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Spectroscopic STM studies of single pentacene molecules on Cu(110)-c(6 × 2)O

Johannes Gall, Peter Zeppenfeld, and Lidong Sun[*]
Institute of Experimental Physics, Johannes Kepler University Linz, A-4040 Linz, Austria

Li Zhang, Yang Luo, and Zhenchao Dong
Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, 230026 Hefei, China

Chunguang Hu
State Key Laboratory of Precision Measuring Technology and Instruments, Tianjin University, Weijin Road, 300072 Tianjin, China

Peter Puschnig[†]
Institute of Physics, Karl-Franzens-University Graz, NAWI-Graz, A-8010 Graz, Austria

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Pentacene adsorbed on the Cu(110)-c(6 × 2)O surface has been investigated using scanning tunneling microscopy and spectroscopy and density functional theory calculations. The molecules lie almost flat on the surface and are anchored via the end carbon ring to a Cu atom of the topmost surface layer, leading to a break of the mirror symmetry of pentacene parallel to the short molecular axis. As a result the molecular electronic structure of the frontier orbitals exhibits a local and gentle modification around the anchoring site but is essentially unaffected in the remaining part of the molecule. The enhancement of the conductance peak related to the second highest occupied molecular orbital (HOMO-2) at the anchoring site, however, is suggestive of a resonance with a surface state or with the Cu *d*-band.

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I. INTRODUCTION

The investigation of the electronic structure of molecules and the corresponding modification upon their interactions with surfaces, molecules, and adatoms at submolecular resolution is essential for the fundamental understanding of single-molecule chemistry [1,2] and the realization of single-molecule devices [3]. In recent years, it has been demonstrated that scanning tunneling microscopy and spectroscopy (STM/STS) can be used to image the molecular orbitals (MOs) of adsorbed molecules [4–7]. The extremely localized tunneling current of the STM allows us to selectively excite vibrational modes of single molecules [8] and molecular luminescence [4,7,9]. Furthermore, in combination with its capability for controlled manipulation of molecules, STM has also been applied to unravel the bond formation between molecules and adatoms with submolecular resolution [2,10]. In order to probe the intrinsic electronic structure of individual molecules adsorbed on metal surfaces with STS, it is essential to decouple, electronically, the MOs from the substrate states. One of the most widely used approaches is to introduce an ultrathin insulating layer between the metal surface and the organic molecules [4,5,11]. Reduced coupling has also been observed between the MOs of organic molecules and the electronic states of bare noble metal surfaces [6,12,13]. Most recently, it has been demonstrated that surface reconstructions induced by atomic oxygen [14] and nitrogen [15] adsorption on noble metal surfaces can efficiently separate the overlap between the MOs and the substrate electronic states.

Until now, most of the STS measurements of MOs were carried out on smooth surfaces with relatively small lattice constants in comparison with the lateral distribution of the delocalized π electrons of the adsorbed organic molecules. For such a case, the influence of the surface corrugation on the intramolecular electronic structure of the individual molecules is not pronounced. On the other hand, for the fundamental understanding of surface adsorption and surface catalysis, it is very interesting to study the possible local modification of the molecular electronic structure upon adsorption on the surface. In this context, we will show that the Cu(110)-c(6 × 2)O surface, obtained after oxygen adsorption and reconstruction of a Cu single crystal [16,17], provides a very weak electronic coupling to the molecules, while at the same time, the binding of the molecules is strong enough to allow STS measurements over a very large energy range. Most importantly, the large unit cell (15.3 Å × 7.2 Å) of the Cu(110)-c(6 × 2)O surface offers an opportunity to investigate the modification of the intramolecular electronic structure as a function of the local atomic structure of the surface. Using combined STM/STS images with submolecular resolution and density function theory (DFT) calculations, we demonstrate that a bending of the carbon backbone of the pentacene (PEN) molecule over the top-layer Cu atom yields a pear-shaped protrusion in the topographic STM images. While the frontier orbitals (highest occupied molecular orbital [HOMO] and lowest unoccupied molecular orbital [LUMO], respectively) are only slightly affected upon adsorption, the HOMO-2 orbital shows a resonance with substrate electronic states located at the anchoring site.

II. EXPERIMENTAL AND THEORETICAL

All experiments were conducted in an ultra-high-vacuum (UHV) environment with a base pressure of less than 1×10^{-10} mbar. The clean Cu(110) surface was prepared by

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[*] Corresponding author: lidong.sun@jku.at

[†] Corresponding author: peter.puschnig@uni-graz.at

several cycles of 900-eV Ar$^+$-ion bombardment and subsequent annealing at 800 K for 5 min. The Cu(110)-c(6×2)O reconstruction was formed by exposing the freshly cleaned Cu(110) surface to about 10^4 L molecular oxygen at room temperature. The preparation was completed by briefly flashing the sample to 550 K. The so-obtained substrate is highly corrugated and features well-separated top-layer Cu atoms in a quasihexagonal arrangement. These top-layer atoms (also termed "super" Cu atoms) slightly stick out of the surrounding Cu-O layer, forming active binding sites for the adsorption of organic molecules [16,17]. The PEN molecules were thermally evaporated out of an organic molecular beam epitaxy (OMBE) source. During deposition, the substrate was kept at room temperature. The STM measurements were carried out with a UNISOKU low-temperature STM working at liquid helium temperature (5 K).

All theoretical results presented here are obtained within the framework of density functional theory (DFT) using the VASP code [18,19] utilizing the projector augmented wave (PAW) method [20]. Calculations for PEN/Cu(110)-c(6×2)O are performed within the repeated slab approach by using five metallic layers with an additional vacuum layer of 15 Å between slabs. To avoid spurious electrical fields, a dipole layer is inserted in the vacuum region [21]. For PEN adsorption, we have assumed the commensurate structure described by the matrix (4; 0/1; 9) with respect to the bare Cu(110) substrate in [001] and [1$\bar{1}$0] directions. This leads to a unit cell containing 36 Cu atoms per layer in the subsurface layers and 30 Cu and 24 O atoms in the reconstructed topmost substrate layer. Geometry relaxations were conducted using a generalized gradient approximation (GGA) exchange-correlation functional [22] and empirical van der Waals corrections according to Grimme [23], while for the subsequent analysis of the density of states, the hybrid functional according to Heyd, Scuseria, and Ernzerhof (HSE) [24] has been used. Simulated STM images are obtained within the Tersoff-Hamann approximation [25].

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows a topographic STM image of the sample surface after deposition of about 0.1 ML of PEN. The PEN molecules appear as pear-shaped protrusions, where one end of the molecule directly resides over a super Cu atom. This can be seen in greater detail in Fig. 1(b), where a topographic STM image of a single molecule is overlaid with the underlying substrate lattice (each crossing point of two lines marks the position of a super Cu atom). Based on the shape, size, and orientation of the protrusion, we have performed DFT calculations of PEN/Cu(110)-c(6×2)O with the molecule oriented along the [1$\bar{1}$0] direction. We have placed the PEN molecule at various relative positions with respect to the super Cu atom and locally relaxed the structure. The structure depicted in Fig. 1(c) turned out to the energetically most favorable one. It should also be mentioned that its corresponding simulated constant-current STM image also compared best to the experimental observations. Here, we colored the Cu atoms of the subsurface in gray and show the Cu atoms of the topmost layer in orange, where the darker color is used to distinguish the super Cu atoms of the topmost layer, which are sticking out by ~0.5 Å with respect to the other Cu atoms (lighter orange). Oxygen atoms are displayed as blue spheres, while the C atoms of the PEN molecule are depicted as small red spheres. We find that PEN prefers to adsorb parallel to the [001] axis with one end ring centered above a super Cu atom such that the remaining carbon backbone rests in the trough between the two neighboring top-layer Cu atoms. Note that we have tested various adsorption positions. For instance, the adsorption site with the last but one PEN ring centered above the super Cu atom has led to a 60-meV weaker adsorption energy.

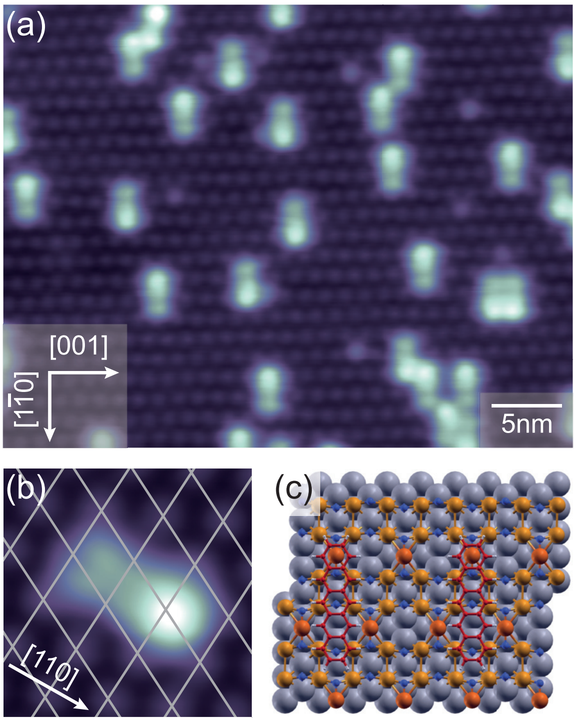

FIG. 1. (a) Overview topographic STM image of the Cu(110)-c(6×2)O surface after deposition of PEN molecules. Two equivalent configurations of adsorbed PEN molecules can be found, in which one end (the top or bottom end) of the molecule lies on top of a super Cu atom. (b) STM image of a single molecule with an overlay of the substrate lattice. (c) Proposed adsorption model showing the super Cu atoms (orange spheres) and one of the two equivalent adsorption geometries of the PEN molecules. Tunneling parameters: $I_{\text{set}} = 50\,\text{pA}$, $V_{\text{bias}} = -1\,\text{V}$; (b) $I_{\text{set}} = 50\,\text{pA}$, $V_{\text{bias}} = -2\,\text{V}$.

In Fig. 2(a), differential conductance (dI/dV) spectra of a single PEN molecule at different tip positions along the molecule are shown. In the spectra we can identify four distinct peaks at 1.3, −1.1, −1.6, and −2.6 V, which can be assigned to the LUMO, HOMO, HOMO-1, and HOMO-2 molecular orbital energies, respectively. These energy positions coincide surprisingly well with those reported by Soe *et al.* for PEN molecules on Au(111) [6]. Only slight differences of the peak positions of the order of ±0.1 V can be observed. The dI/dV spectra show rather sharp, well-defined features which are usually not observed in this quality on metal substrates [6]. Indeed, such sharp features could only be observed for molecules adsorbed on insulating films so far [5]; however, differential conductance spectra have shown a very strongly shifted HOMO resonance compared to our result. This may

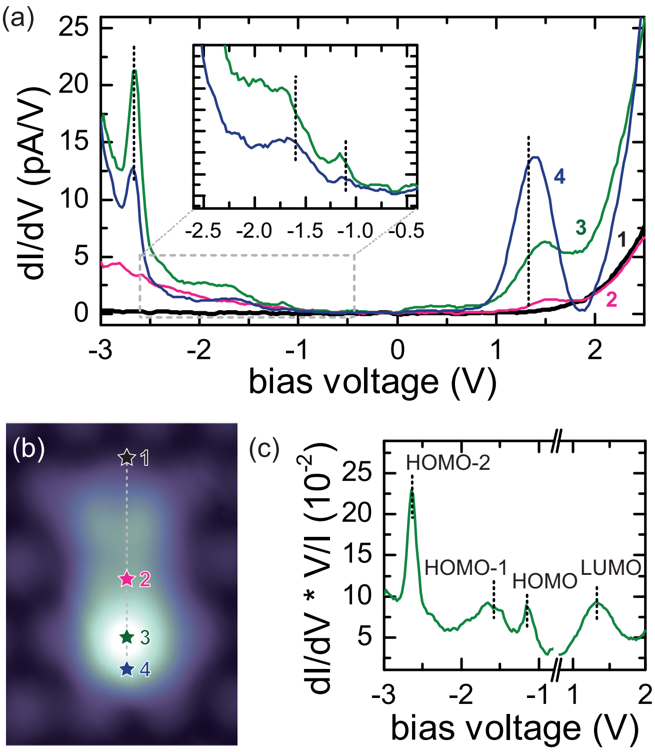

FIG. 2. (a) dI/dV spectra recorded at different tip positions as indicated in panel (b). The spectra are color coded and numbered according to the tip position at which they were acquired. The tip position 1 is directly above an uncovered super Cu atom, whereas the other three tip positions are above the PEN molecule. Four conductance peaks can be discerned, in the spectra taken above the PEN molecule, which can be attributed to resonances of the molecular orbitals: LUMO, HOMO, HOMO-1, and HOMO-2. (b) Topographic STM image of a single PEN molecule adsorbed on the Cu(110)-c(6 × 2)O surface. (c) dI/dV spectrum at tip position 3 from (a), normalized by I/V.

be due to the large band gap of the decoupling layer resulting in weaker polarization shifts of the frontier orbitals [26,27] when compared to our substrate. Besides, usually no more than the HOMO resonance can be observed, as tunneling at too high bias voltages reportedly leads to a decomposition of the molecules [5]. The surprisingly good agreement of the molecular orbital energy levels as compared to those found for PEN on Au(111) stems from the similarity of the work functions. The work function of Cu(110) ($\Phi_{Cu(110)} = 4.5$ eV) increases by $\Delta\Phi_{CuO} = 0.65$ eV upon oxidization [28], resulting in a value close to that of Au(111) ($\Phi_{Au(111)} = 5.35$ eV).

As evidenced in Fig. 2, a clear, asymmetric spatial variation of the molecular resonances across the molecule can be discerned. While at the end of the molecule (tip position 4) contributions from the LUMO resonance dominate, we can find an increased probability for tunneling into the occupied HOMO-2 orbital on top of the bright lobe (tip position 3). As it will become clear later, this can be correlated with a corresponding dark/bright contrast in the dI/dV map at this specific bias voltage. In Fig. 2(c), the dI/dV spectrum 3 recorded on top of the bright lobe is shown after normalization by I/V. This normalization tends to reflect the actual local density of states (LDOS) at higher bias voltages more closely than the bare dI/dV spectrum [29]. Indeed, the intensity differences between the LUMO, HOMO, and HOMO-1 resonances disappear, whereas the HOMO-2 resonance is still very pronounced and sharp.

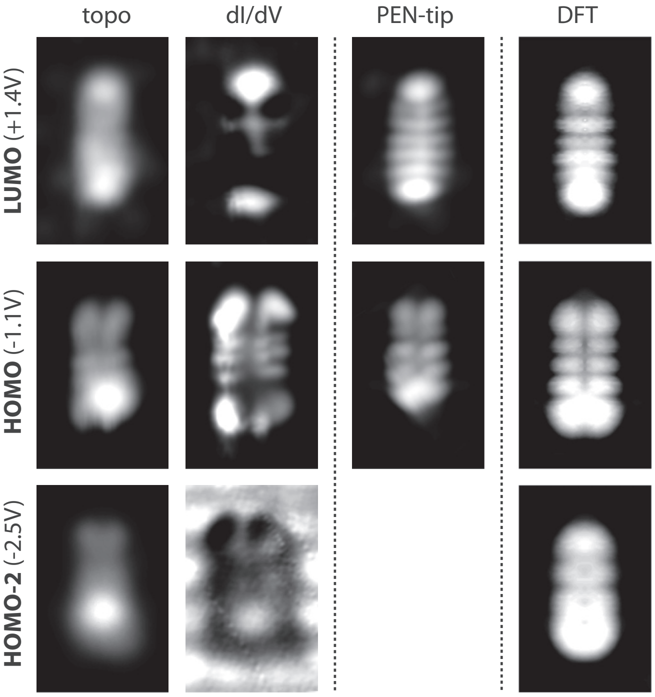

FIG. 3. Left column: topographic STM images of a single adsorbed PEN molecule at different bias voltages. Each row corresponds to a bias voltage related to a specific molecular orbital. The second column shows the respective differential conductance (dI/dV) maps, and in the third column, again topographic STM images are shown, but with a PEN-modified tip (PEN molecule at the tip apex; see text for details). The last column depicts theoretically predicted STM images, obtained from DFT calculations. Tunneling parameters: $I_{\text{set}} = 1$ nA in all images.

To investigate the spatial variation of the differential conductance in more detail, dI/dV maps were acquired. To this end, a sinusoidal modulation was applied to the bias voltage but unlike for dI/dV spectra, the feedback loop was not turned off to sweep the bias voltage. Instead the bias voltage was set to a fixed value, and the sample was scanned in constant current mode. In this case, the feedback loop was tuned to a slow response time in order to not be able to follow the modulation of the bias voltage. dI/dV maps acquired in this mode tend to closely resemble the molecular orbitals [6]. In the left column of Fig. 3, topographic STM micrographs of a single PEN molecule at different bias voltages (corresponding to the LUMO, HOMO, and HOMO-2 molecular orbital resonances) are shown. While at negative bias voltages, the molecule appears as a pear-shaped protrusion, at positive bias, a rodlike shape is obtained. The obviously asymmetric shape of the protrusion with a bright lobe at one end, which is observed for all bias voltages, clearly originates from the directly underlying super Cu atom [see Fig. 1(b)]. The second column of Fig. 3 depicts differential conductance (dI/dV) maps at the very same bias voltages indicated on the left of the figure. The dI/dV map at the LUMO resonance (1.3 V) shows a maximum of the conductance in the vicinity of the underlying super Cu atom. While the undisturbed LUMO orbital of a free PEN molecule should show a seven-lobe modulation of the conductance along the long molecular axis, only three lobes can be discerned. For the dI/dV maps of the HOMO and HOMO-2 resonances the situation is somewhat different: Very similar images as shown for PEN on Au(111) [6] were obtained, but still a maximum intensity around the position of the adsorption site can be identified. In the third column of Fig. 3, topographic STM images are shown where a PEN molecule has been picked up with the STM tip from the surface by a controlled-tip approach before recording the dI/dV maps. Terminating the tip apex with a molecule has been proven to serve as a very sensitive probe for imaging molecular orbitals [5]. Indeed, the image obtained at the bias voltage corresponding to the LUMO resonance accurately resembles the LUMO orbital of a single pentacene molecule. Likewise, the image acquired at -1.1 -V bias voltage nicely resembles the HOMO orbital. Nevertheless, both directly imaged molecular orbitals are slightly asymmetric and exhibit a clear distortion at the end above the underlying super Cu atom. Lower-lying orbitals than the HOMO could not be imaged with a PEN-modified tip, since increasing the bias voltage makes the tunneling junction very unstable and results in a sudden loss of the picked-up molecule. The rightmost column in Fig. 3 depicts simulated STM images from a DFT calculation based on the relaxed adsorption geometry and employing the Tersoff-Hamann approximation. The simulated STM images match the experimental ones extremely well, especially those which were acquired with a PEN-modified tip. In particular, the observed asymmetry is well reproduced. Yet, the experimental dI/dV maps show a quite different contrast: While the HOMO image still resembles the molecular orbital, the LUMO image completely lacks the seven-fold modulation and features a clear depletion in the region above the underlying super Cu atom. The HOMO-2 image even shows an inverted contrast and a bright spot located directly above the underlying super Cu atom.

For a deeper understanding of the electronic structure of the adsorbed PEN molecules and to reveal the origin of the observed asymmetry in the STM images, we have further analyzed our DFT results in Fig. 4. Figure 4(a) shows a side view of the relaxed adsorption geometry. One can immediately see that the PEN molecules do not adsorb flatly on the surface. Instead, the molecules are slightly inclined towards the super Cu atom located on the right side in Fig. 4(a), where a height difference of almost 0.5 Å can be observed. Additionally, the molecule is slightly bent above the super Cu site. Figure 4(a) also shows the charge density difference in a plane perpendicular to the surface and intersecting the PEN molecule. It visualizes the charge rearrangements upon adsorbing the molecule, where red areas correspond to charge accumulations and blue areas correspond to charge depletions. From this representation, one can discern a slight charge accumulation between the super Cu atom and the PEN molecule, whereas on either side of the super Cu atom, an overall charge depletion is observed. These charge rearrangements arise from the Pauli-pushback effect [30] and lead to the formation of an interface dipole, which reduces the work function by 0.32 eV for the PEN coverage used in the simulations.

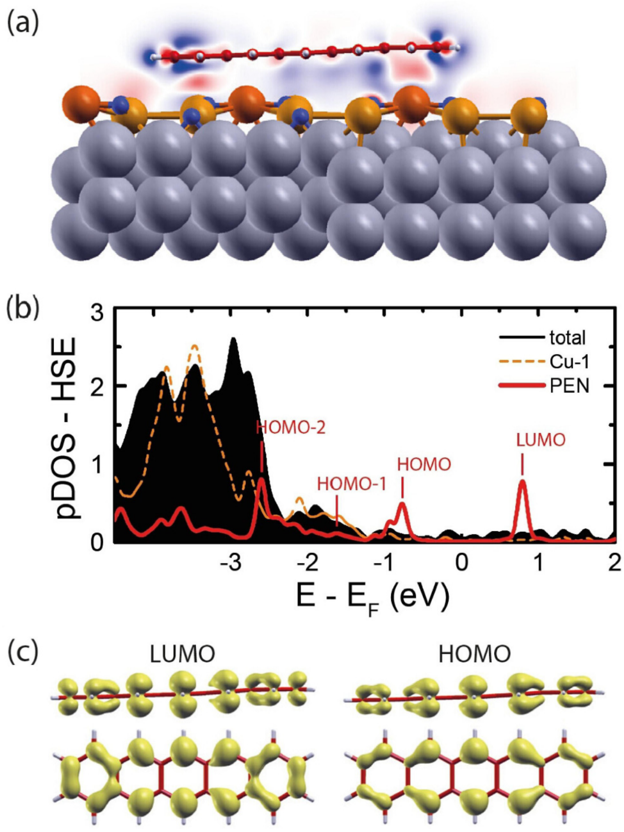

FIG. 4. (a) Adsorption geometry of a PEN molecule on the Cu(110)-c(6 × 2)O reconstructed surface as determined from DFT calculations. A bending of the PEN molecule above the super Cu atom (on the right) can be observed. Additionally, the charge density difference is depicted. Red regions correspond to a charge density accumulation, whereas blue ones correspond to a charge density depletion. (b) Calculated density of states (DOS) of PEN molecule and the substrate. The filled black curve depicts the total DOS of the substrate, whereas the orange dashed curve corresponds to the projections onto the super Cu atoms. The red curve denotes the DOS of the molecule. (c) Frontier molecular orbitals (LUMO and HOMO) of the adsorbed molecule in side and top views.

Figure 4(b) shows the projected density of states (pDOS) of the entire substrate (black) and of the adsorbed molecule (red). In addition, also projections onto the Cu atoms of the first layer are shown, with Cu-1 referring to the super Cu atom. The spectra show no particular sign of significant hybridization; instead clear molecular resonances for the LUMO, HOMO, and HOMO-2 are observed. This is also emphasized in Fig. 4(c), which shows partial charge density plots of the frontier molecular orbitals (LUMO and HOMO) of the adsorbed PEN molecule. Here, only small differences to the undisturbed molecular orbitals of the free molecule can be discerned [31]. This indicates that the observed charge transfer is rather small and that the interaction between the molecules and the substrate is much weaker compared to the adsorption on the bare Cu(110) surface [32]. Only the HOMO-1 orbital resonance broadens into a double feature, which is indicative of a significant hybridization with a substrate atom.

Compared to the dI/dV spectra shown in Fig. 2, the HOMO-LUMO gap in the calculated pDOS (1.6 eV) appears much narrower than the energy (or conductance) gap associated with the HOMO and LUMO states in the STS experiment (2.4 eV). This discrepancy arises from an underestimation of the gap by the hybrid functional DFT calculation. Note that a GGA-DFT calculation would lead to an even smaller HOMO-LUMO gap of the adsorbed system of only 0.9 eV. The sharp HOMO-2 resonance observed in the dI/dV spectra is not equivalently found in the calculated DOS of the molecule. However, Fig. 4(b) shows that the energy position of this resonance coincides with a super Cu atom state, located in the topmost Cu layer (Cu-1), and also with the onset of the Cu d band. Thus, one may speculate that the sharp HOMO-2 resonance could originate from the hybridization with the super-atom-derived resonance state or with the Cu d band. This would also fit nicely with the observed dI/dV map for the HOMO-2 resonance in Fig. 3, where a clear charge density localization at the super Cu atom was observed. The absence of such a sharp resonance in the DFT calculations may again be due to a deficiency of the hybrid functional calculation. Although an improvement over semilocal functionals, it may still lead a wrong relative energy alignment of the localized super Cu d state and the delocalized HOMO-2 state which could prevent the above mentioned hybridization from taking place.

IV. CONCLUSIONS

In conclusion, we have demonstrated that the Cu(110)-c(6×2)O reconstructed surface shows a considerably weaker interaction in comparison with the adsorption on the bare Cu surface, since no clear sign of hybridization between the frontier orbitals of the molecule and the substrate could be observed. We could show that the binding of the PEN molecule to the substrate occurs via the super Cu atoms, which are slightly protruding out of the surface layer and form an active binding site. Indeed, PEN molecules exclusively adsorb with their terminating carbon rings on top of this binding site. This results in a slight modification in the appearance of the molecules in the dI/dV maps with a distinct disturbance in the vicinity of the super Cu atom. This effect is most pronounced for the HOMO-2 orbital, for which we propose a resonance between the HOMO-2 orbital and a Cu state located in the topmost atomic layer. DFT calculations also show a clearly nonplanar adsorption geometry of the PEN molecules. Even more, the molecule is slightly bent over the super Cu atoms with reduced coordination, only resulting in a rather local and gentle modification to the electronic structure of PEN molecules. The detailed understanding provided in this work about the modification of the electronic structure of organic molecules upon surface adsorption is also important with regard to applications in molecular optoelectronics and heterogeneous catalysis.

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[1] B. C. Stipe, M. A. Rezaei, W. Ho, S. Gao, M. Persson, and B. I. Lundqvist, Phys. Rev. Lett. **78**, 4410 (1997).

[2] J. Repp, G. Meyer, S. Paavilainen, F. E. Olsson, and M. Persson, Science **312**, 1196 (2006).

[3] C. Joachim, J. K. Gimzewski, and A. Aviram, Nature (London) **408**, 541 (2000).

[4] X. H. Qiu, G. V. Nazin, and W. Ho, Science **299**, 542 (2003).

[5] J. Repp, G. Meyer, S. M. Stojkovic, A. Gourdon, and C. Joachim, Phys. Rev. Lett. **94**, 026803 (2005).

[6] W.-H. Soe, C. Manzano, A. De Sarkar, N. Chandrasekhar, and C. Joachim, Phys. Rev. Lett. **102**, 176102 (2009).

[7] Y. Zhang, Y. Luo, Y. Zhang, Y. J. Yu, Y. M. Kuang, L. Zhang, Q. S. Meng, Y. Luo, J. L. Yang, Z. C. Dong, and J. G. Hou, Nature (London) **531**, 623 (2016).

[8] N. Ogawa, G. Mikaelian, and W. Ho, Phys. Rev. Lett. **98**, 166103 (2007).

[9] E. Ćavar, M-C. Blüm, M. Pivetta, F. Patthey, M. Chergui, and W. D. Schneider, Phys. Rev. Lett. **95**, 196102 (2005).

[10] J. Mielke, F. Hanke, M. V. Peters, S. Hecht, M. Persson, and L. Grill, J. Am. Chem. Soc. **137**, 1844 (2015).

[11] Y. S. Fu, S. H. Ji, T. Zhang, X. Chen, X. C. Ma, J. F. Jia, and Q. K. Xue, Appl. Phys. Lett. **95**, 063107 (2009).

[12] C. Silien, N. A. Pradhan, W. Ho, and P. A. Thiry, Phys. Rev. B **69**, 115434 (2004).

[13] M. C. Blüm, M. Pivetta, F. Patthey, and W. D. Schneider, Phys. Rev. B **73**, 195409 (2006).

[14] N. Tsukahara, K. I. Noto, M. Ohara, S. Shiraki, N. Takagi, Y. Takata, J. Miyawaki, M. Taguchi, A. Chainani, S. Shin, and M. Kawai, Phys. Rev. Lett. **102**, 167203 (2009).

[15] B. Warner, F. E. Hallak, H. Prüser, J. Sharp, M. Persson, A. J. Fisher, and C. F. Hirjibehedin, Nat. Nanotech. **10**, 259 (2015).

[16] R. Feidenhans'l, F. Grey, M. Nielsen, F. Besenbacher, F. Jensen, E. Laegsgaard, I. Stensgaard, K. W. Jacobsen, J. K. Norskov, and R. L. Johnson, Phys. Rev. Lett. **65**, 2027 (1990).

[17] W. Liu, K. C. Wong, and K. A. R. Mitchell, Surf. Sci. **339**, 151 (1995).

[18] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[19] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[20] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[21] J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992).

[22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[23] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[24] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).

[25] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).

[26] J. B. Neaton, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **97**, 216405 (2006).

[27] J. M. Garcia-Lastra, C. Rostgaard, A. Rubio, and K. S. Thygesen, Phys. Rev. B **80**, 245427 (2009).

[28] X. Duan, O. Warschkow, A. Soon, B. Delley, and C. Stampfl, Phys. Rev. B **81**, 075430 (2010).

[29] K. A. Cochrane, A. Schiffrin, T. S. Roussy, M. Capsoni, and S. A. Burke, Nat. Commun. **6**, 8312 (2015).

[30] O. T. Hofmann, G. M. Rangger, and E. Zojer, J. Phys. Chem. C **112**, 20357 (2008).

[31] S. Berkebile, P. Puschnig, G. Koller, M. Oehzelt, F. P. Netzer, C. Ambrosch-Draxl, and M. G. Ramsey, Phys. Rev. B **77**, 115312 (2008).

[32] T. Ules, D. Lüftner, E. M. Reinisch, G. Koller, P. Puschnig, and M. G. Ramsey, Phys. Rev. B **90**, 155430 (2014).