Plasmon excitation and electron promotion in the interaction of slow Na$^+$ ions with Al surfaces

M. Commissio $^a$, A. Bonanno $^a$, A. Oliva $^a$, M. Camarca $^a$, F. Xu $^a$, P. Riccardi $^{a,*}$, R.A. Baragiola $^b$

$^a$ Laboratorio IIS, Università della Calabria and INFM – Unità di Cosenza, 87036 Arcavacata di Rende, Cosenza, Italy
$^b$ Laboratory for Atomic and Surface Physics, University of Virginia, Engineering Physics, Thornton Hall, Charlottesville, VA 22904, USA

Abstract

We studied the energy distributions of electrons emitted in the interaction of slow Na$^+$ ions with polycrystalline Al surfaces. To study sub-threshold plasmon excitation we performed measurements as a function of emission angle which showed the excitation of bulk plasmons, confirming the kinetic nature of the excitation process. Electron spectra show narrow transition lines due to Auger decay in vacuum of sodium projectiles excited in the 2p-shell by electron promotion in collisions with Al target atoms. Several previously unidentified transition lines could be attributed to the autoionization of doubly excited projectiles.

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1. Introduction

We present first results of experimental studies of electron emission in the interaction of slow Na$^+$ ions with Al surfaces. Aluminum has been widely used as a prototypical free-electron metal surface to study electronic excitations induced by the impact of slow ions. The choice of an alkali projectile is motivated by the fact that, due to their low ionization potential, sodium ions lack enough potential energy to give rise to the so called potential electron emission (PEE) [1]. Alkali projectiles are therefore well suited to study kinetic electron emission (KEE) [2], which is due to the transfer of the kinetic energy of incoming projectiles. Despite of the distinctive advantage of alkali ions to study KEE from metal surfaces, such studies have been undertaken only recently [3,4].

The purpose of our experiments was to study plasmon excitation [5], and inner-shell electron
promotion [6], which has been extensively studied for the analogous Ne\textsuperscript{+}–Al system, allowing a straightforward comparison of the experimental results for two projectiles of vastly different potential energy.

The electron energy spectra reported here show evidence for bulk plasmon excitation, agrees well with previous studies, confirming that bulk plasmon excitation in slow ion-surface interactions [5,7,8] is related to kinetic electron excitation induced by the bombardment.

Electron energy distributions show also several narrow peaks, due to Auger decay in vacuum of sodium projectiles excited in the 2p-level by electron promotion in collisions with Al target atoms. The Auger spectrum of sodium reported in this work is consistent with previously reported spectra [9] and is dominated by the Auger decay of the 2p\textsuperscript{5}3s\textsuperscript{2} state. One of the purposes of this work was to search for and identify the Na peaks with energies above the 2p\textsuperscript{5}3s\textsuperscript{n}nl limit. Promotion of two electrons of the 2p-shell of the projectiles, well established for Ne\textsuperscript{+} impact, helped us to attribute all the atomic features in the Auger spectrum of sodium.

### 2. Experiments

The measurements were performed in a UHV chamber with a base pressure of $3 \times 10^{-10}$ Torr. Na\textsuperscript{+} ions were produced with a Kimball Physics ion gun. The ion beam current was of the order of $10^{-9}$ A and had a Gaussian spatial distribution in both horizontal and vertical directions, as measured with a movable Faraday cup situated in the target position.

The polycrystalline Al samples (purity 99.999\%) was cleaned by sputtering with 6 keV Ar\textsuperscript{+}. Sample cleanness was assured by the absence of oxygen, carbon and sodium signals in electron induced Auger spectroscopy performed right before and after the acquisition of each electron energy spectrum and by the constancy of the energy position of sodium Auger lines during each spectral scan.

Ejected electrons were collected by a hemispherical energy analyzer lying in the incidence plane and operated at a constant pass-energy ($\Delta E = 50$ eV) and therefore a constant transmission over the measured energy range.

### 3. Results and discussion

In Fig. 1 we report energy distributions of electrons emitted from Al surfaces by 1 keV Na\textsuperscript{+} ions...
as a function of observation angle $\Theta_e$ and for fixed incidence angle $\Theta_i = 30^\circ$ (angles are measured with respect to the surface normal).

The broad structure visible in the 10–15 eV electron energy range identifies electron emission from decay of plasmons [5]. Plasmon structures are usually visualized by the derivative of the experimental electron energy distribution [10], shown in Fig. 1(b), where they result in minima at energies $E_m = E_{pl} - \phi$ ($E_{pl}$ is the plasmon energy and $\phi = 4.3$ eV is the work function for polycrystalline Al). Consistent with previous studies [5,7,8], the minimum around 11 eV in Fig. 1(b) is assigned to electron emission from decay of zero-momentum bulk plasmons. This is in contrast to what has been found for noble gas ion impact on Al and Mg surfaces, where the bulk plasmon structure appeared overlapped to another structure assigned to decay of multipole surface plasmons excited by the potential energy released when incoming ions are neutralized by electron capture from the surface [7,11,12].

This attribution is further confirmed by the variation of the intensity of electron emission from bulk plasmon decay with the emission angle $\Theta_e$, shown in Fig. 2 normalized to the intensity for $\Theta_e = 0$. These intensities have been evaluated by subtracting a smooth polynomial background from the derivatives of the spectra and integrating the resulting negative peak [11–13]. Consistent with previous results [8], the plasmon intensity varies like the cosine of emission angle, clearly indicating that bulk plasmon excitation occurs inside the solid and that bulk plasmon decay act as an isotropic internal source of electrons. Deviations from the cosine dependence at large angles most likely results from surface roughness.

The spectra of Fig. 1 show several narrow lines, in the electron energy range 20–45 eV, due to autoionization or Auger decay in vacuum of atomic excited states of reflected Na projectiles, created by electron promotion [6] in binary collisions with Al target atoms. To better illustrate these atomic features, we show in Fig. 3(a) Na autoionization spectrum for $E_p = 800$ eV, $\Theta_i = 70^\circ$ and $\Theta_e = 0^\circ$, while in Fig. 3(b) we amplify the relevant portion of the spectrum after subtracting a smooth secondary electron background. To correct approximately for the Doppler shifts due to the motion of the Na (expected to be rather small in this experimental geometry), the energy scale was adjusted so that peak labeled I assumes the value of 25.7 eV to coincide with the kinetic energy of $2p^63s^2$ autoionization line of neutral sodium [14]. The position of all the features indexed in Fig. 3 are listed in Table 1.

Besides the collisional excitation mechanisms, the identification of the peaks requires consideration of the influence of possible surface neutralization or ionization mechanisms which are peculiar to the ion surface interactions [1]. The most intense peak I is generally attributed to electron emission from Na $2p^53s^2$ decaying in vacuum into the Na$^+$ ground state $2p^6$ [14]. Within the framework of the well known molecular orbital (MO) promotion model [6], excitation of Na-2p electrons is understood by the promotion of the $4\sigma$ MO, correlated to the Na-2p atomic orbital. The crossings with higher lying empty orbitals may result in the excitation of up to two electrons in the $4\sigma$ MO. The origin of peak I can thus be explained by a one electron promotion process during the projectile-target collision, accompanied by electron capture from the surface in the

![Fig. 2](image-url) Fig. 2. The intensity of electron emission from bulk plasmon decay shows a cosine dependence on emission angle.
The Auger spectrum of sodium reported in this work is consistent with that reported in [9]. In that work, peaks II and III were attributed to the decay of the $2p^53s(1P)3p$ and $2p^53s(1P)3d$ configurations of neutral Na. However, it is questionable that the 3d electron is stable against resonant ionization to the metal conduction band. Here, we notice that the energies of electrons from the decay of Na $2p^4(3P)3s^2$ and Na $2p^4(1D)3s^2$ into Na $^+2p^5$ [14] are a better match with the positions of peaks II and III, and in line with studies of the similar system, Ne–Al.

To our knowledge, assignment of peak IV, observed also in gas phase experiments [15], has not been given. We assign it to the decay of Na $^+2p^4(1D)3s^3p$ into Ne $^+2p^5$. An rough estimation of the energy of this transition can be done by applying the approximate Z+1 rule [14], assuming that the difference in energy between the Na $^+2p^4(1D)3s^3p$ and Na $^+2p^4(1D)3s^2$ configurations is equal to the difference (~4.6 eV) between the energies of the states of aluminum ion: Al $^+2p^63s3p^1P$ and Al $^+2p^63s^2$. This yields an expected energy for peak IV equal to 37.5 eV, which agrees well consistent with our measured value.

Finally, we notice that the energy of the weak feature V is consistent with the energy of 41.4 eV estimated in [14] for the decay of the state Na $^+2p^4(1D)3s^23p$.

Assignment of these peaks to the decay of 2p-doubly excited projectiles has significant implications that are consistent with those obtained in the case of Ne $^+$ impact [16–20]. Contribution of $2p^4(3P)$ and $2p^4(1D)$ states to peaks II and III, in fact, implies the occurrence of a core-rearrangement process [16], converting the singlet into the triplet core, which cannot be directly produced by electron promotion.

The comparison with the case of neon projectiles can be further extended. In the case of Ne $^+$ impact, experiments of electron emission [16,18] and ion energy loss [20] showed that simultaneous promotion of two 2p electrons of neutralized and surviving projectiles leads to the formation of Ne $^{**}$ and Ne $^{***}$, which, after autoionization decay, are revealed respectively as backscattered Ne $^+$ and Ne $^{++}$ with a characteristic energy loss. In this context, the production of Na projectiles
with two 2p-vacancies can be understood considering that the ground state of incoming ions is the same of neon atoms. Thus, simultaneous excitation of two electrons via the promotion of the 4f\(_r\) MO leads to the production of the autoionizing states whose decay is observed in our experiments.

4. Conclusions

In this study of plasmon excitation and projectile autoionization by electron spectroscopy we obtained two significant results. First, the spectra show clear features due to electron emission from decay of low momentum bulk plasmons by a projectile that cannot excite plasmons by the potential mechanism. This result is consistent with the conclusions of previous studies, which have not been as direct, that bulk plasmon excitation is indirect, i.e. by fast electrons traveling inside the solid. This implies that secondary effects, such as scattering and electron cascade in the solid can give a significant contribution to electron excitation and emission.

Second, we have observed a number of narrow Auger features in the electron spectra and have proposed identification for all of them, including previously unidentified peaks that can be assigned to decay of 2p doubly excited projectiles.

It is interesting to note that understanding this particular type of experiments requires the consideration of both delocalized solid-state concepts (bulk plasmons) and a local description of two-body collisions (excitation of excited states), thereby stressing the wealth of information on atomic collisions in solids that can be provided by electron spectroscopy.

References