Reviews

Dynamic behavior of highly excited molecular states in the strong monochromatic laser fields

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The dynamic behavior of highly excited molecular states in an external monochromatic field has been investigated in order to establish the general trends in the Rydberg state manifestations in collisional and radiative processes. The effects of interference between direct (background) and resonant interactions and coupling between the continua on the fine structure of collision cross sections and near-threshold photoabsorption spectra are discussed. Analytical expressions for the widths and intensities of the Rydberg lines induced by mixing the field with other quasistationary states are derived and their dependence on the external field strength and frequency are analyzed. It was found that the appreciable stabilization of isolated Rydberg levels observed previously in superstrong fields is also possible in fields much weaker than atomic fields. The possibility of laser control for the energy averaged cross sections and reaction rate constants are considered. All effects are illustrated for the $e^- + H_2^+$ system.

Key words: molecular Rydberg states; laser radiation; dissociative recombination; photoionization; photodissociation.

Introduction

Rydberg states are those highly excited states of atoms and molecules in which one of the electrons possesses a high principle quantum number n and, therefore predominantly moves far from the ionic core (the characteristic size of the electronic orbit is *ca.* a_0n^2, where a_0 is the Bohr radius). At such distances an electron is primarily subjected to the Coulomb field of this core. Large electronic shells and low ionization potentials qualitatively separate highly excited Rydberg states (RS) from the usual low-lying states and makes possible their various practical implementations, including isotope separation, thermonuclear synthesis, developments in infrared and microwave radiation sensors. At the same time, elementary chemical processes involving RS are pertinent to a number of research fields such as the chemical physics of combustion, laser spectroscopy, and aeronomy. This important role is mainly a consequence of the high reactivity of Rydberg

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particles, which is caused by their large size and internal electronic energy (approximately equal to the ionization potential of a neutral particle) which greatly exceeds characteristic vibrational and rotational energies.

In recent years Rydberg atoms and molecules have become the subject of extensively growing studies stimulated by developments in turnable lasers. In the problems of modern laser chemistry,[1] laser photoionization spectroscopy,[2] and radiative collision theory,[3] the dynamics of Rydberg atoms and molecules in external fields is of outstanding importance. Because they are able to govern various phenomena, external fields may serve as a powerful tool for solving new fundamental problems of science and technology, such as, for example, the laser control of chemical reaction dynamics (laser surgery of molecules), hwich has so far challenged experimentalists and theoreticians.

Rydberg atoms and molecules, which form infinite (field-induced) sequences of interacting resonances, in a radiation field, cannot be described within well-known two- or three-level systems. The unique character of the associated phenomena (field-induced stabilization of atoms, interference between different channels of motion, and so on) has necessitated their separation into a specific research area. For simple atoms with a structureless core these phenomena have been studied in sufficient detail.[4–7] For molecules, however, the point core model is entirely invalid because the molecular ion XY^+ possesses vibrational and rotational degrees of freedom and can exchange in energy with a Rydberg electron. Let us discuss the basic features of the isolated $e^- + XY^+$ system from this viewpoint. Fig. 1 shows how dramatically the inelastic excitation of the core may influence the motion of an incident electron captured by the Coulomb well. For the same reason, *i.e.*, due to vibronic coupling, each highly excited state of a molecule XY^{**} generally contains some admixture of levels belonging to other Rydberg series. If the spacing between two adjacent levels of different series is comparable to the interaction between them, then a strong nonadiabatic coupling regime (strong mixture) takes place. The strong coupling regions are marked in Fig. 1 by square brackets.

The autodecay states of the intermediate species XY^{**} are superpositions of infinite series of Rydberg resonances converging on different vibrational v and rotational N states of the XY^+ ion (*i.e.*, $q = \{v, N\}$).

$$E_{nq} = E_q - \frac{1}{2\,(n-\mu_{nq})^2} - \mathrm{i}\,\Gamma_{nq}/2\,.$$

Here E_q is the excitation energy (total energy of a system refers to the ground ion state), μ_{nq} and Γ_{nq} are the quantum defect and decay width of the level n, respectively, and atomic units ($\hbar = m_e = e = 1$) are used hereafter. The characteristic feature of molecular RS is the predissociation, or the X + Y* fragmentation of the XY^{**} molecule due to the configuration interaction. In addition, the RS usually mix with valence, or non-Rydberg, electronic states. The latter may be quasistationary states (states with quasifinite nuclear motion) which, being immersed in the continuum, form an additional set of resonances in the $e^- + XY^+$ system. Generally, a variety of different types of nonadiabatic coupling is characteristic of most Rydberg systems. This implies that the cross sections of elementary processes should exhibit clear resonant features whose shapes may be complicated by wave interference between distinct channels of motion.

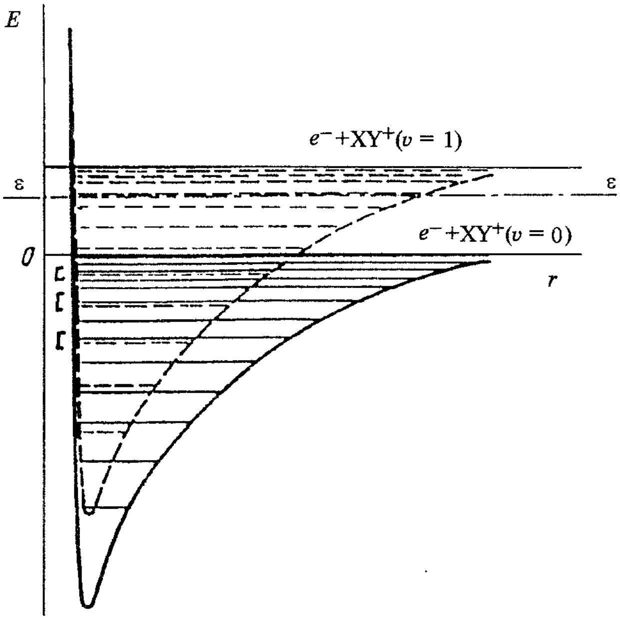

Fig. 1. Schematic overview of the interaction of a slow electron with the XY^+ molecular ion. Dashed line — interaction potential as a function of electron coordinate r and vibronic levels of the first vibrationally excited state of the ion ($v = 1$) for S-scattering. Dash-dotted line — incident electron energy ε. Square brackets indicate the domains of strong nonadiabatic coupling between nuclear and electron motions.

The basic elementary processes involving XY^{**} Rydberg complexes may be qualitatively classified into two groups. The first one includes collision processes

$$\left.\begin{matrix} e^- + XY^+ \\ X+Y^* \end{matrix}\right\} \longrightarrow XY^{**} \longrightarrow \left\{\begin{matrix} e^- + XY^+ \\ X+Y^*\,, \end{matrix}\right. \qquad (1)$$

like elastic and inelastic scattering of slow electrons on XY^+ molecular ions, dissociative recombination (DR) of electrons and ions, associative ionization (AI) of atoms, and various elastic (or inelastic) collisions of atoms in the states which correlate with the dissociative molecular terms lying close to the minimum of the ionic term.

The second important group consists of near threshold photo processes (photoionization and photodissociation)

$$XY + (k+1)\Omega \rightarrow XY^{**} \rightarrow \left\{ \begin{array}{l} e- + XY^+ \\ X+Y^* \end{array} \right. , \qquad (2)$$

induced by single photon ($k = 0$) or multiphoton ($k \neq 0$) absorption of radiation with frequency Ω (or by the simultaneous influence of several fields with different frequencies and intensities). Free radical transitions including bremsstrahlung also belong to this group. Processes (1) and (2) play an important role in the physics of gas lasers, low-temperature plasma, and various atmospheric and astrophysical phenomena.[8]

When considering the dynamic behavior of molecular RS in strong radiation fields it is necessary primarily to understand how the external field may influence the dynamics of elementary processes involving the RS, *i.e.*, to analyze the possibility of laser control for processes (1) and (2). It is also necessary to establish the conditions at which such control and the optical diagnostics of the processes are the most effective. Further, special attention should be paid to the role played by RS in near- and above-threshold multiphoton ionization and dissociation because this problem has not yet been treated theoretically in sufficient detail.

Analyzing the behavior of a quantum system in an external electromagnetic field, the question arises, what does the term "strong" field mean? If the strength of the electric component of the laser field is comparable to or exceeds that of interatomic fields $f_a \geq 5 \cdot 10^9$ V cm^{-1} (corresponding to the intensities ~10^7 W cm^{-2}), the interaction with the electric field should strongly disturb the electronic spectrum, *e.g.*, may result in the detachment of an electron induced by multiphoton absorption as well as in the stabilization of the metastable states above the ionization threshold. This at first glance unexpected phenomena is connected, in the particular case of Rydberg atom X**, with the manifestation of the dynamic Stark effect and Coulomb level shrinkage.[9] The fields possessing the strength $f \geq f_a$ are known as "superstrong". For this reason we apply the terms "strong" or "intense" to a field which, being weak on the atomic scale, strongly mixes states that are stationary (or quasistationary) in the absence of the field. In the case of large mixing coefficients perturbation theory is *a priori* invalid.[10,11]

The treatment given below relies upon the assumption that the external field does not affect the states of the particles at infinite separation. This is certainly true for a free electron if the amplitude of its vibrations in an electromagnetic field ~$f/\omega^2{}_f$ is small compared with its wavelength $\lambda\!\!\!^{-} = 1/p$, *i.e.*, if

$$\xi = \frac{fp}{\omega_f^2} << 1 . \qquad (3)$$

This makes it possible to assign the definite energy $\varepsilon = p^2/2$ (ω_f is the field frequency and p is the electron momentum) to an electron moving in the asymptotic region. If the target is a structureless particle, the only possible channel at small ξ is elastic electron scattering. This makes it evident that the influence of the field on the "electron + target" system may prominently manifests itself only if the system possesses some internal structure. For positive ions this structure is enforced by the formation of the intermediate Rydberg complex XY**. Therefore, under condition (3), the field-induced effects in processes (1) and (2) should exist mainly during the formation of the complex, when the motion of the electron is essentially multichannel. The next restriction assumed for what follows is

$$f\omega_f^{-5/3} << 1 . \qquad (4)$$

This indicates the low probability of free-free transitions in the Coulomb potential ($D \sim \omega_f^{-5/2}$ is the transition dipole moment[12]). Under the conditions formulated above the problem at hand may be investigated within the theory of quantum scattering, which analyzes the perturbations of the continuum states due to the simultaneous interactions of the electron with the target and with the radiation field. This approach has been adopted for studying the dynamics of XY** RS in near-threshold photoionization and photodissociation reactions[13–15] and radiative collisions[16,17] in intense monochromatic laser fields.

Our goal in the present work was to establish the generic trends in the dynamics of a Rydberg molecule in an intense electromagnetic field for a wide range of basic parameters characterizing the system. It is worthwhile to underline that the processes addressed herein take place in the near-threshold region $\varepsilon \sim \omega$ (ω is the vibrational frequency of an XY$^+$ ion) where the Born approximation and semiclassical treatment does not work in principle. In our discussion we will follow the approach developed in Refs. 14—17, namely, the version of multichannel quantum defect theory (MQDT) based on the modified Lippmann—Schwinger equations. This appears to be the most appropriate and transparent for the problems under study. Concrete applications of the theory clearly illustrating the main features of reactions (1) and (2) are given for the H_2 molecule.

Radiative multichannel scattering matrix

If the interaction of the e^- + XY$^+$ system with an external field is described by the time periodic function,

$$u_f = 2\ V^f \cos w_f t, \quad V^f = \frac{\boldsymbol{D}f}{2} \qquad (5)$$

($\boldsymbol{D}$ is the dipole moment operator) and if condition (4) holds, one may utilize the quasienergy representation[18,19] within the stationary MQDT, where the field is accounted for by introducing the quasienergy harmonics and the new channels of motion related to them.[14–17] Thus, the analysis relies upon information on the adiabatic terms of the XY** Rydberg complex, which are thought to be known. The essential ingredients of this picture are shown in Fig. 2. Presented are the Rydberg (U^{**}) and dissociative (U_{X+Y}) terms, as well as the terms of the valence (non-Rydberg) configuration $\underset{\sim}{XY}$ ($U_{\widetilde{XY}}$) with quasifinite nuclear motion. The number of electronic configurations relevant to the problem may be even larger, but after the presentation of the theory, it will be clear that there are no major difficulties in accounting for them. In a rigorous sense, the states shown in Fig. 2 should be considered as diabatic since when they were determined the configuration interaction (V^{CI}), which splits out the terms near their avoided-crossings and is also believed to be known, was ignored. To start our presentation of MQDT, we consider some approaches for studying molecular RS in the absence of external fields (f = 0).

Due to the small value of rotational constant B for molecular ions, the rotationally-adiabatic approximation appears to be valid in almost the entrie energy domain associated with highly excited molecules. Two physical situations, $B = 0$ and $Bn^3 \ll 1$, are of prime practical interest and deserve more detailed discussion.

Fixed molecular axis approximation (B = 0)

The system here is in the coordinate frame defined by the axis of the XY molecules, *i.e.*, is treated within the "strict" adiabatic approximation implying that the rotational constant is infinitely small. In this approximation the zero-order Hamiltonian of the system H_0 can include the interaction potential $V_{nc}{}^0(R_e{}^+)$ between a Rydberg electron and an ionic core XY$^+$ at equilibrium separation $R_e{}^+$. The basis functions therefore are

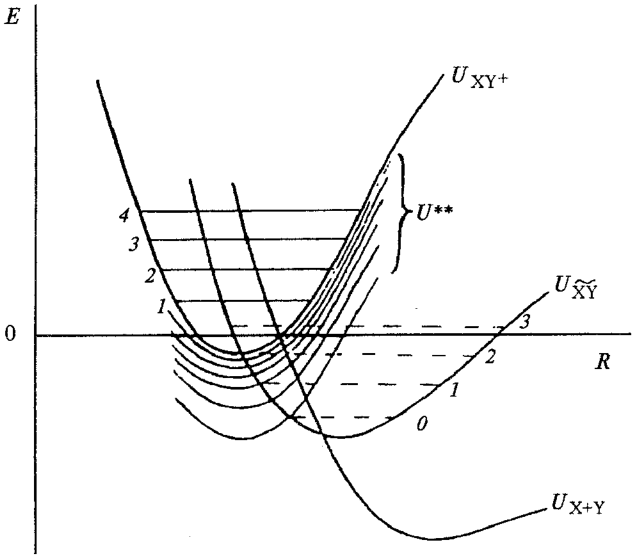

Fig. 2. Diabatic terms of the XY molecule near the continuum threshold. Curly bracket marks the XY** Rydberg series converging to the ionic term. Solid and dashed horizontal lines show vibronic levels of the $\underset{\sim}{XY^+}$ ion and the electronically excited valence (non-Rydberg) $\underset{\sim}{XY}$ state, respectively.

$$|q\rangle = \varphi_{v,\rho\Lambda}\chi_{\upsilon}\phi_{\rho\Lambda}, \tag{6}$$

where $\phi_{v,\rho\Lambda}$ is the radial electronic wave function which differs from the pure Coulomb function beyond the core by the phase shift $\delta_{\rho\Lambda} = \pi\mu_{\rho\Lambda}{}^0$ [$\mu_{\rho\Lambda}{}^0$ is the diabatic quantum defect of the level determined at $V^{CI} = 0$ and at the equilibrium nuclear configuration of the XY$^+$ core, $\mu_{\rho\Lambda}{}^0 = \mu_{\rho\Lambda}(R_e{}^+)$], χ_υ is the vibrational wave function, $\phi_{\rho\Lambda}$ is the angular electronic function, υ is the effective principal quantum number, Λ is the projection of the angular momentum vector onto the molecular axis, and ρ is the effective the angular momentum (for homonuclear diatomics angular momentum l is usually a good quantum number so $\rho = l$, see Refs. 20, 21).

Adiabatic and quasiadiabatic approximations

In case of finite values of B ($Bn^3 << 1$) one can invoke the rotationally adiabatic or the quasiadiabatic approximation where the quantum defect $\mu_{\rho\Lambda}{}^0$ is thought to be a weak function of electron energy and, therefore, the rotational dependence is enforced:

$$\mu_\varkappa{}^0(n) \cong \mu_{\rho\Lambda}{}^0 + g_{\rho\Lambda}{}^J Bn^3 + \ldots\ , \varkappa = \{J,\ \rho,\ \Lambda\}.$$

The expansion coefficients $g_{\rho\Lambda}{}^J$ depend on the total angular momentum of the system J. In this representation the basis functions are

$$|q\rangle = \varphi_{v,\rho\Lambda}\chi_\upsilon\phi_{\rho\Lambda}D_{M\Lambda}{}^J(\hat{R})[\frac{2J+1}{4\pi}]^{1/2}, \tag{7}$$

where $\varphi_{v,\rho\Lambda}$ is given by Eq. (6), $D_{M\Lambda}{}^J$ is the generalized spherical function (Wigner rotational matrix), and $\hat{R}$ denotes the set of angles specifying the orientation of the XY molecule. The advantage of approximations (6) and (7) is that the term $V_{nc}{}^0(R_e{}^+)$, common for all Rydberg states, is eliminated in the total Hamiltonian $H = H_0 + V_{nc}{}^0 + V^{CI}$, so the $V_{nc}{}^0 = V_{nc} - V_{nc}(R_e{}^+)$ term causes only weak perturbation of the basis states. All interactions for the isolated (diabatic) X + Y and $\underset{\sim}{XY}$ configurations are included in the zero-order Hamiltonian H_0 and are treated rigorously.

Nonadiabatic rotational coupling ($Bn^3 \geq 1$)

Since in this case the strong nonadiabatic coupling between the molecular rotations and the motion of an electron makes it imposible to separate out the $V_{nc}(R_e{}^+)$ term, one must adopt the following scheme: the radial wave functions are expressed through the set of Coulomb orbitals R_{vl} in the absence of electron-core interaction, while the angular functions of the Rydberg electron are described by a representation possessing total angular momentum J, its projection M, orbital momentum of an electron l, and rotational momentum N, *i.e.*,[22]

$$\phi_{lN}^{JM}(\hat{r}\hat{R}) = \sum_m Y_{lm}(\hat{r})Y_{N,M-m}(\hat{R})(lNmM-m|JM), \qquad (8)$$

where $\hat{r}$ and $\hat{R}$ are the spherical coordinates of the electron and nuclei, respectively, Y_{lm} are the spherical harmonics, and $(lNmM-m|JM)$ are the vector coupling coefficients. The V_{nc} operator contains the non-Coulomb part of the electron-XY$^+$ interaction. For the X + Y and XY configurations (see Fig. 2) the corresponding diabatic basis functions may be written either in the molecular axis frame ($B = 0$) or in the adiabatic approximation. It is convenient to normalize the radial functions of the open Rydberg and dissociative configurations ($|q>$ and $|\beta>$, respectively) as

$$<q(E)/q(E')> = <\beta(E)/\beta(E')> = \pi\delta(E-E'),$$

whereas the bound-state wave functions $|s>$ associated with the isolated XY configuration should be normalized to unity.

Within all of the above approximations the MQDT equations can be obtained by the general scheme using a scattering T-matrix (the scattering S-matrix is related to the T-matrix by the equation $S = 1 - 2iT$). Once the basis states and interaction operator V are determined, one may turn to the formulation of the radiative collision problem. The energy transfer for the interaction of the e^- + XY$^+$ system with a radiation field is proportional to the electromagnetic field quantum ω_f, so it is convenient to use a quasienergy representation in which the eigenvalues of the system's Hamiltonian are combined with different photon numbers $N + m$ ($N >> 1$). The additional index m specifies the number of photons absorbed by a system. The field induced interaction V^f mixes the new channels corresponding to different m numbers. The resulting energy level diagram for $m = 0$ and $m = -1$ is sketched in Fig. 3, where the initial terms for the ionic and dissociative configurations correspond to $m = 0$ and the valence XY term is not shown for simplicity.

By introducing the compound operator $V = V^e + V^f$ (where $V^e = V_{nc} + V^{CI}$) and the extended basis as explained above, one arrives at the following fundamental operator equation for the radiative multichannel scattering T-matrix

$$T = t - it\sum_p |p><p|T + t\sum_c |c><c|\frac{1}{\lambda(E)}T, \qquad (9)$$

where $|p>$ and $|c>$ are the wave functions of open (p) and closed (c) scattering channels, E is the total energy of the system, and $\lambda(E)$ is the diagonal matrix of the eigenenergies associated with the closed channels of the Rydberg configuration and the energy levels belonging to the isolated valence XY configuration, namely, $\lambda_{cc} = tg\pi\nu_c(E)$ for Rydberg channels and $\lambda_{cc} = E - E_c$ for valence states (ν_c is the effective principal quantum number of the closed channel and E_c are the characteristic energies of the XY configuration). The T-matrix can be found directly from Eq. (9) whose rank N is the sum of N_0, the number of open channels (N_0 enumerates the continuum states of e^- + XY$^+$ system as well as the dissociative channels X + Y), N_c^R is the number of closed Rydberg channels, and N_c^V is the number of states to be accounted for in the XY valence configuration. Equation (9) can also be reformulated as the general formal relation which expresses the desired T_{00} matrix connecting the open channels of $N_0 \times N_0$ rank *via* the submatrices T'_{00} (rank $N_0 \times N_0$), T'_{cc} (rank $N_c \times N_c$), and T'_{0c} (rank $N_0 \times N_c$) obeying the equation

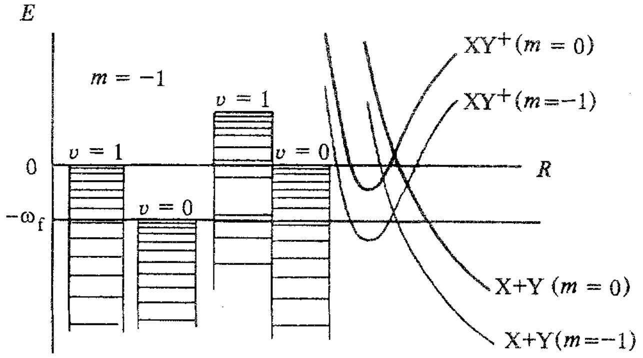

Fig. 3. Diabatic terms of the e^- + XY$^+$ and X + Y configurations. Horizontal lines are the quasienergy representation of the vibronic Rydberg levels XY** converging to the corresponding thresholds for $m = 0$ and $m = -1$.

$$T' = t - it\sum_{p=1}^{N_0} |p><p|T',$$

namely,

$$T_{00} = T'_{00} + T'_{0c}\frac{1}{\lambda(E) - T'_{cc}}T'_{c0}, \qquad (10)$$

where

$$T'_{cc} = t_{cc} - it_{c0}T'_{0c}.$$

Equation (10), as well as the well-known Gailitis—Seaton relation for the multichannel scattering S-matrix (for the Coulomb attraction persisting in all channels of motion),[23,24] is written for the physically observable characteristics. At the same time it more clearly underlines the resonant structure of the transitions: the roots of the determinant

$$\det|\lambda(E) - t_{cc} + it_{c0}T'_{0c}| = 0$$

correspond to the energy levels interacting with the continua of quasidiscrete states. For example, in the case of isolated resonance ($N_c^R = 0$, $N_c^V = 1$) Eq. (10)

reduces to the common Breit—Wigner formula (along with the direct determination of the phase relation between background and resonance contributions). Moreover, the relation obtained above is more general, taking into account the reactive channels and the interacting quasistationary states of arbitrary closed channels, and it is able to describe processes (1) and (2) in the presence of an external periodic field.

Qualitatively, the consequences of laser action on the $e^- + \mathrm{XY}^+$ system may be immediately seen in Eq. (10). Obviously, they originate from the resonant contributions of the second term, *i.e.*, (*i*) the alteration of the decay characteristics for those resonances which are important without a field ($m = 0$ terms); (*ii*) the appearance of laser induced resonances ($m \neq 0$); (*iii*) the overlapping of resonances belonging to different Rydberg series and their mixing by the field (Rydberg states).

Let us now define the operator t in Eq. (9) and establish how its matrix elements are related to the parameters of the adiabatic molecular terms of XY**. Describing the interaction of an electron with an ionic core in the presence of an electromagnetic field, the operator t obeys the equation

$$t = V + VG(E)t, \tag{11}$$

where the Green function excludes the interaction V, smoothly depends on energy, and consists of the Rydberg $e^- + \mathrm{XY}^+$ contributions [except the poles associated with the discrete spectrum of the Coulomb center already accounted for in Eq. (9)] as well as the contributions from the dissociative states X + Y. Thus*

$$G(E) = \frac{1}{\pi}\sum_{q,m} P\int \frac{|q_m\rangle\langle q_m|}{E - E_q - m\omega_\mathrm{f} - \varepsilon}\,\mathrm{d}\varepsilon +$$

$$+ \frac{1}{\pi}\sum_{\beta,m} P\int \frac{|\beta_m\rangle\langle \beta_m|}{E - m\omega_\mathrm{f} - \varepsilon'_\beta}\,\mathrm{d}\varepsilon_\beta\,,$$

where P symbolized the principal value of the integral. The matrix elements

$$\langle q_m|V^\mathrm{e}|\beta_m\rangle,\ \langle q_m|V^\mathrm{e}|\mathrm{s}_m\rangle \text{ and } \langle \beta_m|V^\mathrm{e}|\mathrm{s}_m\rangle, \tag{12}$$

are diagonal in m and represent the $e^- + \mathrm{XY}^+$ and X + Y, $e^- + \mathrm{XY}^+$ and $\widetilde{\mathrm{XY}}$, and X + Y and $\widetilde{\mathrm{XY}}$ state interactions, respectively. The elements $\langle q_m|V^\mathrm{e}|q'_m\rangle$ are responsible for the vibronic transition in the $e^- + \mathrm{XY}^+$ system. The matrix elements of operator V^f couple the states with m and $m' = m \pm 1$. Under the conditions of interest, (3), (4), they should be small compared to the characteristic variations of the Green function $G(E)$.

The structure of Eq. (9) allows one to use the algebraic approach for construction of the unit scattering S-matrix for an arbitrary number of channels. Elements $T_{q_m\beta'_{m'}}$ and $T_{q_m q'_{m'}}$ with indices corresponding to the open channels (*i.e.*, $E > E_q + m\omega_\mathrm{f}$ and $\mathrm{ctg}\pi\nu_q = -\mathrm{i}$) characterize the amplitudes of inelastic scattering and the dissociative recombination reaction (2). In this case the smallness of the configuration coupling together with the condition $A/R_\mathrm{e}^+ \ll 1$ (where A is the zero-point vibrational amplitude of the ionic core) permits one to include a finite number of states in Eq. (9). Since the configuration interaction reflects the particular features of the molecular electronic structure, the smallness of the configuration coupling is not obvious, but for the well-studied $e^- + \mathrm{XY}^+$ systems ($\mathrm{XY}^+ = \mathrm{H_2}^+$, $\mathrm{N_2}^+$, NO^+, O^+, and so on) it indeed occurs (in the sense that matrix elements of (12) are less then unity). This fact allows one to evaluate the matrix elements of operator t iteratively substituting V for t in the right-hand side of Eq. (11). As a result, operator t can be recast in two terms

$$t = t^\mathrm{e} + t^\mathrm{f} \tag{13}$$

with the elements

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

$$t^\mathrm{e}_{q_m\beta_m} = V^\mathrm{e}_{q_m\beta_m} + \frac{1}{\pi}\sum_{q'} P\int \frac{t^{(0)}_{q_m q'_m} V^\mathrm{e}_{q'_m\beta_m}}{E - E_q - m\omega_\mathrm{f} - \varepsilon}\,\mathrm{d}\varepsilon \tag{14}$$

and $t^\mathrm{e}_{\beta_m s_m}$, $t^\mathrm{e}_{q_m s_m}$, and $t^\mathrm{e}_{\beta_m\beta_m}$ having an analogous form. The matrix elements $t^{(0)}_{q_m q'_m}$ in Eq. (14) are related to the diabatic quantum defects by unitary transformation

$$t^{(0)}_{q_m q'_m} = -\sum_{\rho\Lambda} U^J_{lN,\rho\Lambda} \langle \chi_v|\mathrm{tg}\,\pi\mu_{\rho\Lambda}|\chi_{v'}\rangle\, U^J_{\rho\Lambda,l'N'}$$

$$\Big(\sum_{lN} U^J_{lN,\rho'\Lambda'} U^J_{\rho\Lambda,lN} = \delta_{\rho\rho'}\delta_{\Lambda\Lambda'},\ q = \{J, l, N, v\}\Big).$$

Hence, in order to solve the problem it is necessary to obtain information on the diabatic quantum defects $\mu_{\rho\Lambda}$ (also referred to as eigenphases[25]) which parametrically depends on the internuclear distance R in the XY** molecule. The number of these parameters is equal to the total number of states with different l quantum numbers which form the Rydberg state having a definite angular momentum projection Λ and total angular momentum J. In addition, the $c_{\rho\Lambda}{}^l$ coefficients in the expansion of the basis functions over the Coulomb orbitals should also be known in order to specify the transformation matrix U.[26] They can be calculated by the quantum-chemical methods.

The second term in the expansion of operator t (13), which describes the effective interaction with a radiation

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* In the first term of $G(E)$, which corresponds to the contribution from the $e^- + \mathrm{XY}^+$ configuration with isolated poles, the summation over n is replaced by integration and the wave functions of both the discrete and continuum states are normalized to the δ-function of energy.

field, is defined up to terms quadratic in V^{f} as

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

If Eq. (4) is taken into account, it is sufficient to retain the terms linear in f to evaluate t^{f} matrix elements, so

$$t^{f}_{q_m q'_{m\pm1}} = \frac{1}{2} f r_{e} S^{JJ'}_{lN,l'N'}(\mathbf{f}/f)\delta_{vv'}, \tag{15}$$

where the radial part of the transition dipole element is[15]

$$r_{e} \sim \omega_{f}^{-5/3}\cos[\pi(\Delta\mu_{\rho\Lambda,\rho'\Lambda'} + 1/6)]$$

($\Delta\mu_{\rho\Lambda,\rho'\Lambda'} = \mu_{\rho\Lambda}{}^{0} - \mu_{\rho'\Lambda'}{}^{0}$ is the corresponding quantum defect difference), whereas its angular part $S^{JJ'}{}_{lN,l'N'}$ depends on the direction of the vector $\mathbf{f}$ and is analogous to the Hönl—London factors which determines the intensity distribution over the rotational levels.[27]

To describe the energy spectrum of a system and analyze its features, it is convenient to introduce the adiabatic quantum defect $\tilde{\mu}_{\rho\Lambda}(R)$ which accounts for interaction with the dissociative continuum. The action of the external electromagnetic field makes $\tilde{\mu}_{\rho\Lambda}$ dependent on m and ω_{f}. Indeed, it can be shown that quantum defects of the $\rho\Lambda m$-series in the field obey the equation

$$\mathrm{tg}\pi\tilde{\mu}^{(m)}_{\rho\Lambda} - \mathrm{tg}\pi\mu_{\rho\Lambda} = \sum_{\beta}\frac{(V^{(\rho\Lambda)}_{\beta}(R))^{2}}{U_{\beta}(R) - U^{**(m)}_{\rho\Lambda}(R) + m\omega_{f}}, \tag{16}$$

where the adiabatic Rydberg term is defined as

$$U^{**(m)}_{\rho\Lambda}(R) = -\frac{1}{2(n - \tilde{\mu}^{(m)}_{\rho\Lambda}(R))^{2}} + U_{XY^{+}}. \tag{17}$$

The value $V_{\beta}{}^{(\rho\Lambda)}(R)$ is the electronic part of the configuration interaction between the $\rho\Lambda$ and β states. As follows from Eq. (16), near the crossing point $R_{*}{}^{m}$ given by the condition

$$U_{\rho\Lambda}{}^{**(m)}(R_{*}{}^{m}) = U_{\beta}(R_{*}{}^{m}) + m\omega_{f},$$

the adiabatic quantum defect increases by unity.

Radiative collision processes of e^{-} + XY^{+}

Cross sections of laser-induced processes

Let us analyze now the influence of monochromatic IR-radiation on multichannel electron scattering on positive molecular ions at the arbitrary frequency ratio $\omega \neq \omega_{f}$. The external field strongly complicates the spectrum near the threshold creating additional states of the XY** complex with shifted energy $m\omega_{f}$. These laser-induced resonances (possessing a different number of absorbed photons) should manifest themselves in the cross sections of the scattering processes occuring either by direct transitions in the final states, or *via* the formation and subsequent decay of collisional complexes. The influence of these pathways further complicates the energy dependence of the cross sections.

In what follows we will rely upon the rotational adiabatic approximation which, as mentioned above, is valid for the energy range where the condition $Bn^{3} \ll 1$ holds for quasidiscrete states of XY**. It is worth noting that in carrying out this analysis in the molecular fixed frame, it becomes necessary to average the calculated cross section (1) over the orientational angles. In the $Bn^{3} \ll 1$ approximation, which assumes the finite rotational quantum B, the averaging is performed over N_{f}, the projection of rotational momentum N onto the $\mathbf{f}$ vector. Clearly, the latter approach is more general and contains the former one under the relevant limiting conditions.

In the standard scattering problem with fixed directions of the incident and scattered particles, the wave function of the e^{-} + XY^{+}(v, N) system in the JM-representation (J and M are the total angular momentum and its projection in the direction $\mathbf{f}$) has the form*

$$\Psi_{e^{-}+XY^{+}} = \sum_{l\Lambda,JM} i^{l}e^{i\delta_{l\Lambda}}Y_{l\Lambda}(\mathbf{n}_{e})(lN\Lambda M{-}\Lambda|JM) \times \tag{18}$$
$$\times\ (lN\Lambda 0|J\Lambda)|l\Lambda v, JM>,$$

where $\delta_{l\Lambda}$ is the phase shift acquired by an electron at the potential produced by the Coulomb field and the interaction with an XY^{+} core at the equilibrium internuclear distance, namely,

$$\delta_{l\Lambda} = \arg\Gamma(l + 1 - i/p) + \pi\mu_{l\Lambda}{}^{0},$$

where $\Gamma(x)$ is the Gamma-function. The wave function of the reactive X + Y channel can be conveniently expressed in the helical representation[28,29] which, in addition to the direction of the incident particle given by the unit vector $\mathbf{n}_{\beta}$, specifies the projections Λ, Λ' of the electronic angular momentum on $\mathbf{n}_{\beta}$ and $\mathbf{R}$ directions, respectively:

$$\Psi_{X+Y} = \sum_{\Lambda,JM} i^{J}e^{-i\delta_{J}}\sqrt{\frac{2J+1}{4\pi}}D^{J}_{M-\Lambda'}(\varphi_{\beta},\theta_{\beta},0)|\beta\Lambda,JM>. \tag{19}$$

Here δ_{J} denotes the phase of X + Y elastic scattering, φ_{β} and θ_{β} are the azimuthal and polar angles of $\mathbf{n}_{\beta}$ relative to the vector $\mathbf{f}$. It is important that expressions (18), (19) use the same set of basis functions (7), which

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* The previously adopted[30] notations are used for the spherical functions $Y_{l\Lambda}{}^{(n)}$, generalized spherical functions $D_{MK}{}^{J}(\alpha,\beta,\gamma)$, and vector addition coefficients $(lN\Lambda M{-}\Lambda|JM)$.

define the rotationally adiabatic version of the equations for the radiative scattering T-matrix. In this formulation the T-matrix is invariant under the transformation of the reference frame, *i.e.*, it commutes with the operators generating the corresponding rotations. Hence, their matrix elements should depend only on the scalar product of $\boldsymbol{n}_e$, $\boldsymbol{n}_\beta$, and $\boldsymbol{f}$ vectors. The total cross section for any collisional process of type (1) is then

$$\sigma_{if} = \frac{8\pi^2}{E}\sum_S g_S|<\Psi_i|T|\Psi_f>|^2, \tag{20}$$

where g_S is the statistical weight of the state with given spin S, ψ_i and ψ_f are the wave functions of the initial (i) and final (f) scattering channels written in representations (18), (19). The cross section (20) is proportional to the amplitude $<\psi_i|T|\psi_f>$, the superposition of the partial amplitudes $T_{qq'}$. After averaging over the orientations of $\boldsymbol{n}_e$ and $\boldsymbol{n}_{e'}$ (or $\boldsymbol{n}_\beta$) the cross section is expressed through the squared amplitudes $|T_{qq'}|^2$.

Influence of a field on the isolated resonances

When considering the effect of laser irradiation on the RS of an XY** complex it is of prime importance to answer the question of how the field changes the isolated resonances of the system. The latter are either vibronic resonances (existing without the field) or additional resonances created by the field (with definite J, M quantum numbers). Below the vibrational threshold of the XY^+ molecular ion, where the nearest closed channel $v = 1$ supports numerous resonance states (see Fig. 1), the dissociative recombination cross section exhibits an infinite sequence of Fano—Feshbach resonances whose spacing, width, and intensity, decrease by $1/n^3$ as n increases. This generic behavior may be illustrated by the formula for the transition at energy E in the vicinity of arbitrary resonance E_n belonging to this series ($\varepsilon = E - E_n$)

$$|T_{\beta_0 0_0}|^2 = W_0\frac{(\varepsilon-\Delta_n^f-\Delta_n^\beta)^2+(\Gamma_n^f)^2}{(\varepsilon-\Delta_n^f)^2+\Gamma_n{}^2}, \tag{21}$$

$$W_0 = |t^e_{\beta_0 0_0}|^2,\ \Delta_n^\beta = -t^e_{1_0 0_0}t^e_{\beta_0 1_0}/\pi n^3 t^e_{\beta_0 0_0},\ \Gamma_n = \Gamma_n^e + \Gamma_n^f.$$

Here $\Gamma_n^e = \Gamma_n^i + \Gamma_n^\beta$ is the total (autoionization plus predissociation) natural decay halfwidth, and $\Delta_n{}^f$ and $\Gamma_n{}^f$ are the field-induced shift and broadening of level E_n. The equation $\Gamma_n = \gamma/\pi n^3$ relates Γ_n with the partial autoionization, predissociation, to the field-induced decay rates γ^i, γ^β, and γ^f, respectively, which are proportional to the following matrix elements:

$$\gamma^i{}_{v_m} = |t^e{}_{v_m,(v-1)_m}|^2,\ \gamma^\beta{}_{v_m} = |t^e{}_{\beta_m v_m}|^2,$$

$$\gamma^f_{v_m} = \sum_{J'M'l'N'}|t^f_{v_m v_{m-1}}(JMlN\rightarrow J'M'l'N')|^2,$$

where the summation runs over the dipole-allowed $J'M'l'N'$ states. Equation (21) makes it easy to trace the evolution of the Fano profile from $f = 0$ to field strengths at which the field-induced broadening is comparable or even exceeds the natural halfwidths, $\Gamma_n{}^f = \Gamma_n{}^e$. Obviously, the line profile is shifted and spread with increasing f so that the "window of transparency" (the energy domain $E = E_n + \Delta_n{}^\beta$ where the partial cross section vanishes) disappears, and is replaced by the cross section maximum. At the same time the intensity of the resonance line

$$I_n = \pi\frac{\Gamma_n^i\Gamma_n^\beta}{\Gamma_n^e\Gamma_n^f}$$

goes to zero ($\approx 1/f^2$) if $\Gamma_n{}^f \gg \Gamma_n{}^e$.

A field-induced resonance exhibits simple Breit—Wigner dependence ($m = \pm 1$)

$$|T_{\beta_0 0_0}|^2 = \frac{\Gamma^\beta_{n'}\Gamma^f_{n'}}{(\varepsilon-\Delta^f_{n'})^2+\Gamma^2_{n'}}, \tag{22}$$

$$\Gamma_{n'} = \Gamma^\beta_{n'} + \Gamma^f_{n'}$$

since the intensity of the radiative transition in the dissociative continuum is as a rule remarkably lower than that of the dipole transition between the molecular Rydberg states due to the large difference in the electronic energies in the X + Y and XY** configurations. The increase in f also forces profile (22) to spread out,

$$I_{n'} = \pi\frac{\Gamma^\beta_{n'}\Gamma^f_{n'}}{\Gamma_{n'}}$$

whereas the line intensity increases as $\sim f^2$ at low f and approaches the limiting value $I_{n'} = \Gamma_n{}^\beta$ at $\Gamma_n{}^f \gg \Gamma_n{}^\beta$. The above analysis is applicable in the case where the field-induced shift $\Delta_n{}^f$ and width $\Gamma_n{}^f$ do not exceed the Rydberg level spacing, *i.e.*, $\Delta_n{}^f$ and $\Gamma_n{}^f \ll 1/n^3$. The features appearing at $\Delta_n{}^f$, $\Gamma_n{}^f \geq 1/n^3$ will be considered in the next section.

Equations (21) and (22) describe the dissociative recombination of electrons and molecular ions, a process analogous to chemical substitution reactions. At the same time, expressions of the same kind are useful for another important plasmochemical process which controls the kinetic energy distribution function of electrons, namely, the vibrational excitation of molecular ions by slow electrons. Let us consider p-electron scattering

$$e^- + H_2{}^+ (v = 0) \rightarrow H_2{}^{**} (p_{\sigma,\pi},\ v = 2) \rightarrow e^- + H_2{}^+ (v = 1)$$

as a suitable example (the pσ- and pπ-Rydberg series of the $H_2{}^{**}$ molecule are investigated in the most detail).

In the absence of an external field a molecular ion can be excited vibrationally only if $E > \omega$ (ω is the $H_2{}^+$

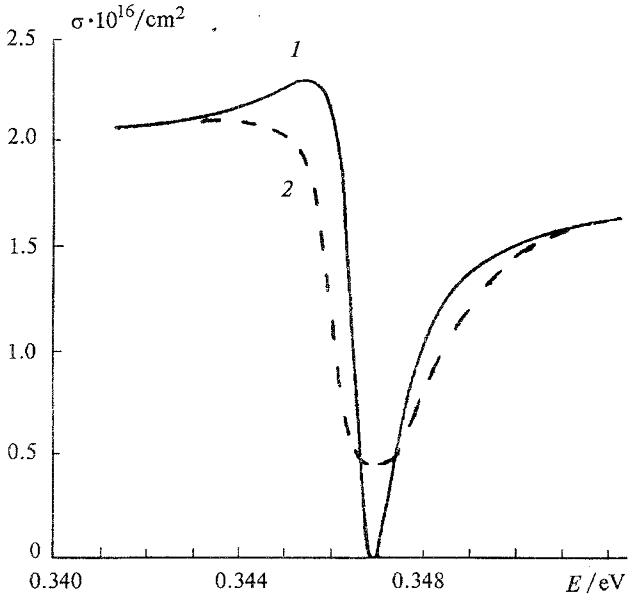

Fig. 4. Energy dependence of the cross section of the inelastic 0→1 transition for electron scattering on the H_2^+ ion near the 8pσ (v = 2) resonance. The solid line (*1*) corresponds to $f = 0$ (two closed channels v = 2 and v = 3 are included in calculation) and the dashed one (*2*) to $f = 10^{-3}$.

vibrational quantum); at $\omega < E < 2\omega$ collisions preferentially populate autoionizing Rydberg series associated with v = 2 and weakly coupled with dissociative channels. For this reason the isolated resonance E_{n_2} is described by a formula close to (21) but with the difference that now for the shift $\Delta^{f}_{n_2} \ll \Gamma^{i}_{n_2}$. Hence, the observed profile has an "antiresonance" character since capture in the v = 2 resonance state requires two quantum transitions. Fig. 4 shows the "antiresonance" transformation in the H_2^+ vibrational excitation cross section upon the application of an electromagnetic field.

It should be noted that in the IR radiation field vibrational excitation of ions is also effective below the threshold (for instance, in the $\omega - \omega_f < E < \omega$ energy range at $\omega_f < \omega$) owing to the population of the intermediate state (v = 1, m = 0) followed by its decay into the channel with the same vibrational excitation (v = 1, m = −1). The probability of this process compared to the background process at $E > \omega$ obeys the relation

$$\frac{1}{\pi n_2^3}\left(\frac{\Gamma^{f}_{n'_1}\Gamma^{i}_{n'_1}}{\Gamma_{n'_1}\Gamma^{i}_{n_2}}\right), \Gamma_{n'_1} = \Gamma^{i}_{n'_1} + \Gamma^{f}_{n'_1} .$$

Along with the energy dependence of the cross sections, prime attention should be paid to the features pertinent to beam experiments, which control the direction of the electron beam relative to the vector f (in the case of linear polarization). The reaction product yield can be a function of the mutual orientation of the electron and light beams. This may be demonstrated by the relation

$$e^- + H_2^+\ (v = 0) + N_0\omega_f \rightarrow H_2^{**} \rightarrow H^* + H + N\omega_f \quad (23)$$

where N is the number of photons in the system, which differs from the initial number by $m = N - N_0$. For the ndσ_g ($^1\Sigma_g^+$) Rydberg series, which predissociates when interacting with a repulsive valence $(2p\sigma_u)^2$ configuration, the angular momentum l = 2 is a good quantum number.[31] The corresponding diagram of the H_2^{**} molecular term is depicted in Fig. 5. The dominant contribution to reaction (23) belongs to the radiationless transitions that form the Rydberg complex (v = 1, m = 0) and to the transitions into the (v = 0, m = 1) states accompanied by emission of a photon.

The results of the calculation of singlet scattering (g = 1/4) by Eqs. (18)—(20) utilizing data[31] on the diabatic quantum defect $\mu_{l\Lambda}(R)$, the dissociative potential curve U_β(R), and interaction $V_\beta(R)$ are shown in Fig. 6. The curve for reaction (23) near the isolated vibronic resonance n_{01} = 8 (v = 1) in the absence of an external field is plotted in Fig. 6, *a* together with previously calculated data.[31,32] The dash-dotted line repro-

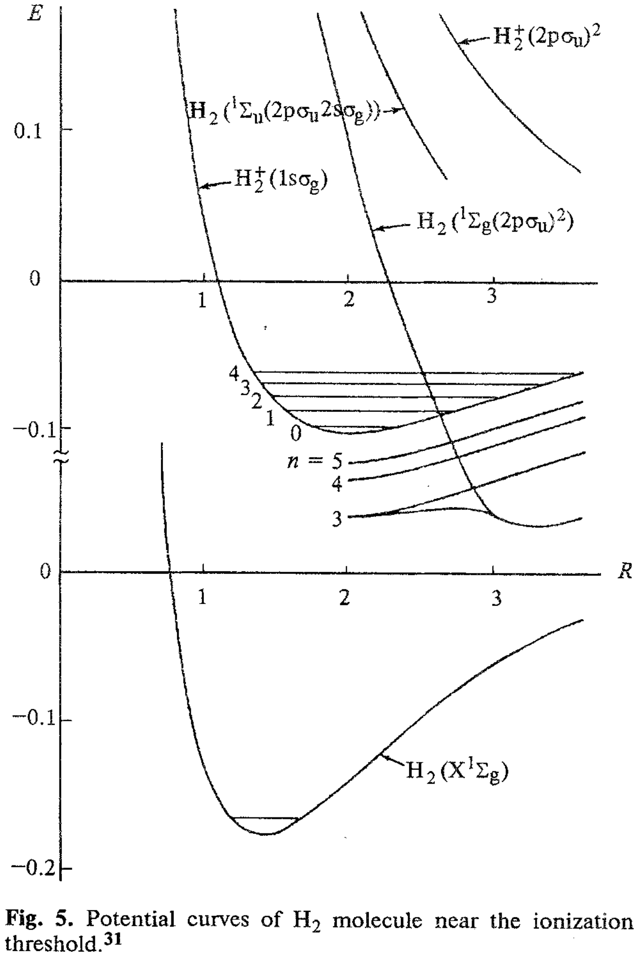

Fig. 5. Potential curves of H_2 molecule near the ionization threshold.[31]

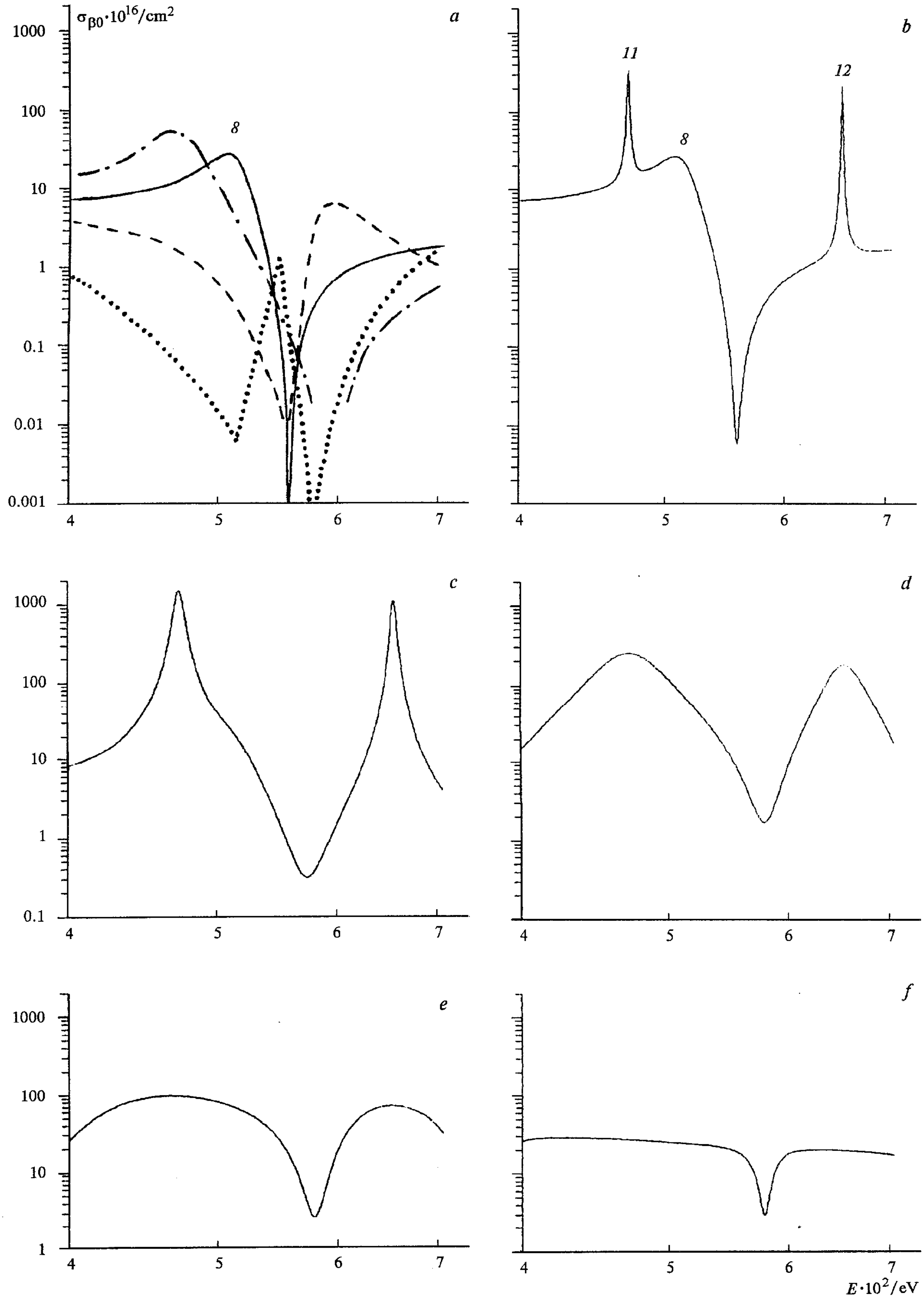

Fig. 6. Dependences of the cross section on electron energy for reaction (23) at $f = 0$ (solid line, see text) (*a*), 10^{-4} (*b*), 10^{-3} (*c*), $2\cdot10^{-3}$ (*d*), $5\cdot10^{-3}$ (*e*), 10^{-2} (*f*).

duces the results of Bardsley's theory,[32] which neglects the interaction of closed channels. The previously suggested version of MQDT[31] takes this effect into account, but ignores the virtual vibrational transition through the dissociative continuum (in other words, the second term in Eq. (14), responsible for such transitions, is omitted in the calculation of $t^e_{q_m q_{m'}}$ matrix elements[31,32]). For this reason the dependencies[31,32] (shown in Fig. 6, *a* by dotted and dashed lines, respectively) exhibit a clear "antiresonance" character pertinent to the case of small profile indexes. In our version of MQDT the vibronic transitions through the dissociative continuum are correctly included (for simplicity, to describe the dissociative recombination in an external electromagnetic field we considered only one closed channel $v = 1$ in the energy region where this simplification is valid), so our results are close to those of Bardsley.[32] However, we used more accurate data[31] for the parameters of the $e^- + H_2^+$ system. The dependence of the DR cross section (23) on the field strength f is demonstrated in Fig. 6, *b—f.* These curves are calculated for $\theta_e = 0$, *i.e.*, for the mutually perpendicular orientation of the incident electron and photon beams. The numbers on the lines of 6 *a, b* indicate the positions of the vibronic ($n_{10} = 8$) and field-induced ($n_{01} = 11$ and 12) resonances ($\omega_f = 0.6\omega$).

Let us now inspect the angular dependence of the cross sections. For low light strengths ($f \sim 10^{-5}$) the simple formula

$$\sigma_{\beta 0}(E, f, \theta_e)/\sigma_{\beta 0}(E, f, 0) = 1 - f^2 W(E, f)\sin^2\theta_e,$$

holds. Here $\theta_e = \arccos(\boldsymbol{n}_e\boldsymbol{f}/f)$ and $W(E, f)$ is a non-monotonic energy function which reaches the maximum in the vicinity of the $\sigma_{\beta 0}$ cross section minimum. The next maximum of this function reflects the field-induced resonance. The least pronounced patterns are observed in the vicinity of vibronic resonance $E_{n_{10}}$. The dependence of $W(E, f)$ on f appears to be rather weak. At $f \geq 10^{-3}$ the angular distribution becomes independent of the field strength and only slightly varies with the energy on a scale of $\sim 1/n^3$. Since at such strengths the resonant patterns of the cross section are degenerate (see Fig. 6, *f*), the same distribution should be the case also for weakly collimated electron beams with effective energy averaging. It should be noted, however, that these features are specific for H_2^{**} complexes, caused by the existence of an isolated predissociative $d\sigma_g$-orbital in the energy range under study. Nevertheless, since the anisotropy of the DR cross sections is completely determined by the types of Rydberg molecular orbitals in the intermediate XY** complex, it should be calculated directly for each particular case.

Now we turn to the dependence of the total cross section on the field strength. At $f \geq 10^{-5}$ the reaction cross section increases as $\sim f^2$. If f increases further, it reaches the maximum at $f \sim 10^{-3}$, *i.e.*, when the field-induced widths match the natural ones. At $\theta_e = 0$ geometry the conditions for field initiation of reaction (23) are the most favorable and the cross section can be enhanced dramatically (by up to an order of magnitude). Averaging over the θ_e angles, which corresponds to plasma conditions, yields for the DR cross section

$$\sigma_{\beta 0}(f) = \frac{2\pi}{E}\sum_S g_S \sum_{l\Lambda,m} \overline{|T^{(l\Lambda)}_{\beta_m 0_0}(f)|^2} , \tag{24}$$

where the squared absolute values of the partial amplitudes ($m = 0, 1$) are

$$\overline{|T^{(l\Lambda)}_{\beta_0 0_0}|^2} = \gamma^{\beta}_{0_0} + \gamma^{\beta}_{1_0}\gamma^{i}_{1_0}/\gamma_{1_0} ,$$

$$\overline{|T^{(l\Lambda)}_{\beta_1 0_0}|^2} = \gamma^{\beta}_{0_1}\gamma^{f}_{0_1}/\gamma_{0_1} .$$

The total decay rates in these expressions are defined as

$$\gamma_{1_0}(f) = \gamma^{i}_{1_0} + \gamma^{\beta}_{1_0} + \gamma^{f}_{1_0}(f) ,$$

$$\gamma_{0_1}(f) = \gamma^{\beta}_{0_1} + \gamma^{f}_{0_1}(f) ,$$

while the corresponding partial rates are related to the squared absolute values of the t-operator matrix elements (14) and (15). According to Eq. (15) $\gamma^{f}_{0_1}(f) = \gamma^{f}_{1_0}(f) = \gamma^{f}$, so for cross section (24) one has

$$\sigma^{(l\Lambda)}_{\beta 0}(f) = \sigma^{(l\Lambda)}_{\beta 0}(\text{direct})[2 - \frac{\gamma_0^{\beta}}{\gamma_0^{\beta} + \gamma^{f}} + \frac{\gamma_1^{\beta}\gamma_1^{i}}{\gamma_0^{\beta}} \cdot \frac{1}{\gamma_1^{i} + \gamma_1^{\beta} + \gamma^{f}}], \tag{25}$$

where the function

$$\sigma^{(l\Lambda)}_{\beta 0}(\text{direct}) = \frac{2\pi}{E} g_S \gamma_0^{\beta(l\Lambda)}$$

is the partial cross section of the direct (background) processes in the absence of an external field (the derivation of Eq. (25) relies upon the additional assumption of the weak energy dependence of predissociation rates, *i.e.*, $\gamma^{\beta}{}_{0_0} = \gamma^{\beta}{}_{0_1} = \gamma^{\beta}{}_{0}$). In the limiting cases of small ($t^f \ll t^e$) and large ($t^f \gg t^e$) strengths, formula (25) admits drastic simplifications. In the weak field limit, for instance, the total DR cross section may be recast into two terms such that one of them does not depend on the field and the other increases with f as f^2. At large strengths cross section (25) appears to be a weak function of f, which approaches the asymptotic value $2\sigma_{\beta 0}{}^{(l\Lambda)}$ (background). If in the field-free regime the background contribution to DR dominates [$\sigma_{\beta 0}(0) > \sigma_{\beta 0}$ (direct)], the external field accelerates the process. On the contrary, if the resonant mechanism prevails and the opposite relation holds, the processes should be retarded under the influence of the external field. The gain in product yield in this case does not exceed 2. Therefore, depending on the particular nature of the XY molecule, the DR reaction rate may be controlled by the external field. In some situations the irradiation will retard the process, in others — it speeds it up. For example in H_2, the predissociation rate $\gamma_0{}^{\beta}$ of the ndσ_g intermediate state is significantly higher than the autoionization rate $\gamma_1{}^{i}$, so the external field enhances the DR cross section. For the NO molecule the ground ionic term $X^1\Sigma^+$ near the equilibrium distance intersects three terms corresponding to the $A'^2\Sigma^+$, $B^2\Pi$, and $B'^2\Delta$ valence configurations.[21] The first state interacts with the npσ series, $B^2\Pi$ interacts with npπ, and $B'^2\Delta$ interacts with the ndσ series. Since in all cases $\gamma_0{}^{\beta} > \gamma_1{}^{\beta}$,[21] the external field should accelerate the DR reaction.

Field-induced mixing of vibronic Rydberg states

Owing to the great number of RS in XY** complexes, the resonances belonging to different series may overlap for almost all ratios between frequencies ω_f and ω. In this case compound (hybrid) vibronic states are emerged. It is noteworthy that the mechanisms of their population and decay in the reaction process are markedly distinct from those considered in the previous section. In particular, newly appearing reaction channels, which correspond to the harmonics that weakly interact with the dissociative terms in the absence of an external field, become effective. Since the condition for the formation of field-induced resonance in $e^- + XY^+$ are sensitive to the positions of the unperturbed resonance levels, the rotational structure of the XY** RS should be generally taken into account by means of the rovibronic basis with rotationally adiabatic (at $Bn^3 \ll 1$) functions (see representation (7)).

The main features of field-induced mixing of resonances may be exemplified by the DR reaction dynamics below the vibrational excitation threshold of the XY^+ ion. Analyzing the scattering of an electron in the state $l\Lambda$ ($v = 0$, $m = 0$), we assume that the "natural" resonance 1 ($nl\Lambda$, $v = 1$, $m = 0$; JM) overlaps with the laser-induced resonance 2 ($nl'\Lambda'$, $v = 1$, $m = \pm 1$; $J'M'$). For brevity, we introduce the notation 0_0 for the continuum state $e^- + XY^+$ with $m = 0$, and β_m for X + Y with $m = 0, \pm 1$. The $0_0 \to \beta_m$ transition, which in the field-free regime follows direct and resonance pathways and exhibits the Fano profile, acquires new qualitative features in its energy dependence [see Eq. (21)]:

$$|T_{0_0\beta_m}|^2 = W_0 \left| \frac{(\varepsilon_1 - \Delta_1^{\beta})(\varepsilon_2 + i\Gamma_2^{e}) - (V_{12}^{f})^2}{(\varepsilon_1 + i\Gamma_1^{e})(\varepsilon_2 + i\Gamma_2^{e}) - (V_{12}^{f})^2} \right|^2 , \quad (26)$$

due to the field mixing by the laser-induced resonance 2 ($nl'\Lambda'$, $v = 1$, $m = \pm 1$; $J'M'$). (Here we assume conditions at which field-induced shifts and broadening may be neglected, *i.e.*, $t^f \ll t^e$.)

Under this circumstance isolated laser-induced resonance does not manifest itself at all, but, according to Eq. (26), it can significantly disturb the line profile if it is located close to the natural resonance. Generally, the resulting pattern is a curve with two asymmetric maxima. The same situation occurs for the "antiresonances" as well, if $\Delta_1{}^{\beta} \ll \Gamma_1{}^{e}, \Gamma_2{}^{e}$. As follows from Eq. (26), the individual "antiresonance" (which at $V_{12}{}^{f} = 0$ corresponds to the $|T_{0\beta}|^2 = W_0\varepsilon_1{}^2/(\varepsilon_1{}^2 + (\Gamma_1{}^{e})^2)$ dependence with absolute maximum) at $V_{12}{}^{f} \gg \Delta_{12}{}^{e}, \Gamma_{1,2}{}^{e}$ ($\Delta_{12}{}^{e} = |\varepsilon_1 - \varepsilon_2|$ is the defect of the levels of $f = 0$) exhibits two "antiresonances" symmetrically shifted with respect to $\varepsilon = \pm V_{12}{}^{f}/2$ with halfwidths $(\Gamma_1{}^{e} + \Gamma_2{}^{e})/2$ at which the cross section reaches the top value.

The second important channel of the $0_0 \to \beta_m$ process is accompanied by an increase ($m = -1$) or decrease ($m = +1$) in the translational energy of dissociation products. Its probability obeys the equation

$$|T_{0_0\beta_m}|^2 = \frac{\Gamma_1^{i}(V_{12}^{f})^2\Gamma_2^{\beta}}{|(\varepsilon_1 + i\Gamma_1^{e})(\varepsilon_2 + i\Gamma_2^{e}) - (V_{12}^{f})^2|^2} , \quad (27)$$

which corresponds to the function with two symmetric maxima at $V_{12}{}^{f} \gg \Delta_{12}, \Gamma_{1,2}{}^{e}$. All the characteristics studied above depend not only on J, but also on M. Averaging over M smooths out the observed patterns. At $V_{12}{}^{f}/J \geq \Gamma_{1,2}{}^{e}$, however, the isolated resonance for each M value can be detected. In our opinion, the dependence of the reaction cross section on M allows one to sense the possibility of fixing the rotation of the reaction products in a definite plane (see below).

Let us illustrate the above statements by reaction (23), which in the absence of an external field occurs in dσ-electron scattering (the sσ-, pσ-, and pπ-orbitals of the closed channels are purely autoionizing, whereas the f-orbitals are weakly penetrative possessing small quantum defects $\sim 10^{-3}$ and negligible autoionization rates $\gamma^{i} \leq 10^{-4}$). As was already noted, if the field-induced widths γ^{f} are much smaller then the natural ones γ^{e} [condition (4)], the RS of the XY** complex are almost insensitive to laser irradiation. However, the situation is changed dramatically if some resonance level of the predissociative Rydberg series ndσ_g overlaps with the field-induced resonance of a neighboring (on l) series (p or f) with $v = 1$. This case deserves more detailed analysis.

Field-induced mixing of the nds- *and* n′ps-*states*

Under this circumstance there are pσ- and dσ-partial waves of electron scattering on the ionic core, so two types of transitions arise. One of them, as has been already mentioned, occurs *via* the radiationless excitation of the hybrid state n′pσ ($v = 1$, $m = 0$) ↔ ndσ ($v = 1$, $m = \pm 1$) upon electron capture in the vibronic resonance pσ ($v = 1$) with the energy

$$E^{(\mathrm{r})\,\cdot}_{\mathrm{n'p}\sigma} = \omega - \frac{1}{2(n' - \tilde{\mu}^{0}_{\mathrm{p}\sigma})^2} \ .$$

The dissociative decay of the latter is governed by the mixing with the field-induced dσ-resonance at the energy

$$E^{(\mathrm{r})}_{\mathrm{nd}\sigma} = m\omega_{\mathrm{f}} + \omega - \frac{1}{2(n - \mu^{0}_{\mathrm{d}\sigma})^2} \ .$$

According to Eq. (27), the amplitude of this transition is not small providing that the electron energy is close to the position of the corresponding p-resonance. Another transition takes place near

$$E^{(\mathrm{r})}_{\mathrm{nd}\sigma} = \omega - \frac{1}{2(n - \tilde{\mu}^{0}_{\mathrm{d}\sigma})^2}$$

[$\tilde{\mu}_{l\Lambda}$ is the adiabatic quantum defect, see Eq. (17)] due to the formation of the hybrid state ndσ ($\upsilon = 1$, $m = 0$) ↔ n′pσ ($\upsilon = 1$, $m = \pm 1$) followed by its dissociative decay. Thus, the resonance conditions hold simultaneously for two channels, that is, for pσ at $E^{(\mathrm{r})}_{\mathrm{n'p}\sigma} = m\omega_{\mathrm{f}} + E^{(\mathrm{r})}_{\mathrm{nd}\sigma}$ and for dσ at $E^{(\mathrm{r})}_{\mathrm{nd}\sigma} = -m\omega_{\mathrm{f}} + E^{(\mathrm{r})}_{\mathrm{n'p}\sigma}$. In other words, if the formation of the compound state in the pσ-channel is accompanied by photon absorption ($m = 1$), then that in the dσ- channel occurs with photon emission ($m = -1$), and *vice versa.*

Field-induced mixing of the ndσ- *and* n′pπ-*states*

The case in which the dσ-state mixes with the doubly generate pπ-states is similar to the previous case with the distinction that the p-states are responsible for two $\mathrm{p}\pi^+$ and $\mathrm{p}\pi^-$ type transitions (the sign ± specifies the wave function parity relative to reflection in the plane containing the molecular axis). Consequently, the $(t^{\mathrm{f}}_{l_1 m l_0})^2$ matrix element characterizing the hybrid state interaction for the dσ- and pσ-fragments is replaced by the corresponding sum of the squared matrix elements responsible for the $\mathrm{d}\sigma$—$\mathrm{p}\pi^+$ and $\mathrm{d}\sigma$—$\mathrm{p}\pi^-$ state interactions.

Field-induced mixing of the ndσ- *and* n′fΛ-*states*

If the dσ- and fΛ-states having fσ, $\mathrm{f}\pi^+$, and $\mathrm{f}\pi^-$ components [*i.e.*, ndσ ($\upsilon = 1$, $m = 0$) and n′fΛ ($\upsilon = 1$, $m = \pm 1$) states coupled by the transition dipole operator] overlap, a transition occurs owing to the admixture of the dσ-component in the hybrid dσ↔fΛ state. Since the natural broadening of the f-levels is very small, the cross section of reaction (23) should exhibit a sharp maximum reflecting the f-level pattern of the $e^- + \mathrm{H_2}^+(\upsilon = 1)$ system.

The efficiency of laser control may be elucidated by comparing the probabilities of the transitions (radiationless and accompanied by photon emission) at low ($t^{\mathrm{f}} \ll t^{\mathrm{e}}$) and sufficiently high ($t^{\mathrm{f}} \geq t^{\mathrm{e}}$) external field strengths *f*. In the first case the photon-emitting transitions disappear and, according to Eq. (26), only the radiationless transitions are allowed. When there is strong field-induced interaction among the resonance states, *i.e.*, at

$$V^{\mathrm{f}} \gg \Gamma^{\mathrm{e}}, \Delta^{\mathrm{e}} \qquad (28)$$

[the field strength *f* here is still fairly low, $(V^{\mathrm{f}})^2 \ll \Gamma^{\mathrm{e}}$], which we illustrate for *p*σ- and dσ-mixing, the isolated (in the field-free regime) resonance $E^{(\mathrm{r})}_{\mathrm{n'p}\sigma}$ in the pσ-scattering channel at certain ω_{f} values may transform into compound resonance with two maxima. This shape follows Eq. (27).

In the vicinity of $E^{(\mathrm{r})}{}_{\mathrm{nd}\sigma}$ the second dσ-scattering resonance builds to form the hybrid state. It is noteworthy that for $m < 0$ this resonance may appear only if $\omega_{\mathrm{f}} < \omega$. The corresponding probabilities in Eq. (28) are described by two Lorentzian curves [*cf.* Eq. (26)] with halfwidths

$$\bar{\Gamma} = \frac{1}{2}[\Gamma^{\mathrm{i}}(\mathrm{p}\sigma) + \Gamma^{\mathrm{i}}(\mathrm{d}\sigma) + \Gamma^{\beta}(\mathrm{d}\sigma)] \qquad (29)$$

[$\Gamma^{\mathrm{i}}(\mathrm{p}\sigma)$, $\Gamma^{\mathrm{i}}(\mathrm{d}\sigma)$, and $\Gamma^{\beta}(\mathrm{d}\sigma)$ are the autoionization halfwidths of the pσ- and dσ-levels, respectively] and the intensities of the $E^{(\mathrm{r})}{}_{\mathrm{n'p}\sigma}$ and $E^{(\mathrm{r})}{}_{\mathrm{nd}\sigma}$ resonances

$$I_{\mathrm{p}\sigma} = \frac{\pi}{2}\,\frac{\Gamma^{\mathrm{i}}(\mathrm{p}\sigma)\Gamma^{\beta}(\mathrm{d}\sigma)}{\bar{\Gamma}}\,;\ I_{\mathrm{d}\sigma} = \frac{\pi}{2}\,\frac{\Gamma^{\mathrm{i}}(\mathrm{d}\sigma)\Gamma^{\beta}(\mathrm{d}\sigma)}{\bar{\Gamma}} \ .$$

In the spectral interval adjacent to the resonant line the translational energy of the DR products increases or decreases depending on the mechanism of the formation of the compound state (by absorption or emission of a photon).

Effect of field-induced mixing on the reaction rate constant

The influence of the field on the characteristics of the process averaged over the energy at strengths obeying condition (28) is determined by the above equations (26), (27) and the particular form of the weighting function $F(E)$. For this determination we will assume that the incident electrons have a Maxwell velocity distribution and their motion does not correlate with the direction of vector ***f*** owing to their averaging over the angle θ_{e}. Assuming that the vibrational temperature of the ions T_{i} is much lower then the electron temperature T_{e}, *i.e.*, $T_{\mathrm{i}} \ll T_{\mathrm{e}} \leq \omega$, one can represent the DR rate constant as

$$k = k^0 + k^{\mathrm{f}}. \qquad (30)$$

Here k^0 is the reaction rate constant in the absence of an external field

$$k^0 = \sqrt{\frac{2\pi}{T_e}}\,\gamma^{\beta}_{0_0}(\mathrm{d}\sigma)\left[1 + \frac{\gamma^{i}_{1_0}(\mathrm{d}\sigma)\gamma^{\beta}_{1_0}(\mathrm{d}\sigma)(1 - e^{-\omega/T_e})}{\gamma^{\beta}_{0_0}(\mathrm{d}\sigma)(\gamma^{i}_{1_0}(\mathrm{d}\sigma) + \gamma^{\beta}_{1_0}(\mathrm{d}\sigma))}\right], \quad (31)$$

where the second term in square brackets accounts for the contribution of the intermediate Rydberg $\mathrm{d}\sigma_g$-states of H_2**. The partial rates $\gamma^{i(\beta)}{}_{v_m}$ in this equation are defined for $m = 0$. The k^f term in Eq. (30) arises from the field effects:

$$k^f = \zeta\frac{\gamma^{i}_{1_0}(\mathrm{p}\sigma)\gamma^{\beta}_{1_1}(\mathrm{d}\sigma)}{(2\pi)^{1/2}T_e^{3/2}\bar{\Gamma}}\left[\frac{F(E^{(r)}_{n'p\sigma})}{(n'_{10}n_{11})^3} - \frac{\gamma^{i}_{1_0}(\mathrm{d}\sigma)}{\gamma^{e}_{1_0}(\mathrm{d}\sigma)}\cdot\frac{F(E^{(r)}_{nd\sigma})}{(n'_{11}n_{10})^3}\right], \quad (32)$$

where $F(E) = \exp(-E/T_e)$ and ξ is the fraction of rotational J-states for which the field-induced interaction V^f exceeds the spacing Δ between the resonant levels [$\xi = 1$ at $V^f > (BT_i)^{1/2}$].

Let us inspect the condition under which the additional term (32) is significant. Note that for the given ω_f/ω ratio the number of hybrid states contributing to Eq. (32) should be finite. In the pσ scattering channel these resonances accelerate the reaction but in the dσ channel they retard it. Depending on the relation between the autoionization [$\gamma^i{}_{10}(\mathrm{p}\sigma)$ and $\gamma^i{}_{10}(\mathrm{d}\sigma)$] and dissociation $\gamma^{\beta}{}_{1_0}(\mathrm{d}\sigma)$ rates in Eq. (32), an increase in the DR rate constant should be expected for $T_e \approx E^{(r)}{}_{n'p\sigma}$ and a decrease for $T_e \approx E^{(r)}{}_{nd\sigma}$. This also requires that the spacing between the neighboring compound resonances (with minimal principle quantum numbers n'_{10} and n_{10}) obey the condition $\Delta E = |E^{(r)}{}_{n'p\sigma} - E^{(r)}{}_{nd\sigma}| > T_e$, which further restricts the range of T_e.* In the opposite case the electromagnetic field only slightly accelerates the reaction.

The maximum enhancement of the reaction is achieved in the process accompanied by field-quantum emission ($m = 1$) and the maximal effect should be expected under the conditions of (28) when $\delta = \omega_f - \omega_f{}^{(r)}$ is small (here $\omega_f{}^{(r)} = E^{(r)}{}_{n'p\sigma} - E^{(r)}{}_{nd\sigma}$). For the resonant $\mathrm{d}\sigma_g$ Rydberg series populated by radiationless transitions the autoionization rate, as noted above, is an order of magnitude smaller than that of predissociation. Thus, at $T_e < \omega$ and $f \leq 10^{-4}$ the ratio $\eta = k^f/k^0$ characterizing the influence of field-induced mixing on reaction (23) is remarkably large. Table 1 presents the η values calculated by Eqs. (31) adn (32) for the external field frequencies $\omega_f = \omega_f{}^{(r)}$ and T_e taken as the energy of the first ($n'_{10} = 8$) the resonance in the pσ scattering channel. Evidently, most of resonances for which $\eta > 0.1$ lie in the infrared region. The η coefficient decreases slightly with T_e. This means that the effects of field-induced mixing on reaction (23) may be observed in low-temperature hydrogen plasma over a wide temperature range.

Table 1. The values of η coefficient (ω_f/ω ratios are given in parentheses)

n_{11}	n'_{10} 8	9	10	11
4	0.16 (2.45)	0.06 (2.63)	0.03 (2.78)	0.02 (2.85)
5	0.15 (1.25)	0.06 (1.43)	0.03 (1.56)	0.02 (1.65)
6	0.15 (0.61)	0.05 (079)	0.03 (0.91)	0.02 (1.00)
7	0.15 (0.23)	0.04 (0.40)	0.03 (0.53)	0.02 (0.62)

Near-threshold photoionization and photodissociation of diatomic molecules under weak UV and strong IR radiation

The study of single-photon UV transitions in the energy domain adjacent to the ionization threshold requires the calculation of the

$$M_{iq} = \langle\psi_i|\boldsymbol{D}|\psi_q\rangle,\ M_{i\beta} = \langle\psi_i|\boldsymbol{D}|\psi_\beta\rangle, \quad (33)$$

matrix elements, where $\boldsymbol{D}$ is the dipole moment operator, ψ_i is the wave function of the initial state, and ψ_q, ψ_β are the wave functions of the $e^- + XY^+$ and X + Y final states, respectively. By means of Eq. (9) these functions can be expressed through the so-called modified states

$$\phi_p = \Omega^e|p\rangle,\ \phi_s = \Omega^e|s\rangle,\ p = \{q, \beta\} \quad (34)$$

[where $\Omega^e = 1 + G(E)t^e$ is an operator smoothly depending on energy, see Eq. (11)] and the same elements $T_{pp'}$, T_{sp} which form the radiative-assisted collision matrix:

$$\Psi_p = \phi_p - i\sum_\beta \phi_\beta T_{\beta p} + \sum_q \phi_q \mathrm{ctg}\,\pi\nu_q T_{qp} + \sum_s \frac{\phi_s T_{sp}}{E - E_s} \quad (35)$$

Here ϕ_p and ϕ_s are real functions describing states dressed by interaction V and constructed from the |p>, |s> basis functions by the Ω^e operator. In the $V \ll 1$ limit one may assume ϕ_s = |s> and ϕ_p = |p>. The basis functions are chosen according to the physical conditions. Here the rotationally adiabatic basis is employed.

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* For example, the first resonance in the pσ scattering channel ($v = 1$) corresponds to the principle quantum number $n'_{10} = 8$ ($E^{(r)}{}_{n'p\sigma} = 1.78 \cdot 10^{-3}$), whereas that in the d$\sigma$-channel — to $n_{10} = 8$ ($E^{(r)}{}_{nd\sigma} = 1.99 \cdot 10^{-3}$), *i.e.*, the spacing between two hybrid states is $\Delta E = 2.1 \cdot 10^{-4}$). Hence, the retardation of reaction (23) in the external field may occur only at $T_e \leq 60$ K when the additional pσ autoionization channel accompanied with emisson of field quantum becomes effective in dσ-scattering.

In the nonresonant case ($\omega_f \neq \omega$) when the (v, m) Rydberg series may be treated as independent of one another within extended spectral intervals, the direct interaction of these states with continua dominates. Obviously, only those ψ_p and ψ_s which correspond to $m = 0$ states or contain them as an admixture should be involved in processes (2) because the UV transition does not change the number of strong-field quanta. It is worth noting that field-induced autoionization accompanied by the vibrational transition of an ion is less probable than vibrational-elastic autoionization (due to the small parameter — the ratio of the zero-point vibrational amplitude and the internuclear separation of the ion). The probability of field-induced decay *via* a repulsive state is also small compared to a direct ionization transition (due to the difference of electron energies in the $e^- + XY^+$ and $X + Y$ configurations). In the region in the immediate vicinity of the threshold, where the product ion is in the ground vibrational state, photodissociation processes of the following types can be discerned. At $-\omega_f < E < 0$, *i.e.*, below the ionization threshold, a strong field quantum can be absorbed and the recoiling electron acquires the energy $\varepsilon = E + \omega_f > 0$. The corresponding amplitude

$$A_{i0_{-1}} = D_{i0_0}\frac{t^{f}_{0_0 0_{-1}}}{z_{0_0}} \tag{36}$$

for the $i \to v$, m process reflects the resonant character of the population of the quasistationary states belonging to the ($v = 0$, $m = 0$) Rydberg series. The denominator of Eq. (36) has the form

$$z_{0_0} = \mathrm{tg}\pi(\nu_{00} + \mu^{0}{}_{\varkappa}) + i\gamma_{0_0}, \tag{37}$$

where $\gamma_{v_m} = \pi n^3 \Gamma_n$ is the decay rate related to the halfwidth Γ_n of the nth Rydberg level, including both natural and field-induced contributions. At $E < 0$ the partial rate $\gamma^{e}{}_{0_0}$ comes entirely from the predissociation of the XY** molecule in the ground vibrational state. According to Eq. (36), the photoelectron spectrum, which is proportional to the squared absolute amplitude, exhibits a clear resonance pattern. The line intensity $I = \int|A_{ip}|^2 F(\varepsilon)d\varepsilon$ [where $F(\varepsilon)$ is the normalized distribution function and integration is performed in the vicinity of isolated resonance E_n] acquires the form

$$I_n = \frac{1}{n^3}\,\frac{\gamma^{f}_{0_0}}{\gamma^{e}_{0_0} + \gamma^{f}_{0_0}}\,|D_{i0_0}|^2 F(E_n)\,. \tag{38}$$

At $0 < E < \omega$, the $v = 1$, $m = 0$ states are efficiently populated in the absence of a field. The photoionization amplitude is given by

$$A_{i0_0} = D_{i0_0} + D_{i1_0}\frac{t^{e}_{1_0 0_0}}{z_{1_0}}\quad, \tag{39}$$

where

$$z_{1_0} = \mathrm{tg}\pi(\nu_{10} + \mu^{0}{}_{\varkappa}) + i\gamma_{1_0}, \tag{40}$$

and γ_{1_0} as above, denotes the total decay rate including autoionization, predissociation, and field-induced broadening. The following formula

$$I_n = \frac{1}{n^3}\,\frac{\gamma^{i}_{1_0}}{\gamma_{1_0}}|D_{i1_0}|^2 F(E_n)$$

holds for the resonant line intensities. Due to the weak field-induced interaction of RS with the X + Y configuration, the photodissociation process ($i \to \beta_m$ transition) under the action of a strong radiation quantum in the presence of an intense IR field obeys the equations

$$A_{i\beta_0} = D_{i\beta_0} + D_{i0_0}\frac{t^{e}_{0_0\beta_0}}{z_{0_0}}\,,\quad E < 0,$$

$$A_{i\beta_0} = D_{i\beta_0} + D_{i1_0}\frac{t^{e}_{1_0\beta_0}}{z_{1_0}}\,,\quad 0 < E < \omega, \tag{41}$$

where the field-induced interaction contributes only *via* the additional broadening of the Rydberg resonance [*cf.* Eqs. (37), (40)]. Having equations (36), (39), and (41) at our disposal, we can qualitatively discuss the essence of the effect of intense IR-radiation on molecular photodissociation in distinct spectral regions. At $0 < I^0 - \Omega < \omega_f$ almost only dissociation may occur, since two-quantum ionization is unlikely to take place under condition (4). Increasing the low-frequency field strength does not remarkably change the yield of X + Y products. At $I^0 - \Omega > \omega_f$ the onset of field-induced ionization processes (assisted by the ω_f quantum) reduces the probability of dissociation, because γ_{0_1} is now equal to $\gamma_{0_1}{}^{\beta} + \gamma_{0_1}{}^{f}$. At $\Omega > I^0$, where the RS associated with the vibrationally excited state ($v = 1$) of the core are populated, the total width is given by the sum $\Gamma = \Gamma^{\beta} + \Gamma^{i} + \Gamma^{f}$, *i.e.*, photodissociation is further suppressed by the opening of a field-free ionization channel.

Analyzing these results one can conclude that for the nonresonant ($\omega_f \neq \omega$) case the effects of radiation become significant when the field-induced and natural widths are comparable, $\gamma^f \sim \gamma^e$. At the same time, a substantially weaker driving field may cause a significant effect if the different Rydberg series overlap. This can be illustrated for the case when the resonant transition from the ground state "0" to some intermediate state "1" induced by low-frequency irradiation Ω is followed by the ionization or dissociation of a molecule, see Fig. 7. This situation is of great importance for the theory of multiphoton dissociation or ionization of molecules, which is growing extensively these days. It is noteworthy, that the conclusions drawn below are also valid when the "0"→"1" transition occurs with the absorption of k strong-field quanta (*i.e.*, at $E_1 - E_0 \approx k\omega_f$) with a low net intensity $|V_{01}|^2$, where V_{01} is a compound matrix element.[4]

Assuming for simplicity that the natural width for level 1 is zero (*i.e.*, that this state does not predissociate), we obtain from Eqs. (33)—(35) for the probability of a transition into the pth continuum (p $= \{q_m, \beta_m\}$):

$$W_p = |V_{01}|^2 \frac{\gamma_2^p |V_{12}|^2}{|(\varepsilon_1 + i\Gamma_1^f)(\mathrm{tg}\pi(\nu_2 + \mu_2) + i\gamma_2) - V_{12}^2|^2} \cdot \quad (42)$$

Here $\gamma_2{}^p$ is the RS decay rate for dissociation ($\gamma_2{}^p = \gamma_2{}^\beta$) and ionization ($\gamma_2{}^p = \gamma_2{}^i$) continua defined for an isolated Rydberg series, $V_{01} = \langle\psi_0|\boldsymbol{D}|\psi_1\rangle$, $\boldsymbol{D}$ is the dipole moment operator for the one-quantum UV transition, and $\nu_2 = (-2E)^{-1/2}$. If the field strength is not too high, $V_{12} < 1/n_2{}^3$ and the resonance conditions are satisfied only for two levels, E_1 and one of the Rydberg series E_{n_2}. Therefore, we reduce problem to the well-known two level model,[11,33,34] and probabilities (42) exhibit two (in general asymmetric) maxima whose form depends on the spacing of the levels spacing $\overline{\Delta} = E_1 - E_{n_2} + \omega_f$, the full widths, and interaction V_{12}.*

Let us now demonstrate for the problem at hand that the overlapping between the interacting resonances not only complicates the spectrum, but also affects the total product yield. For determining the intensity as the integral over the energy range covering both overlapping resonances one has

$$I_p = \pi \frac{\gamma_1 + \gamma_2}{\Delta^2 + (\gamma_1 + \gamma_2)^2} |V_{01}|^2 |V_{12}|^2 , \quad (43)$$

where $\Delta = [(E_1 - E_{n_2} + \omega_f)^2 + 4V_{12}{}^2]^{1/2}$, γ_1 and γ_2 are the splitting and halfwidths of the levels 1 and n_2. They are defined as the zeroes of the two-level system determinant

$$d_2 = (E - E_1 - \omega_f + i\Gamma_1)(E - E_{n_2} + i\Gamma_{n_2}) - V_{12}{}^2 = 0.$$

According to (43), the influence of the field on the elementary photoprocess for mixed resonance is prominent at

$$|V_{12}| \sim \gamma_1, \gamma_2, \quad (44)$$

i.e., at strengths significantly lower than those for the isolated states because $|V_{12}|$, γ_1, $\gamma_2 \ll 1$.

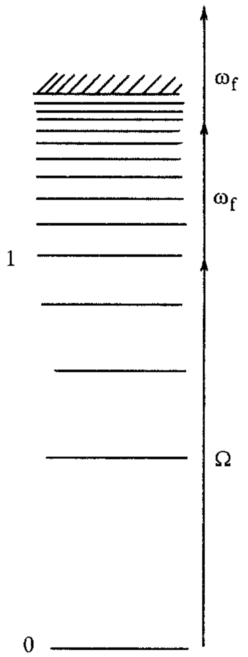

Fig. 7. Diagram of quantum transitions for the resonant photoionization. Shadowed area corresponds to the continuum threshold.

The RS form a dense pattern of levels, so that the conditions under which they can be observed independently of one another in photoabsorption processes, strongly restrict the f value from above. Let us address the opposite case when a large number of RS participate in the process. Then Eq. (42) for the photoelectron spectrum or dissociation product yield may be recast into the form involving the entire series of Rydberg resonances perturbed by a discrete level:

$$W_p = \sum_n I_n^p \frac{\Gamma_n}{(E - E_\nu^{(n)})^2 + \Gamma_n{}^2} . \quad (45)$$

Here Γ_n, $I_n{}^p$ are the line widths and intensities, and the resonant energies $E_\nu{}^{(n)}$ are determined as the roots of the transcendental equation:

$$(E - E_1 - \omega_f)\mathrm{tg}\pi(\nu + \mu) = V_{12}{}^2. \quad (46)$$

It may be shown that the following dependences are relevant in this case:

$$\Gamma_\nu^{(n)} = \frac{\gamma_2}{\pi\nu^3} \cos^2\pi\nu ,$$

$$I_\nu^{(n)} = |V_{01}|^2 |V_{12}|^2 \gamma_2^p \frac{1}{\pi\nu^3} \cos^2\pi\nu , \quad (47)$$

that is, all else being equal, the states with the largest quantum defect $\mu = n - \nu$ (n is an integer) are the most stable. The field-induced quantum defect increases with the strength f. This stabilization effect is a consequence of the collective response of all the Rydberg equations to the perturbation.

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* It should be noted that the number of states actually participating in the two-photon absorption processes rises due to the more complex (than for atoms) selection rules:

$J \to J$, $J \pm 1$; $M \to M$, $M \pm 1$; $\Lambda \to \Lambda$, $\Lambda \pm 1$.

The ideal two-level case corresponds to the condition $f_\Omega \| f$ (f_Ω is the weak field strength vector) for specific transitions without change of the total angular momentum projection M onto the direction f.

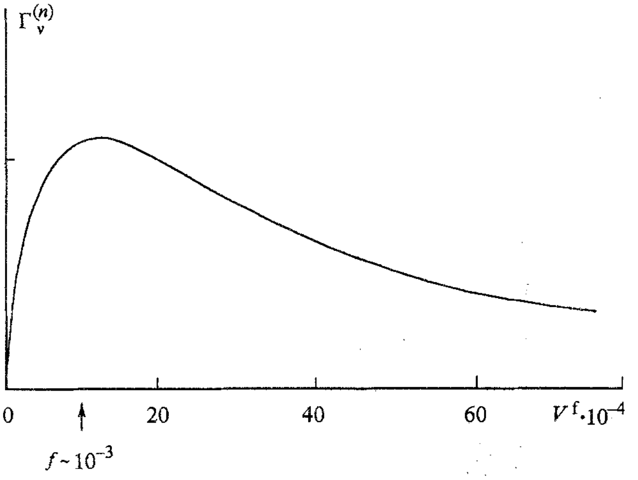

Fig. 8. Dependence of the halfwidth of the *n*th level on the field-induced interaction (V^f).

Unlike the two-level system, in which increasing interaction between the states is known[11] to force the levels infinitely apart, in the Rydberg system the presence of adjacent states suppresses this trend. That is, strong interaction induces "tensions" in the system, which in turn cause the unusual dependence of the widths of the Rydberg levels: they increase quadratically, reach maxima, and then fall-off as $1/f^2$, see Fig. 8. Stabilization of Rydberg atoms in a "superstrong" field has been mentioned in numerous studies (see, for example, Refs. 9, 35, 36). However, the dependence of $\Gamma_v^{(n)}$ and $I_v^{(n)}$ found here indicates that moderately strong fields may stabilize the RS as well, since the condition $|V_{12}| > 1/n^3$ does not contradict criterion (44). It is also important to emphasize that according to Eq. (47) narrowing of a line is accompanied by a decrease in its intensity.

To derive Eqs. (45)—(47) we restrict the considerations to only one Rydberg series despite the fact that a much larger number of RS (with different Λ, *M* quantum numbers and the same ionization potential) participates in strong perturbed near-threshold processes. This simple "one-dimensional" model is currently widely used to describe atomic RS in superstrong fields, since it is able to yield analytical estimations,[34,35] which are confirmed as a rule by quite complex numerical calculations on the real systems. In order to illustrate the above statement, let us consider the photodissociation of the H_2 molecule at $\Omega < I^0$ that occurs as a result of the occupation of the field-induced hybrid state (n′pσ, $^1\Sigma_u{}^+$↔ndσ, $^1\Sigma_g{}^+$):

$$H_2 + \Omega \rightarrow H_2^{**}(n'p\sigma \leftrightarrow nd\sigma,\ v = 0) + \omega_f \rightarrow H + H^*. \quad (48)$$

The main contribution to reaction (48) belongs to the process accompanied by photon emission ($m = 1$). Thus, the situation is close to that considered earlier, except that the absorption of quantum Ω populates the n′pσ Rydberg series. The results of calculations within the fixed molecular axis approximation followed by orientational averaging performed for the data of Refs. 20, 30 are presented in Figs. 9 and 10.

The dependence of the photodissociation spectrum (normalized to unity) on wave selection $\delta = \omega_f - \omega_f^{(r)}$ (the resonant frequency of the external field $\omega_f^{(r)} = 2.455\omega$ corresponds to the formation of the 8pσ↔4dσ, $v = 0$ hybrid state) is depicted in Fig. 9, *a—c*. Obviously, at low *f* values the curve describing the vibronic 8pσ and 4dσ resonance is asymmetric and the intensity of the latter, as should be expected, is small. It is noteworthy that an increase in δ markedly affects only the hybrid state, while the remaining resonances remain almost unchanged. The features of the photodissociation cross section as a function of *f* over a wide range of its variation are clearly demonstrated in Fig. 10 (for the exact δ = 0 resonance). Prominent splitting near the compound resonance is observed for *f* higher than ~10^{-3}. At $f = 10^{-2}$ (dotted line) the width of the resonance (almost symmetric) reach the maxima, and at $f > 10^{-2}$ stabilization of the Rydberg levels takes place.

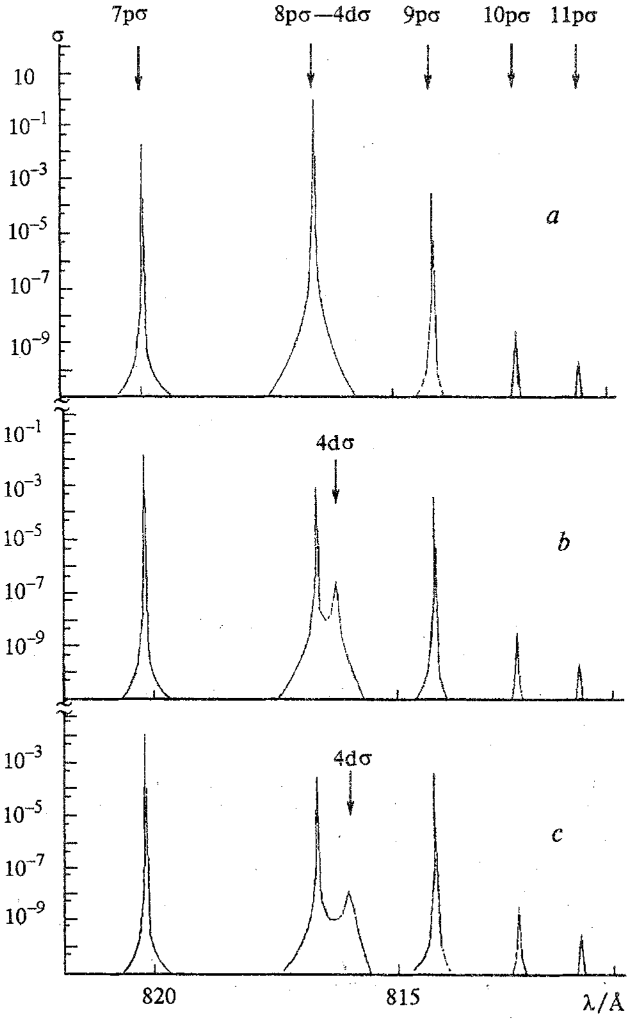

Fig. 9. Photodissociation spectra (48) normalized to unity (at $f = 10^{-5}$ and energy $E_{8p\sigma} = -8.2\cdot10^3$) for $\delta = 0$ (*a*), $3\cdot10^{-4}$ (*b*), $5\cdot10^{-4}$ (*c*). Arrows indicate the resonance positions.

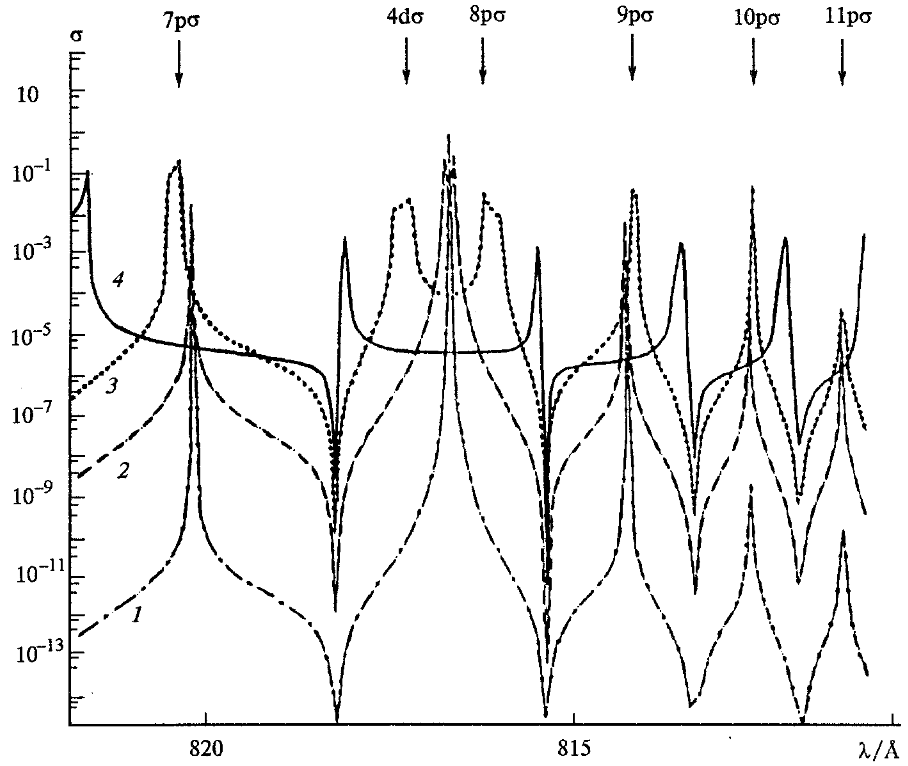

Fig. 10. Reaction cross sections (48) for $f = 10^{-5}$ (*1*), 10^{-3} (*2*), 10^{-2} (*3*), $5 \cdot 10^{-2}$ (*4*). Arrows indicate the resonance positions at $f = 10^{-2}$.

At this strength the position of the cross section minima connected with the poles of the tgπv function are independent of *f*. As *f* increases further, the resonant peaks tighten to these points, *i.e.*, the effective quantum defects (composed of original and field-induced contributions) go to ±1/2 and the intensities of the resonant lines fall-off. These features are completely consistent with the conclusions drawn above.

* * *

In the present work we have concentrated on the purely chemical aspects of the problem, paying most attention to the laser-induced dissociative recombination and near-threshold photoabsorption processes. The interaction of slow electrons with molecular ions (1) and photoabsorption processes (2) exhibit common physical features associated with the formation of intermediate Rydberg states XY** and laser field effects for these states. Hence, it is quite reasonable to consider them in a unique mathematical framework, especially since Eqs. (9) and (10), originally derived for $e^- + XY^+$ scattering events, hold for photoprocesses (2) as well, providing that the excited levels populated by absorption are considered as intermediate states of the "molecule + quantum (quanta)" system. The set of relevant parameters is unambiguously defined and unique for all of the processes mentioned above. These parameters have a precise physical meaning and are related to the characteristics of the adiabatic terms of an XY molecule lying close to the ionization threshold.

Under the same physical conditions, for instance, with field-induced mixing among the same group of molecular states, the various cross sections for processes (1) and (2) differ only quantitatively. The mechanisms responsible for the specific features of the cross sections and spectra for events (1) and (2) are identical and include the interplay of direct and resonant transitions, perturbation of the autodecaying states of XY** in a laser field, interference during complex decay in the common continuum, and multiple transitions to the continuum. The role of the latter factor, described by the T' matrix in Eq. (10), is almost untouched here. Nevertheless, it has become very important for superstrong fields[9] although up to now has been investigated only for oversimplified models and scenarios. Under conditions (3) and (4) multiple transitions in the continuum are significant only above the threshold at $E > \omega$, ω_f and may be accounted for within the approach explained above without difficulties.

The next direction in which the present theory is expected to be very helpful is connected with extensive investigations of the processes in fast molecular beams, particularly those implementing optical detection and probes of the internal states of particles in a beam. One of the most promising schemes is based on the resonant-enhanced multiphoton ionization (REMPI) method, the resonant multiphoton excitation of an intermediate molecular state followed by its photoionization by an additional ionizing field. Measuring the energy spectrum of the resulting charged particles and using tunable pulsing lasers, one can achieve one-to-one inversion of the vibrational-rotational distributions of the original particles. To solve this problem it is necessary to learn the mechanisms controlling the energy spectrum of the products. Since they are closely connected with the dynamics of the e^{-} + XY^{+} system in the laser field, these mechanisms can be understood only if the energy redistribution processes in the ionization continuum are known in detail.

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