Image potential states mediated STM imaging of cobalt phthalocyanine on NaCl/Cu(100)*

Qinmin Guo(郭秦敏)[1], Zhihui Qin(秦志辉)[1], Min Huang(黄敏)[1], Vladimir N. Mantsevich [2], and Gengyu Cao(曹更玉)[1,†]

[1] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China

[2] Faculty of Physics, Moscow State University, Moscow 119991, Russia

(Received 30 September 2015; revised manuscript received 28 December 2015; published online 18 January 2016)

The adsorption and electronic properties of isolated cobalt phthalocyanine (CoPc) molecule on an ultrathin layer of NaCl have been investigated. High-resolution STM images give a detailed picture of the lowest unoccupied molecular orbital (LUMO) of an isolated CoPc. It is shown that the NaCl ultrathin layer efficiently decouples the interaction of the molecules from the underneath metal substrate, which makes it an ideal substrate for studying the properties of single molecules. Moreover, strong dependence of the appearance of the molecules on the sample bias in the region of relatively high bias (> 3.1 V) is ascribed to the image potential states (IPSs) of NaCl/Cu(100), which may provide us with a possible method to fabricate quantum storage devices.

Keywords: image potential states, NaCl ultrathin layer, CoPc, scanning tunneling microscopy

PACS: 68.37.–d, 68.37.Ef **DOI:** 10.1088/1674-1056/25/3/036801

1. Introduction

In the last few decades, many components of molecular circuits, e.g., molecular wires, rectifiers, switches, and transistors, have been fabricated with single molecules.[1–4] The performance of the molecular devices is strongly dependent on the distribution of the molecular orbital. A scanning tunneling microscope (STM) provides with a powerful tool to directly image the molecular orbital in real space. Normally, STM images give us information about both the topography and electronic states of a surface. Since the density of states (electronic structures) of a surface are usually strongly dependent on the energy alignment, the features in STM images are changing with the scanning parameters. Moreover, the electronic states of the adsorbate and substrate would be coupled and contribute to the measured STM images simultaneously. Especially, the electronic states of the STM tips also influence the imaged electronic states greatly. To fully understand the distribution of the molecular orbital, the electronic states involved in STM images have to be clarified.

Electrons in front of metal surfaces would induce image charges and thus feel the attractive force from the image charges. However, they will be reflected by the metal surfaces with high possibility if the metal surfaces, e.g. Cu(100) and Ag(100), have band-gaps involving into the energy of these electrons.[5,6] As a result, electrons above metal surfaces would be trapped by this electrostatic image potential, leading to a pronounced Rydberg-like series of additional surface states existing at these metal surfaces, namely, image-potential states (IPSs). The IPSs can be described as

$$E(n) = -\frac{0.85}{(n+a)^2}\ \text{eV}, \tag{1}$$

where n is a positive integer indicating the order of the IPS, and a is a quantum defect.[5] The IPS investigations are typically carried out by employing two-photon photoemission (2PPE).[7–11] Recently, the studies on IPSs of surfaces for local information are also performed using STM and scanning tunneling spectroscopy (STS).[12–16] Our previous article reported that not only does the Stark shift (electric field effect) but also the molecular adsorption will influence the energetic positions of IPSs in STM/STS studies, giving rise to bias-dependent layer thicknesses of NaCl on Cu(100).[17] Although the molecular orbitals of some molecules, such as pentacene[18] and methylterrylene,[19] have been successfully obtained on NaCl ultrathin layers using STM, there are very few investigations on the influences of IPSs on STM imaging of molecules, which are of crucial importance for understanding the properties of molecules in the systems where IPSs are present.

In this paper, we carry out an STM investigation on a well-known dye molecule, namely, cobalt phthalocyanine (CoPc), on NaCl/Cu(100), where IPSs play a key role.[17] It is found that the molecules on NaCl/Cu(100) appear as dimming holes when the bias voltage exceeds the threshold of 3.1 V. Such an unusual bias-dependent feature of CoPc in STM imaging is ascribed to the IPSs of NaCl/Cu(100). Furthermore, we obtain a highly resolved STM image of the lowest

*Project supported by the National Natural Science Foundation of China (Grant Nos. 21203239 and 21311120059) and RFBR (Grant No. 13-02-91180).

†Corresponding author. E-mail: gycao@wipm.ac.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

unoccupied molecular orbital (LUMO) of CoPc, which is improved by the adsorption of a single molecule on the tip apex. Understanding the influences of IPSs on orbital imaging would help us improve the performance of molecular devices.

2. Methodology

2.1. Experimental details

The experiment was carried out in an ultra-high vacuum (UHV) chamber (base pressure 1.3×10^{-8} Pa) equipped with a commercial low-temperature STM (Unisoku, Japan). The Cu (100) single crystal surface (Mateck, Germany) was cleaned by cycles of Ar^+ sputtering and UHV annealing. The quality of the obtained Cu (100) surface was checked by STM scanning and then the surface was used for deposition. NaCl was thermally evaporated (0.2 ML/min) from a silica evaporator onto Cu (100) kept at room temperature (RT). CoPc molecules, after degassing for more than 20 h, were deposited onto the NaCl/Cu(100). During the deposition, the substrate was kept at 150–200 K in order to reduce the diffusion of molecules as much as possible, and the vacuum was better than 6.6×10^{-8} Pa. An electrochemically etched polycrystalline tungsten wire was used as the STM tip. Before measurement, the tip was treated by electron-beam bombardment to get rid of the contamination and oxidation. The bias voltage refers to the sample voltage with respect to the tip, and all topographic images were obtained in constant current mode at $\sim$ 78 K.

2.2. Computational details

To better understand the adsorption behavior of CoPc on the NaCl/Cu(100) system, we performed plane-wave basis density functional theory (DFT) calculations with Perdew–Burke–Ernzerhof (PBE) generalized gradient corrected approximation (GGA)[20] and ultrasoft pseudopotentials.[21] The cutoff energy for the plane-wave expansion is set to be 400 eV. The Cu(100) surface, cleaving perpendicular to the [100] of the face centered cubic Cu solid, is modeled by a $(8\times8\times3)$ supercell with 64 Cu atoms per layer. The inter-Cu layer distance is around 1.81 Å. Similarly, the NaCl(100) surface is modeled by a $(5\times5\times4)$ supercell containing 4 atomic layers with 25 Na atoms and 25 Cl atoms per layer. The inter-NaCl layer distance is around 2.81 Å. The vacuum thickness of 15 Å is set to avoid the interactions between adjacent supercells. The CoPc ($C_{32}H_{16}CoN_8$) molecule is adsorbed on one side of the supercells and the atomic positions are relaxed according to the Hellmann–Feynman forces until the maximum atomic force is less than 0.02 eV/Å. The coordinates of the atoms in the upper part of the slab (containing the CoPc molecule and 2 atomic layers of substrates) are relaxed while the atoms in the lower part of the slab (1 atomic layer for the Cu(100) surface and 2 atomic layers for the NaCl(100) surface) are constrained to their bulk positions. The optimized distances of the CoPc molecule relative to Cu(100) and NaCl(100) are 2.8 Å and 3.2 Å, respectively. The adsorption energy is calculated by: $E_{\rm ads} = E_{\rm CoPc} + E_{\rm surf} - E_{\rm CoPc/surf}$, where $E_{\rm CoPc}$ is the total energy of an isolated CoPc molecule, $E_{\rm surf}$ is the total energy of the clean supercell slab, and $E_{\rm CoPc/surf}$ is the total energy of the supercell slab with one CoPc molecule adsorbed.

3. Results and discussion

NaCl layers with nominal coverage of 2.2 ML (1 ML refers to a monolayer of NaCl) were grown on Cu(100) at room temperature as shown in Fig. 1. It is found that at the initial growth stage, NaCl forms wetting layers which are usually bilayer in thickness.[17] The third layers in a square shape are prone to forming at the step edges. However, it is noticed that the NaCl layers are not uniform on the entire surface probably due to either the large deposition rate during preparation or the strong interactions between the NaCl layers. The third layers could be formed before the wetting bilayer is closed.

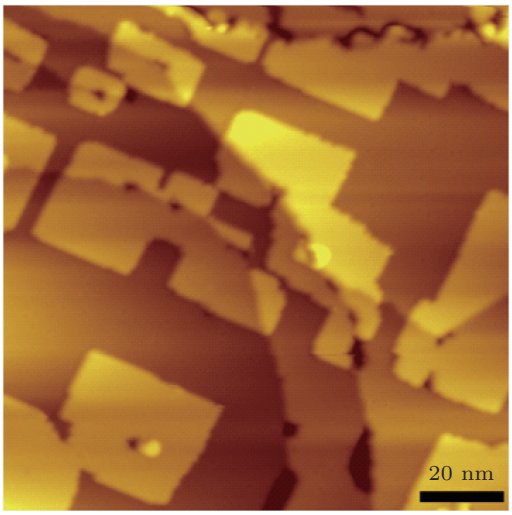


Fig. 1. (color online) Large-scale (200 nm×200 nm, $V_{\rm b}$ = 1.5 V, $I_{\rm t}$ = 100 pA) STM image of NaCl film grown on Cu(100) with coverage of 2.2 ML.

Figure 2(a) shows a region where the bilayer, the third layer, and the substrate Cu(100) are observed simultaneously. The lower side (dark area) in the image refers to the Cu(100) surface, where the post-deposited CoPc molecules with coverage of 0.3 ML are mainly located. Interestingly, the CoPc molecules on Cu(100) exhibit a non-uniform distribution. Our previous investigation revealed that the dominant interaction in a system of CoPc/Cu(100) is the short-ranged intermolecular repulsive force, which induces the dispersed distribution at the initial growth stage on Cu(100).[22,23] In this case, the molecules on Cu(100) near the NaCl step edges are remarkably denser. Where are these molecules from?

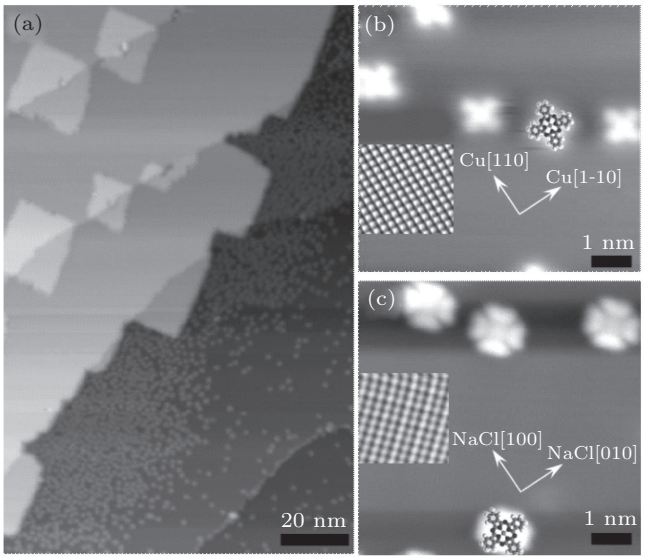


Fig. 2. (a) CoPc molecules adsorbed on NaCl-partially-covered Cu(100) (100 nm×160 nm, $V_b = 3.5$ V, $I_t = 65$ pA). (b) The molecules on Cu(100) (11 nm×11 nm, $V_b = 1.5$ V, $I_t = 80$ pA) and (c) NaCl layers (11 nm×11 nm, $V_b = 2.5$ V, $I_t = 35$ pA). The insets in panels (b) and (c) are the atomically resolved images of Cu(100) and NaCl/Cu(100), respectively.

The calculation reveals that CoPc molecules chemisorb on the Cu(100) surface with an adsorption energy of 0.57 eV and physisorb on NaCl with a low adsorption energy of around 0.15 eV. The results indicate that the molecules interact with Cu(100) more strongly. Therefore, the CoPc molecules could diffuse on the NaCl layer readily and be captured by the Cu(100) surface at the preparation temperature (150–200 K). That is why the density of CoPc molecules on Cu(100) near NaCl layers is much larger than that far from NaCl layers.

Although the molecular adsorption is very weak, there are still some molecules located on NaCl layers. Figures 2(b) and 2(c) are the STM images of CoPc on the Cu(100) and NaCl bilayers, respectively. A close inspection reveals that the CoPc molecules adsorb with their molecular planes parallel to the surface in both cases. Interestingly, the molecular appearances are drastically different. It is known that there is a Co^{2+} ion at the center of the planar CoPc molecule, and the four phenyl lobes outside connect to the central Co^{2+} ion via pyrrole rings whose nitrogen centers are coordinated to the central ion. On Cu(100), the CoPc molecules appear as cross-shaped structures as shown in Fig. 2(b); while on the NaCl ad-layer (Fig. 2(c)), they appear as sub-quadrate, and the similar molecular shape of CuPc was observed on NaBr layers,[24] indicating that the molecular appearance mainly arises from the Pc backbone. The distinguishing molecular contours on NaCl arise from the decoupling effect of the underlying NaCl layers, and thus the appearance of the molecules on NaCl layers gives more information of the spatial distribution of the molecular orbital.[18,19,25] Based on the atomic resolution image of Cu(100) (inset of Fig. 2(b)), two kinds of adsorption configurations on Cu(100) are revealed with the molecular lobes forming $\pm 22.5°$ with respect to the direction Cu⟨110⟩, which are energetically equivalent configurations.[22] In contrast, only one configuration on terraces of the NaCl layer is found, in which the molecular lobes align with NaCl [100] and [010].

Due to its insulator property, NaCl could efficiently decouple the interaction from the free electrons of the underlying metal substrate.[17–19,25–32] NaCl has no energy bands and surface states near the Fermi level, so NaCl layers just act as tunneling barriers at relatively low sample biases (typically below 3.1 V in the case of the NaCl/Cu(100) system). The adsorbed molecules participate tunneling by their frontier orbitals near the Fermi level, and information about the orbitals of the free molecules can be better extracted like the case of pentacene on NaCl/Cu(111).[18] Since the adsorption energy of CoPc on NaCl is only 0.15 eV, it is feasible to gather a single CoPc molecule onto the tip apex just by fast scanning on the surface of CoPc on NaCl layers. Figure 3(a) is a highly resolved STM image of the CoPc molecule on the NaCl layer with a single molecular STM tip. The nodal planes of the molecular orbital are clearly resolved and agree very well with our theoretical calculation on the frontier orbitals of free CoPc molecules in gas phase (Fig. 3(b)). This agreement means that the CoPc molecules on NaCl layers restore the intrinsic electronic properties of free CoPc molecules because NaCl decouples the CoPc molecules from Cu(100) and avoids the hybridization between them.

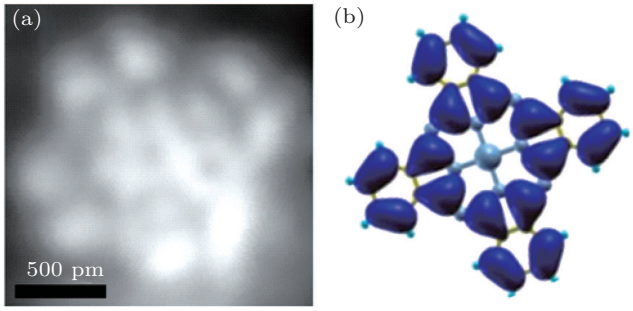


Fig. 3. (color online) (a) STM image of CoPc molecules on NaCl/Cu(100) in sub-molecular resolution (1.8 nm×1.8 nm, $V_b = 1.5$ V, $I_t = 74$ pA). (b) Calculated real-space distribution of LUMO of a free CoPc molecule.

If the tunneling bias exceeds a critical voltage (3.1 V), the tunneling current would suffer a remarkable increase as indicated by the z–V curve in our previous report.[17] We ascribe the increase of the tunneling current to image potential states (IPSs). Indeed, the IPSs originate from the substrate Cu(100), and could be largely blue-shifted by the ad-layer, for example, NaCl layers.[17] Due to the adsorption of the NaCl layers, the first order of IPSs of Cu(100), which is the closest one to the Fermi level (E_F), is shifted from ~ 4.5 eV to ~ 3.1 eV. In order to further investigate how the IPSs influence the adsorbed CoPc molecules, at least one of the IPSs has to be involved in the tunneling process. For simplicity, the first order

of IPSs located energetically at ∼ 3.1 V[17] is chosen here. Unfortunately, we have not acquired STS on CoPc molecules. However, we acquired a series of STM images with different voltages as shown in Figs. 4(a)–4(e).

As shown in Fig. 4(a), under 2.5 V bias voltage, two CoPc molecules exhibit the typical subquadrate feature. With stepwise increasing the sample bias, the appearance of the molecules gradually changes (Figs. 4(b)–4(e)), and finally turns into featureless dark holes under 3.5 V (Fig. 4(e)). It is clearly revealed that the lobes of the CoPc molecules become thinner and thinner (Fig. 4(c)), and then the CoPc molecules exhibit a very faint cross (Fig. 4(d)). The critical sample bias, at which the CoPc molecules become depressed, is ∼ 3.1 V, where the first order of IPSs is just energetically located. It looks like the molecules sink down into the NaCl layer. Actually, as reported previously, we found that the apparent height of the NaCl layer increases very quickly when the bias voltage increases across 3.1 V.[17] Therefore, the transition of the molecular features is predicted to be similar to another abnormal minus the apparent height of the 3rd layer NaCl on Cu(100) at ∼ 3.1 V. Based on the fact that the critical bias is consistent with the energetic positions of the image potential states of the substrate, we propose a model of the tunneling process via IPSs. We believe that the adsorbed molecules have just mediated the tunneling process of electrons between the tip and the substrate, and the proposed model is describing a possible modulating mechanism. As shown in Fig. 4(f), the electrons firstly occupy the molecular orbital and then transfer to the IPSs of the underlying NaCl layer as the STM tip is positioned above one CoPc molecule. The apparent height of the NaCl terraces increases with increasing bias voltage and reaches a very high value when the bias exceeds the first order of IPSs (∼ 3.1 V);[17] on the other hand, the weak coupling of molecules with NaCl layers reduces the tunneling possibility, which results in a relatively low apparent height of molecule (black holes) in comparison with the surrounding NaCl layer.

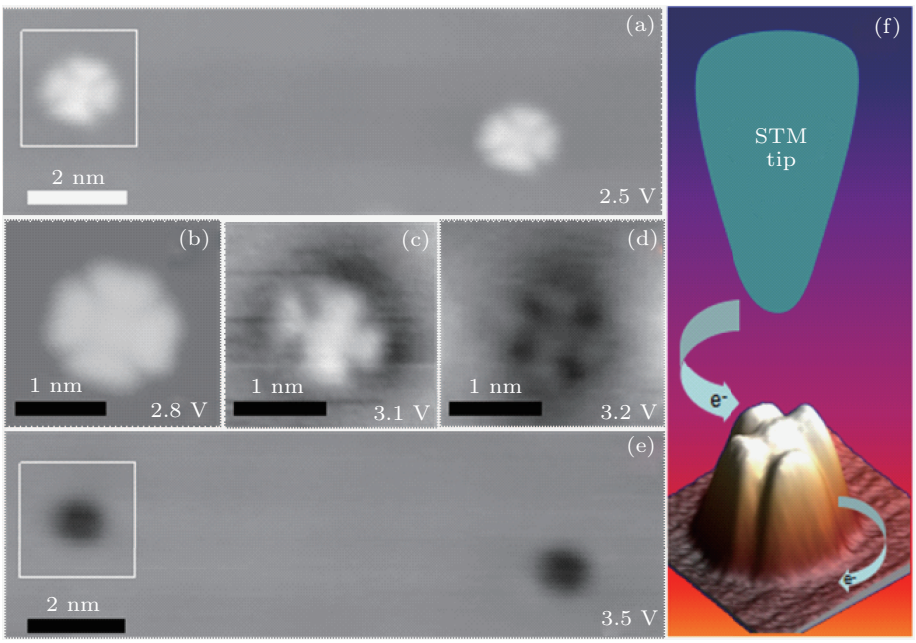


Fig. 4. (color online) A series of STM images obtained at various bias voltages: (a) 2.5 V, (b) 2.8 V, (c) 3.1 V, (d) 3.2 V, and (e) 3.5 V. The STM images in panels (b)–(d) show the CoPc molecule indicated by squares in panels (a) and (e). (f) Two steps of the electron tunneling process in the molecule-covering NaCl region at positive bias voltages. Electrons firstly tunnel from the tip to the empty molecular orbitals and then transfer to the IPSs of the underlying NaCl/Cu(100). The scan sizes of panels (a) and (e) are 4.2 nm×13.0 nm, and the sizes of panels (b)–(d) are 2.5 nm×2.5 nm. The tunneling currents are 16 pA in panels (a)–(e).

4. Conclusion

We have investigated the structural and intrinsic electronic properties of individual CoPc molecules adsorbed on the NaCl bilayer supported by Cu(100). Our high-resolution STM image demonstrates that the CoPc molecules adsorb on the NaCl bilayer with their lobes along the NaCl ⟨011⟩ direction. Due to the decoupling effect of the NaCl layers, the quasi-free CoPc molecular orbital information could be extracted and the best resolution of molecules is achieved using a single molecular tip. Moreover, at bias voltages higher than the first order IPSs of NaCl/Cu(100), the electron tunneling from CoPc into Cu(100) is dominated by the IPSs, resulting in the bias-dependent dimming process of the CoPc molecules. The adsorption of molecules drastically reduces the local density of states of IPSs, which is indicative of the feasibility of fabricating a quantum storage device based on tuning of IPSs by molecular adsorption.

References

[1] Tao N J 2006 *Nat. Nanotechnol.* **1** 173
[2] Tour J M, Wu R and Schumm J S 1991 *J. Am. Chem. Soc.* **113** 7064
[3] Fu X X, Zhang L X, Li Z L and Wang C K 2013 *Chin. Phys. B* **22** 028504
[4] Waldeck D H and Beratan D N 1993 *Science* **261** 576
[5] Plummer W 1997 *Science* **277** 1447
[6] Höfer U, Shumay I L, Reuß C, Thomann U, Wallauer W and Fauster T 1997 *Science* **277** 1480
[7] Shumay I L, Hofer U, Thomann U, Wallauer W and Fauster T 1998 *Phys. Rev. B* **58** 13974
[8] Schuppler S, Fischer N, Fauster T and Steinmann W 1992 *Phys. Rev. B* **46** 13539
[9] Yang Q, Muntwiler M and Zhu X Y 2009 *Phys. Rev. B* **80** 115214
[10] Sangita B, Vyacheslav M S, Robin O, Ivan B, Lucia V, Christian H M, Pierre M, Jean-Yves V, Schneider M A, Evgueni V C, Pedro M E and Klaus K 2010 *New J. Phys.* **12** 023028
[11] Takahashi K, Imamura M, Yamamoto I, Azuma J and Kamada M 2014 *Phys. Rev. B* **89** 155303
[12] Dougherty D, Maksymovych P, Lee J, Feng M, Petek H and Yates J 2007 *Phys. Rev. B* **76** 125428
[13] Dougherty D, Maksymovych P, Lee J and Yates J 2006 *Phys. Rev. Lett.* **97** 236806
[14] Ploigt H C, Brun C, Pivetta M, Patthey F and Schneider W D 2007 *Phys. Rev. B* **76** 195404
[15] Pivetta M, Patthey F, Stengel M, Baldereschi A and Schneider W D 2005 *Phys. Rev. B* **72** 115404
[16] Hanuschkin A, Wortmann D and Blügel S 2007 *Phys. Rev. B* **76** 165417
[17] Guo Q, Qin Z, Liu C, Zang K, Yu Y and Cao G 2010 *Surf. Sci.* **604** 1820
[18] Repp J, Meyer G, Stojković S, Gourdon A and Joachim C 2005 *Phys. Rev. Lett.* **94** 026803
[19] Villagomez C J, Zambelli T, Gauthier S, Gourdon A, Stojkovic S and Joachim C 2009 *Surf. Sci.* **603** 1526
[20] Perdew J, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[21] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
[22] Guo Q, Qin Z, Zang K, Liu C, Yu Y and Cao G 2010 *Langmuir* **26** 11804
[23] Qin Z 2013 *Chin. Phys. B* **22** 098108
[24] Tu X, Mikaelian G and Ho W 2008 *Phys. Rev. Lett.* **100** 126807
[25] Repp J, Meyer G, Paavilainen S, Olsson F E and Persson M 2006 *Science* **312** 1196
[26] Repp J, Meyer G, Olsson F E and Persson M 2004 *Science* **305** 493
[27] Müller M, Ikonomov J and Sokolowski M 2011 *Surf. Sci.* **605** 1090
[28] Sun X, Marcella P F, Petra R and Fabien S 2008 *Nanotechnology* **19** 495307
[29] Liljeroth P, Repp J and Meyer G 2007 *Science* **317** 1203
[30] Swart I, Sonnleitner T and Repp J 2011 *Nano Lett.* **11** 1580
[31] Díaz-Tendero S, Borisov A and Gauyacq J P 2011 *Phys. Rev. B* **83** 115453
[32] Scarfato A, Chang S H, Kuck S, Brede J, Hoffmann G and Wiesendanger R 2008 *Surf. Sci.* **602** 677