Low-energy structural features on the energy dependence of the current of ions reflected from a solid surface

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Various structural features on the energy dependence of the current of ions reflected from a solid surface are analyzed. Structural features of three types (Λ, V, and h) are predicted to result from a competition among various electronic transitions (neutralization through various channels, reionization, deexcitation, and reneutralization) which accompany the motion of an atomic particle. Some new spectroscopic possibilities in experiments on the neutralization of low-energy ions ($E<200$ eV) near a solid surface are discussed.

The interaction of beams of low-energy ($E<500$ eV) ions A^+($A=$He, Ne, Ar, N, N_2, etc.) with a solid surface is known to be accompanied by two easily detected processes: the reflection of these ions and an emission of electrons. Auger-electron spectroscopy is widely used to study the electronic structure of solid surfaces.[1] The spectroscopic possibilities in measurements of the energy dependence of the current of reflected ions, J^+, have not previously been studied. As we will show below, there are some interesting possibilities here.

Some fundamentally new possibilities for experiments on the reflection of low-energy ions from solid surfaces arise because the functions $J^+(E)$ have a variety of structural features: single peaks, slope changes, and combinations of slope changes and peaks. In many cases, these structural features are clearly expressed. They arise from a competition between different electron transitions which accompany the reflection of ions: Auger neutralization, resonant neutralization, reionization, deexcitation, and reneutralization. In general, the energies at which the various structural features are observed fall in the order

$$E_\Lambda < E_h < E_V \tag{1}$$

(we denote the peaks, slope changes, and combinations of slope changes with peaks by Λ, V, and h, respectively).

Figure 1 shows the simplest model which is sufficient to illustrate the mechanisms responsible for the formation of the structural features of all three types. Part a of the figure is the scheme of one-electron terms $\epsilon_i(z)$ of the atomic particle A which is interacting with the solid surface (z is the distance from the particle to the surface; the indices $i=0$, 1 correspond to the ground state and the excited state).

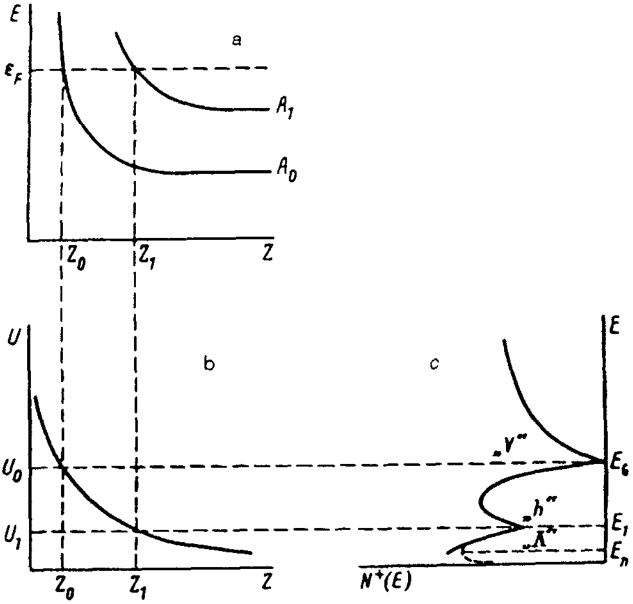

FIG. 1. Mechanisms for the formation of the structural features in the current of reflected ions. a—Scheme of electron terms of particles A_0 and A_1 (ϵ_F is the Fermi level); b—potential of the particle–surface interaction; c—energy dependence of the current of reflected ions corresponding to parts a and b.

At $E \gg \omega \sim 1$ (ω is a characteristic frequency of electron transitions, and $e = \hbar = m = 1$) the motion of particles A^+, A_1, and A_0 can be described by a common trajectory:

$$dz = u(z)dt, \quad u(z) = \{2[E - U(z)]/M\}^{1/2},$$

where M is the mass of the ion, and $U(z)$ is the interaction potential. In this energy interval the interaction potential can be approximated accurately by the Born–Mayer formula[2]

$$U(z) = B\exp(-bz).$$

The sequence of electron transitions evidently begins with the neutralization of an ion, which results in the formation of particle A_1 or (less probably) particle A_0. For the neutralization rates we use the known approximation[1]

$$\Gamma_i(z) = \Gamma_i^0 \exp(-a_i z).$$

According to physical ideas regarding the mechanisms for neutralization in $A^+ \to A_{1,0}$ channels, we would expect the parameters Γ_i^0 and a_i to satisfy $\Gamma_0^0 > \Gamma_1^0$ and $a_0 > a_1$.

The particle A_1 can undergo deexcitation [at a rate $W(z)$] at any distance from the surface. At $z < z_1$ (Fig. 1a) the particles A_1 undergo a reionization, and the ions which form then undergo a reneutralization through the $A^+ \to A_0$ channel ($z > z_0$). At $z < z_0$, the only processes possible are the reionization of A_1 and A_0 and deexcitation ($A_1 \to A_0$).

Since electron transitions are irreversible, the evolution of the electron subsystem of the atomic particle can be described by a method of kinetic equations for the populations of the corresponding states, $n_{0,1}(t)$.

For the case under consideration here (for a system whose terms have the form in Fig. 1a) a solution of the kinetic equations can be written in general form. It contains some deviations from analyticity which arise when the reionization of particles $A_{1,0}$ is taken into account (these deviations correspond to the energy thresholds U_1 and U_0 in Fig. 1b).

Below we construct and analyze the final expressions for the populations of the ion state, $N^+(t) = 1 - n_0 - n_1$, as $t \to \infty$.

For energies $E < U_1$ we have

$$N^+(E) = \exp\left[-2\sum_i \frac{\Gamma_i^0}{bu_0}\left(\frac{E}{B}\right)^{a_i/b} C(a_i b)\right] \equiv N_0^+(E); \tag{2}$$

here $N^+(E) = N^+(t \to \infty)$, $u_0 = u(\infty) = (2E/M)^{1/2}$, and

$$C(a,b) = \int_0^1 x^{a/b-1}(1-x)^{-1/2} dx \tag{3}$$

are numbers on the order of unity (for $a_i \sim b \simeq 2$; Ref. 2).

According to expression (2), under the conditions $b/2 < a_1 < a_0$ we have $(dN_0^+/dE) < 0$; i.e., the current of reflected ions decreases monotonically with increasing energy.[3-5] This case, which is the most common one, is shown by the solid line in Fig. 1b. For $a_1 < b/2 < a_0$, however, the competition between the two neutralization channels gives the function a single peak. The position and half-width of this peak are determined by dynamic parameters (B and b) and spectroscopic parameters (Γ_i^0 and a_i).

The low-energy peak has been observed in, for example, experiments on the reflection of CO_2^+ ions from a Pt (100) surface (see Fig. 11 in Ref. 5). From the position ($E_m \simeq 40$ eV) and half-width ($\Delta E \simeq 40$ eV) of this peak we can easily estimate the ratio of the rates of resonant neutralization and Auger neutralization in this system. For a_1 we can assume $a_1 \ll 1$, $a_0 \simeq b$ (Ref. 3), and $b^{-1} = 0.5$ (Ref. 2). We then find $\Gamma_1^0/_0^0 \approx 10^{-2}$.

With increasing energy of the ions, some additional terms appear in the expression for $N^+(E)$: $\delta N_i^+(E) \sim \eta(E - U_i)$. These additional terms reflect the contributions of ions produced in the reionization of particles A_1 and A_0 [$\eta(x)$ is the unit step function]:

$$N^+(E) = N_0^+(E) + \sum_i \delta N_i^+(E). \tag{4}$$

The term $\delta N_1^+(E)$ is

$$\delta N_1^+(E) = 2P_1P_2P_3 \int_{z_t(E)}^{z_1} dz \frac{\Gamma_1}{u(z)} \cosh\left[\int_{z_t(E)}^{z} (W + \Gamma_1 - \Gamma_0) \frac{dz'}{u(z')} \right] \eta(E - U_1). \tag{5}$$

Here $P_1(E)$ is the probability that particle A_1 reaches the point z_1, $P_2(E)$ is the probability that the ions "survive" as they move from point z_1 to infinity, $P_3(E)$ is the probability that no electron transitions occur as the particle moves on the interval $[z_t, z_1]$, and $z_t(E)$ is the classical turning point: $U(z_t) = E$. The quantities P_1, P_2, and P_3 do not have singularities at $E = U_1$. It is easy to see that at the point $E = U_1$ the function $N^+(E)$, given by (2)–(5), has a characteristic slope change:

$$\frac{dN^+}{dE} < 0, \quad \left| \frac{dN^+}{dE} \right| \sim \text{const} \cdot E^{a_1/b - 3/2} \quad \text{at } E < U_1,$$

$$\frac{dN^+}{dE} > 0, \quad \left| \frac{dN^+}{dE} \right| \sim \text{const} \cdot (E - U_1)^{-1/2} \quad \text{at } \dot{E} > U_1. \tag{6}$$

The square-root singularity in the solution $N^+(E)$ $[\delta N_0^+ \sim \text{const}(E - U_1^{1/2})]$ has the consequence that the probability for the reflection of ions increases sharply just beyond the threshold for the reionization of A_1. Later, when the condition

$$\int_{z_1(E)}^{z_1} \Delta \frac{dz}{u(z)} \sim 1 \quad [\Delta \approx \max(\Gamma_0, W)]$$

becomes satisfied, the function $\delta N_0^+(E)$ falls off exponentially rapidly (because of the factor P_3). In other words, the singularity corresponding to reionization of the electronically excited particles has an extremely characteristic shape, as shown by h in Fig. 1c.

The shape of the threshold singularity corresponding to the reionization of the unexcited particles A_0 is radically different. This singularity is in the term $\delta N_0^+(E)$, which is

$$\delta N_0^+(E) = 2P_1P_2P_3 \sinh\left[\int_{z_t(E)}^{z_0} \frac{\Gamma_0\, dz}{u(z)} \right] \eta(E - U_0). \tag{7}$$

Here $P_1(E)$ is the probability that particle A_0 reaches the point z_0, $P_2(E)$ is the probability that an ion survives as it moves from point z_0 to infinity, and $P_3(E)$ is the probability that A_0 survives on the interval $[z_t, z_0]$.

The function $\delta N_0^+(E)$, like $\delta N_1^+(E)$, has a square-root singularity at $E = U_0$ [the function $N^+(E)$ has a slope change described by Eqs. (6)]. However, since there are no competing processes (deexcitation or reneutralization) on the interval $[z_t(E), Z_0]$, the term $\delta N_0^+(E)$ does not decay for E above the threshold: $(d/dE)\delta N_0^+ > 0$ for all E. At $E \gg U_0$ we have $\delta N_0^+ \sim \exp(-\text{const}/U_0)$; this result corresponds to the Hagstrum formula.[1] The threshold singularity in this case is a single asymmetric dip, marked V in Fig. 1c. These singularities are typically much larger than the h singularities. They are easier to see experimentally (at small values of the angle of incidence α and of the reflection angle β).

Singularities of the V type were first seen[3] experimentally (but not interpreted) in experiments on the reflection of Ar^+, N^+, and N_2^+ ions from Pt (100). These features were later observed by the same investigators for He^+, Ne^+ (Ref. 4), C^+, CO^+, and CO_2^+ ions.[5] Features of the h type have yet to be reported, although they can be seen (in some cases, clearly) on many of the experimental curves in Refs. 3–5. They are found for the A^+/Pt (100) systems, where

$A^+=Ar^+$ (Fig. 2 of Ref. 3, $\alpha=\beta=70°$, $E_h\simeq 25$ eV),

$A^+=N^+$ (Fig. 3 of Ref. 3, $\alpha=\beta\leqslant 70°$, $E_h\simeq 50$ eV),

$A^+=N_2^+$ (Fig. 4 of Ref. 3, $\alpha=\beta\leqslant 70°$, $E_h\simeq 50$ eV),

$A^+=C^+$ (Fig. 9 of Ref. 5, $\alpha=\beta\leqslant 70°$, $E_h\simeq 45$ eV),

$A^+=CO^+$ (Fig. 10 of Ref. 5, $\alpha=\beta\leqslant 70°$, $E_{h_1}\simeq 30$ eV and $E_{h_2}=90$ eV),

$A^+=CO_2^+$ (Fig. 11 of Ref. 5, $\alpha=\beta\leqslant 70°$, $E_h\simeq 50$ eV).

The presence of the h feature in the Ar^+/Pt (100) system is particularly interesting. In the asymptotic region in terms of z, the terms of all of the electronically excited states of Ar lie above the Fermi level (see Fig. 1 in Ref. 3). In this case, a feature of the h type is evidence that an electronically excited collisional complex forms near the Pt (100) surface and that a one-electron term of this complex intersects the Fermi level twice (at a large distance, at which polarization forces are acting, and also at a fairly small distance, at which electron exchange occurs). From the asymptotic resonance defect and the position of the h feature we can easily estimate the binding energy of this complex, E_d, and the position of the point z_1. Specifically, we find $E_d>1$ eV and $z_1=b^{-1}\ln(B/E_h)\simeq 3.5$ [$B=746.3$ (Ref. 2), $b=1.9$ (Ref. 2), and $E_h\simeq 25$ eV (Ref. 3)].

The dependence of the Λ, V, and h features on the basic dynamic and spectroscopic parameters of the collisional complexes, including electronically excited complexes (about which we do not yet have any information to speak of), suggests some interesting new possibilities for experiments on the reflection of slow ions from solid surfaces. Actually realizing these possibilities in full measure will require improving the accuracy of current measurements (primarily, improving the energy resolution) and carrying out a parallel numerical simulation of ion reflection processes incorporating the dependence of the observable quantities on the scattering characteristics. We have carried out a simulation of this sort for the reflection of slow Ar^+ ions from various Pt surfaces [for $E=10$–200 eV and $\alpha(\beta)=5$–$90°$]. The results of these calculations reproduce all features of qualitative importance of the function $J^+(E,\alpha,\beta)$ for this system (this is true of both the features published in Ref. 3 and those of our own experiments). The details of our experiments and of the trajectory calculations will be published separately.

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