Advances in Atom and Single Molecule Machines

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Imaging and Manipulating Molecular Orbitals


Springer
This book encompasses contributions of the third AtMol Workshop in Berlin, September 2012. AtMol is a 4-year research project funded by the European Commission’s ICT-FET programme. It was launched on 1 January 2011 with the objective to construct the first ever complete molecular chip where common microelectronic functionalities are brought and encapsulated at the atomic scale. The core of a molecular chip will make use of the extraordinary properties of individual molecules and surface atomic wires, regarding both their chemical and quantum electronic characteristics that should be of practical use and appealing to future information technologies (IT) manufacturing.

Real space imaging of the electronic cloud of a single atom or molecule is now of prime importance in the field of quantum information transmission, manipulation and storage and in the field of single-molecule mechanics. Also, the intramolecular electronic and magnetic phenomena inside a single molecule are of fundamental scientific interest. This AtMol workshop brought for the first time research groups from all around the world together, working on the theory or experiments on the spatial extension (associated with electronic spectroscopy) of the electronic cloud of a single atom or molecule. When possible, the maps recorded or reconstructed by Fourier Transform can be interpreted on the basis of the spin-orbitals entering in the Slater determinants decomposition of the electronic quantum states of a single atom or molecule. Depending on the used experimental and calculation techniques, the relation between the obtained data and the mathematical concept of orbitals was vividly debated. Manipulation techniques to change the spatial distribution or quantum properties by interacting with single molecules were also discussed.

This workshop was open for contributors in the fields of single atom and single molecule imaging using, for example, the FEM, TEM, Photoemission, Attosecond Tomography, NC-AFM or LT-STM instruments. It was the occasion to celebrate the first recording of the image of a single molecule by E. Müller 60 years ago in Berlin-Dahlem, the precise location of this third AtMol workshop (see Fig. 1).
The topics reported in this book form one of the scientific backgrounds required for building up the future of calculators and memory as recognized at the European Commission level. We thank the ICT-FET programme and A*STAR of Singapore for the financial support in organizing this third workshop, and Springer Verlag and its staff members for the publication of this book.

Fig. 1 The first ever recorded image of a few isolated molecules in real space by Erwin W. Müller in 1950 with a Field Emission Microscope. The imaged molecules are Cu-Phthalocyanines deposited on a broad tungsten tip with about a 200 nm radius of curvature. This image was first submitted on 7 August 1950 and published in the journal Zeitschrift für Naturforschung 5a, 473 (1950). At that time E. Müller was at the Kaiser-Wilhelm-Institut für Physikalische Chemie und Elektrochemie in Berlin. Before this direct space image, these molecules were only known indirectly via a Fourier analysis of the Röntgen X-Ray diffraction pattern of a crystal of Cu-Phthalocyanine molecules as obtained for the first time by J.M. Robertson in 1935 (J. Chem. Soc, 615 (1935))
Contents

Part I  FEM

Observations of Individual Cu-Phthalocyanine Molecules Deposited on Nano-Tips in the Field Emission Microscope .......................... 3
Moh’d Rezeq, Christian Joachim, Ma Han Lwin and Francisco Ample Navarro

High Voltage STM Imaging of Single Copper Phthalocyanine .......... 15
C. Manzano, W.-H. Soe and C. Joachim

Part II  STEM

Motional Analysis of a Single Organic Molecule by TEM Using Nanocarbon Materials: Scope of Atomic Level Imaging and Spectroscopy ................................................................. 29
Masanori Koshino and Kazutomo Suenaga

Part III  Photo-Emission (PE)

Imaging Orbitals by Ionization or Electron Attachment: The Role of Dyson Orbitals ................................................................. 41
B. Mignolet, T. Küs and F. Remacle

Part IV  LT-UHV-STM

Mapping the Electronic Resonances of Single Molecule STM Tunnel Junctions ................................................................. 57
We-Hyo Soe, Carlos Manzano and Christian Joachim
Manipulation and Spectroscopy of Individual Phthalocyanine Molecules on InAs(111)A with a Low-Temperature Scanning Tunneling Microscope ............................. 69
Christophe Nacci, Kiyoshi Kanisawa and Stefan Fölsch

Electronic Structure and Properties of Graphen Nanoribbons: Zigzag and Armchair Edges ............................... 81
Matthias Koch, Francisco Ample, Christian Joachim and Leonhard Grill

Imaging and Manipulation of Molecular Electronic States on Metal Surfaces with Scanning Tunneling Microscopy .......... 91
Robin Ohmann, Lucia Vitali and Klaus Kern

SPM Imaging of Trinaphthylene Molecular States on a Hydrogen Passivated Ge(001) Surface ................................ 105
Marek Kolmer, Szymon Godlewski, Bartosz Such, Paula de Mendoza, Claudia De Leon, Antonio M. Echavarren, Hiroyo Kawai, Mark Saeys, Christian Joachim and Marek Szymonski

Part V STM Theory and Image Interpretation

Simulations of Constant Current STM Images of Open-Shell Systems ............................................................... 117
M. Kepenekian, R. Robles, R. Korytár and N. Lorente

Electronic Transmission Through a Single Impurity in a Multi-configuration Scattering Matrix Approach .............. 137
M. Portais and C. Joachim

Electron Transport Through a Molecular Junction Using a Multi-configurational Description .......................... 159
Martin Vérot, Serguei A. Borshch and Vincent Robert

Visualizing Electron Correlation in Molecules Using a Scanning Tunneling Microscope: Theory and Ab Initio Prediction 181
Massimo Rontani, Dimitrios Toroz and Stefano Corni

Part VI NC-AFM

Submolecular Resolution Imaging of C_{60}: From Orbital Density to Bond Order ............................................. 195
Philip Moriarty
Part I
FEM
Observations of Individual
Cu-Phthalocyanine Molecules Deposited
on Nano-Tips in the Field Emission
Microscope

Moh’d Rezeq, Christian Joachim, Ma Han Lwin
and Francisco Ample Navarro

Abstract Using a field emission microscope (FEM), the first image ever of isolated individual molecules was reported in the 1950s. At that time, the Cu-Phthalocyanine (Cu-Pc) molecule was imaged in different configurations, namely two- and four-leaf patterns. These various apparent shapes were linked to the location of the molecule on particular atomic planes of the relatively quite large FEM tip apex used at that time. We report here on how the fabrication of an extremely sharp FEM tip with an apex of the size of the molecule to be imaged provides a unique opportunity to study the behavior of one molecule at a time on the tip apex. Preliminary data are presented where two adsorption states have been observed according to the electronic cloud FEM images of the molecule. Since the atomic structure of the tip can be determined first from a field ion microscope image, the interaction of the molecule with tip apex surface atoms, and thus the molecule adsorption conformation can be readily determined.
1 Introduction

The remarkable invention of the field emission microscope (FEM) in 1936 by Muller enabled him some years later to turn it into a potential instrument for imaging individual molecules. He actually reported the first images of a single isolated organic molecule, namely a phthalocyanine molecule, in 1950 [1].

The observation of Metal-Phthalocyanine (M-Pc) molecules in the FEM was then reported in several places [2–5]. The thermal vapor deposition of M-Pc molecules on the tip surface usually results in a random distribution of these molecules all over the tip apex area with different shapes. The apparent shapes of the molecule have been classified into two main groups, quadrates which mostly settle on the closely packed (110) planes and doublets that can be seen on the other planes, like (111) and (112). Some other shapes, a doughnut-like shape, have been rarely observed [1–5]. The stability of the molecule on the tip surface has been studied, mainly for the four-leaf pattern. It was found that some molecules disappear gradually during the imaging process at a fixed applied voltage where the remaining molecules are considered the most stable ones; although the majority of the four-leaf molecules and some of the doublets have been found to disappear upon the removal of the applied voltage and turning it back up again. Moreover, the quadruplets can disappear by just increasing or decreasing the applied voltage. It has also been observed that some doublets appear on different sizes and brightness. The various molecular shapes, sizes, brightness, and stabilities indicate different adsorption states on the tip surface. Gomer et al. [2] used I–V measurements to estimate the ionization potential to be 7 V. They found that the images are not the result of diffraction patterns’ superposition, but rather are the results of electron optic effects. Emission measurements of molecules adsorbed on clean tungsten show irregularities of 5–10 Å exist on the cleanest surfaces. The work by Morikawa et al. [4] involved the deposition of H_2-, Fe-, Co-, Ni- and Cu-Pc at liquid nitrogen temperature. They observed four- and two-leaf patterns in a FEM image of a tungsten tip. Most of the four-leaf patterns have been seen on (110) planes. Two-leaf patterns appeared evenly on the whole tip with no preference. Whereas for Co-Pc, almost all the observed molecule images show up only two-leafs. They also found that the adsorption state of Co-Pc two-leaf patterns is the same as the other M-PC molecules with four-leaf patterns. The two-leaf patterns in Co-Pc are stable as the four-leaf patterns in other M-Pc molecules. Nevertheless, the reason for the difference in the appearance between Co-Pc and other M-Pc molecules is not yet understood.

However, the broad tip surfaces that have been used in these images allow the accommodation of a large number of molecules at the same time. Therefore, only statistical information about the molecular adsorption states on the tip surface was possible to obtain.

Reducing the tip size to a very small apex, in the range of the molecular size [6–11], enables the selection of only one molecule to be studied at a time. The atomic structure of the apex is precisely characterized in the field ion microscope.
prior to the molecular deposition process, for an accurate estimate of the molecule location on the tip surface [10, 11]. However, we have observed new states of molecular adsorption that introduce a new insight into the molecular interaction with the surface under the influence of a high electric field. We have found that a flat molecule on the surface can exhibit single, double, triple, and quadruple leaf patterns. In another case, we found that the two-leaf pattern is quite stable and does not convert to other shapes. Furthermore, these doublets do not disappear upon the decrease or increase of the applied voltage. For this stable case the current–voltage data have been taken after the deposition of a single molecule. The I–V plots for the individual molecule have shown unconventional behavior that does not fit in Fowler–Nordheim theory.

The advantages of using an ultrasharp tip for molecular characterization can be summarized as follows: (1) An optimum magnification of the molecule can be obtained. (2) The applied voltage will be a direct function of the field emission from the molecule, as no other parts of the tip will contribute to the field emission current. (3) As the field emission is restricted to one molecule the effect of this molecule on the metal work function can be readily extracted. (4) As the molecule is confined to a small substrate area the position of the molecule on the surface can be estimated with a high precision.

2 Experimental Setup and Molecule Images

The typical field ion and FEM setup [12] is used to shape and characterize the tip [10, 11]. A crucible with Cu-Pc molecule is placed at a normal angle and 20 mm below the tip, whereas the latter faces the screen at a distance 35 mm away, as schematically depicted in Fig. 1. The crucible is embraced by a heating loop from a tungsten wire but does not touch the outside wall of the crucible; this is meant for thermal radiation heating of the crucible. The heating coil and crucible were outgassed several times before the actual molecular vapor deposition.

Fig. 1 The schematic of the FIM setup showing the position of the crucible, which is used for molecular deposition on the tip apex
Then the tip was atomically cleaned in the FIM by the common field evaporation process, as in Fig. 1a, at 8.4 kV. Later, the tip bias was reversed and the field emission was obtained at $-700 \text{ V}$, as in Fig. 1b, at liquid nitrogen temperature (Fig. 2).

Subsequently, the tip voltage was lowered to 1 kV and the molecules were deposited at a filament current 3.5 A for 60 s, while the tip was kept at the liquid nitrogen temperature. The high electric field at the tip, during the deposition mechanism, tends to attract molecules not only to the side that is exposed to the crucible but also to the tip center as we see in Fig. 1c, at $-500 \text{ V}$. The bright area, bottom-right, is the area that is facing the crucible where a large amount of molecules are accumulated. In the same FEM image we can see two Cu-Pc of (four-leaf pattern) molecules at (110) plane. After a short time, the top molecule disappeared and the most stable one sitting on the (110) surface is left with well resolved four-leaf structure, as in Fig. 1(d). Increasing the field further led to the removal of the center four-leaf molecule and to the diffusion of other molecules from the periphery of the tip, the bright area, as in Fig. 5e at $-520 \text{ V}$.

Later, the tip was sharpened using the field assisted nitrogen etching process [10]. The nano-tip size can be estimated by computationally reproducing the atomic structure of the apex, as was done previously in several places [10, 11]. Our approach here, for the characterization of a single molecule, is to reduce the size of the tip to around 1–2 nm in radius and then obtain a field emission of the clean...
The FIM image of the ultrasharp tip is presented in Fig. 3a, at 4.4 kV and estimated to be 1.6 nm in radius, where the electron field emission from the nano-tip apex is imaged in Fig. 3b, at −500 V.

We aim from the FEM of a clean tip to be able to distinguish between the FEM of the molecule and that before the molecular deposition. This is because we will not be able to see any field emission from the tip background after the molecule is deposited, since the field emission will be completely dominated by the molecule.

Fig. 3  
(a) A FIM image of a nano-tip with a radius of 1.6 nm fabricated before the deposition of Cu-Pc.  
(b) A FEM image for the same tip.  
(c–h) A stable two-fold leaf pattern, the shape or position of the pattern does not change upon increase and subsequent decrease of the applied voltage.
We present two interesting cases that highlight the molecular adsorption states. The first case is the extremely stable two-leaf configuration. The molecule is deposited at the established current, time, field, and temperature parameters, i.e., \( I = 3.6 \text{ A}, \ t = 60 \text{ s}, \ V = 160 \text{ V}, \ T = \text{LN} \). Subsequently, and after increasing the voltage gradually from the initial adsorption field the two-fold pattern appeared at a voltage \( = -360 \text{ V} \), which is much lower than the threshold FEM value of the same tip before the molecular deposition as mentioned above, i.e., \(-500 \text{ V}\). This two-leaf pattern only showed an increase in the brightness upon increasing the applied voltage and vice versa. The FEM patterns at different voltages are shown in Fig. 3c–h. We mean here by stability that the molecule does not vibrate or evolve to other shapes as we will see in the next case. In this particular adsorption state the two almost identical leafs are quite stable over a long period of time, more than an hour, and very stable upon increasing or decreasing the applied voltage. Furthermore, the molecule does not disappear even after the removal of the electric field and turning the voltage back up to the imaging values, as in Fig. 3c, where \( V = 365 \text{ V} \) and \( I = 13.21 \text{ nA} \), and in Fig. 3d, where \( V = 365 \text{ V} \) and \( I = 13.22 \text{ nA} \). We have also noticed that the field emission current from the molecule is quite stable and reversible with the applied voltage. This is obvious in Fig. 3e and h, where identical FEM patterns were obtained at 380 V before reaching the highest voltage 440 V in Fig. 3g, and after decreasing the voltage to the same value (380 V). The FE currents were also measured directly at these two cases and were 13.64 and 13.84 nA, respectively, whereas the current at 440 V was 17.32 nA. In fact, this outstanding stability and reversibility in field emission patterns can be rarely seen, even for clean nano-tips.

Later, the tip was atomically cleaned by field desorption of the adsorbed molecules and other contaminates until the atomic structure of the tip is recovered as in Fig. 4a, and its FEM profile in Fig. 4b, where the applied voltages were 4.4 kV and \(-500 \text{ V}\), respectively, which are similar to those of the initial nano-tip. Then the molecule was deposited again at the same setting parameters. We found that the Cu-Pc molecule in this second case exhibits different features that vary between single, two, three, and four leafs and some intermediate cases, as in Fig. 4c–k. In fact, these results represent an example from several experiments that show the same behavior. We also noticed that some leafs appear with different FEM intensities. More importantly, we noticed that the doublet pattern appeared in different orientations as in Fig. 4f, g, k. This suggests that the appearance of various patterns is determined by the binding state between the molecular segments and the surface atoms of the tip, as we will try to explain by models in the Sect. 3.
Fig. 4  a A FIM image of the clean nano-tip.  b The FEM of the same nano-tip just before the molecular depositions.  c–k FEM patterns of the same Cu-Pc molecule
3 Current Voltage Emission Characteristics Through the Molecule

The I–V data have been taken for the above stable doublet case, in Fig. 3, after the deposition of the Cu-Pc molecule, these data are plotted in Fig. 5. The electric current here is measured directly from the tip using a pico-ammeter with an internal voltage source. Two main decisive behaviors can be recognized. First, the relatively high current at small voltages compared to previous studies, which accounts for the ultrasharp tip base fabricated with the nitrogen etching method. The I–V curves do not fit the known Fowler–Nordheim theory, where \( \ln(I/V^2) \) versus \( V \) is linear, but they rather fit the modified field emission theory by Yuasa et al. [13], as we see in Fig. 5a, b. They found that \( I/V^3 \propto \exp(-A/V) \), where \( A \) is a constant, thus \( \ln(I/V^3) \) versus \( V \) is linear. This is also consistent with previous studies which showed that the tip apex maximum electric field, and thus the tunneling current, is a function of the radius of the tip base [14]. Second, it has also been observed that at low current, and below the imaging FE current, the molecular FE current starts at a threshold voltage higher than that of a clean tip and then the current enhances dramatically as the voltage increases, as can be seen in Fig. 6. This indicates that the molecule at low electric field tends to retard the field emission from the surface Fermi electrons into the vacuum. When the electric field becomes high enough at the molecule the resonance tunneling enhances significantly due to the small barrier behind the molecule which results in an enhanced field emission. This enhancement of the field emission accounts for the observation of the FEM image at a lower voltage than needed for a clean tip in the previous both cases. However, more analysis will be needed and it is worth designating a separate and detailed study for these phenomenal behaviors.

![Figure 5](image_url)  
**Fig. 5** a A plot of \( \ln(I/V^2) \) versus \( 1/V \) for a single Cu-Pc molecule deposited on a nano-tip surface. b A plot of \( \ln(I/V^3) \) versus \( 1/V \) for a single Cu-Pc molecule deposited on a nano-tip surface
Fig. 6 Field emission current versus the applied voltage (I–V) from a nano-tip before and after the deposition of Cu-Pc molecule.

Fig. 7 a A Cu-Pc molecule with four arms sitting on the nano-tip apex of (110) plane. b Some arms are detached from the nano-tip surface. c The molecule diffused slightly from the original position. d Side view of the tip showing the Cu-Pc molecule standing on two arms and the other two arms are detached from the surface.
4 Computer Simulation of the Molecule Adsorption on the Nano-Tip Apex

Molecular dynamics simulations were done to understand the behavior of a single Cu-Pc molecule deposited on the tungsten nano-tip (with radius = 1.6 nm and (110) crystal orientation) by means of the ASED+ program [15]. The semi-empirical atom superposition and electronic delocalization molecule orbital (ASED-MO) approach were used to describe the chemical bonds of the molecule and its interactions with the tungsten tip. Our calculations showed that chemical bonds between the molecule and the tungsten tip are rather of a physisorbed nature during the adsorption on the tip surface. The simulations showed multiple conformations of the Cu-Pc molecule on the tungsten nano-tip, as shown in Fig. 7a–d. In these configurations, the molecule can be attached to the surface by the four arms but in some cases, some arms can be detached from the surface. That would explain the observation of different number of bumps when the electric field is emitted through the molecule. Also, the diffusion of the molecule over the tip was observed in the simulations, as in Fig. 7c.

5 Conclusion

We have demonstrated that the fabrication of extremely sharp tips with an apex in the range of 1–2 nm is an ideal method for imaging and characterizing single molecules in the FEM. We have shown that the appearance of the Cu-Pc molecules is not linked to particular atomic planes, but rather to the adsorption state on the surface. This accounts for the observation of single, double, triple, and quadrature FEM patterns for the same Cu-Pc molecule. We have also observed strong, doublet state where the molecule does not change shape upon decreasing or increasing the applied voltage and the field emission current from the molecule is fairly reversible. A computer simulation for the various molecular adsorption states on the tip apex has been presented.

References

High Voltage STM Imaging of Single Copper Phthalocyanine

C. Manzano, W.-H. Soe and C. Joachim

Abstract In this chapter experiments done to investigate the scanning tunneling microscope (STM) imaging at near field emission voltages of single Copper Phthalocyanine (CuPc) molecules deposited on Au(111) are presented. An imaging bias voltage range is explored exceeding the standard tunneling imaging conditions going from the threshold of the tunneling junction barrier up to $-10.0 \text{ V}$. At this voltage regime current transmitted through the tip-molecule–substrate junction is made not only of tunneling electrons but also of electrons overcoming the tunneling barrier and behaving like free electrons. Our interpretation of the process, enabling the visualization of the electronic cloud of single organic molecules under these conditions, is presented.

1 Introduction

In Chap. 1 the far field electron emission imaging technique known as Field Emission Microscopy (FEM) [1] was thoroughly described. The possibility of imaging molecules in real space is, however, not only restricted to the use of high electric fields. In a Scanning Tunneling Microscope (STM) bias voltages of a few volts ($\pm2.0 \text{ V}$) giving access to electronic states near the substrate’s Fermi level are normally used to take images of low-resistance surfaces and molecules or adsorbates deposited on them.