

Directly Probing the Hybrid Bonding of Styrene on Cu(111)

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When a molecule is chemisorbed on a metal surface, its electronic structure is significantly modified by interactions with the substrate electronic states. These interactions typically involve the low-lying unoccupied molecular orbitals (LUMOs) and high-lying occupied molecular orbitals (HOMOs) of the adsorbate and can be described theoretically in terms of hybridization with substrate bands. Experimental information on the electronic structures of these adsorbate–substrate complexes is of central importance for understanding chemical bonding and charge transfer at metal surfaces. Among the methods for probing the interfacial electronic structure between organic molecules and metal electrodes, two-photon photoemission (2PPE), the method we used, is attractive because both occupied levels lying below the Fermi level and, especially, unoccupied levels lying between the Fermi and vacuum levels can be interrogated in a single experiment.^{1–3}

Taking organic light-emitting diodes (OLED) and field-effect transistors (FET)⁴ as technologically important examples, electron injection from a metallic electrode into the lowest unoccupied molecular orbital (LUMO) of an organic overlayer is a critical step. The device performance is intimately related to the interfacial electron-transfer rate, a property determined by the adsorbate–substrate electronic interactions. Commonly used organic materials include poly(*p*-phenylene vinylene) (PPV) and its derivatives.⁴ Although Al and Mg/Ag are common electrodes in OLED devices, we chose Cu(111) and styrene (C₈H₈) to use in a model system for a surface science approach. From a 2PPE perspective, Cu(111) is a well-characterized metal and styrene has some chemical characteristics that model those of PPV. The approach is similar to that recently reported for benzene/Cu(111)⁵ and naphthalene/Cu(111).⁶ Compared to benzene and naphthalene, styrene molecules interact more strongly with Cu(111). The hybrid bonding and antibonding orbitals formed from copper (surface state and d-band orbitals) and styrene (π_1^* and π_2^* orbitals) are both, for the first time, directly probed.

Our experiments were performed in a two-level ultra-high-vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr.⁶ Styrene (C₈H₈, 99%, Aldrich) was used without further purification except for removal of dissolved gases with several freeze–pump–thaw cycles. The exposures are given in units of monolayer (ML), which is defined by saturation of the styrene temperature-programmed desorption (TPD) peak at 278 K.⁷ Except as indicated, experiments were performed with unpolarized light. A styrene-covered surface was irradiated under several different wavelengths for 30 min, with no evidence of laser-induced changes.

The 2PPE spectrum of clean Cu(111) at 90 K is shown in Figure 1a (bottom), plotted as 2PPE intensity versus final kinetic energy relative to the Fermi level. The spectrum contains four main features: a secondary electron onset (the vacuum energy edge), Cu d-band peak, the peak of the Cu(111) surface state (SS), and the Fermi edge. Figure 1a (top) displays the 2PPE spectrum of 0.7 ML styrene adsorbed on the Cu(111) surface. The spectra are

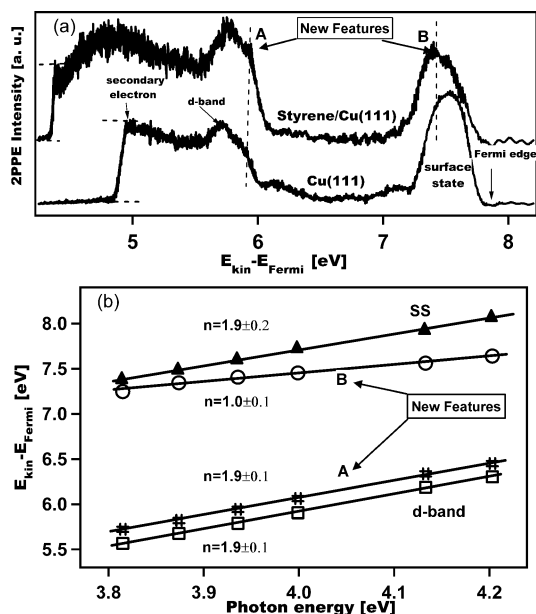


Figure 1. (a) 2PPE spectra of clean Cu(111) (bottom) and 0.7 ML styrene-covered Cu(111) (top) with $h\nu = 3.94$ eV at 90 K. The spectra are normalized at their low-energy cutoffs, where the 2PPE signal is dominated by secondary electrons,⁸ as indicated in Figure 1a. The surface state intensity is suppressed due to the presence of chemisorbed styrene. Two new features appear clearly, at 5.9 eV (A) and 7.4 eV (B). (b) Photon energy dependence of the surface state (SS), the d-band, and the styrene-induced features, A and B.

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In 2PPE spectroscopy, the kinetic energy of photoelectrons varies with the photon energy as

$$\Delta E_{\text{kin}} = 2\Delta h\nu \quad (1)$$

if a transition starts from a fixed occupied state, or

$$\Delta E_{\text{kin}} = \Delta h\nu \quad (2)$$

if photoelectrons are emitted from a fixed intermediate state. Thus, we can discriminate between the two processes by measuring 2PPE spectra at various photon energies.

Figure 1b shows the photon energy dependence of the peak energies of the surface state, the d-band of Cu(111), and styrene-induced features (A and B). The result from A fits to a line with a slope of 2, as do the surface state and the d-band. We attribute A to emission from an occupied state lying below the Fermi level. Extrapolating the fitted line to $h\nu = 0$ eV provides the energy and location of this state— 2.0 ± 0.1 eV below the Fermi level. For B, the kinetic energies vary as $\Delta h\nu$, indicating that this transition

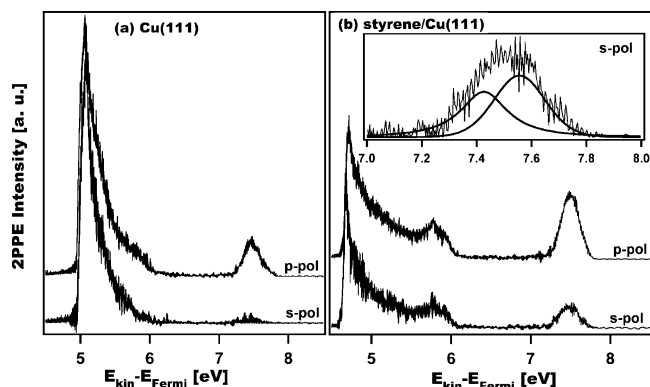


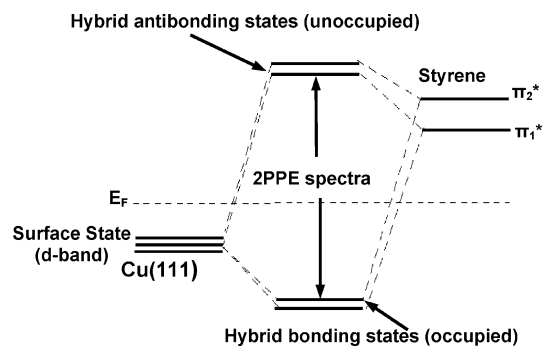
Figure 2. Polarization dependence of 2PPE spectra of clean Cu(111) (a) and 0.2 ML styrene-covered Cu(111) (b). Inset in (b) shows that the styrene-induced feature B contains two components. The two solid curves represent a decomposition into two peaks that give a reasonable fit to the measured curve.

involves an unoccupied intermediate state with an energy lying 3.5 ± 0.1 eV above the Fermi level.

The symmetry of feature B (the unoccupied state) can be deduced from the polarization dependence of the 2PPE intensity. Figure 2b shows 2PPE spectra of 0.2 ML styrene-covered Cu(111) at normal emission with p-polarized (top) and s-polarized (bottom) laser light, respectively. Since intensity in state B is observed for both p- and s-polarized light, an intermediate state with π -symmetry must be involved; observation of intensity along the surface normal for both s- and p-polarized light requires that the component of the electric field parallel to the surface plane contributes in the 2PPE process. This intermediate state cannot be a surface state, since it has σ -symmetry. This is demonstrated in Figure 2a, where the 2PPE signal from the surface state drops almost to zero when we switch from p- to s-polarization. Similar observations are well-established for the image potential states on metal surfaces.^{5,8} We conclude that feature B is dominated by contribution not from states associated with Cu(111), but from the π^* molecular orbital(s) of adsorbed styrene.

The electronic structure of a molecule is a unique fingerprint of its chemical state. Information regarding the nature of the bonding between the adsorbate and a metal substrate can be derived from the changes in the electronic structure upon adsorption.⁹ For example, if the molecules physisorb, the molecular orbitals of the adsorbate undergo a uniform relaxation shift (Coulomb relaxation) toward lower binding energies; this is attributed mainly to extramolecular screening by the substrate (a final-state effect) within the adsorbate layer. For chemisorbed molecules, an additional differential energy shift of one or several molecular orbitals is observed, which reflects the participation of these orbitals in the chemical bond to the substrate (an initial-state effect). The inset of Figure 2b shows that feature B, which is observed for s-polarized light, can be resolved into two components. Regardless of the fitting procedure, the energy difference between these two components cannot be more than 0.2 eV. Our energy resolution is about 60 meV, as determined by fitting the low-energy cutoff with a Gaussian apparatus function.¹⁰ This 0.2 eV difference is much smaller than

Scheme 1



the gas-phase spacing (0.8 eV) between the two lowest unoccupied orbitals of styrene, ${}^2B_1(\pi_1^*)$ and ${}^2A_2(\pi_2^*)$,¹¹ determined using electron transmission spectroscopy. This indicates that styrene chemically interacts with Cu(111).

We assign feature A to an occupied state at 2.0 eV below the Fermi level. It also can be resolved into two components, differing in energy by less than 0.2 eV. These states are not from the HOMO(s) of styrene that are located 4.0 eV below the Fermi level.¹² We conclude that they originate either from the copper bulk or from occupied states located at the surface that have predominantly metal character.

Following the above discussion, Scheme 1 is an energy level model for the bonding of styrene adsorbed on Cu(111). In this model, the two lowest unoccupied molecular orbitals (π_1^* and π_2^*) of styrene are strongly coupled with the surface state and d-band orbitals of Cu(111) to form occupied states 2.0 eV below the Fermi level and unoccupied states 3.5 eV above the Fermi level.

In summary, the interfacial electronic structure of chemisorbed styrene on Cu(111) was successfully investigated with two-photon photoemission spectroscopy. We observed unoccupied states 3.5 eV above the Fermi level and occupied states 2.0 eV below the Fermi level. Polarization results reveal that the occupied and unoccupied states arise from bonding and antibonding orbitals formed by hybridization of copper (surface state and d-band orbitals) and styrene (π_1^* and π_2^* orbitals).

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References

- (1) Petek, H.; Ogawa, S. *Prog. Surf. Sci.* **1997**, *56*, 239.
- (2) Zhu, X.-Y. *Annu. Rev. Phys. Chem.* **2002**, *53*, 221.
- (3) Petek, H.; Ogawa, S. *Annu. Rev. Phys. Chem.* **2002**, *53*, 507.
- (4) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10* (7), 1471.
- (5) Velic, D.; Hotzel, A.; Wolf, M.; Ertl, G. *J. Chem. Phys.* **1998**, *109*, 9155.
- (6) Zhao, W.; Wei, W.; White, J. M. *Surf. Sci.* **2003**, *547*, 374.
- (7) Wei, W.; Zhao, W.; White, J. M., in preparation.
- (8) Wolf, M.; Hotzel, A.; Knoesel, E.; Velic, S. *Phys. Rev. B* **1999**, *59*, 5926.
- (9) Sternrück, H.-P. *J. Phys. Condens. Matter* **1996**, *8*, 6465.
- (10) Schupper, S.; Fischer, N.; Fauster, Th.; Steinmann, W. *Appl. Phys. A* **1990**, *51*, 322.
- (11) Burrow, P. D.; Michejda, J. A.; Jordan, K. D. *J. Chem. Phys.* **1987**, *86* (1), 9.
- (12) Ranke, W.; Weiss, W. *Surf. Sci.* **2000**, *465*, 317.

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