Orientationally Ordered (7 × 7) Superstructure of C_{60} on Au(111)

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Long range orientational order within C_{60} monolayers on Au(111) is observed with low-temperature scanning tunneling microscopy. A unit cell comprised of 49 molecules which adopt 11 different orientations is found. It can be divided in a faulted and an unfaulted half similar to the (7 × 7) reconstruction of Si(111). A model is proposed which shows how, through a Moiré-like effect, the substrate induces minute changes in the orientation of the C_{60} molecules. Intermolecular interactions are shown to play a major role in stabilizing the superlattice.

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Ordering of atoms and molecules in both three- and two-dimensional (3D, 2D) crystals has been studied for decades. Contrary to atoms, most molecules exhibit angular anisotropy and, therefore, often arrange themselves in complex structures which exhibit unique properties not found in atomic crystals such as second harmonic generation, liquid crystal properties, or rotational melting as observed for C_{60} [1].

In the case of 2D assemblies, the influence of the in-plane anisotropy of molecules has been extensively studied. Out-of-plane orientational ordering has less often been discussed, presumably because many of the studied molecules are 2D themselves and adsorb flat on surfaces. Therefore, 3D molecules add an additional rotational degree of freedom and, hence, a new level of complexity. Fullerene molecules, C_{60} in particular, are perfect candidates in this context and are at the focus of numerous studies [2–6]. Although C_{60} is almost spherical, its orientation can be detected with the scanning tunneling microscope (STM) [7,8]. Most studies which reached the required resolution reported random [9] or poorly ordered orientation [10] of C_{60} inside self assembled clusters or monolayers. In some rare cases, strong interaction between C_{60} and substrate impose simple orientational order, such as uniform orientation of all molecules on the surface [11] or ordered alternation of two orientations [12].

Here, we report the first observation of a complex orientational order within C_{60} monolayers organized in a supramolecular $(\sqrt{589} \times \sqrt{589})R14.5°$ lattice on Au(111). The unit cell is comprised of 49 molecules which adopt 11 different orientations. Strikingly similar to the (7 × 7) reconstruction of Si(111), the unit cell can be divided in a faulted and an unfaulted half. A model is proposed, which shows how through a Moiré-like effect, the substrate induces minute changes in the orientation of the C_{60} molecules. Intermolecular interactions are shown to play a major role in stabilizing the superlattice.

The experiments were performed with a low-temperature STM operated at 5.7 K in ultrahigh vacuum (below 10^{-10} mbar). The Au(111) sample as well as etched *W* tips were prepared by argon-ion bombardment and annealing. C_{60} was deposited from a tantalum crucible at a rate of ≈1 ML/ min as monitored by a quartz microbalance. During deposition, a residual gas pressure in the 10^{-8} mbar range was maintained, and the sample was kept at room temperature. The data shown correspond to a coverage of approximately 0.2 C_{60} monolayers. All images were recorded in a constant-current mode.

The quasispherical shape of C_{60} naturally leads to hexagonal compact 2D self assembly on metal surfaces. Nevertheless, different superstructures have been observed depending on the chemistry and crystallography of the underlying surface. In few cases [6], these superstructures correspond to different positions of C_{60} on the underlying atoms, but more frequently [4,5,13–15] they result from reconstructions of the substrate. Grobis *et al.* [5] showed that Ag(110) reconstructs upon C_{60} adsorption to form alternating lines of differently oriented molecules. A simple case of orientational order—all molecules adopting the same orientation—has been observed on Cu(111) and interpreted in terms of small lattices mismatch and high reactivity of Cu [11]. C_{60} monolayers on Au(111) exhibit a commensurate $(2\sqrt{3} \times 2\sqrt{3})R30°$ layer, but no orientational order was reported [9]. Another observed structure was first denoted as (38 × 38) [16], but subsequent measurements revealed more simple unit cell [6,17]. For simplicity of notation, we denote these two structures *A*1 and *A*2.

Figure 1 displays a STM image of the new C_{60} superstructure we found on Au(111). It is hexagonally close-packed and rotated by ≈ 14° with respect to the underlying Au(111) lattice. For used deposition parameters, 20% to 40% of the islands exhibit this misorientation. A phase at this unusual angle has previously been reported from x-ray [18] and electron [19] diffraction data, but, surprisingly, no STM study on this system mentioned it. In addition to islands as shown in Fig. 1, we also observed *A*1 and *A*2 islands at angles of 30° and 0° as reported from earlier STM investigations.

Detailed submolecular resolution [Fig. 1(b)], which was scarcely available in previous STM studies of C_{60} clusters on Au(111), enables a direct determination of the orienta-

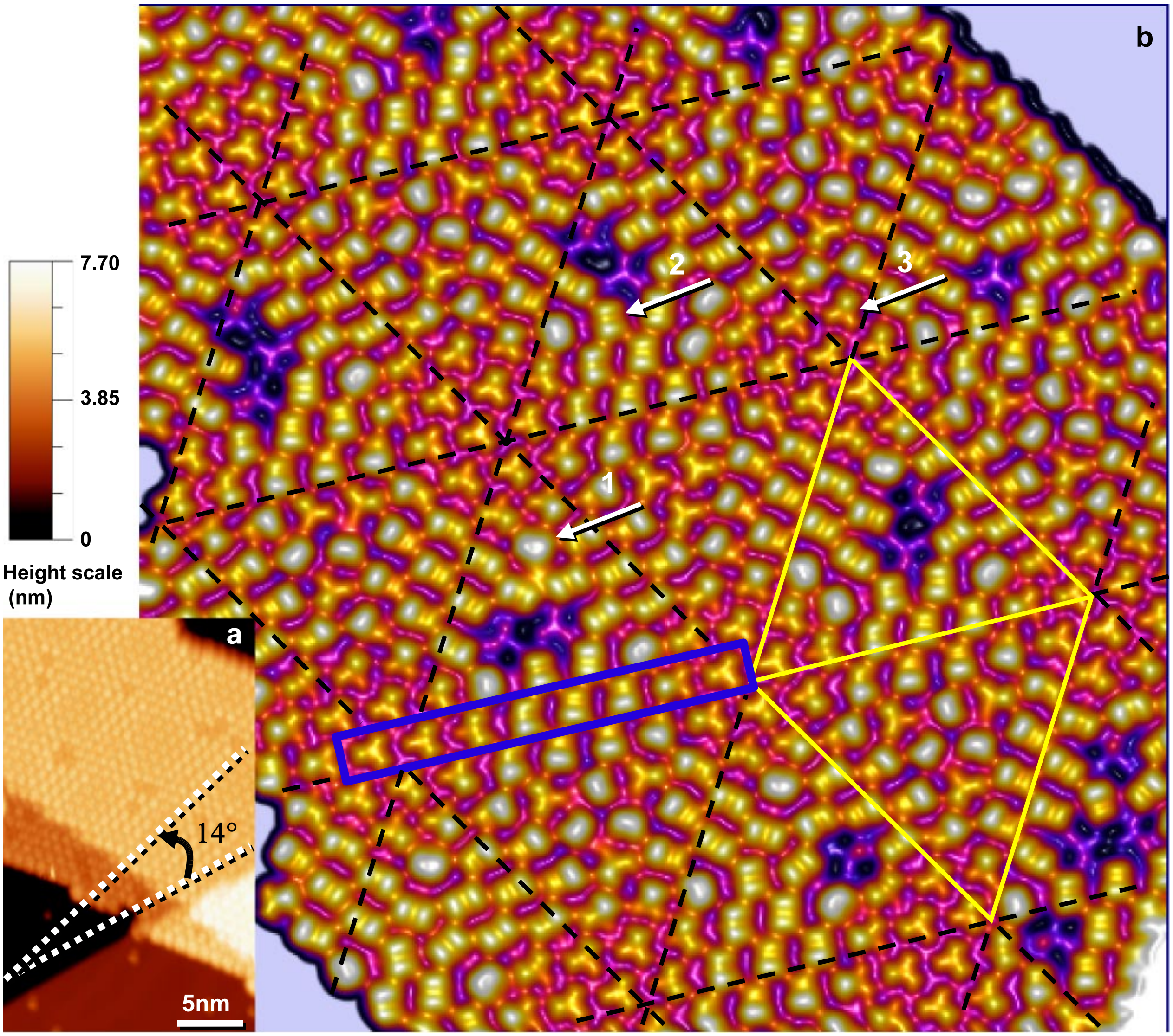

FIG. 1 (color online). (a) $32 \times 20\ \mathrm{nm}^2$ and (b) pseudo-3D $20 \times 20\ \mathrm{nm}^2$ STM images ($I = 0.1$ nA, $V = 1.5$ V) of C_{60} islands deposited at room temperature on Au(111). The height scale correspond to (a). The highlighted rhombus in (b) defines a unit cell. Added dashed lines indicate equivalent cells. Images have been processed with the Nanotec Electronica WSXM software [23].

tion of the molecules in a 14° island. At first glance, three different patterns can be distinguished, which are three or twofold symmetric or rather uniformly bright (indicated by arrows 3, 2, 1 and enlarged in Fig. 2(a)]. As demonstrated by Wang *et al.* [7], at positive sample bias, bright lobes correspond to pentagons of the C_{60} cage. Consequently, the patterns can be assigned to C_{60} adsorbed on a hexagon, a double bond in between hexagons (6:6 bond), and a pentagon (see models in Fig. 2).

Once the out-of-plane orientation of the molecule is determined, different in-plane (azimuthal) orientations can be envisaged. In the case of an epitaxial relation, a limited number of azimuthal orientations should be observed. Given the sixfold symmetry of the (111) surface and the threefold (twofold) symmetry of the molecule around a hexagon (a 6:6 bond), 2 (3) different in-plane orientations are expected. Indeed, we find two different orientations for C_{60} adsorbed on a hexagon and three for the 6:6-bond geometry. Three orientations do also occur for the pentagon adsorption (almost uniformly bright spots) suggesting a slight tilt of the molecular axis. These observations confirm an epitaxial relation between C_{60} and Au(111). Last, few darker molecules, which all exhibit threefold symmetry, are imaged ≈ 0.6 nm lower than the surrounding molecules. This value significantly exceeds the height difference measured between so-called bright and dim molecules ($\lesssim 0.3$ nm) [9,10], suggesting that some Au atoms are missing underneath the darker C_{60}. From a hard sphere model, we estimate that at least 6 atoms have to be removed so that the C_{60} appears 0.6 nm lower on STM pictures. Extraction of atoms was previously observed with more reactive surfaces [4,13,20], but, to our

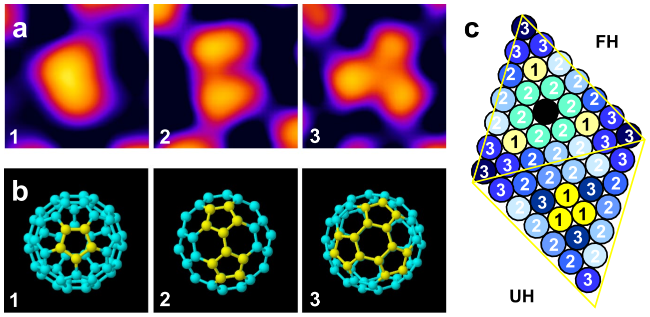

FIG. 2 (color online). (a) STM images of adsorbed C_{60} with one, two, or threefold symmetry axis (1 nm^2). (b) Corresponding top view models. Pentagonal rings are highlighted in yellow in the models because they appear high in STM images at positive bias. (c) Model arrangement of C_{60} in the superlattice. Molecules are labeled by their approximate symmetry in the STM image. Circle background gradation represents the orientation of the molecules according to Fig. 3.

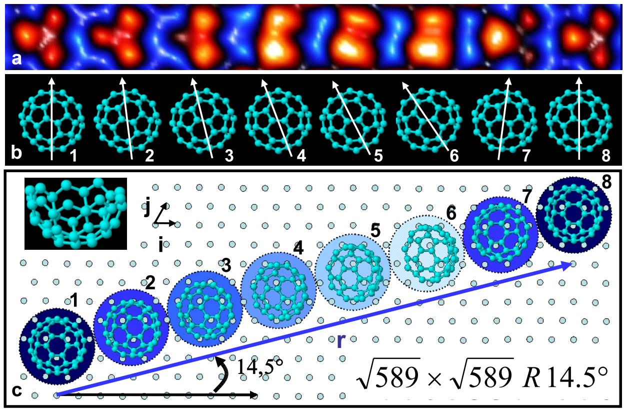

FIG. 3 (color online). (a) Pseudo-3D STM image (0.8 × 8 nm^2) of the C_{60} line marked by a blue rectangle in Fig. 1(b). (b) Side view model of molecular orientation. (c) Top view model of the lateral arrangement of these molecules. Au: small gray circles, C_{60}: large colored circles. Only bottom halves of C_{60} are represented (like in the inset) in order to focus on relative positions of C_{60} lowest atoms to the underlying surface atoms. The circle background gradation corresponds to the orientation indicated by arrows in (b) and is used in Fig. 2(b), too.

knowledge, never on Au(111). To a first approximation, these molecules will be considered as defects.

Having addressed the orientation of individual molecules, we now focus on the most striking observation of the present study. The C_{60} layer displays an orientational superstructure on a large scale. Its unit cell [rhombus in Fig. 1(b)] is composed of 49 molecules in (7 × 7) array. This cell is separated in two halves with distinct arrangements of the molecular axes. Dark molecules (“defects”) are observed in one half only. By analogy with the Si(111) surface, we denote them unfaulted and faulted halves. Probably due to the large scale of the reconstruction, some organizational imperfections are observed; nevertheless, a preliminary model of the lattice can be proposed [Fig. 2(c)]. Each of the molecules is labeled by its approximate symmetry in the STM image. Below, we will see that this model is too simplistic and that the molecules finally adopt 11 different orientations on the surface which are represented, in the model, by the circle background gradation.

The observation of a huge adsorbate unit cell is generally due to long range commensurability with the underlying lattice. The present STM images resemble Moiré patterns, but instead of the height of molecules, it is their orientation which periodically varies. This is analyzed further for the unit cell edge (rectangle in Fig. 1), which comprises 7 C_{60} molecules. A watchful observation of a detailed image of these molecules [Fig. 3(a)] reveals a gradual transition from a threefold to a twofold symmetry. This corresponds to a step-by-step change from adsorption on a hexagon to a 6:6 bond and even further [see model Fig. 3(b)]. Using the position on the hexagon as a reference, we estimate a rotation of 7 ± 1° from molecule to molecule.

A model of the layer has to account for the specific rotation of the superlattice with respect to the Au by 14° and should involve epitaxial positions for each C_{60} molecule which enable a progressive tilt as observed. Such a model is proposed in Fig. 3(c). It relies on the Au(111) reconstruction being lifted by the chemisorption of the C_{60} as commonly reported [6,16]. An intermolecular distance of $d = 1.002$ nm and a Au-Au distance of 0.288 nm—both corresponding to bulk values—along with hexagonal compact structures are used. In terms of the unit vectors **i** and **j** of the hexagonal Au(111) lattice, the superlattice vectors **r** can be described as $\mathbf{r} = m\mathbf{i} + n\mathbf{j}$ with $(m; n) = (20; 7)$. The superlattice is rotated by 14.5° compared to the substrate, in good agreement with the experimental data. It may also be denoted $(\sqrt{589} \times \sqrt{589})R14.5°$. We next consider the molecular positions only and find that a surprisingly good commensurability is achieved with a periodicity of 7 molecules: the mismatch is $\approx 0.35\%$. For comparison, the mismatch values for the previously observed $A1$ and $A2$ structures on Au(111) are 0.43% and 0.60%, respectively. Superlattices with similar size or rotation $(20 \pm 1;\ 7 \pm 1)$ would lead to significantly larger mismatch [$\approx 0.83\%$ in the best case, (21;6)].

We now attempt to place C_{60} in such a way as to reproduce the observed molecular tilt [Fig. 3(a)]. From the threefold symmetry of the leftmost molecule in the STM data, we infer that it adsorbs with a hexagon to a hcp site of the gold [21]. Recent calculations suggest this position to be particularly stable [7]. This hcp site corresponds to C_{60} centered between three Au atoms as shown for molecule 1 in Fig. 3(c). Note that only lower C_{60} halves are shown in this figure. If we now successively rotate the next 5 molecules by angles of 7°, 14°,. . ., we find that the bottom hexagon of C_{60} is still centered at hcp positions. Molecule 7, rather than being tilted further, is rotated about

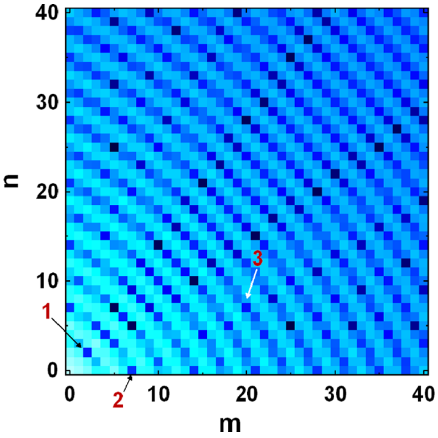

FIG. 4 (color online). Commensurability map of C_{60} superlattices on Au(111). The color code displays the quantity $K = |1 - |m\mathbf{i} + n\mathbf{j}|/(ld)|$ where d is the intermolecular distance and l is an integer chosen as to minimize K. Dark spots correspond to small lattice mismatch.

the same axis but in the opposite direction. In this way, a hexagon remains centered at the adjacent hcp site. Molecule 8 continues this rotation and is identical to molecule 1. The model of Fig. 3(c) accurately reproduces the observed results and suggests that the unusually large reconstruction is induced by the substrate through a long range commensurability or Moiré effect. We will now see that this explanation is not yet complete.

Figure 4 is simple way of representing the degree of commensurability for a range of superlattices indexed (m; n). Better commensurability corresponds to darker squares. The $A1$ (2; 2) and $A2$ (7; 0) structures clearly emerge as dark spots on this map (arrows 1 and 2). The important influence of the size of the unit cell on the stability of a superlattice is not taken into account, and it is obvious that smaller lattices are more likely to be observed. In particular, the $A1$ and $A2$ structures are less commensurable that the $(\sqrt{589} \times \sqrt{589})R14.5°$, but they are frequently observed as they comprise one or two molecules per unit cell only. The map reveals that the $(\sqrt{589} \times \sqrt{589})R14.5°$ superlattice [(20;7), white arrow] provides less mismatch than neighboring lattices. Nevertheless, superlattices with better commensurability and smaller lattice parameters exist, e.g., (15;4) and (18;5), composed of 5 and 6 molecules, respectively. None of these other structures was observed. This is direct indication that considering the interaction between C_{60} molecules and the Au surface alone is insufficient. We conclude that the orientational order is stabilized through intermolecular interactions. This is also consistent with earlier reports on orientational order in C_{60} crystals at low temperature [22] which highlighted the importance of intermolecular interactions. The $(\sqrt{589} \times \sqrt{589})R14.5°$ superlattice provides epitaxial positions for each of the molecules which are suitable to optimize the interaction between neighboring molecules. One of the remarkable properties of the 7 × 7 superstructure is to provide molecules with minute change in orientation which leads to a unique opportunity to address the influence of such small orientational modifications on the conduction properties at the single molecule level.

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