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Interplay between metal-free phthalocyanine molecules and Au(110) substrates

E. Rauls [a,*], W.G. Schmidt [a], T. Pertram [b], K. Wandelt [b]

[a] Lehrstuhl für Theoretische Physik, Universität Paderborn, 33100 Paderborn, Germany
[b] Institute of Physical and Theoretical Chemistry, University of Bonn, 53115 Bonn, Germany

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ABSTRACT

Metal-free phthalocyanine (Pc) molecules adsorbed on the Au(110) surface have been studied both experimentally (STM, LEED) and with density functional calculations. A strong interaction between substrate and adsorbate is observed. On the one hand, a clear template effect of the anisotropic substrate is observed: already at low coverages, the Pc molecules adsorb in various typical row patterns. On the other hand, the molecular adsorption modifies the substrate: at coverages higher than 0.25 monolayers, the usual (1×2) reconstruction is converted to a (1×3) reconstruction. First principle DFT calculations yield adsorption geometries that agree with the measured STM images and adsorption energies in the range of 2–3 eV. The adsorption leads to covalent and van der Waals interactions between adsorbate and substrate and is accompanied by a considerable charge transfer.

Aromatic macrocycles based on the phorphyrin system, known for example from hemoglobin or chlorophyll, have recently attracted considerable attention because of their potential applications in a variety of areas ranging from cancer therapy to solar cells and fuel cells [1]. The adsorption of porphyrine and phthalocyanine (Pc) molecules on surfaces is a topic of investigation in the context of new nanotechnological and nanoelectronic materials [2–7]. In such systems, not only the interaction of the molecules with the surface has to be understood to tailor new materials, but also the interaction of the molecules with each other plays an important role as has been reported for an adsorbate on a graphite substrate [5]. While molecular adsorption on many isotropic surfaces has been investigated, an anisotropic surface may allow for triggering one-dimensional growth. The (110) surfaces of fcc metals have an intrinsic anisotropy. It is even more pronounced in case of the missing row reconstruction, as reported for gold [8,9]. The Au(110) surface is a suitable template for the growth of phthalocyanine molecules and has already been investigated in this context [10–14]. In this combined theoretical and experimental work, the interaction of metal-free H2-Pc with the Au(110) surface is studied in detail. We present adsorption models based on experimental data and ab initio calculations and propose a mechanism for the molecule induced reordering of the underlying substrate. After a short description of the experimental setup and the theoretical modeling, we present the models of adsorbate structures which can explain the scanning tunneling microscopy (STM) images and low energy electron diffraction (LEED) spectra. Finally, we discuss a mechanism for the adsorbate induced change in surface reconstruction.

Our STM and LEED experiments and sample preparation have been performed in two home built UHV systems each working under a base pressure of $5\cdot10^{-10}$ mbar. One equipped with an STM scanner according to the design of Stipe et al. [15]. STM data processing has been performed by using the freeware image processing software WSxM [16]. The STM is able to operate at room and liquid nitrogen temperature cooled by bath cryostat. Electrochemical etched tungsten tips have been used as a probe. The other chamber was equipped with a LEED optics. Additional the UHV systems house a quadruple mass spectrometer (QMS) and Auger electron spectroscopy (AES). The Au(110) single crystal was supplied by MaTeck with a purity of 99.999% and a accuracy of <0.4 to the (110) plane. The metal-free phthalocyanine has been purchased by Sigma-Aldrich with a purity of 98% and was evaporated by a home build knudsen cell. The sample was cleaned by several cycles of argon ion sputtering and annealing and was kept at 300 K during molecule evaporation.

The adsorbate structures have been calculated using first principle density functional theory (DFT) calculations with the Vienna Ab Initio Simulation Package (VASP) [17]. The PW91 functional [19] was used to model the electron exchange and correlation interaction within the generalized gradient approximation (GGA). The electron-ion interaction was described by the projector-augmented wave (PAW) method [18]. As a k-point sampling both the gamma point and a $(2\times2\times1)$ scheme were chosen. The energy cut-off of the plane-wave basis is 400 eV. Molecule–substrate interactions are often influenced by dispersion forces not contained in DFT-GGA. The accurate first-principles description of van der Waals interactions for systems of the size studied here exceeds by far our computational resources. Therefore, long-range

* Corresponding author. Tel.: +49 5251 60 3824; fax: +49 5251 60 3435.
E-mail address: eva.rauls@uni-paderborn.de (E. Rauls).

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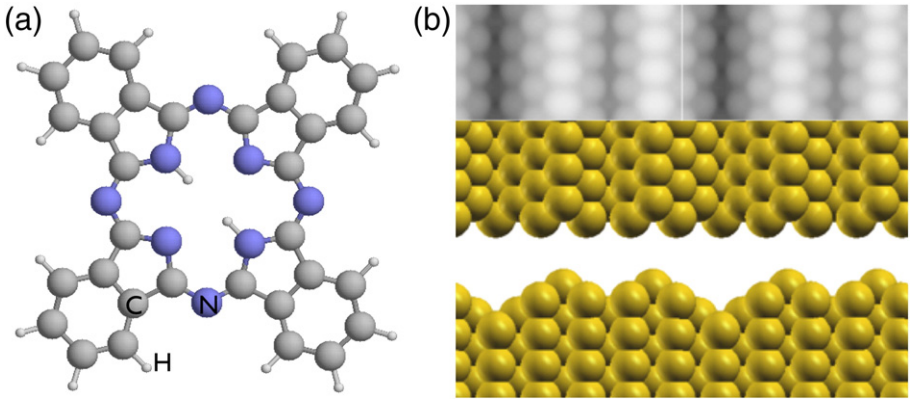

Fig. 1. (a) Structural model of the Phthalocyanine (Pc) molecule and (b) top and side views of the surface slab used. The overlayed simulation illustrates how this structure should look like in an STM.

dispersive interactions were accounted for using the semi-empirical London-type correction described in Ref. [20]. A comparison of the performance of various implementations for the treatment of long range interactions can be found in Ref. [22]. McNellis and co-workers [21] recently tested among others this simple scheme for molecular adsorption on coin metal surfaces and found it to predict adsorption energies that fall close to the measured data. Fig. 1(a) shows a ball-and-stick model of the H2-Pc molecule. We have investigated the adsorption of H2-Pc at varying coverages on the reconstructed Au(110) surface. Usually, the (1×2) reconstruction is observed on this surface, and this is also the case if H2-Pc is evaporated onto the surface in low doses. At high coverages, however, the situation changes.

The (110) surface of gold is special in the respect that it can exhibit a variety of $(1\times r)$ reconstructions at nearly equal energy, r ranging from two to five [23]. Among these, the (1×2) reconstruction is observed most often. The (1×3) reconstruction, however, is slightly lower in energy. Bearing this in mind, it is no surprise that slight perturbations, like e.g. the adsorption of molecules presents, can change the reconstruction. The system under investigation, Pc on Au(110), is a good example for such a process of substrate re-ordering.

In order to determine the translational symmetry of the adsorbed metal free phthalocyanine molecules, we performed LEED measurements at the range of monolayer (ML) coverages. In Fig. 2(a), the typical LEED pattern for a clean Au(110) surface is given. The directions of the surface are marked. The unit cell is indicated with a black square with the spots of the (1×1) unit cell at the corners and the spots of the (1×2) reconstruction between them. After the adsorption of 0.75 ML of H2-Pc molecules, the LEED pattern in Fig. 2(b) is observed. Two spots of a (1×3) unit cell appear in [001] direction additional to the (1×1) spots between them (marked by red arrows). At 0.75 ML coverage of H2-Pc molecules evaporated on the sample at 300 K, the molecules arrange themselves in a sixfold periodicity with respect to the underlying gold substrate. In Fig. 3, the rows of molecule spots are indicated with red arrows. At higher coverages (1.25 ML) and after annealing at 600 K, the molecules form a 5×3 structure as is also observed for several other Pc molecules on Au(110) surfaces [10,13]. Below 0.75 ML coverage, no structural information can be extracted from LEED measurements. Further structural investigations have been performed with STM. All images were taken at a temperature of 90 K. At a coverage of 0.5 ML and a bigger image size (c.f. Fig. 4), the formation of molecule double rows oriented along the [1–1 0] direction are observed. These rows extend over the complete terraces and step edges. The additional brighter areas and the fuzzy step edges in [001] direction may originate from an unavoidable movement of gold atoms during the change from the (1×2) to a (1×3) reconstruction. A closer look as shown in Fig. 5(a) reveals further details concerning the adsorption of the H2-Pc. Supported by a (1×3) reconstruction, rows of double protrusions can be seen, often separated by one row of the (1×2) reconstruction. At dislocations between these two types of reconstructions, single molecules adsorb in the expected fourfold symmetry (as indicated with green arrows in Fig. 5(a)). Surface areas, where no molecules are adsorbed, keep the typical (1×2) reconstruction, as confirmed by the line scan along the black line *s1* in Fig. 5(b). The closest distance between the protrusions is six times the distance of the supporting gold lattice, which is seen in the line scan along the line *s2* as given in Fig. 5(c).

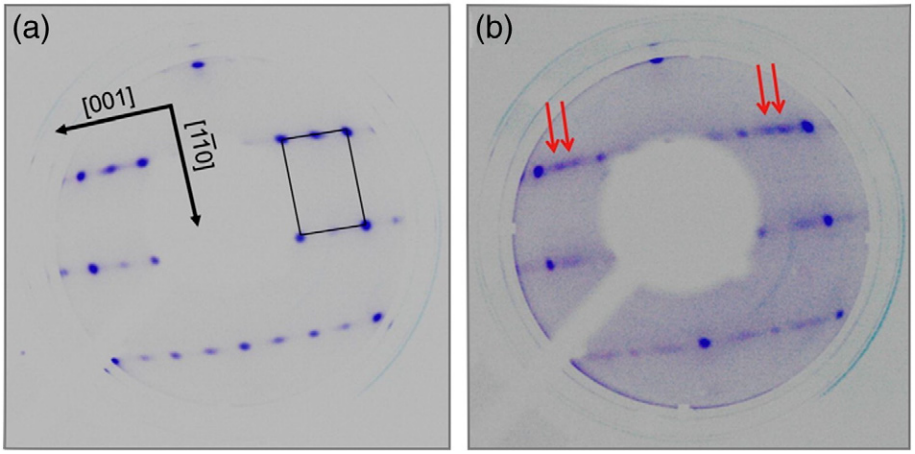

Fig. 2. LEED pattern of the clean Au(110) surface (a) and after the adsorption of 0.75 ML of H2-Pc (b), both taken at T<100 K, 121 eV. Beside the structure of the substrate at lower beam energies, the periodicity of the molecular adsorbate can be seen.

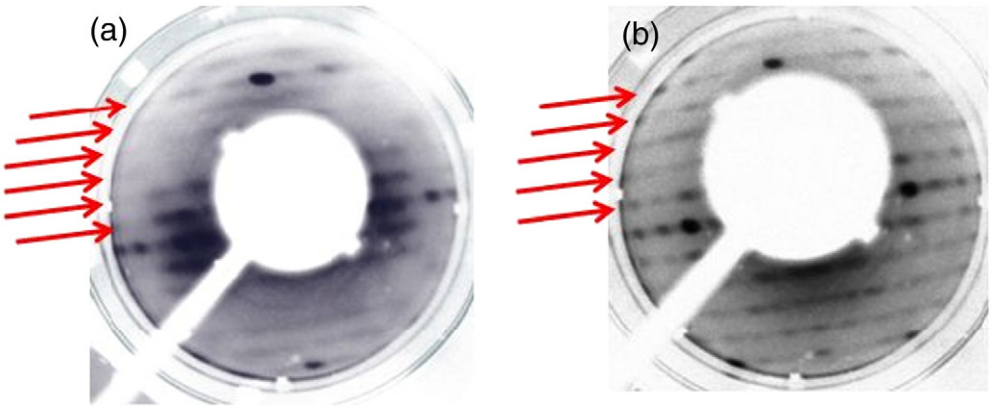

Fig. 3. LEED pattern of 0.75 ML of H2-Pc (a) and 1.25 ML of H2-Pc on Au(110), both taken at 55 eV.

For the modeling of the observed structures, a special surface slab model with periodic boundary conditions was used. This model consists of (1×2) and (1×3) type reconstructions arranged in an alternating manner. Like this, the substrate directly below the molecules as well as in the direct neighborhood resembles the experiments. Fig. 1(b) shows a top and below a side view of this model together with an overlayed simulated STM image. On this special model as well as on pure (1×2) or (1×3) surfaces, Pc molecules (at rather low coverages) have been calculated to exhibit a variety of (meta-)stable adsorbate structures, that differ in energy by 1–2 eV. Binding energies are given in eV per molecule throughout this work.

Upon adsorption, the molecule typically strongly distorts, thus optimizing the van der Waals interaction with the buckled substrate. Fig. 6 shows top and side views of the relaxed geometries of the most stable adsorbate structures. From LEED and STM measurements, we know that – expressed in underlying Au-atoms along the (100) direction –, the Pc molecules arrange themselves along the troughs with distances of most often seven, six or five Au-atoms. In the following, we refer to these structures by d7, d6, or d5, respectively.

Besides the molecule's position and orientation in the adsorbate, the question arises whether or not the center hydrogen atoms reside at their gas phase positions or deprotonate and either diffuse on the surface or leave in form of an H_2 molecule. We calculated these scenarios on both (1×2) and (1×3) surfaces for two molecular orientations differing by 45°, finding for all cases an increase in total energy, leading to repulsive energies of 1.0–1.1 eV. Consequently, the molecules can be regarded as complete also after adsorption.

At low coverages corresponding to larger distances, the d7 is the prevalent structure. As depicted in Fig. 6(a), the molecules adsorb with two of their phenyl rings parallel to the (100) troughs. The slightly asymmetric position above the (1×2) trough is found to be most stable. The wider (1×3) trough induces a symmetric adsorption

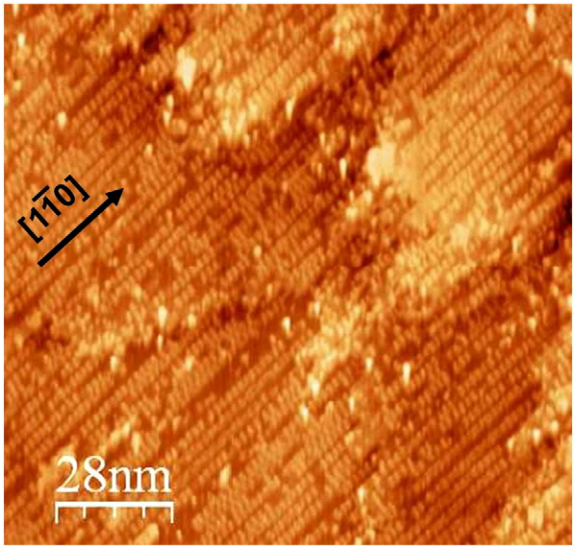

Fig. 4. STM image of the Au(110) surface with 0.5 ML coverage of H2-Pc (−2.3 V, 53.4 pA, T = 90 K).

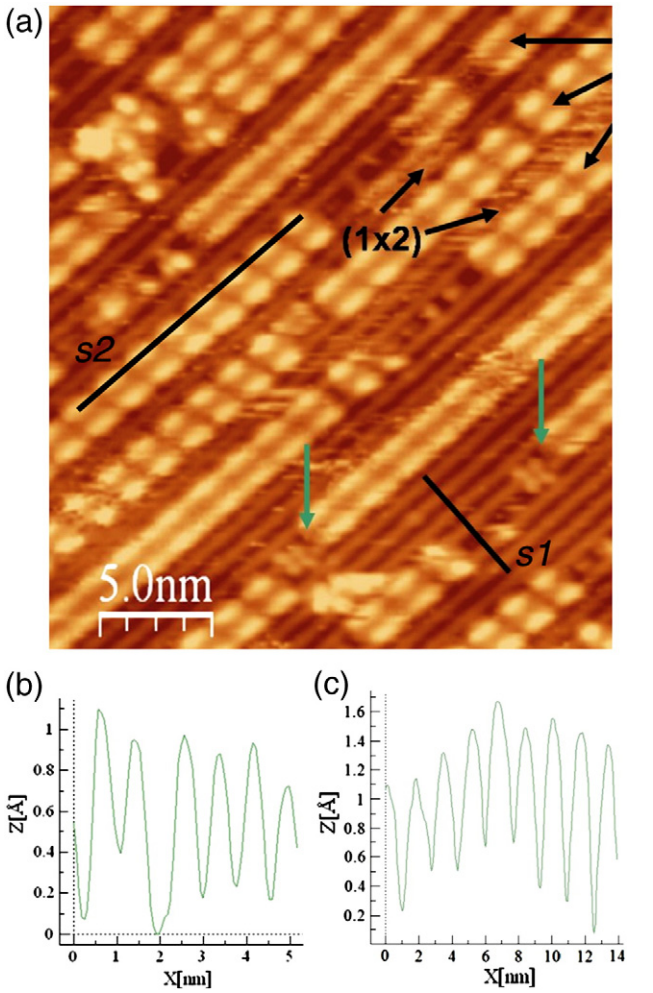

Fig. 5. (a) STM image of the Au(110) surface with 0.5 ML coverage of H2-Pc (−2.3 V, 53.4 pA, T = 90 K). (b) Linescan along the black line *s1* indicated in the STM image, i.e. perpendicular to the Au-rows. (c) Linescan along the (1–10) direction as indicated by the black line *s2* in the STM image.

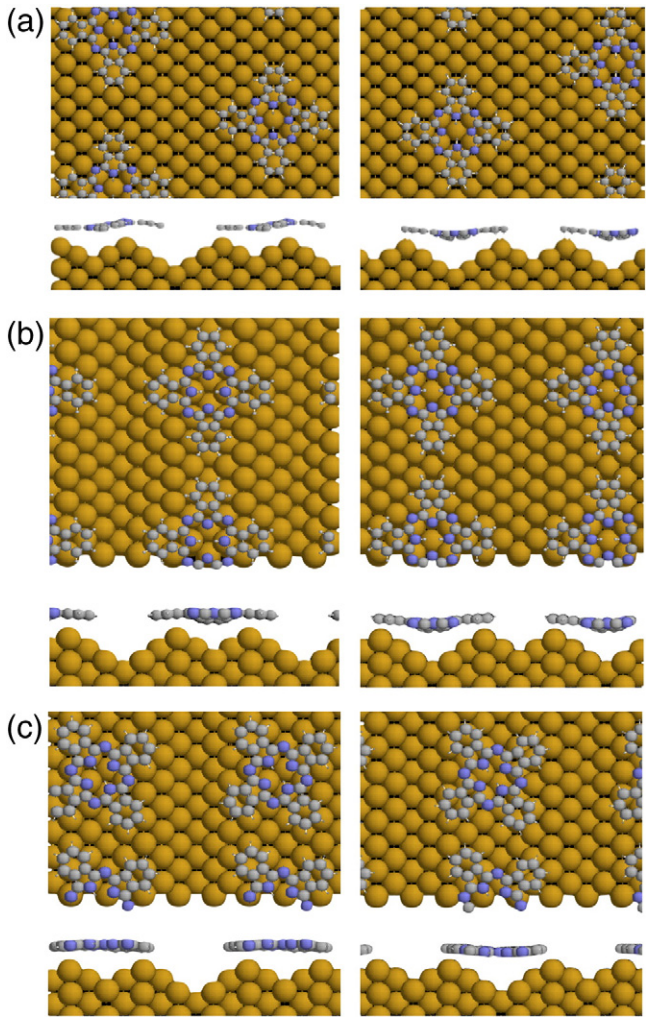

Fig. 6. Top and side views of the most stable adsorbate geometries for different coverages. Structural images show the relaxed geometries for Pc adsorbed with its center on the (1×2) trough (*lefthandside*) or on the (1×3) trough (*righthandside*). In (a), the molecules are adsorbed in a distance of 7 Au atoms along the (100) direction. In (b), the distance is 6 Au atoms, in (c) only 5.

position. The binding energies are −3.23 eV for the (1×2) trough and −2.68 eV for the (1×3) trough, thus 0.55 eV in favor of the (1×2) trough structure. The exact registry of the molecule on the surface and whether adjacent molecular rows are staggered in reverse order or not does nearly not affect the energy of the adsorbate structures. In spite of the varying distortions of the molecule, the potential energy surface corrugation is below 0.1 eV, ensuring molecular mobility. Similarly, the position of the two hydrogen atoms in the center of the molecule does not change energetics by more than 0.1 eV, although the preferred position is along the troughs rather than perpendicularly throughout all structures under consideration. The molecular arrangement of the d7 structure corresponds to a coverage of 24%.

Comparing this result to the experimental observations, we find that the LEED data show that this is still slightly below the "critical coverage" at which structural reordering of the substrate starts. The preferred adsorption of the Pc molecules on the (1×2) trough confirms this, since, at this point, obviously no driving force for a change to the (1×3) reconstruction is induced by the molecules.

The molecule–substrate binding is to a large part covalent and accompanied by a charge transfer from the Au-surface to the molecules. Fig. 7 shows the induced charge density for the d7 structure with the

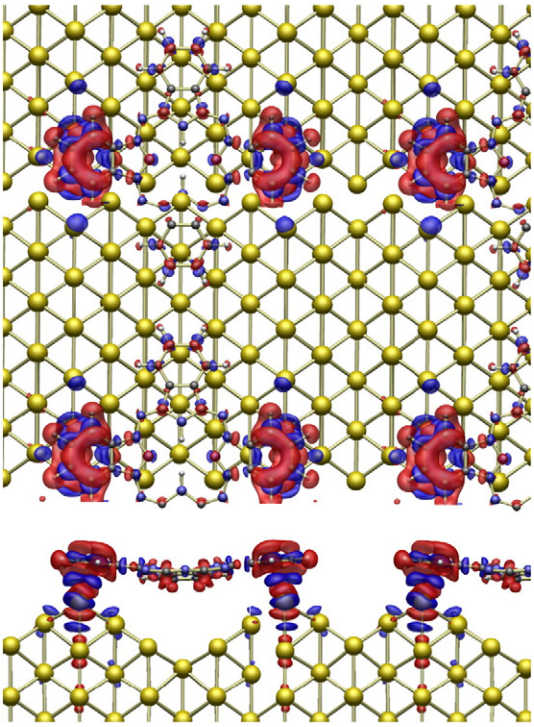

Fig. 7. Top and side views of the calculated charge density differences due to the adsorption of H2-Pc on the (1×3) trough (d7 structure). Red indicates electron depletion, blue electron accumulation.

molecule on the (1×3) trough. The two opposite phenyl groups of the Pc molecule are bent upwards and form covalent bonds to Au-atoms of the ridges on the reconstructed surface. The other two phenyl parts and the center of the molecule are sagging slightly into the trough, as illustrated by the side view in Fig. 7. Mainly the two binding phenyl groups of the molecule experience a rather local charge redistribution. From the substrate, 1.43 electrons are transferred to these parts of the Pc molecule. For comparison, for the molecule adsorbed above the (1×2) trough, this charge transfer amounts to only 1.04 electrons. Along with the charge transfer, the different heights of the Pc-molecules above the surface can be discussed. As a measure for this, we calculated the average height of all atoms in the molecule and calculate the distance to the topmost Au-atoms along the surface normal. For all the structures discussed in this work, it turns out that adsorption on a (1×2) trough leads to heights of 3.7–3.8 Å, while adsorption on (1×3) troughs yields heights of only 3.2–3.3 Å, which is slightly higher than typical distances of Pc-molecules with metal centers. For Copper-Pc on Ag(110), adsorbate–substrate distances are found [25] that range between 2.7 and 3.1 Å. Reducing the intermolecular distance by one Au-atom along (001), the Pc molecules assume a position that minimizes the distance in this orientation in the d6 structure, compare Fig. 6(b). In this structure, the coverage has increased to 33%. The achieved arrangement is considerably less favored than the d7 which might be traced back to repulsion between the hydrogen atoms at the phenyl groups of neighboring Pc molecules and electrostatic repulsion. Similar effects have been reported in Ref. [24]. Nevertheless, Pc can, again, stably adsorb above both troughs. This time, however, the (1×3) trough presents the preferred adsorption site. The binding energy on the (1×3) trough has been calculated to −2.00 eV and is, thus, by 0.35 eV lower than for adsorption above the (1×2) trough. In agreement with the LEED observations, a driving force for re-ordering the substrate reconstruction seems to be initiated.

Finally, increasing the coverage to 40% by bringing the Pc molecules another Au-atom distance closer along (001), we obtain the d5 structure (Fig. 6 (c)). This is, however, not possible if the molecules are not

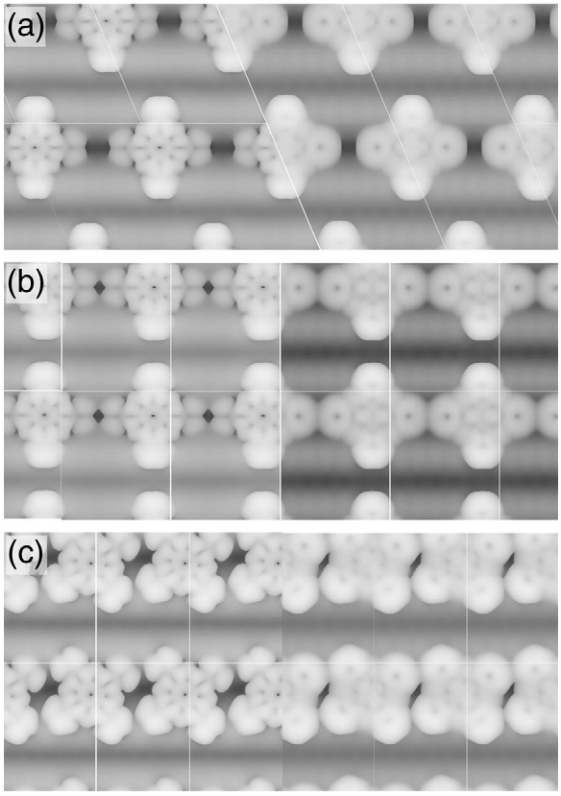

Fig. 8. Constant current STM simulations of the (a) d7 structure, (b) d6 structure, and (c) d5 structure with Pc adsorbed on the (1×3) trough. The left hand parts of the images show the simulations for a voltage of +1 eV applied, the right hand parts for −2.5 eV.

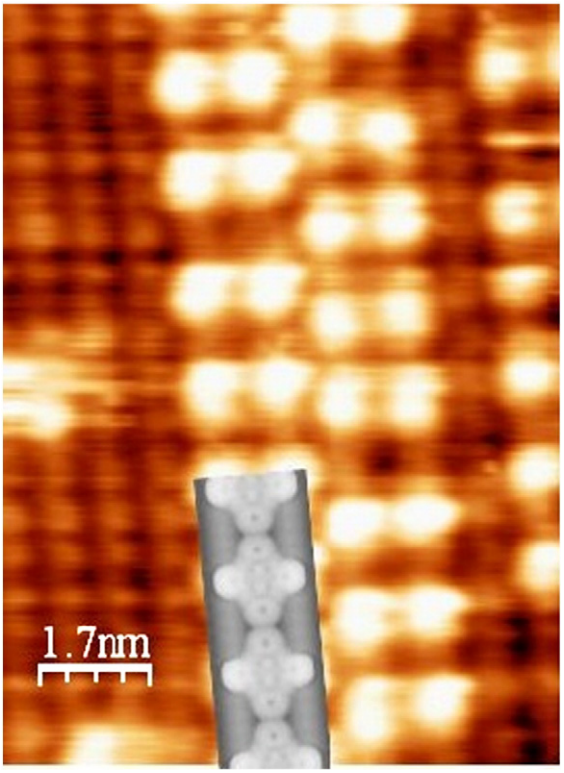

Fig. 9. Superposition of the experimental STM image and the STM simulation for the d6 structure (gray).

rotated and moved at the same time. In the final, energetically lowest, structure, the molecules are approximately 10° rotated against the (001) direction. The centers of the molecules lie centered over the troughs, thus maximizing the overlap of all four phenyl groups of the molecules with the topmost Au rows. Adsorption is possible on both troughs, and the binding energy increases again to −3.7 eV in both cases. A charge transfer of 1.2 electrons from the substrate to the molecule stabilizes the structures. Calculations of the molecular adstructures also without the substrate show nearly no interaction between adjacent molecules, neither for the d7, the d6 nor the d5 structure.

Fig. 8 shows constant current STM simulations of the three structures for two different voltages. For d7 and d6, parts (a) and (b) of the figure, the characteristic bright spots caused by the phenyl rings above the top most Au rows are conspicuous. The other two phenyl rings of the molecules, lying in the troughs, cause some weaker spots, which compares well with the experimental STM observations. The d5 structure in part (c) of the figure gives rise to bright spots over the complete molecule, slightly brighter for the parts above the topmost Au rows of the surface. The bright spots of adjacent molecules start to blur, which is similarly seen in the experimental STM images. Fig. 9 shows a superposition of the experimental STM image and the STM simulation for the d6 structure. The distances of the molecules as identified by the bright spots as well as the blurred enlighted areas between these spots are well represented in the simulation. The d5 structure is supposed to cause the more blurred spots which are observed especially in the lower left corner of the STM image in Fig. 5(a).

The results for the energetic stability and electronic properties of the adsorbate models discussed above suggest a strong coverage dependence of the adsorption mechanism. The flexibility of the Pc molecules and the large variety of adsorption structures with similar adsorption energies make an unambiguous assignment of the calculated structures and mechanisms to the experimental situation difficult. However, also experimentally, different adsorbate structures are observed simultaneously.

Table 1 summarizes the binding energies of the structures discussed above on the (1×2)–(1×3) substrate model (top part) and some further models which were calculated for the pure (1×2) and (1×3) surface reconstructions (bottom), respectively. For the (1×2) surface, this comprises seven models for adsorbate structures with the molecules spaced by seven Au-atoms of the underlying substrate along [100], i.e. like in the d7 model, but with varying rotations of the molecules and with the neighboring rows shifted differently along [100]. Binding energies calculated for these models lie between −1.6 and −3.0 eV, depending strongly on this shift. Repulsive interaction between phenyl groups of molecules in neighboring rows lowers the energetical stability, considerably. For the furthest separated arrangement, the binding energy is −3.0 eV and, thus, comes close to the d7-value (−3.2 eV). In the combined (1×2)–(1×3) substrate model, the repulsion between adjacent rows is avoided due to the separation of the troughs. Furthermore, this model resembles the experimental situation best, where the reconstruction

Table 1
Calculated adsorption energies of favorable adsorption models on the mixed substrate model with the molecules centered above the (1×2) or the (1×3) troughs, respectively (upper part of table), and (bottom) for the molecules centered on trough or ridge on a (1×3) reconstructed surface (bottom). All values in [eV].

Structure	E_{bind} (1×2)	E_{bind} (1×3)
d7	−3.2	−2.7
d6	−1.7	−2.0
d5	−3.7	−3.7
Structure	**E_{bind} (trough)**	**E_{bind} (ridge)**
d6 (1×3)	+0.8	+1.2
d7 (1×3)	−3.0	−2.6
d8 (1×3)	−3.2	−2.6
d7 (1×2)	−1.6–−3.0	–

only changes below the molecular rows but remains unchanged in between. A full surface coverage of either a (1×2) or a (1×3) surface, as is described by the models of the bottom part of the table, has not been observed. However, in regions where two double rows of spots (i.e. two molecular rows) are observed, like in the STM image in Fig. 9, one of the situations in the table can arise. As another result, the energy difference between molecules adsorbed in 6–8 fold distances on top of the gold ridges or above the troughs of the (1×3) reconstruction shows a clear preference of the troughs.

In summary, we performed STM and LEED measurements along with DFT calculations in order to get insight into the various adsorption structures possible for different coverages of Pc on Au(110) surfaces. Three main adsorbate structures have been identified for different coverages. For low coverages, characteristic row patterns are observed on the (1×2) reconstruction, which can be explained by the proposed d7 structure with the Pc binding covalently with two of their phenyl groups to the gold ridges. At higher coverages, another structure appears, the d6 structure, which evolves from the d7 by moving the molecules by one Au–Au distance closer together. Intermolecular repulsion destabilizes this structure in total, but at this coverage, the (1×3) trough gets favored over the (1×2) as adsorption position, indicating the observed re-ordering of the surface reconstruction. At even higher coverages, the STM spots become slightly more blurred, which can be explained by the very stable d5 structure with the molecules centered above the (1×3) troughs, and moved even closer, for which they have to be rotated compared to the d6 or d7 structures. The DFT calculations, thus, provide a microscopic model for the mutual interaction between H2-Pc and the Au(110) substrate. Irrespective of the specific adsorption configuration, we find the molecular bonding to be caused by covalent interactions between molecular phenyl groups and substrate ridge atoms as well as dispersion forces. A considerable charge transfer of the order of one electron occurs from the substrate to the adsorbate. The calculations were performed using grants of computer time from the Paderborn Center for Parallel Computing (PC^2). The Deutsche Forschungsgemeinschaft (DFG) and the Sonderforschungsbereich (SFB) 624 are acknowledged for financial support. We would like to thank P. Königshoven and the mechanical workshop for technical support and C. Becker for fruitful discussions.

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