AUGER IONIZATION INDUCED BY MULTIPLY CHARGED IONS

L. M. KISHINEVSKIĬ and É. S. PARILIS

Institute of Electronics, Uzbek Academy of Sciences

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A collision between a multiply charged ion and an atom gives rise to Auger ionization in which an atomic electron is captured by the ion and another electron is emitted at the expense of the liberated energy. Ionization may proceed along three channels: directly (I), after preliminary single charge exchange (II), or after double charge exchange (III). In the present paper an attempt is made to estimate the Auger ionization for each of the channels, their relative contribution to the total Auger ionization cross section, and the dependence on ion charge and velocity. In all cases the cross section is found to be of the order of 10^{-16}–10^{-15} cm^2. The Auger electron energy spectrum and ion scattering in each of the channels are discussed. Experiments[27] in which additional ionization was observed in collisions between Ne^{3+} or Ne^{4+} and Xe are analyzed. Other pairs of atoms and multiply charged ions for which the phenomenon should be observable are indicated, as well as the velocity range in which it is most effective.

1. When a multiply-charged ion approaches an atom, it forms an excited system. Its upper levels are filled with electrons, and the lower (ion levels) are vacant. Such a system should relax rapidly by nonradiative emission of electrons, in analogy with the Auger effect. In this case one electron of the atom neutralizes the ion, and the other becomes capable of leaving the atom as the result of the released neutralization energy.

This effect can be realized in at least three ways.

I. Auger ionization proper, in which one electron of the atom is immediately captured in the ground state of the multiply charged ion B^{n+}, transferring the excess energy to another electron of the atom A:

$$A + B^{n+} \to A^{2+} + B^{(n-1)+} + e.$$

II. A two-stage process, in which first one electron of the atom A goes over into the excited state of the ion $B^{*(n-1)+}$, which then relaxes with energy transferred to another electron of the atom A:

$$A + B^{n+} \to A^{+} + B^{*(n-1)+} \to A^{2+} + B^{(n-1)+} + e.$$

III. Another two-stage process, namely, two-electron charge exchange in the auto-ionization state of the ion $B^{**(n-2)+}$ with subsequent Auger effect in it:

$$A + B^{n+} \to A^{2+} + B^{**(n-2)+} \to A^{2+} + B^{(n-1)+} + e.$$

Multielectron charge exchange into excited states, which can occur at large values of n, lead qualitatively to the same process.

The Auger ionization of an atom by multiply-charge ion does not require, in principle, kinetic energy of the colliding particles, and could be observed at very low ion velocities[1,2]. The described effect is analogous to impacts of the second kind such as the Penning effect, on the one hand, and to potential emission of electrons from a metal under the influence of positive ions, on the other[3-6].

2. The foregoing possibilities are realized during the time evolution of the $A + B^{n+}$ system as the result of the electronic transitions due to the coming together of the terms at relatively large internuclear distances. In this region, the behavior of the terms is determined in the main by the Coulomb interaction of the ions.

Single-electron charge exchange of multiply-charged ions is calculated by the Landau-Zener formula[7-10]. In the case when the atomic term crosses several terms, the formula can be employed successively several times[11]. The distance R_1 at which the intersection of the terms occurs in single-electron charge exchange, equals

$$R_1 = \frac{n-1}{U^{(n)}_{B^*} - U^{(1)}_{A}}, \tag{1}$$

where $U^{(1)}_{A}$ and $U^{(n)}_{B^*}$ are the ionization potentials of the atoms A and $B^{*(n-1)+}$. We use atomic units throughout ($e^2 = m_e = \hbar = 1$).

Simultaneous transition of two electrons to the ion B corresponds to the crossing of the terms at a distance

$$R_2 = \frac{2(n-2)}{U^{(n)}_{B^*} + U^{(n-1)}_{B^*} - U^{(1)}_{A} - U^{(2)}_{A}}. \tag{2}$$

In addition, two-electron charge exchange can be realized by successive transition of two electrons: one upon intersection at the point R_1 and the other upon intersection of the corresponding terms at the point

$$R_{12} = \frac{n-3}{U^{(n-1)}_{B^*} - U^{(2)}_{A}}.$$

We confine ourselves to the case when the electrons of the atom A go over to the same shell of the ion B. Then,

$$R_{12} \gg R_2 > R_1. \tag{3}$$

Inasmuch as the point R_{12} is at not too large a distance, this transition can be disregarded. Allowance for the possible transition to different shells complicates the calculations, although a similar consideration can be carried out also in this case.

The probability that the system will continue to move along the unperturbed term after passing once through the intersection point, i.e., that the electron will not go over to another atom, equals, in accordance with the Landau-Zener formula,

$$p_i = \exp\left\{-\frac{\pi}{2}\frac{[\Delta U_i(R_i)]^2}{v_{R_i}|F_0 - F_i|}\right\} = \exp\left\{-\frac{v_i}{v_{R_i}}\right\} \quad (i = 1, 2), \quad (4)$$

where v_{R_i} is the radial velocity; $\Delta U_i(R_i)$ is the separation of the terms at the intersection point; F_0 and F_i are the forces of the terms.

Using for ΔU_1 the formula from [9] and an analogous expression for ΔU_2, and taking (4) into account, we get

$$v_2 < 8s^2(R_2)v_1, \quad (5)$$

where $s = \langle\psi_A|\psi_{B^*}\rangle$ is the overlap integral at an internuclear distance $R = R_2$. Inasmuch as R_2 is large, $s(R_2)$ is small and v_2 is at least one order of magnitude smaller than v_1.

3. Upon each passage of the points R_i (i = 1, 2) before and after the turning point, the flux splits into parts p_i and $1 - p_i$. On moving between the intersection points, as a result of the Auger ionization, these fluxes are decreased by a factor ω_k:

$$\omega_k[\rho, R_i(t_i)] = \exp\left(-\int_{-t_i}^{t_i} W_k(R)\,dt\right),$$

where t_i is the instant of the passage through the point R_i (the null point is the instant of closest approach of the nuclei), and $W_k(R)$ are the probabilities of decay per unit time for the different channels (k = I, II, III), calculated at fixed distances between the nuclei. As shown by estimates, process I is effective only in the region $R < R_1$. Then the probabilities of Auger ionization over three channels within the time of transit with velocity v along the trajectory with impact parameter ρ are equal to

$$P_I(\rho, v) = p_1p_2(1 - \omega_I), \quad (6)$$

$$P_{II}(\rho, v) = p_2(1 - p_1)(1 - \omega_{II}), \quad (7)$$

$$P_{III}(\rho, v) = (1 - p_2)[1 - \omega_{III}(1 - p_2)] + p_2(1 - p_2)[p_1^2\omega_I + (1 - p_1)^2\omega_{II}]. \quad (8)$$

In (8) we took into account the fact that the auto-ionization in channel III is possible also after the particles move apart.

The probabilities $W_k(R)$ can be calculated in the adiabatic approximation of perturbation theory, and the role of the perturbation is paid by the Coulomb interaction of the electrons. In general, it is not sufficiently small, but, as will be shown below (formula (10)), and as is also shown in [12], when another smaller perturbation is chosen the contribution to W_k is due only to the electron interaction energy, and the refinement consists in the use of wave functions that are reconciled with the chosen perturbation. The probabilities W_k differ from zero if the initial and final states have the same values of the projection of the orbital angular momentum of the electrons in the axis joining the nuclei (Λ), and the same values of the total spin (S).

Let us consider the probability of the Auger ionization proper (channel I) [13]:

$$W_I(R) = 2\pi|\langle\psi_B(1)\psi_E(2)|1/r_{12}|\psi_A(1)\psi_A(2)\rangle|^2 g_f. \quad (9)$$

Here ψ_A and ψ_B are the quasimolecular wave functions of the electrons, which go over into the atomic wave functions as $R \to \infty$, and ψ_E is the wave function of the continuous spectrum. For brevity, the functions are written in asymmetrical form; g_f is the density of the final states.

When $R \gg 1$, the product $\psi_B(1)\psi_A(1)$ is localized around the ion B, since ψ_B describes the deeper state, and $\psi_A(2)\psi_E(2)$ is localized in the vicinity of the atom A. Thus, the significant regions are where r_{B_1} and r_{A_2} are small, and the perturbation $1/r_{12}$ can be represented in the form of a series in powers of 1/R, the largest term of the expansion, containing r_{A_2} and r_{B_1}, having the form

$$\frac{1}{R^3}\left[\mathbf{r}_{A2}\mathbf{r}_{B1} - \frac{3}{R^2}(\mathbf{r}_{A2}\mathbf{R})(\mathbf{r}_{B1}\mathbf{R})\right]. \quad (10)$$

The magnitude of the product $\psi_B(1)\psi_A(1)$ and, in final analysis, of $W_I(R)$, is determined by the degree of drawing-over of the wave function ψ_A to the vicinity of the multiply-charged ion B.

This drawing-over can be calculated if the atom and the ion are represented by two Coulomb centers with charges $Z_A = 2$, $Z_B = n$ with two electrons. In this case, the variables in the Schrödinger equation are separated. Its solution in the vicinities of the atom A and of the ion B were found by Gershteĭn and Krivchenkov [14]. Joining the solutions together, we obtain

$$\psi_A = \pi^{-1/2}(2p/R)^{3/2}e^{-p\mu}\cdot \times\begin{cases} e^{-p\nu} & \text{in the vicinity of A} \\ D(R)\,e^{p\nu}F\left[\dfrac{Z_A - Z_B}{2p}, 1, 2p(1-\nu)\right] & \text{in the vicinity of B}\end{cases} \quad (11)$$

Here $\mu = (r_A + r_B)/R$ and $\nu = (r_A - r_B)/R$ are elliptical coordinates;

$$p = Z_AR/2 + Z_B/2Z_A + O(1/R).$$

The dependence of the degree of drawing-over of the function ψ_A into the region of the ion B on the distance between the nuclei is determined by the factor

$$D(R) = \Gamma\left[\frac{(Z_A - Z_B)R}{2p}\right](4p)^{Z_B/Z_A}e^{-2p}. \quad (12)$$

A solution of the type (11) can be made continuous also with the wave function of the arbitrary atom A along the axis joining the nuclei, using a procedure described by Smirnov [15]. We obtain

$$D(R) = C\Gamma\left(1 - \frac{Z_B}{\nu} - \frac{Z_B}{\nu^2R}\right)(2\gamma)^{Z_B/\gamma}R^{(Z_B+2)/\gamma-1}e^{-\gamma R}, \quad (13)$$

where $\gamma = \sqrt{2U_A^{(2)} + 2Z_B/R}$, C is a constant determined by joining of the asymptotic solution with the Hartree-Fock solution for the ion A^+ [15]. In the case of two Coulomb centers, (13) goes over into (12).

Assuming that the electron is captured by a Coulomb center B in the ground state 1s, and taking (10)–(13) into account, we obtain

$$W_1(R) = 2^9\omega^{-1}c\sigma_{phot}(\omega)Z_B^5(Z_B + \gamma)^{-2Z_B/\gamma-6}\cdot(Z_B - \gamma)^{2Z_B/\gamma-4}R^{-6}D^2(R) = A_IR^{-6}D^2(R). \quad (14)$$

Here c is the velocity of light, and $\sigma_{phot}(\omega)$ is the cross section for photoionization of the ion A^+ by emission of frequency $\omega = (Z_B^2 - \gamma^2)/2$.

The probability of Auger ionization in channel II is

$$W_{II}(R) = 2\pi|\langle\psi_B(1)\psi_E(2)|1/r_{12}|\psi_{B^*}(1)\psi_A(2)\rangle + \langle\psi_B(1)\psi_E(2)|1/r_{12}|\psi_A(1)\psi_{B^*}(2)\rangle|^2 g_f = 2\pi|V_{II}^{(1)} + V_{II}^{(2)}|^2 g_f. \quad (15)$$

It is seen from (15) that two different transitions are

possible in channel II. 1) direct, with emission of an atomic electron, and 2) "exchange," with emission of an electron from the ion.

The matrix element $V_{II}^{(1)}$ differs from zero if the optical relaxation of the excited state is allowed; its magnitude is determined by the dipole-dipole interaction[16-18]:

$$V_{II}^{(1)} = A_{II}^{(1)}(\pi\omega R^3)^{-1}[c\sigma_{phot}(\omega)f_B]^{1/2}. \quad (16)$$

Here f_B is the oscillator strength for the transition of the ion $B^{*(n-1)+}$ to the ground state; $A_{II}^{(1)}$ is a numerical factor on the order of unity.

In the matrix element $V_{II}^{(2)}$, the product $\psi_B(1)\psi_A(1)$ and $\psi_{B^*}(2)\psi_E(2)$ are localized around the ion, and therefore the perturbation $1/r_{12}$ does not introduce the factor $1/R^3$ and

$$V_{II}^{(2)} = A_{II}^{(2)}D(R), \quad (17)$$

where $A_{II}^{(2)} \approx 0.1 - 0.01$.

When $R \gg 1$ we have $V_{II}^{(1)} \gg V_{II}^{(2)}$, but the quantity $V_{II}^{(1)}$ is smaller in this case by a factor 1.5—2 than in[16-18], since a product $Z_A^{-2}Z_B^{-1}$ appears for the multiply charged ion simultaneously with the factor R^{-3}. Therefore $V_{II}^{(2)}$ may exceed by several times $V_{II}^{(1)}$ at distances on the order of the atomic dimensions, where $D(R) \sim 1$. We note that $V_{II}^{(2)}$ differs from zero not only for the resonant but also for the metastable excited state of the ion $B^{*(n-1)+}$.

The probability $W_{III}(R)$ of the decay of the auto-ionization state of the ion $B^{**(n-2)+}$ is determined by the interaction of the electrons in the ion

$$W_{III}(R) = 2\pi|\langle\psi_B(1)\psi_E(2)|1/r_{12}|\psi_{B^{**}}(1)\psi_{B^{**}}(2)\rangle|^2 g_f.$$

The value of W_{III} can be estimated from[12,19-21] and is of the order of 10^{-4}—10^{-3}.

The auto-ionization state may decay either before or after the separation of the particles, and therefore the probability of the Auger ionization through the channel III is determined mainly by the probability of its formation.

The foregoing estimates show that the probabilities $W_k(R)$ at distances on the order of atomic nuclei have a magnitude 10^{-1}—10^{-2} per atomic unit of time or $\sim 10^{15}$—10^{16} sec^{-1}. These values exceed the probability of the Auger effect in the isolated atom. Indeed, an estimate of W_I for the joined nuclei A and B, carried out for Coulomb centers, yields a much smaller value ($\sim 10^{-3}$)[2]. When the nuclei move apart, W_I increases sharply, reaches a maximum in the region of internuclear distances where the energy of the Auger electron $E_k(R)$ is minimal. This natural correlation between the energy of the Auger transition and its probability explains the course of $W_I(R)$. It could otherwise be attributed to violation of the spherical symmetry and to an intensification of the overlap of the wave functions as the nuclei move apart. Similar factors should lead also to an increase of $W_{III}(R)$ with decreasing R, owing to the deformation of the functions $\psi_{B^{**}}$, introduced by the ion A^{2+}[22].

The probabilities W_I and W_{II} decrease sharply with increasing R, both explicitly, and as a result of the dependence $\sigma_{phot}(\omega) \sim \omega^{-3}$. The dependence on the charge of the ion Z_B is essentially connected with the energy dependence, since $Z_B^2/2$ is the energy of the ground state of the ion. The probability W_{III} for the transition between the given states of the isolated atom, as is well known, depends little on Z_B.

4. Let us calculate the partial cross sections of the Auger ionization over different channels:

$$\sigma_k(v) = 2\pi\int_0^\infty P_k(\rho, v)\,\rho\,d\rho. \quad (18)$$

Taking (6) and (7) into account, and approximating W_I and W_{II} by the exponentials $B_k\exp(-\alpha_k R)$, we obtain

$$\sigma_I(v) \approx \frac{\pi}{\alpha_I^2}e^{-(v_1+v_2)/v}\left[\ln\left(\frac{2{,}5\,B_I}{\alpha_I v}\ln\frac{5B_I}{\alpha_I v}\right)\right]^2, \quad (19)$$

$$\sigma_{II}(v) \approx \frac{\pi}{\alpha_{II}^2}e^{-v_2/v}(1-e^{-v_1/v})\left[\ln\left(\frac{2{,}5\,B_{II}}{\alpha_{II}v}\ln\frac{5B_{II}}{\alpha_{II}v}\right)\right]^2. \quad (20)$$

If the exponential term $V_{II}^{(2)}$ is smaller than the power-law value $V_{II}^{(1)} \sim R^{-3}$ in the region of the effective Auger ionization in channel II, then $W_{II} \sim R^{-6}$. In this case

$$\sigma_{II}(v) \sim e^{-v_2/v}(1-e^{-v_1/v})v^{-7/3}. \quad (21)$$

The cross section for ionization in channel III is

$$\sigma_{III}(v) \approx 2\pi R_2^2\left[\bar{\omega}_{III}\,I\left(\frac{v_2}{v}\right) + \left(1-\frac{R_1^2}{R_2^2}\right)I\left(\frac{R_2 v_2}{v\sqrt{R_2^2-R_1^2}}\right) + \left(\frac{1}{2}-j\left(\frac{v_2}{v}\right)\right)(1-\bar{\omega}_{III})\right], \quad (22)$$

where

$$I(\eta) = \int_1^\infty e^{-\eta x}(1-e^{-\eta x})x^{-3}\,dx, \quad j(\eta) = \int_1^\infty e^{-\eta x}x^{-3}\,dx.$$

An estimate of the cross sections σ_k by means of formulas (19)—(22) yields large values, on the order of the gas-kinetic ones (10^{-15}—10^{-16} cm^2). This is due to the fact that the probabilities W_k reach large values (10^{15}—10^{16} sec^{-1}) at distances on the order of the dimensions of the atom (1—2 Å). To illustrate the velocity dependence of the cross sections, Fig. 1 shows $\sigma_k(v)$ curves calculated for $v_1 = 3\times10^7$ cm/sec, $v_2 = 10^6$ cm/sec, $R_1 = 2$ Å, $R_2 = 2.5$ Å, $B_I = 6\times10^{17}$ sec^{-1}, $B_{II} = 2\times10^{17}$ sec^{-1}, $\alpha_I = 5$ Å^{-1}, $\alpha_{II} = 4$ Å^{-1}, and $W_{III} = 5\times10^{13}$ sec^{-1}.

The cross sections σ_I and σ_{II} pass through the maximum at velocities exceeding v_1 and v_2 by several times, and the cross section σ_{III} does not decrease at small velocities, unlike the cross section for charge exchange in the case of term intersection.

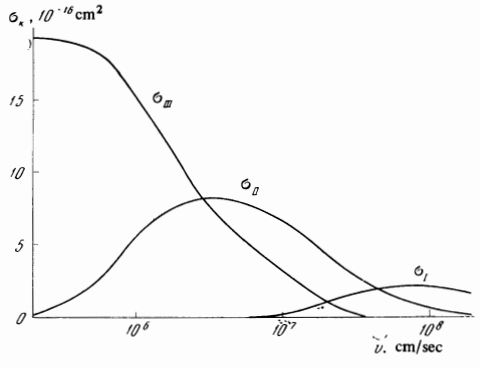

FIG. 1

5. The source of the Auger-electron energy is the ion-neutralization energy. For large R, confining ourselves to the Coulomb interaction, we obtain asymptotic formulas for $E_k(R)$:

$$E_I(R) = E(\infty) - 2(n-1)/R; \quad (23)$$

$$E_{II}(R) = E(\infty) - \frac{n-1}{R} - \frac{n-1}{R_1}, \quad (24)$$

$$E_{III}(R) = E(\infty) - \frac{2}{R} - \frac{2(n-2)}{R_2}. \quad (25)$$

Here $E(\infty) = U_B^{(n)} - U_A^{(1)} - U_A^{(2)}$ is the system excitation energy prior to the collision.

The $E_k(R)$ were calculated at small and medium distances for two Coulomb centers with two electrons in the case $Z_A = 2$ and $Z_B = 4$ (Fig. 2). The symbols on the curves denote the initial state of the system, and in all cases the final state is the ground state $1s\sigma$ of the ion.

Single-electron charge exchange occurs at a distance $(1s)^2$ in the helium atom (state $(2p\sigma)^2$ in the combined atom[14,23]) to the excited states of the ion with principal quantum number n = 2 (in the combined atom these correspond to the states $(2p\sigma)(2p\pi)$, $(2p\sigma)(2s\sigma)$, and $(2p\sigma)(3d\sigma)$[14,23]). The term of the excited states, which is degenerate when $R \to \infty$, splits when the nuclei come closer together. In the calculation of the indicated terms and energies of the Auger electron $E_k(R)$, we used the eigenvalues for one electron in the field of two centers[23] and took into account the electron interaction energy. The separations ΔU_1 upon intersection of the terms $(2p\sigma)(2p\pi)$, $(2p\sigma)(2s\sigma)$, and $(2p\sigma)(3d\sigma)$ with the term $(2p\sigma)^2$ are respectively 0, 0.05, and 0.48 atomic units. Consequently, in accordance with formula (4), the first transition is impossible in the described approximation, while the second and third are effective when $v \lesssim 10^8$ cm/sec and $v \lesssim 10^8$ cm/sec. Two-electron charge exchange corresponds to intersection $R_2 = 9.3 \gg 1$, and therefore $v_2 < 10^4$ cm/sec, i.e., in this case the ionization channel III is of low probability at real velocities. However, the strong coupling between the states, which differ only in the magnetic quantum number m, should lead to transitions between such states, due to the rotation of the internuclear axis[24]. Such transitions leave the system in the auto-ionization state, and consequently should not influence the value of $\sigma_k(v)$ strongly, but they do lead to the appearance of additional peaks in the energy spectrum of the Auger electrons. At large ion velocities, the charge exchange may be connected also with interaction between the orbit and the motion of the nuclei[25,26], which leads to a redistribution of the contributions of the different channels to the ionization cross section.

6. The number of transitions in a spherical layer dR of radius R at a unit flux in the k-th channel is

$$dN_k(R) = 2\pi \int_0^R \omega_k(\rho, R)\, \rho\, d\rho\, W_k(R)\, dR = 2\pi I_k(R) W_k(R) dR. \quad (26)$$

The spectral broadening due to the finite lifetime of the initial state can be described by the factor

$$f(E_k', E_k) = \frac{W_k}{2\pi[(E_k' - E_k)^2 + (W_k/2)^2]}. \quad (27)$$

The time of the radiative transition (10^{-10}–10^{-9} sec) is larger by several orders of magnitude than the time of the Auger effect (10^{-14}–10^{-15} sec), so that the possibility of emission of light can be neglected. Then

$$\frac{dN_k}{dE_k} = 2\pi \int I_k(R) W_k(R) \left|\frac{dR}{dE_k'}\right| f(E_k', E_k)\, dE_k'. \quad (28)$$

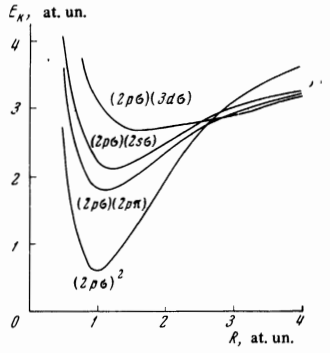

FIG. 2

In relations (26) and (28) it is necessary to take into account, by summation, the ambiguity of $\omega_k(\rho, R)$, which is connected with the fact that the layer dR of radius R is traversed twice (before and after the turning point), and the ambiguity of the function $R = R(E_k)$, since E_k has a minimum. The probability $W_k(R)$ and the derivative dR/dE_k are maximal in the region of the minimum of $E_k(R)$, and this determines the positions of the maxima in the spectrum. Expanding $E_k(R)$ in the vicinity of the minimum, we obtain

$$(dN_k/dE_k)_{max} = 2\pi I_k(R_m) W_k^{1/2}(R_m) (d^2E_k/dR^2)^{-1/2}. \quad (29)$$

Inasmuch as the position of the minima of $E_k(R)$ does not depend on the velocity of the ion, the maxima in the energy spectrum of the Auger electrons are likewise not shifted when the ion velocity changes.

In each channel, besides the described maximum, there can appear on the right side an additional maximum, if the Auger transition has time to occur at large distances, where $I_k(R)$ decreases rapidly at low velocities. Unlike the first maximum, this maximum shifts to the left with increasing velocity.

According to (23)–(25) we have $E_I < E_{II} < E_{III}$, and consequently three sections, corresponding to three possible channels, should be distinguished in the total energy spectrum. The energy spectrum for each channel is normalized to its partial cross section and varies with velocity in analogy with $\sigma_k(v)$. Consequently, with increasing ion velocity, the low-energy maxima increase, and the high-energy maxima decrease.

The energy spectrum of the Auger electrons turns out to be much softer than expected from a comparison of the energy levels of the atom and of the ion at infinity. For example, in the foregoing case, at $E(\infty) = 140$ eV we have $E_I \sim 16$–20 eV and $E_{II} \sim 60$–80 eV. The remaining part of the ion-neutralization energy, ΔE_k, is transferred to the nuclei. According to (23)–(25) we have $\Delta E_k(R) = E(\infty) - E_k(R)$.

The release of energy in the collision process with conservation of the angular momentum should cause an additional scattering of the particles; this scattering is particularly appreciable when the ion energy is comparable with ΔE_k.

7. We select the atom pairs for which this process

is possible by starting from the required energy condition $E_k(R) \geq 0$. It is possible to determine whether this condition is satisfied by using the asymptotic formulas (23)—(25), which give a satisfactory approximation in the region to the right of the minimum of E_k, which is reached at $R = R_m$ on the order of the dimensions R_a of the atom. The ionization in channels II and III is due, in addition, to the possibility of charge exchanges, for which energy conditions can also be formulated. In fact, let $E_{I\,asymp}(R_0) = 0$. Recognizing that $U_A^{(2)} \gtrsim 2U_A^{(1)}$ and consequently $U_{B^*}^{(n)} \approx U_A^{(1)} < U_B^{(n)}/3$, we obtain from (1)—(3) and (23) the inequality

$$R_0 < R_1 < R_2. \qquad (30)$$

It shows that when $R_0 \gg R_a$, when the ionization in channel I is impossible, charge exchange likewise does not occur, or else occurs only at small velocities, since the velocities v_1 and v_2 are small when R_1 and R_2 are large.

Auger ionization is possible when $R_0 \gg R_a$, when the n-th potential of the ion ionization $U_B^{(n)}$ is large, and the sum $U_A^{(1)} + U_A^{(2)}$ is small, and in addition, the dimensions of the atom are large. These conditions are satisfied for light ions and heavy atoms. If at the same time $R_0 \sim R_a \ll R_1$, then ionization is possible only in channel I. For example, for He^{2+} on Xe and Li^{2+} on Ar, the respective values of R_0 are 2.6 and 1.7, while $R_1 > 15$.

With increasing ionization multiplicity n, channels II and III open and the number of ions capable of causing Auger ionization increases. For example, for inert gases the energy condition is satisfied for the doubly charged ions He^{2+} and Li^{2+} on Xe and Li^{2+} on Kr and Ar, for the triply-charged ions Be^{3+}, Li^{3+}, Ne^{3+}, Na^{3+}, and Mg^{3+} on Xe, Be^{3+} and Li^{3+} on Kr and Ar, and Be^{3+} on Ne; for the quadruply-charged ions Be^{4+}, B^{4+}, Ne^{4+}, Na^{4+}, Mg^{4+}, and Al^{4+} on Kr and Xe, and Be^{4+} and B^{4+} on He, Ne, and Ar; for the quintuply-charged ions from B^{5+} to Si^{5+} (except N^{5+}) on Kr and Xe, for the first six of them on Ar, and for B^{5+} and C^{5+} on He and Ne. The condition $E_k(R) \geq 0$ is necessary but not sufficient for the effectiveness of the Auger ionization. Large values of $E_k(R)$ not only do not make it more effective, but, to the contrary, greatly decrease the probability of the transition to the ground state of the ion. Incidentally, in this case when the multiplicity of the ion charge n is very large, Auger ionization with transition to excited states becomes possible. At the same time, the picture of the charge exchanges becomes more complicated and the possibility of multi-step Auger neutralization appears.

8. Observation of Auger ionization against the background of other processes accompanying atomic collisions is facilitated by the large cross sections of this effect, by the characteristic form of the energy spectrum, and by the additional scattering due to the neutralization energy of the ion. Another possibility of observation is afforded by detection of the yield of the A^{2+} ions, which varies with velocity like $\sigma(v)$.

At the present there is only one experiment, performed by Flaks, Ogurtsov, and Fedorenko, in which ionization of Xe by multiply charged ions Ne^{n+} ($n \leq 4$) was investigated[27]. They observed additional ionization in the transition from Ne^{2+} to Ne^{3+} and Ne^{4+}, which they explain in analogy with the potential extraction of

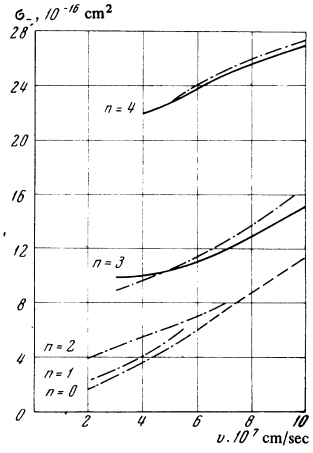

FIG. 3

electrons from a metal, and which regard as a sui generis potential ionization of the atoms (Fig. 3).

The foregoing theory makes it possible to analyze the results of this experiment. For the Ne^{n+}-Xe pairs the value of R_0 is respectively 8, 3.6, and 2.5 at n = 2, 3, and 4, and the atom dimensions $(R_a)_{Xe} \approx 3$. Therefore the condition for Auger ionization ($R_0 \lesssim R_a$) is satisfied only when n = 3 and 4. With the aid of the Slater functions it is possible to estimate the velocities v_1 and v_2. For the pair Ne^{3+}-Xe we have $v_1 \approx 7 \times 10^6$ cm/sec, and the intersection corresponding to two-electron charge exchange is missing. In the case of the pair Ne^{4+}-Xe we have $v_1 \approx 2.5 \times 10^7$ cm/sec and $v_2 \approx 10^6$ cm/sec. Since the experimental data for the Ne^{3+} ions pertain to the velocity region $v > 3 \times 10^7$ cm/sec, and for the Ne^{4+} ions to $v > 5 \times 10^7$ cm/sec, where $\exp(-v_i/v) > 1 - \exp(-v_i/v)$, apparently the main contribution to the cross section is made by the process in channel I.

Comparison with experiment is by matching the value of the cross section σ_I (n = 4) to the difference of the ionization cross sections σ_- (n = 4) $- \sigma_-$ (n = 0) at a velocity $v = 5 \times 10^7$ cm/sec. The matching is attained when the constant B_I in the probability $W_I = B_I \exp[-2\sqrt{2U_{Xe}^{(2)}}R]$ equals 5.85×10^{19} sec^{-1}. The experimental (dash-dot) and theoretical (solid) curves then coincide (Fig. 3). The obtained value of the constant B_I makes it possible to calculate the ionization cross section for n = 3. Thus, in the experiments of[27] they apparently observed Auger ionization in channel I, in the velocity region near the maximum of the function $\sigma_I(v)$ (Fig. 1), where the cross section depends little on the velocity.

The comparison is made difficult by the fact that ionization due to the kinetic energy of the incoming particles is superimposed on the described effect, and allowance for this ionization introduces a certain amount of leeway. In particular, to take this ionization into account it is necessary to assume that its magnitude is independent of the charge of the ion and to extrapolate from the region $v = (2-5) \times 10^7$ to the region $(5-10) \times 10^5$ cm/sec (dashed curve of Fig. 3). At low velocities, where no measurements were made, there should be observed a much larger Auger ionization, which is furthermore not masked by impact ioniza-

tion, since the latter disappears here. Furthermore, in this region ionization appears in channels II and III. It would also be of interest to measure the energy spectrum of the Auger electrons and its dependence on the velocity, making it possible to identify the reaction channels.

[1] L. M. Kishinevskiĭ and É. S. Parilis, Tezisy II Bsesoyuznoĭ konferentsii po atomnym i elektronnym stolknoveniyam (Abstracts of the Second All-union Conference on Atomic and Electronic Collisions), Uzhgorod, 1962.

[2] L. M. Kishinevsky and E. S. Parilis, V. Internat. Conf. on the Physics of Electronic and Atomic Collisions, Leningrad, (1967), p. 100.

[3] Sh. Sh. Shekhter, Zh. Eksp. Teor. Fiz. 7, 750 (1937).

[4] H. D. Hagstrum, Phys. Rev. 96, 336 (1954).

[5] U. A. Arifov, Vzaimodeĭstvie atomnykh chastits s poverkhnost'yu metalla (Interaction of Atomic Particles with Metallic Surfaces), Tashkent (1961).

[6] A. A. Kruithof and M. J. Druyvestein, Physica 4, 450 (1937); A. A. Kruithof and F. M. Penning, Physica 4, 430 (1937).

[7] L. D. Landau, Phys. Zs. d. Sowjetunion 2, 46 (1932).

[8] C. Zener, Proc. Roy. Soc. **A137**, 696 (1932).

[9] D. R. Bates and B. L. Moiseiwitsch, Proc. Phys. Soc. 67, 805 (1954).

[10] T. J. M. Boyd and B. L. Moiseiwitsch, Proc. Phys. Soc. 70, 809 (1957).

[11] Yu. N. Demkov and V. I. Osherov, Zh. Eksp. Teor. Fiz. 53, 1589 (1967) [Sov. Phys.-JETP **26**, 916 (1968)].

[12] S. T. Manson, Phys. Rev. **145**, 35 (1966).

[13] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, 1963, p. 182.

[14] S. A. Gershteĭn and V. D. Krivchenkov, Zh. Eksp. Teor. Fiz. 40, 1491 (1961) [Sov. Phys.-JETP 13, 1044 (1961)].

[15] B. M. Smirnov, Zh. Eksp. Teor. Fiz. 47, 518 (1964) [Sov. Phys.-JETP 20, 345 (1965)].

[16] K. Katsuura, J. Chem. Phys. **42**, 3771 (1965).

[17] B. M. Smirnov and O. B. Firsov, ZhETF Pis. Red. 2, 478 (1965) [JETP-Lett. 2, 297 (1965)].

[18] T. Watanabe and K. Katsuura, J. Chem. Phys. 47, 800 (1967).

[19] B. H. Bransden and A. Dalgarno, Proc. Phys. Soc. **A66**, 904 (1953).

[20] R. Kh. Propin, Opt. Spektrosk. 8, 300 (1960); 10, 289 (1961).

[21] P. G. Burke, D. D. McVicar, and K. Smith, Proc. Phys. Soc. 84, 749 (1964).

[22] R. B. Barker and H. W. Berry, Phys. Rev. 151, 14 (1966).

[23] D. R. Bates and T. R. Carson, Proc. Roy. Soc. **A234**, 207 (1956).

[24] In the Translation Collection Atomnye i molekulyarnye protsessy (Atomic and Molecular Processes), Mir, 1964, pp. 520 and 530.

[25] Yu. P. Mordvinov and O. B. Firsov, Zh. Eksp. Teor. Fiz. 39, 427 (1960) [Sov. Phys.-JETP 12, 301 (1960)].

[26] Yu. P. Mordvinov, Opt. spektrosk. 22, 529 (1967).

[27] I. P. Flaks, G. N. Ogurtsov, and N. V. Fedorenko, Zh. Eksp. Teor. Fiz. 41, 1438 (1961) [Sov. Phys.-JETP 14, 1027 (1962)].

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