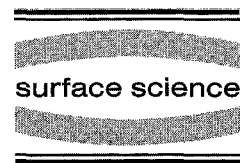




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Femtosecond lifetime investigations of excited adsorbate states: atomic oxygen on Cu(111)

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Abstract

We investigated an excited electronic state induced by atomic oxygen adsorbed on Cu(111) by means of time-resolved two-photon photoemission spectroscopy. In contrast to a system investigated previously, cesium adsorbed on Cu(111), no increase in the relaxation time of the photoexcited electrons due to the resonance time of the excited oxygen state was detected within our time resolution. The difference between the two systems will be discussed, taking the specific adsorption sites of the adsorbates on the Cu(111) surface into consideration.

Keywords: Alkali metals; Copper; Low index single crystal surfaces; Metallic surfaces; Oxygen; Photochemistry; Visible and ultraviolet photoelectron spectroscopy

1. Introduction

The energies and lifetimes of excited electronic states of adsorbates on metal surfaces are suggested to play an important role in photochemical reactions on metal surfaces induced by hot substrate electrons [1]. In a very recent paper we presented the first real-time observation of the resonance time of an excited cesium state adsorbed on Cu(111) by means of time-resolved two-photon photoemission spectroscopy (TR-2PPE) [2]. Our experiments provided evidence for a surprisingly long resonance time in the range of 10 fs for the investigated Cs state.

A first step towards a better understanding of the nature of this large increase in lifetime is a

systematic change in different parameters of the investigated system. Oxygen adsorbed on Cu(111) seems to be very suitable for a comparison with the results we obtained for Cs/Cu(111) because there are several similarities in the excited electronic states appearing in both systems. An excited electronic state induced by atomic oxygen adsorbed on Cu(111) can be found at about 3 eV above the Fermi energy E_F [3,4]. This value is very similar to the location of the excited cesium state on a Cu(111) surface in the coverage range we investigated ($\theta < 0.15$ ML, see Ref. [2]). In addition the nearly equal linewidth, about 350 meV, reported for the two adsorbate states is noticeable [4,5]. Both states are only observable using p-polarized light, suggesting that their symmetry properties are also similar. There are, however, differences between the two systems, reflecting their different binding characters. The binding of

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Cs/Cu(111) depends to a considerable extent on the cesium coverage and changes from an almost ionic character at low coverage to a rather neutral binding near monolayer coverage [6]. This change is accompanied by a strong variation of the work function and the energetic position of the unoccupied cesium state relative to E_F [2,7]. On the other hand, almost no variations with coverage in these two quantities are observed for O/Cu(111) at room temperature, implying a small effective charge transfer between oxygen and copper [3,8,9].

2. Experimental

The experimental set-up of our TR-2PPE investigations is very similar to that reported in Ref. [10]. The Cu(111) crystal, mounted in an UHV chamber, was cleaned by standard procedures, producing a sharp 1×1 LEED pattern. Exposure to oxygen was carried out via a leak valve by flowing O_2 at a pressure of $\sim 1 \times 10^{-6}$ Torr through the chamber. Saturation coverage of the Cu(111) surface is reached at 800 L of O_2 leading to a maximum coverage of 0.3 monolayer with respect to substrate surface atoms [9]. Exposure of Cu(111) to oxygen at room temperature does not produce any ordered overlayer as judged by LEED measurements [8,9].

3. Results and discussion

Fig. 1 shows 2PPE spectra for the clean copper surface and the copper surface after exposure to different amounts of O_2 as a function of the intermediate state energy $E - E_F$. For comparison a spectrum of a cesium-covered surface as it was investigated in Ref. [2] is displayed. For the clean Cu(111) a work function Φ of 4.9 eV was deduced from the low-energy cut-off of the 2PPE spectra. No changes in Φ due to oxygen adsorption were measured within our energy resolution (50 meV), in agreement with previously reported observations [4,8,9]. The peak at the high energy end of the clean spectrum arises from the occupied Shockley surface state S located at 0.39 eV below E_F inside

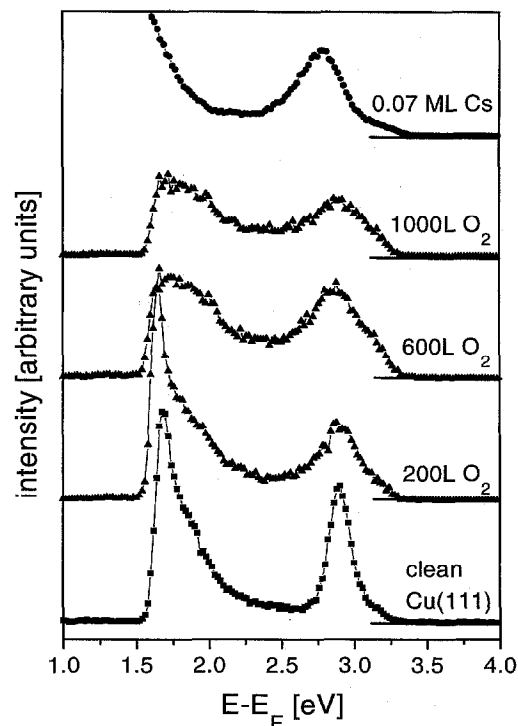


Fig. 1. Two-photon photoemission spectra with $h\nu = 3.3$ eV for a clean and oxygen covered Cu(111) surfaces. The spectrum for a surface covered with cesium is shown at the top.

the sp band gap of the surface [11]. Due to oxygen adsorption, the surface state S is strongly attenuated [3] and a broader state appears in the spectrum. From the photon energy dependence of the energetic position of this state as shown in Fig. 2, this broad feature must originate from the excited oxygen state [12]. We found the energetic position of this state to be 2.9 eV above the Fermi level, in full agreement with the values given in Refs. [3] and [4]. For the linewidth (FWHM) our value of ~ 400 meV was somewhat higher than that reported by Rieger et al. [4]. This deviation can be explained by the relatively low angular resolution of our electron energy analyzer in combination with the known dispersion of the oxygen state at saturation coverage [3]. Although we used a “resonant” excitation energy ($h\nu = 3.3$ eV), no resonant excitation of the surface state to the excited adsorbate state was observed, even at coverages (e.g. 200 L O_2) where a contribution from

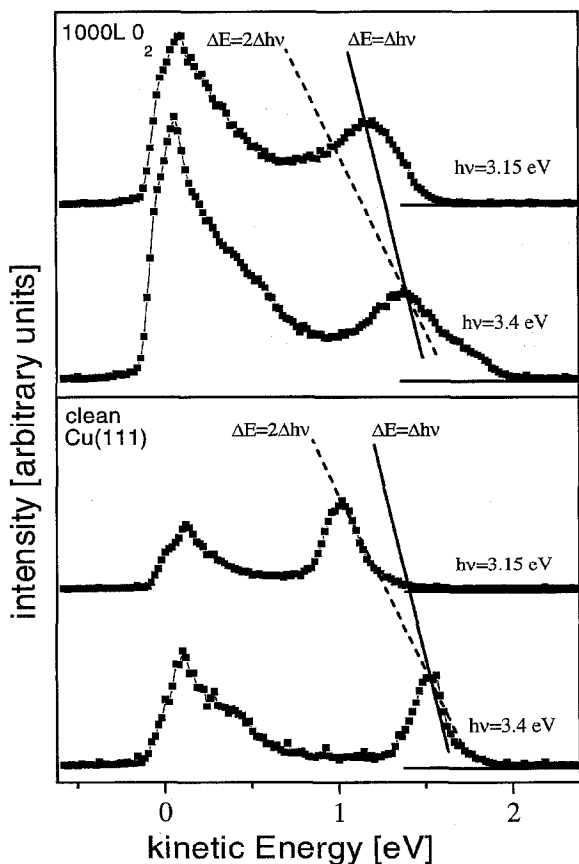


Fig. 2. Comparison of the photon energy dependence for the (occupied) surface state S on the clean Cu(111) surface and the excited (usually unoccupied) oxygen state. Changing the energy of the exciting photons by $\Delta h\nu$, the kinetic energy of electrons emitted from a usually unoccupied feature (oxygen state) varies as the photon energy by $\Delta h\nu$, whereas the kinetic energy of electrons reflecting an occupied feature (surface state S) varies by $2\Delta h\nu$ [12].

the occupied surface state in the spectra is still visible. This is a clear deviation from our observations of the system Cs/Cu(111) [2]. From the energetic position of the highest occupied orbital of oxygen on Cu(111) (about 2 eV below E_F [4]), we also have to exclude intra-atomic excitation of the unoccupied state using an excitation energy of $h\nu = 3.3$ eV. This may be also in contrast to a cesium adsorbate, as from theoretical investigations for alkali adsorption on metal surfaces a broad, partly occupied state at the Fermi edge is expected [13].

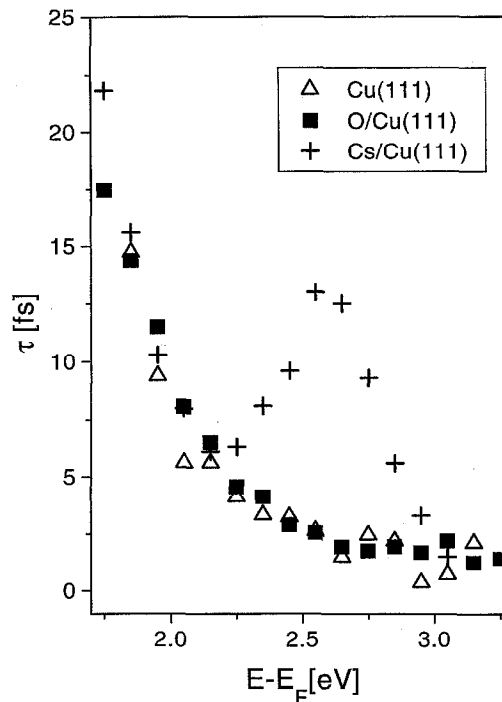


Fig. 3. The deduced lifetime τ as a function of the probed intermediate level for clean (Δ), oxygen-covered (\square) and cesium-covered ($+$) Cu(111) surfaces. In contrast to Cs/Cu(111), no lifetime changes due to the adsorbate state can be obtained for O/Cu(111).

In Fig. 3 the inelastic lifetime τ of electronic excitations versus the excitation energy above E_F for the clean surface and the two different adsorbate systems of Fig. 1 are compared. τ was deduced from the correlation traces determined by TR-2PPE according to Ref. [10]. The increase in the relaxation time of the electrons in the energy range between 2.3 and 2.7 eV due to the Cs-induced state is clearly visible. In contrast, copper after exposure to 1000 L O_2 shows no difference in the electrons' lifetime compared to the clean surface within our time resolution. We also did not observe any indication of an increase at lower oxygen coverage. Thus, quenching of a lifetime effect due to the short-range interaction of the oxygen atoms at saturation coverage [3] can be excluded.

From the observed linewidth (350 meV) of the excited oxygen state the lower limit of the

resonance time can be estimated to be 1.5 fs. It is noteworthy that this limit seems to be close to the value we obtained (in real time) by TR-2PPE. This behavior deviates considerably from the situation at Cs/Cu(111), where the linewidth of the state is obviously determined by other contributions.

Our resonance time results are not surprising if the adsorption structure as well as the electronic structure of O/Cu(111) is considered. The fact that the adsorbate state is located inside the sp bandgap of the Cu(111) surface [3] excludes a direct tunneling of the electron from the oxygen-induced state into the bulk. Therefore, the lifetime (broadening) of the excitation should be determined by the inelastic scattering of the electrons with bulk electrons from below the Fermi edge. The range of τ is then given by the spatial overlap with the bulk electronic states. As atomic oxygen is known to adsorb at three-fold hollow sites on Cu(111), probably inside or below the outermost plane of the copper atoms [9,14], a strong overlap can be expected. The resonance time should be nearly the same as the relaxation time of excited single electrons inside the bulk. According to the theory of Fermi Liquids [15] the lifetime τ of bulk electronic excitations for copper can be estimated to be about 2.5 fs at $E - E_F = 2.9$ eV [16]. The value of 1.5 fs estimated from the linewidth of the state as well as a missing discrepancy between the real-time results of clean Cu(111) and O/Cu(111) within our time resolution is in very good agreement with this picture.

As mentioned above, the situation for Cs/Cu(111) is fundamentally different. We observed a resonance time of the excited state which is strongly increased compared with the lifetime of bulk excitations. At least at monolayer coverage, cesium adsorbed on Cu(111) is known to adsorb on top of the Cu atoms [17] and a recent publication investigating the geometric structure of rubidium on Cu(111) [18] points to the fact that this on top bonding site can also be maintained at the low coverages we investigated (0.1 ML). Hence, the assumption of a weaker interaction of the cesium state with the bulk electronic states of copper than in the case of oxygen adsorption seems to be justifiable. In addition, as proposed in Ref. [2], we also take into

account that the observed cesium-induced excited state may result from hybridization of electronic states of atomic cesium under the influence of the copper surface, as implied by several theoretical investigations [19]. One of the two resulting hybrid states is polarized mainly towards the vacuum side of the cesium atom. This polarization should also give rise to a strong decoupling from the bulk states and hence a strong increase in resonance time.

4. Conclusion

Comparing the different results for the resonance time of the two investigated excited adsorbate states, we would like to add that some (mis)interpretations of the resonance lifetime effect we observed for cesium on Cu(111) can be excluded:

- (1) The high trapping time of electrons inside the cesium state cannot be explained only by a hindered scattering of the electrons into the bulk due to its location inside the sp band gap of the Cu(111) surface. The result for oxygen clearly shows that a very effective relaxation similar to that of bulk electronic excitations can even occur for excited adsorbate states located inside a band gap.
- (2) The possibility that the observed lifetime increase on Cs/Cu(111) is due to an artificial effect (e.g. the proportion of coherent and incoherent contributions to the 2PPE signal) of the difference between excitation via an intermediate (virtual) state inside the band gap and the excitation via a (real) state located at the surface can also be excluded from the result obtained for O/Cu(111). Obviously, a broadening of the autocorrelation trace is not induced just by the existence of an unoccupied (real) state as an intermediate.

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