Anti-phase Boundaries Accumulation Forming a New C₆₀ Decoupled Crystallographic Phase on the Rutile TiO₂(110)- (1×1) Surface

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ABSTRACT. C₆₀ on the rutile TiO₂(110)-(1×1) surface is known to present a well-ordered p(5×2) surface phase. We have identified another crystallographic phase on this surface characterized by a large unit cell containing four C₆₀ molecules. This phase, which exhibits four inequivalent C₆₀ adsorption sites with just two different molecular orientations, is herein explained in terms of an accumulation of the so-called anti-phase boundaries. Among the *a priori* ten possible anti-phase boundary domains, only three of them can result in possible long-range structures attending to geometrical and energetic considerations. In order to fully characterize the structure and energetics of this new C₆₀ / TiO₂(110)-(1×1) phase, an adequate combination of STM and accurate Density Functional Theory-based calculations, including an efficient self-consistent implementation of the vdW interaction, has been used. Results suggest that this new phase is the most stable among all the possible anti-phase boundary domains. On

the other hand, this work rationalizes and enforces the idea of the prevalence of the intermolecular vdW over the molecule-substrate interactions in this particular organic-inorganic interface, which sets TiO₂ as an ideal substrate for decoupled systems.

Keywords: *STM, DFT, fullerenes, organic molecules, 2D-systems, organic-inorganic interfaces*

1. INTRODUCTION

Since C_{60} fullerene was discovered in 1985 by Smalley and coworkers,¹ followed by its synthesis at market-scale, this molecule has attracted an increasing attention. C_{60} has been widely studied – both from experimental and theoretical points of view – given the large variety of novel and interesting properties it shows in many different scientific and technological fields.²⁻⁴ One of the most promising applications of C_{60} Bucky fullerene is molecular electronics, where it has been successfully tested in the fabrication of field effect transistors⁵ or solar cells,⁶ whether by themselves or in combination with other organic molecules. Other industrial applications of C_{60} comprise lubricants, thanks to their spherical shape and hardness,⁷ or medicinal applications as antioxidants, as they present a very high reaction rate with free radicals.⁸ Additionally, they are currently being tested in many other application fields as catalysis, superconductivity, water purification and biohazard protection, non-linear optics, among many others.⁹ Recently, the growing of C_{60} as thin films, together with the most advanced supramolecular chemistry techniques for the modification *a-la-carte* of these molecules to add new functional molecular groups,¹⁰ has permitted the technological development of new organic nanoelectronic devices, as well as more efficient photovoltaic solar cells, among other technological targets.¹¹

Last decade, as a direct consequence of the huge number of possible applications, C_{60} organic layers have been extensively studied by surface science methods using model single-crystal surfaces under ultra-high vacuum (UHV) environments. With this aim, C_{60} has been deposited on metals, semiconductors and insulating materials.^{12,13} When deposited on metals, C_{60} molecules form well-ordered close-packed commensurate superstructures, where molecules are usually fixed on the surface spaced by distances in between 9.8 and 11 Å (close to their van der Waals diameter).¹⁴⁻¹⁷ This implies a weak interaction with the substrate, which, however, is able

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3 to stabilize a specific adsorption geometry for the molecules. In the cases where this interaction
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5 is strong, a modification of the molecular orbitals takes place, together with an alteration of the
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7 intrinsic C_{60} properties.
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10 Nevertheless, previously mentioned model systems, in spite of being adequate for the
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12 understanding the fundamental mechanisms and properties underlying chemistry of interfaces
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14 involving C_{60} molecules, are far from real application fields. In this sense, oxide surfaces, which
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16 exhibit a much wider spectrum of real applications than metal surfaces, represent a step forward
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18 towards the description of more practical interfaces. Following this line, our group has shown
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20 that C_{60} forms a decoupled well-ordered layer when deposited at room temperature on the rutile
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22 $TiO_2(110)-(1\times1)$ surface.¹⁸ Prevalence of intermolecular van der Waals (vdW) over molecule-
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24 substrate interactions yields an electronic and topographical decoupling of the adlayer, resulting
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26 in a net interfacial interaction that preserves the electronic structure of C_{60} monolayers with
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28 spinning molecules.¹⁸ This superstructure was characterized by a $p(5\times2)$ phase, with two C_{60}
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30 molecules per unit cell.^{18,19} Interestingly, in previous literature devoted to the $C_{60} / TiO_2(110)-$
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32 (1×1) system by non-contact atomic force microscopy (NC-AFM), the presence of anti-phase
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34 boundaries (APBs) originated by stacking faults was reported.^{20,21}
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40 In the present work, a novel C_{60} phase on the rutile $TiO_2(110)-(1\times1)$ surface is described. This
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42 $C_{60} / TiO_2(110)$ phase is characterized, at the monolayer limit, by a larger unit cell in comparison
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44 to the $p(5\times2)$ phase, with different C_{60} on-surface adsorption sites. An adequate combination of
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46 STM and accurate Density Functional Theory (DFT)-based calculations – including an efficient
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48 self-consistent implementation of the vdW interaction – shows that the observed new phase
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50 arises as one of the translational domains of the $p(5\times2)$ one based on the accumulation of APBs.
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53 It corresponds to the most energetically and geometrically favorable among all possible APB
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domains. Theory predicts for this new phase a similar adsorption energy per C_{60} molecule as for the $p(5\times 2)$ phase, which enforces the idea of the prevalence of the intermolecular vdW over the molecule-substrate interactions in this particular interface, whatever the considered phase is.

2. METHODS

2.1 Experimental section

Experiments have been carried out in an UHV chamber with a base pressure of 1.5×10^{-10} mbar. A rutile $TiO_2(110)$ single crystal has been prepared by consecutive sputtering and annealing (1000 K-1100 K) cycles under UHV conditions until a sharp LEED pattern has been obtained. The cleanliness of the sample has been checked by Auger electron spectroscopy (AES) and STM. Evaporation of C_{60} molecules has been done from a homemade Ta crucible with a K-thermocouple spot-welded to the Ta envelope. The evaporation temperature has been 700 K and the rate around 0.1 ML / 3 min. For the STM images, a commercial RT-STM (OMICRON) in the constant current mode (CCT mode) has been used. Images have been processed with the WSxM software from NANOTEC.²²

2.2 Theoretical section

As a first consideration, it is worth to remark that there is strong evidence that vdW – or dispersion forces – play a crucial role in the adsorption mechanism of aromatic molecules on oxide surfaces.²³ On this basis, the important role of dispersion forces in the C_{60} / $TiO_2(110)$ interface leads, in comparison with non-vdW DFT-based calculations, to a significant increase of the adsorption energies and distances, and to an improved description of the intermolecular interaction at the high coverage regime.¹¹ For that purpose, and in order to make a direct

comparison between experiments and theory on the C₆₀ / TiO₂(110) phase analyzed in this study, the inclusion of an adequate theoretical vdW implementation to the conventional theory is of paramount importance to obtain realistic structural configurations, as well as adsorption energies.

On the other hand, it is mandatory to investigate in a comparative way the structural properties and energies of both C₆₀ / TiO₂(110) phases experimentally detected so far. For these reasons, we have used for the theoretical analysis of both phases the accurate and efficient plane-wave code PWSCF²⁴ for the characterization and optimization of the atomic configurations, by self-consistently accounting for the van der Waals energy and forces. Therefore, as starting point, the two different C₆₀ / TiO₂(110) phase models have been fully relaxed by means of DFT calculations by including dispersion forces within the DFT+D approach²⁵ as implemented in the PWSCF.²⁴ For this purpose, we have used the revised version of the generalized gradient corrected approximation of Perdew, Burke, and Ernzerhof (rPBE),²⁶ and an empirical efficient vdW R⁻⁶ correction to add dispersive forces to conventional density functionals. Within this approach, the vdW correction is added to the DFT total energy by the expression:

$$E_{vdW} = \sum_{i,j} \frac{C_{ij}}{R_{ij}^6} f(R_{ij}), \quad (1)$$

where C_{ij} and R_{ij} are the vdW coefficients and the distance between atom i and j , respectively. The vdW coefficients can be calculated as described by Elstner *et al.*²⁷ In eq. (1), $f(R_{ij})$ is a damping function that prevents a divergence in the energy as R_{ij} tends to zero as:

$$f(R_{ij}) = \left(1 - \exp \left[-3.0 \left(\frac{R_{ij}}{R_{0ij}} \right)^7 \right] \right)^4, \quad (2)$$

where R_{0ij} is the sum of atomic van der Waals radii. They can be calculated from the vdW radii

provided by Gavezzotti and co-workers^{28–30} – see further details on this approach in Refs. [25] and [31] (and references therein) –.

The ion–electron interaction is modeled by ultrasoft pseudopotentials,³² and the one-electron wave-functions are expanded in a basis of plane-waves, with energy cut-offs of 400 and 500 eV for the kinetic energy and for the electronic density, respectively, which have been adjusted to achieve sufficient accuracy in the total energy. The Brillouin zones of both configurations were sampled by using $[4 \times 2 \times 1]$ and $[2 \times 2 \times 1]$ Monkhorst–Pack grids³³ for the $p(5 \times 2)$ and the recently detected phases, respectively.

Figure 1. STM image of a C_{60} island. In this image we can see two of the main defects present in these molecular layers. Defect I: we observe C_{60} vacancies, which correspond to missing C_{60} molecules (marked by black circles). Defect II: we detect the *anti-phase* boundaries due to a stacking fault during the coalescence of two C_{60} islands (marked by a blue ellipsoid). The $[001]$ direction is indicated by a red arrow. Coverage: 0.6 ML, size: (300×175) $\text{\AA}^2$, $I = 0.12$ nA, $V_s = +1.65$ V.

3. RESULTS AND DISCUSSION

As it has been reported in recent literature,^{18,19} deposition of C₆₀ on the clean rutile TiO₂(110)-(1×1) surface at *RT* yields the formation of well-ordered close-packed islands exhibiting a p(5×2) superstructure. Figure 1 shows a STM image of C₆₀ molecules deposited on the TiO₂(110) surface. It can be observed that, although the C₆₀ islands present an excellent local ordering, it is possible to find some defects. First of all, we can observe the presence of dark features inside the molecular islands, clearly coming from missing molecules (highlighted by black circles in Figure 1 as defect type I). These C₆₀ vacancies cannot be associated to the presence of typical single defects on the substrate such as O_{vac} or OH groups since their density is much higher than the density of missing molecules.¹⁹ Thus, we can envisage two possible origins: they can be due to an unusual accumulation of defects in that area, for example two O_{vac} or two OH groups; or, more likely, they can be originated by a fault in the island formation.

The second type of defects corresponds to linear defects named *anti-phase* boundaries (APB), reported by the first time on TiO₂(110) by Loske *et al.*¹⁹⁻²¹ This kind of defects, highlighted by the blue ellipsoid as defect II in Figure 1, consists of a stacking fault occurring during the island growth. Loske and coworkers recently reported on the experimental evidence of these APBs for this organic-oxide interface.¹⁹ In that work, this kind of defect is rationalized as the mismatch occurring when two different C₆₀ islands coalesce and two molecules in the same substrate Ti_{5f} row get into close contact. This induces the formation of a “boundary” between both islands, where no C₆₀ molecules can be accommodated. The only possibility for the extra C₆₀ molecules is to sit on top of these boundaries, thus protruding from the two coalescing island planes by approximately 0.7–0.8 Å, as measured by STM. These APBs, originated from stacking faults, can only occur along two directions, the [2-25] and the [-225], since these latest crystallographic

directions are the only ones permitting the C_{60} molecules to be separated by an optimal distance close to the molecular van der Waals diameter.

Figure 2. STM image of the $C_{60}/TiO_2(110)$ interface measured in constant-current mode. Coverage: 0.5 ML, size: $(350 \times 290) \text{ \AA}^2$, $I = 0.05 \text{ nA}$, $V_s = +1.8 \text{ V}$. The two coexistent C_{60} phases are highlighted as insets. The unit cell for each phase is represented by a solid-lined blue oblique parallelogram.

Figure 2 shows a constant current STM image of the $C_{60}/TiO_2(110)$ interface for a coverage of 0.5 ML. In this image, two coexistent C_{60} phases can be observed. For clarity, both phases have been highlighted as insets and the unit cell for each phase represented by a blue solid-lined oblique parallelogram. In the left region of the $C_{60}/TiO_2(110)$ island in Figure 2, the previously reported $p(5 \times 2)$ structure,^{18,19} with two spinning C_{60} molecules per unit cell, can be identified (as emphasized in the left inset). On the other hand, in the right inset of Figure 2, a new phase, to our

knowledge not reported so far, can be distinguished. It is worthy to mention that the experimental conditions under which this new phase is observed, do not differ from those used for the growth of the $p(5 \times 2)$ phase. Furthermore, this phase is minority as evidenced by STM. This can be easily rationalized in terms of its slightly less favorable adsorption energy, as it will be shown below. Considering the already observed APBs,^{19–21} one of the possible structural models explaining the new phase in Figure 2 (right inset) would be based on the accumulation of these APBs. However, many different structures can be thought by using APB accumulations. At least, ten distinct translational domains could be formed in the C_{60} / $TiO_2(110)$ system at the interface separating the $p(5 \times 2)$ phase by considering the formation of ordered APB accumulations. We have illustrated the possible models in Figure 3.

Figure 3. (Central panel) Pictorial scheme of the ten different possible APBs accumulation models for the C_{60} / $TiO_2(110)$ system. (Side panels) Pictorial sketches of the representative D1, D4, D6¹⁹ and D8 APB accumulation models (shown as example), including their canonical unit cells (dashed lines), and the two possible homogeneous molecular packing between consecutive APBs (green crosses and triangles). Blue dots represent molecules along the APB lines in the different models.

We have carefully investigated, firstly from a geometrical point of view, the inequivalent models arising from the 10 different translational vectors shown in central panel of Figure 3, which yield the 10 distinct APBs accumulation-types. Considering an arbitrary origin (red dot at (0,0) in central panel of Figure 3), we have used 10 translational cartesian vectors (x,y) to locate adsorbed molecules along the [2-25] direction, giving rise to the ten different domain models, named as D. Thus, domain D0 will be generated by the (0,0) vector, D1 by (1,0), D2 by (2,0), D3 by (3,0), D4 by (4,0), D5 by (0,-1), D6 by (1,-1), D7 by (2,-1), D8 by (3,-1) and, finally, domain D9 by (4,-1) vector (see Figure 3). To facilitate the visualization of the domains, and as representative examples, D1, D4, D6 and D8 domain models are sketched in side panels of Figure 3. Obviously, addition of a further translational vector ($\pm 5,0$), or $(0,\pm 2)$ reproduces each one of the original ten domains (i.e. topmost red dot in central panel of Figure 3). Additionally, from any given domain there are nine distinct boundaries to another domain and, if the gap width can be varied, there will be an even greater number. Side panels of Figure 3 also show the two most homogeneous ways of packing molecules in between consecutive APBs, indicated by green crosses and triangles (named as cross- and triangle-packing in the following). Table I summarizes the distances between consecutive APB lines for the different APB accumulation domain models, d_{APB} (in Å), as well as the minimum and maximum distances between adjacent molecules, d_s and d_l (in Å), within the two molecular packings arising for the different APB accumulation configurations.

It can be clearly distinguished that the case of the domain D0 without APBs accumulation, i.e., without any additional molecular packing between the APB lines, corresponds to the preservation of the $p(5\times 2)$ phase. After a detailed observation it can be identified that the structural configuration of the D7 model (in the triangle-packing configuration) corresponds (as

we will show later) to the phase coexisting with the p(5x2) in Figure 2 observed in the right side of the image.

Table I. Distances between APB lines, d_{APB} (in Å), for the all the APB accumulation models proposed in Figure 3; and short and long intermolecular distances, d_s and d_l (in Å), for the two molecular packing models (green crosses and triangles) proposed in Figure 3. Geometrically feasible APB accumulation domains appear bold-highlighted.

	d_{APB} (Å)	d_s / d_l (Å) cross-packing	d_s / d_l (Å) triangle-packing
D0	13.20	4.97 / 10.57	6.60 / 4.97
D1	13.53	6.16 / 10.15	6.77 / 6.16
D2	14.48	7.46 / 9.94	7.24 / 7.46
D3	15.93	8.82 / 9.94	7.97 / 8.82
D4	17.77	10.22 / 10.15	8.89 / 10.22
D5	19.80	7.58 / 13.71	9.90 / 7.58
D6	20.02	8.41 / 13.39	10.01 / 8.41
D7	20.68	9.49 / 13.22	10.34 / 9.49
D8	21.72	10.51 / 13.22	10.86 / 10.51
D9	23.10	11.71 / 13.39	11.55 / 11.71

As a next step, one can evaluate which ones among all the structures depicted by this simple geometrical model can lead to long and stable crystallographic phases. By carefully inspecting the geometrical distances shown in Table I, it is possible to conclude that most of the APB accumulation models (within both proposed cross and triangular molecular packings) would be directly discarded for being physically unrealistic, showing either too long or too short distances

between adjacent molecules compared to the vdW diameter of the C₆₀ molecules (considering realistic intermolecular distances ranging between 9 and 11 Å). This geometrical observation finds its exception in the obvious D0 model but just in the configuration without any APBs accumulation, D0:p(5×2) – which is the preservation of the p(5×2) phase –, the D4 (cross-packing) model, and the D7 and D8 (triangle-packing) models, which show short / long distances with adjacent molecules of (9.94 / 9.94), (10.22 / 10.15), (10.34 / 9.49) and (10.86 / 10.51) Å, respectively (see Table I). Among the plausible D4, D7 and D8 above mentioned models, D4 is an special case because although this model matches the intermolecular distance close to the vdW diameter criterion, in this configuration the molecules filling consecutive APB lines within the cross-packing fashion do not lie on high-symmetry sites (such as “ontop” atoms, bridges or hollows), which may *a priori* difficult its formation. Thus, we conclude that the only two geometrically feasible possibilities would be the cases of the D7 and D8 APB domains, which exhibit distances between adjacent adsorption sites close to that of the p(5×2) phase.

Additionally, it is important to mention that the D6 model (triangle-packing) corresponds to the APB reported by Loske *et al.*¹⁹ In that case, due to the close intermolecular distance, brighter rows were observed for the APBs and an accumulation of those APBs should lead to alternation of brighter and darker C₆₀ rows in the STM image. However, due to this short intermolecular distance (8.41 Å), the D6 structure cannot lead to long-range ordered phases. The same APB defect type is that shown in Figure 1 as “Defect II”.

On the basis of the aforementioned purely geometrical rationalization, we have carried out DFT+vdW-based calculations on the p(5×2) phase (to compare with previous literature), and on the D4 (cross-packing), D7 and D8 (triangle-packing) APB accumulation models – the result of these calculations will be fully explained in detail below –. Table II shows, after the full

optimization of the structures, the values obtained for the intermolecular distances, d_s / d_l (in Å), the planar molecular densities, σ (in Å² / C₆₀ molecule), and the adsorption energies (in eV / C₆₀ molecule). First of all, it is interesting to notice that, whilst within the p(5×2) phase all the intermolecular distances are around 9.94 Å, for the D4, D7 and D8 models a set of two intermolecular distances appears: a long and a short one. This is due to the oblique configuration of their unit cells. On the other hand, the planar molecular densities (see Table II) provide an accurate measure of the molecular packing. Among the considered D4, D7 and D8 APB accumulation models, the most compact packing is found for the D4 model, followed by the D7 domain, and the D8 domain, the latest exhibiting the less dense packing. The adsorption energies per C₆₀ molecule for the three APB accumulation models and the p(5×2) phase are also given in Table II: 1.72 eV, 1.41 and 1.16 eV for the D7, the D8 and D4 models, respectively, and 1.95 eV for the p(5×2) phase. For the C₆₀ / TiO₂(110) system the results of Table II evidence the p(5×2) phase as the most stable one, followed by the D7 model; this latest corresponding to the C₆₀ phase we report in Figure 2. The calculations suggest that the D4 and D8 domains are less stable, fact that could be expected since they have not been experimentally detected so far.

Table II. Intermolecular distances, d_s / d_l (in Å), planar molecular densities, σ (in Å² / C₆₀ molecule), and adsorption energies (in eV / C₆₀ molecule) obtained within the p(5×2) phase, and the D4, D7 and D8 domains.

	d_s / d_l (Å)	σ (Å ² / C ₆₀)	E^{ads} (eV / C ₆₀)
D0:p(5×2)	9.94 / 9.94	98.2	1.95
D4	10.22 / 10.15	44.2	1.16
D7	10.34 / 9.49	51.4	1.72
D8	10.86 / 10.51	54.0	1.41

In this work, a new structural model is proposed to explain the new C_{60} phase observed in Figure 2 (D7 phase in the following), based on three factors: *i*) the geometrical considerations on the APB accumulations; *ii*) the experimental distances as measured from the STM images; and, finally, *iii*) the theoretical DFT-based calculations, including a self-consistent parametrization of the van der Waals corrections, crucial in highly decoupled systems as explained above. This new D7 model is sketched in Figure 4. In this model, for the new phase region located at the right side of Figure 2, an alternation of C_{60} molecules sitting on top of five-fold coordinated titanium (Ti_{5f}) and bridging oxygen (O_{br}) rows is presented. This new model shows a change in one of the close-packed directions passing from the (5,0;0,2) direction (using a 2D notation for clarity) to the (5,2;2,-3) direction, resulting in a variation in the superstructure unit cell. This oblique lattice characterizing the D7 model contains four C_{60} molecules, one divided into the four corners, two divided into the four sides and one located at the center of the unit cell. Although it may seem an unusually large unit cell, it is the smaller one possible according to the registry with the substrate, and having into account that the four C_{60} molecules are adsorbed on four inequivalent on-surface adsorption sites.

In order to gain insight into the superstructure based on the coexistence of the two different phases on the $TiO_2(110)-(1\times 1)$ surface, DFT+vdW calculations of both the $p(5\times 2)$ and D7 C_{60} phases were performed (also testing the D8 model). To this aim, the $TiO_2(110)$ surface was modeled in a repeated slab geometry: *i*) a slab of three physical $TiO_2(110)$ layers with a distance ~ 25 Å of vacuum between neighboring cells along the axis perpendicular to the surface; as well as *ii*) full periodic boundary conditions representing an infinite $TiO_2(110)$ surface. Each substrate physical layer contained 60 and 114 atoms for the $p(5\times 2)$ and D7 phases, respectively (and 104 and 126 for the testing of the D4 and D8 models, respectively). A perfectly balanced

stoichiometry was used in order to avoid polarization effects, being the obtained size for the unit cells in the direction parallel to the surface, after full lattice optimization, (14.9×13.2) and $(19.9 \times 20.7) \text{ \AA}^2$, for the $p(5 \times 2)$ and D7 phases, respectively (and $(19.9 \times 17.7) \text{ \AA}^2$ and $(19.9 \times 21.7) \text{ \AA}^2$ for testing the D4 and D8 models, respectively). For the full geometry optimizations only the two bottom TiO_2 physical layers were kept fixed. Additionally, in order to check the total energy results for both optimized geometrical configurations, ground-state calculations were recalculated by including an additional oxide layer, with no significant variations w.r.t. the three physical substrate layers case, guaranteeing the energetical convergence in the results for both phases (with an uncertainty below 0.01 eV).

Figure 4. Schematic representation of the D7 structural model. Red and pink balls correspond to O and Ti substrate atoms, respectively. Large blue and red circles frame C_{60} molecules in the $p(5 \times 2)$ and the new D7 structural phases, respectively. Green arrows indicate distances used for the D7 model, measured along the $[001]$ direction (indicated with a black arrow) and perpendicularly to the boundary $[1-11]$, respectively. The unit cells of both phases are also depicted as dashed-lined yellow parallelograms. Right panel shows the particular molecule orientation (w.r.t the $[001]$ direction) of each C_{60} molecule located on the different on-surface adsorption sites.

Figure 5. DFT+vdW optimal models for the two coexistent C_{60} phases on the $TiO_2(110)$ surface. (*Top view*) The superstructure unit cell is represented as a yellow dashed-lined polygon. (*Side view*) Along the $[001]$ surface direction. For both phases, perpendicular distance between the lowest C atoms in the C_{60} molecules and the topmost surface Ti rows is also shown. In top panel, both inequivalent molecules (*1a* and *1b*) present a very similar adsorption height, 3.21 Å. On the other hand, for the oblique phase (bottom panel), molecule-substrate distances range between 3.26-3.32 Å, due to the four inequivalent on-surface adsorption sites in the unit cell (*2a-2d*).

As starting geometrical configuration for the calculation of the $p(5 \times 2)$ phase, we have taken that one previously reported by our group in Ref.¹⁸ The results obtained from the calculations are

practically the same than those shown in Ref.¹⁸ for the p(5×2) phase. This new calculation of the p(5×2) superstructure – within a essentially similar theoretical framework than in Ref.¹⁸ – also predicts an adsorption geometry where molecules are finally located on top and in-between Ti_{5f} atoms as experimentally suggested. Just to clarify, the theoretical results shown for the p(5×2) superstructure in Ref.¹⁸ by our group were obtained within a localized basis set DFT-implementation; whilst, although similar by construction, the theoretical framework applied in the present work is based on a plane-wave parametrization of the DFT formalism. It is important to remark that both methodologies are essentially equivalent. Furthermore, van der Waals energy and forces are accounted in both mentioned DFT-implementations in the same perturbative vdW R⁻⁶ correction to add dispersive forces to conventional density functionals.²³ Besides, both C₆₀ molecules in the unit cell lie around 1.8 Å over the O_{br} lines; 3.21 Å above the Ti_{5f} atoms (see Figure 5). The adsorption energy of the C₆₀ monolayer in the p(5×2) phase predicted by the DFT+vdW theory is 1.95 eV per C₆₀ molecule. All these results support the experimental observation of a weak interaction between C₆₀ molecules and the TiO₂ surface, thus forming a floating organic layer of spinning C₆₀ molecules as previously reported.¹⁸

Once the p(5×2) superstructure has been fully characterized, with an excellent agreement with the previous literature,¹⁸ we applied the same theoretical framework to the calculation of the new D7 configuration proposed in Figure 4. At this point, it is important to remark that the unit cell used in the calculations for this C₆₀/TiO₂ model phase is very large, involving a total amount of atoms above 600. Given that huge amount of atoms, the accurate theoretical treatment by first-principles calculations used here turned into a very challenging task, and a large amount of computational time and effort was necessary to get geometrical and energy converged results. As starting geometrical configuration for this oblique model, we have taken the one shown in the

right part of the left panel of Figure 4, with four C_{60} molecules per unit cell, all of them located on the following inequivalent adsorption on-surface sites: i) on top of an oxygen atom of a O_{br} channel (labeled as $2a$ in Figure 4); ii) on top of a titanium atom of a O_{br} channel (labeled as $2b$); iii) lying in between two titanium atoms of a Ti_{5f} row (labeled as $2c$); and iv) on top of a titanium atom of a Ti_{5f} row (labeled as $2d$). The resulting optimized geometry is shown in bottom panel of Figure 4. The final orientation of the C_{60} molecules labeled as $2a$, $2b$ and $2d$ is essentially the same to that one obtained for molecules in the $p(5\times 2)$ located over Ti atoms in the Ti_{5f} atom rows ($1a$ in top panel of Figure 5) but azimuthally rotated by 90 deg. Therefore, it presents a quasi pentagon-hexagon dimer orientation slightly rotated (around 6 deg) towards the pentagon orientation. Nevertheless, the molecule lying in between two Ti_{5f} atoms ($2c$ in bottom panel of Figure 5) presents, similarly to the other inequivalent molecule in the $p(5\times 2)$ phase ($1b$ in top panel of Figure 5), a hexagon orientation with two Ti atoms in the center of hexagon borders. It is important to notice that for this D7 model, three inequivalent adsorption sites yield the same on-surface orientation of the molecule, and the other inequivalent adsorption site yields a different one, but both of them already predicted in the $p(5\times 2)$ phase. This may be explained in terms of the only two favorable orientations of the molecules in both phases for this C_{60} / TiO_2 interface, which seems to be simply controlled by the fact that whether a C_{60} molecule lies on a surface atom (either an O or a Ti atom), or over a Ti—Ti bridge of a Ti_{5f} row.

The calculation of this new D7 domain model – within the same theoretical framework than for the $p(5\times 2)$ phase – predicts an adsorption geometry, where the four C_{60} molecules in the unit cell exhibit adsorption heights ranging between 3.26 and 3.32 Å above the Ti_{5f} atoms (see Figure 5). It is important to emphasize that, in spite of the four inequivalent adsorption sites in the unit cell, the dispersion in the adsorption heights for all of them is very low, with an average value of

around 3.29 Å, slightly higher than the one obtained for the p(5×2) phase of 3.21 Å. This fact is understood considering the adsorption energy for the new oblique model, which can be quantified in 1.72 eV per C₆₀ molecule. For this new phase, the intermolecular distance is lower than in the p(5×2) phase, which seems to improve the intermolecular interaction by reducing the molecule-substrate interaction, slightly increasing the average distance between the TiO₂ surface and the molecules.

Nevertheless, the small difference in the adsorption energies per molecule for both phases (0.23 eV per C₆₀) – between C₆₀ molecules adsorbed on Ti_{5f} rows (in the p(5×2) phase) and those adsorbed on alternating Ti_{5f} and O_{br} rows (oblique phase) – predicted by the theory may be easily overcome at *RT*. This interesting result implies that due to the low molecule-surface interaction, molecules present a high adsorption height (~3.3 Å). At this height, molecules will not be strongly affected by the surface topography but the intermolecular interaction will prevail; consequently, making no clear distinction between adsorption on Ti_{5f} or O_{br} rows. This is in accordance with our STM images, where no variations in the apparent height between C₆₀ molecules on O_{br} rows and molecules on Ti_{5f} were detected (see right side of Figure 2). According to these results, the model proposed in Figure 4 seems to be highly suitable to explain the new local domain observed in right side Figure 2. Once again, these results enforce the idea of a floating C₆₀ adlayer on TiO₂(110), independently on the local domain considered.

4. CONCLUSIONS

Summarizing, we have found a new phase for C₆₀ molecules on the TiO₂(110)-(1×1) surface. This new phase, not reported so far and characterized by a larger unit cell than the p(5×2) phase, is explained in terms of an accumulation of anti-phase boundaries (APB). Although several

APBs accumulation domains could be *a priori* possible, the one observed by STM in the present work is predicted as the most stable one. An alternation of C₆₀ molecules sitting on Ti_{5f} and O_{br} rows with four inequivalent adsorption sites and two different molecular orientations is found for the new APB phase. The prevalence of the intermolecular over the molecule-surface interaction induces a relatively high adsorption distance, making possible to neglect the effect of the topographic corrugation. This new phase sheds light into the idea of TiO₂ as a suitable substrate for decoupled systems.

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Notes

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