

Research Article Calculations of Constant-Height STM Images of Fullerene C₆₀ Adsorbed onto a Surface

Effat A. Rashed 🝺

Physics Department, Umm Al-Qura University, Makkah 24243-3494, Saudi Arabia

Correspondence should be addressed to Effat A. Rashed; earashed@uqu.edu.sa

Received 16 February 2023; Revised 2 June 2023; Accepted 7 June 2023; Published 21 June 2023

Academic Editor: Carlos Palacio

Copyright © 2023 Effat A. Rashed. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Constant-height scanning tunneling microscopy (STM) images of a C_{60} molecule adsorbed onto a surface were calculated using symmetry-adapted Hückel molecular orbitals (HMOs). Three adsorption orientations of C_{60} are considered. The interaction between the C_{60} molecule and the surface was treated using symmetry arguments only. Projection operators were used to generate symmetry-adapted HMOs of the molecule. These orbitals were then used to construct idealized constant-height STM images using the simple tunneling theory of Tersoff and Hamann. A comparison is made with published experimental STM maps. The results show that, for each orientation of C_{60} , split orbitals of the same symmetry have similar appearances in the constant-height maps. They also show that the map of a molecular orbital of a complete degeneracy is dominated by only one or two of its components.

1. Introduction

In the literature, one finds extensive high-resolution scanning tunneling microscopy (STM) studies on fullerene C_{60} residing on a surface. Most of these studies have used the constant-current mode of STM to investigate the orientation and intermolecular structure of C_{60} under various conditions, including C_{60} interacting with the surface, its neighbours, the scanning tip, a guest molecule situated inside it, or C_{60} isolated from any interactions. This last mode is preferred because it enables probing the fine features of the molecular orbitals, even though it takes a long operation time. In contrast, in the constant-height mode, only the top part of the sample is scanned, and as such, much of the structural details can be lost. However, this mode is preferred when a fast scan of the sample is desired without the need to record its fine topography.

In recent years, Reecht et al. [1] used the constant-height mode to image the molecular orbitals of a C_{60} molecule interacting with a Cu (111) substrate, where the surface-induced splitting of the LUMO (lowest unoccupied molecular orbital) and LUMO + 1 was observed by the STM tip. On the Cu (111) substrate, the C_{60} molecule is adsorbed with a hexagon facing the surface [1–3]. C_{60} can reside on

a substrate with other orientations depending on the adsorption site. For example, on a Au (111) substrate, the preferred orientation is pentagon-down [4], and it is double bond down on a black phosphorous substrate [5]. The adsorption of C₆₀ on a substrate removes the full icosahedral symmetry characteristic of the isolated molecule. The resulting symmetry depends on the orientation of C₆₀ and the symmetry of the adsorption site. Site symmetries available for a C_{60} molecule are $C_{6\nu}$, C_6 , $C_{4\nu}$, C_4 , $C_{3\nu}$, C_3 , $C_{2\nu}$, C_2 , C_s , and C_1 [6]. The reduction in the symmetry of C_{60} lifts the high degeneracies of its molecular orbitals [7]. This effect is now routinely observed in STM experiments, where the split frontier orbitals of C₆₀, namely, the HOMO (highest occupied molecular orbital), LUMO, and LUMO + 1, can be imaged at different biases. The imaged features of the orbitals depend predominantly on the orientation of the C₆₀ molecule and weakly on the adsorption site [8]. Correct assignments of the recorded images to the corresponding orbitals cannot be accomplished by analyzing the STM images alone. Rather, it requires comparison with simulations. Complicated ab initio methods are usually used to make the necessary simulations. However, Hands et al. [6, 7] developed a much simpler analytical method to simulate STM images of the molecular orbitals of C_{60} . This method is based on the Hückel molecular orbital theory and the simple tunneling theory approach of Tersoff and Hamann [9]. It treats any perturbation of the orbitals of C₆₀ purely on the basis of symmetry using group theoretical methods; that is, the effect of the interaction is simply to lift the high degeneracies of the molecular orbitals of C_{60} . The simplicity of the method is that STM images of the orbitals can be created using only their symmetries without any calculations of their energies. Assigning a real STM image can then be made by comparison with the simulated images. The authors have successfully applied their method to simulate and interpret constant-current STM images of C₆₀ and its ions undergoing different interactions [3, 7, 10-12]. They also used the method to simulate constant-height STM images of the unsplit HOMO and LUMO of a C₆₀ molecule residing on a substrate with different orientations [6].

As noted above, most published theoretical STM images of the C₆₀ molecule were produced in the constant-current mode. In this work, the analytical methods were used to simulate constant-height STM images of a C₆₀ molecule adsorbed onto a substrate and subjected only to surface interaction. The aim is to make available what is currently missing in the literature, that is, a library of simulated STM images of C₆₀ that can be used as a reference in constantheight STM scans. The method of projection operators is utilized to form symmetry-adapted HMOs which are then used to construct the STM images. In the simulation, only the effect of the surface interaction on the electronic structure of C₆₀ is taken into account, and none of the complications associated with other experimental parameters are considered. This effect is treated by the group theoretical means developed in [7]. Since the adsorption site has little influence on the captured features of the imaged molecule, [12] is followed and a flat, featureless surface is assumed. Thus, the symmetry of the C₆₀-surface system is determined entirely by the adsorption orientation of C_{60} . Three possible orientations of the adsorbed molecule are considered: a C_{60} molecule adsorbed with a hexagonal face, a pentagonal face, and a double bond prone to the surface. The corresponding overall symmetries of the C_{60} molecule are $C_{3\nu}$, $C_{5\nu}$, and $C_{2\nu}$, respectively [12]. The results for the hexagon-prone orientation are compared with the experimental results in [1]. The results obtained here for a flat surface can be readily linked to any site symmetry by using easy group theoretical methods to correlate the transformation properties of the orbitals considered here to their transformation properties in the site symmetry.

2. Methods

Figure 1 shows the definition of the coordinates used in the simulations when the C_{60} molecule is adsorbed with a double bond prone to the surface (hence, a double bond is facing towards the STM tip). The origin of the Cartesian axes is placed at the center of the C_{60} molecule. The *z* axis is normal to the surface, and as such, it defines the direction of observation. The *x* and *y* axes are parallel to the surface, with each axis defining a C_2 axis of rotation. Accordingly, the symmetry of C_{60} is C_{2v} . To obtain the C_{5v} and C_{3v}

symmetries, the molecule is rotated about the *y* axis by $\tan(-\phi^{-1})$ and $\tan(-\phi-1)$, respectively, where $\phi = (1 + \sqrt{5})/2$ is the golden ratio.

For each symmetry of C_{60} , the method of projection operators was used to generate the HMOs in symmetry-adapted form [13]. The projection operator is defined as follows:

$$P^{i}_{jk} = \frac{d_{i}}{h} \sum_{\hat{O}} \Gamma^{i}(\hat{O})_{jk} \hat{O}, \qquad (1)$$

where *h* is the order of the group, d_i is the dimension of an irreducible representation (irrep.) γ_i of the group, $\Gamma^i(\vec{O})$ is the matrix representation of the symmetry operation \hat{O} , and $\Gamma^{i}(\widehat{O})_{ik}$ is the jk^{th} element of $\Gamma^{i}(\widehat{O})$. Applying the projection operator on a π orbital results in a state of symmetry γ_i if the orbital belongs to that representation or zero if it is not. Therefore, for each point group of the C₆₀ molecule, 60 symmetry-adapted states were obtained in which each state transformed as irrep. of the point group. These states were then used to construct the Hückel matrix in a blockdiagonal form in which each block belonged to irrep. of the point group. Each block was then diagonalized separately to obtain the relative energies and symmetries of the molecular orbitals of C₆₀. The alternation in the single and double carbon-carbon bonds was accounted for [7], in which the corresponding resonance integrals were related by a parameter $\alpha = (\beta_d / \beta_s) = 1.433$ [14], where β_d and β_s are the resonance integrals for the double and single bonds in C_{60} , respectively.

The tunneling theory approach of Tersoff and Hamann [9] was used to simulate the constant-height STM maps of the molecular orbitals. In this approach, the current observed during STM is proportional to the electron density of the surface evaluated at the position of the STM tip:

$$I \propto \sum_{i} |\psi_{i}(\mathbf{r}_{0})|^{2} \,\delta(E_{i} - E_{F}), \qquad (2)$$

where *I* is the tunneling current, ψ_i is the wave function of the surface state of energy E_i , E_F is the Fermi energy, \mathbf{r}_0 is the position of the STM tip, and *i* runs over all the available surface states. A map of an orbital of C_{60} with complete degeneracy was obtained by summing over all the components that would arise from that orbital by surface interaction. The constant-height image of a molecular orbital was constructed by creating a grid of points at a specified tip height and calculating the current at each point.

3. Results and Discussion

The results of the simulations are presented in Figures 2–7. Figures 2 and 3 present the results for a C_{60} molecule adsorbed with a hexagon prone to the surface. This corresponds to the $C_{3\nu}$ symmetry in the simple model assumed here. Figure 2 shows the electron densities and STM maps of the unsplit MOs, including HOMO, LUMO, LUMO + 1, LUMO + 2, LUMO + 3, and combined LUMO + 2 and 3. The latter combination was included to compare the current results with the experimental images obtained in [1]. For this



FIGURE 1: Definition of the Cartesian axes when a double bond is prone to the surface. The pentagon-prone and hexagon-prone orientations are obtained by rotating the molecule, as described in the text.

orientation (and also for the pentagon-prone and doublebond-prone orientations in Figures 4 and 6), the simulated maps for the unsplit HOMO and LUMO are similar to those obtained in [6] using the HMOs of Deng and Yang [15]. In general, the three-fold symmetry of the hexagonal face of C_{60} is present in all images of unsplit and split MOs. The constant-height map for the HOMO, LUMO, or LUMO + 1 appears as three bright lobes arranged as a three-fold ring for the former orbital and as a three-leafed clover for the latter two orbitals. The results for HOMO and LUMO agree with many experimental observations [3, 16, 17]. The maps for LUMO + 1 and LUMO + 2 appear as hexagonal arrangements of 6 bright spots, resulting from the density concentrated on the carbon atoms. A surface interaction of $C_{3\nu}$ symmetry lifts the degeneracies of the MOs of C₆₀ according to irreps. given in the last column in Figure 2. For example, the HOMO orbital is split into three components: a singlet of A_2 symmetry and two doublets of E symmetry. An examination of the maps of all states resulting from the splitting of HOMO, LUMO, LUMO + 1, LUMO + 2, and LUMO + 3 (Figure 3) shows that each takes one of the four unique shapes as per the symmetry of the state: A state of A_1 symmetry is mapped onto a bright protrusion, a state of A_2 symmetry appears as a 6-petaled flower, and a state of E symmetry appears either as a 3-leafed clover or as a bright three-fold ring. Since the two components of the E symmetry produce different images, one of the components is marked as E^* in Figure 3 and also in the text. It is also noted that the map of an MO of complete degeneracy is dominated by the features of one or two of its components. For instance, the map of the HOMO is dominated by the features of one of the two components that transform in $C_{3\nu}$ as a doublet. Similarly, the images of LUMO and LUMO + 1 are dominated by the E components. Thus, care must be taken when analyzing the experimental STM images since an orbital of complete degeneracy may appear as an orbital of a lower degeneracy and vice versa.

To assess the method used here, the simulated electron densities and STM images were compared to the results reported by Reecht et al. [1] The electron densities produced by the simple method of the group theory used here exactly match those simulated by the authors of [1] using the DFT method with the Perdew-Burke-Ernzerhof (PBE) functional. We note that the image obtained for the E^* component arising from the HOMO resembles that obtained for the unsplit HOMO. Both images are similar to the image observed in [1] at V = -1.9 V. The authors of [1] identified this orbital as the HOMO with complete degeneracy; that is, it is unaffected by surface interaction. Splitting of the HOMO when C₆₀ is adsorbed on various surfaces has been observed (see reference [7] and references within) with the E^* component observed at a bias ~ -2 V. If the components of the HOMO in [1] were not well separated by the surface interaction, the constant-height map of the E^* component could have been wrongly attributed to the unsplit HOMO. Experimental maps of the A_1 and E components arising from the LUMO in [1] resemble our simulated images.

However, there is some disagreement regarding the remaining orbitals. The experimental images identified in [1] as the LUMO + 1 A and E components each feature a threeleafed clover. While this matches our simulations for the Ecomponent, it disagrees with the simulation for the LUMO + 1 A_2 component. The electron density of this orbital is shown on the far right of Figure 3. The uppermost part of the electron density features a six-petaled flower, which is expected to be mapped onto a bright, six-fold image in the constant-height map, in disagreement with the experimental image reported in [1]. Lastly, we discuss the results for LUMO + 2, LUMO + 3, and the combination of LUMO2 and 3. The two sets of orbitals and their combination exhibit identical appearances in the simulated constant-height images, each composed of a hexagon of bright spots. [1] does not report individual LUMO + 2 and LUMO + 3. It reports only the map of their combination, which is observed as a bright protrusion. Referring to Figure 3, our simulations suggest that the bright protrusion is the signature of the A_1 state, possibly arising from the splitting of either LUMO + 2 or LUMO + 3.

Figures 4 and 5 present the results for a C₆₀ molecule with a pentagon prone to the surface. Figure 4 shows the HOMO and LUMO +1 orbitals, and each is expected to appear as a five-fold ring and LUMO, LUMO + 2, and LUMO + 3 as bright lumps. The results for unsplit HOMO and LUMO match those simulated by Hands et al. [6]. The image obtained for the LUMO also agrees with the experimental maps [3]. The components arising from these orbitals when the surface interaction has $C_{5\nu}$ symmetry are expected to be mapped by the STM onto one of the four unique shapes: the A_1 component as a bright lump, A_2 as a 10-petaled flower, E_1 as a five-fold ring, and E_2 as a pentagon of bright spots. Moreover, the simulations for LUMO, LUMO + 2, and LUMO + 3 are dominated by the A_1 components and those for HOMO and LUMO + 1 by the E_1 components.



FIGURE 2: The electron densities and STM simulations for hexagon-prone C_{60} . (a) The electron densities obtained from the symmetryadapted HMOs for HOMO, LUMO, LUMO + 1, LUMO + 2, LUMO + 3, and combined LUMO + 2 and 3. (b) Constant-height STM simulations of the orbitals in (a). (c) The irreps. of the split components of each manifold when the surface interaction has C_{3v} symmetry.



FIGURE 3: The appearances of the different components of the molecular orbitals in Figure 2 (labelled by their symmetries in the top row) when they are split by a surface interaction of $C_{3\nu}$ symmetry as would be observed in a constant-height STM probe. Both doublets have the same transformation properties in $C_{3\nu}$ but produce different STM maps, and as such, one of them is distinguished by an asterisk. Far right: the electron density of the LUMO + 1 A_2 component.



FIGURE 4: The electron densities and STM simulations for pentagon-prone C_{60} . (a) The electron densities obtained from the symmetryadapted HMOs for HOMO, LUMO, LUMO + 1, LUMO + 2, and LUMO + 3. (b) Constant-height STM simulations of the orbitals in (a). (c) The symmetries of the components of each manifold arising from the surface interaction of $C_{5\nu}$ symmetry.



FIGURE 5: Simulations of the features of the different components of the molecular orbitals in Figure 4 (labelled by their symmetries in the top row) when they are split by a surface interaction of $C_{5\nu}$ symmetry as would be observed in a constant-height STM probe.

Figures 6 and 7 present the last set of simulations, obtained for a C_{60} molecule with a double-bond prone to the surface. Figure 6 shows the results for the orbitals when they retain their icosahedral degeneracies. The features obtained for the HOMO and LUMO agree with experimental observations [3, 16, 17] and with the simulations reported in [6]. The HOMO appears in the simulations as an oval lobe. LUMO + 2 and HOMO + 3 each features a pair of slightly separated bright spots, which, at low resolution, are expected to appear as a lobe. LUMO and LUMO + 1 each appears as a pair of parallel lobes. Figure 7 shows the simulations for the split orbitals when the surface interaction has $C_{2\nu}$ symmetry.



FIGURE 6: The electron densities and STM simulations for double-bond-prone C_{60} . (a) The electron densities obtained from the symmetryadapted HMOs for HOMO, LUMO, LUMO + 1, LUMO + 2, and LUMO + 3. (b) Constant-height STM simulations of the orbitals in (a). (c) The symmetries of the components of each manifold arising from the surface interaction of $C_{2\nu}$ symmetry.



FIGURE 7: Simulations of the features of the different components of the molecular orbitals in Figure 6 (labelled by their symmetries on the top row) when they are split by a surface interaction of $C_{2\nu}$ symmetry as would be observed in a constant-height STM probe. One of the two singlets transforming as $A_{1(2)}$ is marked by an asterisk because it produces different features in the STM map.

Here, a state of A_1 symmetry appears as a single lobe, while a state of B_1 symmetry features two bright lobes. The additional A_1 component that arises from the LUMO + 3 orbital upon lifting its degeneracy appears as two wellseparated lobes, and as such, it is marked as A_1^* . The last column in Figure 6 shows that the A_1 and B_1 states arise together in the splitting of all but one orbital, LUMO + 1, where only a state of B_1 symmetry arises upon splitting. Seemingly, one or both states dominate the other components in each orbital when the latter maintains its degeneracy.

The simulated images for A_2 and B_2 states all have four bright spots. The additional A_2 state that results from the splitting of the HOMO orbital produces a slightly different STM map, and hence, it is marked by an asterisk in Figure 7 and in the text. In the A_2 and B_2 states, the four spots are rectangular, while they are square in the A_2^* state. Rectangular features have been observed in STM images of C_{60}^{4-} ions on Au (111) at +0.1 eV, and they were attributed to a state arising from the LUMO manifold as a result of a Jahn–Teller distortion of the C_{60}^{4-} ion to D_{2h} [18] or D_{3d} [12]. Hands et al. [7] suggested that these features arose from a LUMO + 1 component (which corresponds to the A_2 component in Figure 7). According to our results, the rectangular features can also arise from the LUMO in neutral C_{60} (the B_2 component) if the molecule is resting on the substrate with a double bond and the surface interaction has a symmetry that does not support any degeneracies.

4. Conclusion

Simulated constant-height STM images of the MOs of C₆₀ when subjected to interaction with a flat surface have been presented. Three common orientations of C₆₀ were considered: when the molecule is prone to the surface with a hexagon, a pentagon, or a double bond. The simulations used the Hückel molecular orbital theory, the group theory method of projection operators, and the Tersoff-Hamann approach of quantum tunneling. The results for the hexagon-prone orientation were compared to previously reported experimental STM images. While many simulated images agreed with the experimental maps, the current simulations suggest that some of the constant-height STM images reported in [1] could have been incorrectly reported. The results of this work are expected to assist in constantheight STM experiments on fullerene C₆₀ by allowing a quick indication of the existence of the surface interaction and fast identification of the orientation of C₆₀ and of the symmetry of its split orbitals.

Data Availability

No underlying data were collected or produced in this study.

Conflicts of Interest

The author declares that there are no conflicts of interest.

References

- G. Reecht, B. W. Heinrich, H. Bulou, F. Scheurer, L. Limot, and G. Schull, "Imaging isodensity contours of molecular states with STM," *New Journal of Physics*, vol. 19, no. 11, Article ID 113033, 2017.
- [2] T. Hashizume, K. Motai, X. Wang et al., "Intramolecular structures of C_{60} molecules adsorbed on the Cu (111)-(1× 1) surface," *Physical Review Letters*, vol. 71, no. 18, pp. 2959–2962, 1993.
- [3] J. Leaf, A. Stannard, S. P. Jarvis, P. Moriarty, and J. L. Dunn, "A combined Monte Carlo and huckel theory simulation of orientational ordering in C₆₀ assemblies," *Journal of Physical Chemistry C*, vol. 120, no. 15, pp. 8139–8147, 2016.
- [4] E. I. Altman and R. J. Colton, "Determination of the orientation of C₆₀ adsorbed on Au (111) and Ag (111)," *Physical Review B: Condensed Matter*, vol. 48, no. 24, pp. 18244–18249, 1993.

- [5] X. Cui, D. Han, H. Guo et al., "Realizing nearly-free-electron like conduction band in a molecular film through mediating intermolecular van der waals interactions," *Nature Communications*, vol. 10, p. 3374, 2019.
- [6] I. D. Hands, J. L. Dunn, C. S. Rawlinson, and C. A. Bates, "Jahn-teller effects in molecules on surfaces with specific application to C₆₀," in *The Jahn-Teller Effect*, H. Köppel, D. R. Yarkony, and H. Barentzen, Eds., vol. 97, pp. 517–551, Springer, Berlin, Germany, 2009.
- [7] I. D. Hands, J. L. Dunn, and C. A. Bates, "Calculation of images of oriented C₆₀ molecules using molecular orbital theory," *Physical Review B: Condensed Matter*, vol. 81, no. 20, Article ID 205440, 2010.
- [8] J. G. Hou, J. Yang, H. Wang et al., "Identifying molecular orientation of individual C₆₀ on a Si (111)–(7× 7) surface," *Physical Review Letters*, vol. 83, no. 15, pp. 3001–3004, 1999.
- [9] J. Tersoff and D. R. Hamann, "Theory of the scanning tunneling microscope," *Physical Review B: Condensed Matter*, vol. 31, no. 2, pp. 805–813, 1985.
- [10] I. D. Hands, J. L. Dunn, and C. A. Bates, "Visualization of static jahn-teller effects in the fullerene anion C₆₀"," *Physical Review B: Condensed Matter*, vol. 82, no. 15, Article ID 155425, 2010.
- [11] A. J. Lakin, C. Chiutu, A. M. Sweetman, P. Moriarty, and J. L. Dunn, "Recovering molecular orientation from convoluted orbitals," *Physical Review B: Condensed Matter*, vol. 88, no. 3, Article ID 035447, 2013.
- [12] A. J. Lakin, H. S. Alqannas, and J. L. Dunn, "Theoretical modelling of jahn-teller distorted C₆₀ anions on a surface," *Journal of Physics: Conference Series*, vol. 428, Article ID 012001, 2013.
- [13] M. Tinkham, Group Theory and Quantum Mechanics, Dover, Illinois, IL, USA, 2003.
- [14] I. D. Hands, J. L. Dunn, C. A. Bates, and V. Z. Polinger, "An enhanced bonding model for C₆₀ and its ions," *Chemical Physics*, vol. 278, no. 1, pp. 41–51, 2002.
- [15] Y. Deng and C. N. Yang, "Eigenvalues and eigenfunctions of the Hückel Hamiltonian for carbon-60," *Physics Letters A*, vol. 170, no. 2, pp. 116–126, 1992.
- [16] F. Rossel, M. Pivetta, F. Patthey, E. Cavar, A. P. Seitsonen, and W.-D. Schneider, "Growth and characterization of fullerene nanocrystals on nacl/Au (111)," *Physical Review B: Condensed Matter*, vol. 84, no. 7, Article ID 075426, 2011.
- [17] L. Tang, Y. Xie, and Q. Guo, "Complex orientational ordering of C₆₀ molecules on Au (111)," *The Journal of Chemical Physics*, vol. 135, no. 11, Article ID 114702, 2011.
- [18] A. Wachowiak, R. Yamachika, K. Khoo et al., "Visualization of the molecular jahn-teller effect in an insulating K_4c_{60} monolayer," *Science*, vol. 310, no. 5747, pp. 468–470, 2005.