

Influence of Subsurface Layers on the Adsorption of Large Organic Molecules on Close-Packed Metal Surfaces

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The adsorption behavior of molecules and adatoms on surfaces is governed by adsorbate–substrate interactions, such as physisorption and chemisorption. Provided the adsorbates have sufficient energy to overcome the migration barriers, the preferred adsorption sites are those of minimum energy. Besides the chemical nature and positions of atoms in the upper layer, the potential landscape on surfaces is determined also by the atomic arrangement of subsurface layers. On close-packed surfaces, such as Cu(111), the hollow-sites of the first layer are not equivalent, but can be distinguished between so-called hcp- and fcc-sites according to their relative location with respect to atoms in lower-lying layers. This leads to a lifting of the degeneracy in the adsorption energy, as was demonstrated for single adatoms about 20 years ago by Wang *et al.*¹ The resulting site-selection for adatoms plays an important role, for example, in determining the nucleation sites during epitaxial growth.² The local site preference can also prompt specific structures on larger scales, as revealed by the growth of metal islands with triangular shape, displaying favored orientations.³ However, it is unclear to what extent the subsurface layers influence the adsorption of more complex adsorbates like molecules. Studies on small molecules, such as NO or benzene, on various close-packed metal surfaces suggest, depending also on the type of the metal substrate, preferences for one or the other hollow-site.^{4–8} Experimentally it is, however, a difficult task to determine the exact molecular locations, due to limitations in imaging and identification of subsurface layer atoms. Additionally, for too large molecules the selectivity may be hindered as the various groups of the molecules could be

ABSTRACT The asymmetric molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) adsorbed on Cu(111) is characterized by scanning tunneling microscopy (STM) and density functional theory (DFT) to determine the influence of subsurface atomic layers on the adsorption. In contrast to the 6-fold symmetry of the first atomic layer of close-packed surfaces, we find that the arrangement of the isolated molecules follows predominantly a 3-fold symmetry. This reduction in symmetry, where the molecule selects a specific orientation along the $\langle -211 \rangle$ axes, reveals the contribution of lower-lying Cu layers to the molecular arrangement. Our calculations rationalize the interaction of the substrate with the molecule in terms of electrostatic screening and local relaxation phenomena.

KEYWORDS: metal–organic interfaces · adsorption · subsurface layers · local relaxation · scanning tunneling microscopy · density functional theory

forced, because of the spatial extent of the molecules, to occupy both types of hollow-sites averaging out possible site preferences. So far experimental studies in this direction are rare,⁹ and a clear rationale elucidating the possible mechanisms behind the selectivity is missing.

In the present work, we show unequivocally *via* a combined experimental and theoretical study the direct influence of subsurface layers on the arrangement of large organic molecules adsorbed on a metal surface. These not only cause the selectivity for the orientations, but also control the local relaxation and screening of the potential perturbation of the adsorbed molecule. Using the particular geometry of close-packed surfaces, and adsorbing a nonsymmetric molecule (*i.e.*, with differing end-groups), we show that the molecules bind preferably in three orientations. This is in contrast to the 6-fold symmetry of the top atomic layer of the substrate, but compatible with the reduced symmetry achieved once the subsurface layers are taken into account, indicating a strong influence of these on the adsorption.

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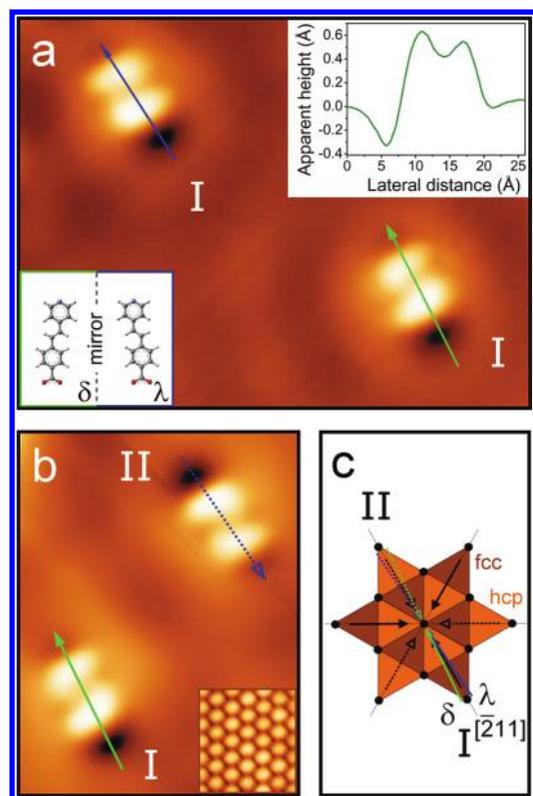


Figure 1. STM topography images of PVBA molecules on Cu(111) taken at bias = 0.1 V: (a) two single PVBA molecules with different chirality in configuration I (inset top: height profile of a single PVBA molecule) (inset bottom: sketch of deprotonated δ - and λ -PVBA); (b) two PVBA molecules in different orientations (bottom left configuration I and top right configuration II); (inset: atomically resolved image (to scale)); (c) scheme illustrating the adsorption angle with respect to the surface. For clarity only one of three orientations for the favored I and unfavored II configuration is shown. The green and blue arrows denote the direction of δ - and λ -PVBA, respectively. Image sizes in \AA^2 : (a) 55.3×72.3 , (b) 51.7×39.4 .

Specifically, we studied the organic molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) on the Cu(111) surface, where single isolated molecules can be observed, as we have reported previously.¹⁰ PVBA consists of two different functional end-groups, a pyridyl ring on one side and a benzoic acid at the other connected by a vinyl bridge. By scanning tunneling microscopy (STM) the two sides of the PVBA molecules can be distinguished¹⁰ allowing in contrast to previous studies^{9,11} a clear distinction and selection of the orientation of the molecule with respect to the substrate registry.

Our studies are supported by Density Functional Theory (DFT) calculations addressing the specific adsorption geometries. This allows us to rationalize the influence of lower atomic layers on the adsorption in terms of adsorption energy, local relaxation, and charge distribution.

RESULTS AND DISCUSSION

Figure 1a shows a typical STM topography image of single PVBA molecules on Cu(111) acquired at a

TABLE 1. PVBA on Cu(111): Number of Molecules Found in Certain Adsorption Orientations (Left), Calculated Energetic Difference (Right)

STM		
I	II	DFT ΔE (meV)
84	5	47

voltage of +0.1 V. PVBA appears as two protrusions and one large depression at one end, which we have previously associated with the deprotonated carboxyl side.¹⁰ The protrusion near the depression is hence attributed to the phenylene ring of the benzoic-acid moiety and the other one to the pyridyl ring. This enables us to assign to the molecule a specific intrinsic direction which is identified by an arrow pointing from the oxygen to the nitrogen terminated side. The distance between the protrusions (see top inset Figure 1a) is comparable to the distance of 6.62 \AA between the centers of the rings of the free molecule obtained from our calculations, suggesting a planar adsorption of the molecule. The two protrusions show different apparent heights and a slightly triangular shape giving rise to two motifs that are resolved in the topographic images (indicated by a green and blue line, respectively). The two motifs are mirror symmetric and occur with equal probability. These reflect the two different chiral species (enantiomers) of PVBA that are induced by the 2D confinement at the surface (see bottom inset Figure 1a).

Given the 6-fold symmetry of the top atomic layer of the close-packed Cu(111) surface each enantiomer is expected to adsorb in six orientations every 60° degrees. If the adsorption of the molecule were exclusively determined by the top layer, these molecular orientations would be equally likely. Although six orientations are indeed observed, we find that among these, three orientations are, however, strongly preferred, which we label as configuration I. The other three orientations, which are unfavored and pointing opposite to the former ones, are referred to as configuration II. Table 1 shows a statistical analysis of the number of molecules in each configuration, revealing a more than 90% preference for configuration I. Figure 1b shows a topography image of two molecules in the two different configurations. The molecules are aligned parallel to a common axis, while their orientation is opposite to each other. In the image the dotted line symbolizes one of the orientations of the molecules that are only rarely observed (configuration II, see Table 1). The three preferred orientations, which constitute the large majority, occur every 120° with respect to each other, displaying effectively a 3-fold symmetric arrangement of the molecules in contrast to the 6-fold symmetric pattern of the top-layer atoms of the Cu(111) surface (see black dots symbolizing the first layer atoms in Figure 1c). Note, that for a symmetric molecule, such as

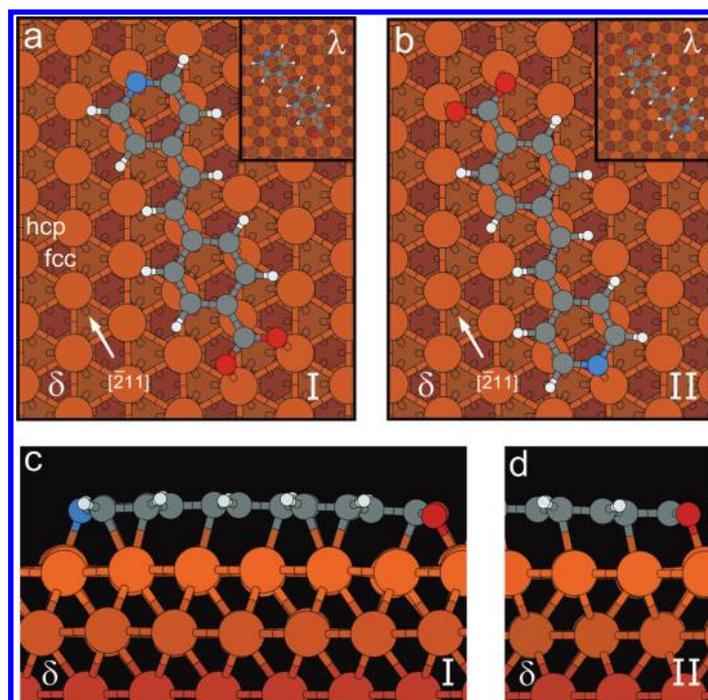


Figure 2. Calculation of PVBA (deprotonated) on Cu(111) showing in panels a and b the favored I and the unfavored II adsorption configuration for δ -PVBA. The insets show the λ -PVBA case respectively. (c) Sideview of δ -PVBA for case I. PVBA is adsorbed in an almost planar configuration with a slight apparent arc, where the nitrogen-side and oxygen-side are by 0.11 Å and 0.25 Å closer to the surface than the central part.¹⁸ (d) Sideview of δ -PVBA for configuration II.

pentacene,⁹ the distinction between the two orientations of the molecule along a given axis would not be possible. Atomically resolved STM images (see inset Figure 1b) reveal that PVBA adsorbs close to the $\langle -211 \rangle$ axes. Depending on the enantiomer, a small clockwise or counter-clockwise angle of approximately $4 \pm 2^\circ$ with respect to these axes is observed (see arrows in Figure 1a,b and the corresponding illustration in Figure 1c).

To explain the preference of one configuration over the other, the second and the subsequent Cu layer must be taken into account. These differentiate the hollow-sites of the first layer into alternating hcp (Cu atom in the second layer) and fcc sites (vacancy in the second layer), imposing the nonequivalent directions “fcc to hcp” and “hcp to fcc” (full and dotted lines in Figure 1c, respectively). These repeat every 120° as the two configurations. In other words, the inclusion of the subsurface layers reduces the 6-fold symmetry of the surface to a 3-fold symmetry as can be seen in Figure 1c. The predominant 3-fold symmetric arrangement of PVBA molecules experimentally observed on Cu(111) hence highlights a strong influence of the second and subsequent Cu layer (*i.e.*, subsurface atoms) on the adsorption. Before we discuss the molecule–surface interaction in detail, we shortly comment on the occurrence ratio of the two configurations. In the case of single adatoms the ratio between favored and unfavored sites has been shown to follow the Boltzmann statistics.² As neither diffusion nor rotation of the molecules was observed at the imaging

temperature of 6 K, the ratio between the two sites is a frozen image determined at some temperature during the cooling down process from the deposition temperature (~ 300 K).¹² The transition between configuration I and II requires a 60° in-plane rotation of the molecule, which is associated with an energy barrier. We theoretically evaluated a barrier of 0.42 eV for a rigid translational movement of PVBA on Cu(111)¹⁴—a lower value is expected for a rotational movement.¹⁵ At the deposition temperature the thermal energy of the molecule is sufficiently high to overcome these barriers and both configurations will occur on the surface, with a ratio determined by their relative energy difference. Upon system cooling, the ratio will drift toward a population consisting of molecules almost exclusively in the energetically preferred configuration, while the thermal energy will progressively become too low for molecules to overcome the barrier. The observed ratio at low temperatures results hence from an interplay between the reaction kinetics and the thermodynamic driving force.

To achieve a deeper understanding of the adsorption of PVBA on Cu(111) the system was modeled by DFT calculations. The molecule is found to adsorb nearly planar on the surface (see Figure 2), in agreement with the experimental observations. The functional groups at the ends of the molecule are slightly closer to the surface (see Figure 2c,d) than the aromatic backbone as a consequence of their strong bonding character.¹⁰ Previous reports have shown that these groups may even force a molecular backbone in an

upright or tilted configuration.^{16,17} In Figure 2a,b relaxed structures of the two most stable arrangements, corresponding to configuration I and II, are reported. The aromatic rings of the molecules are aligned along the $\langle -211 \rangle$ directions. However, due to the kinked vinyl moiety, a small angle between the molecular axis (defined by the line of the N atom to the carboxyl C atom) and these directions is actually present. This, which is of about 7° , has either a clockwise or counterclockwise sense characterizing the two different enantiomers δ - and λ -PVBA, respectively. These angles correspond well to those experimentally observed, allowing an unambiguous assignment of the specific chiral species. Moreover, experimentally we find that each of the two angles is linked to one of the two specific topographic motifs. This enables a direct assignment of the chirality, based only on the topographic appearance (*i.e.*, electronic structure) of the enantiomers. Since the $\langle -211 \rangle$ directions identify mirror symmetry planes orthogonal to the surface, the adsorption energy is independent of the chirality, so that the two enantiomers are predicted to occur with equal probability, as experimentally observed.

We now examine in detail the differences between configuration I and the less frequently observed configuration II. Their calculated energy difference is 47 meV. The most stable configuration I is assigned to molecules oriented in the direction which is predominantly observed. In this configuration (see Figure 2 a) the nitrogen atom of PVBA is located almost on top of a Cu atom, with a slight shift of the molecule along $\langle -211 \rangle$ toward a nearby hcp-hollow site. Rotating the molecule in-plane by -60° (or $+60^\circ$, or 180°) should result in the same adsorption geometry if we considered only the first layer. However, the position of the molecule with respect to the second metal layer is not equivalent in the two cases. The site below the N atom turns from an hcp-hollow site to an fcc-hollow site after any of the rotations above, with no second-layer Cu atom present below the N atom. Hence, the difference in energy is ascribed to the different stacking layout of subsurface metal atoms.

Inspection of the different relaxations and screenings obtained from our calculations reveals a wealth of further information supporting a different response of the subsurface atoms for the two configurations. The analysis shows that the two relaxed adsorption geometries differ noticeably already in the way the molecule positions itself with respect to the first Cu layer. Whereas in configuration I the nitrogen atom is closer to the on-top site, it lies 0.32 \AA further away laterally for case II, resulting in an overall rigid displacement of the molecule along the $\langle -211 \rangle$ axes. In both configurations, the centers of the aromatic rings are positioned slightly toward the hcp-site. We note that theoretical calculations of benzene on Cu(111)⁸ suggest that benzene prefers the hcp-site over the fcc-site. This tendency could then be responsible for some of the driving force

associated with the shift along the molecular axis obtained in our calculations. Indeed, the distance between the rings in PVBA matches very well the one between two geometrically equivalent hollow-sites (either hcp or fcc). This allows the two aromatic rings to experience the same substrate environment which could reinforce any effect predicted for a single aromatic ring.

In both configurations the molecule is chemically bonded to the surface, with almost identical Cu–N and Cu–O bond lengths. Slight local relaxations of surface atoms and molecule atoms occur to allow for a displacement under these constraints. Specifically, in configuration I the oxygen atoms are 0.13 \AA closer to the surface than in configuration II (see Figure 2c,d). By contrast, the nitrogen atom, more rigidly coupled to the pyridine ring, sits similarly close to the surface in the two cases. To preserve the Cu–N bond length the first layer Cu atom is, therefore, lifted by 0.14 \AA in configuration II.

So far, the adsorption of PVBA seems to be governed by an interplay between the interactions of the aromatic groups with the surface mediated by anchoring bonds through the N and O atoms. In this scenario, the driving force for the relaxation is the tendency to achieve the “correct” stacking of aromatic rings over hcp sites. The energy difference between the two configurations is correspondingly ascribed to subtle differences in the relaxation behavior due to equivalently long chemical bonds occurring in slightly different adsorption geometries. This view is further supported by a projected density of states (PDOS) analysis. This reveals almost no difference for the carbon atoms between configuration I and II, consistent with the fact that the C atom adsorption sites are similar in the two cases. For the N-atom and the O-atoms slight differences in the occupied densities of in-plane p -states (p_x , p_y) are found, while the vertical p_z -states are not significantly altered. These findings are consistent with the fact that no noticeable change was detected in the appearance of the two configurations in the STM images (see Figure 1b).

We next turn to the discussion of the screening capabilities of the two adsorption configurations. Given the deprotonation of the PVBA molecule upon the adsorption on the copper surface a horizontal dipole is formed along the molecule and oriented from the deprotonated carboxyl group to the pyridyl group. This induces an image charge electrostatic response by the metal substrate corresponding to an image dipole in opposite orientation. The different response from configuration I and II is investigated by the following procedure: At first, the electron density displacement $\Delta\rho^1(\mathbf{r})$ is evaluated for configuration I by subtracting the neutral density of the separated molecule and substrate from the total (“interacting system”) density obtained for the relaxed structure.¹⁰ Neglecting the small lateral displacement of the PVBA molecule, configurations I and II only differ by the position of the second and third copper layer. By swapping

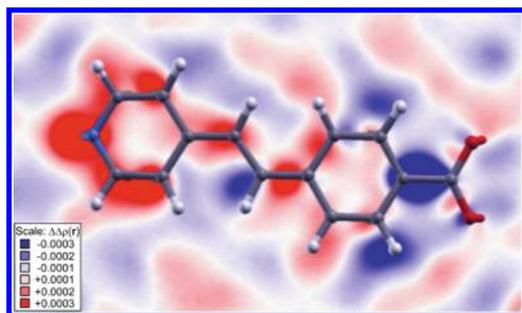


Figure 3. Map of the differential adsorption charge transfer $\Delta\Delta\rho(\mathbf{r})$ between configuration I and II of PVBA on Cu(111). Considering the more stable configuration I as reference, red areas denote larger negative charge accumulation, blue areas denote larger positive charge accumulation (*i.e.*, electron depletion). The projection is on a plane between the molecule and the surface. The larger electron accumulation around the pyridine ring and the larger depletion around the carboxylate region denote a more efficient screening of the horizontal PVBA dipole for configuration I over configuration II.

hcp- and fcc-sites, which corresponds to a rotation of 180° of the subsurface layers, a second density displacement $\Delta\rho^{\text{II}}(\mathbf{r})$ is then calculated. This is associated with the molecule in configuration II. Finally, the difference of the two quantities $\Delta\Delta\rho(\mathbf{r}) = \Delta\rho^{\text{I}}(\mathbf{r}) - \Delta\rho^{\text{II}}(\mathbf{r})$ can be safely inspected in the molecule and first layer region to investigate the coupling between substrate stacking and screening response (performing the same procedure starting from configuration II yields almost identical results). To screen the molecular dipole electrons must withdraw from below the carboxylate and accumulate around the pyridyl group. Indeed, electron density depletion is obtained below the carboxylate group in both configurations, accompanied by an electron density accumulation located below the pyridyl ring.¹⁰ However, the effect is significantly larger for configuration I. Namely, a larger electron density depletion is obtained below the carboxylate group for the energetically preferred configuration I, accompanied by a correspondingly larger electron density accumulation below the pyridine ring. This is revealed by inspecting the calculated electron density difference pattern $\Delta\Delta\rho(\mathbf{r})$ in the region between the surface and the molecule. The pattern is shown in Figure 3 indicating that configuration I allows for a more efficient electron redistribution than con-

figuration II. This behavior must reflect the different locations of Cu atoms in the second layer for configuration I compared with configuration II. In the present system, the slightly better screening of the molecular dipole in configuration I can be related to the larger amount of valence charge available for local screening when the metal atoms in the second layer are positioned more directly underneath the most electrostatically charged (and chemically active) atoms of the adsorbed molecule.

CONCLUSION

We have presented a combined experimental and theoretical study on single PVBA molecules adsorbed on Cu(111). We find that PVBA is predominantly adsorbed in only three orientations. This reflects the reduced symmetry of the surface once the subsurface atoms are included. In particular, this shows that the second and subsequent Cu layers can play a major role in the bonding of large organic molecules on Cu(111). We believe that our results can be generalized to other close-packed surfaces. Furthermore, the influence of subsurface layers shown here for single molecules, can potentially also play a role for supramolecular assemblies, composed of nonsymmetric molecules, in terms of geometrical arrangement and electronic properties.

METHODS

STM Investigation. The single crystal Cu(111) was prepared by repeated cycles of Ar^+ ion sputtering and subsequent annealing. PVBA was evaporated ($T_{\text{cell}} = 456$ K) in ultrahigh vacuum for 5–10 min leading to submonolayer coverage. The temperature of the sample was kept at room temperature during deposition. After the preparation the sample was transferred into the low-temperature STM where it was cooled down to 6 K.

DFT Calculation. The PVBA on Cu(111) system was modeled by Density Functional Theory (DFT) calculations by means of the Quantum-ESPRESSO package¹⁹ and treating the electronic exchange and correlation terms within the local density approximation (LDA). We used ultrasoft Perdew–Zunger pseudopotentials with energy cutoff of 25 Ryd to model the interaction between the atomic cores and the valence electrons. The

Cu(111) surface was modeled with a four-layer periodic slab with 36 Cu atoms per layer. The size of the hexagonal cell was $a = b = 16.71$ Å, and Brillouin zone sampling was limited to the Gamma point only. A c value of 22.4 Å was used, so that 10 Å of vacuum separate the slab from its periodic images along the z direction orthogonal to the slab. The bottom layer was kept fixed at the bulk Cu values to mimic the behavior of the metal substrate.

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