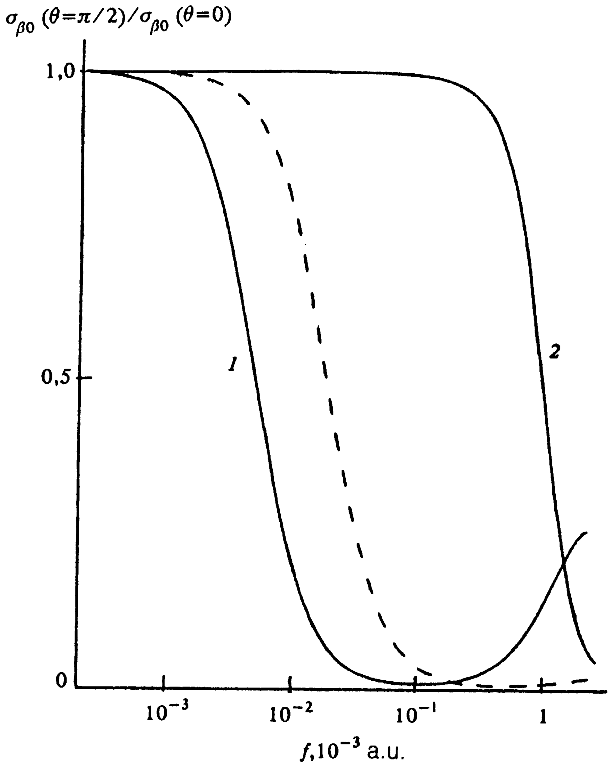

FIG. 3. The ratio $\sigma_{\beta 0}(\theta=\pi/2)/\sigma_{\beta 0}(\theta=0)$ versus the field intensity f. Dashed line: Energy of a field-induced resonance ($n_{01}=11$). Solid lines: The minimum at $E_1=5.59\cdot 10^{-2}$ eV (1) and the maximum at $E_3=5.08\cdot 10^{-2}$ eV (2) of the cross section for reaction (28) in the absence of a field.

where

$$w=Af^2 \times\frac{z^2_{10}(E)+2\gamma^e_{1_0}cf^2+\gamma^{e2}_{1_0}}{(z_{10}(E)+B)^2(z^2_{01}(E)+\gamma^{e2}_{0_1})+(z^2_{10}(E)+\gamma^{e2}_{1_0})Cf^2}, \qquad (33)$$

and the quantities A, B, and C are defined by

$$A=\frac{45}{1024\pi^2}\left(a^2_{10}+\frac{6}{5}a_{10}a_{11}+a^2_{11}\right), \quad B=t^e_{\beta_0 1_0}t^e_{1_0 0_0}/t^e_{\beta_0 0_0},$$

$$C=\frac{3}{32\pi}(a^2_{10}+2a^2_{11}).$$

The elements $a_{1\Lambda}$ are given by expressions (31). It follows from this expression that the strongest f dependence at a given θ should occur near the point E_1, which characterizes the position of the minimum of the cross section $\sigma_{\beta 0}$, at which we have $z_{10}(E_1)=B$. The following maximum of the function $w(E,f)$ corresponds to the position of a field-induced resonance, found from the condition $z_{01}(E_2)=0$. The most poorly expressed region is the vicinity of the vibron resonance $z_{10}(E_3)=0$, in which we have $w \propto Af^2(\gamma^e_{1_0})^2/B^2$. These conclusions are illustrated in Fig. 3 for the angle $\theta=\pi/2$ (the laser beam is directed along the electron beam). We see that the relative cross section begins to decrease significantly with increasing θ at $f\sim 10^{-4}$;

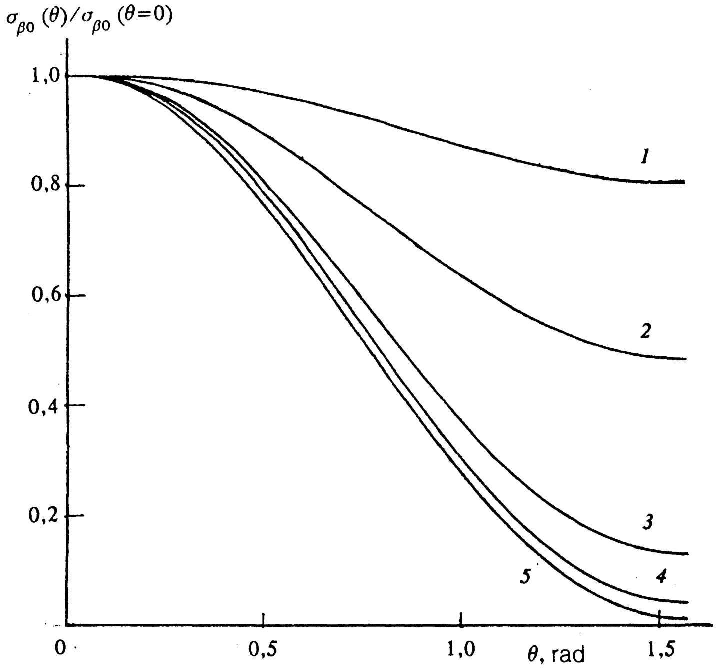

FIG. 4. The ratio $\sigma_{\beta 0}(\theta)/\sigma_{\beta 0}(\theta=0)$ versus the angle θ near a field-induced resonance (for $n_{01}=11$). *1*—10^{-5}; *2*—$2\cdot 10^{-5}$; *3*—$5\cdot 10^{-5}$; *4*—10^{-4}; *5*—$\gtrsim 10^{-3}$.

according to (32), this cross section reaches a minimum at $\theta=\pi/2$. Figure 4 shows the angular distribution of this cross section near the field-induced resonance $n_{01}=11$ (which has the energy $E_2=4.7\cdot 10^{-2}$ eV) for the frequency $\omega_f=0.6\omega$ and for various values of f. For $f\gtrsim 10^{-3}$ the angular distribution corresponds to curve 5 in Fig. 4 and varies only weakly with f. Since the resonance structure in the total cross section is poorly defined at these field levels (Fig. 2d), this distribution should also apply to poorly collimated electron beams, in which case there would be effective averaging over the energy. It should be noted, however, that the properties we are discussing here are determined by the specific features of the H_2^{**} complex which stem from the existence of a special predissociation $d\sigma_g$ orbital in this energy region.

Figure 5 shows the total cross section for reaction (28) versus the field for the angles $\theta=0$ and $\pi/2$. Curve *1* corresponds to the energy of the field-induced resonance $n_{01}=11$, while curve *2* corresponds to the vicinity of the minimum of the cross section ($E_1=5.59\cdot 10^{-2}$ eV). It is

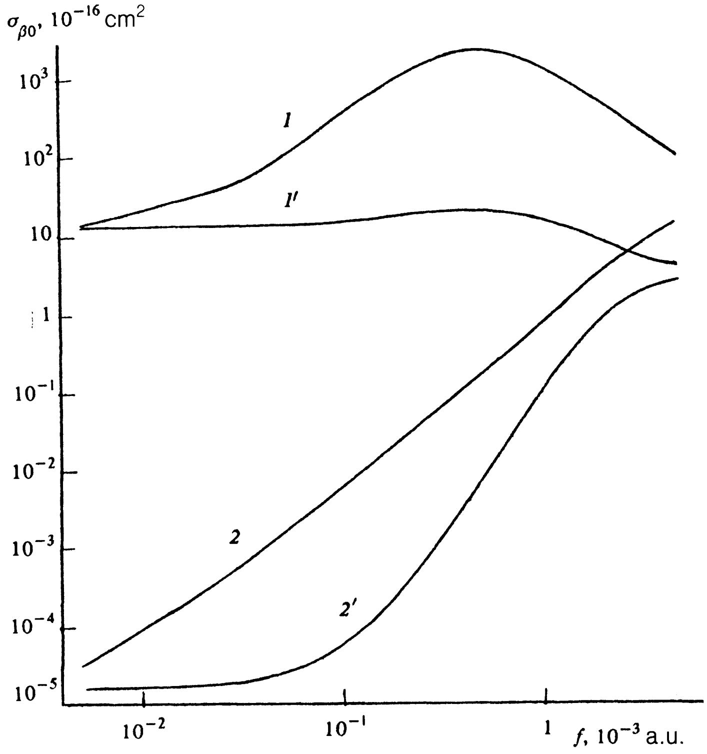

FIG. 5. Cross section for reaction (28) versus the field intensity f for $\theta=0(1,2)$ and $\pi/2(1',2')$ and for a field frequency $\omega_f=0.6\omega$. Curves 1 and 2 correspond to the energies of the field-induced resonance ($n_{01}=11$) and the minimum of the cross section ($E_1=5.59\cdot 10^{-2}$ eV).

not difficult to see that for $f \gtrsim 10^{-5}$ the cross section increases as f^2. With a further increase in f the cross section reaches a maximum whose position corresponds to $f \sim 10^{-3}$, when the field-induced widths are comparable to the natural widths. In the case $\theta = 0$ we have the most favorable conditions for field induction of a dissociative recombination, in which there may be a substantial increase in the cross section (by at least an order of magnitude). If, on the other hand, we take an average over all angles θ, we see that for $f > 10^{-3}$ the external field leads to roughly doubling of the cross section.

4. FIELD-INDUCED MIXING OF RYDBERG VIBRON STATES

Because of the rich resonance structure in Rydberg complexes, resonances belonging to different series may overlap for essentially any relation between the frequencies ω and ω_f. Under these conditions, compound resonant vibron states arise for which the filling and decay mechanisms in the course of dissociative recombination are quite different from those discussed above. Some new channels for the process open up when those $l'\Lambda'$ harmonics which are shut out of the process in the absence of a field, because the configurational interaction with dissociation channels is weak, also become effective. Since the conditions for the formation of field-induced compound resonances of the $e^- + XY^+$ system are extremely sensitive to the position of the unperturbed resonance levels, it is generally necessary to take account of the rotational structure of the XY** Rydberg complexes. This is done by using a rovibron basis with adiabatic (under the condition $Bn^3 \ll 1$) electronic-rotational wave functions in Eqs. (7) and (8). The transition matrices incorporating the interacting resonance states in the adiabatic rovibron basis and in a basis with a fixed molecular axis are written in the same way [see Eqs. (34) and (35) below]. They differ only in the definition of the matrix elements which they contain. The basic conclusions concerning the intensities and the characteristics of the process averaged over energy (whose determination is the ultimate goal of this study) do not depend on the particular basis used.

Reaction (28) in the $e^- + H_2^+$ system, which we are discussing here for definiteness, occurs in the absence of a field during the scattering of an electron in a $d\sigma$ state (the $s_{\sigma-}$, $p_{\sigma-}$, and p_π orbitals of the closed channels are purely autoionization orbitals, while the f orbitals are weakly penetrating orbitals characterized by small quantum defects, $\mu_{f\Lambda} \sim 10^{-3}$, and by negligible autoionization rates, $\gamma^i \sim 10^{-4}$). As we mentioned earlier, under conditions (4), with the field-induced widths small in comparison with the natural widths ($\gamma^f \ll \gamma^e$), the states of isolated series of the XY** Rydberg complex are essentially unaffected by the laser radiation. The situation changes fundamentally, however, if some resonance level of the predissociation Rydberg $nd\sigma_g$ series overlaps a field-induced resonance belonging to the next series in terms of l (p or f) for $v = 1$. To examine this situation in more detail, we distinguish three cases.

Field-induced mixing of *ndσ* and *n′pσ* states

Active in this case are the $p\sigma$ and $d\sigma$ harmonics of the scattering of the electron by the ion core; correspondingly, there are two types of transitions. The first occurs during radiationless excitation of the $p\sigma$ component ($v = 1$) of the hybrid state $n'_{10} p\sigma(v = 1,\ m = 0) - n_{1m} d\sigma(v = 1,\ m = \pm 1)$ and its decay to the $d\sigma$ dissociation channel. The corresponding transition amplitude, whose construction incorporates the interaction of these series, is ($m = \pm 1$)

$$T^{(r)}_{\beta_m 0_0}(p\sigma \to d\sigma)$$

$$= \frac{t^e_{\beta_m 1_m}(d\sigma)\, t^f_{1_m 1_0}(p\sigma \to d\sigma)\, t^e_{1_0 0_0}(p\sigma)}{D(p\sigma, d\sigma)}, \tag{34}$$

where

$$D(p\sigma, d\sigma) = \kappa_{1_0}(p\sigma)\,\kappa_{1_m}(d\sigma) - [t^f_{1_0 1_m}(p\sigma \to d\sigma)]^2.$$

For convenience we have introduced some notation here:

$$\kappa_{v_m}(l\Lambda) = \mathrm{tg}[\pi(\nu_{vm} + \tilde{\mu}^0_{l\Lambda})] + i\gamma^e_{v_m}(l\Lambda),$$

$$\tilde{\mu}^0_{l\Lambda} = \tilde{\mu}_{l\Lambda}(R^+_e), \quad \gamma^e = \gamma^i + \gamma^\beta.$$

In determining $\kappa_{v_m}(l\Lambda)$ we made use of the small value of the elements $t^e_{v_m v_m}$ and expression (22) for the adiabatic quantum defect $\tilde{\mu}_{l\Lambda}$. The amplitude in (34) is not small if the electron energy is close to the position of some resonance of the $p\sigma$ series.

The other transition occurs near the point $E = \omega - 1/2(n_{10} - \tilde{\mu}^0_{d\sigma})^2$ during the formation of a hybrid $[n_{10} d\sigma(v = 1, m = 0)] - [n'_{1m} p\sigma(v = 1, m = \pm 1)]$ state due to the filling of a vibron resonance $nd\sigma$ state and the subsequent radiationless decay of this state into the dissociation channel. The amplitude for this transition is

$$T^{(r)}_{\beta_0 0_0}(d\sigma \to d\sigma) = \frac{t^e_{\beta_0 1_0}(d\sigma)\,\kappa_{1_m}(p\sigma)\, t^e_{1_0 0_0}(d\sigma)}{D(d\sigma, p\sigma)}. \tag{35}$$

We need to stress that the denominators in (34) and (35) are not the same (their zeros correspond to different energies). We also note that at $f = 0$ expression (35) becomes the resonance term in the amplitude (20), taken without the field-induced broadening.

Mixing of *ndσ* and *n′pπ* states

The case of mixing of $d\sigma$ states with doubly degenerate $p\pi$ states is described by expressions like (34) and (35), with the new features that transitions of two types arise because of p states: $p\pi^+$ and $p\pi^-$ (the plus and minus signs here specify the parity of the electron wave function under reflection in a plane passing through the axis of the molecule), and the quantity $[t^f_{1_0 1_m}(p\sigma \to d\sigma)]^2$ in expression (34) for the determinant is replaced by the sum of squares of the field-induced interaction of the $d\sigma - p\pi^+$ and $d\sigma - p\pi^-$ states.

Field-induced mixing of $nd\sigma$ and $n'f\Lambda$ states

In the case of an overlap of coupled dipole transitions of $d\sigma$ and $f\Lambda$ states ($f\sigma$, $f\pi^+$, and $f\pi^-$), i.e., of the states $n_{10}d\sigma(v=1)$ and $n'_{1m}f\Lambda(v=1, m=\pm 1)$, the transition occurs because of an admixture of the $d\sigma$ component in the hybrid $d\sigma-f$ state. Since (as we have already mentioned) the natural broadening of the f levels is exceedingly slight, some clearly expressed minima reproducing the positions of the f levels of the $e^-+H_2^+$ $(v=1)$ system should be observed in the reaction cross section in this case.

We can get an idea of the effectiveness of the laser radiation for this system by comparing Eqs. (34) and (35) for the cases of low ($t^f \ll t^e$) and fairly high ($t^f \gtrsim t^e$) external fields f. In the former case, transitions of the form (34) disappear, and we are left simply with transitions of the second type, for which expression (35) becomes the expression for a one-resonance approximation in the vicinity of the $n_{10}d\sigma$ resonance:

$$|T^{(r)}_{\beta_0 0_0}(d\sigma\to d\sigma)|^2=\frac{\Gamma^e_i(d\sigma)\Gamma^e_\beta(d\sigma)}{(E-E^{(r)}_{nd\sigma})^2+[\Gamma^e(d\sigma)]^2}. \qquad (36)$$

Here $\Gamma^e_i(d\sigma)$ and $\Gamma^e_\beta(d\sigma)$ are the autoionization and predissociation half-widths of the resonance vibron level $E^{(r)}_{nd\sigma}=\omega-1/2(n_{10}-\tilde{\mu}^0_{d\sigma})^2$, given by

$$\Gamma^e_i=\frac{|t^e_{1_0 0_0}|^2}{\pi n^3}, \quad \Gamma^e_\beta=\frac{|t^e_{\beta_0 1_0}|^2}{\pi n^3}, \qquad (37)$$

and the total natural width is

$$\Gamma^e=\Gamma^e_i+\Gamma^e_\beta.$$

In the case of a strong field-induced interaction of the resonance states (which are discussed below in the example of mixing of the $p\sigma$ and $d\sigma$ series), a compound resonance can arise at the position of an individual (in the absence of a field) resonance $E^{(r)}_{n'p\sigma}$ level in the $p\sigma$ scattering channel at certain values of ω_f. This compound resonance is described by a curve with two peaks, whose positions are

$$E_{1,2}(p\sigma)=\tfrac{1}{2}(E^{(r)}_{n'p\sigma}+E^{(r)}_{n_m d\sigma})\pm\delta^{(m)}_{(p\sigma)},$$

$$\delta^{(m)}(p\sigma)=[(\bar{V}^f_m)^2+\Delta^2_m]^{1/2}, \quad \Delta_m=\frac{1}{2}(E^{(r)}_{n'p\sigma}-E^{(r)}_{n_m d\sigma}),$$

where $E^{(r)}_{n_m d\sigma}$ is the position of the field-induced resonance (at $m=\pm 1$), given by

$$E^{(r)}_{n_m d\sigma}=m\omega_f+\omega-\frac{1}{2(n_{1m}-\tilde{\mu}^0_{d\sigma})^2}>0,$$

and $\bar{V}^f_m$ is the interaction. We assume that this interaction satisfies the following condition:

$$\bar{V}^f_m=\frac{|t^f_{1_m 1_0}(p\sigma\to d\sigma)|}{\pi(n'_{10}n_{1m})^{3/2}}\gg\Gamma^e,\Delta_m. \qquad (38)$$

This is true although the field f is still fairly weak, i.e., although the inequality $\bar{\Gamma}^f_m\ll\Gamma^e$ holds, where $\bar{\Gamma}^f_m=(\bar{V}^f_m)^2$. Furthermore, a second compound resonance in the $d\sigma$ scattering arises near the point $E^{(r)}_{nd\sigma}$. For $m<0$, these resonances form only if $\omega_f<\omega$. The corresponding behavior of the squares of the matrix elements in this case is described by

$$|T^{(r)}_{\beta_m 0_0}(p\sigma\to d\sigma)|^2 =\frac{\Gamma^e_\beta(d\sigma)\bar{\Gamma}^f_m\Gamma^e_i(p\sigma)}{[(E-E_1(p\sigma))^2+\bar{\Gamma}^2][(E-E_2(p\sigma))^2+\bar{\Gamma}^2]}, \qquad (39)$$

$$|T^{(r)}_{\beta_0 0_0}(d\sigma\to d\sigma)|^2 =\frac{\Gamma^e_\beta(d\sigma)[(E-E^{(r)}_{n'_m p\sigma})^2+(\Gamma^e_i(p\sigma))^2]\Gamma^e_i(d\sigma)}{[(E-E_1(d\sigma))^2+\bar{\Gamma}^2][(E-E_2(d\sigma))^2+\bar{\Gamma}^2]}, \qquad (40)$$

where $\Gamma^e_i(p\sigma)$, $\Gamma^e_i(d\sigma)$, and $\Gamma^e_\beta(d\sigma)$ are the autoionization half-widths of the $p\sigma$ and $d\sigma$ levels and the predissociation half-width of the $d\sigma$ level. Here also, $\bar{\Gamma}=[\Gamma^e_i(p\sigma)+\Gamma^e_i(d\sigma)+\Gamma^e_\beta(d\sigma)]/2$. The intensities of the lines under the conditions (38) are

$$I_{p\sigma}=\frac{\pi}{2}\frac{\Gamma^e_i(p\sigma)\Gamma^e_\beta(d\sigma)}{\bar{\Gamma}}, \quad I_{d\sigma}=\frac{\pi}{2}\frac{\Gamma^e_i(d\sigma)\Gamma^e_\beta(d\sigma)}{\bar{\Gamma}},$$

and the ratios of these intensities for the case in which the compound resonances are not far apart is

$$\frac{I_{p\sigma}}{I_{d\sigma}}=\frac{\Gamma^e_i(p\sigma)}{\Gamma^e_i(d\sigma)}.$$

According to (39), in the spectral interval adjacent to the resonance line $E^{(r)}_{n'p\sigma}$, the products of the dissociative recombination either accelerate ($m=-1$) or slow down ($m=1$), depending on how the compound resonance of the system is formed:

$$-\frac{1}{2(n'_{10}-\tilde{\mu}^0_{p\sigma})^2}=m\omega_f-\frac{1}{2(n_{1m}-\tilde{\mu}^0_{d\sigma})^2} \quad (m=\pm 1).$$

5. EFFECT OF FIELD-INDUCED MIXING OF RESONANCES ON THE RATE CONSTANT FOR DISSOCIATIVE RECOMBINATION

The effect of the field on the characteristics of the process, averaged over the energy, at field levels corresponding to condition (38) is determined by expressions (39) and (40) and by the explicit functional dependence $F(E)$, used to carry out the averaging. For definiteness we assume that the incident electrons have a Maxwellian velocity distribution and that their motion is uncorrelated with the direction of the field vector f (i.e., we are assuming that a corresponding average is taken over the angle θ). The distribution function then takes the form

$$F(E)=\sqrt{\frac{2\pi}{T^3_e}}\exp\left(-\frac{E}{T_e}\right),$$

where T_e is the electron temperature. Making the further assumption that the vibrational temperature of the ions satisfies $T_i\ll T_e\lesssim\omega$, we can write the rate constant for dissociative recombination as

$$k=k_d+\sum_m \int_0^\infty \left| \sum_{l\Lambda} T^{(r)}_{\beta_m 0_0}(l\Lambda\to d\sigma)\right|^2 F(E)dE, \quad (41)$$

where

$$k_d=\int_0^\infty F(E)\gamma^\beta_{0_0}(d\sigma)dE=\sqrt{\frac{2\pi}{T_e^3}}\,\gamma^\beta_{0_0}(d\sigma).$$

Separating out the field-independent terms in (41), and going through the necessary calculations, we finally find

$$k=k^0+k^f, \quad (42)$$

where the first term is the reaction rate constant in the absence of an external field, i.e.,

$$k^0=k_d\left[1+\frac{\gamma^i_{1_0}(d\sigma)\gamma^\beta_{1_0}(d\sigma)[1-\exp(-\omega/T_e)]}{\gamma^\beta_{0_0}(d\sigma)[\gamma^i_{1_0}(d\sigma)+\gamma^\beta_{1_0}(d\sigma)]}\right]. \quad (43)$$

[The second term in square brackets in (43) shows the contribution from intermediate Rydberg $d\sigma_g$ states of H_2^{**}.] The next term is caused by the field and is given by

$$k^f=\frac{\gamma^i_{1_0}(p\sigma)\gamma^\beta_{1_1}(d\sigma)}{2\pi\bar{\Gamma}}\left[\frac{F(\widetilde{E}^{(r)}_{n'p\sigma})}{(n'_{10}n_{11})^3}-\frac{\gamma^i_{1_0}(d\sigma)}{\gamma^e_{1_0}(d\sigma)}\frac{F(\widetilde{E}^{(r)}_{nd\sigma})}{(n'_{11}n_{10})^3}\right]. \quad (44)$$

Here $\widetilde{E}^{(r)}_{n'p\sigma}$ and $\widetilde{E}^{(r)}_{nd\sigma}$ are the positions of the field-perturbed compound resonances in the $p\sigma$ and $d\sigma$ channels, respectively, for electron scattering.

Let us clarify the conditions under which the quantity k^f is not small, and the field-induced mixing of resonance plays a major role. For a given ratio ω_f/ω there should exist a finite number of compound resonances which can contribute significantly to (44). In the $p\sigma$ scattering channel, these resonances increase the rate constant for dissociative recombination, while in the $d\sigma$ channel they decrease this rate constant. Depending on the relations between the half-widths for autoionization, $\Gamma^e_i(p\sigma)$ and $\Gamma^e_i(d\sigma)$, and predissociation, $\Gamma^e_\beta(d\sigma)$, which appear in (44), we can expect an effective increase in the rate of dissociative recombination at temperatures $T_e\simeq \widetilde{E}^{(r)}_{n'p\sigma}$ and we can expect slowing at $T_e\simeq\widetilde{E}^{(r)}_{nd\sigma}$. Here we must also require that the distance between the compound resonances with the lowest principal quantum numbers, n'_{10} and n_{10}, satisfy the condition $\Delta E=|\widetilde{E}^{(r)}_{n'p\sigma}-\widetilde{E}^{(r)}_{nd\sigma}|\gtrsim T_e$. This condition imposes further restrictions on the electron temperature[5] T_e. In the opposite case, the electromagnetic field leads to a slight increase in the rate constant.

The maximum increase in the rate of dissociative recombination is reached in a process accompanied by the emission of a field photon ($m=1$). The effect should be greatest when the frequency detuning satisfies $|\omega^{(r)}_f-\omega_f|\ll\bar{V}^f_m$, where the resonant frequency $\omega^{(r)}_f$ is given by

$$\omega^{(r)}_f=\frac{1}{2(n_{11}-\widetilde{\mu}^0_{d\sigma})^2}-\frac{1}{2(n'_{10}-\widetilde{\mu}^0_{p\sigma})^2}. \quad (45)$$

TABLE I. The coefficient η versus the ratio ω_f/ω.

n_{11} \ n'_{10}	8	9	10	11
4	2,45	2,63	2,78	2,85
	0,16	0,06	0,03	0,02
5	1,25	1,43	1,56	1,65
	0,15	0,06	0,03	0,02
6	0,61	0.79	0,91	1,00
	0,15	0,05	0,03	0,02
7	0,23	0,40	0,53	0,62
	0,15	0,04	0,03	0,02

For each n_{11}, the upper row gives the ratio ω_f/ω, and the lower one the value of η found from (46).

For the resonant Rydberg series $d\sigma_g$, which is filled in a radiationless transition, the autoionization rate $\gamma^i_{1_0}(d\sigma)$ is an order of magnitude smaller than the predissociation rate. At temperatures $T_e\ll\omega$, the ratio of constants characterizing the effect of the field-induced mixing of resonances on the rate of reaction (28) can thus be written

$$\eta=\frac{k^f}{k^0}$$

$$\approx\frac{\gamma^i_{1_0}(p\sigma)\gamma^\beta_{1_1}(d\sigma)}{T_e(\gamma^i_{1_0}(p\sigma)+\gamma^\beta_{0_0}(d\sigma)}\,\frac{\exp(-\widetilde{E}^{(r)}_{n'p\sigma}/T_e)}{[\gamma^i_{1_0}(p\sigma)n^3_{11}+\gamma^\beta_{1_1}(d\sigma)n'^3_{10}]}, \quad (46)$$

where the quantity $\gamma^\beta_{0_0}(d\sigma)$, which depends only weakly on the energy (on the scale of the change, $\sim 1/n^3$), is calculated for an energy $E\simeq T_e$, and $\gamma^\beta_{1_1}(d\sigma)$ is calculated at the energy $\widetilde{E}^{(r)}_{n'p\sigma}-\omega_f$. The results of a calculation from (46) for external-field frequencies $\omega_f=\omega^{(r)}_f$ are listed in Table I. [Here we have taken T_e to be the energy of the first ($n'_{10}=8$) vibron level in the $p\sigma$ scattering.] The largest number of resonances with a coefficient $\eta\gtrsim 0.1$ is in the IR range. As the temperature T_e rises, the coefficient η decreases, but it does not become negligible. This result means that the effect of the field-induced mixing on the dissociative recombination can be seen in a low-temperature hydrogen plasma over a broad temperature range.

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[1] The external electromagnetic field is incorporated in the definition of the Hamiltonian $\mathbf{H}_0$.

[2] The introduction of the quantum defects $\mu_{l\Lambda}(R)$ does not require the assumption that the interaction $\mathbf{V}^e$ in an isolated configuration of e^-++XY^+ is small.

[3] We are using the notation of Ref. 20 for the spherical harmonics $Y_{l\Lambda}$ and for the coefficients of the vector addition $(ll'\Lambda\Lambda'|JM)$.

[4] From (19) we also find a generalized representation for the reactance matrix $\mathbf{R}$ (found by formally replacing $\mathbf{T}'$ by $\mathbf{t}$):

$$\mathbf{R}_{oo}=\mathbf{t}_{oo}+\mathbf{t}_{oc}\frac{1}{\mathbf{E}_{cc}-\mathbf{t}_{cc}}\mathbf{T}_{co}.$$

This representation includes as a particular case (in the absence of a field and in the absence of non-Rydberg channels) Seaton's relation[18] for the $\mathbf{R}$-matrix (our definitions of the $\mathbf{t}$- and $\mathbf{R}$-matrices differ in sign from those of Ref. 18).

[5] For example, the first resonance in the $p\sigma$ scattering channel (for $v=1$) corresponds to $n'_{10}=8$ ($E^{(r)}_{n'p\sigma}=1.78\cdot 10^{-3}$), and that in the $d\sigma$ channel to $n_{10}=8$ ($E^{(r)}_{nd\sigma}=1.99\cdot 10^{-3}$). In other words, the distance between the hybrid states is $\Delta E=2.1\cdot 10^{-4}$.

[1] S. L. Guberman, in *Physics of Ion-Ion and Electron-Ion Collisions* (ed. F. Brouillard), Plenum, New York, 1983.

[2] N. B. Delone, S. P. Goreslavsky, and V. P. Krainov, J. Phys. B **22**, 2941 (1989).

[3] V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. **66**, 1981 (1974) [Sov. Phys. JETP **39**, 975 (1974)].

[4] Yu. I. Geller and A. K. Popov, *Laser Induction of Nonlinear Resonances in Continuous Spectra*, Nauka, Novosibirsk, 1981.

[5] N. B. Delone and V. P. Krainov, *Atoms in Strong Light Fields*, Springer-Verlag, New York, 1985.

[6] P. Lambropoulos and P. Zoller, Phys. Rev. A **24**, 379 (1981).

[7] A. I. Andryushin, A. E. Kazakov, and M. V. Fedorov, Zh. Eksp. Teor. Fiz. **82**, 91 (1982) [Sov. Phys. JETP **55**, 53 (1982)]; **88**, 1153 (1985) [**61**, 678 (1985)].

[8] G. Alber and P. Zoller, Phys. Rev. A **27**, 1373 (1983).

[9] A. L'Huillier, A. X. Tang, and P. Lambropoulos, Phys. Rev. A **39**, 1112 (1988).

[10] S. I. Yakovlenko, *Radiation-Collision Phenomena*, Energoizdat, Moscow, 1984.

[11] V. S. Dubov, Ya. E. Lapsker, and L. V. Gurvich, Khim. Fiz. **1**, 1642 (1982).

[12] L. Dimou and F. H. M. Faisal, Phys. Rev. Lett. **59**, 872 (1987).

[13] A. Giusti-Suzor and P. Zoller, Phys. Rev. A **36**, 5178 (1987).

[14] A. M. Movsesyan and M. V. Fedorov, Zh. Eksp. Teor. Fiz. **99**, 411 (1991) [Sov. Phys. JETP **72**, 228 (1991)].

[15] G. K. Ivanov and G. V. Golubkov, Zh. Eksp. Teor. Fiz. **99**, 1404 (1991) [Sov. Phys. JETP **72**, 783 (1991)].

[16] G. K. Ivanov, A. S. Vartazaryan, and G. V. Golubkov, Dokl. Akad. Nauk SSSR **303**, 390 (1988).

[17] A. S. Vartazaryan, G. K. Ivanov, and G. V. Golubkov, Opt. Spektrosk. **63**, 557 (1989) [Opt. Spectrosc. (USSR) **63**, 327 (1989)].

[18] M. J. Seaton, Rep. Progr. Phys. **66**, 167 (1983).

[19] E. M. Balashov, G. V. Golubkov, and G. K. Ivanov, Zh. Eksp. Teor. Fiz. **86**, 2044 (1984) [Sov. Phys. JETP **59**, 1188 (1984)].

[20] A. S. Davydov, *Nulclear Theory*, Fizmatgiz, Moscow, 1958.

[21] M. L. Goldberger and K. M. Watson, *Collision Theory*, Wiley, New York, 1964.

[22] K. Nakashima, H. Takagi, and H. Nakamura, J. Chem. Phys. **86**, 726 (1987).

[23] G. Herzberg and G. Ch. Jungen, J. Mol. Spectrosc. **41**, 425 (1972).

[24] A. Giusti-Suzor, J. N. Bardsley, and C. Derkits, Phys. Rev. A **28**, 682 (1983).

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