Nonadiabatic transitions and decay reactions during slow collisions of polarized atoms

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(Submitted 14 June 1989)
Zh. Eksp. Teor. Fiz. **70**, 114–126 (January 1990)

The elementary processes occurring in slow collisions between polarized atoms X with arbitrary total electron angular momentum $\mathbf{J}$ and atoms in the ground state $Y(^1S_0)$ are considered. The effect of polarization on the spectral distribution of the electrons or photons emitted during the collision is analyzed for the decay processes (Penning ionization, collision-induced emission) of polarized metastable atoms. The cross sections and spectral distributions for arbitrary polarization of the atoms are expressed in terms of the cross sections σ_M and spectral distributions $d\sigma_M/d\varepsilon$ for the $X(J)$ atoms with fixed projection M of the angular momentum $\mathbf{J}$ on the direction of the initial relative velocity of the colliding atoms. As examples, the processes taking place in the collisions $\mathrm{Kr}(5^3P_2)$, $\mathrm{Xe}(6^3P_2)$ + Ne are considered. It is found that the cross sections for the inelastic transitions $^3P_2 \rightarrow {}^3P_1$ differ by an order of magnitude for different polarizations of the Kr* and Xe* atoms. The polarization effect for these reactions significantly exceeds the analogous effect for the processes which have been studied hitherto.

INTRODUCTION

In recent years a number of experimental and theoretical studies of nonadiabatic transitions and ionization during slow collisions of polarized (oriented or aligned) atoms in intersecting beams have been carried out (see reviews 1–3). A peculiarity of elementary processes involving polarized atoms is the dependence of the reaction cross sections on the polarization of the colliding particles.

In the present paper for a wide class of reactions of the type

$$X(J)+Y(^1S_0)\rightarrow \text{Products} \qquad (1)$$

and arbitrary polarization of the $X(J)$ atoms, the cross section of the process is expressed in terms of the cross section σ_{M_v} ($M_v = 0,1,...,J$) for the $X(J)$ atoms with fixed initial projection M_v of the total electron angular momentum $\mathbf{J}$ on the direction of the initial relative velocity $\mathbf{v}$ of the atoms and the parameters which characterize the polarization of the $X(J)$ atoms. The effect of polarization of the $X(J)$ atoms on the cross sections and the spectra of the decay reactions (Penning ionization and collision-induced radiative decay of the metastable state) is considered as well as its effect on the cross sections of the inelastic transitions.

Actual calculations have been carried out for the following reactions of metastable atoms

$$\mathrm{Kr}\,(5s^3P_2)+\mathrm{Ne}\rightarrow\mathrm{Kr}\,(4p^6\,{}^1S_0)+\mathrm{Ne}+\hbar\omega, \qquad (2)$$

$$\mathrm{Xe}(6s^3P_2)+\mathrm{Ne}\rightarrow\mathrm{Xe}(5p^6\,{}^1S_0)+\mathrm{Ne}+\hbar\omega, \qquad (3)$$

$$\mathrm{Kr}\,(5s^3P_2)+\mathrm{Ne}\rightarrow\mathrm{Kr}\,(5s^3P_1)+\mathrm{Ne}, \qquad (4)$$

$$\mathrm{Xe}\,(6s^3P_2)+\mathrm{Ne}\rightarrow\mathrm{Xe}\,(6s^3P_1)+\mathrm{Ne} \qquad (5)$$

in which the most widespread isotopes with zero nuclear spin participate. We show that for various polarizations of the Kr* or Xe* atoms the cross sections (4) and (5) differ by an order of magnitude, and the polarization effect for these reactions substantially exceeds the analogous effect for processes occurring during slow collisions which have been investigated hitherto. The possibility of experimentally determining the polarization dependences of reaction cross sections (2)–(5) is discussed.

The atomic system of units is used in this paper.

REACTION CROSS SECTIONS FOR THE POLARIZED ATOMS

A semiclassical study of the effect of polarization of the $X(J)$ atoms on the reaction cross sections of type (1) for $J = 1$ was carried out in Refs. 4–7 in the instance of the inelastic transitions $5^1P_1 \rightarrow 5^3P$ during the collisions Ca* + He, Ne. Below we will consider reaction (1) for polarized atoms $X(J)$ with arbitrary values of J for the typical case in which, during the collision $X(J) + Y$ with relative energy E and impact parameter ρ, a change of the type of angular momentum coupling $e \rightarrow c$ (Hund's classification) takes place in the vicinity of the large internuclear distance $R_d(E,\rho)$.[8,9] Thus, during the approach of the atoms at large $R > R_d$ the initial projection M_0 of the angular momentum $\mathbf{J}$ on some fixed axis z_0 remains constant (coupling type e). For $R < R_d$ the projection Ω of the total electron angular momentum of the quasimolecule on the rotating internuclear axis z remains constant (coupling type c).[1)] If reaction (1) does not take place, type-e coupling is again realized as the atoms separate.

As to the mechanism of process (1), it is further assumed that for initial energy E the cross section is determined predominantly by the collisions with impact parameter $\rho < \rho_m(E)$, and the transitions take place in the region $R < R_m(E)$, where $R_m < R_d(\rho_m)$. A possible variant of the qualitative scheme of quasimolecular terms for reaction (1) for $J = 2$ is shown in Fig. 1. For $\rho \leqslant \rho_m$ the $e \rightarrow c$ coupling change takes place in the hatched region $R \geqslant R_{dm} = R_d(\rho_m)$. Note that as ρ increases from 0 to ρ_m the magnitude of $R_d(\rho)$ decreases from $R_d = \infty$ to $R_d = R_{dm}$. The regions of transitions significant for reaction (1) are indicated in Fig. 1 by thickening of the quasimolecular terms.

As is well-known (see Refs. 8 and 9), an $e \rightarrow c$ coupling change takes place in the region of internuclear distances $R_d - \Delta R_d < R < R_d + \Delta R_d$, where the characteristic splitting ΔU between the degenerate (in the limit $R \rightarrow \infty$) quasi-

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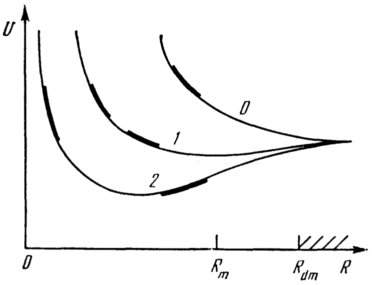

FIG. 1. Qualitative picture of the quasimolecular terms for reaction (1) for $J=2$. Change of coupling type takes place in the hatched region $R \gg R_{dm}$. The transition regions are indicated by thickening of the quasimolecular terms. The numbers alongside the terms are the values of $|\Omega|$.

molecular $\Omega(J)$-states of the system $X(J)+Y$ goes from values $\Delta U(R_d-\Delta R_d) \gg V_{\rm cor}$ to values $\Delta U(R_d+\Delta R_d) \ll V_{\rm cor}$ [$V_{\rm cor}(R) \sim v\rho/R^2$ is the Coriolis interaction of the $\Omega(J)$-states of the quasimolecule $X(J)+Y$, which is due to rotation of the internuclear axis]. If the splitting $\Delta U(R)$ varies rapidly in the vicinity of $R_d(\rho)$ at values of the impact parameter $\rho<\rho_m$ which are important for reaction (1), then the coupling-type change region is quite narrow [for the systems considered below the exponential approximation $\Delta U \sim \exp(-\beta' R)$ is valid near R_d] and the width of the change region $\Delta R_d \sim 1/\beta'$ is of the order of $0.5a_0$. In this case if $\Delta R_d \ll R_d - R_m$ then it is possible to use the approximation of sudden change of coupling type to describe the passage of the system through the vicinity of R_d.[8-10] The question of the choice of the radius $R_d(v,\rho)$ of coupling type change is discussed in Ref. 10. In what follows we will take for R_d the root of the equation (see Ref. 10)

$$|\Delta U(R_d)|=2v\rho/R_d^2, \tag{6}$$

where ΔU is the maximal splitting between the $\Omega(J)$-states. The existence of some indeterminacy in the choice of R_d is of no consequence if the variation of the splitting ΔU in the region of change from coupling type e to coupling type c is rapid.

In the approximation of sudden change of coupling type the population of the $\Omega(J)$-states in the region $R<R_d$ is determined by the projections of the initial state $|i\rangle$ of coupling type e onto the states of coupling type c at the internuclear distance R_d. To analyze reaction (1) in more detail, it is convenient to introduce alongside the arbitrary fixed coordinate system $x_0y_0z_0$ the fixed system $x_vy_vz_v$ with quantization axis z_v parallel to the initial velocity $\mathbf{v}$ (M_v is the projection of $\mathbf{J}$ the z_v axis). We then obtain for the probability $P_{\Omega M_0}$ of populating the quasimolecular Ω-state in the region $R>R_d$ via the collision $X(J,M_0)+Y$ with fixed value of the projection M_0 of the angular momentum $\mathbf{J}$ the arbitrary fixed axis z_0

$$P_{\Omega M_0}=\Big|\sum_{M_v=-J}^{J} d^{(J)}_{M_vM_0}(\alpha)\, d^{(J)}_{\Omega M_v}(\theta_d)\exp(iM_v\varphi)\Big|^2, \tag{7}$$

where $\hat{d}^{(J)}(\beta)$ is the matrix of finite rotations with Euler angles $(0,\beta,0)$, α is the angle between the z_0 and z_v axes, θ_d is the angle between the z_v and z axes at internuclear distance R_d, and φ is the azimuthal angle of the z axis in the coordinate system $x_vy_vz_v$. Note that for a wide class of reactions of type (1) $e\to c$ coupling change takes place at large internuclear distances; in this case the approximation of rectilinear motion is valid in the region $R \gtrsim R_d$ and

$$\theta_d=\arcsin(\rho/R_d). \tag{8}$$

If as a result of populating each of the $\Omega(J)$-states the reaction (1) takes place in the region $R \leqslant R_m < R_d$ with probability P_Ω but the contribution of the transitions in the region $R>R_m$ is negligibly small, then the total probability of the process (1) during the collision $X(J,M_0)+Y$ is

$$P_{M_0}=\sum_{\Omega=-J}^{J} P_\Omega P_{\Omega M_0}. \tag{9}$$

It is assumed in Eq. (9) that the action between R_m and R_d is large, and interference terms are neglected.

During the collisions $X(J,M_0)+Y$ in intersecting beams the angle φ takes on arbitrary values from 0 to 2π. After integrating over φ and ρ we obtain for the cross section σ_{M_0} of reaction (1) for collisions with fixed initial projection M_0 of the angular momentum $\mathbf{J}$ on the z_0 axis

$$\sigma_{M_0}=\sum_{M_v=-J}^{J}|d^{(J)}_{M_vM_0}(\alpha)|^2\sigma_{M_v}, \tag{10}$$

where

$$\sigma_{M_v}=\sum_{\Omega=-J}^{J}2\pi\int_0^{\rho_m}P_\Omega|d^{(J)}_{\Omega M_v}(\theta_d)|^2\rho\,d\rho \tag{11}$$

is the cross section of reaction (1) for collisions with fixed initial projection M_v of the angular momentum $\mathbf{J}$ on the z_v axis ($z_v \parallel \mathbf{v}$).

Note that for unpolarized atoms the cross section averaged over the initial states

$$\bar{\sigma}=\frac{1}{2J+1}\sum_{M_0=-J}^{J}\sigma_{M_0} \tag{12}$$

is given by the usual formula

$$\bar{\sigma}=\frac{1}{2J+1}\sum_{\Omega=-J}^{J}2\pi\int_0^{\rho_m}P_\Omega\rho\,d\rho. \tag{13}$$

Formulas (7) and (9)–(11) describe both nonadiabatic transitions in the region $R<R_m$ and the decay of quasistationary states during collisions of polarized atoms. In the latter case it is assumed that the probability of decay in the region $R>R_m$ is negligibly small.

For a wide class of reactions, $P_{-\Omega}=P_\Omega$ and $\sigma_{-M_v}=\sigma_{M_v}$. Thus, in the approximation of sudden change of coupling type the cross section of process (1) for arbitrary polarization of the $X(J)$ atoms is expressed in terms of the quantities $\sigma_{M_v}=0$, $\sigma_{M_v},\dots,\sigma_{M_v}=J$, which number $J+1$ in all, and parameters which characterize the polarization of the $X(J)$ atoms, e.g., α and M_0.

CROSS SECTIONS OF DECAY REACTIONS IN THE COLLISIONS OF POLARIZED METASTABLE ATOMS

The semiclassical description of the decay reactions of the metastable states during atomic collisions (such a Penning ionization or collision-induced fluorescence of the metastable state) is based on the introduction of internuclear-distance-dependent values of the autodecay width $\Gamma_\Omega(R)$ of the adiabatic quasimolecular $\Omega(J)$-states (see, e.g., Refs. 9 and 11). Thus, for immobile nuclei the probability of decay (per unit time) of the quasimolecular $\Omega(J)$-state with emission of an electron or a photon is $\Gamma_\Omega/\hbar$.

If the width Γ_Ω is small enough and falls off fast enough with growth of R, such that in the region $R > R_m(E) > R_{dm}(E)$ it can be neglected, then the total probability of decay of the quasimolecular $\Omega(J)$-state during a collision with initial energy E and impact parameter ρ is given by

$$P_\Omega(E,\rho)=\frac{2}{v}\int\limits_{R_{t\Omega}}^{R_m}\frac{\Gamma_\Omega(R)\,dR}{(1-\rho^2/R^2-U_\Omega(R)/E)^{1/2}}, \tag{14}$$

where $U_\Omega(R)$ is the interaction potential in the state $\Omega(J)$ and $R_{t\Omega}(E,\rho)$ is the turning point. Formula (14) is valid for $P_\Omega \gg 1$ if for negative values of U_Ω the condition $|U_\Omega| \gg E$ is fulfilled. The latter condition is violated at low energies. In this case it is possible to use the approximate given in Ref. 12. If necessary, the transitions in the region $R > R_d(\rho)$ can be taken into account, as in Refs. 13 and 14, by using the joining approximation. Note that even though in Refs. 13 and 14 were considered ionization reactions during collisions of unpolarized atoms, allowance was made there for coupling-type change during the course of the collision.

For a wide class of processes involving Penning ionization (see, e.g., the review[15]) and radiative quenching of metastable states,[16-18] in the region of internuclear distances which contribute significantly to the cross sections the autodecay width Γ is determined by the exchange interaction of the atoms and has the exponential form

$$\Gamma_\Omega(R)=C_\Omega\exp(-\beta_\Omega R). \tag{15}$$

If the parameter β_Ω is large enough, the main contribution to the cross section comes from collisions with small ρ, and the transitions take place near the turning point, where the potential $U_\Omega(R)$ is also determined by the exchange interaction and the approximation

$$U_\Omega(R)=A_\Omega\exp(-\alpha_\Omega R) \tag{16}$$

is valid.

Let us consider the calculation of the probability P_Ω on the basis of formula (14) at moderate impact parameters ρ which contribute significantly to the cross section and for which the potential U_Ω (16) substantially exceeds the centrifugal potential $E\rho^2/R^2$ near the turning point $R_{t\Omega}(\rho)$. The radiative width Γ_Ω [see Eq. (15)] falls off rapidly with the growth of R. In this case the probability $P\Omega$ is determined by the radiative transitions near the turning point and the main contribution to the integral in formula (14) comes from the narrow region $R_{t\Omega}(\rho) \lesssim R \lesssim R_{t\Omega}(\rho) + 1/\beta_\Omega$. Therefore for $\alpha R_{t\Omega} > 1$ an approximate value of $P_\Omega(\rho)$ can be found by replacing the centrifugal term ρ^2/R^2 in the integrand by the constant expression $\rho^2/R^2_{t\Omega}$ and extending the integration to infinity (the contribution of the region $R > R_m$ is negligibly small). Then

$$P_\Omega(E,\rho)=\frac{2C}{\alpha v}\left(\frac{E}{A}\right)^{\gamma}\mathrm{B}\left(\gamma,\frac{1}{2}\right)\left(1-\frac{\rho^2}{R_t^2(\rho)}\right)^{\gamma-1}, \tag{17}$$

where $B(x,y)$ is the beta function, $\gamma=\beta/\alpha$ (the index Ω is omitted to simplify the expressions). Comparison (Fig. 2) of the results calculated on the basis of formulas (14) and (17) for the interaction parameters corresponding to reactions (2) and (3) shows that at values of the impact parameter ρ which contribute significantly to the cross section approximation (17) only insignificantly increases the probability of radiative decay. For $\rho = 0$ formula (17) is exact [for exponential dependences (15) and (16)].

A rougher (see Fig. 2) estimate of the probability P_Ω is given by the formula

$$P_\Omega'(E,\rho)=P_\Omega(E,\rho=0)(1-\rho^2/R_0^2)^{\gamma-1}, \tag{18}$$

obtained from Eq. (17) by replacing $R_t(\rho)$ by $R_0 = R_t(\rho=0) = \alpha^{-1}\ln(AE^{-1})$.

Thus it is possible to use approximation (17) for the probabilities P_Ω in formulas (9)–(13) in the analysis of the decay processes in the collisions of polarized atoms. Note that for unpolarized atoms the total cross section $\bar{\sigma}$ of the decay reaction, allowing for the repulsive nature of the potentials U_Ω, can be represented in the form (see, e.g., Ref. 9 and 11)

$$\bar{\sigma}=\frac{1}{2J+1}\sum_{\Omega=-J}^{J}\frac{4\pi}{v}\int\limits_{R_{0\Omega}}^{\infty}R^2\Gamma_\Omega(R)\left(1-\frac{U_\Omega(R)}{E}\right)^{1/2}dR. \tag{19}$$

Substitution of the estimate (18) of the probability into formula (13) gives the approximate value

$$\bar{\sigma}=\frac{1}{2J+1}\sum_{\Omega=-J}^{J}\pi R_{0\Omega}^2\frac{4C_\Omega}{\alpha_\Omega v}\left(\frac{E}{A_\Omega}\right)^{\gamma_\Omega}\mathrm{B}\left(\gamma_\Omega,\frac{3}{2}\right), \tag{20}$$

which corresponds to replacing R^2 in the integrand of Eq. (19) by $R_{0\Omega}^2$.

The values of the cross sections $\bar{\sigma}$ of reactions (2) and (3) calculated according to formula (19) and formula (13) with probability (17), which are shown in Table I, confirm the feasibility of using approximation (17) to analyze the decay processes. Approximation (20) also gives reasonable results for the cross sections $\bar{\sigma}$ of reactions (2) and (3).

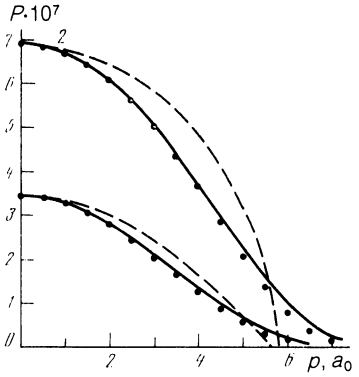

FIG. 2. Dependence of the decay probability $P_{\Omega=1}$ on the impact parameter ρ for reaction (2) for $E = 0.05$ eV (curves 1) and reaction (3) for $E = 0.1$ eV (curves 2). The solid and dashed curves were calculated on the basis of approximate formulas (17) and (18), respectively, and the points represent calculation according to the exact formula (14).

TABLE I. Cross sections of reactions (2)–(5) for the polarized ($\sigma_{|M_v|}$) and unpolarized ($\bar{\sigma}$) atoms.

E, eV	σ_c, Å^2	σ_1, Å^2	σ_2, Å^2	σ_1/σ_2	$\bar{\sigma}$, Å^2	$\bar{\sigma}$*, Å^2	$\bar{\sigma}$**, Å^2
			Reaction (2)				
0,025	$7,2\cdot10^{-7}$	$1,0\cdot10^{-6}$	$3,5\cdot10^{-7}$	2,8	$6,8\cdot10^{-7}$	$6,4\cdot10^{-7}$	$5,8\cdot10^{-7}$
0.050	$1,8\cdot10^{-6}$	$2,7\cdot10^{-6}$	$8,7\cdot10^{-7}$	3,1	$1,8\cdot10^{-6}$	$1,7\cdot10^{-6}$	$1,5\cdot10^{-6}$
0,075	$3,2\cdot10^{-6}$	$4,8\cdot10^{-6}$	$1,5\cdot10^{-6}$	3,2	$3,2\cdot10^{-6}$	$2,9\cdot10^{-6}$	$2,6\cdot10^{-6}$
0.100	$4,7\cdot10^{-6}$	$7,2\cdot10^{-6}$	$2,2\cdot10^{-6}$	3,3	$4.7\cdot10^{-6}$	$4,3\cdot10^{-6}$	$3,9\cdot10^{-6}$
			Reaction (3)				
0,025	$1,5\cdot10^{-6}$	$1,9\cdot10^{-6}$	$7,3\cdot10^{-7}$	2,6	$1,3\cdot10^{-6}$	$1,3\cdot10^{-6}$	$1,1\cdot10^{-6}$
0,050	$2.8\cdot10^{-6}$	$3,6\cdot10^{-6}$	$1,4\cdot10^{-6}$	2,6	$2,6\cdot10^{-6}$	$2,4\cdot10^{-6}$	$2,1\cdot10^{-6}$
0,075	$4,0\cdot10^{-6}$	$5,3\cdot10^{-6}$	$2,0\cdot10^{-6}$	2,7	$3,7\cdot10^{-6}$	$3,5\cdot10^{-6}$	$3,4\cdot10^{-6}$
0,100	$5,3\cdot10^{-6}$	$7,0\cdot10^{-6}$	$2,5\cdot10^{-6}$	2,8	$4,9\cdot10^{-6}$	$4,6\cdot10^{-6}$	$4,0\cdot10^{-6}$
			Reaction (4)				
0,175	$5,6\cdot10^{-9}$	$9,2\cdot10^{-8}$	$1,9\cdot10^{-9}$	90	$3,9\cdot10^{-8}$	–	–
0,200	$1,1\cdot10^{-7}$	$1,6\cdot10^{-6}$	$3,9\cdot10^{-8}$	41	$6,7\cdot10^{-7}$	–	–
0,225	$1,0\cdot10^{-6}$	$1,2\cdot10^{-5}$	$3,5\cdot10^{-7}$	34	$5,3\cdot10^{-6}$	–	–
0,250	$5,5\cdot10^{-6}$	$6,1\cdot10^{-5}$	$1,9\cdot10^{-6}$	32	$2,6\cdot10^{-5}$	–	–
0,275	$2,1\cdot10^{-5}$	$2,2\cdot10^{-4}$	$7,3\cdot10^{-6}$	30	$9.6\cdot10^{-5}$	–	–
			Reaction (5)				
0.175	$3.9\cdot10^{-9}$	$6,0\cdot10^{-8}$	$1,3\cdot10^{-9}$	46	$2,5\cdot10^{-8}$	–	–
0.200	$6,9\cdot10^{-8}$	$8,8\cdot10^{-7}$	$2.4\cdot10^{-8}$	37	$3,8\cdot10^{-7}$	–	–
0.225	$5,5\cdot10^{-7}$	$6,1\cdot10^{-6}$	$1,9\cdot10^{-7}$	32	$2,6\cdot10^{-6}$	–	–
0.250	$2.7\cdot10^{-6}$	$2.7\cdot10^{-5}$	$9,3\cdot10^{-7}$	29	$1.2\cdot10^{-5}$	–	–
0.275	$9,6\cdot10^{-6}$	$8.9\cdot10^{-5}$	$3,3\cdot10^{-6}$	27	$3.9\cdot10^{-5}$	–	–
0.300	$2.8\cdot10^{-5}$	$2.4\cdot10^{-4}$	$9.6\cdot10^{-6}$	25	$1,1\cdot10^{-4}$	–	–
0.325	$6.8\cdot10^{-5}$	$5.5\cdot10^{-4}$	$2,3\cdot10^{-5}$	24	$2.4\cdot10^{-4}$	–	–

*Calculation according to formula (19).

**Calculation according to formula (20).

SPECTRA OF DECAY REACTIONS WHICH OCCUR DURING COLLISIONS OF POLARIZED ATOMS

Let us consider the influence of the polarization of the $X(J)$ atoms on the shape of the spectral distribution of the electrons or photons emitted in the decay reaction $X(J) + Y$.

For unpolarized $X(J)$ atoms the probability of emission during the collision of an electron (photon) with energy in the interval from ε to $\varepsilon + d\varepsilon$ is given by the well-known formula[11]

$$\frac{d\bar{P}(v,\rho,\varepsilon)\,d\varepsilon}{d\varepsilon}=\frac{1}{2J+1}\sum_{\Omega=-J}^{J}\sum_{R_{c\Omega}}\frac{2\Gamma_{c\Omega}\,d\varepsilon}{|\Delta F_{c\Omega}|\,v_{c\Omega}}. \tag{21}$$

The inner sum is taken over all the classically accessible Condon points $R_{c\Omega}$—the roots of the equation

$$\Delta U_{\Omega}(R_{c\Omega})=\varepsilon, \tag{22}$$

where ΔU_{Ω} is the energy difference between the initial and final quasimolecular states (if there are more than one final quasimolecular states, then there is an additional sum over the final states), $\Gamma_{c\Omega} = \Gamma_{\Omega}(R_{c\Omega})$,

$$|\Delta F_{c\Omega}|=|d\Delta U_{\Omega}/dR|_{R=R_{c\Omega}}$$

$$v_{c\Omega}=v(1-\rho^2/R_{c\Omega}^2-U_{c\Omega}/E)^{1/2},$$

and $U_{c\Omega} = U_{c\Omega}(R_{c\Omega})$. The corresponding cross section of the decay reaction

$$\frac{d\bar{\sigma}(E,\varepsilon)}{d\varepsilon}\,d\varepsilon=\frac{1}{2J+1}\sum_{\Omega=-J}^{J}\frac{4\pi R_{c\Omega}^{2}\Gamma_{c\Omega}}{v|\Delta F_{c\Omega}|}\left(1-\frac{U_{c\Omega}}{E}\right)^{1/2}d\varepsilon \tag{23}$$

is found by integrating the probability (21) over the impact parameter. Formulas (21) and (23) assume that coupling type c is realized in the region of internuclear distances $R\sim R_{c\Omega}$ and are valid far from the extrema of the spectral distributions associated with the extrema of the difference potentials, where $|\Delta F_{c\Omega}| = 0$.

In the analysis of the collisions of polarized atoms it is necessary to remove the averaging over the initial states and to introduce the probabilities of populating the corresponding quasimolecular Ω-states. For collisions with prescribed projection M_0 of the angular momentum **J** on the z_0 axis we obtain

$$\frac{dP_{M_0}(v,\rho,\varepsilon)}{d\varepsilon}=\sum_{\Omega=-J}^{J}\sum_{R_{c\Omega}}\frac{2\Gamma_{c\Omega}P_{\Omega M_0}}{|\Delta F_{c\Omega}|\,v_{c\Omega}}, \tag{24}$$

where the probability $P_{\Omega M_0}$ is given by formula (7).

The spectral distribution of the cross section $d\sigma_{M_0}(E,\varepsilon)/d\varepsilon$ is related by a formula of type (10) with the spectral distributions

$$\frac{d\sigma_{M_v}(E,\varepsilon)}{d\varepsilon}=\sum_{\Omega=-J}^{J}\sum_{R_{c\Omega}}\frac{4\pi\Gamma_{c\Omega}}{v|\Delta F_{c\Omega}|}\times\int_0^{\rho_{c\Omega}}|d_{\Omega M_v}^{(J)}(\vartheta_d)|^2\rho\left(1-\frac{\rho^2}{R_{c\Omega}^2}-\frac{U_{c\Omega}}{E}\right)^{-1/2}d\rho \tag{25}$$

for the collisions $X(J,M_v) + Y$ with prescribed projection M_v of the angular momentum **J** on the z_v axis. Here $\rho_{c\Omega} = R_{c\Omega}(1 - U_{c\Omega}/E)^{1/2}$ is the maximum value of the impact parameter at which the internuclear distance $R_{c\Omega}$ is attained. In Eq. (25) it is assumed that $R_d(\rho_{c\Omega}) > R_{c\Omega}$. The averaged spectral distribution

$$\frac{d\bar{\sigma}(E,\varepsilon)}{d\varepsilon}=\frac{1}{2J+1}\sum_{M_0=-J}^{J}\frac{d\sigma_{M_0}(E,\varepsilon)}{d\varepsilon} \qquad (26)$$

coincides with distribution (23).

Thus, at energies ε for which the spectral distribution is built up by transitions in the region of type-*c* coupling the values of $d\sigma/d\varepsilon$ for arbitrary polarization of the $X(J)$ atoms are expressed in terms of distributions (25), as is also the case for the total cross sections (10).

THE INTERACTION Kr(5*s*), Xe(6*s*)+Ne

The interaction potentials of the atoms $\mathrm{Kr}(4p^5 5s)+\mathrm{Ne}$ and $\mathrm{Xe}(5p^5 6s)+\mathrm{Ne}$ (Fig. 3) were calculated in Refs. 17–20 using the effective-Hamiltonian method.[20] In the region of internuclear distances important for processes (2)–(5) (at energies $E \gtrsim 0.1$ eV) the adiabatic potentials U_Ω of the interaction $X(^3P_1, {}^3P_2)+\mathrm{Ne}$ are approximated by exponential functions such as in Eq. (16). The splitting of the degenerate (in the limit $R\to\infty$) quasimolecular terms is due to the ion–atom interaction $X^+ + \mathrm{Ne}$ and is proportional to the quantity $\Delta V = V_\Pi - V_\Sigma$ (see Ref. 20), where V_Σ and V_Π are the potentials of the ion–atom interaction in the Σ- and Π-states, we obtain without taking the spin-orbit splitting into account. In particular, at $J=2$ for ΔU in Eq. (6)

$$\Delta U=|U_2-U_0|={}^2/_3\Delta V. \qquad (27)$$

The nondiagonal matrix elements of the effective Hamiltonian in a quasimolecular basis of products of atomic wave functions are also proportional to ΔV.[20] To determine the $\Delta V(R)$ dependence, we used semiempirical ion–atom potentials[21] which allow for the interaction of the ion configurations $X^+ + \mathrm{Ne}$ and $X+\mathrm{Ne}^+$. In the regions of transitions (2)–(5) the dependences $\Delta V(R)$ are determined by the ion–atom exchange interaction and have exponential form.

In the calculation of the spectral distributions of reactions (2) and (3) we used the interaction potentials[22] of the atoms in the ground state to determine the difference potentials $\Delta U_\Omega(R)$ (Fig. 3).

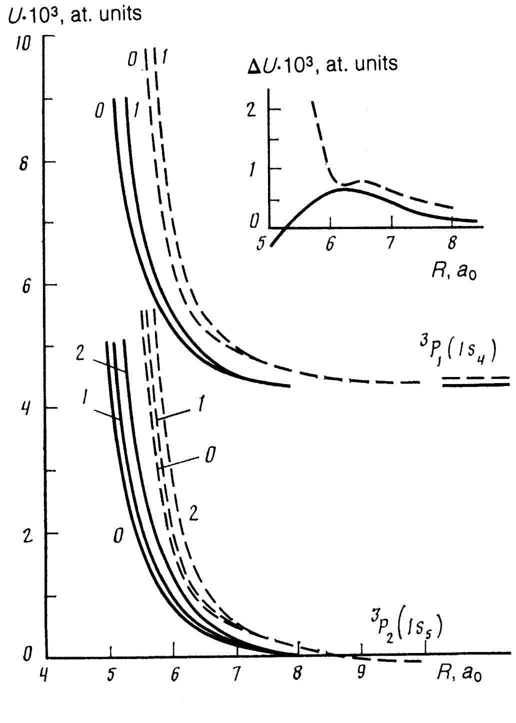

FIG. 3. Adiabatic potentials $U_{|\Omega|}$ of the interaction $\mathrm{Kr}(^3P_1, {}^3P_2)+\mathrm{Ne}$ (solid curves) and $\mathrm{Xe}(^3P_1, {}^3P_2)+\mathrm{Ne}$ (dashed curves). The numbers labeling the curves are the values of $|\Omega|$. The inset is a plot of the corresponding difference potentials $\Delta U_{|\Omega|}$ ($\Omega=1, J=2$).

RADIATIVE DECAY OF THE METASTABLE STATE $^3P_2$ DURING COLLISIONS OF THE POLARIZED ATOMS Kr* AND Xe* WITH Ne ATOMS

One of the possible channels of destruction of the metastable states during slow atomic collisions is radiative decay during the approach of the atoms. On the whole, these processes are characterized by small cross sections ($\sigma \lesssim 10^{-20}$ cm^2); however, it is just radiative decay which determines the radiation of the reaction zone at frequencies close to the frequency of the forbidden atomic line, and also the destruction of the metastable states under those conditions in which the inelastic transitions are adiabatic and low-probability, and in which Penning ionization is impossible (see, e.g., Refs. 16–18).

Radiative quenching in processes (2) and (3) is due to mixing of the wave functions of the metastable $[X(^3P_2)+\mathrm{Ne}]$ state and the resonant $[X(^{1,3}P_1)+\mathrm{Ne}]$ states of a quasimolecule with $|\Omega|=1$ as a consequence of the interatomic interaction. In the region of internuclear distances accessible at energies $E\lesssim 0.1$ eV the radiative width of the adiabatic quasimolecular state $\Omega=\pm 1$ ($J=2$) can be represented in the form

$$\Gamma_{\Omega=\pm1}(R)=\Gamma_0\frac{b^2}{4}\left(\frac{\Delta V(R)}{\Delta E_1}-\frac{\Delta V(R)}{\Delta E_2}\right)^2, \qquad (28)$$

where Γ_0 is the radiative width of the resonant atomic level $^1P_1$; ΔE_1 and ΔE_2 are the splittings between the atomic levels $^1P_1$ and $^3P_2$ and the levels $^3P_1$ and $^3P_2$, respectively; $b=\langle {}^3P_{1,ic}|{}^3P_{1,LS}\rangle$ ($|{}^3P_{1,ic}\rangle$ is the atomic wave eigenfunction of intermediate coupling and $|{}^3P_{1,LS}\rangle$ is the *LS*-coupling atomic wave function). The factor $[\omega(R)/\omega_0{}^3]$, where $\omega(R)$ is the quasimolecular transition frequency and ω_0 is the frequency of the resonant atomic transition $^1P_1$–$^1S_0$, has been omitted in Eq. (28).

The dependences of the potentials $U_{\Omega=\pm1}$ and of the widths $\Gamma_{\Omega=\pm1}$ on distance, which were calculated in Refs. 17–19, are approximated by the exponential functions (15) and (16) with the following parameters (in atomic units): $C=0.92$, $\beta=4.1$, $A=138$, and $\alpha=2.0$ for Kr* + Ne and $C=0.51$, $\beta=3.7$, $A=3650$, and $\alpha=2.4$ for Xe* + Ne.

The cross sections σ_{M_0} of reactions (2) and (3) were calculated using formula (11) and are listed in Table I. The approximate formula (17) was used for the probabilities $P_{\Omega=\pm1}$ in the calculation of the cross sections; for $|\Omega|\neq 1$ one obtains $P_\Omega=0$. Expression (8) holds for the angle θ_d.

As was assumed in the derivation of formulas (9)–(11), the transition region (a narrow vicinity of the turning point R_t) and the region of coupling type changeover R_d (see Figs. 4 and 5) do not overlap for those impact parameters ρ which contribute significantly to the cross section.

As follows from the formulas

$$\sum_{\Omega=\pm1}|d_{\Omega0}^{(2)}(\theta)|^2=3(\cos^2\theta-\cos^4\theta), \qquad (29)$$

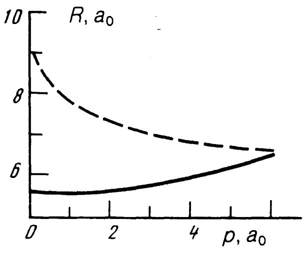

FIG. 4. Dependence of the variation R_d of the type of coupling radius change (dashed curve) and of the turning point R_t (solid curve) on the impact parameter ρ for reaction (2) at $E = 0.05$ eV.

$$\sum_{\Omega=\pm1} |d_{\Omega1}^{(2)}(\theta)|^2 = {}^1/_2(4\cos^4\theta - 3\cos^2\theta + 1), \tag{30}$$

$$\sum_{\Omega=\pm1} |d_{\Omega2}^{(2)}(\theta)|^2 = {}^1/_2(1 - \cos^4\theta), \tag{31}$$

the cross sections $\sigma_{M_v=0}$ and $\sigma_{M_v=2}$ are determined by collisions with larger impact parameters in comparison with the cross section $\sigma_{M_v=1}$ (Fig. 5).

Processes (2) and (3) are most efficient for collisions with unity projections ($|M_v| = 1$) of the angular momentum **J** on the direction of the initial relative velocity, and are least efficient for collisions with $|M_v| = 2$. The ratio of the maximal cross section [upon variation of the parameters which characterize the polarization of the $X(^3P_2)$ atoms] to the minimal cross section is $\sigma_{|M_v|=1}/\sigma_{|M_v|=2} \sim 3$ (see Table I).

The spectral distributions (23) and (26) for the photons studied in reaction (20) and (3) during collisions of unpolarized and polarized atoms are shown in Fig. 6 ($\Delta\varepsilon = \varepsilon - \varepsilon_0$, ε_0 is the energy of the forbidden transition). The spectral distributions $d\sigma/d\varepsilon$ have maxima of two types. the maxima of the first type with $\Delta\varepsilon_1 \sim 140$ cm^{-1} (for Kr* + Ne) and $\Delta\varepsilon_1 \sim 170$ cm^{-1} (for Xe* + Ne) are associated with the extrema of the difference potentials ($\Delta F = 0$). Formulas (23) and (26) are therefore inapplicable in these regions for a quantitative description of the spectrum and allow one only to confirm the existence of peculiarities (maxima) in the dependences of $d\sigma/d\varepsilon$ near $\Delta\varepsilon_1$. Maxima of the first type arise at energies large enough for the attainment of internuclear distances R_1, where $\Delta F(R_1) = 0$. The location of these maxima remains practically unchanged with further increase of the energy.

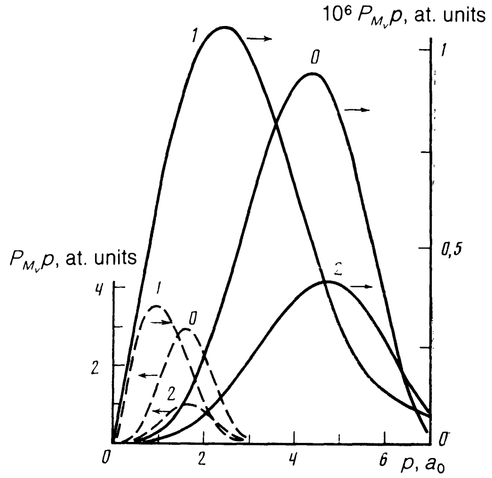

FIG. 5. Dependences on the impact parameter ρ of the integrands of formula (11), summed over Ω, for reaction (3) at $E = 0.1$ eV (solid curves) and reaction (5) at $E = 0.2$ eV (dashed curves). The numbers labeling the curves are the values of M_v. For reaction (5) at $M_v = 0$ and $M_v = 2$ values $10^8\, P_{M_v}$ are given.

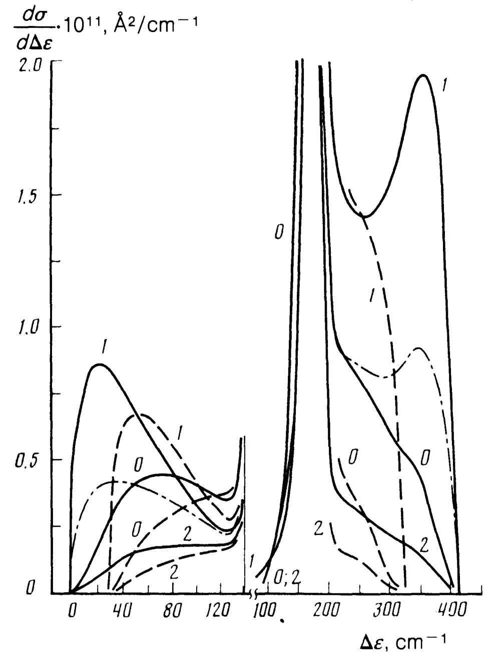

FIG. 6. Spectral distributions (23) and (25) of the photons emitted in reactions (2) (the spectrum in the region $\Delta\varepsilon \lesssim 140$ cm^{-1}, $n = 7$) and (3) (the spectrum in the region $\Delta\varepsilon \gtrsim 100$ cm^{-1}, $n = 8$). The numbers labeling the curves are the values of $|M_v|$. The solid curves show the distributions (25) for the polarized atoms at $E = 0.1$ eV; the dot–dash curves are distributions (23) for the unpolarized atoms at $E = 0.1$ eV; the dashed curves are the distributions (25) for the polarized atoms at $E = 0.75$ eV.

The maxima of the second type are associated with the extremum of the product $\Gamma\Omega(1 - U_\Omega/E)^{1/2}$ in the vicinity of the turning point (at $E = 0.1$ eV $\Delta\varepsilon_2 \sim 20$ cm^{-1} for Kr* + Ne and $\Delta\varepsilon_2 \sim 350$ cm^{-1} for Xe* + Ne). The location of these maxima shifts as the collision energy E increases. Thus, as E increases for the system Kr* + Ne the value of $\Delta\varepsilon_2$ falls off, and for the system Xe* + Ne it grows. This difference in the behavior of the spectral distributions of reactions (2) and (3) is due to the different character of the potentials $\Delta U_\Omega(R)$ for the systems Kr* + Ne and Xe* + Ne (Fig. 3).

The peculiarities of the spectral distributions for reactions (2) and (3) under gas-cell conditions were discussed in Ref. 18. A satellite of the forbidden line Xe($^3P_2$–$^1S_0$) in neon was experimentally observed under gas-cell conditions.[23] The location of the experimental satellite agrees with the results of the calculations in Refs. 18 and 20.

NONADIABATIC TRANSITIONS $^3P_2$–$^3P_1$ IN COLLISIONS OF POLARIZED Kr* and Xe* ATOMS WITH Ne ATOMS

The nonadiabatic transitions (4) and (5) are due to the interaction of quasimolecular states with $|\Omega| = 1$. As was shown in Ref. 19, where collisions of unpolarized atoms under gas-cell conditions were considered, the probabilities $P_{\Omega=\pm 1}$ in reactions (4) and (5) (at energies $E \lesssim 0.2$ eV for Xe* + Ne and $E \lesssim 0.15$ eV for Kr* + Ne) can be calculated in the distorted-wave approximation[19]

$$P_{\Omega=\pm 1}=\left(\frac{2\mu\Delta E^2}{\alpha^2 A}\right)^{\lambda}\left(\frac{2\pi C}{\Delta E\Gamma(\lambda)}\right)^{2}$$

$$\times\exp\left\{-\frac{2\pi}{\alpha}[(2\mu E_r)^{1/2}-(2\mu(E_r-\Delta E))^{1/2}]\right\},$$

$$E_r=E(1-\rho^2/R_t^2),\quad \lambda=2\beta/\alpha,$$
$$R_t=\alpha^{-1}\ln(A/E),$$

where $\Gamma(\lambda)$ is a gamma function, R_t is the turning point for the collision with zero impact parameter, and ΔE is the reaction defect. The interaction parameters were determined in Ref. 19 and take for Kr* + Ne the following values: $A = 160$, $\alpha = 2.0$, $C = 64.1$, and $\beta = 2.05$, and for Xe* + Ne: $A = 3900$, $\alpha = 2.39$, $C = 37.1$, and $\beta = 1.85$ (in atomic units).

The transitions in reactions (4) and (5) are localized near the turning point, and for those impact parameters which contribute significantly to the cross section the transition region and the coupling-type-change region do not overlap (see Figs. 4 and 5).

The cross sections for the polarized and unpolarized atoms calculated according to formulas (11)–(15) are given in Table I. As in the case of reactions (2) and (3), the cross sections $\sigma_{M_v=0}$ and $\sigma_{M_v=2}$ of reactions (4) and (5) are determined by collisions with larger impact parameters than those of the collisions which determine the cross section $\sigma_{M_v=1}$ (Fig. 5). Processes (4) and (5) are characterized by a very strong polarization dependence of their cross sections (the ratios of the maximal cross sections $\sigma_{|M_v|=1}$ to the minimal $\sigma_{|M_v|=2}$ are given in Table I) since these cross sections are determined by collisions with small impact parameters (Fig. 5), for which the expression (30) substantially exceeds expressions (29) and (31). Note that the cross sections of reactions (4) and (5) grows rapidly with increasing energy, whereas reactions (2) and (3) are characterized by a quite weak energy dependence of their cross sections.

CONCLUSION

Our results can be used in the theoretical analysis of a wide class of elementary processes of type (1) occurring in slow collisions of polarized atoms. Relations (10) for the total cross sections and the spectral distributions allow one to determine from the experimental data for a few polarization types the corresponding values for arbitrary polarization.

From our analysis of formulas (6), (8), and (11) we conclude that the strongest polarization dependences of the cross sections of processes of type (1) occur under those conditions in which only one quasimolecular $|\Omega|(J)$-state takes part in the reaction and the cross section of the process is determined primarily by collisions with small impact parameters for which $\rho \gg R_d\ (\rho)$.

Reactions (2)–(5) and similar processes in the collisions of other polarized atoms of the rare gases can be observed using intersecting atomic beams or a beam of relatively fast metastable atoms and a sufficiently cold gaseous target, when the relative velocity of the colliding atoms is simply the velocity of the polarized metastable atoms. Note that the problem of creating a beam of polarized metastable atoms of rare gases in the state $^3P_2$ was solved in Ref. 24. The difficulty of measuring the absolute values of the cross sections, which characterizes beam experiments, is increased further by the smallness of the cross sections of reactions (2)–(5). It therefore appears most promising to investigate polarization effects for reactions (2)–(5) by measuring the polarization dependence of the relative intensities of the satellites of the forbidden lines $^3P_2$–$^1S_0$ which accompany reactions (2) and (3) or the intensities of the resonant lines $^3P_1$–$^1S_0$ excited in reactions (4) and (5). The slow intensity increases with increase of the collision energy (see Table I) and of the density of the atoms of the target N_t. At the same time, the density of the atoms of the target is limited by collisional depolarization of the metastable atoms, i.e., the condition $N_t \ll (\sigma d)^{-1}$ must be satisfied, where $\sigma \sim 30$ Å^2 is the depolarization cross section of Kr($^3P_2$) or Xe($^3P_2$) atoms colliding with Ne atoms, and d is the target thickness. In the opposite case collisional destruction of the initial polarization of the metastable atoms precedes processes (2)–(5).

In the experimental investigation of processes (2)–(5) it is necessary to take into account the influence of the reactions

$$X(^3P_2)+X(^1S_0)\to X(^1S_0)+X(^1S_0)+\hbar\omega, \tag{33}$$

$$X(^3P_2)+X(^1S_0)\to X(^3P_1)+X(^1S_0) \tag{34}$$

in symmetric collisions of the atoms in the beam (X = Kr,Xe). The influence of processes (33) and (34) can be eliminated by making the beam monokinetic to decrease the relative energy of $X^* + X$ collisions of like atoms. In this case the cross section of reaction (34) is negligibly small in comparison with the cross sections of reactions (2)–(5), and reaction (33) is accompanied by luminescence at wavelengths longer than that of reactions (2) and (3).

The author is grateful to A. Z. Devdariani for discussion of the elementary processes in which polarized atoms take part and to Yu. N. Demkov and the participants of his seminar for a discussion of the work.

[1)] The case of weak spin–orbit coupling, when coupling type *b* is realized at sufficiently small *R*, is not considered here.

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Translated by P. F. Schippnick