

Low-Temperature Orientationally Ordered Structures of Two-Dimensional C₆₀

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Abstract: Orientationally ordered structures of two-dimensional (2D) C₆₀ at low temperature have been investigated theoretically and experimentally. Using total energy optimization with a phenomenological potential, we find the ground state is a close packed hexagonal lattice in which all the molecules have the same orientation. Several local minima of the potential energy surface are found to be associated with other 1×1 lattices as well as 2×2 lattices. The energies of the orientational domain boundaries of the 1×1 lattices are also computed, and two kinds of which yield negative values. A majority of these theoretical findings are confirmed by our low-temperature scanning tunneling microscopy study of a 2D C₆₀ array supported on a self-assembled monolayer.

A recent effort in nanomaterial research has led to the emergence of a new class of exotic materials that are composed of complex building blocks such as stable large molecules and clusters. In these materials, there exists an important parameter that is absent in a more conventional material: the orientational degrees of freedom of the building blocks. A solid C₆₀ is a quintessential example. Because of the high symmetry of the C₆₀, the binding force between C₆₀ molecules in solid C₆₀ depends strongly on their separation but only weakly on their relative orientations. This gives rise to a phase transition that is primarily related to the mutual molecular orientations and takes place only at low temperatures.¹ At room temperature (rt), the C₆₀ molecules rotate freely in a face-centered-cubic lattice, known as the *orientationally disordered phase*. When a C₆₀ solid is cooled to 260 K, it undergoes a first-order phase transition. The molecular orientations become ordered, and the lattice is transformed into a simple cubic of the *Pa* $\bar{3}$ space group, known as the *orientationally ordered phase*.² In this ordered phase, there are two kinds of nearly degenerate orientations for each C₆₀. Below 90 K, the transition time between the nearly degenerate orientations exceeds the laboratory time scale, and the lattice is now in a *glassy phase*.³

Two-dimensional (2D) C₆₀ also exhibits complex orientational ordering and disordering. For example, orientationally dependent surface melting of a solid C₆₀ has been reported.⁴ This experiment has led to the proposed two-stage rotational disordering mechanism, whereby a fraction of molecules undergoes the orientational disorder transition at a lower temperature than that of the remaining ones.⁵ Recently, we have reported a novel orientational domain topology in a 2D C₆₀ revealed by the low-temperature scanning tunneling microscopy.⁶ The C₆₀ molecules form a 2D orientationally ordered phase where all molecules have an *identical* orientation. As a result, a unique domain structure is also created in which the correlation function of the molecular orientation within a domain is spatially uniform and changes abruptly at domain boundaries. A remarkable character of these *molecular orientational domains* is that the domain wall is perfectly sharp.

Experimental results have clearly demonstrated that the orientational order in a 2D C₆₀ differs significantly from that in its 3D counterparts. It is, therefore, important to gain some theoretical insight into these unique orientational orders and domain structures. In this paper, on the basis of the total energy optimization using a semiempirical approach, we show that the energies for the identical orientational orders such as the ones observed experimentally are, indeed, among several local minima, if not the global minimum. Furthermore, an orientational order involving a 2×2 unit cell also gives rise to several local minima in the potential energy surface. As we shall show,

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- (1) Heiney, P. A.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; Denenstien, A. M.; McCauley, J. P., Jr.; Smith, A. B., III *Phys. Rev. Lett.* **1991**, *66*, 2911.
- (2) (a) David, W. I. F.; Ibberson, R. M.; Matthewman, J. C.; Prassides, K.; Dennis, T. J. S.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, *353*, 147. (b) Sachidanandam, R.; Harris, A. B. *Phys. Rev. Lett.* **1991**, *67*, 1467.

- (3) David, W. I. F.; Ibberson, R. M.; Dennis, T. J. S.; Hare, J. P.; Prassides, K. *Europhys. Lett.* **1992**, *18*, 219.

- (4) Goldni, A.; Cepek, C.; Modesti, S. *Phys. Rev. B* **1996**, *54*, 2890.

- (5) Laforge, C.; Passerone, D.; Harris, A. B.; Lambin, P.; Tosatti, E. *Phys. Rev. Lett.* **2001**, *87*, 085503.

- (6) Hou, J. G.; Yang, J. L.; Wang, H. Q.; Li, Q. X.; Zeng, C. G.; Yuan, L. F.; Wang, B.; Chen, D. M.; Zhu, Q. S. *Nature* **2001**, *409*, 304.

a majority of these theoretical predictions are confirmed by our low-temperature STM experiment on 2D C_{60} arrays grown on a self-assembled monolayer.

Although complete first-principles calculations for a C_{60} lattice is still beyond the present-day computational ability, phenomenological descriptions of such systems have been improved significantly and have shown good success for obtaining properties in good agreement with experimental results.^{7–9} Here we adopt the approach of Lamoen and Michel (denoted as the LM model from this point on).⁸ The LM model, designed to reproduce the experimental 3D C_{60} orientational order parameters, is particularly applicable for predicting the relative energies of different orientations, which are what we are concerned about in our paper. Recently, this model has been used to predict the two-stage rotational disordering of the C_{60} surface.⁵ The LM intermolecular potential consists of three terms: van der Waals attraction, Born–Mayer repulsion, and Coulomb interaction:

$$V = \sum_{i,i'} \frac{A}{r_{i,i'}^6} + \sum_{j,j'} B_{j,j'} \exp(-C_{j,j'} r_{j,j'}) + \sum_{k,k'} \frac{q_k q_{k'}}{r_{k,k'}}$$

The first term is the van der Waals attraction with $A = 3.05421 \times 10^5 \text{ K } \text{Å}^6$ and the summation is taken over the 60 carbon atoms. The second term is the Born–Mayer potential that replaces the repulsive term in the Lennard–Jones potential. To better describe the orientational dependence, LM introduces 210 interaction centers on each molecule: 60 are at the carbon atoms, 60 are at the midpoints of the 60 single bonds, and 90 are evenly distributed along the 30 double bonds. The parameters $B_{j,j'}$ and $C_{j,j'}$ are dependent on the types of interaction centers j and j' and can be found in ref 8. The last term is the Coulomb potential, which is calculated from a fitted point charge model of the multipole moments with the local-density approximation.¹⁰ The relative positions and the charges at the 153 points on a molecule are given in ref 10.

In our calculations, we regard C_{60} molecules as rigid bodies and their centers of mass are placed in a 2D closed-packed hexagonal lattice. The total energy is the pairwise summations of the interaction energies between the nearest neighbors. The orientational optimizations are performed by adjusting the three Euler angles (α , β , γ) representing the orientational space with the steepest descent method. The Euler angles are relative to a standard orientation of C_{60} in which three 2-fold axes define the x , y , and z directions (as Figure 1A in ref 9). As noted by refs 8 and 9, the LM model is unsatisfactory in predicting the lattice constant, hence the absolute cohesive energy. To avoid this demerit of the LM model, we fix the intermolecular distance to be 9.93 Å, the same as the value in the bulk $Pa\bar{3}$ phase. This setting is supported by our STM experiment from which the intermolecular distance of 2D C_{60} is estimated to be 9.95 ± 0.1 Å. Moreover, we have repeated theoretical calculations with intermolecular distances increased/decreased by 0.1 Å and found no real difference in the conclusions.

We first optimize the system with the constraint that all molecules have the same orientation, that is, a 1×1 lattice or

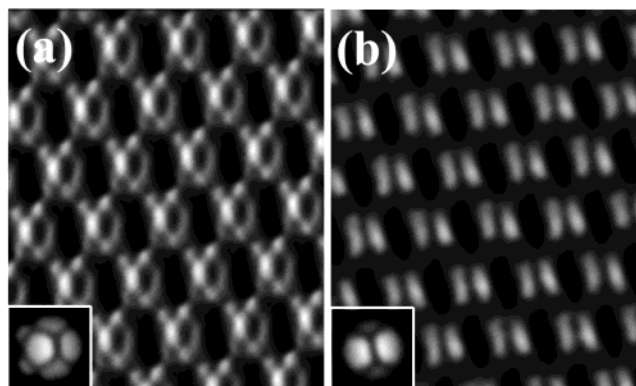


Figure 1. 48 Å × 58 Å STM images of the 1×1 C_{60} lattices with two different molecular orientations. The sample bias voltage is 2.0 V. Insets are the theoretical simulations with the A and B orientations.

one C_{60} per unit cell. The overall theoretical results are summarized in Table 1. Because of the hexagonal symmetry of the lattice, the total energy is invariant with two symmetry operations performed simultaneously on all the molecules: rotation about the c axis (normal to the plane) by $n \times 60^\circ$ and reflection about the perpendicular planes through the basis vectors **a** or **b**. To use these symmetries explicitly, we define the polar (θ) (azimuthal (ϕ)) angle of an orientation as the angle between c (**a**) axis and a characteristic direction typically projected from the center of the molecule to a high symmetry point on its surface (see Table 1 for detail). Thus, the lattice with an orientation of $\theta = \theta_0$ and $\phi = \phi_0$ is isoenergetic to that with $\theta = \theta_0$, $\phi = \pm\phi_0 + n \times 60^\circ$ ($n = 0, 1, 2-5$). So generally, there will be 12 isoenergetic orientations of a local minimum and only a characteristic polar angle ϕ_0 between 0° and 30° needs to be reported. We note that, since either θ or ϕ_0 could be zero and the C_{60} molecule possesses the high point group symmetry, the actual number of isoenergetic orientations is usually less than 12. The orientation dependent part of the interaction between two molecules is mainly determined by how the molecules face each other. Because of the hexagonal symmetry of the lattice C_{60} , the interface orientations between a molecule and its two opposite neighbors are identical. Thus, there are at most three kinds of different interface orientations in a 1×1 lattice. Moreover, the center inversion symmetry of the C_{60} determines that the geometrical elements (vertex, pentagon, hexagon, etc) of an interfacing must be the same, as shown in Table 1.

We find three local potential energy minima, -0.384 , -0.294 , and -0.268 eV per molecule, and denote them as phase A, B, and C of the 1×1 lattice, respectively. The orientation of the A phase is at $\theta = 1.9^\circ$ and $\phi_0 = 0.0^\circ$, shown in the third column of Table 1. There are only two distinct interface orientations, both having a hexagon of one molecule facing a hexagon of another, staggered as in the fourth column. The dot at the center is the normal projection of the line joining the centers of the two molecules. The former interface orientation shown in Table 1 accounts for $2/3$ of the intermolecular “bonds”, while the latter accounts for the remaining $1/3$. For the B phase, a double bond faces upward and the orientation is set at $\theta = 0.0^\circ$ and $\phi_0 = 19.6^\circ$. There are three different interface orientations for this orientation. Finally, the C phase has the highest symmetry with a hexagon facing the top and only has one type of interface

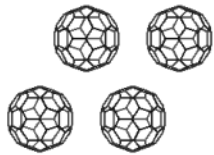
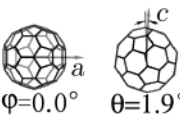

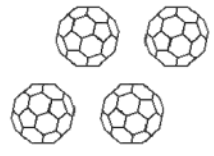
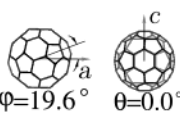
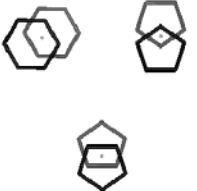
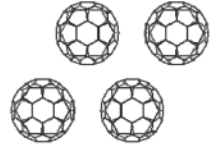
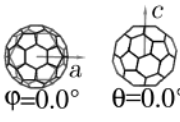

(7) Lu, J. P.; Li, X. P.; Martin, R. M. *Phys. Rev. Lett.* **1992**, *68*, 1551.

(8) Lamoen, D.; Michel, K. H. *J. Chem. Phys.* **1994**, *101*, 1435.

(9) Savin, S.; Harris, A. B.; Yildirim, T. *Phys. Rev. B* **1997**, *55*, 14182.

(10) Yildirim, T.; Harris, A. B.; Erwin, S. C.; Pederson, M. R. *Phys. Rev. B* **1993**, *48*, 1888.

Table 1. Summary of the Theoretical Results for the Three Kinds of 1×1 Lattices^a

Lattice	Orientation	parameters	interface orientation
1×1.A (-0.384)		 $\varphi=0.0^\circ$ $\theta=1.9^\circ$ $\alpha=109.3^\circ, \beta=294.5^\circ, \gamma=242.8^\circ$	
1×1.B (-0.294)		 $\varphi=19.6^\circ$ $\theta=0.0^\circ$ $\alpha=316.4^\circ, \beta=0.0^\circ, \gamma=63.2^\circ$	
1×1.C (-0.268)		 $\varphi=0.0^\circ$ $\theta=0.0^\circ$ $\alpha=270.0^\circ, \beta=339.1^\circ, \gamma=120.0^\circ$	

^a The energies (eV/molecule) are listed in the parentheses. In the column "orientation" are shown the top views of the lattices. In the column "parameters" are displayed the top views and side views of a molecule and three Euler angles. In the column "interface orientation" are displayed the facing situations of the neighbor molecules, with dots showing the intersection points of the line connecting the molecular centers with the molecular faces. The high symmetry points used to define the characteristic directions are the highest C atom, the midpoint of the highest double bond, and the center of the highest hexagon for the A, B, and C lattices, respectively.

orientation. For the A, B, and C phases, the numbers of equivalent orientations are 6, 6, and 1, respectively.

Two out of the above three 1×1 structures are confirmed experimentally. Figure 1 is the STM images of two close pack hexagonal arrays of C_{60} formed on a self-assembled monolayer (SAM) of alkylthiol grown on a gold (111) substrate. The SAM is atomically flat and interacts very weakly with the C_{60} molecules.¹¹ At rt, the C_{60} arrays are unstable: molecules at the edge of an array can detach readily and diffuse to other parts of the same array or other nearby arrays. High-resolution STM images show that the C_{60} displays a smooth hemispherical protrusion, suggesting that the C_{60} molecules are rotating freely at rt. This is in strong contrast to the case of C_{60} adsorbed on metal or semiconductor surfaces where the molecular rotation are frozen even at room temperature because of the strong binding of C_{60} on the substrate.¹² At 77 K, the C_{60} molecule appears as a hemisphere, a tilted donut, or an asymmetric dumbbell, each being consistent with a rotating pattern around a fixed axis. When the sample is cooled further to 5 K, the STM images begin to reveal internal fine structures of the C_{60} , as shown in Figure 1. From the temperature evolution of the

C_{60} internal patterns, we conclude that final C_{60} orientational order is resulted primarily from the C_{60} - C_{60} interactions, not from the C_{60} -substrate interactions. It has been shown that, by comparing the theoretical simulation with high-resolution STM images, the orientation of the C_{60} can be unambiguously determined.¹² The insets to Figure 1a and b are two simulated images based on the A and B orientations, respectively. We adopt Tersoff and Hamann's formula¹³ and its extension to simulate STM images, where the tunneling current in the STM is proportional to the local densities of states of the C_{60} molecule. The electronic structure of the C_{60} molecule is calculated using the density functional theory with the local density approximation within DMol package.¹⁴ The agreement between the experiment and theory is quite good.

Our STM experiment also reveals a 2×2 C_{60} lattice, shown in Figure 2a. It can be seen that there are four differently oriented molecules in each unit cell. It is interesting to note that the (111) face of the $Pa\bar{3}$ C_{60} solid also shows a 2×2 surface lattice. We next consider the results of the optimization performed with a 2×2 unit cell. It is found that, even when the 1×1 constraint is relaxed to 2×2 , the A and B phases of the 1×1 lattice are still

(11) Evans, S. D.; Ulman, A. *Chem. Phys. Lett.* **1990**, *170*, 462.(12) Hou, J. G.; Yang, J. L.; Wang, H. Q.; Li, Q. X.; Zeng, C. G.; Lin, H.; Wang, B.; Chen, D. M.; Zhu, Q. S. *Phys. Rev. Lett.* **1999**, *83*, 3001.(13) Tersoff, J.; Hamann, D. R. *Phys. Rev. B* **1985**, *31*, 805.

(14) DMol, version 960; Density Functional Theory electronic structure program; Molecular Simulations Inc., 1996.

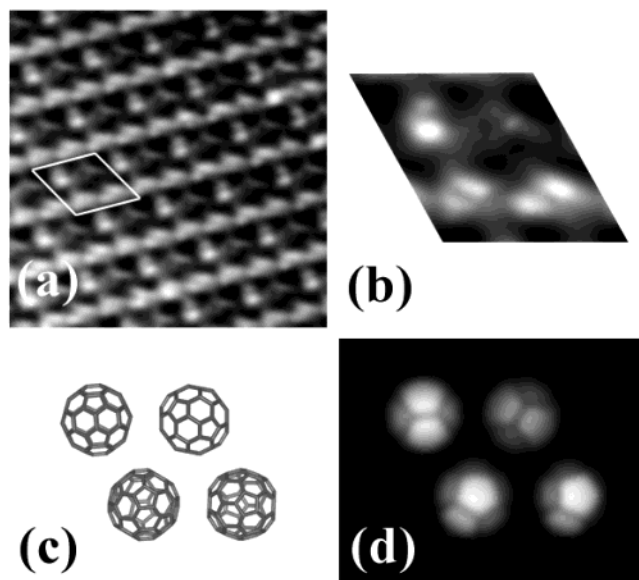


Figure 2. (a) $110 \text{ \AA} \times 105 \text{ \AA}$ STM images of a 2×2 C_{60} lattice taken with the sample bias voltage at 2.0 V; (b) a unit cell of the whole lattice; (c) the theoretical C_{60} orientations; and (d) the simulated images of the theoretical lattice.

at the potential energy minima but the C phase is unstable against distortion. We note that a recent first-principles calculation of a C_{60} monolayer used the (1×1) C phase as the model and its stability was not investigated.¹⁵ In addition, several other energy minima are found to be associated with the 2×2 lattices but all having energies higher than that of the (1×1) A phase. In this sense, the (1×1) A phase is the ground state of the 2D C_{60} , which is quite different from the case of the 3D counterpart. We find that a kind of 2×2 structure (Figure 2c), whose energy is $-0.369 \text{ eV/molecule}$, gives a remarkable match to the experimental image (Figure 2d). In this 2×2 structure, all four molecules show different orientations and heights, giving rise to six different facings. Because of the different heights, a molecule in the unit cell looks relatively dark in the image. However, the 2×2 structure corresponding to the (111) face of the $Pa\bar{3}$ C_{60} solid does not yield energy minimum, indicating again that the orientational order critically depends on dimensionality.

A combination of A and B arrays can give rise to 66 domain structures. We define the domain boundary energy per unit length to be $E_0 = (E_{12} - E_1 + E_2)/2$, where E_1 and E_2 are the energies of a single domain for two orientations, respectively, and E_{12} is the energy of an array containing half of domain 1 and half of domain 2. We find two kinds of negative domain boundary energies out of 66 possible domain structures. The lowest energy, -0.0035 eV/\AA , is formed by a B array and its mirror array (Figure 3a). The other, around -0.0003 eV/\AA , is for the boundary between an A array and a B array, as shown

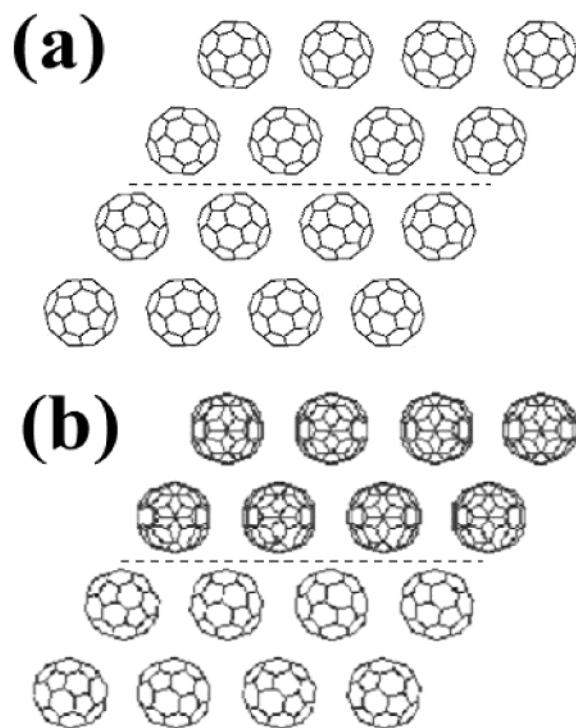


Figure 3. Theoretical domain structures with negative boundary energies: (a) a B array and its mirror array; (b) an A array and a B array.

in Figure 3b. So far, only the latter one has been observed experimentally.⁶ This could be understood by noting that the B array is much higher in energy than the A array. The small gain in domain boundary energy is also consistent with the experimental observation that the boundary fluctuates in time but is otherwise stable.

In summary, through model computation as well as STM experiment, we have shown that orientational ordering in a 2D C_{60} is drastically different from that in a C_{60} solid. In particular, the reduced dimensionality allows the molecules a greater degree of freedom in adjusting their mutual orientations. Although the interface orientations have lower symmetry than those in the 3D case, they better minimize the system energy and the domain boundary energies and lead to a deliberate unorientational molecular order for a 2D C_{60} and a new topological order for the orientational domains. These findings will have implications in other molecular lattices as well as in lattices made of more complex building blocks such as clusters.

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(15) Nakamura, J.; Nakayama, T.; Watanabe, S.; Aono, M. *Phys. Rev. Lett.* **2001**, *87*, 048301.