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ELECTRON CAPTURE BY ALKALINE METAL IONS SCATTERED BY INERT GAS IONS

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We consider one-electron nonresonance charge exchange of alkaline metal ions and inert gas atoms. The electron terms of the quasi-molecules formed in the collisions are determined under the assumption that the polarization interaction between the alkali metal atoms and the ions is the principal one. A characteristic feature of these terms is the fact that the unperturbed frequency exhibits a minimum. The cross-sections are determined from the theory of nonadiabatic transitions. Numerical calculations are given for the reactions Li^+, Na^+, K^+, $Cs^+ \rightarrow He$ and $Li^+ \rightarrow Ne$, Ar. All results are found to be in satisfactory agreement with the experimental data.

INTRODUCTION

AT the present time it can be regarded as established that the cross-sections for nonresonance processes and their dependence on the velocities of the colliding particles in the adiabatic region $\eta \gg 1$ (η is the adiabatic parameter of Massey) are determined by the behavior of the electron levels of the quasi-molecule that is formed in the interaction process. Mathematically the problem reduces to a search for the "region of nonadiabaticity" and the extrapolation of approximate asymptotic solutions of the appropriate differential equations through the so-called "turning points" (the points of discontinuity of the asymptotes) rather than numerical integration over the entire range of variation of the independent variable. When we can limit ourselves to a minimum number of turning points the method is most simple and convenient; however, even this simple variant of the theory encounters difficulties in application to actual systems. These difficulties derive from the electron terms in the compound systems.

This circumstance is one of the principal reasons that the application of the theory to the calculation of cross-sections for inelastic processes (if we neglect thermal collisions) is limited essentially to the case of charge exchange of multiply charged ions. In this case it is possible to use a simple description of the potential curves; essentially one takes account of the strong Coulomb repulsion of the particles in the final state. Calculations already reported by one of the authors[1] based on this simplified picture of the interaction between the atom and the ion are in satisfactory agreement with the available experimental data; nevertheless, the approximations made in these calculations (neglecting the configuration terms p^N and the excited states of the reaction products) are such that it is impossible to judge the degree of accuracy of the theory and the nature of possible discrepancies.

In a paper by Nikitin and Bykhovskii[2] an investigation has been made of the effect of remote zeroes of the adiabatic frequency on the probability for charge exchange of multiply charged ions in the two-state approximation; in this case the results exhibit a strong discrepancy with experimental data. A consistent analysis of this process goes far beyond the framework of the two-state approximation and requires taking account of the "turning points" in more than two differential equations; it can be shown that these lie at approximately the same distance from the real axis. However, the mathematical difficulties that are encountered in this approach make it impossible to solve the problem. In view of these considerations it is of interest to apply the theory to other processes and to compare the results which are obtained with the reliable experimental data which are presently available.

In the present work we compute the cross sections for single nonresonance charge exchange of alkali metal ions in slow collisions with inert gas atoms. The investigation of the behavior of the electron levels reduces to taking account of the strong polarization interaction of the particles in the final state on the basis of ideas developed in the theory of electron-atom collisions. A comparison with the experimental data indicates the general validity of the theory; in particular, the validity of the assumptions made in the approximate calculations of the potential curves, is established.

1. APPROXIMATE FORMULATION OF THE ELECTRON LEVELS OF THE QUASI-MOLECULE

The reactions we consider are of the following forms:

$$A^+({}^1S) + B({}^1S) \rightarrow A({}^2S) + B^+({}^2S) - \Delta E, \quad (1)$$

$$A^+({}^1S) + C({}^1S) \rightarrow A({}^2S) + C^+({}^2S) - \Delta E;$$

$$A^+ = (\mathrm{Li}^+, \mathrm{Na}^+, \mathrm{K}^+, \mathrm{Cs}^+); \quad B = \mathrm{He}, \quad C = (\mathrm{Ne}, \mathrm{Ar}). \quad (2)$$

In the range of relative velocities being considered[1] the minimum value of the adiabatic parameter of Massey is approximately equal to 4 or 5 units and the adiabaticity condition can be regarded as satisfied. Furthermore, in treating the processes in Eqs. (1) and (2) we neglect the contribution of excited states of the alkali metal atoms. The validity of this approximation is generally not evident a priori since the excited atoms exhibit a strong polarizability (in this case the role of the exchange forces also becomes more important). In the work of Van Eck[3] for example, the 4D → 2P line of the Li atom was observed in charge exchange between Li^+ and He. However, the strong endothermal nature of the reaction ($\Delta E \sim 0.5 - 0.7$) and other experimental results[2] yield some justification for neglecting the excited states.

According to the Wigner spin conservation rule, in reactions such as (1) we can limit ourselves to terms ${}^1\Sigma^+(A^+ + B)$ and ${}^1\Sigma^+(A + B^+)$ and in reactions of type (2) to terms ${}^1\Sigma^+(A^+ + C)$, ${}^1\Sigma^+(A + C^+)$ and ${}^1\Pi(A + C^+)$ of the quasi-molecule. The term ${}^1\Sigma^+$ of the initial state in (1) and (2), which characterizes the interaction of atomic systems with closed electronic shells, has been studied extensively by direct calculation (cf. for example [5, 6]) and by analysis of the data on the mobility of alkali metal ions in inert gases. This term can be written in the form

$$\mathscr{E}_1(R) = E_b - U_1(R), \quad (3)$$

where E_b is the energy of the ground state of the inert gas atom and $U_1(R)$ is the potential energy; the potential energy has different analytical representations for different values of R (R is the internuclear distance). To the best of our knowledge an exact quantitative calculation is not available for the terms ${}^1\Sigma^+$ and ${}^1\Pi$ (p^6 configuration) of the final state; hence, we introduce the following simplification. We limit ourselves to the approximation in which these terms are degenerate. In this case $\mathscr{E}_2(R)$ can be written in the form

$$\mathscr{E}_2(R) = E_a - U_2(R) - U_{pol}(R),$$

$$U_{pol}(R) = -\alpha(R) / 2R^4, \quad (4)$$

where $U_2(R)$ is the potential associated with the electrostatic forces while $U_{pol}(R)$ is the polarization potential, whose representation is given below.

In order to estimate the difference $U_1(R) - U_2(R)$ we have carried out numerical calculations using the Hartree-Fock functions in the approximation which neglects the effect of the other atoms A and C. These estimates indicate a relatively weak effect of this difference on the unperturbed transition frequency $\omega_0(R)$, which is given by the following approximate expression

$$\omega_0(R) \approx \Delta E - \alpha(R) / 2R^4. \quad (5)$$

Thus, for an approximate representation of $\omega_0(R)$ we use a model of the alkali metal atom in the field of the Coulomb centers B^+ and C^+. The polarization potential in the system consisting of A plus the Coulomb centers is determined as follows.

It is known that the polarizability of alkali metal atoms is determined by the valence electron while the effect of the other electrons can be neglected. The polarization potential of the atom is then given by

$$U_{pol}(R) = \int \varphi_a(\mathbf{r}) \frac{1}{|\mathbf{R} - \mathbf{r}|} g(\mathbf{r}R)\, d\tau, \quad (6)$$

where $\varphi_a(\mathbf{r})$ is the wave function for the valence electron while $g(\mathbf{r}R)$ is a function which characterizes the perturbation of state $\varphi_a(\mathbf{r})$ by the field of the positive charge. This function can typically be found by a variational method. Experimental work of this nature[7, 8] shows that a test function of the form

$$g(\mathbf{r}R) = \vartheta f(\mathbf{r}, a_k) \frac{r}{R^2} \varphi_a(\mathbf{r}) P_1(\cos\theta), \quad \cos\theta = \frac{(\mathbf{r}\mathbf{e}_z)}{r},$$

$$\vartheta = \begin{cases} 0, & r > R \\ 1, & r \leqslant R \end{cases}, \quad (7)$$

leads to good agreement with $U_{pol}(R)$ as found from numerical calculations for an appropriate choice of the function f. This choice affects the quantity α_∞ and the behavior of $U_{pol}(R)$ at small R.

The polarization potential in the adiabatic ap-

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[1] In all calculations we make use of atomic units.

[2] Data on stripping of alkaline metal atoms[4] indicate a small fraction of excited states.

proximation (more precisely, the dipole part) must satisfy

$$U_{pol}(R) \to -\alpha_\infty / 2R^4, \quad R \to \infty, \tag{8}$$

$$U_{pol}(R) \to \mathrm{const}\cdot R^2, \quad R \to 0. \tag{9}$$

In view of these conditions and assuming that $\varphi_a(\mathbf{r})$ can be written in the form

$$\varphi_a(\mathbf{r}) = N r^{n-1} e^{-\sigma r}, \tag{10}$$

we take

$$g(\mathbf{r}R) = \vartheta\lambda_n \frac{r^{4-2n}}{R^2}\varphi_a(\mathbf{r}) P_1(\cos\theta)$$

$$= \vartheta\lambda_n N \frac{r^{3-n}}{R^2} e^{-\sigma r} P_1(\cos\theta). \tag{11}$$

This representation guarantees that (9) is satisfied at small R and allows us to obtain the proper asymptotic behavior for $U_{pol}(R)$ if we normalize λ_n as follows:

$$\lambda_n = -\frac{1}{5\pi}\frac{\alpha_\infty \sigma^6}{N^2}. \tag{12}$$

Computing $U_{pol}(R)$ from Eq. (6) with $g(\mathbf{r}R)$ taken from Eq. (11) when $R > 1$ ($\rho = \sigma R$) we find

$$\omega_0 = \Delta E - \frac{\alpha_\infty \sigma^4}{2\rho^4}\left[1 - e^{-2\rho}\left(1 + 2\rho + 2\rho^2 + \frac{4}{3}\rho^3 + \frac{2}{3}\rho^4 + \frac{4}{15}\rho^5\right)\right]. \tag{13}$$

The restriction $R > 1$ arises for the following reason. For small R ($R \lesssim 1$) there is an appreciable difference $U_1(R) - U_2(R)$ which starts to dominate U_{pol}. However, since this term is not taken into account in the approximation for ω_0 (13) the expression has meaning at distances where the polarization potential predominates, that is to say, when $R > 1$.[3)] The function $\omega_0(R)$ is shown in Fig. 1; the dashed line indicates the assumed behavior of the correct function $\omega_0(R)$ for $R \sim 1$ and smaller, i.e., this curve takes account of ΔU_{12}. The minimum resonance defect is

$$\omega_{0\,min} = \Delta E - 0.87\,\alpha_\infty \sigma^4 10^{-2}. \tag{14}$$

2. TRANSITION PROBABILITIES

In order to find the probability for charge exchange we must solve the system of differential equations

$$i\dot{a}_{\cdot} = -V\exp\left(\pm i\int^t \omega_0 dt'\right) a_{2,1} \tag{15}$$

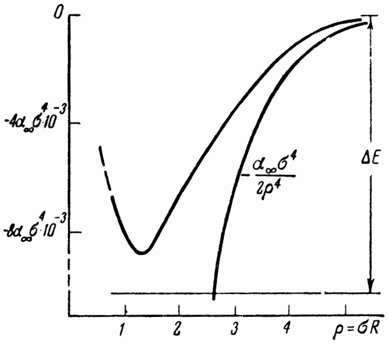

FIG. 1. Unperturbed frequency $\omega_0 = \Delta E - \alpha(R)/2R^4$. For purposes of comparison we show the behavior of the term $\alpha_\infty/2R^4$.

with the boundary conditions $|a_1(-\infty)| = 1$; $a_2(-\infty) = 0$ where V is the interaction matrix element, given by

$$V = \frac{V_{12} - SV_{22}}{1 - S^2},$$

$$V_{12} = \left\langle 1 \left| -\frac{1}{r_b} + \frac{1}{R} - \frac{v_\theta}{R} i\hat{L}_y \right| 2 \right\rangle; \tag{16}$$

$$V_{22} = \left\langle 2 \left| -\frac{1}{r_b} + \frac{1}{R} - \frac{v_\theta}{R} i\hat{L}_y \right| 2 \right\rangle,$$

$$S = \langle 1 | 2 \rangle. \tag{17}$$

Here $\langle 1|$ is the wave function for the valence electron in atom A, $\langle 2|$ is the wave function for the electron in the inert gas atom, r_b is the distance from B^+ to the active electron and the term $v_\theta i\hat{L}_y/R$ (v_θ is the velocity component of the relative motion along the $\mathbf{e}_\theta$ axis, $\hat{L}_y$ is the operator for the projection of the electron orbital angular momentum along the axis perpendicular to the plane of motion) is due to the rotation of the internuclear axis (the wave functions $\langle 1|$ and $\langle 2|$ can be regarded as being written in a moving coordinate system with z axis parallel to the line that joins the nuclei).[9]

Transitions of σ and π electrons occur respectively under the effective perturbations

$$-1/r_b + 1/R, \qquad -v_\theta i\hat{L}_y / R.$$

The perturbed transition frequency is computed from the expression

$$\omega^2(R) = \omega_0^2(R) + 4V^2(R). \tag{18}$$

Since the resonance defects are large ($\Delta E \sim 0.5 - 0.7$) and the Massey parameter is much greater than unity the region of transitions is concentrated in a small circle around the point $R = R_x$ for which we can use the following approximation for ω_0 and V, which reflects the basic features of the interaction in this region:

[3)] By the same token we neglect transitions for which $R \lesssim 1$.

$$\omega_0(R) = \omega_{0x} + {}^1/_2\,\omega_{0x}''(R - R_x)^2, \qquad V = V_x = \text{const},$$

$$\omega_{0x}'' = \left.\frac{d^2\omega_0}{dR^2}\right|_{R=R_x}; \qquad \omega_{0x} \equiv \omega_{0\,min}. \tag{19}$$

This case differs considerably from the usually treated case of quantum transitions in the presence of linear overlapping terms in the zeroth approximation and a constant interaction matrix element (the Landau-Zener case). In the semiclassical approximation we can go from the variable R to t making use of the relation $R - R_x = V_R(t - t_x)$ and treat the problem in the complex plane of the variable t. In this case the unperturbed frequency has two first-order zeros at the points

$$t_x \pm i2\omega_{0x} / (v_R^2\omega_{0x}''),$$

which, under the effect of a constant perturbation V_x, are split into four zeroes of the adiabatic frequency (zeroes of half multiplicity).

This case has been treated recently in a paper by Nikitin, Bykhovskii, and Ovchinnikov[10] in connection with the problem of determining the transition probability when the turning point lies close to the pseudo-intersection points. If, following this work, we introduce the dimensionless parameters

$$\varepsilon = -\omega_{0x} / 2V_x; \qquad b = 4V_x^{3/2}[\omega_{0x}''^{1/2}v_R]^{-1}, \tag{20}$$

and the dimensionless variable $\tau = 2V_x(t - t_x)$ our case becomes analogous to the case of a nonadiabatic transition which occurs by tunneling for a large imaginary velocity ($\varepsilon \ll -1$). In the case of weak spreading of the zeros ($\varepsilon \ll -1$) the usual perturbation theory applies and leads to the following result for the transition probability:

$$P = \frac{2\pi y^2}{\varepsilon^2}\Phi^2(y), \qquad y = 2^{1/3}\omega_{0x}''^{-1/3}v_R^{-2/3}\omega_{0x}. \tag{21}$$

Here, $\Phi(y)$ is the Airy function as given by Fock.[11] When $y > 1$ (this condition is satisfied in all the reactions studied here) the Airy function approaches its asymptotic value; hence, the final result is

$$P = \frac{\pi y^{3/2}}{2\varepsilon^2}\exp\left(-\frac{4}{3}y^{3/2}\right). \tag{22}$$

If the splitting of the zeros is not small[4] but we can limit ourselves to strong coupling of only two zeroes[5] the problem can be solved by extending the adiabatic solutions by the method of parabolic equations as described in [12]. This procedure yields the following result for P

$$P = \frac{2\delta\sin^2\pi\delta}{\pi}\Gamma^2(\delta)\,\delta^{-2\delta}e^{2\delta}\exp\left(-2\operatorname{Re} i\int_0^{\tau_0}\omega(\tau)\,d\tau\right) \tag{23}$$

$$\delta = V_x^2[(2\omega_{0x}\omega_{0x}'')^{1/2}v_R]^{-1}. \tag{24}$$

This result has also been obtained by Bykhovskiĭ et al.[10]

In all of the reactions treated here the following inequalities are satisfied:[6]

$$\delta \ll 1, \qquad \varepsilon < -2, \tag{25}$$

in which case Eqs. (22) and (23) coincide. Integrating with respect to the impact parameter between the limits 0 and R_∞ we obtain the following expression for the capture cross section for a single σ-electron:

$$\sigma_0 = 2.36\pi R_x^2\varepsilon^{-2}\eta J_0(\eta),$$

$$\eta = 1.88\omega_{0x}^{3/2}(\omega_{0x}''^{1/2}v)^{-1}; \qquad J_0(\eta) = \int_1^\infty x^{-2}e^{-\eta x}\,dx, \tag{26}$$

where R_x is the distance for which $\omega_0' = 0$ and v is the velocity of the colliding atom.

In considering transitions of a π-electron we must take account of the fact that the matrix element for the transition is $v_\theta V_{1x}$ where $V_{1x} = R^{-1}\langle 1 | -iL_y | 2\rangle$; hence, the cross section is given by

$$\sigma_1 = 2.36\pi R_x^2\varepsilon^{-2}\eta v^2(V_{1x} / V_x)^2 J_1(\eta),$$

$$J_1(\eta) = \int_1^\infty x^{-2}e^{-\eta x}(1 - x^{-2})\,dx. \tag{27}$$

The matrix element V_{1x} is nonvanishing only for the function $\langle 1 |$ which is symmetric with respect to the plane of motion of the heavy particles. Assuming that there are two σ electrons in (1) and two σ and four π electrons in (2), in the approximation in which exchange is neglected the total cross sections can be written from the following:

$$\sigma = 2\sigma_0 \qquad \text{for reaction (1)}$$

$$\sigma = 2\sigma_0[1 + v^2(V_{1x}/V_x)^2 J_1(\eta)/J_0(\eta)] \qquad \text{for reaction (2)} \tag{28}$$

These expressions will be used below for carrying out numerical calculations.

3. RESULTS OF NUMERICAL CALCULATIONS

Results of calculations of the cross-sections for single charge exchange Li^+, Na^+, K^+, Cs^+ in

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[4] It is easy to show that the zeroes of the adiabatic frequency in the complex plane of τ are located symmetrically with respect to the real and imaginary axes at the ends of two diameters of the line $2b(q + \epsilon^2)^{1/4}$ and that they form an angle $Q = \arc\tan|\epsilon|^{-1}$ with the imaginary axis.

[5] According to [10] the conditions that must be satisfied for this analysis to be valid are the inequalities $\epsilon \ll -1$ and $|\epsilon|^{1/2}b^{1/3} \gg 1$; both of these are in fact satisfied in the present case.

[6] For most reactions the inequality $\epsilon < -6$ is satisfied.

He, Ne, and Ar were carried out for Eqs. (26), (27) and (28); in the case of charge exchange in helium we have used the first formula in (28) and in the case of Ne and Ar we have used the second formula. The matrix elements for the interaction (16) and (17) were computed with one-electron functions of the Slater type; the parameters were chosen to make these functions coincide with the Hartree-Fock functions at large distances. The values of α_∞ were taken from the work of Karule.[13] All of the parameters used in the calculations are given in the figure captions.

In all the reactions studied here the following condition is satisfied

$$v^2(V_{1x}/V_x)^2 J_1(\eta)/J_0(\eta) \ll 1, \qquad (29)$$

which indicates a small contribution of π electrons in the charge exchange cross-section. This feature is a consequence of the rather large energy defect at $R \sim R_X$ ($\omega_{0X} \sim 0.2-0.3$) and the small magnitude of the perturbation due to the rotation of the internuclear axis, which is proportional to the velocity of the colliding particles. The situation changes when the levels cross (the Landau-Zener case) in which case transitions of the π electrons can play a dominant role.

In Figs. 2 and 3 we show the results of calculations compared with the experimental data obtained by Flaks, Kikiani, and Ogurtsov;[4] In Fig. 2 we show the data for a single target (He) with different incoming particles; in Fig. 3 we show different targets and one incoming particle Li$^+$. A comparison shows that in all cases these results are in satisfactory agreement with experiment and that both the magnitude of the cross-section and its velocity dependence are correct. In the case of one target He and different incoming particles (Li$^+$, Na$^+$, K$^+$ and Cs$^+$) the cross-sections are not located along the resonance defect (as must be the case for the adiabatic hypothesis) but along the polarizability; the cross section increases with polarizability (there are no experimental data for Cs$^+$). It should be noted that changes of several hundredths in σ or several tenths in polarizability can change the cross-section by a factor of two or three.

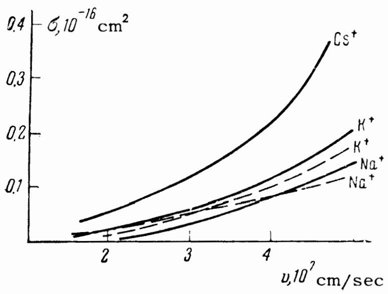

FIG. 2. Cross-sections for charge exchange of the ions Na$^+$, K$^+$, and Cs$^+$ on He atoms (the dashed lines show the experimental results[4] and the solid lines the calculated results). The values of the parameters are as follows: (Na$^+$, He) – $\Delta E = 0.715$, $\alpha_\infty = 161$, $\sigma = 0.73$; (K$^+$, He) – $\Delta E = 0.745$, $\alpha_\infty = 303$, $\sigma = 0.67$; (Cs$^+$, He) – $\Delta E = 0.764$, $\alpha_\infty = 449$, $\sigma = 0.62$.

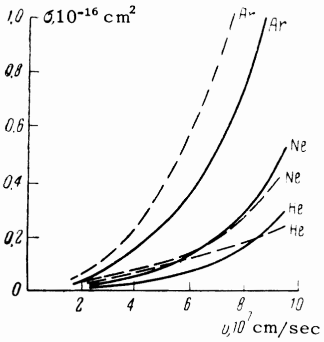

FIG. 3. Cross-sections for charge exchange of Li$^+$ ions on He, Ne, and Ar (the dashed lines show the experimental results[4] and the solid lines the calculated results). The values of the parameters are as follows: (Li$^+$, Ne) – $\Delta E = 0.594$, $\alpha_\infty = 168$, $\sigma = 0.68$; (Li$^+$, Ar) – $\Delta E = 0.382$.

The discrepancy between theory and experiment increases, as is evident from the figures, as the velocity increases; this is evidently due to the approximate nature of the transition probability calculation. Thus, the theory given here gives a satisfactory explanation of all these processes, which do not fall within the framework of the adiabatic hypothesis, in spite of the large resonance defect at small velocities. The case of a minimum in the unperturbed frequency (which differs from the Landau-Zener case in which $\omega_0(R_X) = 0$) is frequently encountered in slow collisions of heavy particles and allows a relatively simple treatment of the problem. Taking account of remote zeros of the adiabatic frequency and the excited states would require a more rigorous analysis of the energy levels.

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237