Force microscopy on insulators: imaging of organic molecules

To cite this article: O Pfeiffer et al 2005 J. Phys.: Conf. Ser. 19 166

View the article online for updates and enhancements.
Force microscopy on insulators: Imaging of organic molecules

O Pfeiffer, E Gnecco, L Zimmerli, S Maier, E Meyer
NCCR Nanoscale Science, Institute of Physics, Klingelbergstrasse 82, 4056 Basel, Switzerland

L Nony
L2MP, Equipe Nanostructuration, Faculté des Sciences de Saint-Jérôme, 13397 Marseille, France

R Bennewitz
Department of Physics, McGill University, 3600 University Street, Montreal QC, H3A 2T8 Canada

F Diederich, H Fang, D Bonifazi
Laboratorium für Organische Chemie, ETH-Hönggerberg, HCI, 8093 Zürich, Switzerland
E-mail: oliver.pfeiffer@unibas.ch

Abstract. So far, most of the high resolution scanning probe microscopy studies of organic molecules were restricted to metallic substrates. Insulating substrates are mandatory when the molecules need to be electrically decoupled in a electronic circuit. In such a case, atomic force microscopy is required. In this paper we will discuss our recent studies on different organic molecules deposited on KBr surfaces in ultra-high vacuum, and then imaged by AFM at room temperature. The distance between tip and surface was controlled either by the frequency-shift of the cantilever resonance or by the excitation signal required to keep the oscillation amplitude constant. Advantages and drawbacks of both techniques are discussed. The high mobility of the molecules, due to their weak interaction with the substrate, hinders the formation of regular self-assembled structures. To overcome this problem we created artificial structures on the surface by annealing and by electron irradiation, which made possible the growth of the molecules onto step edges and their confinement into rectangular pits.

1. Introduction

In the last few years, the global interest in organic electronic devices, based on ordered films of organic molecules on flat surfaces, has grown rapidly. The operation of such devices should be governed by the electronic properties of a single or a few molecules. While the scanning tunneling microscope (STM) is an established technique to analyze organic molecules on metallic substrates [1, 2], the imaging of molecules on insulators by atomic force microscopy (AFM) is still in early stages [3, 4]. Insulating surfaces are necessary to avoid coupling between the electrons of the molecules and the substrate. Apart from the advantage of being independent of the substrate conductivity, AFM offers the possibility to perform local force vs. distance curves. The
application of force microscopy on single molecules of Cu-tetra (3,4-di-t-butylphenyl) porphyrins (Cu-TBPP) revealed that different molecular conformations can be detected. In addition, the energy required to switch the molecules between different states was quantified [5].

The use of AFM and of insulating substrates for the deposition of organic molecules is quite challenging. In this paper we discuss some problems encountered when performing force microscopy investigations of molecules on insulators, and possible strategies to overcome them.

2. Experimental setup
All measurements were performed with a homebuilt combined STM-AFM in ultra-high vacuum at room temperature. The instrument characteristics have been reported elsewhere [6]. As force sensors, highly n-doped silicon cantilevers (Nanosensors™) with typical resonance frequencies of $f_0 = 160$ kHz and spring constants of $k = 30$ Nm$^{-1}$ were used. The quality factor of these cantilevers for the normal bending is around $Q \approx 30'000$.

To image the surfaces, the non-contact FM-AFM mode was chosen. In this mode, the cantilever is excited at its resonance and the amplitude $A$ of the tip oscillation, is kept constant by adjusting the amplitude of the exciting signal, $A_{\text{exc}}$ [7]. Typical values of the amplitude $A$ are 10-20 nm.

The topography of the samples is usually recorded by scanning the surface while the distance between tip and sample is controlled by the resonance frequency $f$, which shifts due to tip-sample interactions. Using this technique contrasts down to the atomic scale were achieved in UHV [8, 9, 10]. For large amplitudes compared to the interaction length, the frequency-shift $\Delta f$ can be converted into forces [11].

When the oscillating tip interacts with the surface, energy can be dissipated. This leads to an additional damping of the cantilever oscillation, which is added to the intrinsic damping of the oscillator [12]. To observe the changes in the damping, the cantilever excitation $A_{\text{exc}}$, which is needed to maintain the constant oscillation amplitude, is recorded during scanning.

When working with a conducting sample, a bias voltage can be applied between tip and surface. Then the tunneling current averaged over the tip oscillation, $\langle I_t \rangle$, can be measured or used for distance control.

2.1. The organic molecules
In this work four different organic molecules were used: Figure 1 shows the structural formulae of these molecules: a) Cu-tetrakis(3,4-di-t-butylphenyl)porphyrin (Cu-TBPP) [5], b) $1',4'$-Dihydronaphtho[2',3':1,9](C$_{60}$-Ih) [5,6]fullerene-6'-carboxylic acid (carboxyfullerene, C$_{69}$H$_{8}$O$_{2}$) [13], c) chloro[sub-phtalocyaninato]boron(III) (SubPc) [14] and d) 5, 15-bis (3,5-dicyanophenyl)-10, 20-bis [3, 5-di(tetrt-butyl)phenyl]porphyrinatoN21,N22,N23,N24zinc(II) (tetracyanoporphyrin). The tetracyanoporphyrin derivative was prepared in analogy to previously reported similarly substituted porphyrins [15]; details will be published elsewhere.

The organic molecules were evaporated in UHV from a small Al$_2$O$_3$ crucible which was heated by a tantalum wire coil. The deposition rates were calibrated using a quartz microbalance.

3. AFM imaging of molecules
3.1. Comparison of high-resolution imaging with STM and non-contact AFM
Scanning tunneling microscopy has been the most common technique to visualize molecular-scale structures so far. STM uses the tunneling current flowing between the tip and the sample as a feedback signal for the tip-sample distance regulation. Due to the short decay length of the tunneling current, only a few atoms at the tip apex probe the electronic overlap between tip and sample (see fig. 2a). STM provides a high spatial resolution and a simple experimental setup. However, STM cannot be applied to the imaging of insulating materials.
Figure 1. a) Cu-tetrakis(3,4-di-tert-butylphenyl)porphyrin (Cu-TBPP), b) carboxyfullerene, C_{69}H_{8}O_{2}, c) chloro[sub-phtalocyaninato]boron(III) (SubPc), and d) tetracyanoporhyrin.

In contrast, non-contact AFM is capable of imaging insulating materials. Atomic resolution can be readily achieved on flat, homogeneous terraces, but it is rather difficult to get it at step sites or on heterogeneous surfaces. In force microscopy, tip asperities which are a few nanometers away from the surface can contribute to the interaction and therefore blur the imaging-contrast (see fig. 2c)). Compared to STM, the sharpness of the AFM-tip is therefore a prerequisite to achieve a high vertical and lateral contrast on heterogeneous surfaces.

In AFM, the optimum imaging parameters depend on the interplay between long-range forces, such as van der Waals and electrostatic forces, and short-range forces, such as ionic repulsion and chemical forces. Due to the different contributions, the total force consists of an attractive and a repulsive branch, which complicates the distance control by $\Delta f$ (see Figure 2).

Another difficulty in nc-AFM on heterogeneous surfaces is the variation of long-range forces between substrate or molecular islands and the AFM-tip, for example due to variations in the work function. Optimum parameters for simultaneous imaging both the substrate and the molecules may be difficult to be achieved.

Figure 2 summarizes the differences of STM- and AFM-mode when imaging Cu-TBPP molecules on Cu(100). In STM mode, the mean tunneling current increases monotonically upon approaching. Due to the short decay length only a few tip-atoms contribute to the feedback signal and a high resolution is achieved. In nc-AFM mode, the feedback-signal $\Delta f$ shows an attractive and a repulsive part as well as a long-range contribution. Therefore, the resulting image is not as sharp as the one obtained by the tunneling-feedback. A reduction of the oscillation amplitude may lead to a relative reduction of long-range forces compared to short-range forces. However, due to the signal-to-noise ratio, amplitudes of 10-20 nm are required in our setup.

3.2. Distance control on damping as an alternative?

While scanning a surface in nc-AFM mode, the excitation signal $A_{exc}$ is often recorded simultaneously to obtain additional information about non-conservative interaction forces.

Figures 3b) and c) show the $A_{exc}$-signal, while the tip-surface distance was controlled to maintain a constant frequency-shift $\Delta f$. In these images, an enhancement of the damping at the step edges can be observed. The contrast in the $A_{exc}$-signal strongly depends on the atomic composition of the tip apex. In fact, the damping signal depends more on the tip-radius than the frequency-shift [12]. Depending on the state of the tip, there is no contrast in the $A_{exc}$-signal at all; even when the tip oscillates in tunneling range. With other tips, atomic contrast is revealed [16, 6] or a clear contrast between the different materials on heterogeneous surfaces is shown [17].

As mentioned before, the long-range contributions to the frequency shift $\Delta f$ often hinder a high resolution on heterogeneous surfaces. The $A_{exc}$-signal increases monotonically and steep when approaching the surface. This is illustrated in the plot in fig. 3a) for an approach-curve on Cu(100). The long range part of this signal can be neglected if an applied bias-voltage
Figure 2. a) and c) are illustrating the distance dependence of $I_t$ and $\Delta f$. $\Delta f$ exhibits a longe range contribution; therefore a blurred topography is expected. Measurements on Cu-TBPP molecules on Cu(100) controlled by a constant mean tunneling current in b) and by a constant frequency-shift in d) confirm this expectation.

Figure 3. a) Typical distance dependence of the frequency-shift $\Delta f$ and the excitation amplitude $A_{exc}$ on Cu(100). b) and c) are showing the excitation signal $A_{exc}$ when the distance is controlled on a constant frequency-shift $\Delta f$ on NaCl/Al(111) and NaCl/Cu(111). An enhancement of the excitation signal can be observed at the step edges. An enhancement of the excitation signal can be observed at the step edges. If the surfaces under study are rough, the control on a constant $\Delta f$ is often unstable on large scan ranges. On the contrary, if the distance is controlled on a constant excitation amplitude $A_{exc}$, the advantage of the monotonicity of the $A_{exc}(z)$-signal can be used, which offers a very
stable imaging on large scales. The damping-feedback indeed operates very efficiently on large scan ranges, as fig. 4 shows.

In principle it is also possible to image surfaces with atomic resolution using the damping-feedback. Theoretically, controlling on dissipation should offer a higher resolution than controlling on $\Delta f$, as the decay length is shorter. But in practice, better results are achieved when $\Delta f$ or $I_t$-feedback are used. When the distance is controlled by the damping, two controllers are cascaded: the amplitude-controller and the distance-controller. This can lead to additional problems, as the two controllers affect each other. To overcome this problem, the time constant of the inner controller, i.e. the amplitude controller, should be an order of magnitude faster than the outer controller. Otherwise, errors of the inner controller are corrected by the outer controller, so that the outer controller affects the inner. In our case, the amplitude controller works at 10 kHz; the speed of the analogue distance controller is given by the P- and I-gains and can be of the same size as 10 kHz. Using a setup with such time-constants it is not guaranteed, that the two controllers are decoupled. When imaging with atomic-resolution, corrugations in the sub-Angström range have to be measured, which might be hindered by the two controllers influencing each other.

Another way to obtain images with molecular resolution in damping regulation is to use very low gains for the distance-controller. This also helps to circumvent the mentioned problem of the time constants of the two controllers. Using very low gains leads to a quasi constant-height mode, in which the height is corrected slowly preventing from drifting into the sample. This method was used for Figure 5, where Carboxy-fullerenes are evaporated on Cu(100). In the image, the frequency-shift signal is shown. The tip-changes, which occurred during the imaging can clearly be seen, but they don’t affect the stability of the distance-control. Molecular resolution was clearly obtained in the $\Delta f$-signal.
4. Organic molecules on insulators

Apart from the challenge to find the right imaging conditions, it is also difficult to prepare suitable insulating surfaces at room temperature with optimum molecule-substrate interaction. As insulating materials are less reactive than metals, physisorption is weaker. The large energy gaps of insulators implies a weaker polarizability and weaker van der Waals interaction with a given molecule, roughly a factor of two smaller than for metals [19]. The molecule-substrate interactions are found to be weak, often weaker than the molecule-molecule interactions, which hampers suitable self-assembly. Due the reduced interaction, the molecules tend to be very mobile on the insulators.

Furthermore, the effective substrate corrugation experienced by isolated aromatic molecules without suitable legs is typically so weak, that they easily diffuse at room temperature even on metals. The mobility of Cu-TBPP, an organic molecule with legs which self-assembles nicely on Cu(100), is demonstrated in Figure 6, where the molecular lattice was accidentally destroyed by the AFM-tip. More dramatic effects are expected on insulators.

**Figure 6.** a) shows an island of Cu-TBPP porphyrin molecules deposited on Cu(100). The image in b) shows the region marked by the white square in the left image and was taken in a second time. At the height of the arrow a scan accident happened and, after this, the lattice appears locally broken. It can be deduced, that the interaction force is low even on this metallic substrate. Indicated by the circles are a few molecules, which are propably degraded.

Figure 7a) shows Cu-TBPP molecules on KBr(100). Although the molecules aggregate at the step edges, no self-assembly of the molecules can be observed, which indicates high mobility of the molecules. The observed aggregation of clusters at steps is probably due to the interaction of the lateral electric field generated at a step with the dipole induced in the extended $\pi$-system of the aromatic cores of the molecules. Figure 7b) shows a simple simulation of this situation. The virtual molecules (pixels) were randomly placed on a stepped surface, using a coverage of about 20%. Then they are randomly selected and moved one pixel in a random direction, but only if (i) the molecule does not lay on a step and (ii) all the neighboring sites are empty. The resulting distribution looks close to the measurement.

The high mobility of organic molecules on insulating surfaces was further confirmed by the experiment shown in Figure 8, where tetracyanoporphyrin molecules were deposited on KBr(100) (see fig. 1d) for the molecular structure). During a set of distance-curves, some molecules were picked up by the tip and where later deposited on the clean KBr-surface.

To enhance the molecule-substrate interaction the molecules can be functionalized using more reactive end groups. An example is given by the carboxylic group added to the fullerene molecule in Figure 1. Another solution is to freeze the mobility by measuring at low temperatures. As an
alternative at room temperature, the local morphology of the ionic crystals can be modified to increase their local reactivity. For example, when the surface of KBr(001) is shortly irradiated by an electron beam, small pits of some nanometers in size are formed. Previous measurements from our group revealed that the pits are filled by perylene molecules, and they thus act as molecular traps [20]. Polar molecules like SubPc form indeed well-ordered structures, where molecular resolution is achieved [21] (see Figure 9). The periodicity of the molecules is best visible in the error-signal which is shown in fig. 9b). In the damping-image in fig. 9c) enhanced dissipation can be observed at some borders of the molecular island. This could be attributed to the lower coordination of the molecules at the border. As well, mobile molecules on the second layer exhibit increased damping. Thus, damping and molecular mobility might be related. It has to be mentioned, that the contrast in the $A_{exc}$ signal only appeared after a tip-change.
Figure 9. Sub-phtalocyanine on KBr(100). a) shows the topography, where the distance is controlled by $\Delta f = -10$ Hz. b) shows the error signal of $\Delta f$, where the periodicity of the molecules are visible. c) shows the excitation amplitude $A_{exc}$. The damping is enhanced at the steps and over the molecules at the edges.

5. Conclusions
In conclusion, we described the main difficulties encountered when AFM is applied to image structures formed by organic molecules on insulating surfaces. High-resolution AFM imaging is often hindered by the convolution of long- and short-range forces. On the other side, AFM provides important information on mechanical processes occurring between tip and surface. From the frequency-shift of the cantilever oscillating close to the surface, the interaction forces can be evaluated. Dissipative processes in the interaction region can be recognized in the damping signal. On large scales, damping can also be used as feedback signal to image with improved stability.

Furthermore, the molecules tend to be more mobile on insulators than on metals. Of course, this problem might be easily overcome by imaging at low temperature. As potential applications of molecular electronics need to be operated at room temperature, different solutions have to be considered. One possibility is given by functional groups added to the molecules to enhance their interaction with the substrate, and consequently reduce their mobility. Alternatively, artificial nanopatterns can be created on the crystal surface to confine the molecules. The enhanced electric field surrounding these structures was used to orient polar molecules (SubPc) on KBr surfaces.

6. Acknowledgment
We acknowledge the Swiss National Center of Competence in Research on Nanoscale Science and the National Science Foundation for financial support. We thank D. Schlettwein and W. Michaelis (University of Oldenburg) for providing the SubPc molecules and A. Gourdon and C. Joachim (CEMES-CNRS, Toulouse) for providing the Cu-TBPP molecules.

7. References
[1] V.J. Langlais, R.R. Schmittler, H. Tang, A. Gourdon, C. Joachim, and J.K. Gimzewski. Spatially resolved tunneling along a molecular wire. Phys. Rev. Lett., 83:2809, 1999.
[2] M. de Wild, S. Berner, H. Suzuki, H. Yanagi, D. Schlettwein, S. Ivan, A. Baratoff, H.-J. Güntherodt, and T.A. Jung. A novel route to molecular self-assembly: Self-intermixed monolayer phases. ChemPhysChem, 3(10):825, 2002.
[3] S.A. Burke, J.M. Mativetsky, R. Hoffmann, and P. Grutter. Nucleation and submonolayer growth of c-60 on kbr. Phys. Rev. Lett., 94:096102, 2005.
[4] T. Kunstmann, A. Schlarb, M. Fendrich, T. Wagner, R. Moller, and R. Hoffmann. Dynamic force microscopy study of 3,4,9,10-perylenetetracarboxylic dianhydride on kbr(001). Phys. Rev. B, 71:121403, 2005.
[5] C. Loppacher, M. Guggisberg, O. Pfeiffer, E. Meyer, M. Bammerlin, R. Lüthi, R. Schlittler, J.K. Gimzewski, H. Tang, and C. Joachim. Direct determination of the energy required to operate a single molecule switch. *Phys. Rev. Lett.*, 90:066107, 2003.

[6] R. Bennewitz, A.S. Foster, L.N. Kantorovich, M. Bammerlin, Ch. Loppacher, S. Schär, M. Guggisberg, E. Meyer, H.-J. Güntherodt, and A.L. Shluger. Atomically Resolved Steps and Kinks on NaCl islands on Cu(111): Experiment and Theory. *Phys. Rev. B*, 62:2074, 2000.

[7] Ch. Loppacher, M. Bammerlin, F.M. Battiston, M. Guggisberg, D. Müller, H.R. Hindler, R. Lüthi, E. Meyer, and H.-J. Güntherodt. Fast Digital Electronics for Application in Dynamic Force Microscopy Using High-Q Cantilevers. *Appl. Phys. A*, 66:215, 1998.

[8] F.J. Giessibl. Atomic resolution of silicon(111)7x7 by atomic force microscopy through repulsive and attractive forces. *Science*, 267(68):1451–1455, 1995.

[9] M. Bammerlin, R. Lüthi, E. Meyer, A. Baratoff, J. Lü, M. Guggisberg, Ch. Gerber, L. Howald, and H.-J. Güntherodt. True Atomic Resolution on the Surface of an Insulator via Ultrahigh Vacuum Dynamic Force Microscopy. *Probe Microscopy*, 1:3, 1997.

[10] S. Orisaka, T. Minobe, T. Uchihashi, Y. Sugawara, and S. Morita. The atomic resolution imaging of metallic ag(111) surface by noncontact atomic force microscope. *Appl. Surf. Sci.*, 140:243, 1999.

[11] F.J. Giessibl. A direct method to calculate tip-sample forces from frequency shifts in frequency-modulation atomic force microscopy. *Appl. Phys. Lett.*, 78(1):123, 2001.

[12] O. Pfeiffer, L. Nony, R. Bennewitz, A. Baratoff, and E. Meyer. Distance Dependence of Force and Dissipation in NC-AFM on Cu(100) and Al(111). *Nanotechnology*, 15(2):101–107, 2004.

[13] Ch. Loppacher, M. Bammerlin, M. Guggisberg, S. Schär, R. Bennewitz, A. Baratoff, E. Meyer, and H.-J. Güntherodt. Dynamic force microscopy of copper surfaces- Atomic resolution and distance dependence of tip-sample interaction and tunneling current. *Phys. Rev. B*, 62:16944, 2000.