Strong irregular excitation-energy dependence of the inelastic transition and collisional ionization cross sections of highly excited molecules

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(Submitted 22 May 1992)
Zh. Eksp. Teor. Fiz. **103**, 374–395 (February 1993)

It is predicted that the cross sections of inelastic vibronic transitions and ionization of Rydberg molecules depend strongly (resonantly) on the principal quantum number n in slow collisions with atoms and the nature of this effect is analyzed. The effect is associated with the manifestation of nonadiabatic vibronic coupling, resulting in mixing of the low-lying vibronic states of a Rydberg molecule which belong to different excited states of the ionic core. Together with pronounced peaks (whose amplitude is two to three orders of magnitude higher than the values in the plateau region), the cross sections should exhibit interference dips resulting from oscillations of the quasiclassical wave function of the outer electron as a function of n. A comparison is made with the impulse approximation, widely employed in such problems, and it is shown that for $nV_c \ll e^2/\hbar$, where V_c is the relative velocity of the colliding particles, this approximation is inapplicable for the processes considered. The theory developed is employed to describe collisions of N_2^{**} molecules with inert-gas atoms.

1. INTRODUCTION

Rydberg states (RSs) of molecules have, as is well known, a number of unique features which are due to strong nonadiabatic coupling of the electronic and nuclear motions. Among other phenomena, these features lead to, for example, irregular dependence of the quantum defects of highly excited molecules on the principal quantum number n (Ref. 1) and of the near-threshold photoabsorption spectra on the frequency of the incident light,[1,2] the presence of bound states superposed on the continuum background,[3] and the stroboscopic effect.[4]

In the present paper we show that the nonadiabatic interaction also leads to an interesting physical phenomenon: strong (resonance) dependence of the cross sections for inelastic transitions and ionization of highly excited molecules XY^{**} on the principal quantum number n in slow collisions with atoms A

$$XY^{**}(n,q)+A \begin{array}{l} \nearrow XY^{+}(q')+A+e^{-} \\ \searrow XY^{**}(n',q')+A \end{array} \qquad (1)$$

where q is the collection of quantum numbers describing the internal state of the ion XY^+. We demonstrate the existence of this effect in which the collision velocities V_c of the colliding particles are low ($V_c \ll n^{-1}$), when the dynamical behavior of the system $XY^{**}+A$ is studied after the structural features of the potential energy surfaces (PES) are investigated.[1)] This approach, which is an alternative to the impulse approximation (see Ref. 1 and the literature cited there), has been widely employed in problems of the interaction of Rydberg atoms with atoms and molecules in the electronic ground state.[5–8] In contrast to Refs. 5–8, however, here we must solve the problem of the perturbation of a series of interacting Rydberg states by the field of a neutral particle. In so doing, it is assumed that in the energy range considered $|E| \ll 1$, where E is the total energy of the system $XY^{**}+A$ with fixed distance between the particles XY^+ and A and is equal to the binding energy of the Rydberg electron for the ground vibrational state of XY^+, the atom A does not have resonance states responsible for the formation of the ionic configuration XY^+A^-. Our investigation includes two stages.

First, we use the asymptotic method proposed in Refs. 9 and 10 to analyze the characteristic features of the vibronic PESs of the system $XY^{**}+A$ in the energy range $E<\omega$, where ω is the vibrational frequency of the ion XY^+. The peculiarity of this system is that it contains a weakly bound electron, moving in the field produced by a Coulombic center and the interactions with the ionic core and atom A. The ionic core perturbs states with low electron angular momentum l relative to the Coulombic center ($l=0$, 1 and 2). The field of the atom, in turn, affects only those superpositions of the states of the Coulombic center that have low electron angular momentum L with respect to the atom A. We refer to the two "heterocenter" groups of terms, characteristic of a purely Coulombic center, briefly as l and L terms.

Next, we study the collision dynamics, employing an approach based on analysis of the quasicrossing regions of the terms of the PESs using the model of independent Landau–Zener transitions at the crossing points of the terms (rigorous justification of this model is given in Ref. 11 for the case of the crossing of parallel terms by a linear term). It should be noted that the Rydberg states of molecules are, as a rule, predissociation states and decay in the nuclear continuum on account of configurational mixing with dissociative states, correlated at infinity with low-lying electronic states of the atoms X and Y. Under the condition $V_c \gg \gamma_d n^{-1}$, where γ_d is the configuration interaction constant and $\gamma_d \ll 1$, the characteristic predissociation time $\tau_d \sim \gamma_d^{-1} n^3$ is much longer than the collisional time $\tau_c \sim n^2 V_c^{-1}$. This makes it possible to exclude from the description of the processes (1) the dissociative valence configurations.

As an illustration of the theory developed we calculate the cross sections of inelastic transitions and collisional ionization of Rydberg molecules N_2^{**} by inert-gas atoms as a function of the initial excitation energy and the relative velocity.

1063-7761/93/020200-10$10.00

2. GENERAL EQUATIONS OF THE THEORY

It is convenient to analyze the behavior of a weakly bound electron in the field of the perturbing atom A by means of an asymptotic method similar to the one proposed in Refs. 9, where the position of the lower energy levels of the electron in the system $XY^{**}+A$ with fixed distance R between the atom and the molecule is determined from an integral equation for the level-shift operator, which is a rearranged Lippmann–Schwinger equation for the eigenvalue problem

$$\tau = \mathrm{W}(\mathrm{G}-\mathrm{g})\tau, \tag{2}$$

and W is an operator satisfying the equation

$$\mathrm{W} = \mathrm{V} + \mathrm{VgW}. \tag{3}$$

The operator V in Eq. (3) describes the effective $e^- + A$ interaction, which, generally speaking, is not weak; $\mathbf{g}$ is the weakly energy dependent part of the Green's function operator $\mathbf{G}$ of the molecule XY^{**}. In this formulation the equation (2) contains only singular terms, which characterize the contributions of the discrete states $XY^{**}+A$.

The behavior of the terms of the quasimolecule $XY^{**}A$ at $XY^+ - A$ distances R corresponding to the classically accessible motion of the Rydberg electron $R\,|\varepsilon_v|<1$, where $\varepsilon_v = E - E_v$ and E_v is the vibrational excitation energy of XY^+, is important for the processes (1) which we are investigating. In order to describe them it is necessary to know the explicit form of the operator $\mathbf{G}$ in the neighborhood of the perturbing atom A,[9] i.e., for electron coordinates r such that

$$|\mathrm{r}-\mathrm{R}| \ll R.$$

For this purpose, we employ an adiabatic basis, in which the vibrational state and orientation of the molecule and the position of the perturbing atom are given and it is assumed that the direction of the molecular axis does not change much during the characteristic time of a transition from one term to another. This means essentially that the rotational motion of the molecule XY^{**} is treated classically on an equal footing with the translational motion, which is described by the motion of the image point over the collection of PESs. We also drop the spin variables, since they can easily be included in the general scheme when necessary.

With these restrictions the operator $\mathbf{G}$ can be represented in the following form:[10]

$$\mathrm{G} = \mathrm{g} + 2\sum_{\substack{LMv\\ L'M'v'}} |\chi_v j_L Y_{LM}\rangle\langle\chi_{v'} j_{L'} Y_{L'M'}| \times (k_v \operatorname{ctg}\pi\nu_v\,\delta_{LM,L'M'}\delta_{vv'} + \tilde{\alpha}_{Lv,L'v'}(\mathrm{R})\delta_{M0}\delta_{M'0}), \tag{4}$$

where the part of the Green's function operator that depends weakly on the energy E is defined as

$$\mathrm{g} = -\sum_v |\chi_v\rangle \frac{\cos k_v|\rho-\rho'|}{2\pi|\rho-\rho'|}\langle\chi_v|.$$

Here χ_v is the vibrational function of the ion XY^+, $j_L(k_v\rho)$ is a spherical Bessel function of the first kind, $k_v = [2(1/R - \varepsilon_v)]^{1/2}$ is the quasiclassical momentum of the electron, $Y_{LM}(\hat{\rho})$ are spherical harmonics ($\hat{\rho}$ describes the angles which determine the direction of the vector $\boldsymbol{\rho}$ relative to $\mathbf{R}$, where $\boldsymbol{\rho} = \mathbf{r} - \mathbf{R}$), M is the projection of the angular momentum L on the direction of the vector $\mathbf{R}$, and $\nu_v = [-2(\varepsilon_v)]^{-1/2}$ is the effective principal quantum number.

The matrix $\tilde{\alpha}_{Lv,L'v'}(\mathbf{R})$ is related to the electron scattering matrix $T^{(\Lambda)}_{lv,lv'}$ of the ion core by the expression

$$\tilde{\alpha}_{Lv,L'v'}(\mathrm{R}) = 2\pi^2 \sum_{l\Lambda} \frac{(\nu_v\nu_{v'})^{3/2}}{\sin\pi\nu_v \sin\pi\nu_{v'}} [(2L+1)(2L'+1)]^{1/2} \times T^{(\Lambda)}_{lv,lv'}\tilde{\varphi}_{Lv,E}(R)\tilde{\varphi}_{L'v',E}(R)\,|Y_{l\Lambda}(\hat{R})|^2 \tag{5}$$

where $\hat{R}$ denotes the angles determining the position of the atom A in the coordinate system of the molecule and Λ is the absolute magnitude of the projection of the electron angular momentum l on the axis of the molecule.

The elements of the matrix $T^{(\Lambda)}_{lv,lv'}(E)$ are found from the system of equations

$$T^{(\Lambda)}_{lv,lv'} = t^{(\Lambda)}_{lv,lv'} + \sum_{v''} t^{(\Lambda)}_{lv,lv''} \operatorname{ctg}\pi\nu_{v''} T^{(\Lambda)}_{lv'',lv'},$$

$$t^{(\Lambda)}_{lv,lv'} = -\langle\chi_v|\operatorname{tg}\pi\mu_{l\Lambda}(\xi)|\chi_{v'}\rangle,$$

where $\mu_{l\Lambda}(\xi)$ is the adiabatic quantum defect of the Rydberg level and depends parametrically on the interatomic distance. The radial function $\tilde{\varphi}^{(l)}_{Lv,E}(R)$ is defined outside the ion core as[10]

$$\tilde{\varphi}^{(l)}_{Lv,E}(R) = \frac{W_{\tilde{\nu}_v,\, l+1/2}(2R/\tilde{\nu}_v)}{R\tilde{\nu}_v[\Gamma(\tilde{\nu}_v - l)\Gamma(\tilde{\nu}_v + l + 1)]^{1/2}},$$

$$\tilde{\nu}_v = \begin{cases} \nu_v & \text{for} \quad L = 2m \\ \nu_v - 1/2 & \text{for} \quad L = 2m+1 \end{cases},$$

where $W_{\mu\nu}(x)$ is the Whittaker function, $\Gamma(x)$ is the gamma function, and $m = 0,1,2,\ldots$. We neglect l-mixing in the scattering of an electron by the ion core, since for many diatomic molecules l is a good quantum number.[1] Since the representation (4) for the operator $\mathbf{g}$ contains standing-wave electron Green's functions, the K scattering matrix corresponds to the elements of the $\mathbf{W}$ operator.[9] Thus, substituting Eq. (4) into Eq. (2) reduces the homogeneous integral equation with a singular kernel to the following system of algebraic equations:

$$\tau_{LMv} = K_{Lv}(k_v \operatorname{ctg}\pi\nu_v \tau_{LMv} + \delta_{MO}\sum_{L'v'}\tilde{\alpha}_{Lv,L'v'}\tau_{LOv'}). \tag{6}$$

Due to the spherical symmetry of the field of the perturbing atom the K matrix is diagonal with respect to the indices L and M, and for this reason the first term in Eq. (6) does not include summation over L. The equation (6) describes vibronic PESs, whose definition includes nonadiabatic coupling of the electronic and vibrational motions.

According to Eq. (6) only terms with $M=0$ interact effectively with one another. Thus the following equation is sufficient for finding the terms:

$$1 - k_v K_{Lv}\operatorname{ctg}\pi\nu_v - K_{Lv}\tilde{\alpha}_{Lv,Lv}(\mathrm{R}) = 0, \tag{7}$$

The solution of this equation includes two groups of vibronic terms of the compound system $XY^{**}A$, which correspond, respectively, to two independent electron scattering centers (the ion core XY^+ and the atom A). The first group corresponds to R-independent Rydberg l terms (see Ref. 10)

$$E_{n_v l\Lambda} = E_v - \frac{1}{2(n_v - \mu_{l\Lambda v})^2}, \tag{8}$$

where $\mu_{l\Lambda v}$ is the quantum defect of the $l\Lambda v$ series. The position of these terms is given by the poles of the T collision matrix. The second group consists of the covalent L terms, split from the Coulombic levels by the field of the perturbing atom A. These terms are determined by the equation

$$1 - k_v K_{Lv} \operatorname{ctg} \pi\nu_v = 0 \tag{9}$$

and are written as

$$U_{n_v}^{(L)}(R) = E_v - \frac{1}{2\left[n_v + \frac{1}{\pi}\operatorname{arctg}(k_v(R)K_{Lv})\right]^2}. \tag{10}$$

The collision of the particles XY^{**} and A induces nonadiabatic transitions between the Rydberg l and covalent L terms near the quasicrossings of the terms. These transitions are accompanied by a simultaneous change in the vibrational state of the ion and an abrupt change in the angular momentum l (from $l \sim 1$ to $l \sim n_v$).

3. PERTURBATION OF THE INTERACTING RYDBERG SERIES BY THE FIELD OF THE NEUTRAL PARTICLE

The region of the spectrum corresponding to simultaneous excitation of two interacting series of $n_{v'} l$ and $n_v l$ Rydberg terms by the covalent L term is of principal interest for the processes (1) which we are considering. After we identify in Eq. (5) the pole terms, we are interested in, which have definite values of l and Λ, Eq. (7), describing terms of the quasimolecule $XY^{**}A$ taking into account nonadiabatic coupling between the nearest v and $v' = v - 1$ Rydberg series of XY^{**} (i.e., in the two-channel representation for $T_{lv,lv}^{(\Lambda)}$) assumes the form

$$(\operatorname{tg} \pi\nu_v - k_v K_{Lv})[(\operatorname{tg} \pi\nu_v - t_{lv,lv}^{(\Lambda)})(\operatorname{tg} \pi\nu_{v'} - t_{lv',lv'}^{(\Lambda)}) - (t_{lv,lv'}^{(\Lambda)})^2]$$
$$= B_{l\Lambda Lv} K_{Lv} \frac{\pi\nu_v^3}{\cos^2 \pi\nu_v} [(t_{lv,lv}^{(\Lambda)})(\operatorname{tg} \pi\nu_{v'} - t_{lv',lv'}^{(\Lambda)}) - (t_{lv,lv'}^{(\Lambda)})^2], \tag{11}$$

where the coefficient

$$B_{l\Lambda Lv} = 2\pi(2L+1)|\tilde{\varphi}_{Lv,E}^{(l)}(R)|^2 |Y_{l\Lambda}(\hat{R})|^2 \tag{12}$$

characterizes the probability of finding an electron near the perturbing atom A.

Neighborhoods of quasicrossing points $R_{n_{v'}}^{(c)}$ of the Rydberg $n_{v'} l$ and covalent $n_v L$ terms, corresponding to different vibrational states of the ion XY^+, make the largest contribution to the cross section of the processes (1). In order to investigate the behavior of the terms in these regions we employ the fact that the coefficients $B_{l\Lambda Lv}$ are small and we rewrite the left-hand side of Eq. (11) as

$$(E - U_{n_v}^{(L)}(R))(E - E_{n_{v'} l\Lambda})(E - E_{n_v l\Lambda}),$$

which explicitly determines the position of the terms of the system taking into account nonadiabatic vibronic coupling in the $l\Lambda$ states of the molecule XY^{**}. Then in the neighborhood of the crossing points $R_{n_{v'}}^{(c)}$ of the $n_{v'} lv'$ and $n_v Lv$ terms, where $E_{n_{v'} l\Lambda} = U_{n_v}^{(L)}(R)$, Eq. (11) can be rewritten as follows:

$$(E - E_{n_{v'} l\Lambda})(E - U_{n_v}^{(L)}(R)) = V_{n_v L, n_{v'} l}^2,$$

which makes it possible to determine the interaction $V_{n_v L, n_{v'} l}^2$ between them:

$$V_{n_v L, n_{v'} l}^2 = \frac{B_{l\Lambda Lv} k_v K_{Lv}^2 \cos^2 \pi\nu_v}{\pi\nu_v^3} f_{n_v n_{v'}}^{(l)}, \tag{13}$$

where the factor

$$f_{n_v n_{v'}}^{(l)}(E_{n_{v'} l\Lambda})$$
$$= \frac{(t_{lv,lv'}^{(\Lambda)})^2}{(\nu_{v'}/\nu_v)^3 (\cos \pi\nu_v / \cos \pi\nu_{v'})^2 (\operatorname{tg} \pi\nu_v - t_{lv,lv}^{(\Lambda)})^2 + (t_{lv,lv'}^{(\Lambda)})^2} \tag{14}$$

is defined as the nonadiabatic mixing factor. This factor plays an important role in the theory being developed here and, as will be shown below, it is responsible for the effects we are investigating.

We now consider the two limiting cases of weak and strong mixing. In the first case (nonresonance situation), when the splitting between isolated vibronic $n_{v'} l$ and $n_v l$ levels is quite large, i.e., the inequality

$$|E_{n_v l\Lambda} - E_{n_{v'} l\Lambda}| \gg |t_{lv,lv'}^{(\Lambda)}| (n_v n_{v'})^{3/2},$$

is satisfied, the term $(t_{lv,lv'}^{(\Lambda)})^2$ in the denominator in Eq. (14) can be neglected. Then the expression (13) will describe the case of weak interaction of the series of $n_{v'} l$ Rydberg terms with the covalent $n_v L$ term, as studied in Ref. 10. At resonance $\tan \pi\nu_v = t_{lv,lv}^{(\Lambda)}$ (when the factor $f_{n_v n_{v'}}^{(l)}$ is equal to unity), the quantity (13) is the squared interaction of the covalent $n_v L$ and Rydberg $n_v l$ terms. Here a transition is observed to the case of the quasicrossing of two terms with the same vibrational quantum number v (strong mixing).

The behavior of the autoionization terms of the quasimolecule $XY^{**}A$ is described by Eq. (7) with the formal substitution $\tan \pi\nu_{v'} = i$. The solution gives the following expression for the covalent term

$$U_{n_v}^{(L)}(\mathrm{R}) = E_v - \frac{1}{2n_v^2} + \frac{k_v(R)K_{Lv}}{\pi\nu_v^3} - i\frac{\Gamma_{n_v L}(\mathrm{R})}{2}, \tag{15}$$

where the autoionization width$^{2)}$ is

$$\Gamma_{n_v L}(\mathrm{R})$$
$$= \sum_{l\Lambda} \frac{2B_{l\Lambda Lv} k_v K_{Lv} (t_{lv,lv'}^{(\Lambda)})^2}{(\operatorname{tg}[\pi\{2(E_v - \mathrm{Re}\,U_{n_v}^{(L)}(R))\}^{-1/2}] - t_{lv,lv}^{(\Lambda)})^2 (1 + \Delta_{v'v}^{(\Lambda)})^2},$$
$$\Delta_{v'v}^{(\Lambda)} = t_{lv',lv}^{(\Lambda)} + \frac{1}{(\operatorname{tg}[\pi(2E_v)^{-1/2}] - t_{lv,lv}^{(\Lambda)})^2}. \tag{16}$$

It is obvious that ionization of the molecule XY^{**} is efficient when in the region of classical motion of the electron the covalent $n_v L$ term crosses the limit E_{v-1} or, in other words, the equation

$$U_{n_v}^{(L)}(R_{n_v}^*) = E_{v-1} \tag{17}$$

has at least one solution. If

$$|n_v - (2\omega_v)^{-1/2}| n_v^3 \ll 1 \quad (\omega_v = E_v - E_{v-1})$$

the roots of Eq. (17) (at least some of them) lie in the asymptotic region $2n_v^2 > R_{n_v}^* \gg 1$. In order to analyze the asymptotic solutions we employ the wavelength representation ($L = 0, \beta k_v^2 \ll 1$):[13]

$$K_{0v} = a + \frac{\pi\beta}{3} k_v + \frac{4}{3}\beta k_v^2 a \ln(k_v) + \gamma k_v^2, \tag{18}$$

where a is the scattering length of the electron scattered by atom A, β is the polarizability of the atom A, and the values of the coefficient γ for scattering of an electron by inert-gas atoms are given in Ref. 14.

We now indicate the conditions under which the $n_v l$ resonance level, leading to effective mixing of the vibronic v and v' states of XY^{**}, falls into the energy range from the minimum of the term $U_{n_v}^{(L)}(R_{\min})$ to the spectrum limit $E = 0$. This happens for positive a if

$$n_v - (2\omega_v)^{-1/2} < \mu_{l\Lambda v} < 0, \tag{19}$$

and for $a < 0$ if

$$n_v - (2\omega_v)^{-1/2} < \mu_{l\Lambda v} < n_v - (2(\omega_v - U_{n_v}^{(L)}(R_{min})))^{-1/2}. \tag{20}$$

An example satisfying simultaneously the conditions (19)–(20) is the system $N_2^{**}(nd\delta_g) + A$, where A is an inert-gas atom. The behavior of the $n_1 L$ terms $U_{n_1}^{(L)}(R)$ for the case $L = 0$ is displayed in Fig. 1 (a and b). The terms with $L \neq 0$ deviate significantly less from their asymptotic values and are not considered here.

We note that in the case $a < 0$ the matrix elements K_{Lv} with $L = 0$ can vanish (Ramsauer effect), i.e., $K_{0v}(\tilde{R}) = 0$, where the point $\tilde{R}$ corresponds to the position of the unperturbed level

$$U_{n_v}^{(L)}(\tilde{R}) = E_v - 1/2n_v^2.$$

At distances in the range $\tilde{R} < R < 2n_v^2$ the PESs of the compound system $XY^{**}A$ (see Fig. 1) have small potential wells, whose depth increases with decreasing n_v. The characteristics of these terms are presented in Table I.

4. IONIZATION PROBABILITY AND CROSS SECTION

We now calculate the probabilities and cross sections of collisional ionization of vibrationally excited Rydberg molecules ($v' = 0$, $v = 1$). For this we employ, as is done in the similar problem of ionization of a Rydberg atom due to perturbation by the term crossing the spectrum limit,[7,16,17] the model of independent Landau–Zener transitions in a system with multiple crossing of terms.[11] The model has been strictly justified for the linear term and is applicable under our conditions, if the region $\Delta R = R_{n_0}^{(c)} - R_{n_1}^* \ll R_{n_0}^{(c)}$ makes the main contribution to the ionization cross section; this condition imposes, generally speaking, certain restrictions on both the choice of collision partners and the initial excitation of the molecule XY^{**}. Since the asymptotic region of large R plays the main role in the collisional processes (1), under the condition

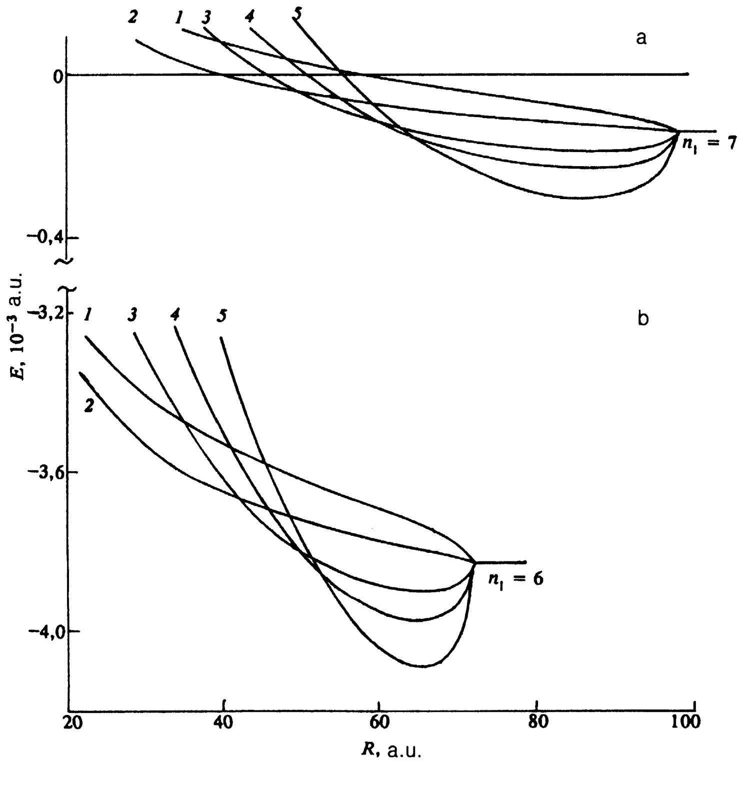

FIG. 1. Terms of the system $N_2^{**} + A$ ($A = \{$He, Ne, Ar, Kr, Xe$\}$) for $n_1 = 7$ and $n_1 = 6$, classified according to the type of scattering ($L = 0$) by the perturbing center. The numbers indicate the sequence of $n_1 L$ terms from He to Xe.

TABLE I. Parameters a, β, γ in the expansion of the K matrix for $e^- - A$ scattering [Eq. (18)] and characteristics of the covalent n_1L terms of the system $N_2^{**} + A$ (in a.u.).

Atoms				Covalent n_1L terms*							
A	a	β	γ	$n_1 = 7$					$n_1 = 6$		
	[15]	[15]	[14]	R_{min}	$U_{n_1}^{(L)}(R_{min})$	$\tilde{R}$	$R_{n_1}^*$	$\frac{\Gamma_{n_1L}^* R_{n_1}^*}{V_c}$	R_{min}	$U_{n_1}^{(L)}(R_{min})$	$\tilde{R}$
He	1,15	1,383	6	—	—	—	58,1	6,87(−4)	—	—	—
Ne	0,3	2,68	6,5	—	—	—	39,9	4,56(−3)	—	—	—
Ar	−1,69	11,08	−5	86,6	−1,88(−4)	65,5	45,9	2,93(−2)	65,6	−3,91(−3)	53,0
Kr	−3,2	16,74	−40	85,5	−2,33(−4)	63,5	50,6	7,83(−2)	65,0	−3,97(−3)	51,5
Xe	−6,0	27,06	−210	86,0	−3,07(−4)	64,0	55,6	1,28	65,4	−4,09(−3)	51,5

*The autoionization parameters $\Gamma_{n_1L}^* R_{n_1}^* / V_c$ were calculated for the relative velocity $V_c = 2\cdot 10^{-4}$.

$$V_c \gg (\beta/M_c)^{1/2} (R_{n_1}^{(c)})^{-2}$$

where M_c is the reduced mass of the colliding particles, the ionization cross section can be calculated in the rectilinear-trajectory approximation.

For fixed impact parameter b the ionization probability can be written as[11]

$$W_{n_1n_0}(b) = p_{n_1n_0}(b) q_{n_1n_0+1}(b)(1 - S(b)), \tag{21}$$

where $p_{n_1n_0}$ is the probability of the first nonadiabatic transition from the n_0l Rydberg term to the n_1L covalent term, and $q_{n_1n_0+1}$ is the probability of entering the continuous spectrum at the point $R_{n_1}^*$ along the diabatic n_1L-term. The quantity S is the probability of remaining on the covalent term as the image point moves into the range $R \lesssim R_{n_1}^*$ [in this region the term is determined by the expression (15)].

In order to describe a transition between two crossing terms we introduce, as usual, the Landau–Zener parameter characterizing the probability of transitions in the model:[18]

$$\eta_{n_1n_0} = 2\pi \frac{\overline{V_{n_1L,n_0l\Lambda}^2}}{F_{n_1} V_c}, \tag{22}$$

where F_{n_1} is the magnitude of the difference of the forces acting along the trajectory, i.e.,

$$F_{n_1}(R_{n_0}^{(c)}) = \frac{|K_{L1}| [(R_{n_0}^{(c)})^2 - b^2]^{1/2}}{\pi n_1^3 k_1 (R_{n_0}^{(c)}) (R_{n_0}^{(c)})^3}.$$

The overbar in Eq. (22) denotes averaging over all orientations of the molecule XY^{**}. Substituting Eq. (13) into Eq. (22) and using the quasiclassical representation for the electron wave function $\tilde{\varphi}_{L1,E}^{(l)}$, we can easily derive the following expression:

$$\eta_{n_1n_0} = \frac{2(2L+1) k_1 (R_{n_0}^{(c)}) |K_{L1}| \cos^2 \pi\nu_1 \sin^2 \Phi}{V_c [1 - (b/R_{n_0}^{(c)})^2]^{1/2}} f_{n_1n_0}^{(l)}, \tag{23}$$

where $\Phi = (8R_{n_0}^{(c)})^{1/2} + \frac{2^{1/2}}{3} \varepsilon_0 R_{n_0}^{(c)^{3/2}} + \pi\mu_{l\Lambda0} + \pi L/2 - \pi/4$ is the corresponding quasiclassical phase. In the presence of resonance, whose existence is determined by the conditions (19)–(20), the mixing factor $f_{n_1n_0}^{(l)}$ near an isolated n_1l level

$$E_r = E_1 - \frac{1}{2[n_1 + \pi^{-1} \operatorname{arctg}(t_{l1,l1}^{(\Lambda)})]^2}$$

acquires a pronounced resonance character

$$f_{n_1n_0}^{(l)} = \frac{d_r^2}{(E - E_r)^2 + d_r^2}. \tag{24}$$

The quantity d_r here is the "effective width" of the resonance and is given by

$$d_r = \left| \frac{\cos \pi\nu_1 \cos \pi\nu_0}{\pi(\nu_1\nu_0)^{3/2}} t_{l1,l0}^{(\Lambda)} \right|.$$

The capture probability $p_{n_1n_0}$ in the formula (21) is related to the probability of remaining in the n_1L covalent term (on passage through the quasicrossing point $R_{n_0}^{(c)}$)

$$w_{n_1n_0}(l, \Lambda, b) = \exp(-\eta_{n_1n_0}(l, \Lambda, b))$$

by the expression $p_{n_1n_0} = 1 - w_{n_1n_0}$. The probability that the system is transferred in the continuous spectrum is defined as the product of the separate probabilities of remaining in the n_1L term, taking into account all transitions at the points of quasicrossings with Rydberg terms ($n_0' \geqslant n_0 + 1$, $l' \leqslant n_0 - 1, \Lambda' \leqslant l'$)

$$q_{n_1n_0+1} = \prod_{n_0' \geq n_0+1}^{n-1} \prod_{l'=0}^{l'} \prod_{\Lambda'=0} w_{n_1n_0'}(l', \Lambda'). \tag{25}$$

Assuming the transition region ΔR to be well localized, in calculating $q_{n_1n_0+1}$ in Eq. (25) the summation over n_0' can be replaced by integration. The quantity $S(b)$ in Eq. (21) (neglecting nonabatic transitions in the continuous spectrum) can be written in the form

$$S(b) = \exp(-2 \int_0^{T(b,E)} \Gamma_{n_1L}(t) dt)$$

where $T(b,E)$ is the residence time in the region $b \leqslant R \leqslant R_{n_1}^*$ and Γ_{n_1L} is the autodecay width (16). In the rectilinear-trajectory approximation

$$S(b) = \exp\left(-\frac{2\Gamma_{n_1L}^* R_{n_1}^{*2}}{V_c b} \operatorname{arctg} \left[\left(\frac{R_n^*}{b} \right)^2 - 1 \right]^{1/2} \right)$$

$$(\Gamma_{n_1L}^* = \Gamma_{n_1L}(R_{n_1}^*)). \tag{26}$$

Performing the integration over the impact parameter b, we can represent the ionization cross section as the product of the cross section for the system to be captured in the n_1L state and the effective ionization probability $p_{10}^{(i)}(V_c)$ (the indices l and Λ are dropped), i.e.,

$$\sigma_{n_0}^{(i)}(V_c) = \pi R_{n_1}^{*2} P_{10}^{(i)}(V_c), \tag{27}$$

where

$$P_{10}^{(i)}(V_c) = 2\int_0^1 x \left[1 - \exp\left(-\frac{A}{V_c}(1-x^2)^{-1/2}\right)\right]$$
$$\times \exp\left(-\frac{Q}{V_c}(1-x^2)^{-1/2}\right)(1 - S(x))dx \quad \left(x = \frac{b}{R_{n_0}^{(c)}}\right). \tag{28}$$

The quantities A and Q, which are related, respectively, to the probability of the first Landau–Zener transition from the initial Rydberg n_0l term to the covalent n_1L term ($\sim A/V_c$) and the probability of remaining in this term ($\sim\exp(-Q/V_c)$), are given by the expressions

$$A(n_0) = \frac{1}{\nu_0^3} Z(R_{n_0}^{(c)}) f_{n_0 n_1}^{(l)}, \tag{29}$$
$$Q(n_0) = Z(R_{n_1}^{(c)}) d_r \operatorname{arcctg}\left(\frac{|E_r^*| - I_0'}{d_r^*}\right),$$

where we have introduced the following notation:

$$Z = 2(2L+1)k_1K_{L1}\left[\frac{(t_{01})^2}{1+(t_{00})^2}\right]\left(\frac{\cos^2\pi\nu_1}{\pi\nu_1^3}\right)^2 \frac{\sin^2\Phi}{d_r^2},$$

$$E_r^* = E_r + \Delta_r, \quad \Delta_r = -\frac{d_r^2}{E_r},$$

$$d_r^* = -\frac{d_r I_0'}{E_r}, \quad I_0' = \frac{1}{2(n_0+1)^2}.$$

We now analyze the cross section (27), making the assumption that in the energy range under consideration strong nonadiabatic mixing of n_0l and n_1l states occurs in only one region. According to Eq. (29) the functions $A(n_0)$ and $Q(n_0)$ vary significantly near the corresponding n_1l level and are virtually energy independent far from this level. The half-width of the transition region is quite narrow, $\Delta n \gtrsim 1$. The function $A(n_0)$ in this region increases rapidly, reaching at the point E_r the maximum value

$$A_{max} = \frac{1}{\nu_0^3} Z(R_{n_1}^{(c)}).$$

The function $Q(n_0)$, however, after passing the resonance point E_r^*, decreases rapidly with n_0. The rate of decrease is $\sim k_1K_{L1}/n_1^3$. For this reason, the peak in the cross section (27) should be, strictly speaking, asymmetric with respect to E_r. Physically, this is related with the fact that for $E_{n_0} < E_r$ the molecule XY^{**} is efficiently vibrationally excited due to the transition from the covalent n_1L term of the Rydberg n_1l term. The rapid growth of the cross section near the point E_{n_0} is caused by the increase in $A(n_0)$ due to mixing of n_0l and n_1l Rydberg configurations.

If the energy of the initial state E_{n_0} lies above E_r, then according to Eq. (28) the probability $P_{10}^{(i)}(V_c)$ is

$$P_{10}^{(i)}(V_c) = \frac{\pi^2 \Gamma_{n_1L}^* R_{n_1}^*}{2V_c} E_3\left(\frac{2Q}{\pi V_c}\right), \tag{30}$$

where $E_n(x)$ is the integral exponential function.[19] This corresponds to a nonresonance situation. For $Q(n_0)/V_c \ll 1$ the ionization cross section as a function of V_c in this case is proportional to $\sim 1/V_c$.

Since near the point E_r, $A(n_0)$ starts to increase with increasing n_0 and $Q(n_0)$ starts to drop rapidly at the point $E_r^*(|E_r^*| < |E_r|)$, the position of the maximum of the probability (28) should correspond to the energy E_r. The maximum then is

$$P_{10}^{(i)}(\max) \simeq \frac{\Gamma_{n_1}^* R_{n_1}^*}{4V_c}.$$

For this reason, the ratio of $\sigma_{n_0}^{(i)}(E_r)$ to the cross section in the plateau region $\sigma_{n_0}^{(i)}(E \neq E_r)$ is larger than or of order 10^3, i.e., the cross section (27) should have a pronounced peak near $E = E_r$.

We note that the ionization cross section (27) should contain, together with sharp peaks, oscillations due to the n_0-dependence of the quasiclassical phase Φ. The scale of these oscillations

$$\delta n_0 = \frac{\pi}{2|\Phi'(n_0)|} \tag{31}$$

is proportional to $\sim |dU_{n_1}^{(L)}/dR|^{1/4}$. Hence it follows that the cross sections for the sloping $n_v L$ covalent terms are characterized by a higher oscillation frequency ($\sim \delta n_0^{-1}$).

Similar oscillations in the broadening cross section in the case of quenching of nonhydrogen-like Rydberg states of alkali atoms in a rubidium atmosphere due to formation of an ionic ^3P-configuration were investigated in Ref. 20, and were also mentioned in Ref. 17.

5. VIBRONIC TRANSITIONS IN THE SYSTEM $XY^{**}+A$

We now consider inelastic collisions accompanied by single-quantum vibrational excitation of the molecule XY^{**}. Here vibronic transitions into the n_1L state (accompanied by a change in the angular momentum of the electron $l' \neq l$, $l' \lesssim n_1$), i.e.

$$XY^{**}(n_0, l, v'=0) + A \to XY^{**}(n_1, l' \gg 1, v=1) + A, \tag{32}$$

and transitions into the n_1l state with conservation of $l(l'=l)$

$$XY^{**}(n_0, l, v'=0) + A \to XY^{**}(n_1, l, v=1) + A \tag{33}$$

are of greatest interest.

In contrast to the ionization process, the inelastic $(n_0, v=0) \to (n_1, v=1)$ vibronic transitions occur because the image point passes through the regions of pseudocrossing of the Rydberg and covalent terms twice. Since transitions between them are unlikely, the total cross sections of the processes (32)–(33) are sums of separate cross sections, each of which corresponds to a single capture in the n_1L state (with the particles approaching one another and moving apart, respectively). In addition, in the case (33), in contrast to the case (32), an additional factor describing the probability of leaving the n_1L term in the vicinity of $E = E_r$, must also be included in the overall scheme of the calculation.

Two regions corresponding to different values of n_1 must be distinguished in the dependence of the cross sections on the initial energy E_{n_0}. In the first region the n_1L terms lie near the limit of the continuous spectrum and they cross this limit at the points $R^*_{n_1}$ (see Fig. 1a). For this reason, the possibility of an autoionization term must be taken into account here.

In the second region (see Fig. 1b) the covalent n_1L terms lie in the discrete spectrum ($E<0$). The cross section of inelastic transitions in this case can be represented in the form

$$\sigma_{01} = 2\pi R^{(c)^2}_{n_0}\left[E_3\left(\frac{\overline{Q}(n_0)}{V_c}\right) - E_3\left(\frac{\overline{Q}(n_0)+A(n_0)}{V_c}\right)\right], \qquad (34)$$

where $\overline{Q}$, in contrast to Eq. (29), presupposes summation over a finite number of states. Under nonresonance conditions the excitation cross section (34) is

$$\sigma_{01}(E \neq E_r) = \pi R^{(c)^2}_{n_0}\frac{A(n_0)}{V_c}. \qquad (35)$$

Near the point $E=E_r$, however, it is of order

$$\sigma_{01}(E_r) = \pi R^{(c)^2}_{n_0},$$

and for this reason the ratio of the maximum cross section to the cross section in the region of the plateau is $\sigma_{01}(E=E_r)/\sigma_{01}(E\neq E_r)\gg 1$. Therefore, the pronounced "resonance" structure in the energy dependence $\sigma_{01}(E_{n_0})$ should also be manifested in the cross sections for inelastic transitions (by analogy to ionization).

Another important feature of the processes (1) arises when the molecule XY^{**} interacts with atoms A characterized by the presence of the Ramsauer effect in $e^- + A$ scattering ($a<0$). Near the level $E_{n_0} = \omega - 1/2n_1^2$ (where the matrix element K_{L1} vanishes) the probability of capture in the state n_1L [corresponding to the factor A/V_c in Eq. (28)] becomes small, and as a result the cross sections decrease sharply in this energy range.

6. COMPARISON WITH THE IMPULSE APPROXIMATION

It is natural to compare the results obtained to the impulse approximation, which is widely employed in similar calculations but completely ignores the specific structure of the PESs of the quasimolecules. Such a comparison is helpful for clarifying the usefulness of the impulse approximation for describing collisional processes in $XY^{**}+A$ systems, characterized by quasicrossing of terms.

The cross section for the transfer of energy $\Delta E = |1/2n_0^2 - 1/2n^2|$ with $\Delta E \gg 1/n_0^3$ by the impact impulse mechanism can be estimated as

$$\frac{d\sigma^{(i)}_{imp}}{dE} = 2\pi|F(\varkappa)|^2\int|\psi_{nl}(\mathbf{k})|^2\delta(E-\varkappa V_c)dk\, d\cos\theta_c.$$

Here $|F(\varkappa)|$ is the amplitude of elastic scattering of an electron by an angle θ_c and $\varkappa$ is the momentum transferred ($\varkappa = |\mathbf{k}-\mathbf{k}'|$). Since for $n_0V_c\ll 1$ the amount of energy transferred is small compared with the kinetic energy $k^2/2$, in the main region of the transitions ($I_0 = 1/2n_0^2$) the ionization cross section can be represented in the form

$$\frac{d\sigma^{(i)}_{imp}}{d\Omega} = |F|^2\int_{I_0/2V_c}^{\infty}|\psi_{nl}(\mathbf{k})|^2\frac{(k-I_0/2V_c)^2}{k^2}dk. \qquad (36)$$

Using the well-known expression for the electron momentum distribution in the hydrogen atom[21] and the fact that the minimum momentum in the integral (36) satisfies $k_{\min} = I_0/2V_c \gg 1/n_0$, we obtain for the total ionization cross section

$$\sigma^{(i)}_{imp} = 2^7\left(1+\frac{l}{n}\right)\frac{\Gamma(3/2)\Gamma(n_0+l)(4n_0V_c)^{2l+3}|F|^2}{\Gamma(l+3/2)\Gamma(n_0-l)(l+2)[(2l+4)^2-1]}. \qquad (37)$$

The expression (37) with $l=0$ is identical to the cross section calculated according to classical mechanics,[15] i.e.,

$$\sigma^{(i)}_{imp} = \frac{256\sqrt{2}}{15\pi}\sigma_0(I_0^{-1/2}V_c)^3 \quad (\sigma_0 = 4\pi|F|^2). \qquad (38)$$

From Eqs. (29)–(30), the ionization cross section (27) under nonresonance conditions ($n_0 > (2|E_r|)^{-1/2}$) can be estimated as

$$\sigma^{(i)}_{n_0} \simeq \frac{|K_{L1}|^3 t_{01}^4}{n_0^3 n_1^2 V_c} \sim \frac{\omega|K_{L1}|t_{01}^4}{n_0^3V_c^2}, \qquad (39)$$

where ω is the vibrational frequency of the ion XY^+.

Comparing Eqs. (38) and (39), the following relations are easily obtained:

$$\sigma^{(i)}_{n_0} \gg \sigma^{(i)}_{imp} \quad \text{for} \quad n_0 < v_i^*,$$

$$\sigma^{(i)}_{n_0} < \sigma^{(i)}_{imp} \quad \text{for} \quad n_0 > v_i^*,$$

where

$$v_i^* = \left(\frac{\omega|K_{L1}|^3 t_{01}^4}{\sigma_0 V_c}\right)^{1/6}$$

is the effective principal quantum number, for which $\sigma^{(i)}_{n_0}\sim\sigma^{(i)}_{\rm imp}$. For the characteristic values $\sigma_0\sim|K_{L1}|^2\sim 1$, $|t_{01}|\sim 10^{-1}$ and $V_c\sim 10^{-4}$, this number is on the order of $v_i^*\sim 10^3$. Thus in the case $n_0 < v_i^*$, corresponding to the condition $n_0V_c\ll 1$, the ionization process proceeds mainly by the term-quasicrossing mechanism. Under these conditions the impulse approximation in the velocity range $V_c \approx 1/n_0^2$ does not give a correct estimate of the cross section for collisional ionization in the $XY^{**}+A$ system.

7. IONIZATION AND VIBRONIC TRANSITIONS DURING THE INTERACTION OF N_2^{**} MOLECULES WITH INERT-GAS ATOMS

We now apply the foregoing theory to the example of collisional excitation and inelastic $(n_0, v=0)\to(n_1, v=1)$ vibronic transitions in the system

$$N_2^{**}(n_0>40, d\delta_g, v=0) + A \to \begin{cases} N_2^+ + A + e^-, & (40') \\ N_2^{**}(n_1=7, l\gg 1, \\ \quad v=1)+A, & (40'') \\ N_2(n_1=7, d\delta_g, \\ \quad v=1)+A & (40''') \end{cases}$$

(where $A = \{\mathrm{He,Ne,Ar,Kr,Xe}\}$), whose covalent L terms cross the spectrum limit (Fig. 1a). This system with energy $E_r = -1.148\cdot10^{-4}$ corresponding to $n_r = 66$, is characterized by strong nonadiabatic mixing of the Rydberg $d\delta_g$ states ($v = 0$ and $v = 1$). The dependence of the cross sections of the processes (40) on the initial excitation, which were calculated using the formulas (27)–(29) with the parameters[22,23]

$$\omega = 1{,}006\cdot10^{-2},\quad \xi_e = 2{,}11,$$

$$\mu_{d\delta_g}(\xi) = -0{,}01 + 0{,}158(\xi - \xi_e) \qquad (41)$$

(ξ_e is the equilibrium interatomic distance in the ion N_2^+) and the initial data taken from Table I, are displayed in Figs. 2 and 3. These cross sections are characterized by sharp peaks, encompassing a small group of Rydberg states. The resulting distributions are, as expected, asymmetric with re-

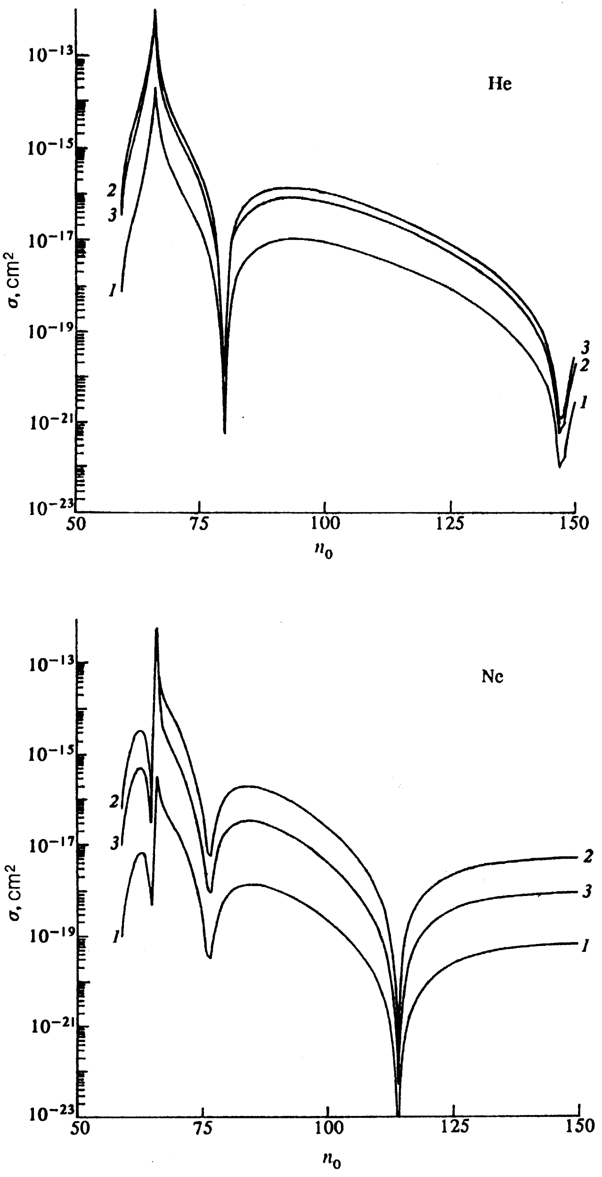

FIG. 2. Cross section for collisional ionization (*1*) and vibronic transitions $v = 0 \rightarrow v = 1$ with (*2*) and without (*3*) a change in the electron angular momentum for the system $N_2^{**}(n_0, d\delta_g, v = 0) + A$, where $A = \{\mathrm{He\ and\ Ne}\}$. The calculations were performed for the relative velocity $V_c = 2\cdot10^{-4}$ a.u. with the parameters (41) and the data given in Table I.

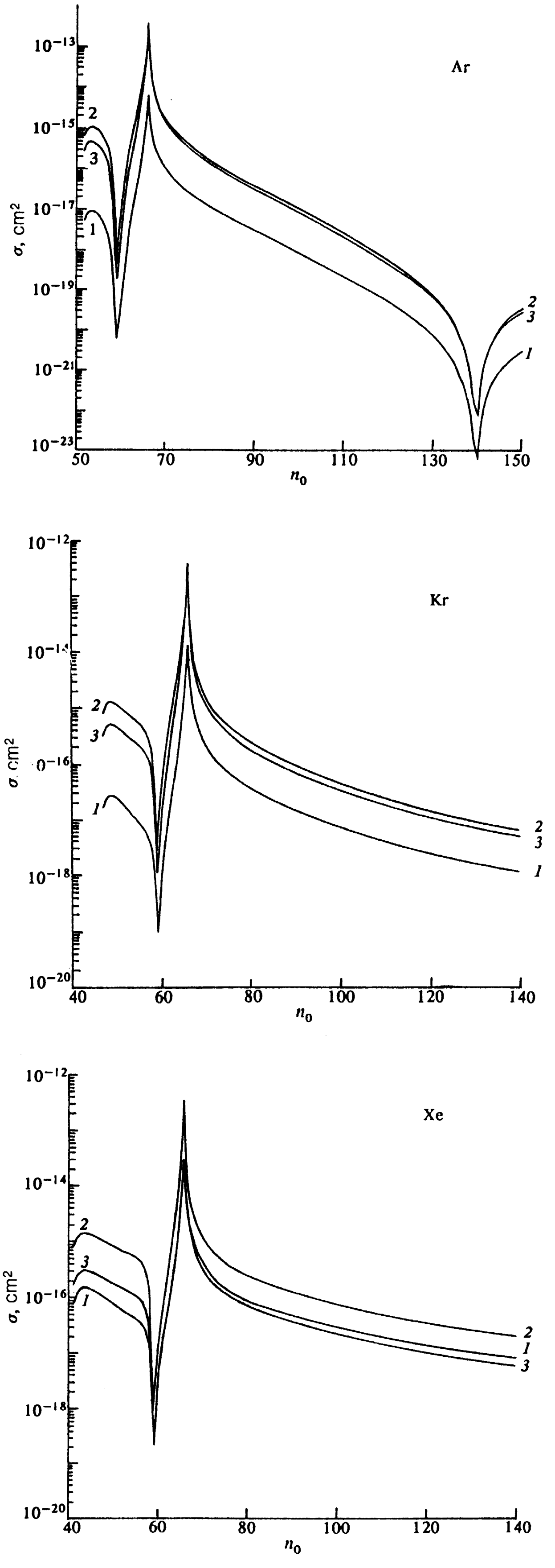

FIG. 3. Cross sections for collisional ionization (*1*) and vibronic transitions $v = 0 \rightarrow v = 1$ with (*2*) and without (*3*) a change in the electron angular momentum for the system $N_2^{**}(n_0, d\delta_g, v = 0) + A$, where $A = \{\mathrm{Ar,Kr,Xe}\}$. The calculations were performed for the relative velocity $V_c = 2\cdot10^{-4}$ a.u. with the parameters (41) and the data given in Table I.

TABLE II. Cross sections of inelastic transitions $v = 0 \rightarrow v = 1$ with a change in the electron angular momentum in a collision of the molecules $N_2^*(n_0, d\pi_g, v = 0)$ with inert-gas atoms.

n_0	$\sigma_{01}(n_0)$, 10^{-16}cm^2*				
	He	Ne	Ar	Kr	Xe
11	—	—	—	—	30,0
12	466,0	22,8	108,0	6,18	84,0
13	0,58	2,39	0,92	4,38	1,41
14	0,04	0,11	0,51	0,58	0,02
15	0,04	0,61	0,03	0,03	—

*The cross sections were calculated for the relative velocity $V_c = 1 \cdot 10^{-3}$ a.u.

spect to the position of the level $n_r = 66$.

The next general property of the processes (40) is the interference suppression of cross sections for values of n_0 approximately corresponding to $\sin \Phi(n_0) = 0$. For example, for the He atom the first interference minima occur at the points $n_0 = 80$ and $n_0 = 147$. In the case of Ne atoms, where the $n_1 L$ term is the most gently sloping (see Fig. 1a), the function $\sigma(n_0)$ has three oscillations at $n_0 = 65$, 77, and 114, respectively. Due to the closeness of the first interference minimum to the position of the level $n_r = 66$ the processes (40′) and (40″) are found to be partially suppressed here.

A characteristic feature of the interaction with Ar, Kr, and Xe atoms (whose scattering length is negative) is the appearance of the Ramsauer effect, due to which the cross section near the level $n_0 = 59$ decreases. This effect should also be observed in inelastic collisions of X^{**} Rydberg atoms with A atoms.[1] In contradistinction to atomic systems, where the Ramsauer minima are quite flat, however, here we have narrow localized dips (Fig. 3). This is because the cross section for the processes (1) reproduce the characteristic features of the energy dependence of the K matrix and not its average characteristics (as in the case of collisions proceeding by the impulse mechanism[1]).

For all inert gases (with the exception of Xe atoms) the autoionization parameter $\Gamma^*_{n_1 L} R^*_{n_1} / V_c$ is small (see Table I). For this reason, here, the ionization cross section is found to be less than the cross sections for inelastic transitions. The cross sections of the processes (40) are comparable only in the case of Xe atoms (where ionization proceeds quite efficiently).

We now proceed to the region of the spectrum $n_1 = 6$ (see Fig. 1b). In this region the most efficient transitions should be the vibronic transitions into the covalent $n_1 L$ state with the participation of the $n_0 d\pi_g$ Rydberg series of the N_2^{**} molecule. Strong nonadiabatic mixing of states with $n_0 \sim n_r = 12$, which appreciably increases the cross sections, should also occur here. The results of calculations performed with the adiabatic quantum defect[22,23]

$$\mu_{d\pi_g}(\xi) = -0,11 + 0,166(\xi - \xi_e)$$

are presented in Table II. We note that the cross sections obtained near $n_r = 12$ are two orders of magnitude larger than the gas-kinetic cross sections.

8. CONCLUSIONS

Our investigation is based on an asymptotically exact determination of the potential energy surfaces of the systems considered and an approximate (using the model of Ref. 11) description of their dynamical behavior. As we have already been mentioned, the conditions under which this model is applicable are, in the main, satisfied. It can be expected, however, that the qualitative conclusions that the excitation energy dependence of the cross sections of the processes is irregular will remain valid also in more general cases, since the effect considered is associated with mixing of higher-lying vibrational states of a Rydberg molecule, and the relative role of these states is determined by the sharply n_0-dependent function (14).

According to the results obtained in this work, similar features should be observed in the cross sections of charge-exchange processes, occurring by the harpoon mechanism, in collisions of Rydberg molecules with atoms and molecules having a positive electron affinity. Sharp n_0 dependence should also be manifested in inverse three-particle electron-ion recombination processes, giving rise to light flashes on optically allowed transitions.

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1) Here and below the atomic system of units $\hbar = m_e = e = 1$ is employed.

2) This result is obtained in the two-channel approximation and holds in the region $E_v > U^{(L)}_{n_v}(R) > E_{v-1}$, where the strongest coupling with the closest (with respect to v) continuum state of the system is taken into account. In order to determine the autodecay properties of the system in the region $E_{v-1} > U^{(L)}_{n_v}(R) > 0$ the equations (5) and (6) must be solved using the multichannel T collision matrix.

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Translated by M. E. Alferieff