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Unoccupied adsorbate states of CO/Cu(111) analyzed with two-photon photoemission

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Abstract

The unoccupied electronic states of the CO-(1.4×1.4) overlayer on Cu(111) have been studied with two-photon photoemission (2PPE). For excitation with $3.5 \leq h\nu \leq 4.5$ eV the kinetic energy of photoelectrons emitted from a CO induced state is found to shift as $\Delta E_{kin} = 1 \cdot \Delta h\nu$. This provides evidence for emission from a normally unoccupied state, located 3.35 ± 0.1 eV above the Fermi level, which is transiently populated in the 2PPE process. Based on the polarization dependence of the adsorbate induced feature this state is identified as being derived from the $2\pi^*$ affinity level of CO adsorbed on Cu(111). No dispersion of the CO $2\pi^*$ level is observed along $\bar{\Gamma}\bar{K}$.

1. Introduction

Electronic excitations of adsorbed molecules play an important role in chemisorption and various activated surface processes, particularly in surface photochemistry. The spectroscopy of unoccupied electronic states is generally the domain of inverse photoemission (IPE) [1,2]. An alternative technique is two-photon photoemission (2PPE), which is restricted to intermediate states located between the Fermi and vacuum levels [3,4]. Compared with inverse photoemission, better energy resolution can be achieved with 2PPE and the polarization of the exciting laser light simplifies the determination of symmetry properties. In addition, 2PPE is a very promising technique for time-resolved studies of the electron surface dynamics using ultra-short laser pulses to stimulate and subsequently probe the state of excitation [5–7].

In two-photon photoemission spectroscopy the life-time of the intermediate state must be sufficiently long,

particularly if lasers with nanosecond pulse duration are used. The longer lifetime of image potential states compared to bulk states has led to a great success in the study of the properties of these states with high energy resolution 2PPE spectroscopy [3,8–11]. Recently image-potential derived surface resonances have also been observed [12].

At present, most 2PPE studies of adsorption systems have been restricted to *atomic* chemisorption systems [13–15]. Recently Munakata et al. studied NO/Cu(111) with 2PPE [16]. However, the overlap of two-photon emission from the occupied NO 2π level made it difficult to resolve the unoccupied adsorbate states in this system [17].

In this Letter we demonstrate for CO/Cu(111) that 2PPE can be used to probe the excited states in a molecular chemisorption system. In the traditional picture for CO chemisorption on transition metals, the Blyholder model, it is believed that the CO–surface bond is formed by the interaction of the 5σ and $2\pi^*$ orbitals with the substrate d band [18]. The 2π-resonance

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model proposed by Avouris et al., suggests a much larger contribution of the metal sp conduction band electrons in the CO–metal bond [19]. For CO on copper a recent analysis by Bagus et al. shows that the Cu 4sp electrons make the dominant contribution to the CO–Cu bond [20].

In a simple molecular orbital picture of the CO–Cu bond, the interaction is derived from the CO $2\pi^*$ orbital and the Cu $3d_\pi$ and $4p_\pi$ levels must be included. This results in one occupied orbital with mainly $3d_\pi$ character and two unoccupied states arising from the bonding–antibonding combination of the 4p Cu and the $2\pi^*$ CO orbitals [19]. Indeed, a double-peak structure of the $2\pi^*$-derived states of CO/Cu(100) has been observed with IPE and was interpreted as the bonding–antibonding combination of the $2\pi^*$ CO orbital with the substrate sp continuum [21]. However, Tsuei and Johnson found that the two adsorbate-induced peaks show a different dispersion, indicating a different symmetry [22]. Based on tight binding calculations the authors assigned the peak at lower binding energy to the CO $2\pi^*$ level and the other structure to the ($n=0$) surface resonance shifted by the interaction with the CO 5σ level.

On Cu(111) we observe for the ordered CO-(1.4×1.4) overlayer a single unoccupied adsorbate-induced state. Taking advantage of the polarization of the laser light we show that this feature has indeed π-symmetry. Because of the sp-band gap along the Γ–L direction, the only unoccupied substrate orbitals that could resonantly interact with the $2\pi^*$ affinity level are 4 eV above E_F. We find no evidence for a splitting as proposed by the 2π-resonance model. This suggests that the CO bond results primarily from the interaction of CO $2\pi^*$ orbital with the *occupied* substrate orbitals of π-symmetry.

2. Experimental

The experiments were performed in an UHV chamber equipped with a retractable electron time-of-flight (TOF) spectrometer, combined LEED and Auger optics, an ion gun, and a quadrupole-mass spectrometer (see Fig. 1). The 6.4 eV and 3.5–4.0 eV output of an excimer or dye laser was used for one- and two-photon photoemission, respectively. Additional photon energies of 3.96 and 4.48 eV were generated by shifting the
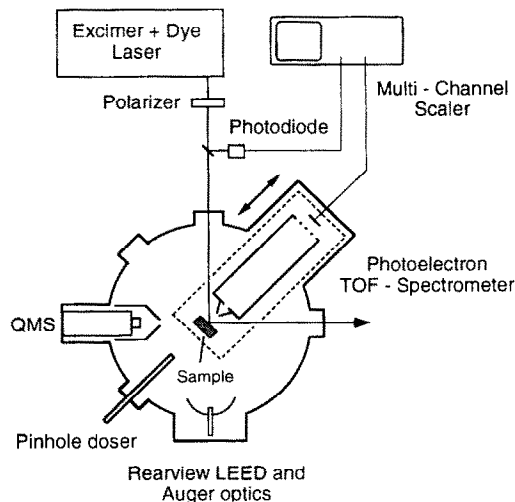

Fig. 1. Schematic overview of the experimental set-up. The polarized laser beam is incident upon the Cu(111) sample at 45° and exits the chamber through a second viewport. Photoelectrons are detected along the surface normal in an electrically and magnetically shielded time-of-flight (TOF) spectrometer. A fast photodiode serves as a trigger for the multi-channel counting electronics.

5.0 eV output of an excimer laser in a stimulated Raman process in H_2 gas [23]. If not otherwise noted, the polarized laser beam is incident on the sample under 45° with respect to the surface normal. For p-polarization (s-polarization) the electric field vector is parallel (perpendicular) to the plane of incidence. Photoemitted electrons are detected within $\pm 3.5°$ along the surface normal after drifting through the 300 mm field free region of the TOF spectrometer. The signal is recorded by counting electronics with 5 ns time resolution. The overall energy resolution is limited by the width of the laser pulses (<13 ns) and was estimated from the measured width of the Cu(111) surface state to be 180 meV at 2 eV kinetic energy. For 2PPE the laser fluence was kept below 5 mJ/cm² and by varying the laser fluence it was verified that the spectra were not distorted by space charge broadening.

The Cu(111) sample was mechanically polished and attached to a liquid nitrogen cooled manipulator. It could be cooled to ∼ 85 K and resistively heated to 770 K. The sample was cleaned by repeated cycles of Ar^+ ion sputtering, followed by annealing to 770 K. From the total width of the 2PPE spectra the work function was determined as $\Phi_{Cu(111)} = 4.85 \pm 0.1$ eV in agreement with other reports [10,13]. CO was dosed below 90 K up to saturation coverage ($\Delta\Phi_{CO} = -0.03$ eV
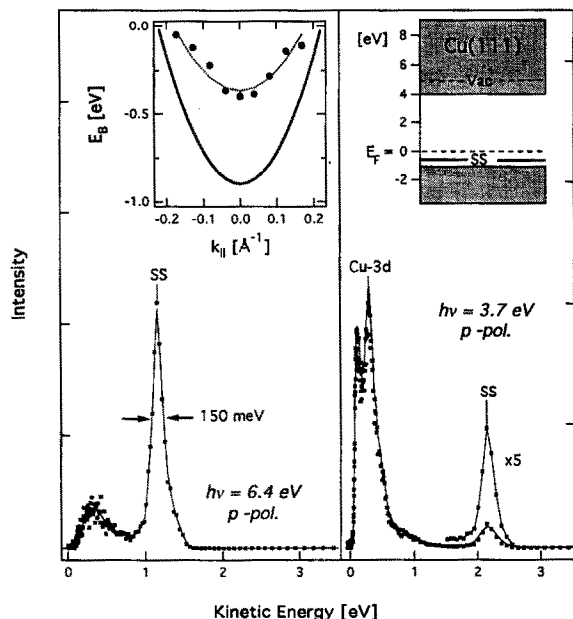
Fig. 2. Left panel: One-photon photoelectron spectra of Cu(111) recorded at $h\nu = 6.4$ eV photon energy with p-polarized light. The dominant peak at $E_{kin} = 1.15$ eV is due to emission from the occupied surface state (SS). The inset shows the $k_\parallel$ dispersion of the surface state (●) obtained with $h\nu = 6.4$ eV along $\bar{\Gamma}$–$\bar{K}$). The thick line indicates the bulk projected band gap. Right panel: Two-photon photoelectron spectra of Cu(111) obtained with $h\nu = 3.7$ eV. The signal from the surface state (SS) is multiplied by a factor of five. The inset shows the electronic structure of Cu(111) for $k_\parallel = 0$. The surface projected bulk bands are shown as shaded areas.

[24]) resulting in a (1.4×1.4) LEED pattern, as described previously [24]. All spectra were recorded at 85 K sample temperature and a pressure below 3×10^{-10} mbar.

3. Results and discussion

As a test of the performance of the TOF spectrometer the occupied ($n = 0$) surface state in the sp-gap of Cu(111) has been studied with one- and two-photon photoemission. At $\bar{\Gamma}$ this state is located 0.4 eV below E_F and disperses parabolically upward as the parallel momentum, $k_\parallel$, is increased [25]. An energy diagram of the electronic structure for $k_\parallel = 0$ is shown in Fig. 2 (inset). The left panel displays a kinetic energy spectrum for normal emission from the Cu(111) surface recorded with p-polarized light at 6.4 eV photon energy. The sharp peak at $E_{kin} = 1.15$ eV originates

from the surface state consistent with a binding energy of $h\nu - E_{kin} - \Phi_{Cu(111)} = -0.4$ eV with respect to E_F. The measured dispersion (see inset) is in agreement with the high resolution UPS work of Kevan [25]. We note that the emission from the surface state is completely quenched by CO adsorption (not shown). The right panel of Fig. 2 displays a 2PPE spectrum obtained with p-polarized light at $h\nu = 3.7$ eV. The peak at $E_{kin} = 2.15$ eV results from two-photon emission from the surface state. The peak at $E_{kin} = 0.3$ eV is attributed to 2PPE from the Cu d-bands. The presence of the sp-band gap suggests that a virtual state serves as an intermediate in the excitation process.

Fig. 3 (left panel) compares 2PPE spectra ($h\nu = 4$ eV) for the clean Cu(111) surface and after saturation with CO at 85 K. On the clean surface with s-polarized light no emission from the surface state is observed in accordance with the σ-symmetry of this state [26]. After adsorption of CO the emission from the d-bands is enhanced and a new peak appears at $E_{kin} = 2.4$ eV. Because this feature is observed for both s- and p-polarization a pure σ-symmetry can be ruled out. The intensity of the adsorbate-induced feature changes by a factor of two between s- and p-polarization. This ratio compares well with the squared ratio of the electrical
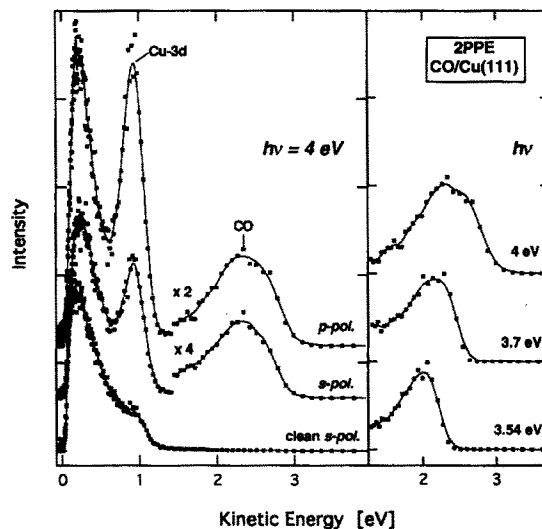

Fig. 3. Two-photon photoemission spectra from Cu(111) before and after saturation with CO (left panel). All spectra were recorded at $h\nu = 4.0$ eV with the same incident fluence. For $E_{kin} > 1.4$ eV the CO/Cu(111) spectra taken for p- and s-polarization have been multiplied by a factor of two and four, respectively. The dependence of the CO induced feature on photon energy is shown in the right panel.
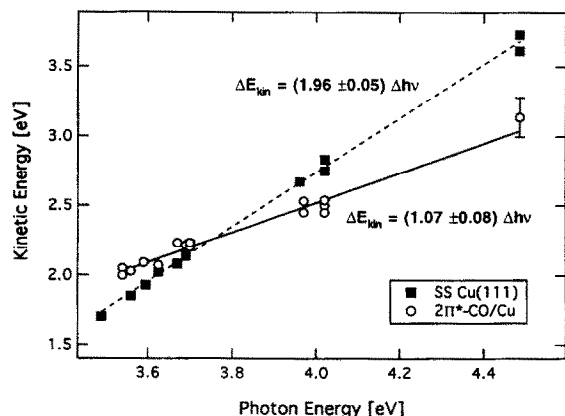
Fig. 4. Dependence of the kinetic energy of the Cu(111) surface state (■) and CO derived state (○) on the photon energy. The peak position of the adsorbate induced state (○) was determined by fitting the high energy side with a single Gaussian. The dashed and solid lines are a linear fit ($\Delta E_{kin} \approx \Delta h\nu$) to the data. In two-photon photoemission peak positions of occupied (unoccupied) states shift with twice (one times) the photon energy. The CO induced feature must, therefore, originate from an *unoccupied* state.

field intensities within the surface plane, $(\langle E_{p,x}^2 \rangle / \langle E_s^2 \rangle)^2 = 1.85$ [27]. A fact, which suggests that the component of the electric field normal to the surface plane, $\langle E_{p,z}^2 \rangle$ does not contribute in this 2PPE process. Two-photon excitation leading to the CO induced peak must, therefore, involve an intermediate state with predominately π-symmetry.

Two-photon photoemission probes both occupied as well as unoccupied electronic states. Starting from a fixed occupied state (like the sp-surface state) the kinetic energy of the final state will scale with twice the photon energy, i.e., $\Delta E_{kin} = 2 \cdot \Delta h\nu$, whereas for a fixed intermediate state, $\Delta E_{kin} = 1 \cdot \Delta h\nu$. In order to discriminate between occupied and unoccupied states we have compiled 2PPE spectra at various photon energies (see right panel of Fig. 3). The dependence of the surface state and the CO induced feature on photon energy is presented in Fig. 4 for $3.5 \leq h\nu \leq 4.5$ eV. As expected, the kinetic energy of the surface state varies as $\Delta E_{kin} = 2 \cdot \Delta h\nu$. The same dependence is found for the emission from the Cu d bands (not shown). However, for the adsorbate-induced peak we find a slope very close to one. We conclude that this feature results from an *unoccupied* CO derived state and because it has π-symmetry, it is assigned to the CO $2\pi^*$ affinity level [28].

From the data in Fig. 4 the binding energy of the CO $2\pi^*$ level is determined as 3.35 ± 0.1 eV above E_F. In

earlier inverse photoemission work with lower energy resolution, a single CO $2\pi^*$ derived peak has been reported approximately 4 eV above E_F with a half width of 1.7 eV [1,21]. In two-photon photoemission the CO $2\pi^*$ level is observed much closer to the Fermi level with a half width < 600 meV. In principle, binding energies obtained with 2PPE and IPE could differ because the final state is a system with $(n-1)$ or $(n+1)$ electrons, respectively. Interestingly, an oxygen induced peak on Cu(111) was observed 200 meV lower in energy with 2PPE [13] compared with IPE [29]. However, in view of the experimental errors and the small data basis obtained with 2PPE it seems too speculative to generalize these differences and to draw conclusions regarding the excitation process.

Having identified the $2\pi^*$ level of CO/Cu(111) it remains to consider the dispersion. At $h\nu = 3.7$ eV 2PPE spectra were recorded for various detection angles with respect to the surface normal. Fig. 5 shows the resulting $k_{\parallel}$ dependence for the emission from the surface state and the CO $2\pi^*$ level. The surface state exhibits the well-known upward dispersion [25] while for the CO $2\pi^*$ level no dispersion is observed for $|k_{\parallel}| < 0.4$ Å^{-1}. If we consider the dispersion of the occupied bands [30], the $k_{\parallel}$ range probed in the 2PPE experiment seems to be too small to establish the dis-
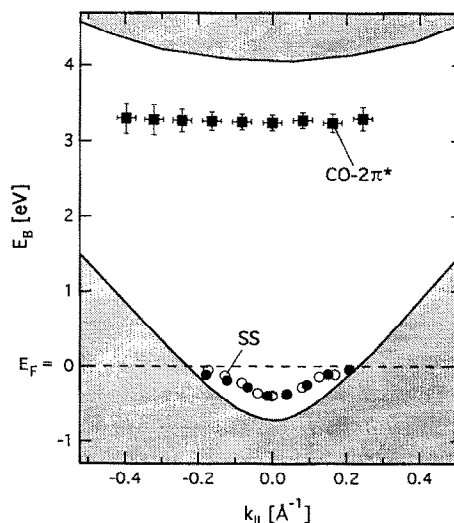

Fig. 5. $k_{\parallel}$ dispersion of the Cu(111) surface state (●) and the CO $2\pi^*$ level on Cu(111) (■) obtained at $h\nu = 3.7$ eV. No dispersion is found for the CO $2\pi^*$ level. In all measurements the sample is rotated along $\bar{\Gamma}$–$\bar{K}$. The data obtained with one-photon photoemission ($h\nu = 6.4$ eV) are shown for comparison (○).

persion for the whole surface Brillouin zone. Comparison with other compressed CO adsorption systems [31] and a theoretical analysis [32] suggests only a very modest dispersion at a CO–CO nearest neighbor distance of 3.6 Å in the CO-(1.4×1.4)/Cu(111) overlayer [33].

In summary, using nanosecond laser pulses we have demonstrated the versatility of two-photon photoemission to study excited states of molecular adsorbates. We have identified the unoccupied $2\pi^*$ derived level of CO adsorbed an Cu(111) located 3.35 ± 0.1 eV above E_F. In contrast to the splitting proposed in the 2π-resonance model [19], only a single CO derived level is resolved. This suggests that the CO $2\pi^*$ orbitals interact primarily with the *occupied* substrate orbitals of the appropriate symmetry. Our results are in agreement with IPE data for the CO/Cu(100) system, where the $2\pi^*$ derived level was assigned to a CO-induced peak 3.6 eV above E_F showing very little dispersion [22]. The second CO-induced feature on Cu(100), which was attributed to the ($n=0$) surface resonance, cannot be observed on Cu(111) since the ($n=0$) surface state is located below the Fermi level.

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