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PHYSICAL REVIEW B **73**, 115433 (2006)

Hindered rotation of a copper phthalocyanine molecule on C_{60}: Experiments and molecular mechanics calculations

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If copper phthalocyanine (CuPc) molecules are deposited on a Au(111) surface covered with a monolayer of C_{60}, the molecules are found to adsorb individually onto the close-packed layer of C_{60}. As the adsorption site of the CuPc is not symmetric with respect to the underlying C_{60} layer, the CuPc molecule has six equivalent orientations according to the hexagonal packing of the C_{60}. Scanning tunneling microscopy (STM) measurements reveal that at room temperature, the molecules may hop between these adsorption sites due to thermal activation and therefore appear as a ring with six maxima. This paper reviews the STM measurements carried out by Stöhr *et al.* in the light of molecular force field calculations. The potential energy for an individual CuPc molecule has been calculated as a function of the lateral position on the C_{60} layer based on the van der Waals interactions between molecules. For each position, the minimal energy has been evaluated, taking the vertical and the rotational degrees of freedom into account. A map of the potential energy not only reveals the preferred adsorption sites, it also indicates several favorable paths between these minima. The calculations consistently explain the experimental observations at low and ambient temperature.

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I. INTRODUCTION

During recent decades, nanotechnology has become one of the most important fields of research. For future electronics, not only does the size of an individual device have to be reduced enormously, but also the energy that is required to switch from one to the other state. Promising candidates in light of both aspects are individual organic molecules adsorbed at surfaces. To develop new concepts, it is necessary to understand in detail the interactions of a molecule with the surface as well as with neighboring molecules. The manipulation of individual atoms and molecules on a surface has been demonstrated, e.g., by Eigler *et al.*[1,2] Moresco *et al.*[3] have investigated the switching of the internal configuration of Cu-tetra-3,5 di-tert-butyl-phenyl porphyrin (Cu-TBPP) deposited on Cu(211) by low-temperature scanning tunneling microscopy (STM) manipulation. Using atomic force microscopy (AFM), Loppacher *et al.*[4] could even determine the energy required to switch one leg of this molecule between two well defined positions.

A different type of molecular switching was observed by Stöhr *et al.*:[5,6] If copper phthalocyanine (CuPc) molecules are deposited on a closed packed layer of C_{60} on a Au(111) surface, a hindered rotation of the CuPc around a central C_{60} is found at room temperature. At lower temperatures (50 K), this motion is frozen. Originally, we were interested in mixed layers of these molecules because of possible applications in organic electronics. But as presented in this paper, the system offers another very interesting perspective: If one could systematically manipulate the individual (or several) CuPc on C_{60}, this could be applied as a "bit" providing not only two but six states.

So far, different approaches have been introduced to predict the geometry for the adsorption of molecules on a surface and the involved interaction energies. *Ab initio* or density functional theory (DFT) calculations are well suited for this purpose. The latter have been used, e.g., to determine the adsorption for 3,4,9,10-perylenetetracarboxylic-dianhydride (PTCDA) on Ag(111) (Ref. 7) and for C_{60} on Ag(111) and Au(111) surfaces.[8] However, the computational effort of these techniques increases rapidly with the number of atoms that have to be included. The molecules of interest for organic electronics, e.g., dye molecules are relatively large (~30 atoms and more). Hence corresponding calculations are barely feasible, even for semiempirical quantum mechanical methods.

Full quantum mechanical calculations may be avoided using force field calculations if a loss of accuracy is accepted. This method yields a good approximation for weakly interacting systems, i.e., van der Waals (vdW) and electrostatic interactions in contrast to chemisorption. The applicability of force field calculations has been shown recently by Mannsfeld *et al.*,[9] who investigated the growth of PTCDA on highly oriented pyrolytic graphite (HOPG). The experimental results were confirmed by calculations considering only the vdW and electrostatic interactions. Yim and Jones[10] succeeded in confirming their experimental results for phthalocyanines on InAs and InSb surfaces by force field calculations. We have applied this technique to the heterogeneous system of copper phthalocyanine (CuPc) on C_{60} in order to validate experimental results that have been obtained by Stöhr *et al.* and to achieve a deeper understanding of these results. Assuming that chemisorption does not play an important role for the growth of CuPc on C_{60}, force field calculations only considering the vdW interactions between a layer of C_{60} molecules and one CuPc molecule have been performed.

II. EXPERIMENTAL RESULTS

The experiments have been carried out in an UHV system equipped with a variable temperature STM (Omicron). The

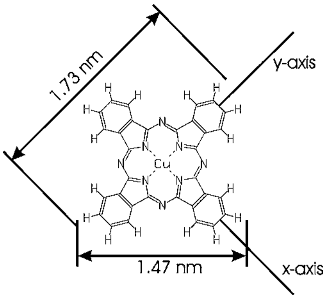

FIG. 1. A CuPc molecule. The sizes given here consider the vdW radii of the H atoms. The z axis of the molecule is perpendicular to the paper plane.

STM allows the cooling of the sample by a liquid helium flow cryostat. For the current measurements, we operated the microscope in the temperature range between 50 K and room temperature. The sample preparation was done in a seperate chamber connected by a transfer system to the STM. A (111) oriented gold film grown on mica was used as substrate. A submonolayer of C_{60} was deposited from a homebuilt crucible onto the gold film at room temperature. Before evaporating a fraction of a monolayer of CuPc, the C_{60} layer was annealed with a linear temperature ramp of 1K/s up to 600 K.

STM images of the heterogeneous system of CuPc on a submonolayer of C_{60} grown on Au(111) obtained at room temperature show sixfold symmetric rings [see Figs. 2 and 3(c) for more details]. The diameter of the ring structures is about 2.5 nm, which is too large to be a single CuPc molecule at rest. Taking van der Waals radii into account, the maximum extension of a single CuPc molecule is only 1.73 nm (see Fig. 1). Hence the size of the protrusion cannot be explained by a convolution of the STM tip with the molecule. On the other hand, the feature in the STM image is too small to include several molecules—neither CuPc nor C_{60}. Furthermore, the structures imaged by STM exhibit six minima along the ring in contrast to the fourfold symmetry of the CuPc molecule with its D_{4h} symmetry (see Ref. 11 and Fig. 1).

However, the observed sixfold symmetry may be explained by a superposition of six equivalent positions each corresponding to a minimum of the potential energy. Assuming a small energy barrier between this position, there should be a frequent and random switching between the adsorption sites. If the scanning frequency of the STM is much lower than the hopping rate of the molecule, this motion will not be resolved.

Figure 3 shows the same sample at different temperatures. The black circles within the images indicate the positions of the central C_{60}. The lines represent the directions of the unit cell vectors for the hexagonal C_{60} structure. For 300 and 100 K, the protrusion due to the coadsorbed CuPc is clearly centered on one C_{60} molecule. Furthermore, the apparent size is identical for both cases. However, the images observed at 300 and 100 K differ by their appearance. The one at lower temperature appears to be much noisier within the CuPc structure. This can be related to changes in the topography assuming that the dwell time of the tip over the feature is in the range of the inverse hopping rate of the adsorbate.

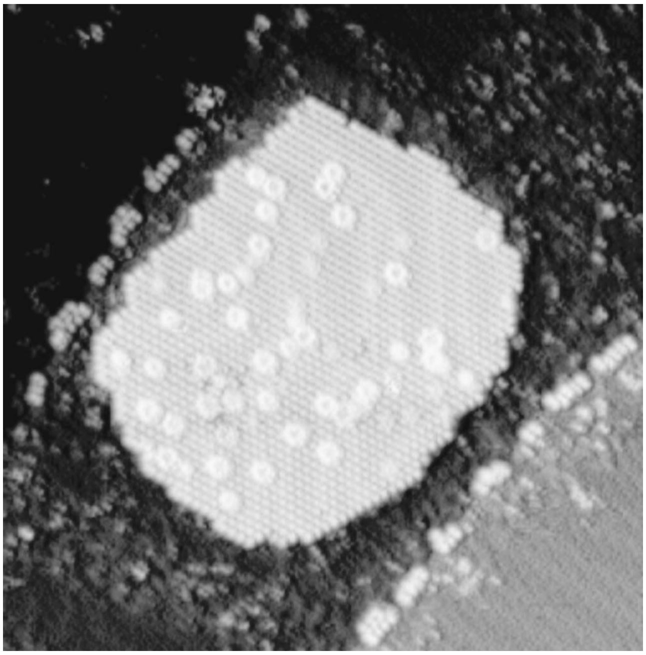

FIG. 2. STM image of C_{60} and CuPc on Au(111) taken at room temperature. In the middle, a close-packed island of C_{60} with several CuPc molecules on top can be seen; the ring structure of individual CuPc molecules is clearly visible. To the lower right, a gold terrace only covered by CuPc can be seen. The scanned area is 65×65 nm^2 (from Ref. 5).

If the sample was further cooled to a temperature of 50 K [see Fig. 3(a) for details], the rotational motion of the individual CuPc molecules was frozen. In particular, the individual CuPc molecule is no longer mobile on the C_{60} layer but seems to be "pinned." From Fig. 3(a) and the cross sections in Fig. 4, it can be deduced that the resting CuPc molecule is adsorbed in an asymmetric position according to the underlying C_{60} lattice. The maximum of the protrusion is shifted by 0.35 nm from the center of the anchoring C_{60} toward the hollow site. Assuming that the molecule is tilted relative to the plane of the C_{60} island, the shift should be smaller. By taking the mean value of the positions at half of the height of the molecule, an estimate of 0.14 nm is obtained.

The subject of the present paper is to understand these results based on a model calculation. Furthermore, we were interested in the trajectory of the molecule during its "rotation" and the energy barrier between two equivalent positions that had been (very roughly) estimated to be $E_B \approx 100$ meV.[5]

The value of E_B was obtained from an Arrhenius plot using the (assumed) hopping frequencies observed at different temperatures. Estimating that the hopping rate ν is determined by an Arrhenius law,

$$\nu(T) = \nu_0 e^{-E_B/k_B T}$$

(ν_0 is an initial rate), one obtains E_B from a semilogarithmic plot displaying the hopping rate versus the inverse thermal energy $1/k_B T$ (Fig. 5). For room temperature (300 K

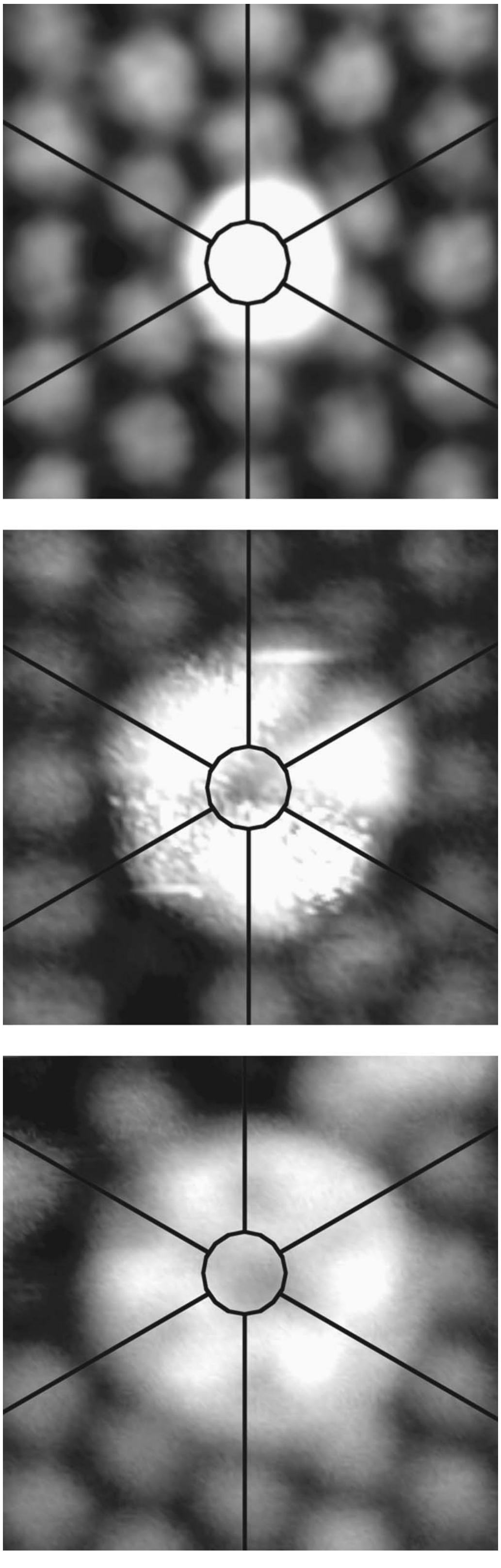

FIG. 3. STM images of a single CuPc molecule on top of a C_{60} layer at different temperatures. The displayed areas are 5×5 nm^2. All images were corrected for thermal drift. The black drawings within the images indicate the central C_{60} molecule and the directions of the unit cell vectors. For the image taken at 50 K, the CuPc is not adsorbed symmetrically on top of the underlying C_{60} molecule.

$\triangleq 37.6/\text{eV}$), we assume a hopping rate of $\nu(T=300\text{ K}) = 10^6$ Hz, which is significantly higher than the inverse of the interaction time (IIT) between tip and feature, i.e., the protrusion, within one scan line. The IIT was roughly estimated to be $\approx 25\text{ s}^{-1}$, due to the scan speed: Scanning 50 nm/s, the dwell time of the tip over the protrusion is approximately 40 ms. When the temperature was lowered to 100 K ($\triangleq 115.9/\text{eV}$), the image became fuzzy, so the IIT can be assumed to be only one or two orders of magnitude smaller than the hopping rate: $\nu(T=100\text{ K}) = 10^3$ Hz. For $T=50$ K ($\triangleq 231/\text{eV}$), no hopping was observed, hence the hopping frequency has to be much smaller than the IIT: $\nu(T=50\text{ K}) = 10^{-2}$ Hz. For all hopping frequencies, an error of 90% is assumed. The slope of the fitted line is $1/E_B = 10.5/\text{eV}$, so that we obtain an energy barrier of $E_B = 95 \pm 50$ meV. (Within the error bars, slopes between $1/E_{B,\max} = 7/\text{eV}$ and $1/E_{B,\min} = 20/\text{eV}$ are obtained, yielding $E_{B,\min} = 50$ meV and $E_{B,\max} = 142$ meV, respectively.)

III. CALCULATIONS

A. The mathematical tools

To perform the calculations, we used the computational chemistry software "HYPERCHEM" and the software "POWERGRID."[12] For some preliminary calculations, the semiempirical PM3 method[13] was used. To calculate the interaction energy between a single CuPc molecule and a C_{60} island, we used the set of vdW parameters from the AMBER molecular force field.[14–16] AMBER uses a 6-12 Lennard-Jones (LJ) potential. The energy is given by

$$E_{\text{vdW}} = \sum_{i,j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} \right],$$

i and j denoting all pairs of atoms with distance R_{ij} in the C_{60} layer (i) and the CuPc molecule (j). A_{ij} and B_{ij} are specified by the parameters r^* and ϵ, which are given for each atom type (see Table I). The combination rules are

$$A_{ij} = \left(\frac{r_i^*}{2} + \frac{r_j^*}{2} \right)^{12} \sqrt{\epsilon_i \epsilon_j},$$

$$B_{ij} = 2 \left(\frac{r_i^*}{2} + \frac{r_j^*}{2} \right)^{6} \sqrt{\epsilon_i \epsilon_j}.$$

To find the path between local minima, the so-called nudged elastic band (NEB) method described, e.g., by Henkelman and Jónsson[17] was applied. Four intermediate states between two minima were used. The path was then interpolated linearly.

B. The model

Altman and Colton[18] have reported two superstructures of close-packed layers of C_{60} on Au(111): A (38×38) and a $(2\sqrt{3} \times 2\sqrt{3})R30°$ reconstruction, both providing a spacing of 1.0 nm between the C_{60} molecules. DFT calculations for the $(2\sqrt{3} \times 2\sqrt{3})R30°$ superstructure by Wang *et al.*[8] indicate that the C_{60} molecule is adsorbed on the Au(111) substrate at a

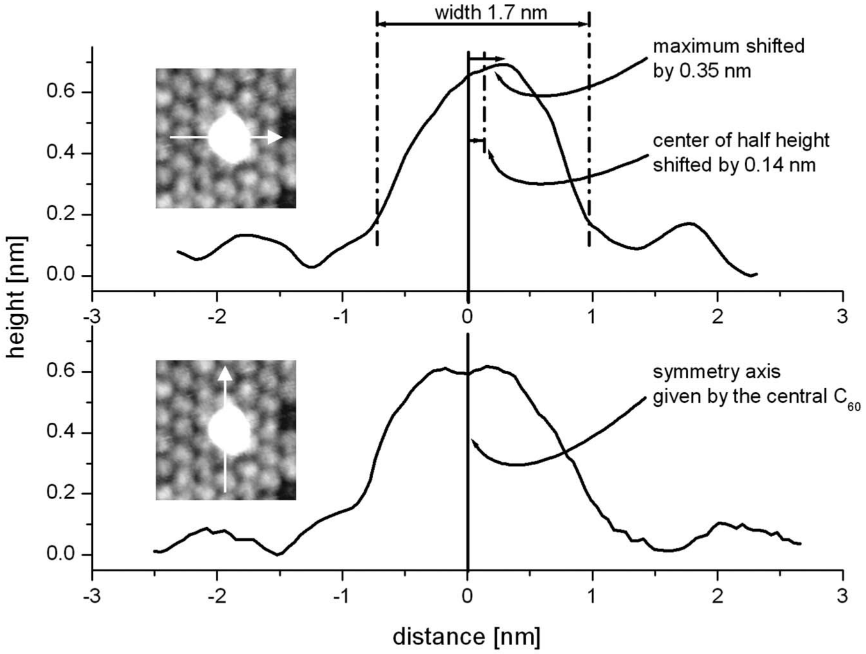

FIG. 4. Cross sections taken along the white arrow through the CuPc protrusion at 50 K. The maximum of the vertical profile (upper part of the image) is clearly shifted by 0.35 nm according to the position of the central C_{60} molecule. The shift of the center of the molecule taken at the half height of the protrusion is found to be 0.14 nm. The horizontal profile is symmetrical to the underlying C_{60}. The diameter of the protrusion is about 1.7 nm.

hcp site facing the Au substrate with a hexagon. They also calculated the energy barrier for a rotation of the C_{60} molecule with the axis of rotation perpendicular to the Au(111) plane and found an energetic barrier of $E_{\mathrm{rot}}=0.2$ eV. This value gives evidence that the rotation is essentially frozen at temperatures of 50 and 100 K. At room temperature, a rotation of the C_{60} molecules is nevertheless likely, as stated by Wang *et al.*[8] as well as by Altman *et al.*[18] However, we did not take the rotation into account for the calculation. Giving the C_{60} molecules rotational degrees of freedom would increase the computational effort by several orders of magnitude, so we made the assumption that the rotation would not have a major influence on our results.

For our calculations we assumed 37 C_{60} molecules in the x-y plane [parallel to the Au(111) plane]. The molecules were assembled in the $(2\sqrt{3}\times 2\sqrt{3})R30°$ phase. As the spacing between the C_{60} is the same for both phases and the Au substrate is neglected, the choice of the phase is of minor importance for our calculations. Neglecting the gold substrate is justified, since the adsorption geometry of C_{60} molecules on Au(111) was already achieved by the DFT calculations[8] and the vdW interactions between the CuPc and the substrate are negligible over a distance of >0.8 nm. To model the molecules, structure data from the HYPERCHEM package were taken for C_{60} and from x-ray diffraction (XRD) data by Brown[11] (see Fig. 1) for CuPc. Tests with more than 37 C_{60} molecules showed that this number is sufficient to exclude edge effects.

We assumed the CuPc and the C_{60} layer to be rigid because otherwise the calculations would not be feasible in a reasonable time. In order to find the trajectory of the CuPc molecule, we "scanned" an area of 1.0×0.5 nm^2 (using Car-

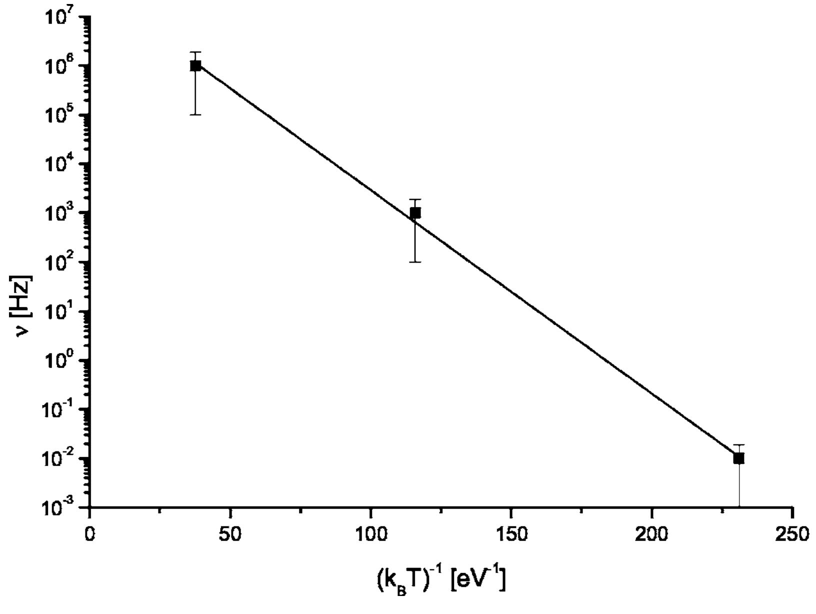

FIG. 5. Arrhenius plot of the assumed hopping rates for different temperatures ($T=300,100,50$ K). From the slope of the fitted line, we obtain an energy barrier of $E_B=95\pm 50$ meV.

TABLE I. Parameters for the atoms in the CuPc/C_{60} system.

Atom	AMBER atom type	r^* (nm)	ϵ (kcal/mol)
C	CA	0.185	0.12
N	NA/NP[a]	0.175	0.16
H	H	0.100	0.02
Cu	CU	0.120	0.05

[a] Both atom types have equivalent LJ parameters.

tesian coordinates instead of the hexagonal unit cell of the C_{60} superstructure, see Fig. 6). The origin of the scanned area (0,0,0) is in the center of a C_{60} molecule; the increment in the x and y directions was 0.001 nm. With this spatial resolution, we obtained a smooth energy hypersurface; tests with a resolution of 10^{-4} nm showed no increase in accuracy. In the following text, the angle ϕ_j denotes an active rotation of the CuPc molecule about its inertial j axis $(j=x,y,z)$. For $\phi_x=\phi_y=\phi_z=0$, those axes coincide with the Cartesian axes of the system.

Note that the C_{60} molecules are in fact no "balls" and only have a threefold rotational symmetry (if adsorbed with a hexagon facing the substrate). Thus we cannot expect a perfect sixfold symmetry of the potential map. In order to estimate the magnitude of the energetic differences arising from these small asymmetries, we have scanned a larger area than necessary for a perfectly sixfold symmetric substrate. For every (x,y) position of the center of the CuPc, we optimized the four other coordinates (z and three angles ϕ_x, ϕ_y, and ϕ_z) for CuPc. This was done by a direct search algorithm.

IV. RESULTS

From the calculations we obtain a map of the potential energy of the CuPc motion [see Fig. 7 (Ref. 19)]. One can see a smooth energy hypersurface.

Three energetically favorable positions are found within the scanned area (see Fig. 8), as listed in Table II. Some asymmetries can be seen by looking at the path and at the values of the potential energy. However, they can easily be understood by the symmetry of the C_{60} molecules. Next to

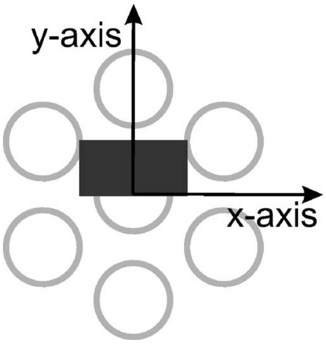

FIG. 6. Sketch of the scanned area: The circles mark the positions of the C_{60} molecules, the rectangle indicates the scanned area of 1.0×0.5 nm^2. For the calculations, Cartesian coordinates with the axes given in the sketch are used.

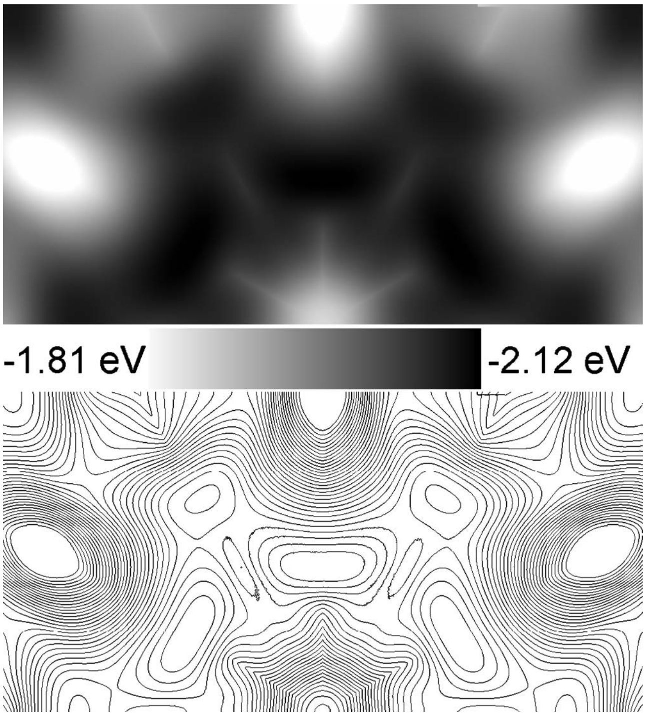

FIG. 7. Potential map of one CuPc on a C_{60} layer. The scanned area is 1.0×0.5 nm^2. As the contrast of the grayscale plot is not that good in the energetically favorable regions, a contour plot is given below.

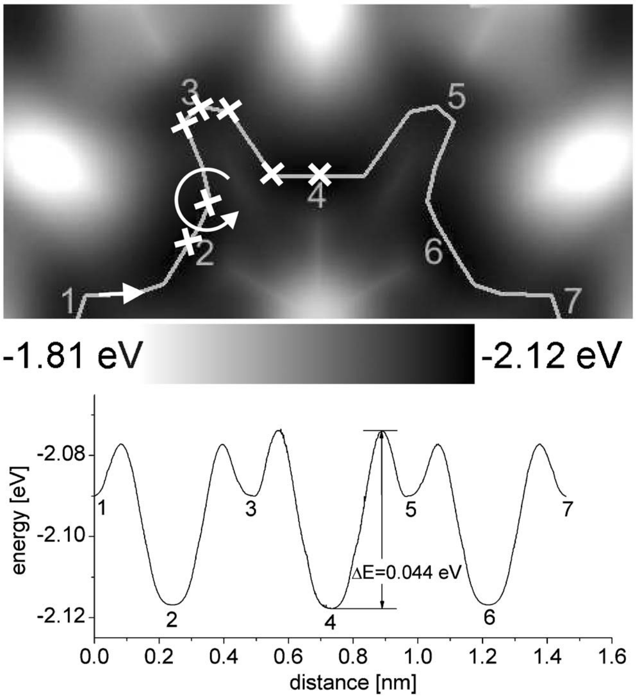

FIG. 8. Potential map of one CuPc on a C_{60} layer. A path leading over three energetically favorable positions is marked, the potential energy along this path is plotted below. When running the path in clockwise direction, the CuPc rotates around its inertial z-axis anti-clockwise, as indicated by the crosses along the path.

TABLE II. Values of the coordinates and angles at the energetically favorable positions (numbers: see Fig. 8). Estimating an error of $\Delta E_{\mathrm{pot}} = \pm 0.1$ meV for the energy, we obtain $\Delta z = \pm 0.5$ pm and $\Delta \phi_i = \pm 0.12°$.

pos.	x (nm)	y (nm)	z (nm)	ϕ_x (deg)	ϕ_y (deg)	ϕ_z (deg)	E_{pot} (eV)
2	−0.209	0.118	0.5875	−6.90	−6.91	15.18	−2.1316
4	0.00	0.224	0.5877	−7.16	7.10	44.57	−2.1323
6	0.209	0.118	0.5875	−6.89	6.89	−15.29	−2.1316

the hexagon carbon ring on top, pentagon and hexagon rings are alternating, causing small differences in the potential energy landscape. At positions 2 and 6, the CuPc is "facing" a hexagon, at position 4 a pentagon ring. The energy barrier between two minima we obtain from the calculations is $E_{B,\mathrm{rot}} = 44$ meV, which is in good agreement with the value we estimated very roughly from the experimental data.

The given path is the energetically favorable one and was found by the NEB algorithm. However, one may think of other paths that are less "complicated" and only cost slightly more energy. We have marked three different paths between the minima positions 2 and 4 in Fig. 9. Path (a) requires the lowest energy, however (c) exceeds the potential energy only by 3.3 meV or 8%. Therefore, this path also seems possible for the motion of the CuPc molecule.

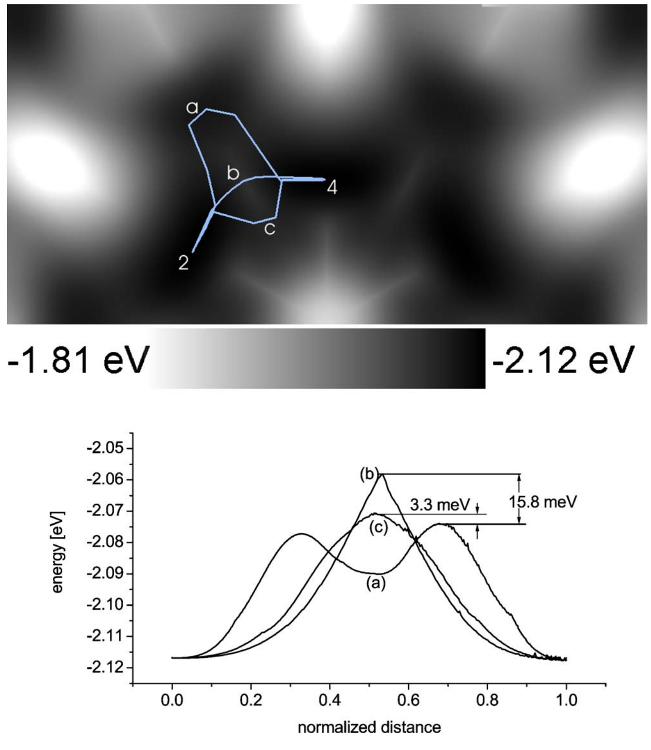

FIG. 9. In addition to the favorable path (a) (see Fig. 8), two other reasonable paths are marked, a circle line (b) and a path that is obtained when we start the NEB algorithm with different initial intermediate points (c). The potential energy along the three paths is plotted below, the path length has been normalized. One can see that path (c) has a slightly higher potential energy than path (a). The increase is less than 8%.

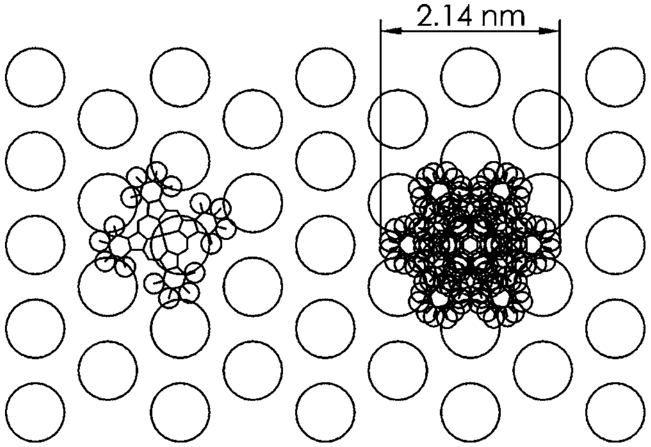

FIG. 10. New model of the adsorption of CuPc on a C_{60} layer: On the left side, a single CuPc molecule at position 2 is shown, on the right side one can see the superposition of the six energetically favorable positions around one central C_{60}. Comparing the superposition image with the STM data (Figs. 2 and 3), the similarity can be clearly seen.

Comparing the adsorption site derived from the STM data taken at 50 K with the calculations, a good agreement between measurement and calculations is obtained. We can deduce that the CuPc is indeed not lying in the x-y plane but is tilted by a small angle. Now, we can draw a schematic picture (see Fig. 10, left). The superposition of the six equivalent positions is also given and reflects the STM images at room temperature very well (Fig. 10, right). The starlike

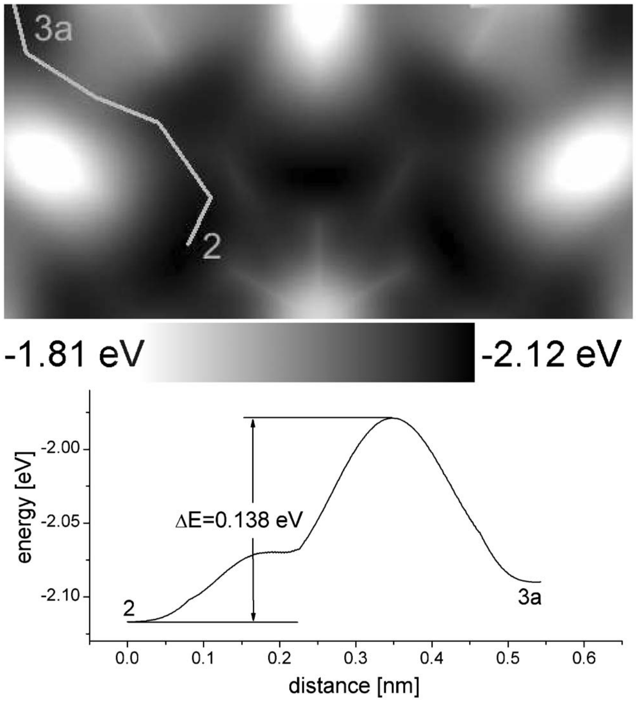

FIG. 11. Potential map of one CuPc on a C_{60} layer. A path leading from an energetically favorable position to a local minimum belonging to the neighboring C_{60} molecule is marked; the potential energy along this path is plotted below.

structure and the ring size are explained by this model. A feature that cannot be explained by this model calculation is the hole in the middle of the protrusions. However, STM images relate to the electronic structure of a sample, which cannot be simulated by our calculations based on Lennard-Jones potentials.

On the upper edges of the map (Fig. 8), one can see two local minima of potential energy "belonging" to the next C_{60} molecule at ($x = \pm 0.485$ nm, $y = 0.5$ nm). They are equivalent to those at (±0.382 nm, 0 nm). Again, we used the NEB algorithm to find the path from this local minimum to position 2 (see Fig. 11). The energy barrier between two neighboring C_{60} molecules is $E_{B,\mathrm{jump}} = 138$ meV, i.e., 3.5 times as high as the barrier for the "rotation." This is also in agreement with the experiment: In most cases the CuPc molecules seemed to be "pinned" to one C_{60}. A diffusion over the C_{60} layer was observed very rarely.

V. CONCLUSION

In summary, the results obtained from the force field calculations reproduce the experimental STM data quite well, even though we have made a simplified model of the CuPc-C_{60} system in which the molecules are assumed to be rigid and the C_{60} molecules do not rotate. Although this might not be correct at room temperature, we are able to give a convincing explanation of the experimental results within this simplified model. The hindered rotational motion of the CuPc molecule described here is energetically favorable compared to the diffusion across the C_{60} layer. The simple model obtained by Stöhr *et al.* from the STM data was refined. The new refined model gives a value of $E_B = 44$ meV that is much better than the 100 meV roughly estimated from the experimental data.

The molecular force field approach leads to good results, without high computational effort: All calculations were performed on a Pentium 4 2.6 GHz machine; the scanning of the 1.0×0.5 nm^2 sized area took <10 days of computation.

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