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## STM and STS of coronene on HOPG(0001) in UHV – adsorption of the smallest possible graphite flakes on graphite

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**Abstract** The adsorption of the aromatic molecule hexabenzobenzene (coronene) on an HOPG(0001) surface was investigated under UHV conditions by means of variable temperature scanning tunneling microscopy (STM) and spectroscopy (STS). Imaging on a mesoscopic scale showed a distribution of coronene islands. These islands are mobile on the surface and can be pinned at step-edges. Zooming in on areas apart from the islands reveals an hexagonal arrangement of coronene molecules in a closed layer. Submolecular resolved molecules consist of bright spots with varying intensity. This variation in intensity is explained with the commensurability of the adlayer. STS investigations were performed for various tip-sample distances, adjusted by the tunneling current setpoint. A gap can be seen for every setpoint, but its width is dependent on the setpoint. The gap for the largest tip-sample distance and therefore the smallest tip-sample interaction is compared with the theoretical value.

**Keywords** STM · STS · Coronene · Adsorbate · HOPG

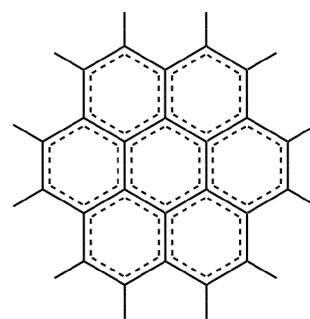
### Introduction

The basic study of organic molecule adsorption on crystalline substrates 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, provide a further challenge to study selected organic molecules on well-defined substrates.

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



Coronene (Fig. 1) is an interesting substance for several reasons: the molecule is planar with a sixfold 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 highly oriented pyrolytic graphite – HOPG(0001) – was studied by LEED [2] and STM [3] as well. An hexagonal close-packed  $\sqrt{21} \times \sqrt{21} R10.9^\circ$  superstructure of the coronene molecules was found. 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 proposed Stranski-Krastanov growth mechanism [2] is visualized by STM imaging on a mesoscopic scale. Images with submolecular resolution are presented and the internal molecular structure is discussed. In addition, STS has been performed with a variation of the setpoint to reveal the influence of the distance-dependent tip-sample interaction.

## Experimental

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 low temperatures (around 20 K) to immobilize the weakly bound molecules. The sample was cooled with a liquid helium flow cryostat; however, the tunneling tip cannot be cooled in our STM and always remains nearly at room temperature. All given tunneling voltages are referred to the sample. Electrochemically etched tungsten tips were used, which were cleaned in situ by Ar ion sputtering and subsequent annealing at temperatures around 750 °C.

The HOPG crystal was cleaved in air by means of an adhesive tape and immediately transferred into the vacuum chamber. Annealing up to 550 °C for one hour was applied to desorb contaminations.

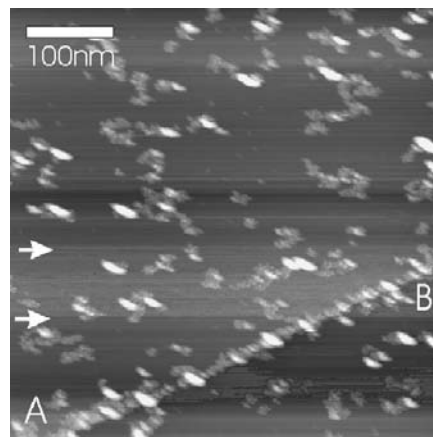
The molecules were deposited by thermal evaporation in the preparation chamber of a commercial two-chamber STM-LEED system. Coronene was provided by Aldrich with a purity of 97% and was used without further ex situ purification. Prior to the sublimation, the evaporant was outgassed with temperatures slightly below the temperature applied during the deposition. A simple home-built thermal evaporator with quartz glass 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 monitored with a quartz microbalance and found to be in the order of  $1 \text{ \AA min}^{-1}$ . 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.

## Results and discussion

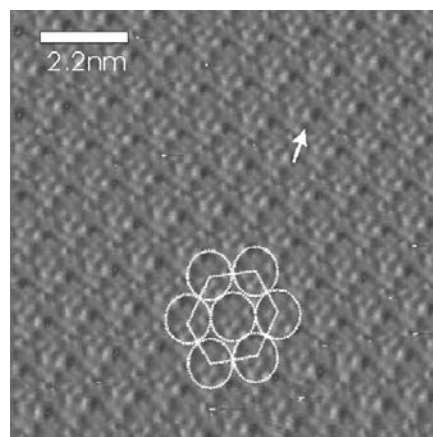
After preparation, the sample was immediately cooled down without prior investigation at room temperature to avoid contamination of the tip. First, the sample was investigated on a mesoscopic scale as shown in Fig. 2. In this image, bright coronene islands can be observed with heights of 1.5–2.5 nm. Concerning the shape of the islands, their elongation might be an artifact caused by thermal drift. Likewise, influence of the tip on the shape of the islands cannot be ruled out. As proposed for this system, based on LEED investigations [2], a Stranski-Krastanov growth is to be expected. First, molecules adsorb in a closed layer and incline to form islands if more material is deposited. A step edge is clearly visible in Fig. 2; this pins the mobile coronene islands and it is therefore decorated with molecular agglomerates. The observable height variation of the background is caused by tip changes. Because there are a lot of mobile molecular clusters on the substrate, the tip collects and deposits material from the substrate, thus leading to a change of the effective tip length. Hence, the apparent height of the background is changing abruptly; such sudden changes are marked in Fig. 2.

Zooming in on areas between the islands reveals a hexagonal arrangement of coronene molecules in a closed monolayer, as depicted in Fig. 3. Single molecules appear as group of bright spots with different intensity. As a guide to the eye, in Fig. 3 an hexagonal arrangement of molecules is marked with white circles.

All seven carbon rings of the molecule are visible via their  $\pi$ -electron clouds, in concordance with theoretical calculations of the frontier molecular orbitals [3].

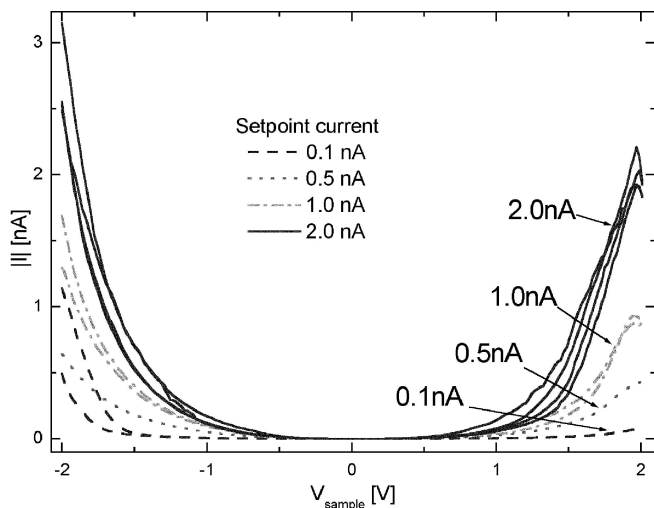


**Fig. 2** Constant current image of coronene on HOPG(0001). Bright spots correspond to islands according to the Stranski-Krastanov growth mode. A step edge (between A and B) is decorated with pinned islands. Arrows mark tip changes leading to a change of the average height ( $-720 \text{ mV}$ ,  $300 \text{ pA}$ ,  $500 \times 500 \text{ nm}^2$ )



**Fig. 3** Submolecularly resolved constant height image of a closed monolayer. The white circles mark single molecules, which are hexagonally arranged. Explanations are given in the text. ( $+864 \text{ mV}$ ,  $161 \text{ pA}$ ,  $11 \times 11 \text{ nm}^2$ )

Within the submolecular structure, one of the spots (marked with an arrow in Fig. 3) is the brightest of the group. Its relative position within each molecule is always the same, and the intensity ratio between different spots is also equal for every molecule. An explanation for these experimental findings is based on the commensurability of the coronene adlayer on HOPG(0001). That means the ratios of the adsorbate and substrate lattice vectors are whole-numbered. Hence, every coronene molecule has a similar adsorption position and senses the same interaction with the substrate. This molecule-substrate interaction is the reason for breaking the sixfold symmetry of the molecular states. If no substrate interaction were present, every outer ring of the molecules would be equal and would have the same contribution in STM images. Interaction with the substrate changes the tunneling probability of each single ring, but – because of the commensurability of the superstructure – in exactly the same way for



**Fig. 4** STS data of the adlayer. Each curve represents an average of about 100 single measurements. Furthermore, STS was performed for varying tip-sample distance determined by the setpoint current

each molecule. The comparison of copper-phthalocyanine adsorbed on  $\text{MoS}_2$  and HOPG [4] shows that even interaction with weakly bonding van der Waals substrates can cause changes in the STM image. However, also a geometrical effect such as the tilt of the molecular plane found for coronene on  $\text{Ag}(111)$  by means of STM [5, 6] and NEXAFS [7] cannot be completely ruled out.

### Scanning tunneling spectroscopy

STM is not only capable of real space imaging, but also performing local spectroscopy of occupied and unoccupied electronic states. The most common way is to record I-V curves with deactivated feedback and a constant tip-sample distance. This distance, that is the width of the tunneling gap, is an important parameter determined by the tunneling current setpoint before switching the feedback off.

Here, STS was performed for the setpoint currents 0.1, 0.5, 1.0, and 2.0 nA and results are depicted in Fig. 4. Each single curve represents an average of about 100 single measurements, performed in a regular grid over the image. During the acquisition, simultaneous imaging ensured that the adlayer was not destroyed.

For each setpoint current, a gap between the two onset points is clearly visible, reflecting the gap of molecular states between HOMO and LUMO. However, the shape of the curve and the width of the gap respectively, depend on the tip sample-distance. This behavior indicates an interaction between tip and sample leading to a reduced gap for decreasing tip sample-distance and stronger influence,

respectively. Hence, it is difficult to determine the true HOMO-LUMO gap by STS. Furthermore, the STS gap is different to the optical gap, because of the exciton binding energy having great impact on the optical gap. STS measures a one-particle excitation – the so-called polaronic gap. By comparison with the optical gap it is possible to extract the exciton binding energy [8]. Nevertheless, the gap (onset defined when current is above 10 pA = noise amplitude of the preamplifier) deduced for the largest tip-sample distance (setpoint 0.1 nA) amounts to 2.5 eV. Ab initio calculations of the HOMO-LUMO gap according to the method described in Sternberg et al. [9] provide a value of 3.0 eV. The deviation could be caused by molecule-substrate interactions, a remaining tip influence and the polaron binding energy.

### Conclusion

Imaging of coronene on HOPG(0001) on a large scale showed a Stranski-Krastanov mode, with islands mainly pinned by step edges. Zooming in on the closed layer shows a hexagonal arrangement, as expected by LEED measurements. Each single molecule consists of seven bright spots, representing the  $\pi$ -electron clouds of the carbon rings. However, the  $\pi$ -electron systems of each ring do not have equal intensity. Interaction with the van der Waals substrate is discussed, but also geometric effects cannot be ruled out. STS investigations did show a gap between HOMO and LUMO. However, this gap is dependent on the tip-sample distance during the measurement. The value found for the weakest tip-sample interaction is in reasonable agreement with theoretical calculations.

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