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STM investigations of C_6Br_6 on HOPG and MoS_2

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Abstract

Monolayers of the organic molecule hexabromobenzene on HOPG and MoS_2 have been imaged with scanning tunneling microscopy. The flat lying molecules form an ordered close-packed array with unit cell parameters corresponding to their van der Waals radii. In both cases the overlayers are incommensurable to the substrate. In the images with submolecular resolution, the molecules appear different on the two substrates. On HOPG the observed STM image contrast shows a detailed submolecular pattern depending on the tunneling voltage, whereas on MoS_2 the molecules appear with a less pronounced inner structure. Neither on HOPG nor on MoS_2 the observed submolecular contrast depends on the adsorption site.

1. Introduction

Since the invention of scanning tunneling microscopy in 1982, it is increasingly used for the characterisation of organic and bioorganic materials [1], but the STM image contrast of organic molecules is still under discussion [2–4]. One reason for this is the small number of systematic investigations of the submolecular contrast of aromatic molecules.

Benzene coadsorbed with CO on Rh(111) forms an ordered commensurable overlayer of chemisorbed molecules, which were imaged by Othani et al. [5]. At low temperatures Weiss and Eigler [6] showed the influence of the adsorption site on the image contrast of statistically distributed benzene molecules on Pt(111). Hallmark et al. [7] have imaged naphthalene, azulene and a series of related molecules on

Pt(111) in an irregular arrangement. They compared their images with simple extended Hückel calculations and found good agreement with the experimental data. For chemisorbed benzene on Rh(111) the STM image contrast was calculated by Sautet and Joachim [8], who used an electron scattering quantum chemistry treatment. Recently Fisher and Blöchl [9] have published the first calculations for benzene physisorbed on the most commonly used substrates for STM, graphite and MoS_2 . They found that the image contrast on graphite should depend on the adsorption site and the tunneling voltage.

In this work we report about the first high resolution images of a physisorbed benzene derivative. On weak interacting substrates at room temperature, the immobilisation of molecules necessary for high resolution STM images can only be achieved by an ordered two-dimensional arrangement of the molecules. Because of its high vapor pressure benzene does not form ordered arrays on graphite at room temperature [10]. To overcome this difficulty

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we studied hexabromobenzene (C_6Br_6) on graphite and MoS_2 . Since the melting point of C_6Br_6 lies above $300^\circ C$, the preparation of well ordered monolayers by organic molecular beam epitaxy becomes possible even at room temperature. Thin films of C_6Br_6 on MoS_2 were also characterized by transmission electron microscopy from Kobayashi [11].

2. Experimental methods

STM investigations were carried out with a microscope specially developed for the characterisation of physisorbed molecules. For fast sample inspection and in order to increase the signal to noise ratio, it operates with a scan rate up to 20 frames/s. In connection with an on-line averager this leads to high resolution images even at noisy conditions. All measurements were made with a mechanically cut Pt/Ir-tip in a nitrogen atmosphere at room temperature. For an improvement of the image quality we subtracted a constant background in the Fourier-transformed images. However no digital or analog low or high pass filtering was used. The voltage sign in the figure captions refers to the sample.

The molecular layers were prepared by evaporation from a graphite effusion cell at a pressure less than 10^{-7} mbar. Before evaporation the freshly cleaved substrates were heated to $250^\circ C$ in order to desorb contaminations and then cooled to $10^\circ C$ for preparation. Evaporation rates were typically 0.05 monolayers/s which corresponds to a temperature of the effusion cell of about $150^\circ C$.

The positions of the monolayer molecules relative to the substrate were determined by the "scrape off" technique, i.e. imaging of the underlying substrate after monolayer removal by slowly approaching the tip to the substrate, as described previously [12].

3. Results and discussion

Fig. 1 shows a $200 \text{ \AA} \times 200 \text{ \AA}$ image of C_6Br_6 on HOPG recorded in the constant height mode with a frame rate of 4 frames/s and averaged over 4 frames. The hexagonal arrangement of the molecules is clearly visible. Due to different lattice constants and different orientations of the lattice vectors of adsor-

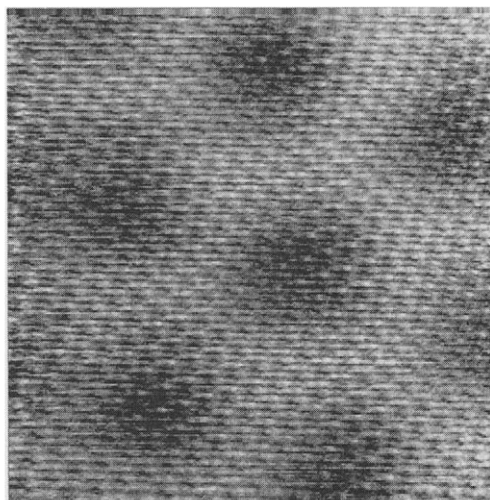


Fig. 1. $200 \text{ \AA} \times 200 \text{ \AA}$ image of C_6Br_6 on HOPG recorded with a scanning speed of 4 frames/s and averaged over 4 frames. The dark spots are a moiré pattern due to the incommensurability of the overlayer ($U = 1.2 \text{ V}$, $I = 1.9 \text{ nA}$).

bate and substrate the overlayer shows a moiré pattern. The dark spots of the moiré pattern form a hexagon with a distance between adjacent spots of about 80 \AA . By comparison of this image with the image of the underlying substrate, which becomes visible after scraping off the molecules by the tip, we obtained the unit cell parameters of the C_6Br_6 layer with respect to the substrate. The molecules form a closed-packed hexagonal structure with a distance corresponding to their van der Waals radii, which is incommensurable to the substrate.

To determine the crystallographic structure with high accuracy we start modelling the adsorption geometry with the unit cell parameters obtained by the scrape off technique and then correct these parameters until the observed moiré pattern is reproduced by the calculation in a self-consistent way. Fig. 2 shows a detailed model of the ordering of C_6Br_6 on HOPG obtained in this way. To indicate the position of each individual molecule the underlying substrate is drawn in lines with the center of each molecule transparent, so that the substrate underneath becomes visible. The crossing points of the hexagonal graphite lattice represent maxima in the STM image of graphite with a distance of 2.46 \AA . The circles in Fig. 2 mark regions with equivalent adsorption sites. We obtained for the lattice constant

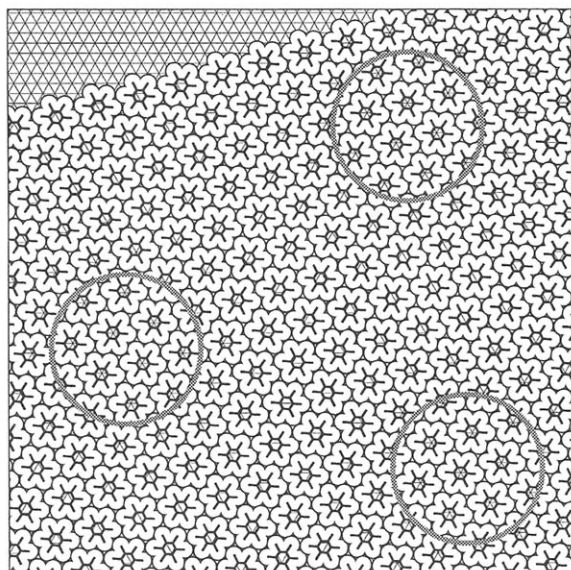


Fig. 2. Structural model of the ordering of C_6Br_6 on HOPG. The center of each molecule is transparent to emphasize the different adsorption sites.

$9.14 \pm 0.04 \text{ \AA}$ and for the angle between the substrate and the overlayer lattice vector $\Phi = 14.5 \pm 0.1^\circ$. The nearest commensurable structures with similar lattice constants are the $p(\sqrt{13} \times \sqrt{13})$ and a $p(4 \times 4)$ superstructure with a lattice constant of 8.87 and 9.84 \AA , respectively. This would require a lattice mismatch of the close-packed structure of more than 3%. These values are far away from our margins of error, so that we are sure that the C_6Br_6 overlayer is incommensurable to the graphite lattice. The crystallographic results are summarized in Table 1.

Fisher and Blöchl [9] calculated the binding energies and the vertical separation of benzene from graphite and MoS_2 . They found that the separation between molecule and substrate exhibits a corrugation of 0.2–0.3 \AA , with the smallest value for benzene centered on a site with threefold symmetry

above a substrate atom. In the framework of this calculation the reason for the dark moiré areas of Fig. 1 could be a vertical distance modulation. But in the proposed superstructure of Fig. 2 this would be valid only for the substrate C-atoms visible in the STM. The theoretical model used for the calculations however did not regard the fact that only half of the carbon sites at the graphite surface is imaged. Nevertheless we expect that the origin of the dark spots is topographic, but electronic perturbations cannot be excluded.

Fig. 3a shows a constant height image of C_6Br_6 on HOPG with submolecular resolution. The individual molecules appear in this image with threefold symmetry and a pronounced minimum in the center of each molecule. The image contrast of individual molecules does not vary significantly over the scan area of 50 \AA , although the overlayer is incommensurable to the substrate. This implies that the specific adsorption site does not influence the submolecular contrast, which is in contradiction to the calculations of Fisher and Blöchl [9]. In their model the benzene molecules appear in the low voltage range used here with threefold symmetry when centered at a carbon atom and with twofold symmetry when the benzene ring is located between two carbon sites.

Not in all cases it was possible to reproduce the image contrast of Fig. 3a. Sometimes we observed under the same tunneling conditions a tunneling current distribution with fourfold symmetry as can be seen in Fig. 3b. However, in all cases the submolecular image contrast did not vary over the whole scan area extending over $100 \text{ \AA} \times 100 \text{ \AA}$, so that we assume that the difference between Figs. 3a and 3b is possibly caused by a tip influence and not by the influence of the specific adsorption site.

At higher voltages we obtained an image contrast with the full sixfold symmetry of the molecule, which is shown in Fig. 4. Here the six outer maxima are located at the positions of the bromines. The lobes are oriented along the three symmetry equivalent directions of the graphite lattice. For this voltage range Fisher and Blöchl [9] expected a tunneling current distribution showing the highest molecular orbitals with near sixfold symmetry, but with no pronounced submolecular details.

For C_6Br_6 on MoS_2 we also observe a moiré pattern, but in this case the distance between the dark

Table 1
Unit cell parameters of C_6Br_6 on HOPG and MoS_2

| | $ g_1 \text{ (\AA)}$ | $ a \text{ (\AA)}$ | $\Phi = \angle(a, g) \text{ (deg)}$ |
|----------------------|-----------------------|---------------------|-------------------------------------|
| C_6Br_6 on HOPG | 2.46 | 9.14 ± 0.4 | 14.5 ± 0.1 |
| C_6Br_6 on MoS_2 | 3.16 | 9.16 ± 0.4 | 19.7 ± 0.1 |

spots is only 39 \AA due to the larger lattice constant of MoS_2 . Here we obtained in the way mentioned above for the lattice constant $9.16 \pm 0.04 \text{ \AA}$ and for the angle $\Phi 19.7 \pm 0.1^\circ$. As on HOPG the overlayer is incommensurable to the MoS_2 lattice. Fig. 5 shows a high resolution image recorded with a frame rate of 14 frames/s and averaged over 8 frames. Due to the

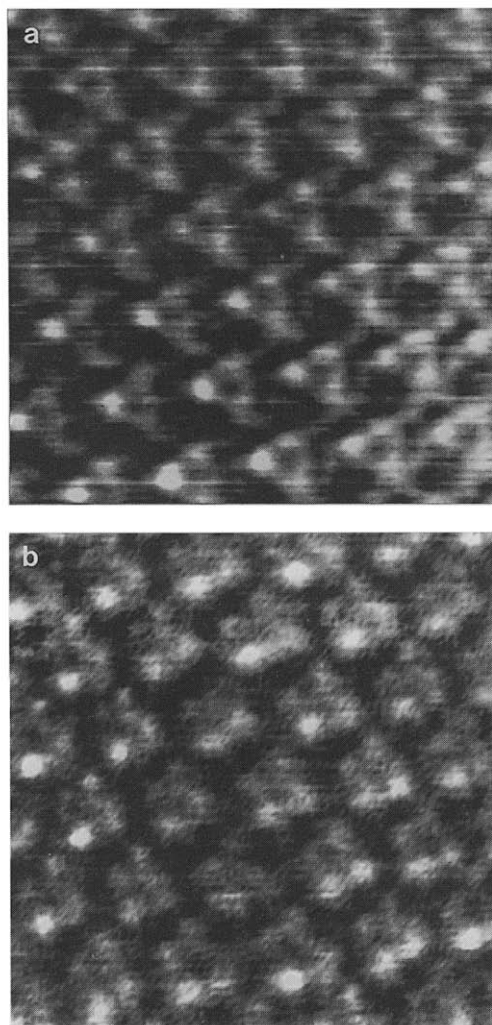


Fig. 3. High resolution images of C_6Br_6 on HOPG. The image contrast of individual molecules is tip dependent. (a) The molecules appear with threefold symmetry with a pronounced minimum in the center. (b) The molecules appear with a more quadratic tunnel current distribution. Over the entire scan area there is no significant influence of the specific adsorption sites on the image contrast visible in both images. (a) $U = -390 \text{ mV}$, $I = 1 \text{ nA}$, (b) $U = -250 \text{ mV}$, $I = 0.6 \text{ nA}$.

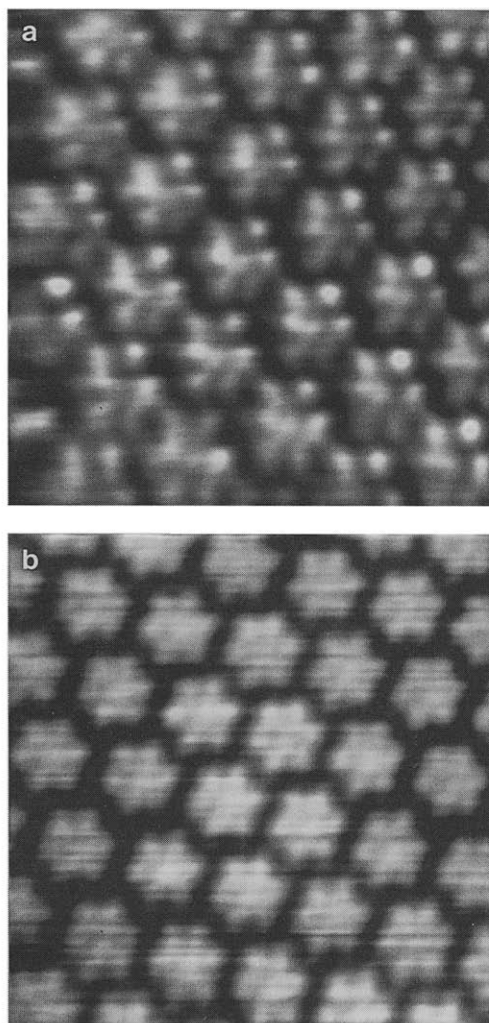


Fig. 4. High resolution images of C_6Br_6 recorded at higher tunneling voltages showing the full sixfold symmetry of the molecule. (a) On HOPG the molecules appear with a more detailed inner structure ($50 \text{ \AA} \times 50 \text{ \AA}$, $U = -1.8 \text{ V}$, $I = 1.8 \text{ nA}$, 14 frames/s, 8 frames averaged). (b) On MoS_2 the submolecular image contrast is less pronounced ($50 \text{ \AA} \times 50 \text{ \AA}$, $U = 1.4 \text{ V}$, $I = 0.27 \text{ nA}$, 14 frames/s, 8 frames averaged).

small scan area only a part of the hexagonal moiré pattern is visible. The molecules show a sixfold symmetry with the lobes oriented parallel to the symmetry directions of the substrate, but with less submolecular details. No dependence of the image contrast of individual molecules on the specific adsorption site is observed. However, as the calculations from Fisher and Blöchl [9] show, on MoS_2 the

interaction with the substrate broadens the tunneling current distribution.

On HOPG we obtained molecular resolved images for both polarities, but the images with the highest resolution were always recorded with a negative sample bias. Because of its rectifying behavior, on MoS₂ only images with positive polarity could be recorded. With respect to the comparison of our results with the calculations of Fisher and Blöchl [9], the main difference between C₆Br₆ and C₆H₆ is the much larger van der Waals radius of the bromines. This may lead to a different epitaxial growth [10]. However, the symmetry of the molecular orbitals remains unchanged. Only the energy levels are slightly shifted, which should not change the submolecular contrast significantly. The larger van der Waals radius of the bromines can lead to a larger molecule–substrate distance and thereby to a smaller interaction of the π -electrons of the aromatic ring with the substrate. Our results agree qualitatively with the calculations regarding the image contrast on MoS₂ as well as for the vertical variation of the molecule–substrate distance caused by different adsorption sites.

A detailed comparison of the experimental data with theoretical predictions requires a quantitative analysis of the image contrast.

4. Conclusion

In summary, we have shown that it is possible to prepare well ordered monolayers of C₆Br₆ on HOPG and MoS₂ by organic molecular beam epitaxy. The molecules form a close-packed hexagonal overlay, which is in both cases incommensurable the substrates. In the high resolution images the submolecular contrast is different for the two substrates. On HOPG the individual molecules appear with three-

or fourfold symmetry depending on tip conditions in the low voltage range and with the expected sixfold symmetry with a detailed inner structure at voltages above –1.5 V. The accurate knowledge of the orientation of the monolayers relative to the substrate allows us to exclude an influence of the specific adsorption site on the observed submolecular image contrast. This is in contradiction to calculations published previously [9]. On MoS₂ the molecules show in the high resolution images also the expected sixfold symmetry but with less submolecular details.

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