π Resonance of Chemisorbed Alkali Atoms on Noble Metals

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We have performed a joint experimental and theoretical study of the unoccupied electronic structure of alkali adsorbates on the (111) surfaces of Cu and Ag. Combining angle- and time-resolved two-photon photoemission spectroscopy with wave packet propagation calculations we show that, along with the well known σ resonance oriented along the surface normal, there exist long-lived alkali-localized resonances oriented parallel to the surface (π symmetry). These new resonances are stabilized by the projected band gap of the substrate and emerge primarily from the mixing of the p and d Rydberg orbitals of the free alkali atom modified by the interaction with the surface.

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For atoms and molecules in front of the metal surfaces, electronic states of the joint system reflect the bound state—continuum interaction between the localized molecular orbitals and the propagating states of the substrate. Resonances appear, with widths (inverse of the lifetimes) corresponding to the rates of the electron (hole) escape from the atom or molecule into the metal. A detailed understanding of this phenomenon and the ability to predict the energies and lifetimes of the quasistationary states are of paramount importance for various processes from projectile-surface charge transfer [1] and catalysis [2] to molecular electronics [3] and electron transport in tunneling junctions [4]. Moreover, electron and photon induced reactions at surfaces can be promoted when the lifetimes of adsorbate-localized resonances are sufficient for the energy transfer between electrons and nuclei [5,6].

The development of time-resolved two-photon photoemission (TR-2PP) spectroscopy with femtosecond laser pulses has greatly expanded our understanding of the ultrafast interfacial charge transfer dynamics, and, more generally, time evolution of the excited electronic states at surfaces [7–11]. In particular, the case of alkali atom chemisorption on noble metal surfaces has been a subject of numerous studies [12–16]. This system has become the benchmark for developing increasingly sophisticated theories of (ad)atom surface interactions [17–20].

Until now the only known unoccupied spectroscopic feature of the alkali chemisorption interface has been the alkali-localized resonance appearing at ~2 eV below the vacuum level in the low coverage limit [12–16,18,19,21,22]. This resonance is oriented perpendicular to the surface, and it is formed essentially by the ns and np_z valence orbitals of the alkali atom with σ ($m = 0$) symmetry [16,23–25]. Here m is the projection of the angular momentum on the surface normal (z axis). On noble metal surfaces with a projected band gap the lifetime of the σ resonance can attain tens of femtoseconds [12–14,16,23]. Thus, transient occupation of the σ resonance can initiate surface femtochemistry [15]. It is noteworthy that an excited sp_z resonance has been also reported in theoretical and scanning tunneling microscopy studies of Au and Cu adatoms on metal surfaces [26], as well as in core excited noble gas adatoms [27,28].

In this Letter we show that, in agreement with recent predictions [16], alkali atom adsorption is associated with resonant states of several symmetries and not only the σ one. We report a joint experimental and theoretical study of the angle- and time-resolved photoemission from alkali atom covered noble metal surfaces [Na, K and Cs on Cu (111) and on Ag(111)]. In addition to the σ resonance we find a new alkali induced feature located at 0.3–0.7 eV higher energy. Comparison between calculated and measured data allows its unambiguous assignment to an adsorbate-localized state oriented parallel to the surface and formed by the mixing between the p and d valence orbitals of the alkali atom with π ($m = \pm 1$) symmetry. Long lifetimes of 20–30 fs are obtained from interferometric two-pulse correlations (I2PCs) of 2PP [29], in good agreement with theory and consistent with the resonance stabilization by the projected band gap of the substrate.

2PP measurements for alkali atom covered noble metal surfaces were performed as described previously [25].

Alkali atoms were deposited at background pressures of $<4 \times 10^{-10}$ bar from SAES getter sources onto cleaned and annealed Cu(111) or Ag(111) surfaces. The coverages where kept below 0.1 ML to insure large adsorbate-adsorbate spacing and the absence of ordered structure [12,14,17,27]. 2PP signal was excited by ~16 fs, 3.1 eV pulses from the second harmonic of a Ti:sapphire laser oscillator. The p-polarized excitation light was incident at 45° with respect to the lens axis of a hemispherical electron energy analyzer. Angle-resolved photoemission was obtained by rotating the sample with respect to the fixed laser and analyzer axes. The analyzer lens had an angular acceptance of ±1°. I2PC scans for specific photoelectron energies and angles were measured [29].

Figure 1 shows representative angle-resolved 2PP spectra. The corresponding surface-projected band structures of Cu(111) and Ag(111) as well as the energy diagram for 2PP is sketched in Fig. 2. For finite alkali coverage, the 2PP signal is dominated by resonant excitation out of occupied dispersive Shockley surface state and bulk lower sp band of the substrate to the unoccupied resonances localized on the adatom. The latter do not disperse with the electron momentum parallel to the surface. The σ resonance appears as a prominent feature with associated angle-resolved spectra dominated by emission perpendicular to the surface [24].

In addition, at 0.3–0.7 eV higher energy, for the K and Cs covered surfaces we observe a new nondispersive, i.e., adsorbate-localized feature. It is characterized by a distinctly different angular dependence of the electron emission, pointing at the different symmetry of the underlying state. Namely, the 2PP intensity of this new feature on Cu (111) has a *minimum* in the direction perpendicular to the surface whereas pronounced maxima appear at emission angles of ±17° ± 2° with respect to the surface normal. For Ag(111), the same angular dependence is observed, but the emission maxima are distorted by the participation of the adsorbate resonance as the intermediate state in the lower to upper sp-band ($L_{\text{sp}} \rightarrow U_{\text{sp}}$) two-photon transition at $k_{\parallel} = \pm 0.46$ Å^{-1}. Based on the comparison with theoretical calculations presented below, we assign the new resonances to the $m = \pm 1$ states with π symmetry. They are formed by the hybridization of the np and $(n-1)d$ valence orbitals of chemisorbed K and Cs atoms. The π resonance does not appear for Na/Ag(111). Its high excitation energy (as calculated here, see Table I) makes this state unobservable at this coverage with 3.1 eV photons.

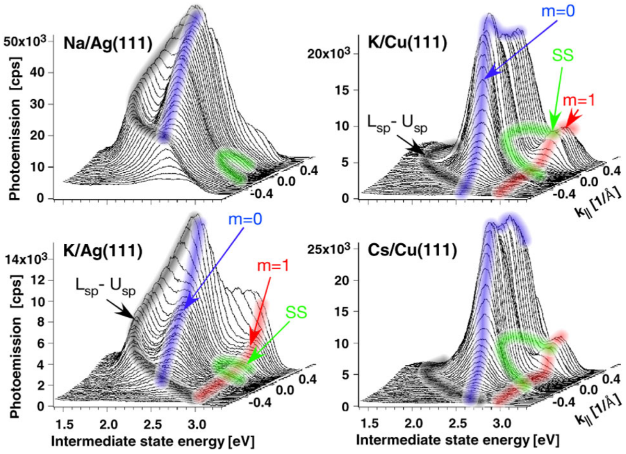

FIG. 1 (color online). Waterfall plots of 2PP spectra for Na/Ag(111), K/Ag(111), K/Cu(111), and Cs/Cu(111) plotted against emission wave vector parallel to the surface $k_{\parallel}$. Spectroscopic features highlighted by the colored lines and labels correspond to the two-photon absorption from the lower sp band (L_{sp}) to the upper sp band (U_{sp}), two-photon absorption from the surface state (SS), and transitions through alkali-localized $m = 0$ (σ) and $m = \pm 1$ (π) intermediate states.

In order to explain the experimental data we have performed a wave packet propagation (WPP) study of the energies, decay rates (widths) via resonant one-electron transfer into the metal, and wave functions of the quasistationary states of the alkali-adsorbate on metal-surface system. The method and its particular application for the alkali adsorbates including finite coverage effect is detailed in Refs. [23,32].

Figure 3 shows the calculated energy and width of the lowest lying resonances of σ and π symmetries for a single K atom in front of the Cu(111) surface. Including finite but small coverage results in the shift of the resonance energy towards the Fermi level, while the width is mainly unaffected (see also Ref. [32] and below). Similar data are obtained for all alkali atoms studied here on both surfaces. The results are shown from large alkali-surface separations down to chemisorption distances. Thus, we identify the σ

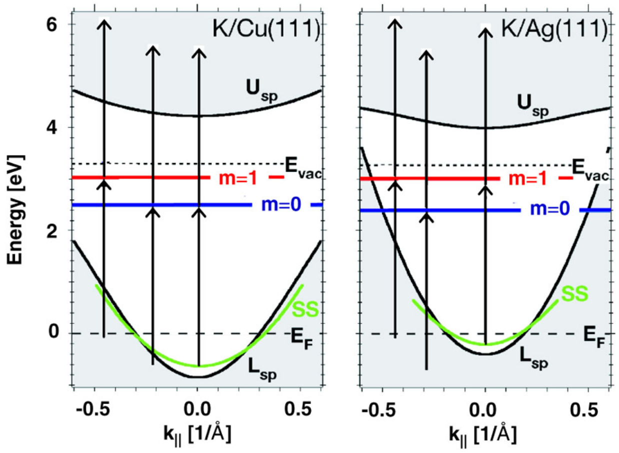

FIG. 2 (color online). Energy diagram of the states and the 2PP excitation pathways (arrows). Alkali coverage corresponds to Fig. 1, where the associated work function decrease is 1.6 eV for Cu(111) [1.2 eV for Ag(111)]. Energy with respect to Fermi level E_F is shown as a function of the electron momentum parallel to the surface $k_{\parallel}$. E_{vac} is the vacuum level energy. The projected band gap extends from L_{sp} to U_{sp}; SS stands for the surface state. For the energetics of the clean surfaces, see Ref. [31].

TABLE I. Summary of theoretical results for the π resonance. Vanishing coverage limit. The adsorption distance $Z_{\rm ads}$ (atomic units) is given with respect to the image plane [23,25,30]. E (eV), is the resonance energy with respect to the vacuum level. $\Gamma_{1\bar{e}}$ (meV) is the one-electron decay rate. τ (fs) is the lifetime obtained with the many-body decay taken into account (see the text).

	Cu(111)				Ag(111)			
	$Z_{\rm ads}$	E	$\Gamma_{1\bar{e}}$	τ	$Z_{\rm ads}$	E	$\Gamma_{1\bar{e}}$	τ
Na	2.58	−0.97	28	13	2.55	−0.88	30	13
K	3.38	−1.15	4.4	27	3.39	−1.09	9.5	22
Rb	3.65	−1.2	6.4	24	3.67	−1.15	6.1	25
Cs	3.5	−1.16	65	8	4.0	−1.22	45	10

resonance as originating from the $4s$ parent orbital of the free-standing alkali atom, and two degenerate π resonances originating from the $4p(m = \pm 1)$ parent orbitals oriented parallel to the surface. As the K atom approaches the surface the energies of the alkali-localized resonances are upshifted by the interaction with the image of the alkali ion core [16,20,32]. Remarkably, excited states originating from the np Rydberg orbitals, have been also reported for the core excited noble gas adatoms [33,34].

The widths of the resonances first increase exponentially for decreasing atom-surface distance because of the increasing coupling with the metal. When K moves into the chemisorption distance range, however, the widths stabilize and even strongly decrease because of the combination of two effects [16,23,32]: (i) Close to the surface the $4s$–$4p_z$ (σ-state) and $4p$–$3d$ (π-state) hybridization pushes the electronic density of the hybrid states away from the surface, and the coupling with metal is reduced; (ii) as illustrated in Fig. 2, because of the projected band gap the alkali-localized states are in energy resonance with electronic states of the substrate only for finite values of $k_{\|}$. The resonant decay of the adsorbate-localized states via electron transfer into the substrate along the "easiest" direction of the surface normal is thus not possible.

A representative example of the wave function of the alkali-localized π resonance is shown in Fig. 4(a) for the single Cs adsorbate on Cu(111). The resonance wave function is pushed away from the surface by the $6p$–$5d$ hybridization of the Cs valence orbitals. The node in the direction of the surface normal results from the $m = 1$ symmetry of the state. The electron density inside the metal corresponds to the outgoing flux because of the decay of the quasistationary state. In Fig. 4(b) we show the calculated angular distribution of the electrons photo emitted from the resonant state by the "probe" pulse of 3.1 eV polarized along the surface normal. We have explicitly checked that results are robust with respect to inclusion of the Fresnel factors and the finite (small) coverage. In agreement with experimental data, the distribution is characterized by a maximum at 21° and no emission in the direction of the surface normal because of the symmetry of the resonance.

Theoretical results are summarized in Table I. For all studied systems, alkali atom adsorption induces a long-lived adsorbate-localized excited electronic state of π-symmetry oriented parallel to the surface. This state coexists with the well-documented unoccupied resonance of σ symmetry. The latter shows a nearly adsorbate-independent energy of the order of -2 eV with respect to the vacuum level as calculated here (see also [16,25]). Therefore, calculations predict the π resonance to be located typically 0.8–1.1 eV above the σ resonance so that, e.g., for the Cs/Cu(111) case the $6s/6p$ energy separation of 1.46 eV for the free atom is reduced to $\Delta E_{\sigma/\pi} = 0.8$ eV

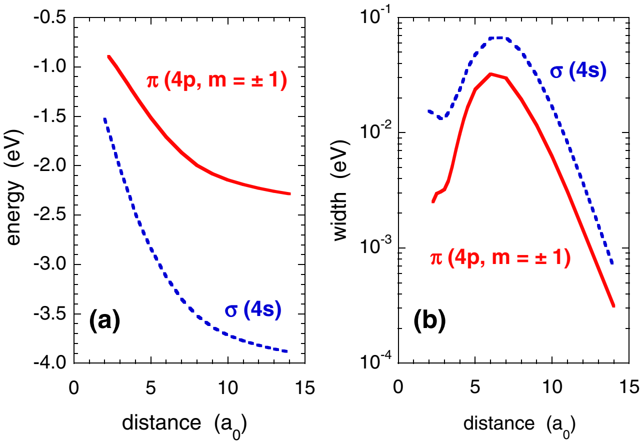

FIG. 3 (color online). (a) Energies and (b) widths of the alkali-localized states of σ and π symmetry for a single K atom in front of Cu(111). The energy is given with respect to the vacuum level. Results are shown as a function of alkali distance from the image plane [30]. The labels reflect the symmetry of the state and the parent orbital of the free-standing alkali atom.

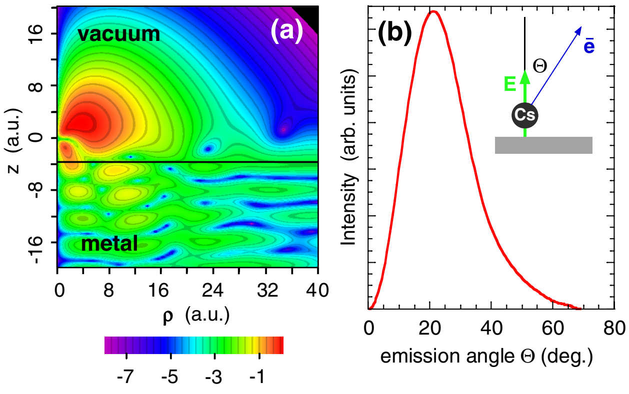

FIG. 4 (color online). (a) Logarithm of the electron density of the quasistationary π state for the Cs/Cu(111) system. Single adsorbate case. Origin of cylindrical coordinates (ρ, z) is on the adsorbate. z axis is perpendicular to the surface. The black horizontal line shows the image plane. (b) Calculated angular distribution of the electrons photo emitted from the quasistationary state shown in panel (a). Arrow labeled E shows the polarization of the laser pulse.

at the surface. The calculated $\Delta E_{\sigma/\pi}$ is larger than experimentally observed values of 0.3–0.7 eV. We attribute this difference in part to the effect of the finite adsorbate coverage used in the experiments. The adsorbate dipole layer induces a shift of the resonance energy towards the Fermi level [22,25,32]. In particular, this enables the observation of both σ and π resonances for K and Cs with present 3.1 eV photons. The energy shift appears different for σ and π states. For Cs/Cu(111), using model approach of Ref. [32], we calculate $\Delta E_{\sigma/\pi} = 0.66$ eV at the coverage corresponding to the work function reduction by 1.6 eV. The corresponding experimental value is 0.43 ± 0.03 eV. Besides the electrostatic effect, interaction between π orbitals located at neighboring adsorbates cannot be excluded.

The lifetime of the π resonance has been evaluated as: $\tau = 1/(\Gamma_{1\bar{e}} + \Gamma_{ee})$ [23]. Here, $\Gamma_{1\bar{e}}$ is the present WPP one-electron resonant decay rate. Γ_{ee} is the multielectron decay rate resulting from the inelastic interactions between adsorbate-localized and substrate electrons. Based on the previous studies for the σ state it has been estimated at ≈20 meV [23]. The obtained lifetime of the π resonance is in the 10–30 fs range in agreement with the present experimental measurements. Thus, the π resonance has a lifetime comparable to that of the σ resonance [12–16].

In conclusion, combining experiment and theory, we could observe and describe a new alkali-adsorbate induced feature in the unoccupied part of the electronic density of states at chemisorption interface. For alkali atom adsorption on (111) faces of Cu and Ag, along with the well studied σ resonance, an alkali-localized state of π symmetry has been found. Results reported here should be of general nature for the substrates presenting a projected band gap and adsorbates with strong electron donation to the surface. Finally, the discovery of a new type of long-lived resonances oriented parallel to the surface and thus responding differently to an external excitation, as compared to the previously known σ resonance, extends the possibilities to induce and control various processes involving excited electrons.

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