ADVANCED MATERIALS

Imaging Organic Molecules with the Scanning Tunneling Microscope

By Jürgen P. Rabe*

Atomic resolution has become a common feature in Scanning Tunneling Microscopy (STM) of inorganic semiconductor surfaces, both in vacuum and in a number of fluid ambients. A review has been given recently in this journal.[1] Moreover, the physics involved in the imaging process for these materials is well enough understood to allow detailed electron-spectroscopic investigations on an atomic scale to be performed. For organic materials, however, the method is much less developed. Clearly, this cannot be attributed to a lack of interest but rather to the characteristics of organic systems; above all the lack of electrical conductivity. In an attempt to circumvent this particular problem the imaging of single organic molecules as they are adsorbed on a conducting substrate has been attempted, since in this case the distance required for the probing electrons to tunnel is minimized. However, for these systems another typical feature of organic materials, molecular mobility, may still remain a problem. To date, due to these difficulties, only few systems have successfully been imaged by STM and it is this lack of experimental data which contributes to a third problem, namely the lack of a good understanding of the contrast mechanism in STM imaging of organics. Therefore, it is of particular interest that recently a number of new organic systems have been imaged.

In Figure 1 an STM image of Cu-phthalocyanine on Cu(100) is shown as obtained under ultra-high vacuum conditions by *Lippel* et al.[2] It shows isolated Cu-phthalocyanine molecules adsorbed flat with two different rotational orientations. Notably, studies of the same adsorbate on Ag(111), Au(111) and Si(111) 7 × 7 surfaces gave considerably less clear and stable images, indicating that the STM can resolve the internal structure of a flat isolated molecule, provided that the interaction between adsorbate and substrate is strong enough to sufficiently reduce molecular motion. The important question of contrast generation is also addressed by the authors. They interpret their images as representing the charge distributions of free molecule states near to the Fermi level. Like in the case investigated earlier[3] of benzene and carbon monoxide coadsorbed on Rh(111), the authors favor this explanation rather than an adsorbate induced change of the local work function.

In Figure 2 another high resolution STM image obtained by *J. K. Spong* et al.[4] is shown: The adsorbate layer at the interphase between a conducting solid substrate (graphite) and a liquid crystalline ambient (5-nonyl-2-*n*-nonoxylphenylpyrimidine). This example is representative of a whole

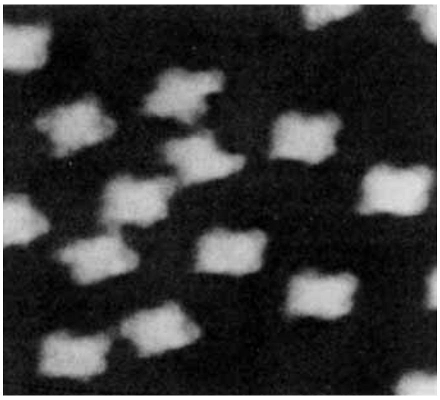

Fig. 1. STM image of Cu-phthalocyanine on Cu(100), as obtained by *P. H. Lippel* et al. [2]. The isolated molecules are adsorbd flat with two different rotational orientations. The scan dimensions are 15 nm × 15 nm.

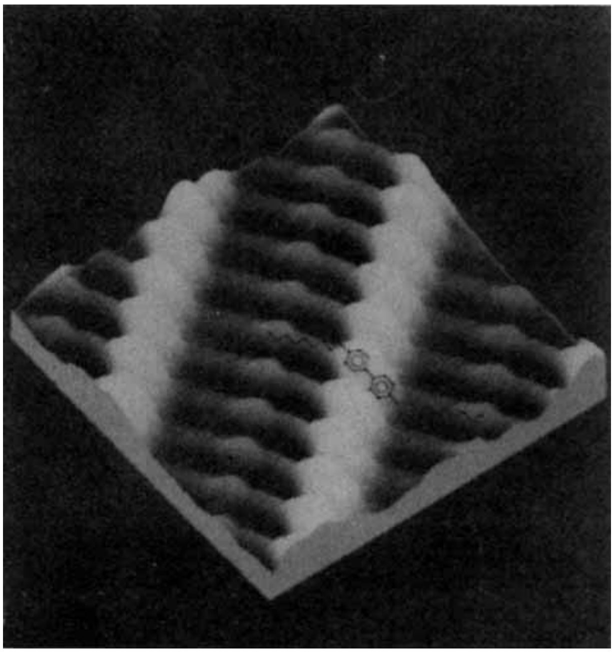

Fig. 2. Three dimensional display of an STM image of 5-nonyl-2-*n*-nonoxylphenylpyrimidine on graphite, as obtained by *J. K. Spong* et al. [4]. The scan dimensions are 4.3 nm × 5.2 nm. The image has been unit cell averaged.

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class of liquid crystalline materials on graphite.[4, 5] Evidently, the molecules are imaged as they are adsorbed flat on graphite, quite like the phthalocyanine rings on copper. However, in this case no isolated molecules, but rather an ordered array is imaged. The intermolecular interaction within the monolayer may stabilize the position of any particular molecule, thereby reducing molecular motion sufficiently for STM imaging. The contrast is attributed in this case to the modulation of the local work function of the substrate by the polarizable molecular adsorbates. Indeed, functional groups which are electronically as dissimilar as benzene and cyclohexane can have similar contrast when imaged by the STM. This is explained by their comparable polarizability. However, it should be noted that alkane residues also have similar polarizabilities but give a different contrast in the STM. Obviously, the issue of contrast generation still remains a matter of debate.

A quite general way to reduce molecular motion is to increase the number of segments per molecule interacting with the substrate, a feature typical in polymer adsorption. Interestingly, high resolution STM images of DNA and double stranded RNA have recently been obtained by *T. P. Beebe* et al.[6] and *G. Lee* et al.[7] Both groups could resolve, minor and major grooves of the double helices adsorbed on graphite. However, the pitch periodicity was found to vary considerably. This can be attributed to the combined forces of the surface, partial dehydration and possibly intercalation with ionic species. To draw conclusions about the contrast mechanism is very difficult in these cases, since the samples were prepared by allowing buffer solutions of DNA and RNA to evaporate on graphite and the STM investigation was performed in air immediately after the last amounts of water were observed to evaporate. It cannot be excluded, therefore, that traces of electrolyte may contribute to the conductivity. Furthermore, it should be mentioned that due to the thickness of the molecule it is more complicated to interpret high resolution images of this material, than it was in the examples given before.

Our understanding of the processes involved in imaging organic adsorbates is considerably improving. This is both stimulating and encouraging for those working in this research area.

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[2] P. H. Lippel, R. J. Wilson, M. D. Miller, C. Wöll, S. Chiang, *Phys. Rev. Lett. 62* (1989) 171.

[3] H. Ohtani, R. J. Wilson, S. Chiang C. M. Mate, *Phys. Rev. Lett. 60* (1988) 2398.

[4] J. K. Spong, H. A. Mizes, L. J. LaComb Jr., M. M. Dovek, J. E. Frommer, J. S. Foster, *Nature 338* (1989) 137.

[5] J. S. Foster, J. E. Frommer, *Nature 333* (1988) 542.

[6] T. P. Beebe Jr., T. E. Wilson, D. F. Ogletree, J. E. Katz, R. Balhorn, M. Salmeron, W. J. Siekhaus, *Science 243* (1989) 370.

[7] G. Lee, P. G. Arscott, V. A. Bloomfield, D. F. Evans, *Science 244* (1989) 475.

Phase Equilibria under Stress

By Robert W. Cahn *

Ever since the Phase Rule was first formulated more than a century ago, it has been recognized that hydrostatic pressure is a variable that must affect phase equilibria; the normal neglect of this variable in the construction of ordinary metallurgical equilibrium diagrams is merely a recognition that atmospheric pressure is minimal, and a flourishing research field is centered upon the investigation of new polymorphs and new transition temperatures under large pressures. Nevertheless, in the last few years the whole field has been given a quite new impetus by a small group of thermodynamics theorists who have examined the whole issue afresh.

Before we look at these new developments, let us dispose of some of the other ways in which an applied stress can affect phase dispositions. Here the major interest attaches, not to hydrostatic pressure but to uniaxial stress – a simple tension or compression. One important category is that of martensitic transformations, as in ordinary carbon steel. Here, a phase transforms by combining a macroscopic shear with more complex localized strains. When a cubic crystal transforms, it can typically form 24 crystallographically equivalent orientations or variants. An applied stress in the elastic range will favor a few of these orientations, or even a single one, over all the others. This has often been experimentally confirmed (e.g. by *Kochendörfer* and *Müller*,[1] who in this way created virtually a single crystal of a martensitic phase). This same phenomenon is crucially involved in the much studied family of shape-memory alloys, which return to an 'imprinted' shape on gentle heating.[2]

Again, when a single crystal of a cubic disordered phase is cooled so as to create a non-cubic superlattice, then a very small applied compression can pick out one of the, e.g., three

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