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Study of the electronic structure at the interface between fluorene-1-carboxylic acid molecules and Cu(110)

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Abstract

The interface electronic properties of fluorene-1-carboxylic acid (FC-1) adsorbed on Cu(110) have been studied by ultraviolet photoemission spectroscopy (UPS) and first-principles calculations. Both the molecular orbitals and the Cu valence band are significantly modified upon adsorption. FC-1 is chemically bonded to Cu(110) through charge donation and back donation involving the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the molecule. An observed reduction of the work function can be attributed to the adsorption induced charge redistribution, and the positive interface dipole.

1. Introduction

Ultra-thin films of organic molecules have recently received considerable attention because of their potential applications, e.g. in molecular electronics and organic LEDs [1, 2]. An important feature of functional organic materials is that their physical and chemical properties are readily tunable by molecular design, with virtually unlimited degrees of freedom. The performance of organic devices, however, depends not only on the molecules themselves, but also on their arrangement in the thin films. One of the most important problems in molecular electronics is to understand the properties of molecule–metal contacts and to learn how to control them [1–4].

Molecular ordering on surfaces is ruled by a delicate balance between intermolecular forces and substrate–molecule interactions. Much effort has been devoted to investigating phenomena such as the molecular orientation and detailed geometric structure at interfaces, intra-layer ordering properties, thin film growth mechanisms and the chemical properties of molecular layers [4, 5]. The molecular orientation and geometric

structure at the interface can have important implications for the film growth, as well as for its electrical, electronic, and perhaps optical properties [6]. The interaction at the interface may give rise to a charge transfer or polarization, and hence influences the direction and size of the interface dipole, the position of the charge neutrality level, the band bending and the relative position of the occupied and unoccupied bands derived from the molecular orbitals.

When a planar conjugated molecule, e.g. pentacene or PTCDA, is adsorbed on a transition metal or noble metal surface, bonding to the surface is achieved through the interaction between the substrate and the π orbitals of the molecule, via aromatic ring and oxygen atoms. In such cases the molecules strongly interact with the metal surfaces, forming ordered supra-molecular structures commensurate with the substrate periodicity. Examples for such a behavior are PTCDA on Ag(110) [6] and Ag(111) [7]. Ordered structure can also be found on the moderately interacting systems by molecule self-assembly, within the balance of intramolecular interaction and molecule–substrate interaction, such as pentacene on Cu(119) [8, 9] and Cu(110) [10], and perylene on Ag(110) [11]. Much less attention has been given to non-planar molecules.

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Here we are concerned with the adsorption of fluorene-1-carboxylic acid (FC-1, $\text{C}_{14}\text{H}_{10}\text{O}_2$), a non-planar molecule composed of fluorene with a carboxylic group at the first carbon. The adsorption of a non-planar molecule is different from other normal aromatic molecules, such as tetracene, pentacene, etc. Many ordered supra-molecular structures from the planar molecules have been formed by molecule self-assembly, but less attention has been given to non-planar molecules. Actually, the FC-1 molecule is planar in the central aromatic part except for the CH₂ hydrogens, with each hydrogen lying above or below the molecular plane. The adsorption of this molecule on Cu(110) has recently been studied by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and first-principles calculations [12]. When the surface was saturated with one monolayer, a (4×4) *pg* ordered structure is observed with LEED after the substrate was annealed at about 120 °C, but no ordered overlayer structure was formed with the coverage lower or higher than one monolayer. STM images reveal that this ordering is confined to small local areas. STM also indicates that the molecular aromatic plane of FC-1 is parallel to the substrate. Interestingly, the adsorption structure shows a chiral property. Two FC-1 molecules in one unit cell have their carboxylic groups bent in an identical geometry and equivalent orientation, but with opposite chirality [12]. In this paper, we focus on the electronic structure of this adsorption system using ultraviolet photoemission spectroscopy (UPS) and first-principles calculation in the framework of density function theory (DFT).

2. Experimental setup

Sample preparation and photoemission experiments were carried out in the same ultrahigh vacuum system using a VG ADES-400 electron spectrometer [13]. The base pressure of the chamber was better than 5×10^{-10} mbar. He I light with a photon energy of 21.2 eV was used. The Cu(110) surface was cleaned by several cycles of argon-ion sputtering (2000 eV for 20 min), followed by an annealing to 500 °C. The surface ordering and cleanliness were confirmed by both a sharp $p(1 \times 1)$ LEED pattern and photoemission spectroscopy measurements. FC-1 powder (Sigma, 99%) was purified thoroughly by pre-heating in a Ta-boat at about 110 °C overnight. The deposition of FC-1 was performed when the source temperature was about 200 °C, with a deposition rate of 0.5 monolayers (ML) per minute, while the substrate was held at room temperature. The temperature of the sample was measured by a K-type thermocouple attached to the sample stage. The thickness of the organic ad-layer was monitored using a calibrated quartz crystal oscillator. A negative bias of -5 V was applied on the sample to obtain the correct, sample determined, secondary electron cutoff during the data measuring.

3. Results and discussion

UPS spectra recorded at room temperature from the Cu(110) surface with different amounts of organic molecules are shown

in figure 1(a). The spectra were collected along the surface normal direction with a photon incidence angle of 30°. The nominal thickness of the organic film was 0.0, 0.2, 0.5, 0.7, 1.0, 2.0, 4.0, and 10.0 ML respectively. The deposition of a sub-monolayer coverage of FC-1 on the surface leads to an intensity decrease of the emission features of the copper substrate, while features originating from FC-1 appear at 1.45, 3.45, 6.90, and 9.00 eV below the Fermi level (labeled as α , β , γ and δ , respectively, in figure 1). The experimental error on the measured binding energies is 0.05 eV from the fitting procedure. When further increasing the organic film thickness, peaks α , β , and γ increase in intensity and shift towards the higher binding energies. When the coverage reaches about 10.0 ML, the features of FC-1 are located at binding energies of 1.55, 3.80, 7.05, and 9.05 eV. From previous studies and other reports, we could conclude that such a coverage-dependent shift in binding energy can be ascribed to the electronic difference between molecules at the interface and molecules in the multilayer, since there is less interference from the substrate in the case of the multilayer. At the interface, charge redistribution takes place, caused by the strong chemical interaction between the adsorbed molecules and the substrate [6, 7, 12].

The low-energy cutoff in the UPS is determined at the position where the crossover point is between two lines fitted to the background and the decline edge of the curve respectively, as shown in the figure 1(b). Based on the low-energy cutoff in the UPS, the change in work function of the surface can be obtained, as shown in figure 1(c). The work function of the clean surface is 4.20 eV. The minimum in work function, of 3.90 eV, corresponds to the completion of one monolayer. The work function increases considerably with further deposition, the value 4.05 eV representing the work function of a thick organic film. The change in the work function first decreases then increases by a similar order of magnitude, indeed indicating molecular interaction at the monolayer stage, and the interaction and polarization on the interface should both be taken into account, as suggested in [7, 13–15].

To investigate the intimate nature of the interface electronic states close to the Fermi level, we undertook a theoretical study of FC-1 on Cu(110) by means of first-principles DFT calculations. Simulations were performed with the Dmol3 package in the Materials Studio of Accelrys Inc. [16]. The physical wavefunctions were expanded in terms of accurate numerical basis sets. The electron–ion interaction was described by density functional semicore–pseudopotentials for metals [16–18], and the generalized gradient corrected (GGA) functional method developed by Perdew *et al* was used to deal with the exchange–correlation functional [19]. A Fermi smearing of 0.1 eV was used in order to minimize the errors in the Hellmann–Feynman forces, due to the entropic contribution to the electronic free energy [20]. A real-space cutoff of 4 Å was adopted to improve the computational performance, and the k -points $(1 \times 2 \times 1)$ were obtained from the Monkhorst–Pack scheme [21]. The tolerance of energy, gradient, and displacement convergence were 5×10^{-4} eV, 1×10^{-1} eV Å⁻¹, and 5×10^{-3} Å, respectively. Under the

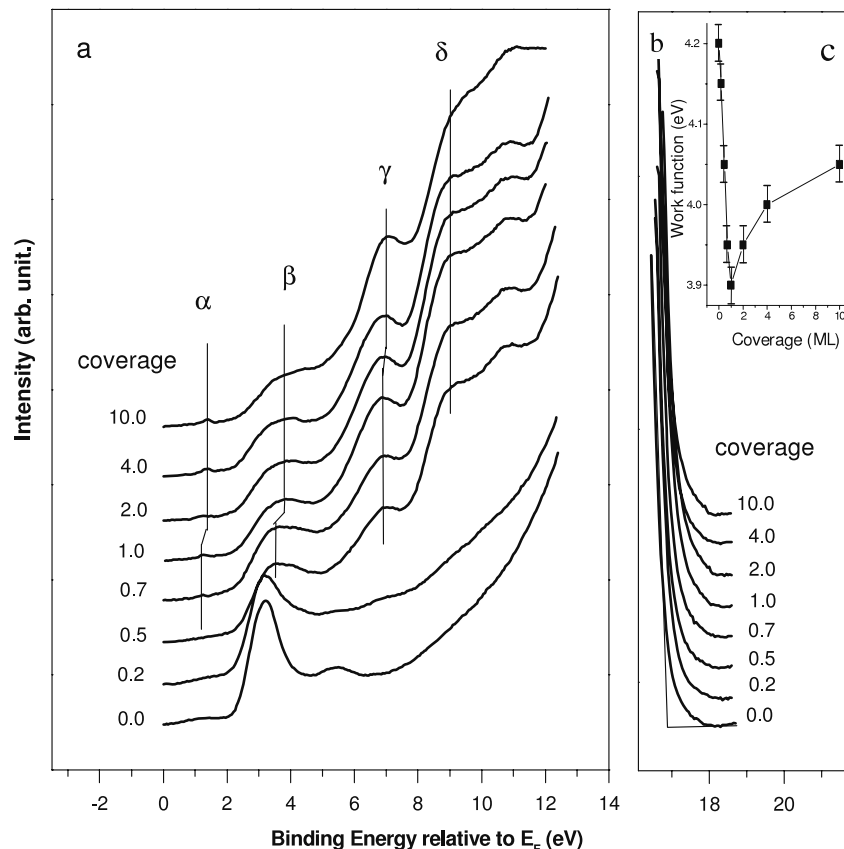


Figure 1. (a) Photoemission spectra ($h\nu = 21.2$ eV) of FC-1 molecules adsorbed on Cu(110) as a function of coverage (in monolayers); (b) low-energy intensity cutoff as a function of film coverage; (c) change in work function with film coverage.

Table 1. Theoretical ionization potentials of some occupied molecular orbitals in the free molecule and corresponding experimental values for the adsorbed molecules on Cu(110) (observed binding energies plus measured work function).

Level	Type	Ionization potential in free molecule		UPS of monolayer on Cu surface	UPS of multilayer on Cu surface
			Label		
1	π	5.64	α	5.35	5.60
2	π	7.82	β	7.35	7.85
3	π	11.47	γ	10.80	11.10
4	σ	13.24	δ	12.90	13.10

present conditions, the lattice parameter of the Cu slab was calculated as 3.64 \AA , in good agreement with the experimental value of 3.61 \AA [22].

According to the calculation, the free FC-1 molecule should show photoemission peaks at 5.64, 6.24, 7.82, 8.97, 9.87, 10.58, 11.47, 13.24, 14.95, and 15.63 eV, but not all of these have a high photoionization cross-section and are, in fact, observed for FC-1 on Cu(110). Based on the symmetry of our measurement, only some orbitals give a strong intensity and can be resolved in the spectrum, e.g., the B1g, B2g, B3g and Au orbital symmetry; on the other hand, the peaks can hardly be resolved in the UPS, for example, B1u, B2u and so on. Table 1 shows the sub-set of calculated ionization potentials for the occupied molecular orbitals which have been assigned to the experimentally observed peaks. For a convenient comparison, the data from the UPS spectra have been corrected by the corresponding work function of 3.90 eV for one monolayer and 4.05 eV for a multilayer. If we

assume that the molecular orbitals have similar energies for the multilayer and the free molecule, the emission features from a FC-1 multilayer on Cu(110) located at binding energies of 1.55, 3.80, 7.05, and 9.05 eV can be considered as coming from the same orbitals as for the free molecules located at ionization potentials of 5.64, 7.82, 11.47, and 13.24 eV, respectively. The peak at 1.55 eV (α in figure 1), should correspond to the highest occupied molecular orbital, since there are no other states within this energy range. The agreement between the IP (orbital energies) and UPS data in the multilayer situation is, again, a sign of a much stronger interaction, charge transfer and back donation at the monolayer stage, and less influence from the interface in the multilayer.

The peak shift with increasing coverage, and the change in work function cannot be expected, but a change in molecular orbitals must be considered, since an increase of 150 meV in the work function is less than the shift in the binding energy of the peaks. For the multilayer, the signal from the substrate

is very weak and the peak we see in the spectrum is from molecular orbitals, as seen from the change of spectrum as a function of coverage. The peak from the copper surface state gradually vanishes, and the peaks from the organic film are step by step more visible. Although the intensity for the peak β is not so strong, and the shift is small compared to other peaks, it is from a certain orbital of the molecule, as it still remains in the multilayer coverage. Furthermore the peaks shift by different values, peaks α , β and γ shift 100, 350 and 150 meV, respectively, while peak δ hardly shifts upon increasing the coverage. Based on the change in work function with different coverage, the shift relative to vacuum level is 250, 500 and 300 meV for α , β and γ , respectively. The differences in electronic structure between molecules in a monolayer and in a multilayer also indicate a smaller influence from the Cu substrate at higher coverage, which will be discussed in detail in the following. The greater shift in binding energy for peaks α , β and γ than for peak δ suggests that the π orbital of the molecule interacts more strongly with the substrate than the σ orbital. As for the different photoionization cross-section for the molecular orbitals, it is a simple approach to describe this in the method of using He II. In this work, we did not check the spectral signal with He II photons (with photon energy 40.8 eV) for the limitation of the experimental setup. The difference in photoionization cross-section for the molecular orbitals is not obviously observed, due to the low intensity of He II.

We now inspect the electronic properties of the interface theoretically by comparing the projected density of states (PDOS) of FC-1⁵, in the case of one monolayer and two layers on a Cu(110) surface, as well as that of the substrate, as presented in figures 2(A) and (B). The PDOS was calculated on the adsorption structure, which was optimized with minimum energy, and the optimizations were performed via the conjugate-gradient (CG) technique by adjusting the adsorbate in height and orientation. The geometry of the second layer is similar to that of the first layer, flat, lying on the surface without any distortion, which is deduced from the information that it is less influenced by the substrate on the multilayer, and also seen in the UPS and work function change. The binding energy, in the figure, is relative to the Fermi level. The PDOS of the second layer in the 2 layer system can be depicted with that of multilayer, since it does not show any apparent change compared to that of the third layer in the 3 layer system. When the molecule is adsorbed on the substrate, a substantial modification of its density of states takes place between one monolayer and the second layer of 2 layers, indicating a strong interaction between the adsorbate and substrate. The valence states of the Cu substrate undergo a change upon the adsorption with one monolayer, in both the peak intensity and binding energy location, as shown in figure 3(b). This also suggests that an interaction beyond physical adsorption occurs at the interface [23]. In the case of physical adsorption, no change in the valence states of the Cu substrate was observed [24].

⁵ Herein the adsorption geometry for the first layer has been assumed to be the point of the absolute energy minimum, as described in [12], and the second layer was considered to be flat, lying on top, and less influenced by the substrate indicated from the UPS.

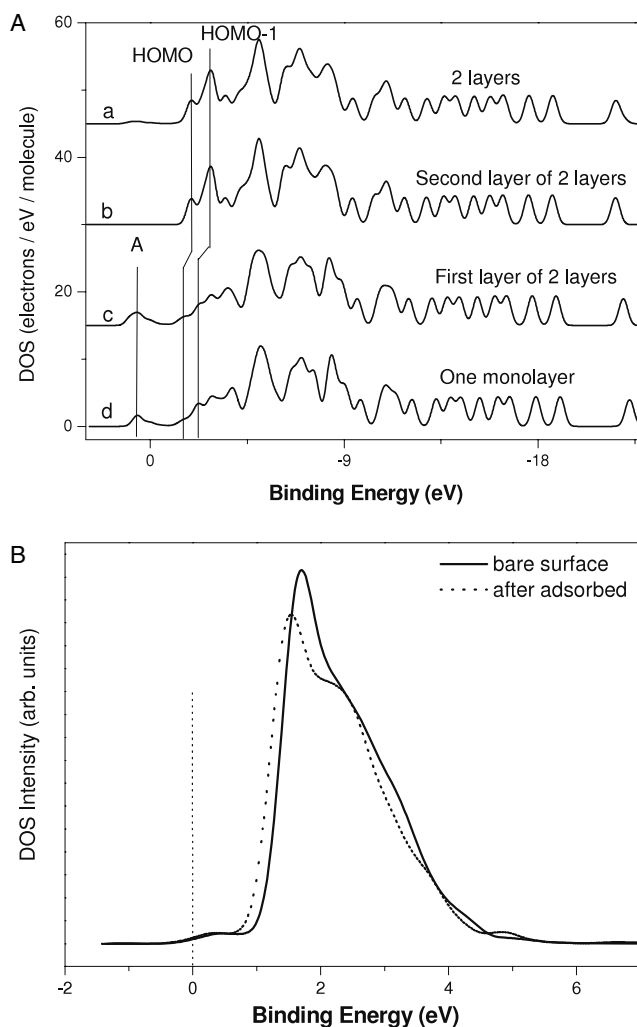


Figure 2. (A) Projected density of states (PDOS) of an FC-1 molecule on a Cu(110) surface. (a) The coverage is 2 layers, calculated from the FC-1 molecule in these two layers; (b) the coverage is 2 layers, calculated from the FC-1 molecule in the second layer of two layers; (c) the coverage is 2 layers, calculated from the FC-1 molecule in the first layer of two layers; (d) the coverage is one monolayer, calculated from the FC-1 molecule in the layer. (B) Projected density of states (PDOS) of the Cu substrate. The solid curve was calculated from the bare Cu substrate and the dotted curve was calculated from the Cu substrate with one monolayer of FC-1 molecules.

Of particular interest are the peaks corresponding to the HOMO of the FC-1 molecule. The peak α in figure 2(A), corresponding to the HOMO of the molecule is located at a binding energy of -1.70 eV for one monolayer, but at -1.90 eV for the second layer of 2 layers. This is apparently consistent with a difference of about 100 meV between the monolayer and multilayer observed in figure 1. As expected, in addition, HOMO, 'HOMO-1', 'HOMO-2', and 'HOMO-3' (the 4 highest peaks visible in the UPS; these are the 4 highest orbitals in the adsorbed state, not the orbitals of the free molecule) also shift in the DOS, especially HOMO-1, which can be easily attributed to the charge transfer and interaction between the molecules and the substrate. Another interesting phenomenon is the change of peak A in the figure, which lies

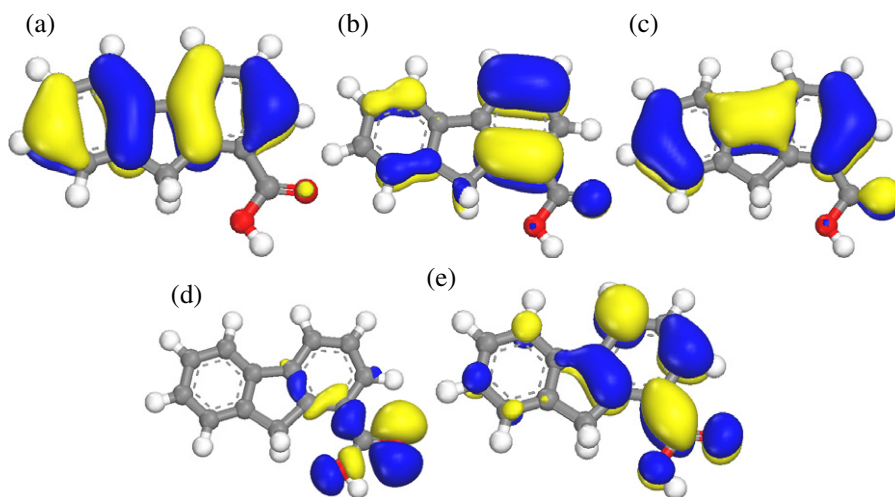


Figure 3. The schematic drawing of molecular orbitals. (a)–(c). (d) HOMO (peak α) and corresponding peaks (β , γ , δ) in the UPS. (e) LUMO of the FC-1 molecule.

(This figure is in colour only in the electronic version)

about 0.6 eV above the Fermi Level when the organic film is one monolayer. This peak can also be observed in the DOS of 2 layers, it should be a peak formed after adsorption because of hybridization and admixing of Cu 4s states. However, it is not clearly distinguished from the experimental UPS, possibly because of a low cross-section or the energy resolution limit of the experimental setup. In all, the formation of peak A indicates a significant charge transfer from the substrate into the region between the LUMO and HOMO of the molecule, which, in a simplified picture, would imply a work function change.

This apparent contradiction can, however, be resolved by noting that there is not only a charge donation from the metal into the LUMO, but also a charge back donation involving at the former HOMO and other orbitals, with a significant energy shift of these orbitals [25]. A schematic drawing of the HOMO, ‘HOMO-1’, ‘HOMO-2’, ‘HOMO-3’, and LUMO of the FC-1 molecule is given in figure 3. The density distribution of the HOMO is concentrated on the aromatic plane of the molecule, while the density distribution of the LUMO is concentrated on the carboxyl O atom (=O) and the hydroxyl O atom (–O), which acts as an electron acceptor. Upon adsorption charge back donation involving the former HOMO and other orbital occurs, while charge is donated to the former LUMO. As a result of the charge transfer to the LUMO of the molecules, the copper atoms in the topmost layer become slightly positively charged. The carboxylic oxygen, being negatively charged, is then attracted by the substrate. Also, the local Cu–O attraction leads to a distortion of FC-1 from planarity [12]. Due to the charge transfer, a negative charge is assembled near the interface between the FC-1 molecule and the substrate; however, meanwhile more positive charge is assembled near the higher level of the FC-1 molecule. The overall formed positive interface dipole thus contributes to the reduction of work function.

We then have a quantized analysis of the work function change. Usually, for a metal, a change in work function

results partly from a change of the dipole formed at interface [7, 14, 26]. When the charge transfer happens at the interface after adsorption, different contributions, such as charge transfer and back donation, charge redistribution, and orbital overlap, are likely to happen and compensate each other simultaneously. In order to make this complex mechanism simple, the dipole contribution to the change in the work function is studied first. In the case of FC-1, to a first approximation, $e\Delta\phi_{\text{dip}}$ is related to the contribution of the dipole moment p of the adsorbate/substrate interface by the following equation [27, 28]:

$$e\Delta\phi_{\text{dip}} = -\frac{e}{\varepsilon_0}pn_{\text{dip}}\left[1 + \frac{9\alpha}{4\pi}n_{\text{dip}}^{3/2}\right]^{-1}$$

where ε_0 is the vacuum permittivity. The density of adsorbed molecules is estimated as $n_{\text{dip}} = 6.78 \times 10^{13} \text{ cm}^{-2}$ assuming one FC-1 molecule adsorbed per (4×4) substrate unit cell for the first monolayer [12], and a polarizability $\alpha = 26 \times 10^{-23} \text{ C}^3 \text{ m}^3$ is obtained from the above DFT calculations [26] for an isolated FC-1 molecule on the Cu(110) surface. A value of interface dipole $p \cong 3.35 \times 10^{-30} \text{ C m}$ (about 1 D) is obtained after adsorption, according to the charge transfer induced charge redistribution and adsorption height, which indicates a work function decrease of 0.21 eV following the equation above. Compared to the experimental data of 0.3 eV reduction at a monolayer, this is a sign of an inaccurate description with a pure dipole model, which works reasonably for the multilayer case. The role of interface interaction and screen effect has to be taken into account to explain the work function change comprehensively, as mentioned by Betti *et al* [14, 15]; a complete theoretical model including the charge transfer, Pauli repulsion, molecular dipoles, and interface screening will consistently interpret the work function change. At sub-monolayer and monolayer coverage, assuming a flat molecule lying on the Cu(110) surface [12], a value of -0.1 eV is obtained for the contribution to the interface work function

change, based on a combined theoretical model [14, 15, 27] without any contribution from interface screening.

Concurrent experimental and theoretical results on the electronic structure of FC-1 on Cu(110) result in a picture for the interaction at this kind of interface. Both the adsorbed molecular orbital characters and the valence state of the Cu substrate undergo a substantial change upon adsorption. In particular, charge donation and back donation involving HOMO and other orbital of FC-1 are observed. This leads to the formation of a positive interface dipole and to a reduction in work function. These results show that the adsorption of FC-1 on Cu(110) cannot be described by a pure van der Waals bonding, but is a mixture of chemical adsorption together with physical adsorption and hybridization [6, 7, 27].

4. Conclusion

The adsorption of a non-planar FC-1 molecule on Cu(110) has been studied both experimentally and theoretically. Both the molecular orbitals and the Cu valence band are significantly modified upon adsorption. FC-1 is chemically bonded to Cu(110) through charge donation and back donation involving the LUMO and HOMO of the molecule. Moreover, an apparent reduction of the work function is also observed, which can be attributed to the formation of an adsorption induced positive interface dipole, and the charge redistribution mechanism.

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