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Absence of reionization in low-energy Na$^+$ scattering from Al surfaces

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Inner-shell excitation during low-energy atomic collisions in the gas phase is driven by the formation of transient molecules, in which some electronic levels are promoted to higher energies. For collisions occurring in solids, it is commonly believed that electrons are promoted into the empty conduction states of the embedding system. To verify this assumption, we scattered slow, singly charged neon and sodium ions from polycrystalline aluminum surfaces, focusing on the Auger decay of projectiles excited in the $2p$ level, during a binary collision with a target atom. We observed double promotion of $2p$ electrons in collisions involving neon projectiles and neonlike sodium ions. Double $2p$ excitation is anticipated also for neutralized sodium projectiles, but only single excitation is observed. This implies that the collision-induced excitation is governed by the occupancy of the $3s$ level of the sodium projectile, with the electrons being excited into the Rydberg states of the collision system, rather than being transferred to the solid.

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Since Rutherford's experiments, the scattering of energetic ions has been the basic mechanism for several techniques of spectroscopy and microscopy of solid surfaces, relying on the classical dynamics of binary elastic collisions. More interesting and often controversial have been inelastic effects associated with electronic excitations during nonadiabatic processes, some of which are just beginning to be satisfactorily addressed [1–3]. In particular, electronic excitations, during binary atomic collisions of incoming projectiles with target atoms, have been long investigated for their crucial role in determining the charge and excitation states of the scattered projectiles [4–8], and are currently emerging as an important mechanism for electronic stopping of heavy projectiles [9]. These excitations for sufficiently slow collisions have been successfully interpreted in terms of electron promotion within a molecular orbital (MO) model [10].

Originally developed for collisions in the gas phase, the MO promotion model describes the collision system as a transient molecule, in which some electronic levels are raised to higher energies when the internuclear distance decreases below a critical value. Therefore, electron promotion processes are characterized by a well-defined threshold in impact energy, which depends on the particular combination of collision partners. This threshold energy can be experimentally determined and theoretically estimated from adiabatic MO correlation diagrams. Because of the nonadiabaticity of the collision, promoted electrons can be transferred to higher-lying states at the adiabatically forbidden crossing between the MOs [10]. This results in the production of one or two core holes that are experimentally identified by their decay, via photon or Auger electron emission, and by the characteristic energy loss of scattered projectiles [4,5,11–13].

When the atomic collisions occur in solid targets, because the Rydberg orbitals of the molecular complex are embedded into the continuum of the valence and conduction levels, the promoted electrons are assumed to diffuse irreversibly into the empty conduction band states of the solid, meaning that after the collision they are not localized into specific atomic orbitals [6,7]. This band effect is generally referred to as *(re)ionization* [6,8,9,14], because most of the projectiles are neutralized during the approach to the surface. Here, we show that such a commonly accepted view of electron promotion in atomic collisions in solids is quite far from reality. In the following, we demonstrate that the electrons promoted in collisions of slow sodium projectiles with Al target atoms are located into atomic outer shells, rather than being transferred into the empty conduction states of the metal surface. The analogy with other projectiles, primarily neon, clearly indicates that the conclusions are a general characteristic of low-energy ion-surface collisions.

To achieve our goal, we discuss the Auger decay of $2p$ excitations in the projectiles, produced by electron promotion in close atomic encounters with target atoms, which occurs when singly charged sodium and neon ions are scattered off an Al surface.

The experiments were performed in a previously described UHV chamber setup [15–17], with a base pressure of 3×10^{-10} Torr. Noble gas ions were produced in an electron impact source, operated at low discharge voltage to avoid significant amounts of doubly charged ions reaching the surface with twice the energy. Na$^+$ ions were produced with a Kimball Physics ion gun. The ion beam currents were of the order of 10^{-9} A and had a Gaussian spatial distribution in both horizontal and vertical directions, as measured by a movable Faraday cup situated in the target position. The energy distributions of emitted electrons were acquired by a hemispherical analyzer mounted on a rotatable goniometer. The analyzer, lying in the incidence plane, had semiacceptance

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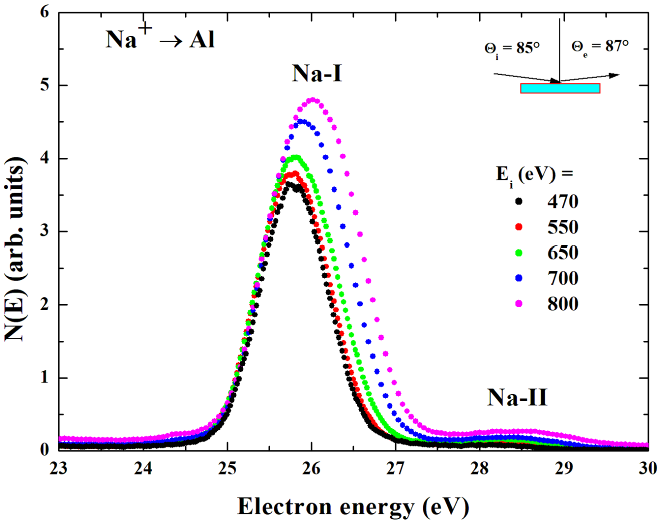

FIG. 1. Auger spectra of singly excited sodium with increasing kinetic energy of incoming projectiles. The spectra are shown normalized to the beam current and width and have been acquired under grazing incidence and observation angles to reduce the background of electrons emitted from the solid.

angles of 1.5° and was operated at a constant pass energy of 50 eV. The polycrystalline Al samples (with 99.999% purity) were sputter cleaned by 6-keV Ar$^+$ bombardment. Sample cleanness was attested to by the absence of oxygen, carbon, and sodium signals in electron-induced Auger spectroscopy, performed right before and after the acquisition of each spectrum, and by the constancy of the energy position of sodium Auger lines during each spectral scan.

Our analysis is based on the energy distributions of Auger electrons emitted in the interaction of sodium and neon ions with the Al surface. Within the framework of the MO model [10], the promotion of the $4f\sigma$ state, correlated to the $2p$ atomic orbital of the lighter collision partner, results in inner-shell excitation in Na and Ne colliding with Al atoms. The decay of $2p$ excitations in sodium and neon projectiles produces the spectral features shown in Figs. 1–4. The spectra are reported normalized to the beam current and width and compare very well with those reported in previous studies [11,17–19].

For sodium projectiles, the decay of these excited states is revealed by the characteristic Auger peaks reported in Figs. 1, 2, and 3(a) for different experimental conditions. For the spectra in Figs. 1 and 2 the incidence angle was $\Theta_i = 85°$ (angles are measured with respect to the surface normal) and the observation angle was $\Theta_e = 87°$. This scattering geometry reduces the background of secondary electrons emitted from the solid, allowing a clearer resolution of the Auger transition lines. Assignments for the observed transition lines are listed in Table I. The position and width of the peaks is indicative of the fact that they originate from the Auger decay in the vacuum of backscattered projectiles. In fact, we observe that the Auger peaks in Figs. 1 and 2 shift towards higher electron emission energies and their widths become larger. The broadening itself is asymmetric, extending towards the high-energy side of the peaks. This is an interesting feature of ion induced Auger electron emission. Since electrons are emitted by atoms moving with respect to the spectrometer, the measured electron energy will be “Doppler” shifted and broadened [20], according to the distribution of the velocity components of the decaying atoms in the direction of observation. Thus, the Auger spectra contain information on the spatial distribution of the scattered particles. In our case, the asymmetry of the distributions, and the fact that the low-energy side of the peaks is essentially unaffected by a change in impact energy, is a clear indication that all decaying atoms are moving with velocity components towards the analyzer.

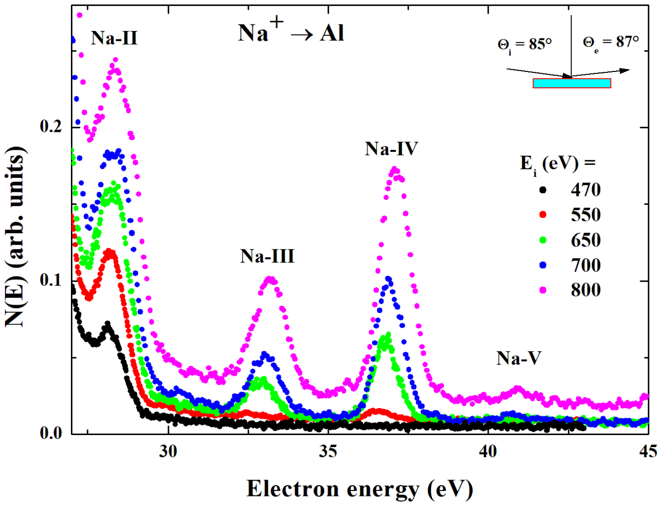

FIG. 2. Auger spectra of doubly excited sodium ions at varying incident energy under the same scattering geometry of Fig. 1.

The spectra in Fig. 1 are characterized by two Auger peaks, which originate from the decay of singly excited Na atoms in the $2p^5 3s^2$ and $2p^5 3s3p$ states [21]. These peaks, labeled Na-I and Na-II, respectively, are the only distinctive features of the spectra at impact energies up to about 500 eV, starting from threshold impact energies as low as 200 eV. On the other side, double excitation in the Na projectiles is observed at impact energies higher than about 500 eV. It is shown in Fig. 2 which focuses on the spectral features in the electron energy range of 27–45 eV, where the spectra present several narrow peaks at electron energies above the $2p^5 3snl$ limit. These peaks are consistent with those reported in previous works [15,21]. In particular, the largest peaks around 33 eV (Na-III) and 37 eV (Na-IV) are ascribed, respectively, to the decay of sodium projectiles excited to the $2p^4(^1D)3s^2$ and $2p^4 3s3p$ state.

It is useful to compare the collision-induced excitation in sodium with those revealed in the case of neon projectiles, which has been extensively investigated [4,11,18]. This comparison is performed in Fig. 3, which reports spectra of electrons excited by neon and sodium at impact energies close to the threshold for $2p$ excitation and under identical scattering geometries ($\Theta_i = 60°$, $\Theta_e = 0°$). As for the spectra of Figs. 1 and 2, the spectra of Fig. 3(a) show that up to an impact energy of about 500 eV the Auger spectrum of sodium reveals only the single $2p$ excitation, starting from a threshold impact energy of about 200 eV, whereas the Auger decay of double excitations is revealed at higher impact energies (not shown). Thus, at impact energies below this threshold, our results show that double excitations in sodium are not observed

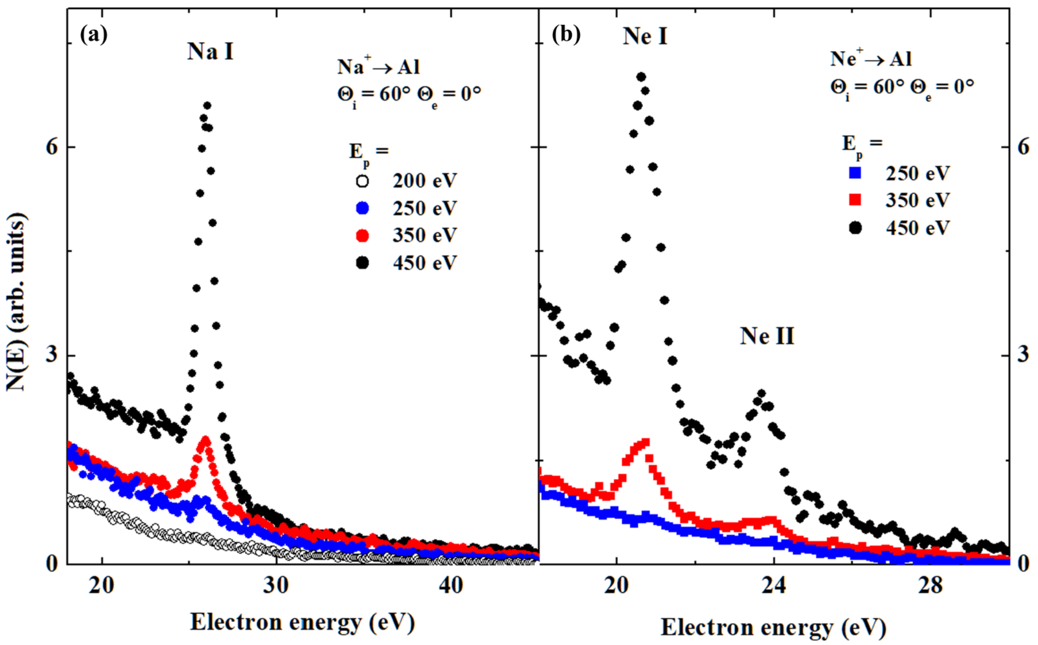

FIG. 3. Auger spectra of sodium projectiles (a) compared with that of neon (b) at impact energy close to the threshold for $2p$ excitations and under identical experimental conditions. Double excitation is observed for neon but not for sodium.

for the two different scattering geometries of Figs. 2 and 3(a). Moreover, earlier studies [15,17], which were performed over an extended variety of impact energies and scattering geometries, are consistent with the present findings. Therefore, we conclude that the absence of double $2p$ excitation is a general property of the scattering of slow sodium ions at Al surfaces.

In the case of neon projectiles, in contrast, the double excitation is observed at impact energies as low as 200 eV. Actually, the spectra of electrons emitted by the decay of $2p$ excitations in neon projectiles reported in Fig. 3(b) can reveal only the occurrence of two-electron excitation events, while single-electron excitation in neon has been detected by the UV photon emission from the decay of the $2p^5 3s$ state [13]. Figure 3(b) is dominated by the two peak structures, labeled Ne-I and Ne-II, which are due, respectively, to the decay of a triplet $[2p^4(^3P)3s^2]$ and a singlet $[2p^4(^1D)3s^2]$ excited state. The formation of these states has been investigated in electron emission experiments as well as in energy loss studies and is well known to occur in collisions involving projectiles that have been neutralized during their approach to the surface [4,11,18,22].

At impact energies higher than those of Fig. 3(b), the spectra show also several other weaker atomic features that have been scrutinized elsewhere [11]. The most intense of them, labeled Ne-III, is also reported over a magnified intensity scale in Fig. 4, reporting the spectrum induced by the impact of 1-keV Ne$^+$. These Auger features, appearing at electron energies larger than 30 eV, above the $2p^4 nln'l'$ transition limit, are due to autoionization decay of triply excited neon states. Triply

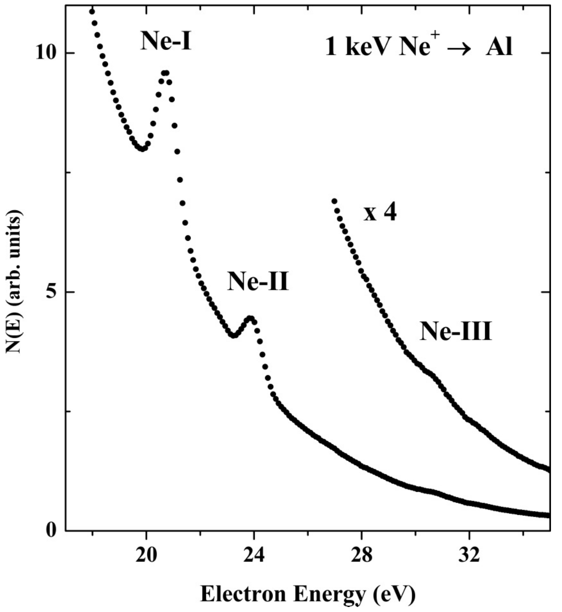

FIG. 4. Autoionization spectrum of neon at 1 keV under the same scattering geometry as Fig. 3. The peak Ne-III is due to a triply excited state formed in collisions involving ions that have survived neutralization at the surface.

TABLE I. Sodium Auger transition lines and proposed assignment.

Label	Expected energies (eV)	Initial state	Final state
I	25.7[a]	$2p^5 3s^2$	$2p^6$
II	28.7[a]	$2p^5 3s3p$	$2p^5$
	and		
	28.9	$2p^4(^3P)3s^2$	
III	32.6[a]	$2p^4(^1D)3s^2$	$2p^5$
IV	37.5[b]	$2p^4 3s3p$	$2p^5$
V	41.4[a]	$2p^4(^1D)3s^2 3p$	$2p^5 3s$

[a] From Ref. [4].
[b] $Z + 1$ rule [21].

excited states are produced at impact energies higher than a threshold of about 500 eV [4,11] by the promotion of the two electrons in the $4f\sigma$ MO in collisions with Al target atoms of incoming ions, which have survived neutralization at the surface with a hole in the $2p$ level correlated to the $3d\pi$ MO [11], as also confirmed by the absence of these excitations in measurements using neutral Ne projectiles [23].

Similarly to the case of neon impact, the observation of the different energy thresholds for the single and double $2p$ excitation of sodium implies that these excitations occur in different collision processes, which involve, respectively, neutralized projectiles and ions that have survived neutralization [15]. In fact, the ground-state electronic configuration of a Na^+ ion is the same as that of a Ne atom. Therefore, collisions involving surviving sodium ions produce both the single and double $2p$ excitation with the same threshold energy, which is consistent with the results for neon and fluorine projectiles [4,5,11,13]. With respect to collisions involving neutralized sodium projectiles, excitation in surviving ions requires a smaller distance of closest approach for the $2p$ level promotion and, therefore, a higher threshold energy, similarly to the case of neon projectiles and consistent with calculated MO orbital correlation diagrams [17]. At impact energies lower than 500 eV, the absence of structures due to decay of doubly $2p$ excited states excludes contributions of collisions involving neonlike sodium ions to the Auger spectrum.

On the other side, the striking observation of Fig. 3 is that at impact energies below 500 eV double excitations are revealed for neon but not for sodium. If one assumes that electrons can be promoted into the empty states of the solid, this observation is quite counterintuitive. In fact, the formation of doubly $2p$-excited states in neutralized sodium would require one or both promoted $2p$ electrons to be transferred to the solid. For example, a transition in a neutral sodium projectile, in which one electron is promoted into the empty $3s$ level and the second one into the conduction band, would lead to the production of the $2p^4(^1D)3s^2$ state. This, in turn, would lead to the observation of the Na-III peak with the same threshold as the Na-I and Na-II peaks, which is clearly not the case. Indeed, a similar transition, leading to formation of the $2p^43s$ state, has been considered in the case of neon projectiles as a possible contribution to the fraction of singly charged backscattered ions from several surfaces [24]. Therefore, the fact, that double electron promotion is not observed for neutralized sodium provides clear evidence that reionization into the empty conduction states is not an important process. This conclusion explains straightforwardly all the excitations revealed for neonlike projectiles, including both the single and the long debated double $2p$ excitation ([4–6], and references therein). We judge that the same conclusion holds also for helium, for which autoionization of doubly excited states has been observed in earlier works [19] but not always analyzed as such [25]. For noble gas projectiles, neutralization into the ground and excited states [25] and their interplay with the collisional excitation produce a variety of charge and excitation states for scattered particles that have prevented so far from an unambiguous determination of the dominant promotion processes.

It is important to remark that the solid environment is not merely a spectator of the collisional excitation. This is better evidenced in the case of neon projectiles by the observation of the intense emission from the $2p^4(^3P)3s^2$ triplet state, which cannot be produced directly by promotion of the $4f\sigma$ MO. Excitation of the triplet state occurs therefore from the conversion of the singlet $2p^4(^1D)3s^2$ state. The singlet-to-triplet conversion has been ascribed to an Auger rearrangement mechanism in which a valence electron of the solid drops into the empty $4f\sigma$ MO, and an electron of the $3d\pi$ MO is excited simultaneously above the Fermi level [26]. This conversion process occurs in the immediate vicinity of the excitation sites with two colliding atoms still in a coupled molecular state, and its rate strongly depends on the local electronic properties around the target atomic site [26]. In the case of sodium projectiles, the Auger electrons from the decay of the triplet $2p^4(^3P)3s^2$ state have energies similar to those due to the decay of the $2p^53s3p$ state. We observe here that the reduced intensity of the Na-III peak with respect to the Na-IV peak is indicative of the occurrence of a singlet-to-triplet conversion also for sodium projectiles.

In conclusion, we have studied Auger electron spectra excited by electron promotion in binary atomic collisions during the scattering of slow sodium ions at aluminum surfaces. We have pointed out that double $2p$ excitation is observed for collisions involving Na ions that have survived neutralization during the approach to the surface. Collisions involving neutralized projectiles result in the promotion of one electron. This provides clear evidence that electron promotion occurs into bound Rydberg states of the collision system and is governed by the actual charge state of Na projectiles during the collision, i.e., by the occupancy of its $3s$ level, rather than by the availability of empty conduction states of the solid. Comparison with other projectiles and examination of the literature indicate that this conclusion is a general property of low-energy ion scattering, being straightforwardly applicable also to noble gas projectiles.

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