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

Robin Ohmann,*† Giacomo Levita,‡§ Lucia Vitali,‡ Alexander De Vita,†* and Klaus Kern†*

The asymmetric molecule 4-[trans-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA) adsorbed on Cu(111) 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 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 endgroups), 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.

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 (−211) 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
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(b) 51.7

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distribution.

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fication of the molecule with respect to the substrate registry.

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 Å²: (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 con-
nected by a vinyl bridge. By scanning tunneling micros-
copy (STM) the two sides of the PVBA molecules can
be distinguished10 allowing in contrast to previous studies5,11 a clear distinction and selection of the orienta-
tion 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
fluence 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

tage of ±0.1 V, PVBA appears as two protrusions and
one large depression at one end, which we have pre-
viously 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 dis-
tance between the protrusions (see top inset Figure 1a)
is comparable to the distance of 6.62 Å 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 spe-
cies (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 exclu-
sively determined by the top layer, these molecular
orientations would be equally likely. Although six orienta-
tions are indeed observed, we find that among these,
three orientations, which are, however, strongly preferred, which
we label as configuration I. The other three orienta-
tions, 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% pre-
fereedness for configuration I. Figure 1b shows a topo-
graphy 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

<table>
<thead>
<tr>
<th>Configuration</th>
<th>STM</th>
<th>DFT ΔE (meV)</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>84</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td>5</td>
<td>47</td>
</tr>
</tbody>
</table>

TABLE 1. PVBA on Cu(111): Number of Molecules Found in Certain Adsorption Orientations (Left), Calculated Energetic Difference (Right)
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 $\lambda_{211}$ axes. Depending on the enantiomer, a small clockwise or counter-clockwise angle of approximately 4° 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.\textsuperscript{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 \((-211)\) 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 \(7^\circ\), has either a clockwise or counterclockwise sense characterizing the two different enantiomers \(\delta\)- and \(\lambda\)-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 \((-211)\) 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 2a) the nitrogen atom of PVBA is located almost on top of a Cu atom, with a slight shift of the molecule along \((-211)\) toward a nearby hcp-hollow site. Rotating the molecule in-plane by \(-60^\circ\) (or \(+60^\circ\), or \(180^\circ\)) 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 Å further away laterally for case II, resulting in an overall rigid displacement of the molecule along the \((-211)\) 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)\textsuperscript{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 Å 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 Å 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 \(\Delta \rho(r)\) 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.\textsuperscript{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
The larger electron accumulation around the pyridine ring and the larger depletion around the carboxylate group in both configurations, accompanied by an electron density accumulation located below the pyridyl ring. 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 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 (Tevapor = 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.

REFERENCES AND NOTES


12. Along with single molecules supramolecular structures are formed. These consist of two molecules in opposite orientations. Therefore the ratio of I to II will not be altered. Notably, in these structures the two configurations respond differently to the tunnel current as reported. For deposition below room temperature, deprotonation was less frequently observed, hindering a temperature depended study.


14. The value was calculated by means of the nudged elastic band (NEB) method, in which the initial and final images were fixed at the relaxed geometries of the PVBA molecule adsorbed on two adjacent sites. Eleven intermediate points were considered to satisfactorily represent the rigid translational movement between these two anchoring sites.

15. Manipulation experiments reveal that the molecules are more easily rotatable around the oxygen side than inducing a translational movement.


18. In the DFT approach van der Waals forces are not adequately treated. In the here chosen treatment of the exchange-correlation terms, they are usually overestimated.