Resonant multiphoton ionization and dissociation of molecules with simultaneous action of a weak field and intense monochromatic radiation

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A study is carried out of resonant multiphoton ionization and dissociation of molecules in a monochromatic laser radiation field with preliminary excitation of a lower-lying intermediate level by a weak (probe) field. The method employed is based on the determination and analysis of the properties of the radiative collision matrix of the photoabsorption products and allows one to calculate line profiles under conditions of formation of intermediate hybrid states of complex type with appropriate account of their interaction with the continua. Analytic studies are carried out of two-level and some multilevel schemes of resonant processes in diatomic molecules. The effect of interference suppression in the photoelectron spectra and the spectrum of dissociation products of one of the components of the intermediate complex formed from an odd number of rotational states of the molecule is demonstrated. Experimentally realizable transition schemes are indicated which should allow one to obtain rotationally oriented molecular ions, i.e., to realize a unique sort of selection of their energetically indistinguishable states. © *1995 American Institute of Physics.*

1. INTRODUCTION

Resonant multiphoton ionization (RMI) and dissociation (RMD) are processes that take place as a result of the interaction of intense laser radiation with molecular systems when their stationary or spontaneously decaying states are efficiently populated at an intermediate stage of the reaction (preceding the transition to the continuum). A study of these phenomena presupposes the necessity of a detailed consideration of the field coupling of resonant discrete and quasidiscrete states and their interaction with the continuum.

The first studies of multiphoton ionization made wide use of perturbation theory based on the assumption that there are no random coincidences between the values of the quasienergy $-I_i+k\omega_f<0$ (I_i is the ionization potential and ω_f is the frequency of the external monochromatic field) and the discrete levels of the system. Then the process corresponds to a direct multiphoton absorption mechanism and is described by the combined matrix elements, the recipe for constructing which is well known.[1–3]

In the case in which the process passes through an isolated intermediate resonance (e.g., for k^*-photon absorption, if $k^*<k_m$, where k_m is the minimum number of quanta $\hbar\omega_f$ necessary for ionization) the photoelectron spectra are described by formulas of the Breit–Wigner type, in which the width of the resonant level corresponds to a k_m-k^*-photon transition from this level to the continuum.[4,5] This case corresponds to the single-resonance approximation, in which a simple sort of compound state arises in the intermediate stage.

The next step in the development of the theory consisted in a special study of situations in which resonant conditions are created simultaneously at two intermediate states, populated, for example, by k^*-1 and subsequent k^*-photon absorption. In Refs. 6–8 such situations were investigated with the help of equations for the amplitudes of the populations of isolated states in the instantaneous turn-on regime, in which the effective field interaction between these two states is turned on instantaneously. The concrete cases considered in Refs. 6–8 required a special procedure for accounting for the interaction via the continuum (since the relaxation matrix method, widely used in the theory of the interaction of atoms with external fields, is not suitable here).

The overwhelming majority of results from the theory of resonant multiphoton ionization have been obtained for atomic systems. Molecules are a substantially more complicated object of study. Intermediate molecular states are, as a rule, degenerate (e.g., in the projection M of the angular momentum J for $J\geqslant 1$). The upper levels ordinarily predissociate, i.e., here one has a well-developed system, more developed than in the case of atoms, in which molecular states decay.

The model of two-photon ionization and dissociation of molecules is generally considered to be the best worked out model in the theory of the interaction of monochromatic laser radiation with molecular systems.[9] In this model, one or several of the noninteracting states are populated at the intermediate stage of the process.

The aim of the present paper is an analytic study of the mechanisms of formation of the photoelectron spectra and the spectra of the photodissociation products of the molecules under conditions of the formation at the intermediate stage of a coherent superposition of spontaneously decaying states of complex type (including predissociation states). In addition, we will show that the results of Refs. 6–8, which correspond to the formulation of the problem considered by us, are obtained as special cases.

The method we use is based on the determination and analysis of the properties of the T-matrix of radiative collisions, which describes the interaction of an electron e^- and a

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molecular ion XY^+ and its dissociation products X+Y. Equations for the radiative T-matrix were obtained and used to solve various problems in our previous papers.[10-13] In a subsequent paper,[14] which examined the specific details of the manifestation of Rydberg states of atoms in the presence of multiphoton absorption, it was shown that this method can also be used in the theory of resonant multiphoton ionization.

In the present paper we analyze the purely molecular aspect of the problem, which reduces to an examination of the role of rotational motion in the formation of the states of the intermediate complex. Therefore, before we present the factual material we will formulate the method of the T-matrix of radiative collisions applied to molecular systems. The solutions obtained correspond to the regime of continuous irradiation, in which the first state (counting from the ground state) is populated as a result of a weak probe field or a nonresonant multiphoton transition from the ground state and mixes with higher-lying discrete or autoionization states under the action of a strong electromagnetic field. The latter is assumed to be monochromatic, linearly polarized, and weak on the scale of atomic units ($e=\hbar=m_e=1$), i.e.,

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

where ω_f and f are the frequency of the electromagnetic field and the electric field strength. Condition (1) means that break-up fragments (electron and ion) are not subject to the action of the external field. However, its influence on the processes under consideration is substantial, and is not described using perturbation theory. Also it is assumed that the field does not act on the XY^+ ion and the isolated atoms in the dissociative channel.

2. THE METHOD OF THE RADIATIVE COLLISION MATRIX IN THE THEORY OF RESONANT MULTIPHOTON IONIZATION AND DISSOCIATION OF MOLECULES

It is well known that the Schrödinger equation for systems subjected to a periodic perturbation reduces to a set of time-independent equations.[2] In Refs. 10–13 this possibility was realized (in contrast, e.g., to Ref. 15) in the form of integral equations for the scattering problem, in which the boundary conditions are automatically taken into account upon fulfillment of inequality (1).

The equations for the T-matrix obtained in Refs. 10–13 and the representations for the continuum wave functions for the states e^-+XY^+ and X+Y found in them can be applied directly in the theory of resonant multiphoton ionization and dissociation if these functions are constructed in such a way that they contain information about those sets of intermediate states that are important for the multiphoton absorption processes under consideration.

The system e^-+XY^+ with the interaction V^c between the configurations e^-+XY^+ and X+Y turned off is characterized by states of the continuous spectrum $|q\rangle$ and discrete spectrum $|s\rangle$, which we will determine (as well as the functions $|d\rangle$ of the dissociative channel) in the adiabatic approximation (with regard to the rotational motion) by prescribing the total angular momentum J of the system and its projection M onto the direction **f**:

$$\begin{aligned} |q\rangle &= \Psi^{JM}_{e^-+XY^+} = \Phi^q_\Lambda D^J_{\Lambda M}(\alpha,\theta,0)\chi_v(R), \\ |d\rangle &= \Psi^{JM}_{X+Y} = \Phi^d_\Lambda D^J_{\Lambda M}(\alpha,\theta,0)\chi_d(R), \end{aligned} \tag{2}$$

where Φ_Λ and $D^J_{\Lambda M}$ are the radial and angular parts of the electronic wavefunction in the coordinate system fixed to the axis of the molecule, Λ is the projection of the angular momentum of the electrons onto this axis, $\chi_v(R)$ is the vibrational wavefunction of the ion XY^+, $\chi_d(R)$ is the wave function of the nuclei in the dissociative channel (here R is the interatomic distance, $D^J_{\Lambda M}(\alpha,\theta,0)$ is the generalized spherical harmonic, and α and θ are the azimuthal and polar angles of the vector **R** relative to **f**). The wave functions $|q\rangle$ and $|d\rangle$ are assumed to be normalized as follows:

$$\langle q_\varepsilon | q_{\varepsilon'}\rangle = \pi\delta(\varepsilon-\varepsilon'), \quad \langle d_E | d_{E'}\rangle = \pi\delta(E-E').$$

The function $|s\rangle$ is written in a way analogous to that in which the function $|q\rangle$ is written, with the one difference that Φ^s_Λ is normalized to unity. We will combine that part of the interaction with the ion shell not taken into account in the system e^-+XY^+, $V'=V_{nc}(R)-V_{nc}(R_e^+)$, and responsible for the vibronic transitions, into the operator $V^e=V^c+V'$ (where R_e^+ is the equilibrium distance in the ion XY^+).

For a collision taking place in a field of intense monochromatic radiation, the treatment in Refs. 10–13 is carried out in the representation of quasi-energy harmonics, whose energetic characteristics are shifted, one from the other, by the displacement $k\omega_f$, where k is a positive or negative integer. The coupling between these states in the case of linear polarization is a result of the interaction

$$V^f = \tfrac{1}{2}(\mathbf{Df}), \tag{3}$$

where **D** is the dipole moment. The basis functions are now $|q_k\rangle$, $|s_k\rangle$, and $|\beta_k\rangle$. They are distinguished by the number of photons and are defined with energy $E-k\omega_f$, where E is the total energy of the system, which it is convenient to reckon from the boundary of the spectrum of e^-+A^+.

Recall that, strictly speaking, it is possible to consider e^-+XY^+-scattering in the radiation field within the framework of the ordinary formulation of the scattering problem only under the condition of smallness of the matrix elements of the transition between the states of the continuous spectrum (1), when the break-up fragments e^- and XY^+ are not subject to the action of the external field. In the opposite case $f/\omega_f^{5/3} \geqslant 1$, it is necessary to introduce a superposition of quasiharmonics—in this case we are speaking of scattering of the corresponding wave packets (at present such a problem has been solved for pure potential scattering without account of the effect of bound states[16,17]).

The equation for the T-matrix in the problem of the perturbation of the continuum states of the system due to the combined interaction $V=V^e+V^f$, including the interaction with the ion shell V', the configurational coupling V^c between the states e^-+XY^+ and X+Y, and the field interaction V^f, is written, in analogy with Ref. 11, in the form

$$T = t - it\sum_{p,k} |p_k\rangle\langle p_k| T + t\sum_s \frac{|s_k\rangle\langle s_k|}{E-k\omega_f-E_s} T. \tag{4}$$

Here E_s is the energy of the s level reckoned from the continuum (q and d are included in the general index of open channels $p=\{q,d\}$). The operator t in Eq. (4), smooth in the energy, consists of two terms, $t=t^e+t^f$, the first of which is responsible for transitions between the p, d, and s configurations, and the second of which describes the field effects:

$$t^f=V^f+V^f\sum_k |k\rangle G(E-k\omega_f)\langle k|V^f+\dots, \qquad (5)$$

where $|k\rangle$ is the photon part of the total wavefunction and $G(E-k\omega_f)$ is the Green's function of the system with the pole singularities taken into account in Eq. (4) excluded. As it is written, expression (5) takes account of the second-order perturbation theory in V^f, which allows us to take account of Stark level shifts in a natural way. Here the matrix elements of the t^e operator are diagonal in m:

$$t^e_{p_k p'_{k'}}=t^e_{p_k p'_k}\delta_{kk'}, \quad t^e_{p_k s_{k'}}=t^e_{p_k s_k}\delta_{kk'} \qquad (6)$$

The elements of the operator V^f in turn are responsible for the coupling between the states with indices k and $k'=k\pm 1$.

The total wavefunction of the final (continuum) state of the system is expressed in terms of the modified functions

$$\Phi_{p_k}=\hat{\Omega}|p_k\rangle, \quad \Phi_{s_k}=\hat{\Omega}|s_k\rangle \qquad (7)$$

and elements $T_{pp'}$ and T_{sp} of the radiative collision matrix, i.e.,

$$\Psi_{p_k}=\Phi_{p_k}-i\sum_{p',k'}\Phi_{p'_{k'}}T_{p'_{k'}p_k}+\sum_{s,k'}\frac{\Phi_{s_{k'}}T_{s_{k'}p_k}}{E-k'\omega_f-E_s} \qquad (8)$$

[here Φ_p and Φ_s are real functions which describe the "dressed" states ("dressed" by the interaction V) and which are made up of linear combinations of the basis functions $|q\rangle$ and $|s\rangle$ affected by the weakly energy-dependent operator $\hat{\Omega}$]. Taking into account the smallness of the configurational coupling, which is the case for the majority of diatomic molecules, we can set $\Phi_p\simeq|p\rangle$ and $\Phi_s\simeq|s\rangle$.

It is convenient to define the elements of the radiative collision T-matrix entering into expression (8) by means of the formally general relations[13]

$$T_{00}=T'_{00}+T'_{0c}\frac{1}{\varepsilon-T'_{cc}}T'_{c0},$$
$$T_{c0}=\frac{1}{\varepsilon-T'_{cc}}T'_{c0}, \quad T_{0c}=\frac{1}{\varepsilon-T'_{cc}}T'_{c0} \qquad (9)$$

(ε is the diagonal matrix with elements $\varepsilon_{cc}=E-E_c$, where $E_c=E_s-k\omega_f$), i.e., to express it in terms of the auxiliary submatrices T'_{00} (of rank $N_0\times N_0$), T'_{cc} (of rank $N_c\times N_c$), and T'_{c0} (of rank $N_c\times N_0$) constructed on the basis of the open channels

$$T'=t-it\sum_{\rho}^{N_0}|\rho\rangle\langle\rho|T' \qquad (10)$$

(N_0 and N_c correspond to the open $\rho=\{p,k\}$ and closed $c=\{s,k\}$ channels of motion). Here the elements of the matrices T'_{cp} and $T'_{cc'}$ are expressed in terms of the elements of the matrix of open channels in the following way:

$$T'_{cp}=t_{cp}-i\sum_{p'}t_{cp'}T'_{p'p},$$
$$T'_{cc'}=t_{cc'}-i\sum_{p}t_{cp}t_{pc'}-\sum_{p,p'}t_{cp}T'_{pp'}t_{p'c'}. \qquad (11)$$

Note that Eqs. (9)–(11) take account of the influence of cascade transitions in the continua on the discrete states of the quantum system. Below we assume that the laser transitions in the near-threshold region are preceded by a resonant transition from the ground state "i" to the intermediate level "0". This transition proceeds under the action of weak UV-radiation (with frequency Ω) or as a result of direct k-photon absorption ($k\omega_f\simeq E_0-E_i$) and is characterized by a weak resultant intensity V_{i0}. The two variants of population of the intermediate level differ only in the way in which the matrix element V_{i0} is written. For example, for a single-quantum UV-transition

$$V_{i0}=\langle\psi_i|\hat{D}|\psi_0\rangle,$$

where $\hat{D}$ is the dipole moment operator. In the case of k-photon absorption V_{i0} is a combined matrix element, which is written in the usual way.[1]

Considering for definiteness the case of single-quantum population of the set of intermediate levels s_0, we can represent the matrix element of the transition to the p-continuum in the form

$$M_{ip_k}=D_{ip_k}\delta_{0k}+\sum_{s_0}\frac{D_{is_0}T_{s_0p_k}}{E-E_{s_0}}, \qquad (12)$$

and express it directly in terms of the radiative collision matrix elements (9) (the subscripts i and s_0 correspond to $k=0$). Formula (12) describes photon-initiated dissociation and ionization with allowance for the entire cascade of radiative transitions induced by the strong field under the condition $\tau_0\omega_f>1$, where τ_0 is the duration of the pulse of radiation of the weak (probe) field (ensuring excitation of the molecule to the first intermediate level). The total amplitude of the process, according to formula (12), is a superposition of partial amplitudes, each of which contains a product of the matrix elements D_{is_0} of the dipole transitions to one of the lower-lying intermediate states, and the matrix elements $T_{s_0p_k}$. It is precisely this circumstance that shapes the complex resonance structure of the energy dependence of the cross sections of the radiative–collisional processes, characterized by the corresponding resonance lines, their positions, and widths. These lines differ only in their intensities and the details of the spectra which are a result of interference of the amplitudes of various kinds of transitions.

It can be shown that the results obtained with the help of Eqs. (9)–(12) are completely equivalent to those obtained by the nonstationary approach under conditions of continuous action of the monochromatic radiation (with constant amplitude f) on the system finding itself at the intermediate level s_0 after instantaneous turn-on of the field at time $t=0$. Note also that it is easy to account for the relaxation associated

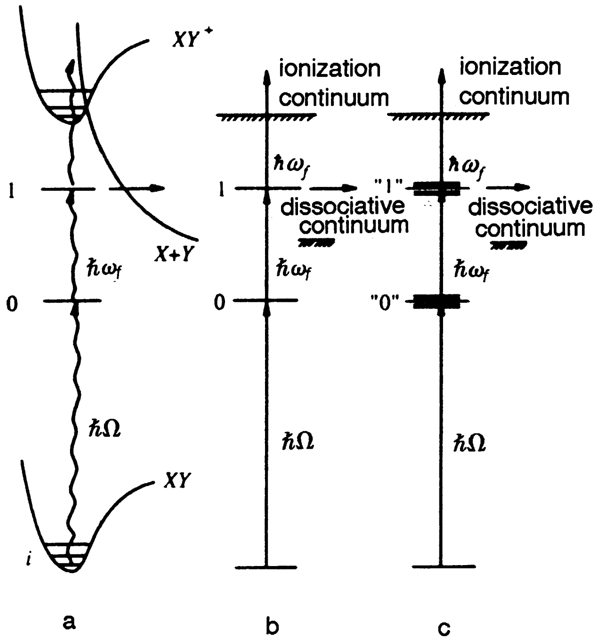

FIG. 1. Terms of a diatomic molecule and diagram of intramolecular transitions: a) system terms, b) diagram of J-selected transitions, c) transitions between groups of J-levels.

with spontaneous emission within the framework of the stationary theory, but not for the interaction with the surrounding medium.

3. RMI AND RMD OF MOLECULES INVOLVING TWO INTERMEDIATE STATES

Let us first consider a system in which one state "0," populated by the weak probe field with frequency Ω, is mixed upon reemission of quanta of the strong field with a higher-lying state "1" (see Fig. 1). Note that an analogous system was discussed in detail in the theory of RMI of atoms.[6–8] Molecules, as opposed to atoms, possess a larger number of degenerate states and are characterized by more complicated selection rules: $J\rightarrow J$, $J\pm 1$; $M\rightarrow M$; $\Lambda\rightarrow\Lambda$, $\Lambda\pm 1$. However, under the condition

$$|V_{01}^f|\ll B(J+1)$$

(B is the rotational constant), when the field interaction V_{01}^f is much smaller than the distance between rotational sublevels of the molecule XY, a two-level situation arises (see Fig. 1b). It is precisely this case that we will look at in this section.

We will denote the positions of the levels by E_0 and E_1 and assign the magnitudes of the detunings from the resonant values of the energy $\varepsilon_0=-I_i+\Omega-E_0$ and $\varepsilon_1=-I_i+\Omega+\omega_f-E_1$, where I_i is the ionization potential of the initial ith state. Next, introducing the spontaneous decay characteristics of these levels

$$\gamma_m=\sum_{p_k}|t_{mp_k}|^2,\quad \gamma_{ml}=\sum_{p_k}t_{mp_k}t_{p_kl}\quad (m,l=0,1,2,\ldots) \tag{13}$$

and the interactions V_{i0} and V_{01}, we have for the amplitude of the $0\rightarrow p$ transition (the Stark field shifts are included in the definition of the energy)

$$M_{ip}=V_{i0}D^{-1}[t_{p0}\varepsilon_1+t_{p1}V_{01}+i(t_{p0}\gamma_1-t_{p1}\gamma_{01})], \tag{14}$$

where the denominator is equal to

$$D=(\varepsilon_0+i\gamma_0)(\varepsilon_1+i\gamma_1)-(V_{01}-i\gamma_{01})^2.$$

On the basis of formula (14) the probability of transitions to either the "0" or the "1" continuum can be written in the following form:

$$|M_{ip}|^2=|V_{i0}t_{p0}|^2\,\frac{\left(\varepsilon_1+\dfrac{t_{1p}}{t_{0p}}V_{01}\right)^2+\left(\gamma_1-\dfrac{t_{1p}}{t_{0p}}\gamma_{01}\right)^2}{|D|^2}. \tag{15}$$

Here the probabilities of transitions to their own continua for the "0" and "1" levels are given by

$$\begin{aligned}|M_{ip}|_0^2&=|V_{i0}|^2\,\frac{(\varepsilon_1^2+\gamma_1^2)}{|D|^2}\,\gamma_{0p},\\ |M_{ip}|_1^2&=|V_{i0}|^2\,\frac{(V_{01}^2+\gamma_{01}^2)}{|D|^2}\,\gamma_{1p}.\end{aligned} \tag{16}$$

Expression (16) have a simple physical meaning. Indeed, the factor $|V_{i0}|^2$ reflects the the preliminary excitation of the molecule by the weak probe field, the second factor reflects the stage of evolution of the intermediate complex, and, finally, the third factor (γ_{0p} or γ_{1p}) is the probability of decay via the assigned channel of motion.

The specifics of molecular systems are manifested here only in the structure of the matrix elements entering into formulas (14)–(16). Note that these formulas are also applicable to the case of RMI of atoms involving discrete or autoionization states. It can be shown that formulas (14)–(16) reproduce the corresponding results of Refs. 6–8, obtained under more particular assumptions. For example, the dependence (5.19) found in Ref. 6 for the probability of the process is valid for the case in which the resonating levels have one common decay continuum. The final formulas (38)–(39) given in Ref. 8 were obtained for the case in which each mixed state has its own proper decay continuum and one common decay continuum. It should be emphasized that formulas (14)–(16) are applicable to any number of correlated and uncorrelated continua. We thus arrive at a natural generalization of the results of Refs. 6 and 8.

The total ionization probability can be obtained within the framework of the approach just presented by summing the squares of the amplitudes $|M_{ip}|^2$. Along with that, there also exists a simpler way of solving this problem: the probability W can be defined as the imaginary part of the level "i" populated at the intermediate stage of the process $e^-+\mathrm{XY}^+$ taking place according to the scheme

$$p\overset{\omega_f}{\rightleftarrows}1\overset{\omega_f}{\rightleftarrows}0\overset{\Omega}{\rightleftarrows}i.$$

Then, from the expression for the determinant of the three-level system, with allowance for the smallness of $|V_{i0}|^2$, we have

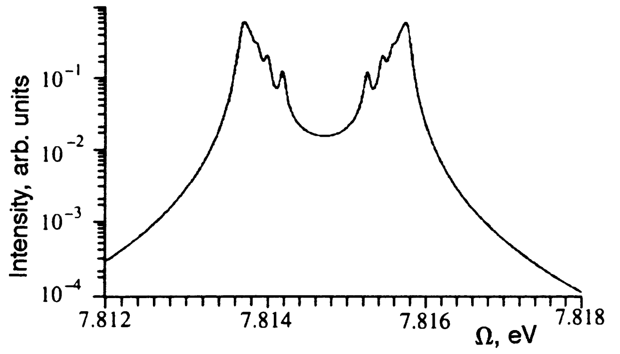

FIG. 2. Photoelectron spectrum averaged over the projection M of the total angular momentum J for three-photon ionization of the NO molecule $[X^2\Pi(J=6)]$ through the states $E^2\Sigma^+(J=7)$ and $R^2\Sigma^+(J=6)$ (in arbitrary units).

$$W=\gamma_i+V_{i0}^2\,\frac{\gamma_0\left(\varepsilon_1+V_{01}\dfrac{\gamma_{10}}{\gamma_0}\right)^2+(\gamma_1\gamma_0-\gamma_{10}^2)\left(\gamma_1+\dfrac{V_{10}^2}{\gamma_0}\right)}{|D|^2}. \tag{17}$$

Here γ_i is the auto-ionization width due to the direct transition to the continuum. Note that formula (17) reduces to the special case in Ref. 7.

Note that formulas (14)–(16) and the parameters entering into them depend on the projection M of the total angular momentum onto the electric field vector **f**. The resulting picture of the photoelectron spectra consists of a superposition of a large family of double-peaked curves. The resonances that proceed from different M do not overlap if the difference in the magnitude of V_{01} for the states M and $M\pm 1$ exceeds the intrinsic widths of the levels ($\Delta V_{01}\sim V_{01}J^{-1/2}>\gamma_{0,1}$ for $J\gg 1$). In this case the most favorable conditions for determining the plane of rotation of the just-formed molecular ion XY^+ relative to the electric field vector **f** arises, which is of interest for the problem of forming ionic and molecular beams with prescribed microscopic properties.

It should be kept in mind that in this way only the projection M of the total angular momentum J of the system e^-+XY^+ is determined, which is composed of an ionic component M^+ and an electronic component m, thus:

$$M=M^++m.$$

Thus, the quantity M^+ is determined with some uncertainty or spread ΔM^+, which is fixed by the possible values of m for the process under consideration. The relative spread $|\Delta M^+/M|$ (for $M\gg 1$) decreases with decreasing effective angular momentum l of the injected electron.

To illustrate the effect under consideration, Fig. 2 gives a graph of the results of a calculation of the spectrum of photoelectrons formed by the irradiation of molecules of NO, i.e.,

$$X^2\Pi(J=6)\xrightarrow{\Omega}E^2\Sigma^+(J=7)\overset{\omega_f}{\leftrightarrows}R^2\Sigma^+(J=6)$$
$$\rightarrow\text{continuum}$$

(the characteristics of the transitions and their parameters are discussed in the following section). The spectrum was calculated according to formula (14) with the matrix element t_{p0} equal to zero. The curve plotted in the figure was found by averaging M spectra corresponding to experimentally observable processes. As a consequence of the dependence of the angular part of the matrix element V_{01}^f on M ($V_{01}^f\sim(J^2-M^2)^{1/2}$, each pair from the series of close-lying resonances corresponds to different values of $|M|$ (here $|M|$ runs from 0 to 6).

4. HYBRIDIZATION (COHERENT MIXING) OF GROUPS OF INTERMEDIATE STATES FOR RMI AND RMD OF MOLECULES

The electronic–vibrational states of diatomic molecules are characterized by an extensive system of close-lying rotational sublevels

$$E_{vJ}=E_v^e+BJ(J+1), \tag{18}$$

where E_v^e is the position of the electronic–vibrational level. For the principal atmospheric molecules (N_2, NO, O_2, CO) the constant B is of the order of 10^{-5}, i.e., the distance between the rotational sublevels for $J\sim 10$ stands at $\Delta E_r\simeq 10^{-4}$. Therefore, in accordance with the selection rules for the dipole matrix elements $J\rightarrow J$, $J\pm 1$ of the (0–1) transitions for field strengths $V_{01}^{JJ'}\geqslant\Delta E_r$, large groups of states are entrained into the $(\Omega+2\omega_f)$ absorption processes. In other words, for these processes it is possible to expect the appearance of hybrid states of complex type (see Fig. 1c). Below we will show that they lead to specific features in the spectra of the photoelectrons and dissociation products which do not take place in the two-level resonance approximation,[6–8] nor do they take place in the theory of two-photon absorption developed in Ref. 9.

A rotationally excited molecule ($J=0$) undergoing a transition through the Σ-state is a three-level system. In transitions with $\Lambda\neq\Lambda'$ there arises a more complicated superposition of states. The general expression for the transition amplitude in the three-level case has the form

$$B_{0p}=-\frac{(V_{01}t_{1p}\varepsilon_2+V_{02}t_{2p}\varepsilon_1)-V_{12}(V_{01}t_{2p}+V_{02}t_{1p})}{\varepsilon_0\varepsilon_1\varepsilon_2+2V_{01}V_{02}V_{12}-V_{02}^2\varepsilon_1-V_{01}\varepsilon_2-\varepsilon_0V_{12}}. \tag{19}$$

Here

$$\varepsilon_0=\Omega-(I+E_0),\quad \varepsilon_1=\varepsilon_0-\Delta_1+i\gamma_1,\quad \varepsilon_2=\varepsilon_0-\Delta_2+i\gamma_2,$$

$$\Delta_1=E_1-\omega_f-E_0,\quad \Delta_2=E_2-\omega_f-E_0,$$

(Δ_1 and Δ_2 are the resonance defects reckoned from the value $E_0+\omega_f$). The definition of the remaining quantities was given earlier.

In the case of a "fine" resonance, when $\varepsilon\sim\gamma$ and the field coupling between the "0" and "1" states satisfies the condition $|V_{01}|\gg\{\Delta_1,\Delta_2,\gamma_1,\gamma_2\}$, we obtain the simple expression

$$B_{0p}=-\frac{(V_{01}t_{1p}+V_{02}t_{2p})(\epsilon+\Delta'+i\gamma')}{\left(\varepsilon-\bar{V}+\frac{i}{2}\gamma_\Sigma\right)\left(\varepsilon+\bar{V}+\frac{i}{2}\gamma_\Sigma\right)(\epsilon+\tilde{\Delta}+i\tilde{\gamma})}, \tag{20}$$

where we have introduced the following notation:

$$\gamma_\Sigma=2\gamma-\tilde{\gamma},\ \ \gamma=\frac{V_{01}^2\gamma_1+V_{02}^2\gamma_2}{V_{01}^2+V_{02}^2},\ \ \tilde{\gamma}=\gamma+\frac{2V_{01}V_{02}}{V_{01}^2+V_{02}^2}\gamma_{12},$$

$$\gamma'=\frac{V_{01}t_{2p}+V_{02}t_{1p}}{V_{01}t_{1p}+V_{02}t_{2p}}\gamma_{12}+\gamma,\ \ \bar{V}=\sqrt{V_{01}^2+V_{02}^2}+\frac{1}{2}\Delta_\Sigma,$$

$$\Delta_\Sigma=\Delta_1+\Delta_2-\tilde{\Delta},\ \ \tilde{\Delta}=\frac{V_{01}^2\Delta_1+V_{02}^2\Delta_2}{V_{01}^2+V_{02}^2},$$

$$\Delta'=\frac{V_{01}t_{1p}\gamma_2+V_{02}t_{2p}\gamma_1}{V_{01}t_{1r}+V_{02}t_{2r}}. \tag{21}$$

It follows from Eq. (20) that the parameter γ_{12}, which according to Eq. (13) represents the interference of waves taking place during the decay to the total continua, influences, by way of the quantities γ_Σ, $\tilde{\gamma}$, and γ', the line profile of the photoabsorption accompanying the transition of the system to the p-continuum. According to Eq. (21), the presence of a common decay continuum can also be seen in the transitions to the isolated continua.

Despite the three-component structure of the intermediate hybrid state, the cross section of the process has only two pronounced peaks at $\varepsilon+\pm\bar{V}$ (with maximum cross section $\sigma\sim 1/\gamma$). The third state is manifested in the form of a weak singularity, i.e.,

$$\sigma\sim\frac{\Omega^2}{4\bar{V}^2}\frac{\varepsilon^2+\gamma'^2}{\varepsilon^2+\tilde{\gamma}^2},\quad(\varepsilon\sim\tilde{\gamma}) \tag{22}$$

where $\Omega=V_{01}t_{1p}+V_{02}t_{2p}$. Thus if $\gamma'<\tilde{\gamma}$, then this singularity has the character of an antiresonance. Beyond the limits of the energy interval $-\bar{V}<\varepsilon<\bar{V}$ the cross section rapidly tends to zero.

As an illustration, we will carry out a calculation of the spectra of the photoelectrons and dissociation products for RMI and RMD of the NO molecule, taking place according to the scheme (case "*b*" according to the Hund rules), i.e.,

$$\mathrm{NO}\{X^2\Pi(v_i=0,J_i=0)\}\overset{\Omega}{\rightarrow}\mathrm{NO}\{E^2\Sigma^+(v_0=1,J_0=1)\}\overset{\omega_f}{\leftrightarrows}\mathrm{NO}\begin{Bmatrix}R^2\Sigma^+(v_1=1,J_1=0)\\R^2\Sigma^+(v_2=1,J_2=2)\end{Bmatrix}\overset{\omega_f}{\rightarrow}\mathrm{NO}^+\begin{Bmatrix}X^2\Sigma^+(v_f=1,J_f=1)\\X^2\Sigma^+(v_f=1,J_f=3)\end{Bmatrix}+e^-. \tag{23}$$

We also assume that the transition from the ground (rotationally unexcited) state $X^2\Pi$ to the intermediate state $E^2\Sigma^+$ takes place under the action of a weak source of radiation with frequency $\Omega=7.815$ eV while the subsequent transition from the state $E^2\Sigma^+$ to the Rydberg states $R^2\Sigma^+$ takes place upon absorption of a quantum of the strong field $\omega_f=1.011$ eV. The double arrows in Eq. (23) signify multiple reemission of quanta of the strong field at the stage of formation of the three-component hybrid state. The upper state in braces in Eq. (23) corresponds to the R-branch, and the lower state, to the P-branch. The two dissociative continua $I^2\Sigma^+$ and $A'^2\Sigma^+$, as a rule, mix with the Rydberg configuration $R^2\Sigma^+$ (Ref. 18). The corresponding predissociation half-widths of levels "1" and "2" are equal to

$$\gamma_1^d=1.633\cdot 10^{-6},\quad \gamma_2^d=1.627\cdot 10^{-6}.$$

We calculated the field interaction V_{01}^f and V_{02}^f of the hybrid 0–1 and 0–2 states and the amplitudes of the transitions to the continua according to the well-known formulas[19]

$$V_{01}^f=S_{01}^e\langle J=1,M=\Lambda=0|D_z|J'=0,M=\Lambda=0\rangle,$$

$$V_{02}^f=S_{02}^e\langle J=1,M=\Lambda=0|D_z|J'=2,M=\Lambda=0\rangle,$$

where $\langle JM\Lambda|P_z|J'M\Lambda'\rangle$ is the angular part of the matrix element of V^f, S_{01}^e is the radial part of the transition matrix element (the z axis points in the same direction as the vector **f**). Since the state $E^2\Sigma^+$ (like the state $R^2\Sigma^+$) is highly excited, we used the quasiclassical formula[20] to determine S_{01}^e, including a factor of π in it in accordance with the normalization of the wave function, thus

$$S_{01}^e=\Gamma(2/3)(4/3)^{1/2}\omega_f^{-5/3}\cos\pi(\mu_{p\sigma}-\mu_{s\sigma}-1/6), \tag{24}$$

($\Gamma(x)$ is the complete gamma function, $\mu_{s\sigma}=1.104$ and $\mu_{p\sigma}=0.682$ are the corresponding quantum defects of levels 0, 1, and 2 (Ref. 18), with positions $E_0=-1.4453$ eV, $E_1=-0.4353$ eV, and $E_2=-0.4338$ eV (Ref. 21). For transitions to the ionization continua, which, by the way, are described by the elements t_{1p} and t_{2p}, formula (24) must be used after deleting $\mu_{s\sigma}$. Here we are considering the spectral region $\Omega>I_i+E_{vJ}(v_f=1,\ J_f=3)-2\omega_f$, where the continua are homogeneous. As a result we obtain the following values for the matrix elements:

$$V_{01}^f=-30.0f,\quad V_{02}^f=-26.8f,$$

$$t_{1p}=-68.6f,\quad t_{2p}=-30.7f. \tag{25}$$

Figure 3 shows photoelectron spectra corresponding to transitions from the excited state $R^2\Sigma^+$ to the total continuum (left) and the isolated continuum (right) for three values of the field strength: $f=5\cdot 10^4$, $5\cdot 10^5$, and $2.5\cdot 10^6$ V/cm. Since the field-induced levels correspond to the rotational quantum numbers $J_1=0$ and $J_2=2$, according to the selection rules the states ($J=1$, $\Lambda=1$) and ($J=3$, $\Lambda=1$) belong to the common continuum and isolated continuum, respectively.

For moderate field strengths $f\simeq 10^4-10^5$ V/cm (see the top two figures) the intensity of the resonance line corresponding to the state $R^2\Sigma^+$ ($v_1=1$, $J_1=0$) for transitions to the isolated continuum ($v_f=1$, $J_f=3$) turns out to be markedly lower than for the transition to the common continuum ($v_f=1$, $J_f=1$). Thus, for $f\simeq 5\cdot 10^4$ V/cm it is generally impossible to make it out. In the case $f\simeq 2.5\cdot 10^6$ V/cm the resonance curves for the transitions to the common continuum and the isolated continuum are essentially identical. In this case, as could be expected from formula (19), we observe strong field broadening and splitting of the rotational levels, and also suppression of the central maximum corresponding to the state $E^2\Sigma^+$.

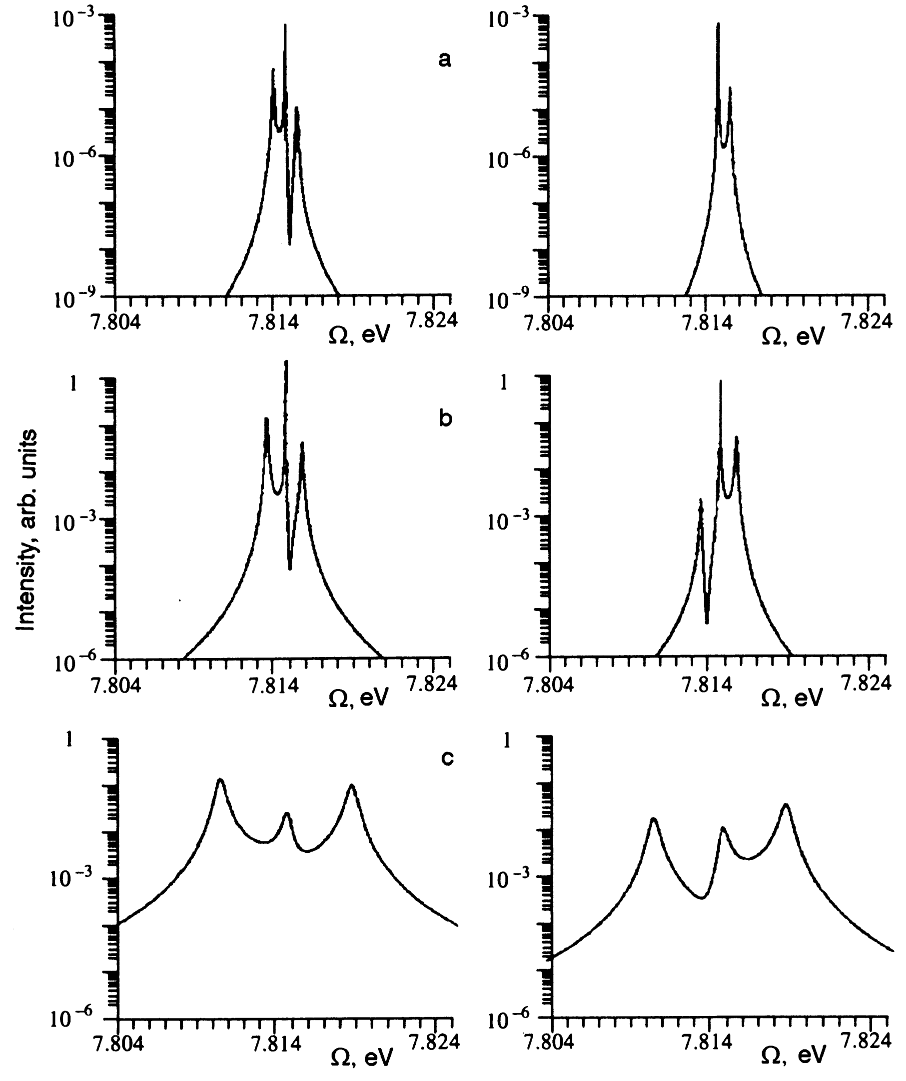

FIG. 3. Spectra of electrons formed in the process of ionization according to scheme (23) during transitions to the total (left) and isolated (right) ionization continua for field strengths of $5\cdot 10^4$ V/cm (a), $5\cdot 10^5$ V/cm (b), and $2.5\cdot 10^6$ V/cm (c) (in arbitrary units).

Note that the indicated regularity (i.e., the abrupt decrease in the intensity of one of the lines of the intermediate complex at sufficiently high field strengths) also takes place in the more general case, when an odd $(2n+1)$ number of strongly field-mixed states of the molecule take part in the generation of photoelectrons. Analysis of expression (19) shows that the shape of the photoelectron spectrum is very critical to the assortment of "0" and "1" intermediate states and each case has its own individual character. This property can be used to solve the problem of optical diagnostics of vibrational and rotational states in molecular beams.

5. CONCLUSION

Let us now discuss the most important results of this paper. First of all, note that for RMI and RMD processes taking place according to the scheme of $\Omega + k\omega_f$-absorption, a direct connection has been established to radiative collisions of slow electrons with molecular ions. This is an extraordinarily interesting and useful circumstance since it allows us to substantially broaden the possibilities of the theory for describing all of the phenomena taking place in an intense laser radiation field (including reverse processes, such as dissociation and photorecombination, bremsstrahlung, etc.).

Also noteworthy is the possibility of intramolecular transitions when in the presence of a one-photon transition at the frequency Ω and two-photon absorption at the frequency of the strong field ω_f the ordinary two-level scheme [see Eqs. (14)–(16)] is realized, which admits a generalization of known results.[6–8] This latter fact is especially important since it provides the simplest interpretation of the experimentally observed spectra.

In conclusion, we point out that under certain conditions rotationally oriented molecular ions can be observed during RMI, i.e., a unique kind of selection of their energetically indistinguishable states is possible, which can be of significant interest in the problem of forming ion beams with prescribed microscopic properties.

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