Resonance lifetime and energy of an excited Cs state on Cu(111)

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Using time-resolved two-photon photoemission spectroscopy, we investigated the resonance lifetime and energy of an excited Cs state on Cu(111) in the low-coverage case. We found a pronounced lifetime increase of up to 11 ± 3 fs on a copper surface covered with cesium as compared to a clean copper surface in the energy range of an excited electronic Cs state in the spectrum. This result is in agreement with recent theoretical predictions of hybridization among excited atomic levels of alkali atoms near metal surfaces. [S0163-1829(97)06215-2]

Many photoinduced processes between adsorbed species and metal surfaces are proposed to be stimulated by energy transfer due to exchange of hot electrons rather than by thermal activation.[1] Motivated by recent femtosecond-laser–induced desorption results, several theoretical investigations of hot-carrier–induced reactions have been undertaken.[2,3] The results show that one of the most important parameters for understanding the enhanced energy transfer between the hot electron and the adsorbate is the duration of stay of the hot electron inside the adsorbate. This resonance lifetime is directly associated with the energy gain by the adsorbate per electron-transfer process. Unfortunately, our knowledge of excited states close to metal surfaces is not nearly as complete.

Investigations of lifetimes of image states of a Ag(111) (Ref. 4) and a Cu(111) surface[5] have proven that time-resolved two-photon photoemission (TR 2PPE) is a suitable tool for studying the electron dynamics of unoccupied surface states in the femtosecond time domain. In spite of impressive progress, TR 2PPE experiments on unoccupied adsorbate states were reported only by Schmuttenmaer *et al.*[6] and Knoesel *et al.*,[7] who investigated the $2\pi^*$ resonance of CO on Cu(100) and on Cu(111), respectively. In both cases, however, no measurable lifetime effect due to the resonance of the excited electrons in the adsorbate was detected.

The present paper reports a real time observation of the lifetime of an excited electron in an adsorbate. We investigated a usual unoccupied cesium-induced state on a Cu(111) surface by means of TR 2PPE. As seen in the top panel of Fig. 1, there is a clear increase in the lifetime of single excited electrons from a clean Cu(111) surface (open circles) as compared to the same surface covered with a small amount of Cs (filled circles) exactly in the energy range where we found an excited Cs state in the 2PPE spectrum (see inset). The result is in agreement with recent theoretical predictions of hybridization among excited atomic levels of alkali atoms near metal surfaces.[8,9]

The experimental setup has also been used to measure the lifetimes of excited electronic states in various noble and transition metals and is described in more detail elsewhere.[10] In brief, our time-resolved two-photon photoemission experiments were performed with an 82-MHz pulsed Ti sapphire laser, tunable from 730 to 830 nm. The system delivers transform-limited and sech[2] temporal shaped pulses of up to

9 nJ/pulse with a duration of 40 fs. The linearly polarized output is frequency doubled in a 0.2-mm-thick beta barium borate (BBO) crystal to produce UV pulses at $h\nu = 3 - 3.4$
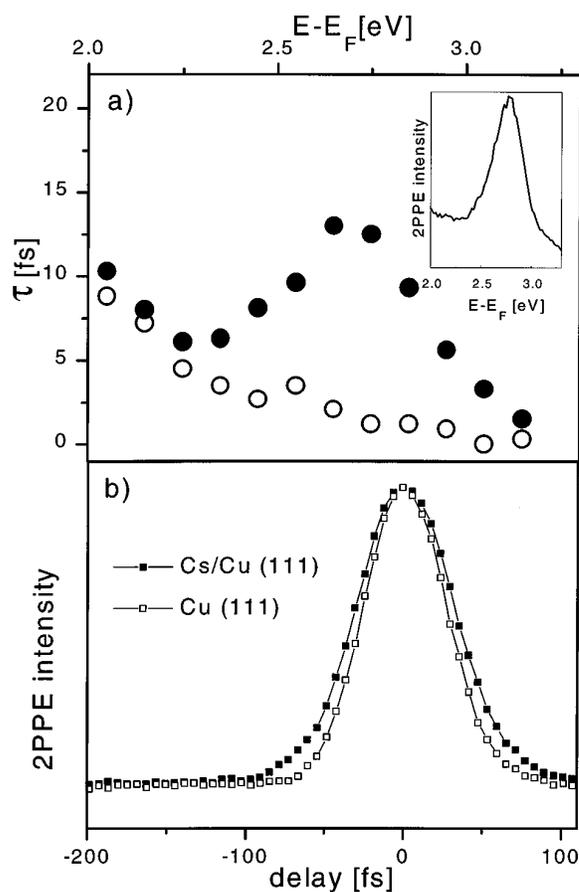

FIG. 1. Increase in lifetime of excited electrons due to the cesium adsorbate state. Top panel: the deduced lifetime τ as a function of the probed intermediate level for the clean (○) and adsorbate-covered (●) copper surface; the inset shows a detail of the corresponding 2PPE spectrum with the cesium state. Lower panel: comparison of the correlation traces corresponding to the values of the top panel at $E - E_F = 2.6$ eV for the clean (□) and covered (■) surfaces, respectively. The values for the FWHM of the curves were determined to be 62 and 74 fs.

eV. The pulses are split by a beam splitter to equal intensi-ty(pump and probe pulses), and one path is delayed with respect to the other by a computer-controlled delay stage. Both beams are combined colinearly by a second beam split-ter and are focused under 45° incidence at the sample sur-face.

The Cu(111) sample is mounted in an UHV chamber (base pressure 8×10^{-11} mbar) equipped with a cylindrical sector analyzer. In general, we use a pass energy of 4 eV, leading to roughly 50-meV resolution. A 4.0-V bias is ap-plied to the sample to eliminate the effects of any stray elec-tric fields. The cesium was deposited by evaporation from a normal commercial SAES getter source. The pressure during evaporation was maintained in the low 10^{-10}-mbar range. From the lowest work function value ϕ we measured and referring to the work of Lindgren and Wallden,[11] we esti-mated a maximum Cs coverage of 0.15 ML in our experi-ments. In order to avoid single photoemission at $\phi < h\nu$, higher Cs coverages were not investigated within the scope of this experiment.

Figure 2 shows a series of 2PPE spectra for increasing coverage of Cs on the Cu(111) crystal, measured with one of the laser beams blocked (photon energy $h\nu = 3.3$ eV). The data are plotted as a function of the intermediate state energy E relative to E_F. Since the work function ϕ is very sensitive to alkali adsorption,[12] the change in ϕ, deduced from the onset of the 2PPE spectra, is used to verify the cesium cov-erage under consideration of Ref. 11. The right peak of spec-trum (a) arises from the occupied surface state S of the clean Cu(111) surface, located 0.39 eV below E_F for $k_\parallel = 0$.[13] At 0.02 ML Cs [spectrum (b)] a double-peak structure is visible at the high-energy end. The surface state S has downshifted, in full agreement with the coverage dependency reported for the system Na/Cu(111).[12] The second peak A can be attrib-uted to an unoccupied Cs state. The presence of unoccupied alkali valence states on different metal surfaces has been reported previously (for an overview see Ref. 12 and refer-ences therein). At even higher coverage [see spectra (c) and (d)], peak A shows a downward shift, whereas the contribu-tion from the surface state is strongly reduced. This can be deduced from the excitation energy dependency of the ener-getic position of peak A. When varying the photon energy by $\Delta h\nu$, a shift of peak A by $\Delta E_{kin} = \Delta h\nu$ is obtained as ex-pected for an unoccupied state, whereas an occupied surface state would shift with $\Delta E_{kin} = 2\Delta h\nu$.[14] The second peak $J1$ in Fig. 2(d) is attributed to the $(n = 1)$ image state of the Cu(111) surface. At the highest coverage we investigated even the $(n = 2)$ image state $J2$ appears in our 2PPE spectra. The existence and energetical position of these states, result-ing from the interaction of an electron in front of a metal surface with its polarization charge, are very sensitive indi-cators of the conditions at the surface. Furthermore, it is noteworthy that, at a certain cesium coverage (about 0.03 ML for $h\nu = 3.3$ eV), we observe resonant excitation of the adsorbate state A by the surface state S, which leads to a drastic enhancement of the 2PPE signal.

The energies of all observed states relative to E_F are plot-ted in Fig. 3 as a function of the work function. The binding energies for all three states are very similar to the values deduced from Fischer and co-workers for sodium adsorbed on Cu(111).[12] They gave a value of $E_A^0 = 2.86$ eV for the
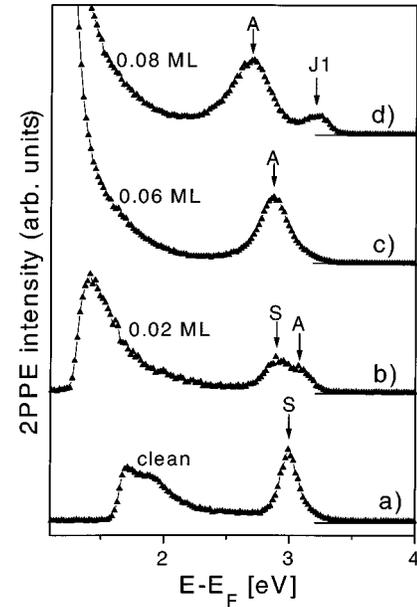

FIG. 2. Two-photon photoemission spectra for various cesium coverages. The coverage values were deduced from the measured change in the work function ϕ. Spectrum (a) shows the clean sur-face with the occupied surface state S. At low coverages the unoc-cupied adsorbate state A appears and dominates the upper two spec-tra (c) and (d). The additional state $J1$ in spectrum (d) is characterized as the first image state of the Cu(111) surface.

energetic position of the excited sodium state A above E_F in the zero-coverage limit. We attained $E_A^0 \cong 3.1$ eV for the ex-cited Cs state. Furthermore, the decreasing binding energy with increasing coverage of the $(n = 1)$ image state, which can be deduced from the slight upward slope of $J1$ in Fig. 3, is in full agreement with the results obtained for the system Na/Cu(111).

We now present our results for time-resolved investiga-tions of the cesium-induced unoccupied state A: Figure 1(b)
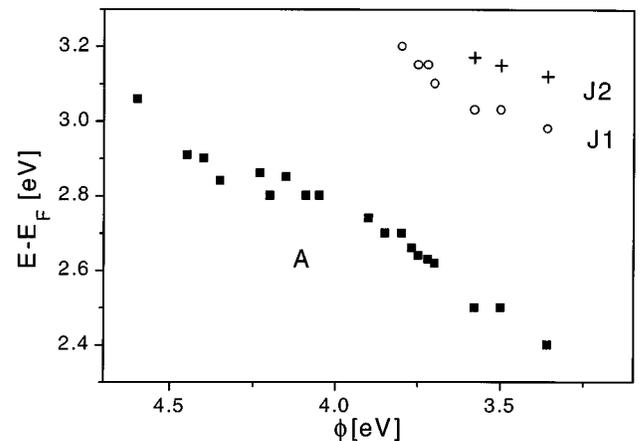

FIG. 3. Experimentally observed energies of the excited states for Cs on Cu(111) as functions of the measured work function; the Cs coverage increases from left to right. State A is attributed to a Cs-induced state; $J1$ and $J2$ indicate the position of the image states of the Cs/Cu(111) surface.

shows a comparison of the pump-probe scans for a clean and a Cu(111) surface covered with Cs. The correlation traces were taken at room temperature at a fixed intermediate-state energy $E - E_F = 2.7$ eV corresponding to the energy of the unoccupied Cs peak A in the 2PPE spectrum [see inset of Fig. 1(a)]. The difference in the full width at half maximum (FWHM) between the two traces indicates that there is a pronounced variation in the electron relaxation dynamics between a clean and a Cu surface covered with Cs. Assuming that the two excitation steps via the intermediate (investigated) state can, as a first approximation, be described sufficiently by Fermi's golden rule, we extracted the inelastic lifetime of excited electrons by means of the method of reconvolution described in Ref. 10.

Figure 1(a) presents the deduced lifetime τ as a function of the probed intermediate level for the clean and an adsorbate-covered copper surface; the inset shows a detail of the corresponding 2PPE spectrum with the cesium state. There is a striking difference between the two lifetime measurements exactly in the energy range of the observed unoccupied Cs state in the 2PPE spectrum, indicating the strong influence of an excited adsorbate state on the relaxation time of optically excited electrons. From the maximum lifetime difference between the two measurements, we estimate the resonance lifetime of the excited Cs state on Cu(111) $\tau_R = 11 \pm 3$ fs. Resonant excitation from the surface state gave no measurable difference in our results.

How can this pronounced lifetime effect be brought into line with theoretical predictions? The general view is that atomic states of chemisorbed adatoms on metal surfaces are broadened due to the hybridization with the substrate states.[15] More specifically, the broadening of the linewidth of atomic levels near a metal surface is explained by the reduced lifetime of the electron due to the strongly increased interaction with the metallic electronic states.[16,17] Therefore, the linewidth depends very much on the distance d of an adsorbate state from a surface[3,8,18] and, hence, on the bonding character.

Using a simple wave-function-matching technique to calculate the width of resonances at a given adatom-substrate separation d, Muscat and Newns[18] predicted a spectral linewidth of 0.8–1.8 eV for Cs adsorbed on Ni in the chosen interval (3.8 a.u. $< d <$ 4.5 a.u.). Yu and Lang calculated a width of 1 eV for Cs adsorbed on aluminum.[19] All these values correspond to lifetimes far below 1 fs. In contrast, surprisingly small experimental linewidths determined by means of 2PPE for alkali-induced states have been reported before. In a recent paper, Nielsen and Thowladda reported a linewidth of 700 meV for a potassium state on Ag(100), located 2.4 eV above E_F.[20] Fischer and co-workers[12] gave a value of 410 ± 30 meV for sodium on Cu(111), pointing out that this observed width was not only determined by the finite lifetime of the electronic state. This implies that the resonance lifetime is longer than 1.5 fs. We observed a linewidth of 250 meV at resonant excitation from the surface state and about 350 meV out of the resonance corresponding to a lifetime of $\tau \cong 2$ fs. Even this value, which marks the lower limit of the real lifetime, differs from the theoretical predictions. Our real time experiments, however, gave evidence of a resonance time in the range of up to 10 fs. However, it is well known that the direct comparison of excited

electron lifetimes with experimentally determined linewidths is complicated by the many contributing factors to experimental line broadening.

Because their calculated linewidth of 0.8–1.8 eV of the $6s$ state is comparable to the $6s$-$6p$ energy separation of 1.44 eV for the free cesium atom, Muscat and Newns predicted a strong $s - p$ hybridization for the adsorbed cesium atom.[9] That means not only the interatomic polarizability mechanism (Gurney lifetime broadening), but also the intraatomic polarizability mechanism must be taken into account. As Muscat and Newns mentioned, this results in an unoccupied $|6s + 6p_z\rangle$ state directed away from the surface, coupled only weakly to the metal states, and a $|6s - 6p_z\rangle$ hybrid, located between the adatom core and the surface. This picture is also supported by self-consistent electronic-structure calculation of the Na overlayer on a semi-infinite jellium surface by Ishida.[21] He showed that, due to the strong adatom-substrate interaction, the Na $3s$ and $3p_z$ states do not form separated peaks. The single main peak in the total state density of Na on the jellium in his calculation cannot be attributed to a pure, almost empty Na $3s$ state but rather to a hybridized state of Na $3s$ and $3p_z$, which strongly polarizes to the vacuum side of Na. In addition, Nordlander and Tully showed that different electronic states of an atom can behave very differently in their broadening when approached to a surface, depending on their relative orientation to the surface.[8] Even though there may be only small differences in the real part of the energies of different hybridized states (e.g., $ns + np_z$ and $ns - np_z$), the state whose wave function is mainly orientated to the vacuum side of the adsorbate, away from the substrate, can show much higher electron lifetimes than one located between adsorbate and substrate. In contrast to Muscat and Newns, in the case of a cesium atom near a jellium surface, they assume a hybridization of the (closer lying) $5d_z^2$ and $6p_z$ levels. However, in both cases, the resulting states exhibit a very similar orientation. In general, they reported much longer calculated excited-state lifetimes than reported previously by including the repulsive electron-core image interaction.

Considering the extended lifetime in the observed excited Cs state A in our 2PPE spectra, we propose that this state A originates from the formation of an antibonding hybridized state, caused by a strong adatom-substrate interaction, which strongly polarizes to the vacuum side of Cu. This assumption is supported by the fact that the state A can be observed only by using p-polarized light. Possible candidates for such a hybrid state are the $|6s + 6p_z\rangle$ hybrid state[9] or the $|5d_z^2 - 6p_z\rangle$ hybrid state.[8] As Nordlander and Tully pointed out, excited electrons in such states are strongly decoupled from the bulk electronic states and, hence, the backscattering into the bulk is probably considerably diminished. As shown in Fig. 1, our real time results support this theoretical picture quite well.

We did not observe any indications of the expected counterpart of the state A, the hybrid state located between adsorbate and surface. We do not agree with the interpretation of Nielsen et al.[20] that a missing second peak in the spectrum is proof enough that the observed exited alkali state at an energy of 2–2.6 eV above the Fermi level must originate from the pure s resonance. Rather, due to the location of the hybrid state close to the metal electronic states, it has to be

expected to be strongly lifetime broadened. It is very difficult to distinguish a smooth structure with a broadening of up to 2 eV from the background, especially when the spectrum is dominated by the sharp and pronounced peak *A* close to the same energy range.

In summary, we used two-photon photoemission to identify an unoccupied Cs state on a Cu(111) surface. *Time-resolved* 2PPE investigations show that the lifetime of the electrons in the Cs state lies 11 ± 3 fs above the value mea-

sured for electrons inside the Cu. To our knowledge, this is the first direct observation of an increase in the lifetime of exited electrons at metal surfaces due to an excited adsorbate state. We explain this pronounced lifetime effect by a weak overlap of the investigated hybrid state of the excited cesium to the bulk electronic structure due to hybridization of atomic Cs states near a surface.

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