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Spectral properties of Cs and Ba on Cu(111) at very low coverage: Two-photon photoemission spectroscopy and electronic structure theory

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The adsorption of Cs and Ba on Cu(111) is investigated by means of one- and two-photon photoemission experiments and theoretically by first-principles calculations. The spectral properties of these systems, induced by both surface and adatom states, are studied at submonolayer coverage through angle-resolved measurements. A coverage-dependent analysis is also exploited in the assignment of the observed electronic states. The comparison with *ab initio* calculations allows identification of all the spectral features induced by Cs and Ba chemisorption. The theoretical analysis concerns the limiting single adatom case, treated in an embedding approach with a one-dimensional potential for the surface. The agreement between the calculated density of states and the experimental spectra confirms that the model substrate retains all the relevant physics entering in the adsorption process. The differences between the electronic structures of Cs and Ba on the Cu(111) surface can be attributed to the group-dependent screening of the core potentials as manifested by the ionic radii and ionization potentials (alkali vs alkaline earth).

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I. INTRODUCTION

The adsorption of a single atom on a metal surface represents a challenging topic in surface physics. The surface-atom interaction induces a modification in the local electronic properties of the system. It takes place via the mutual hybridization of the electronic states of the substrate and the atomic levels of the adsorbate. Depending on the degree of hybridization between surface- and atomic-wave functions and on their symmetry and binding energy, they can give rise to broad resonances or sharp features in the density of states (DOS). These parent single-adatom states define the electronic properties of the interface that develops at higher coverages through adsorbate-surface and interadsorbate interactions. In this work the electronic properties arising from the interaction between Cs and Ba atoms with clean Cu(111) surface will be discussed in relation to the coverage-dependent evolution of one-photon (1PP) and two-photon photoemission (2PP) spectra. Alkali-atom metal-surface systems have been widely studied in the past[1–8] because of the simplicity of single *s* electron interaction and relevance to the principles of the ionic chemisorption. By contrast, hardly any effort has been devoted to the study of alkaline-earth metals in which two *s* electrons participate in the bonding. Whether the chemisorption of Ba still exhibits the simplicity of ionic chemisorption or new effects arise through, for instance, onsite electron-electron interaction is not clear.

Although the changes in the surface electronic structure upon alkali-atom chemisorption have been of enduring interest because they mostly occur in the unoccupied spectrum, systematic studies have become available only through the development of 2PP spectroscopy.[9–11] The high sensitivity of 2PP with respect to more conventional techniques such as inverse photoemission and inelastic electron scattering has made possible systematic studies as a function of coverage, period, and emission angle. Recently we reported on the hybridization of *ns* and *np* orbitals of alkali atoms (Li through Cs) into σ and π symmetry resonances on Cu(111) and Ag(111) surfaces.[11,12] The high sensitivity and resolution of 2PP spectroscopy made it possible to determine accurately the asymptotic zero-coverage energies of their σ resonances, which were surprisingly independent of the alkali atom period. Moreover, we independently investigated the alkali chemisorption-induced changes in the occupied DOS, by laser-excited 1PP spectroscopy.[13]

In order to provide the corresponding characterization of the electronic properties of a single adatom on the surface from a theoretical point of view, one has to deal necessarily with the lack of periodicity both normal and parallel to the surface. The first *ab initio* investigations of the electronic properties of a single adatom on metals dealt with a jellium modelization of the surface.[14–18] In these works the Dyson equation is solved self-consistently in the density-functional theory (DFT), considering the Green's function of the substrate as the unperturbed one. An alternative description of both the substrate electronic properties and the effect induced by the adsorption of a single atom, can be obtained using the embedding method of Inglesfield.[19,20] In this approach the single-particle Kohn-Sham equation is solved only in the perturbed space, applying appropriate boundary conditions that guarantee the matching with the Green's function of the unperturbed system. The embedding method was applied to study isolated adsorbates on jellium[21] and, in a more sophisticated formulation, to investigate realistic clean surfaces and overlayers.[22–24] Although the jellium model for the substrate allows to describe the main adatom-induced electronic properties, it cannot account for the presence of a projected band gap and gives an erroneous estimation of the work function. Both these aspects strongly influence the reorganization of the electronic states due to the adsorption of an adatom. The theoretical *ab initio* results presented here have been obtained using a one-dimensional potential for the substrate that correctly reproduces both the projected band gap and the work function of the surface.[25,26] The same potential has been successfully adopted to study alkali adatom electronic structure on Cu(111) using the wave-packet propagation procedure.[27] In this paper the electronic properties of Ba/Cu(111) will be discussed both from the experimental and theoretical point of view. The results will be compared with the case of Cs/Cu(111). To the best of our knowledge no 1PP and 2PP experiments on Ba/Cu(111) have been performed previously while the experimental investigation of Cs/Cu(111) has been the subject of recent publications on alkali adatoms on both Cu(111) and Ag(111) surfaces.[11,12,28] Despite of the detailed analysis present in literature for both alkali and noble gas atoms on metals, theoretical investigation of adatoms with two valence electrons has only been performed within the Anderson-Newns model in relation to resonant tunneling spectroscopy.[29,30]

Because of its relatively large ionic size and significant chemisorption-induced charge transfer, the chemisorption of Ba on metal surfaces induces a large surface dipole. For this reason Ba has been recognized as superior adsorbate for enhancing thermionic emission because of its effect on suppressing the work functions of metals. Very little experimental or theoretical information exists, however, that would connect the atomic chemisorption structure of Ba with its effect on the macroscopic work function of metals.[31,32]

The paper is organized as follows: in Sec. II the experimental apparatus for the 1PP and 2PP measurements is briefly described. In Sec. III we outline the theoretical *ab initio* method. In Sec. IV the analysis of both the experimental spectra and theoretical DOS is performed toward a characterization of the electronic properties of the system. Finally, in Sec. V the conclusions are drawn.

II. EXPERIMENTAL SECTION

Adsorbate atom coverage and emission angle-dependent 2PP spectra were measured as described previously.[11,33] Briefly, clean and annealed Cu(111) surface was cooled to ~130 K inside the ultrahigh vacuum photoemission apparatus. 2PP and 1PP measurements at normal emission and in the angle-resolved mode were performed, respectively, with excitation by the second harmonic (SH; photon energy—3.14 eV) and fourth harmonic (FH; 5.93 eV) of a ~10 fs pulse duration Ti:sapphire laser oscillator.[11,33] Effusive Cs and Ba atom beams were generated by resistively heating the respective getter sources. The sources were collimated and aligned onto the sample to avoid creation of work-function differences and the concomitant lateral-surface-potential gradients. The spectra were recorded sequentially under constant flux of atoms after opening a shutter to expose Cu(111) surface. The measurements were terminated when the work function decreased to ~3.4 eV because high density of photoelectrons generated by 1PP with the SH light led to distortion of 2PP spectra. Because the unfiltered SH light generated a large interfering photoemission signal, the 1PP spectra with FH excitation also suffered from the same coverage limitation. Angle-resolved photoemission measurements were performed by rotating the sample about the axis normal to the optical plane.[12,34]

III. THEORETICAL METHOD

Various theoretical methods have been developed in order to describe surface electronic structure. In the case of a clean surface, the lack of periodicity in the normal direction is commonly restored by a repeated slab approach in which the slab and the vacuum regions alternate. In this way the three-dimensional periodic boundary conditions can be used, reducing the computational effort.[35] This supercell approach has the disadvantage of describing a semi-infinite system with a finite one along the normal to the surface so that the continuous character of the semi-infinite bulk cannot be accounted for and no qualitative difference between substrate states and discrete surface features can be appreciated. The treatment of the single atom on a surface is still more demanding. Within the slab approach the presence of a single adsorbate can be approximated by a low-density array of adsorbates.[36,37] Despite of its computational efficiency, even this method could introduce fictitious interactions between the adsorbates.

In order to overcome these drawbacks we take advantage of the embedding method of Inglesfield.[19] The application of this method to the study of a single adatom on the surface consists of two computational steps that are performed in the DFT approach. First of all, the clean surface is treated as perturbation to the infinite bulk system. Subsequently, the adatom is considered as perturbation to the clean surface system.

We apply the Inglesfield approach to the unperturbed clean surface described by the one-dimensional modulated Chulkov potential.[25,26] We consider the Chulkov potential's ability to correctly reproduce the work function, the projected band gap and the Shockley surface state as the most important aspects for a good description of the adsorbate-induced surface features. The absence of corrugation parallel to the surface in this potential is not relevant in the single-atom-adsorption phenomena. In fact the lack of translational invariance upon adsorption of single atoms corrupts $k_{\parallel}$ as a good quantum number and makes the integrated contribution of the whole-surface Brillouin-zone operative in the interaction with the adatom. Based on this consideration, the use of a potential depending only on the coordinate normal to the surface is justified.

The embedding calculation for the clean surface has been performed in a region containing three atomic layers and 10 Å of vacuum. The modulated potential is treated as the effective potential in the Kohn-Sham equation. The second

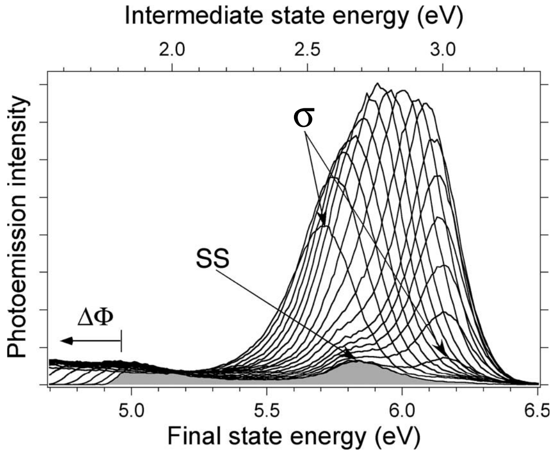

FIG. 1. Normal-emission 2PP spectra for Cs/Cu(111) during continuous alkali atom deposition up to ~0.08 ML coverage at sample temperature of 130 K (Ref. 11). The gray highlighted spectrum is of the clean surface before deposition, where the Shockley SS is the only spectral feature. The σ resonance (indicated at low and high coverage) shifts to lower energy through a one-photon resonance with SS.

step embedding calculation is performed in a sphere of radius 6.35 Å; the surface-adatom distance is set equal to 2.61 Å for Ba. The theoretical equilibrium Ba distance is calculated, as was 3.33 Å for Cs, from DFT calculations for the adatom 7×7 overlayer structures.[11] For the calculation in the sphere, the external potential is obtained as superposition of the nuclear potential and the ionic term of the clean surface as reported in Ref. 38. The problem is then solved self-consistently. The basis set inside the embedding sphere is composed of linearized augmented spherical waves. The expansion in angular momentum has been considered up to $l=18$. More details about the implementation will be discussed elsewhere.

IV. RESULTS AND DISCUSSION

In this section an analysis of both experimental and theoretical results is performed, toward a coherent characterization of the surface electronic structure induced by Cs and Ba adsorption. The 2PP spectra in Fig. 1 show the chemisorption-induced changes in the surface electronic structure when the Cs coverage is progressively increased from 0 to ~0.08 ML. The spectra are taken under constant Cs atom flux starting with the clean surface spectrum (shaded feature in Fig. 1). As already discussed elsewhere,[11] the formation of a surface dipole layer by chemisorption of Cs substantially changes the substrate work function Φ. Consequently, as the Cs coverage increases, the vacuum edge (low-energy cutoff in Fig. 1) of the 2PP spectra shifts to lower energies with respect to the Fermi level (E_F) by $\Delta\Phi$. The main feature in the spectra is the unoccupied resonance appearing at 3.0 eV above the E_F, which has been identified as the antibonding σ resonance derived by hybridization of the $6s$ and $6p_z$ atomic levels.[12] The binding energy of this feature changes as a function of the coverage according to $\Delta\Phi^{3/2}$ (see Ref. 11).

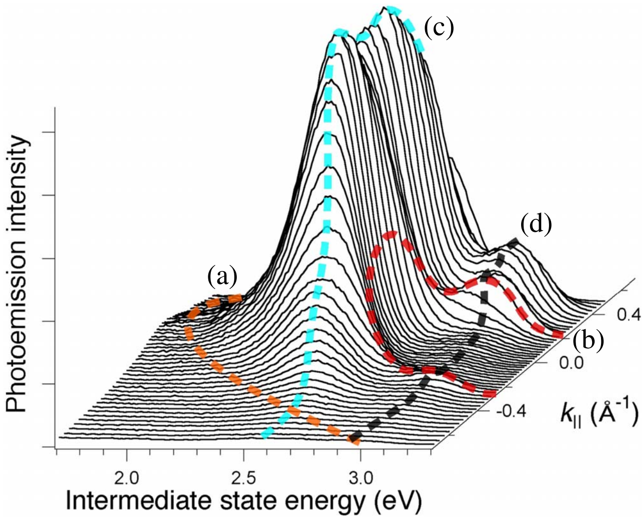

FIG. 2. (Color online) Angle-resolved 2PP spectra for Cs/Cu(111). The dashed lines denote the angular dependence of the lower-to-upper *sp*-band two-photon transition (a), 2PP from the Shockley surface state (b), and σ (c) and π (d) resonance of Cs. The estimated coverage for this measurement is 0.08 ML of Cs (Ref. 13), which is approximately the same as the highest coverage in Fig. 1.

Further information on the nature of alkali-atom-induced resonances can be obtained from the angle-resolved 2PP measurements. The angle-resolved spectra in Fig. 2, which show that for the main feature (c) the emission strength peaks near normal emission, confirm the $m=0$ symmetry of the σ resonance (m is the projection of the orbital momentum l onto the surface plane). By contrast, the next-higher resonance (d), which appears approximately at 0.5 eV above the σ resonance, is characterized by the intensity maximum off normal and a node for normal emission.[12] The presence of the node allows to assign this state to $|m|=1$ (i.e., π) symmetry. This resonance is formed by the hybridization of the $6p_x$ and $6p_y$ atomic levels with $5d$ levels. Such resonances with maximum emission intensity at $\approx 15°-19°$ emission angle have been observed for K and Cs on Cu(111) and Ag(111) surfaces.[12] Actually, the observed intensities are also modified by Fresnel factors for the incoming laser beam that change when the sample is rotated with respect the analyzer and laser axes during the angle-resolved measurements. In addition, the angle-dependent intensities of the nondispersing, adsorbate-localized states are also affected by the $k_{\|}$ dispersion of the substrate bands. Specifically, the adsorbate-localized states can act as intermediate states in two-photon transitions from the lower to the upper *sp* bands in the copper bulk[34] and from the occupied Shockley surface state (SS) of Cu(111) [respectively, (a) and (b) in Fig. 2].

Comparison between the present experimental and theoretical results confirms these assignments. In Fig. 3, the DOS of a single Cs adatom on Cu(111) is decomposed into separate panels corresponding to the atomic-orbital angular momentum l and each l component is further decomposed into its constituent m contributions. All the DOS in this work have been calculated in a sphere with a radius of 2.65 Å.

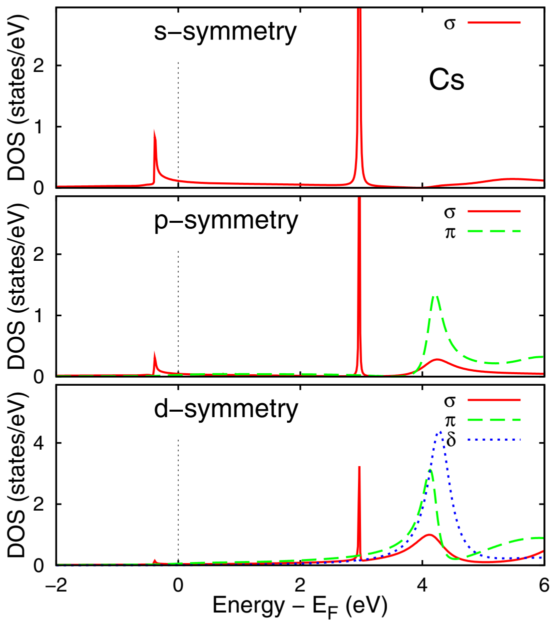

FIG. 3. (Color online) DOS of Cs/Cu(111) resolved into l and m components. Upper panel: s symmetry ($l=0$), middle panel: p symmetry ($l=1$), and lower panel: d symmetry ($l=2$).

It is worth noting that because of the lack of spherical symmetry due to the adsorption, l is not a good quantum number, and the adatom-induced electronic states are better characterized on the basis of projection of l onto its components labeled by their quantum number m. Some of these components become nondegenerate because the presence of the surface potential causes the energy splitting of the m components of the atomic levels. Nevertheless the analysis of the l character of the features in the DOS can still give qualitative information, useful for relating the observed resonances to their parent atomic electronic levels.

The primary feature in the unoccupied DOS of Cs/Cu(111) is the sharp resonance at 3.0 eV. It has $m=0$ symmetry and mainly s character but contribution from p_z (σ in the middle panel of Fig. 3) is also notable. As previously reported,[39] it correlates with the 6s atomic level of Cs as the adatom-surface distance increases. This is consistent with the picture describing the adsorption of Cs atom in a fully ionized state with the valence electron completely transferred to the substrate and the excitation occurring through a photoinduced charge-transfer process to create transiently the neutral Cs atom at the equilibrium position of the ionic ground state.[40]

The extremely small extrapolated linewidth of this state, i.e., ~0.01 eV, is explained by its position within the band gap of the surface-projected bulk band structure for a broad range of $k_{\|}$ points of the surface Brillouin zone. In addition, its symmetry (i.e., $l=0$ and $m=0$) limits coupling with the substrate, characterized by high $k_{\|}$ states.[41] The energy position of this empty state fully agrees with the experimental σ resonance. The present calculation, which does not assume any hypothesis about the atom-surface interaction, is also in excellent agreement with the result reported in Ref. 11, where the 6s resonance energy was calculated using the Chulkov potential for Cu(111) and pseudopotential for Cs atom to describe the noninteracting system and image charge model as the dominant atom-surface interaction.

A second feature in the computed DOSs is a broader resonance at 4.1 eV, characterized by $|m|=1(\pi)$. It is well described by the mixing of 6p (p_x and p_y) and 5d atomic states (see middle and lower panels of Fig. 3). Its linewidth is ~0.4 eV.

The difference in the linewidth of the two adsorbate-induced resonances reflects the degree of interaction of atomic wave functions with the substrate states. In fact the $|m|=1$ component at zero Cs coverage is resonant with the surface-projected band of Cu(111). Furthermore, the higher is the l component the larger is the overlap with the substrate states. In comparison with the experimental π resonance, the theoretical energy position in the single adatom limit is higher than the experimental energy of 2.9 eV at ~0.08 ML coverage. As in the case of the σ resonance, the π resonance is also stabilized by formation of the surface dipole layer. The experimental linewidth is narrower than predicted by theory, probably because at finite Cs coverage the π resonance belongs to the surface-projected band gap.

In the lower panel of Fig. 3 is reported the DOS characterized by $l=2$ (d symmetry). It contains all the m contributions up to $m=2$, slightly split due to the hybridization into the already discussed resonances by the surface potential.

As far as the occupied DOS is concerned, the effect of the adatom adsorption consists of the localization of the Shockley surface state caused by the attractive potential of the Cs^{+} ion core.[42–45] The simple electronic structure and nearly complete ionization of chemisorbed Cs atoms make the assignment of the experimental and theoretical spectra straightforward. In the case of Ba/Cu(111), however, the assignment of the spectra is more challenging but is facilitated by the analogies with the Cs case.

As in the case of Cs, the continuous deposition of Ba onto the surface introduces an unoccupied state, which is clearly observed at the initial stage of growth in the 2PP spectra of Fig. 4. This intense peak initially observed at an intermediate energy of 2.22 eV, is seen to increase in intensity and shift to lower energy as the Ba coverage is increased, similar to the case of Cs deposition. At the maximum coverage of our measurements, we observe two additional spectral features at intermediate-state energies of 2.50 and 2.93 eV. The 2.93 eV feature is probably a higher lying unoccupied state of Ba. We will refer to the lower and higher energy Ba-induced peaks as the σ and σ' resonances, being both visible at normal emission. We assign the 2.50 eV feature to the occupied SS of Cu(111), which is observed through nonresonant 2PP. Upon deposition of Ba, the SS peak upshifts, then disappears, and then reappears with a downshift. This complex behavior, which is contrary to the monotonic change in SS intensity and binding energy that is observed in 1PP, may be a manifestation of interference between parallel excitation pathways that couple the same initial and final states in 2PP process through different, i.e., surface vs bulk, intermediate states. The influence of such coherent interference effects has been noted in 2PP spectra but is still poorly understood.[46,47]

Because our measurements are in a low-coverage regime, where we do not expect orbital overlap between adjacent Ba atoms to be significant, the Ba-induced features should not

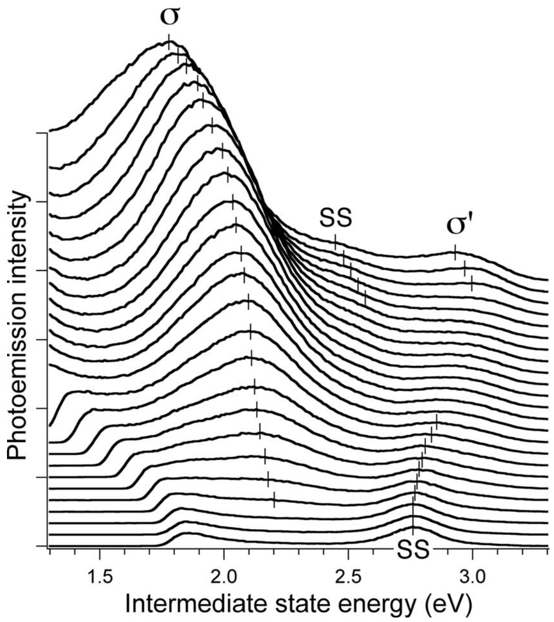

FIG. 4. 2PP spectra of Ba/Cu(111) for varying Ba coverage. The spectra are displaced vertically for clarity. The vertical lines indicate peak positions of spectroscopic features at different coverages.

disperse with $k_{\parallel}$, whereas the intrinsic surface and bulk bands of Cu(111) do retain their dispersions. The Ba-localized states manifest their symmetry through angle ($k_{\parallel}$)-dependent intensity changes as in the case of Cs/Cu(111). The angle-resolved 2PP measurements, reported in Fig. 5, show the nondispersive character of the σ resonance and confirm the assignment to the Ba-induced resonance while the SS disperses as expected. We note also the presence of another spectral feature in 2PP spectra of Ba/Cu(111) in Fig. 5 at an intermediate-state energy of 2.64 eV, which appears only for $k_{\parallel} > 0.1$ Å^{-1}. This is consistent with the $|m|=1$, or π resonance of Ba, which would not appear for normal emission on account of its symmetry. Its energy in Fig. 5 is 0.5 eV above the σ resonance, implying zero-coverage energy of ≈ 2.7 eV. The intensity of the π resonance in Fig. 5 is probably enhanced by the doubly resonant transition from the lower to the upper *sp* band as in the case of the σ resonance of Cs/Cu(111) at $k_{\parallel} \sim 0.2$ Å^{-1} for the coverage conditions in Fig. 2.

The comparison between the experimental spectra and the theoretical DOS allows interpretation of the adatom-induced electronic resonances in the very low-coverage regime. Figure 6 presents the DOS obtained for a single Ba atom on Cu(111).

We consider first the states of *s* character because the excitation of the *s* component of Ba would have a larger transition moment than the *p* and *d* components. On the basis of the DOS (upper panel in Fig. 6), we suggest that the 6*s* atomic level is divided into two contributions: one is at 2.2 eV while the other is just below E_{F} in the energy range proper of the Shockley surface state. The p_z component also contributes to the empty state (see middle panel of Fig. 6) as we found for Cs. The energy position of the empty *s* component nicely agrees with the experimental σ resonance but the linewidth of 0.22 eV is considerably narrower than the experimental linewidth of ~ 0.4 eV.

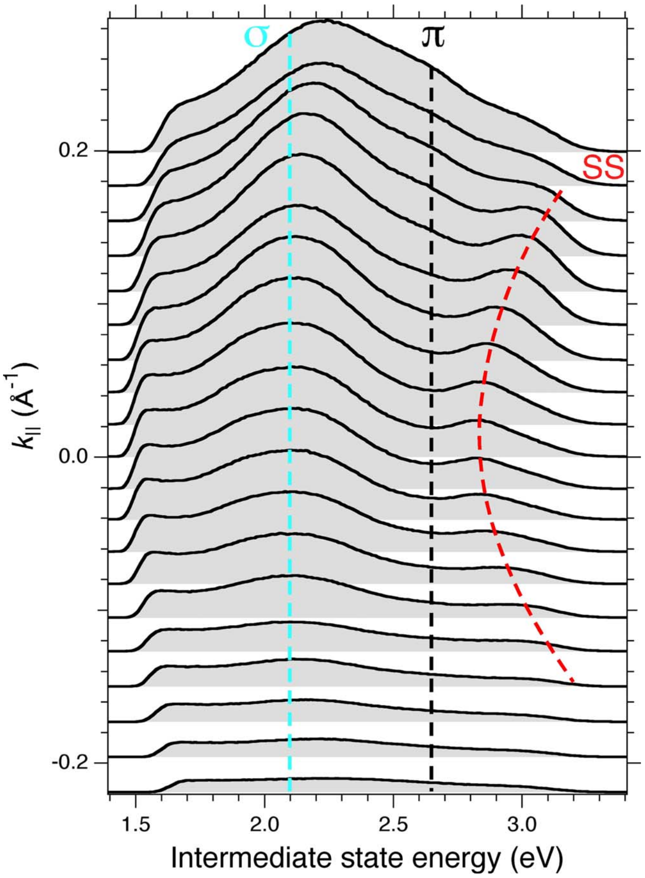

FIG. 5. (Color online) Angle-resolved 2PP spectra for Ba/Cu(111). The dispersive feature belongs to SS.

The energy of the empty 6*s* resonance can also be accounted for by using simple arguments recently proposed by Zhao *et al.*[11] and Gadzuk.[48] They estimate the binding energy E_b of the *s* resonance of alkali adatoms with respect to the vacuum level E_{vac} via the simple relationship: $E_b = 1/4R_{\mathrm{ads}} - I$, where R_{ads} is the image plane-adatom distance and I is the atomic ionization potential. While this expression holds quite well for alkalies, i.e., for fully ionized bonding, we verified that it is also valid for the Ba-adsorption case. In fact by using E_b given by this simple approach one obtains 2.11 eV, to be compared with our *ab initio* value of 2.18 eV.

Next, we consider the *p* component of the DOS, reported in the middle panel of Fig. 6. The p_z resonance ($m=0$) coincides in energy with the empty *s* state, previously discussed, contributing to the σ resonance although to a minor extent. The p_x and p_y resonance (π) appears at higher energy and the first maximum falls at 0.5 eV above the σ component. This state can be related to the π resonance at 2.7 eV reported in Fig. 5.

From the $l=2$ resolved DOS (lower panel in Fig. 6) one can observe a broad peak at about 2 eV. It contains all the m components, up to $m=2$, split by the surface potential.

We have no experimental evidence of such $l=2$ states, for either Cs or Ba, most likely because the optical cross section for excitation to $l=2$ states is small. The $l=2$ character of the unoccupied resonances, however, has been reported in angle-dependent inverse photoemission spectra of Cs covered copper surfaces.[49]

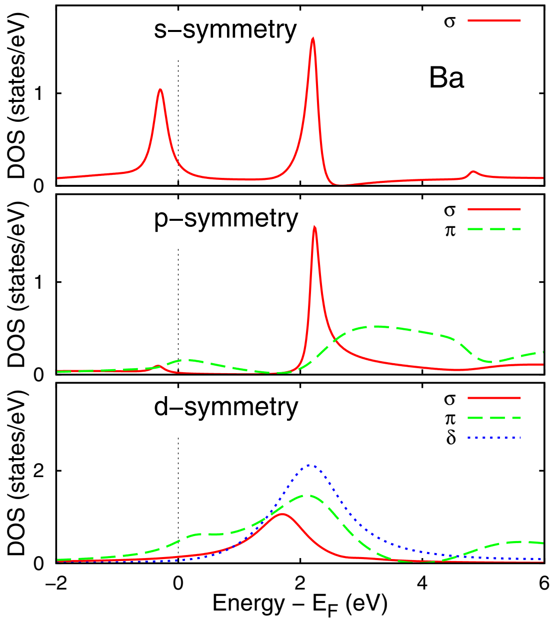

FIG. 6. (Color online) DOS of Ba/Cu(111) resolved into l and m components. Upper panel: s symmetry ($l=0$), middle panel: p symmetry ($l=1$), and lower panel: d symmetry ($l=2$).

Whereas there are strong similarities between the interpretation of 2PP spectra and the calculated adsorbate-induced electronic structures of Ba and Cs on Cu(111), based on the calculations it is also possible to underline some differences.

First of all the different energy position of the Ba resonances with respect to the alkali adatom case is due to the stronger attractive potential of the Ba core that draws the Ba-adatom-induced features lower in energy. The different computed linewidth of the resonances is determined by the energy positions with respect to the substrate gap. In the Ba case the empty state is lower in energy and a higher hybridization with the substrate states is expected. A further reason for Ba having a larger resonance width than Cs is the shorter adsorption distance and consequently a larger overlap with the substrate. The linewidth of the Ba resonance is comparable with that of Na on Cu(111), which has a slightly shorter adsorption distance than Ba.[11]

The main difference between Cs and Ba is the occupation of the s state. In Cs it is fully unoccupied due to the complete ionicity of the bonding, whereas in Ba, the partially occupied s state below E_F reflects a more complex electronic structure. This is consistent with the charge-transfer analysis, which suggests that one valence electron still remains on the Ba adatom, forming a bound state.

A deeper analysis of the adatom charge distribution, reported in Fig. 7, for both Cs and Ba cases, gives evidence for some qualitative differences. The Cs/Cu(111) case (upper panel) shows only the image charge localized on the image plane of Cu(111), giving a further evidence of the fully ionic interaction. In the Ba/Cu(111) case, there is an additional charge distribution centered on the adatom. One valence electron of Ba, is still located around the nucleus in an s-like state, at the same energy as the Shockley surface state (see upper panel of Fig. 6). The 1PP spectra, both angle and coverage dependent, of Ba/Cu(111) can support this interpretation.

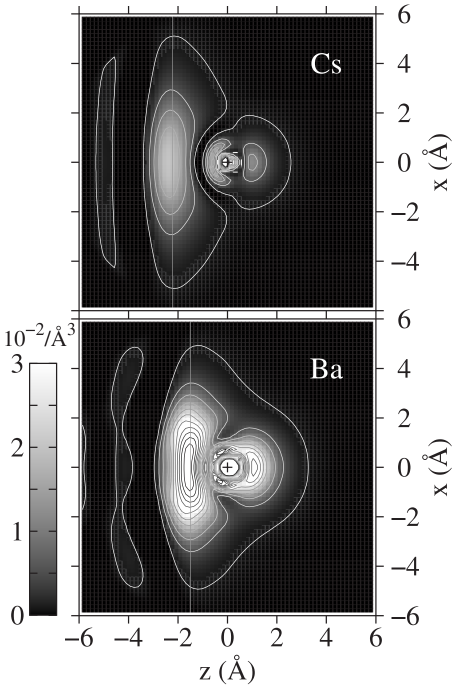

FIG. 7. Spatial distribution of the electronic charge density for Cs/Cu(111) (upper panel) and Ba/Cu(111) (lower panel). The origin (cross) corresponds to the position of the adatom. Vertical lines indicate the image plane position.

Figure 8 shows a series of 1PP spectra during the continuous Ba atom deposition. The main feature in the 1PP spectra of clean Cu(111) is the SS that exists 0.4 eV below E_F at the $\bar{\Gamma}$ point. The initial deposition of Ba causes the SS intensity to decrease and its linewidth to broaden as expected from previous photoemission studies for alkali covered Cu(111) surface.[50] For higher coverage, the lineshape is asymmetric

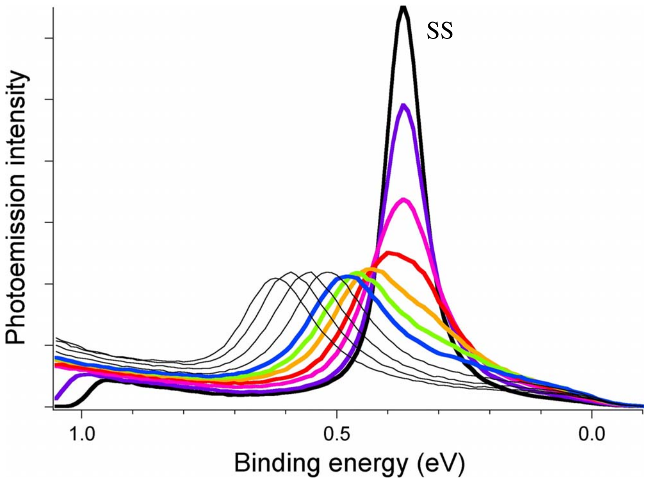

FIG. 8. (Color online) 1PP spectra of Ba/Cu(111) for increasing Ba coverage. The maximum amplitude peak corresponds to SS of clean surface. The thicker spectra emphasize the complex lineshapes that may signify the contributions from both the localized and delocalized DOS.

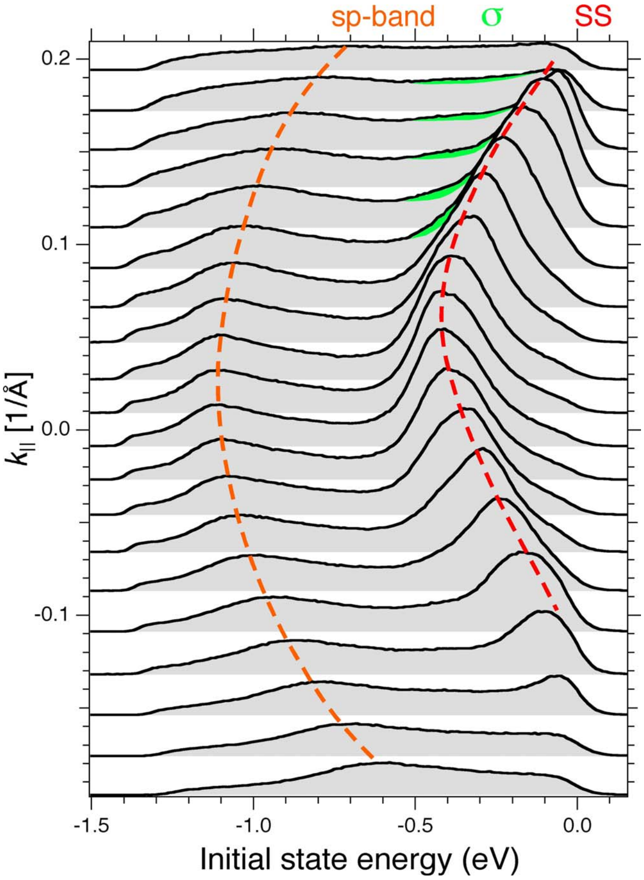

FIG. 9. (Color online) Angle-resolved 1PP spectra for Ba/Cu(111).

having a tail that extends toward the E_F edge. This lineshape is complex due to contributions from both the low- and high-coverage profiles.

The initial coverage-independent binding energy of SS was also observed in 2PP spectra of Fig. 4 and is indicated by the black vertical dashes. The asymmetric shape of SS resonance when it starts to shift suggests the coexistence of two species; one related to the perturbation of SS by the ionic impurity and the other corresponding to the partially occupied 6*s* bonding resonance. This hypothesis is supported also by the angle-resolved spectra, reported in Fig. 9. In these spectra, in addition to the expected parallel dispersion of the Shockley state corresponding to the effective mass of 0.4 times the free-electron mass m_e, a hint of a nondispersive feature can be distinguished for $k_{\|} > 0.1$ Å^{-1}, that could be a further evidence of a nondispersive adatom-localized feature. On the basis of further *ab initio* calculations we observe that this accidental degeneracy of the Shockley state and the 6*s*-derived resonance disappears on other substrates, such as Ag(111).

V. CONCLUSIONS

The electronic structure of chemisorbed Cs and Ba on Cu(111) has been explored by 1PP and 2PP techniques. The 2PP spectra in both cases are dominated by charge-transfer excitation to the unoccupied, or in case of Ba, singly occupied 6*s* resonance. The main difference in the unoccupied electronic structures, namely, the lower energy and larger bandwidth of the Ba resonance, as compared with the corresponding Cs resonance, can be attributed to the difference in screening of the core potential. The stronger attraction between 6*s* electron and the ionic core for Ba, as apparent from the higher ionization potential of the free atom than for Cs, is responsible for the larger binding energy with respect to E_{vac} of the *s* resonance. Likewise, the smaller size of the Ba ionic core leads to a smaller bonding distance to the surface, and therefore, stronger coupling to the substrate, as manifested by the resonance linewidth.

The theoretical simulation of the electronic properties of these single adatoms assigns unambiguously all the experimental features. The model potential for the substrate used in our treatment allowed us to take into account the effects of the surface-projected band structure to the adsorption properties. In particular, by contrast to the simpler jellium model, the degree of hybridization of the atomic states strongly depends on their energy position and, furthermore, on their symmetry. For *s* states lying in the projected gap, the classical picture of adsorption on a metal surface must be modified. Indeed the substrate does not supply states to hybridize the atomic one. Consequently a "molecular" scenario is a better description, as accounted for by the seminal Anderson-News approach,[18] in the case of a "narrow band."

The adsorption of Ba on Cu(111) can now be understood: it does not present a broad, partially filled resonance, with a variable degree of ionization. It is clearly described by the formation of two molecular states, one occupied and the other empty. Consequently, Ba loses exactly one electron, giving rise to a charge transfer very similar to the alkali adsorption. Nevertheless, one electron still remains in the valence shell of Ba positioned in a relatively broad resonance near E_F where it is able to play a role in phenomena such as transport and spin-dependent interactions. This scenario could change significantly if the surface substrate has different electronic structure, allowing charge transfer of a noninteger number of electrons in case of absence of an energy gap.

In conclusion, our joint experimental and theoretical study provides a description of chemisorption of alkaline-earth metals on noble-metal surfaces. Most aspects of Ba chemisorption have direct parallel in the now well-established electronic structure of chemisorbed alkali atoms. The physical properties imparted by the partially occupied 6*s* state, however, have yet to be explored.

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