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Orientation dependence of charge transfer for C₆₀ on Cu(100)

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Scanning tunneling microscopy was used to characterize the lowest unoccupied molecular orbitals (LUMO), up to LUMO+3, of individual C_{60} molecules within monolayer films on Cu(100). On this surface C_{60} orients in four distinct configurations with respect to the substrate. Tunneling spectroscopy and spectroscopic imaging were used to identify the energies and spatial distributions of the molecular orbitals. We find that the LUMO shifts by ~200 meV depending on the orientation of the molecule, which suggests charge transfer between the surface and molecule is orientation dependent. Orientation-dependent shifts were also observed for the higher unoccupied molecular orbitals. © 2011 American Institute of Physics. [doi:10.1063/1.3569719]

Since their discovery in 1985, C_{60} fullerenes have been extensively used in a variety of devices including diodes, transistors, and solar cells. As with traditional semiconductor devices, the successful implementation of organometallic device architectures requires understanding and engineering of the interface to electrodes. Precise knowledge of nanoscale morphology, molecule/metal band alignments, and interfacial charge transfer is necessary. For example, hole injection in organic heterostructures has been enhanced by a C_{60} interlayer which favorably alters the energy bands of the hole transporting layer relative to the electrode Fermi energy.¹

Scanning tunneling microscopy (STM) has contributed to the understanding of the molecular orientations and local electronic structure of C₆₀ on a variety of metal and semiconductor surfaces. For example, the highest occupied molecular orbital (MO), lowest unoccupied MO (LUMO) as well as the next LUMO (LUMO+1) have been measured, with respect to the Fermi level of the substrate, for C_{60} on Ag,² Au,³ and Al⁴ as well as different surface orientations such as Cu(111)⁵ and Cu(100).⁶ Perhaps due to limited tip stability and dynamic range of STM current amplifiers, there have been few studies of the MOs at higher energies (i.e., LUMO+2, +3 etc.).⁶ The alignment of such orbitals with unoccupied bands in the respect to metal substrate influences, for example, photoinduced electron transfer.

Here we present an STM study of individual C_{60} molecules, which adopt one of four orientations within monolayer-thick films on Cu(100). Tunneling spectroscopy reveals peaks associated with unoccupied MOs up to LUMO+3. We find that the LUMO varies by ~0.2 eV for different molecules in the film, indicating that charge transfer depends on the molecular orientation. We also observe variation in the peak positions for the LUMO+1, +2, and +3 states, which may reflect a spatially dependent overlap of the MOs with the underlying copper lattice. Spatial maps of the local density of states (LDOS) associated with the unoccupied MOs compare well to available calculations.

Data were collected using a Createc LT-STM at 5.3 K in ultrahigh vacuum ($<1 \times 10^{-10}$ mbar). The Cu(100) sample was cleaned with cycles of Ar⁺ sputtering and annealing to 550 °C. An average C₆₀ coverage of ~0.5 monolayers was

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achieved by 2 min of thermal evaporation from an alumina crucible onto the sample at room temperature, followed by 1 min of annealing at 330 °C. Data were collected using a cut Ir tip prepared with in situ field emission, voltage pulses, and controlled contact with the surface. To characterize the electronic states of C₆₀, we employed two tunneling spectroscopy modes. In "constant height" mode, the STM feedback was turned off, and the tunnel current, I, was recorded as a function of voltage V. The differential conductance, $dI/dV|_{Z}$, was measured by lock-in amplifier detection of the ac tunnel current induced by adding a 5 mV_{rms} , 855 Hz modulation to the voltage. At low voltages, $dI/dV|_Z$ is proportional to the convolved tip and sample LDOS. To resolve the local electronic structure of C₆₀ over a larger voltage range, we also employed a "constant current" mode, where the STM feedback loop maintains a constant current by varying the tunneling gap as the voltage is varied.⁸ This mode also allowed us to spatially map the density of states at a fixed energy by simultaneously recording the lock-in signal as the tip was scanned. Because the large electric field in the tunnel junction may change the tip's termination or the molecular film, we regularly checked tunneling spectra and images to avoid possible artifacts.

Figure 1(a) shows an STM image of a monolayer-thick island of C_{60} ; bright and dim stripes appear oriented along



FIG. 1. (Color online) STM images of C_{60} on Cu(100) (a) Large scale image illustrating the characteristic bright and dark rows. (2.25 V, 500 pA). (b) Ball and stick representations of four orientations on Cu(100). (c) High resolution STM image. Color and filtering were applied to emphasize contrast. (1.5 V, 300 pA).



FIG. 2. (Color online) Spectroscopy and imaging of unoccupied MOs. (a) Tunneling spectroscopy showing peaks from LUMO up to LUMO+3. dI/dV data for V < 1 V are taken at constant tip height (2.25 V, 300 pA). dI/dV data for V > 1 V are taken at constant current (300 pA). (b) STM image of the pentagon orientation (1.5 V, 300 pA). (c) Constant height dI/dV spectra taken at the points indicated in (b). (d) Spatial map of dI/dV corresponding to the LUMO+1 (1.59 V, 300 pA, modulation 20 mV_{rms}).

the [011] or [011] directions which are attributed to a missing row reconstruction of the underlying Cu surface.^{2,9} Bright molecules bridge a single missing row of Cu while dark molecules bridge two missing rows. In addition to this structure, Schull et al. has previously reported four distinct orientations of C₆₀ on Cu(100).⁶ The orientations are characterized by the molecular feature closest to surface (and by symmetry, the tip): 5:6 bond (i.e., the bond between a pentagon and hexagon), 6:6 bond, hexagon ring, and pentagon ring [Figs. 1(b) and 1(c)]. We find the dark rows contain the pentagon and hexagon orientations while the bright rows contain the 6:6 and 5:6 orientations. An understanding of the origin and ordering of the four orientations on Cu(100) requires further experimental studies (such as predeposition and postdeposition temperature dependence) and density functional theory calculations to determine the adsorption energetics. We note that STM studies at temperatures above 100 K do not show clear evidence for these multiple orientations.¹⁰ On other surfaces, charge transfer, surface reconstruction, and strong intermolecular interactions are thought to contribute.^{11–15}

The differential conductance spectra in Fig. 2(a) show a series of peaks corresponding to unoccupied MOs of C₆₀. The LUMO is assigned to the first peak above the Fermi energy $(E_F=0V)$; subsequent peaks are assigned to higher MOs: LUMO+1, LUMO+2, and LUMO+3. Upon absorption, charge is transferred from the metal surface to the electron affine C₆₀, partially occupying the LUMO. It is generally thought that proximity of the LUMO to $E_{\rm F}$, which is closer for metals with smaller work functions,¹⁶ correlates with greater charge transfer. For example, prior STM studies of C_{60} on Au(111) [ϕ =5.4 eV (Ref. 17)] and Cu(100) [ϕ =4.6 eV (Ref. 18)] show LUMO peaks at 1 eV (Ref. 3) and 0.4 eV^6 , respectively. Averaged across orientations of C₆₀ on Cu(100), we find a LUMO peak at 0.37 V, consistent with prior STM studies.⁶ Based on this peak position, we conclude that the magnitude of charge transfer from the Cu(100)surface to C_{60} is larger than from Au(111).

Averaged across orientations, we observe the higher LUMO+1,+2,+3 at 1.57 V, 3.02 V, and 3.69 V, respectively. Our STM measurement of the higher lying unoccupied MOs is in qualitative agreement with inverse photoemission data¹⁹ for multilayer C_{60} on Cu(100). A quantitative comparison

TABLE I. Peak positions of the unoccupied MOs.

Orientation	LUMO (eV)	LUMO+1 (eV)	LUMO+2 (eV)	LUMO+3 (eV)
Hexagon	0.34	1.60	3.11	3.80
Pentagon	0.49	1.63	2.94	3.75
5:6 bond	0.34	1.57	3.07	3.60
6:6 bond	0.29	1.58	2.94	3.60
Average	0.37	1.57	3.02	3.69
Literature (avg) ^a	0.43	1.71		

^aReference 6.

with this study is difficult due to the different coverage regimes studied. It is known that MO energies shift for multilayer coverages since the second and higher layers are partially decoupled from the interface.²⁰

Closer inspection of Fig. 2(a) indicates that MO peak positions vary with molecular orientation. To quantify these variations, we must first study the dependence of tunneling spectra on the tip's position over the molecule.^{2,3} We measured $dI/dV|_{Z}$ (for the LUMO and LUMO+1 states) and $dI/dV|_I$ (for the LUMO+2,+3) at up to 13 spatially distinct points for each molecular orientation. Figures 2(b)-2(d)show data for the LUMO+1 of pentagon-down C_{60} . As spectra are taken at different locations on the molecule [e.g., colored points in Fig. 2(b)], MO peak positions may vary by up to 0.2 eV [e.g., Fig. 2(c)], comparable to or larger than variations due to different orientations. While these position dependent shifts have been attributed to the tip induced electric field,²¹ Grobis *et al.* observed no shifts in MO energies when systematically changing the local field by varying the tunneling gap distance.² Variation in dI/dV spectra with tip position over the C₆₀ molecule may instead reflect a superposition of MO's with underlying copper states, MO overlap (particularly for the closely spaced LUMO+2,+3) or perhaps spatial variation in electron-phonon coupling.⁴

Therefore, in assigning a specific voltage for each MO peak, we believe it is important to first locate the tip to maximize the associated LDOS. In Fig. 2(c), for example, the LUMO+1 for the pentagon-down orientation has maximum LDOS at the edges of the molecule, rather than at the center. We confirm this spatial variation by also acquiring spatial maps of dI/dV for each MO, such as in Fig. 2(d) for the LUMO+1. The bright regions in this map indicate maximum LDOS near the edges, while the dark region corresponding to minimum LDOS occurs at the center. We thus report in Table I the peak voltage with the tip positioned at the edge [e.g., blue curve in Fig. 2(c)] for the LUMO+1 of the pentagon-down orientation.

Figure 3 shows similar dI/dV maps up to LUMO+3 for the four orientations observed on Cu(100). The spectra in Fig. 2(a) were acquired with the tip positioned to maximize each MO resonance, consistent with these spatial maps. Table I summarizes the extracted MO peak voltages up to LUMO+3 for each orientation. The LUMO peak positions vary by 150 meV with orientation, suggesting some sensitivity of charge transfer to molecular orientation. Prior STM measurements by Schull *et al.* showed approximately 40 meV variations with orientation, but these data were collected at the molecular center, where the LUMO may have low LDOS.⁶ Based on the proposed missing row reconstruction of the underlying Cu surface,^{6,9} the 5:6 and 6:6 orienta-



FIG. 3. (Color online) Spatial mapping of the unoccupied MOs. (a) STM topographic images (2.25 V, 300 pA) of the four orientations. [(b)-(e)] Spatial maps of dI/dV, taken at the noted voltages (300 pA, 20 mV_{rms}). For optimal visualization of the orbitals, the images have been Gaussian filtered and have independent color scales. Blue (pink) corresponds to low (high) LDOS. All images are 11 Å in diameter.

tions are closer to Cu atoms, and thus, we expect a greater degree of charge transfer to the molecule. The two ring-down orientations are further from the Cu atoms, and thus, we expect a lesser degree of charge transfer. This is qualitatively consistent with the relative LUMO peak positions shown in Table I. The two bond-down orientations have LUMO peaks which are closest to $E_{\rm F}$ while the two ring-down orientations have LUMO peaks shifted away from $E_{\rm F}$.

Table I shows that the LUMO+1, +2, and +3 resonances vary with orientation by ~ 0.06 eV, 0.17 eV, and 0.20 eV, respectively. However, we find no consistent trend in order of the orientational shift. This indicates that charge transfer does not rigidly shift the ladder of higher lying MOs, but rather, each MO shifts independently. These shifts may arise from varying degrees of MO overlap with Cu atoms for different orientations. Another possibility is that charge transfer to the molecule causes slight deformations which alter the MO spectrum and is different for each orientation.

The dI/dV maps in Fig. 3 compare well with published STM results^{2,6,23} (available up to LUMO+2) and with calculated images^{21,24} on other substrates. Additionally, the data reveal an alternating even/odd parity of the MOs. For example, while maximum LDOS for the LUMO and LUMO +2 is found near the center of the pentagon-down orientation, this corresponds to minimum LDOS for the LUMO +1 and LUMO+3. A similar even/odd character is evident for the MOs of molecules in the other orientations. We note that in addition to MO states, delocalized "superatom MOs (SAMOs)" may be present in C₆₀ films on metal substrates.²⁵ Previous STM studies of C₆₀ on Cu(111) showed a lack of

intramolecular contrast at voltages corresponding to these SAMOs.^{25,26} We do not observe a clear loss of intramolecular contrast for any dI/dV maps within the range 3.38–5.01 V for C₆₀ on Cu(100). However, we do observe weakened contrast along C₆₀ rows, especially near the LUMO+3 voltage for the 6:6 and hexagon-down orientations, which could reflect some coupling to SAMOs.

In conclusion, we have studied the energy and spatial distribution of unoccupied MOs for C_{60} on Cu(100). The variation in LUMO energy with orientation suggests that different degrees of charge transfer contribute to the adsorption energetics for the four orientations. We hope that this study will motivate further theoretical work on the orientational dependence of the MOs of as well as the higher lying LUMO states of C_{60} on surfaces.

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