

Coronene on Ag(111) Investigated by LEED and STM in UHV

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The adsorption of the aromatic molecule hexabenzobenzene (coronene) on a Ag(111) single crystal surface was investigated under UHV conditions by means of LEED and variable temperature STM. For a very low coverage randomly distributed individual molecules adsorbed on terraces were found. All molecules are surrounded by concentric rings caused by scattering of surface electrons, leading to the formation of standing waves. These surface electrons mediate an additional intermolecular interaction with an oscillatory potential in the distance between molecules. The balance of all forces leads to a typical spacing of 2.4 nm for isolated molecular dimers. For monolayer coverage, a long-range ordered close packed structure was found. Calibration of the coronene LEED pattern with the substrate spots provided the superstructure unit cell parameters. These were used for distortion correction and a subsequent correlation analysis, which improves the quality of the submolecular resolved images. The zoom shows a tilt of the molecules against the substrate plane.

Introduction

The basic study of organic molecule adsorption on a crystalline substrate is of fundamental interest because of the huge variety of existing molecules and their widespread physical and chemical properties. Also the impressive opportunities for applications of organic–inorganic interfaces, mainly for electronic devices, are a further challenge to study selected organic molecules on well-defined substrates.

Coronene (structure given in Figure 1) is an interesting substance for several reasons: the molecule is planar with a 6-fold symmetry axis (spacegroup D_{6h}), which makes coronene suitable for theoretical calculations; it can be considered as the smallest possible flake of a graphite sheet saturated by hydrogen atoms; on the other hand, coronene is one of the most complex molecules encountered in interstellar space and possibly plays a basic role in interstellar extinction.¹

Adsorption of coronene on graphite(0001) was studied by LEED² and STM.³ There was found a hexagonal close packed $\sqrt{21} \times \sqrt{21} R \pm 10.9^\circ$ superstructure of the coronene molecules. This superstructure is commensurate (i.e., all superstructure matrix elements are integers), despite the incommensurability of the molecular dimensions with the graphite unit cell due to the hydrogen atoms surrounding the graphite kernel of coronene. Furthermore it was found that the very weak adsorbate–substrate interaction is of a purely van der Waals type.³

In this paper the coronene adsorption on a metal surface is studied. In this case a stronger adsorbate–substrate interaction should be expected, which is dominated by the interaction of the molecular π -electron systems with the conduction band and surface state electrons of the metal. There was previous effort to investigate coronene on Ag(111) by means of STM.⁴ But

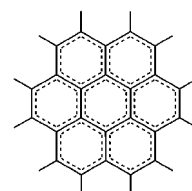


Figure 1. Structure of coronene ($C_{24}H_{12}$).

only thick layers around 100 nm were investigated, and no submolecular resolution could be obtained.

This paper is organized as follows. First of all the experimental conditions are described. In the result section, at first, low coverage is considered, which represents an approach to the single-molecule adsorbate. Then close packed monolayers with long-range order are discussed.

Experimental Section

All experiments were carried out in a UHV system without breaking the vacuum between sample preparation and analysis. STM imaging was done with the sample held at room temperature and low temperatures around 20 K as well. The sample is cooled with a liquid helium flow cryostat, however the tunneling tip cannot be cooled in our STM and remains always nearly at room temperature. Electrochemically etched tungsten tips were used, which were cleaned in-situ by Ar^+ -ion sputtering and subsequent annealing. All given tunneling voltages are referred to the sample. The Ag(111) single crystalline surface was cleaned by cycles of Ar^+ -ion sputtering and subsequent annealing up to 550 °C.

Coronene layers were prepared by thermal evaporation in the preparation chamber of a two-chamber STM-LEED system from Omicron GmbH. Coronene was provided by Aldrich with a purity of 97% and was used without further ex-situ purification. Prior to sublimation the evaporant was outgassed at temperatures slightly below the applied temperature during the deposition. A simple home-built thermal evaporator with quartz-glass

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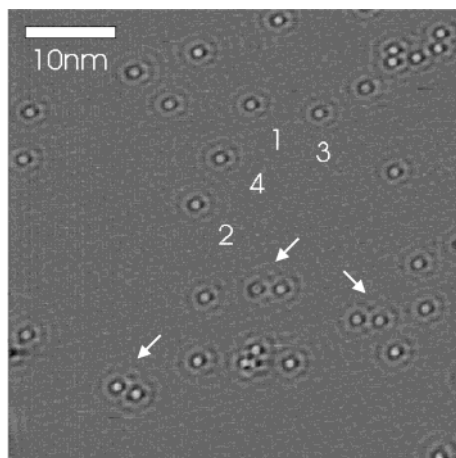


Figure 2. Constant height image of coronene adsorbed on Ag(111), taken at room temperature ($V = -774$ mV, $I = 408$ pA, 50×50 nm²).

crucibles and a chromel-alumel thermocouple was used. For a reproducible and stable adjustment of the evaporation temperature, an electronic controller was applied. The deposition rate was measured with a quartz microbalance to be in the order of $1 \text{ \AA}/\text{min}$. During the deposition the substrate was held at room temperature and the background pressure in the preparation chamber did not exceed the 10^{-10} mbar regime.

The LEED is a conventional four grid rear-view system from Omicron with LaB₆ cathode and was used to check the substrate preparation and investigate the coronene adlayers as well. The diffraction patterns were recorded with an ordinary CCD camera.

Results and Discussion

At first the Ag(111) surface was covered with very low coverage in the order of 1.5% of a monolayer, leading to isolated molecules. In this regime, the formation of islands could not be observed. A constant height image, recorded at room temperature, is depicted in Figure 2 with the bright spots corresponding to individual coronene molecules.

These single molecules are surrounded by concentric rings of standing electron waves, uniquely detected by STM, being sensitive to the local density of states (LDOS) at the position of the tip.^{5,6} A great feature of the STM is that the energy range of the LDOS mapping can be set by the tunneling voltage. If another molecule is within the decay length of these rings, interference with neighboring molecular rings leads to complex patterns. The electrons constituting these patterns come from surface states known for the densely packed (111) noble metal surfaces.⁷ These electrons behave like an almost free 2D electron gas with a nearly parabolic dispersion relation.^{8,9}

All—as far as we know—STM images of surface state electron scattering on adsorbates were obtained at low temperatures, mostly below 10 K. This was done for two reasons: to avoid diffusion of the adsorbate acting as scattering centers during the time needed for scanning. The second reason is to have a sufficient mean free path of the electrons, for the coherent superposition of the electron waves. The image in Figure 2, however, was taken at a sample temperature of 300 K. It turned out that the coronene molecules are quite strongly adsorbed at the Ag(111) surface; even the single molecules were not brushed away by the tip, as seen in subsequent images. The reason for the strong chemisorption might be a massive charge transfer between molecule and substrate and a hybridization of the molecular orbitals. For the aromatic PTCDA molecule, which has also a conjugated π -electron system, on Ag(111) the binding

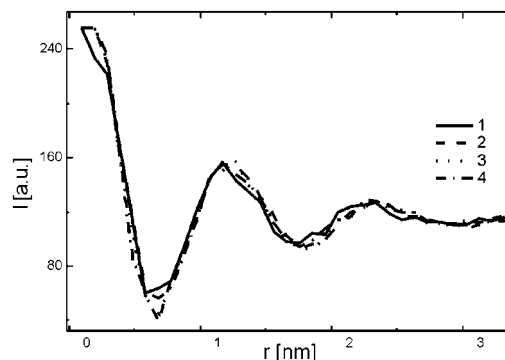


Figure 3. Radial average of the tunneling current vs distance to the center of the molecules (numbering refers to Figure 2).

energy is so large that decomposition of the molecules occurs during thermal desorption.¹⁰

These standing electron wave patterns are basically two-dimensional Friedel oscillations, first predicted for the three-dimensional case by Friedel,¹¹ where the screening of perturbing charges happens not with a monotonically decreasing density of free charge carriers, but oscillating with a period of half the Fermi-wavelength. We assume the perturbing charges in our case come from the conjugated π -electron system, which protrudes out of the molecular plane and penetrates into the substrate. The tunneling current averaged over the circumference of the concentric ring vs distance to the center is shown in Figure 3. For this representation molecules which are hardly influenced by neighboring molecules were chosen and are numbered in Figure 2. These curves are almost identical and decay very rapidly after only a few oscillations. The decay in amplitude of the charge density oscillation is to be expected for Friedel oscillations. The loss of coherence due to scattering may play a minor role on this length scale for the clean single-crystal surface.

The screening electrons are also mediating a long-range oscillatory interaction^{12,13} between adsorbates. Each molecule creates an additional potential with minima and maxima for distances, which are only dependent on the Fermi wavelength and the scattering phase shift for surface electrons. An analytically derived expression for this potential obtained by scattering theory is given by Hyldgaard et al.¹³ This long-range oscillatory potential influences other adsorbates in the surrounding of the scatterer. So the equilibrium distance between molecular dimers is determined by the balance of the oscillatory force contribution and the generally occurring intermolecular forces, like the attractive van der Waals force.

For low coverage of coronene on Ag(111), this leads to an average distance of molecular dimers of 2.4 nm (examples are marked with arrows in Figure 2), which is more than twice the next nearest neighbor distance of close packed monolayers, as described below. In the case of close packed coronene monolayers the contribution of the van der Waals force dominates and the next nearest neighbor distance decreases to 1.15 nm. Because of the monotonic decay of the van der Waals force we believe the main contribution in the case of isolated molecular dimers is due to the oscillatory force contribution caused by the scattering of surface electrons.

For increasing film thickness the formation of close packed layers was observed. Because of their long-range order LEED could be applied for the large scale characterization. In contrast to STM images, LEED provides an average over relatively large areas of the sample. The formation of ordered coronene and perylene adlayers on Ag(110), Au(110), and Au(111) was

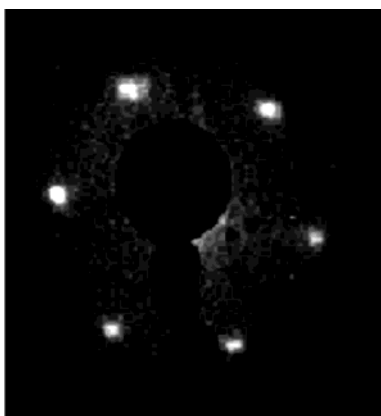


Figure 4. Hexagonal LEED pattern of the coronene superstructure for 15.4 eV.

intensively studied by MBE-LEED for varying coverage by Seidel et al.¹⁴

In the LEED measurements coronene adlayers appear as a hexagonal pattern for the first-order spots, Figure 4, shows an example with an acceleration voltage of 15.4V. The densely packed Ag(111) surface shows a hexagonal LEED pattern as well. For thin coronene layers the adlayers could be observed with LEED and at higher acceleration voltage other spots, arising from the underlying substrate, became visible as well, without destroying the coronene layer. After switching back to low electron energies the coronene spots were still visible, indicating an intact adlayer. Due to its conjugated π -electron system coronene is rather stable with respect to electron bombardment. Using low beam-currents, the samples could be investigated for a long time without remarkable damage. Also, storage for a few days under UHV conditions had no remarkable influence on sample quality.

The coronene superstructure on Ag(111) was found to be in registry with the substrate, in contrast to graphite(0001), where a rotation of the coronene superstructure of $\pm 10.9^\circ$ with respect to the substrate was found by means of LEED² and STM.³ For the measured lattice constants a parallel adsorption of the molecular plane to the graphite substrate was suggested.

Due to the limited screen size the substrate and adlayer spots could not be seen simultaneously, so the calibration of the superstructure lattice vector with the substrate was done with a sequence of LEED patterns, recorded for various acceleration voltages. Such a sequence was taken for the substrate LEED pattern for electron energies from 59.4 to 145.5 eV and the superstructure LEED pattern for electron energies from 10.3 to 30.4 eV as well. Then an arbitrary distance in the LEED pattern—e.g., the distance between diametral or neighboring spots—was drawn vs $1/\sqrt{E}$. This was done for the substrate and the adlayer as well and fitted with a straight line through the origin each, as shown in Figure 5. For a fixed energy the higher value for the spot distance in reciprocal space corresponds to lower distances in real space. Therefore the steeper line corresponds to the Ag substrate, also indicated by the lower $1/\sqrt{E}$ values—higher E values—constituting the line.

As described in ref 15, the square root of the ratio of the energy values for each arbitrarily chosen spot distance—spot distance set here to 1.0—equals the inverse ratio of the lattice constants.

$$\frac{a_{\text{coronene}}}{a_{\text{Ag}}} = \sqrt{\frac{E_{\text{Ag}}(\text{reflex distance} = 1.0)}{E_{\text{coronene}}(\text{reflex distance} = 1.0)}}$$

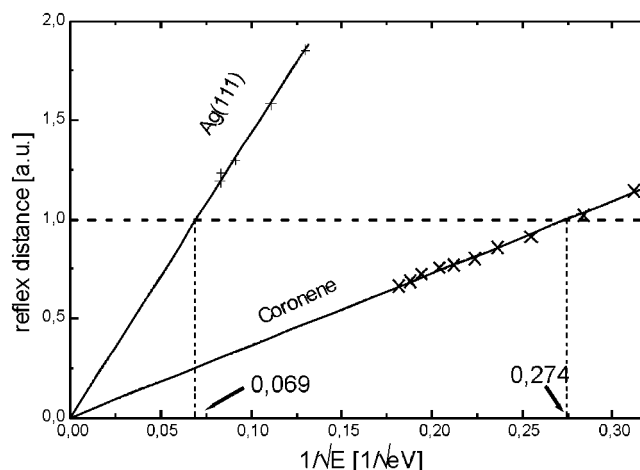


Figure 5. Spot distances deduced from LEED sequences of the same sample for various electron energies.

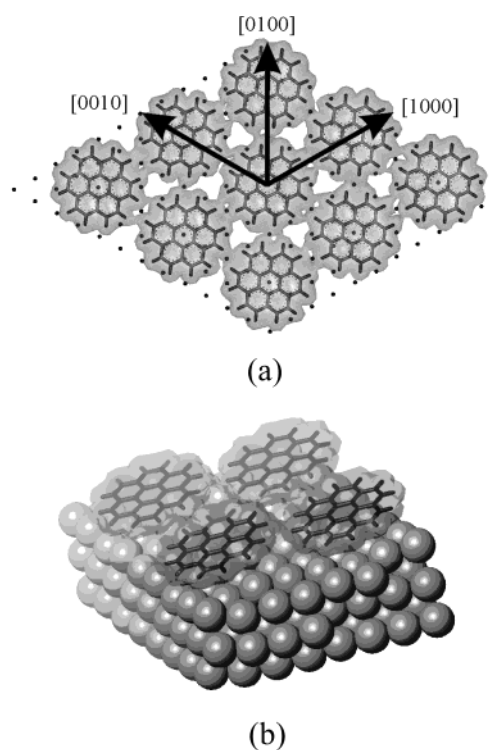


Figure 6. (a) Real space model of the commensurate 4×4 superstructure; molecules are shown with van der Waals radii of the atoms. (b) Three-dimensional view of the force field calculation.

Using 4.08 \AA^{16} as the lattice constant and $a_{\text{Ag}} = 2.88 \text{ \AA}$ for the nearest neighbor distance on a Ag(111) surface, we end up with a nearest neighbor distance of $11.5 \pm 0.1 \text{ \AA}$ for the coronene layer. This number is very close to the van der Waals radius of the molecule, indicating a dense packing. Because of the quite strong adsorbate—substrate interaction a commensurate 4×4 superstructure—Figure 6a shows the real space model—is suggested. The associated next nearest neighbor distance of 11.54 \AA agrees with the LEED measurements within the experimental errors. This results in an area per unit cell of 1.16 nm^2 . Comparison with the value of 1.13 nm^2 for the coronene superstructure on graphite(0001) reveals a less dense packing on Ag(111).

In the STM image of Figure 7 the molecular positions within a single hexagon are marked by a white line. This hexagon is supposed to be symmetric, as demanded by the 6-fold symmetry

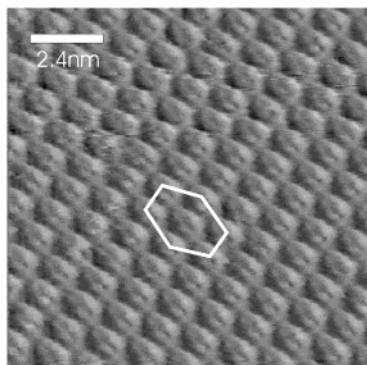


Figure 7. STM image (raw data, constant height) of a close packed coronene layer on Ag(111), recorded at 20 K ($V = -600$ mV, $I = 120$ pA, 12×12 nm²).

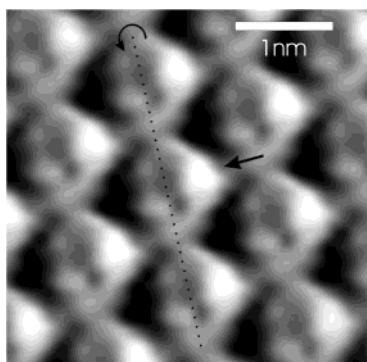


Figure 8. Correlation analysis (explained in the text) of a cut-out with the drift corrected image in Figure 7 (3.7×3.7 nm²).

in the LEED measurements. Due to drift and piezo hysteresis, the image is distorted. This distortion was corrected, using the unit cell parameters deduced from the quantitative analysis of the LEED pattern. To reduce noise an average image was processed and is shown in Figure 8. Therefore a cross correlation of a selected cut-out, containing one molecular hexagon, with the distortion corrected image of Figure 7 was calculated. A peak in the cross correlation occurs at the positions where this cut-out matches the periodic main image. This peak positions were applied for averaging over the molecular hexagons of the main image. (feature of the image processing software: SPIP 2.1105 by Image Metrology ApS).

For the back and forth scan, all single molecules appear bright at the side marked by the arrow in Figure 8. This cannot be explained as an intrinsic electronic effect of the molecular density of states, because the molecular orbitals reflect the 6-fold symmetry of the atomic structure. This was shown in a combined tight-binding and STM study.³ Therefore a geometric effect is assumed. The molecule is not adsorbed in a planar geometry, but somewhat tilted as also indicated by NEXAFS investigations¹⁷ with coverage around 1–2 monolayers. In the real space model of Figure 6a each molecule is depicted with its van der Waals radius. The superstructure lattice constant is so small that neighboring molecules are hindering each other, indicated by the overlap of their van der Waals radii. Force field calculations, similar to the calculations described by Edelwirth et al.,¹⁸ using the Dreiding force field result in a tilt of the molecular planes against the substrate. Figure 6b shows a pseudo-three-dimensional view of the energy-minimized structure.

So molecule–molecule and molecule–substrate interactions lead to a relaxation through tilt of the molecular plane around an axis in [1000] direction (outlined in Figure 8). The fact that no tilt could be observed for the still more dense packing of coronene on graphite(0001) is not fully understood.

The tilt reduces the interaction of the π -orbitals with the substrate and is the result of a crucial balance between molecule–substrate and molecule–molecule interactions. Even simple molecular mechanical considerations, applying force field calculations result in a tilt of the molecules.

Summary

The adsorption of coronene on Ag(111) for an extreme low coverage and a close packed monolayer was investigated by means of LEED and variable temperature STM. For individual molecules we found concentric rings surrounding each molecule, which are identified as standing electron waves constituted from surface state electrons. If two molecules are close to each other, interference of the rings occurs. The substrate mediated long-range interaction between molecules is expressed in typical distances for molecular dimers. For monolayer coverage a close packed hexagonal arrangement of the coronene molecules was found. Quantitative analysis of the LEED measurements results in a commensurate 4×4 superstructure. A correlation averaging analysis of a distorted image yields enhanced submolecular resolution. This detailed view showed tilted molecules, due to a relaxation caused by interaction between neighboring molecules.

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