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 pre-
dict 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 tunnel-
ing 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 gen-
erally, 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 \(np\) valence orbitals of the alkali atom with \(\sigma\) \((m = 0)\)
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 \(\sigma\) resonance can attain tens of femtoseconds [12–
14,16,23]. Thus, transient occupation of the \(\sigma\) resonance can initiate surface femtochemistry [15]. It is noteworthy
that an excited \(sp\) 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 \(\sigma\) 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 \(\sigma\) 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 \(\pi\) \((m = \pm 1)\) 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 \( \sim 16\) 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 \( \pm 1° \). 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 emission perpendicular to the surface [24]. In addition, at 0.3–0.7 eV higher energy, for the K and Cs adsorbates 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 \( \pm 17° \pm 2° \) 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 \( (L_{sp} \rightarrow U_{sp}) \) two-photon transition at \( k_{||} = \pm 0.46 \text{ Å}^{-1} \). Based on the comparison with theoretical calculations presented below, we assign the new resonances to the \( m = \pm 1 \) states with \( \pi \) symmetry. They are formed by the hybridization of the \( np \) and \((n - 1)d \) valence orbitals of chemisorbed K and Cs atoms. The \( \pi \) 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.

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 \( \sigma \) and \( \pi \) 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 \( \sigma \)
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 \( \pi \) 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 \( \pi \)-symmetry oriented parallel to the surface. This state coexists with the well-documented unoccupied resonance of \( \sigma \) 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 \( \pi \) resonance to be located typically 0.8–1.1 eV above the \( \sigma \) 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 \( \Delta E_{\pi}/\sigma = 0.8 \) eV.

![Image](image_url)

**FIG. 3** (color online). (a) Energies and (b) widths of the alkali-localized states of \( \sigma \) and \( \pi \) 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 \( \pi \) state for the Cs/Cu(111) system. Single adsorbate case. Origin of cylindrical coordinates (\( \rho, z \)) 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 $\sigma$ and $\pi$ resonances for K and Cs with present 3.1 eV photons. The energy shift appears different for $\sigma$ and $\pi$ 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 $0.43 \pm 0.03$ eV. Besides the electrostatic effect, interaction between $\pi$ orbitals located at neighboring adsorbates cannot be excluded.

The lifetime of the $\pi$ resonance has been evaluated as: $\tau = 1/(\Gamma_{ie}^\pi + \Gamma_{ee}^\pi)$ [23]. Here, $\Gamma_{ie}^\pi$ is the present WPP one-electron resonant decay rate. $\Gamma_{ee}^\pi$ is the multielectron decay rate resulting from the inelastic interactions between adsorbate-localized and substrate electrons. Based on the previous studies for the $\sigma$ state it has been estimated at $\approx 20$ meV [23]. The obtained lifetime of the $\pi$ resonance is in the 10–30 fs range in agreement with the present experimental measurements. Thus, the $\pi$ resonance has a lifetime comparable to that of the $\sigma$ 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 $\sigma$ resonance, an alkali-localized state of $\pi$ 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 $\sigma$ resonance, extends the possibilities to induce and control various processes involving excited electrons.

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[30] Position of the image plane with respect to the last atomic plane is 2.11/2.22a$_0$ for Cu(111)/Ag(111) [31].