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Jun-Hyung Cho and Dong-Hwa Oh
Department of Physics, University of Texas, Austin, Texas 78712-1081

Kwang S. Kim
Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea

Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712-1081

The adsorption of 1,4-cyclohexadiene on the Si(001) surface is studied by first-principles density-functional calculations within the generalized gradient approximation. The ''pedestal'' structure where the two C=C double bonds react with different Si dimers is found to be more stable than the ''upright'' structure where only one of the two C=C bonds reacts with a Si dimer. However, the $[2+2]$ cycloaddition reaction can easily form the upright structure but not the pedestal one. The latter structure can be obtained from the former through a high energy barrier of ~0.95 eV, indicating a small reaction rate at room temperature. Our results provide the theoretical basis for the interpretation of recent low-energy electron diffraction and photoelectron spectroscopy data in which the upright structure was seen. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Recently, cyclic unsaturated hydrocarbons such as cyclopentene,[1] 1,4-cyclohexadiene,[2] and 1,5-cyclooctadiene[3] have been used for the fabrication of ordered organic monolayer films on Si(001) surfaces. These hybrid organic-silicon systems are promising for the development of molecular electronics because of the possibility of combining the wide range of functionality of organic molecules with the existing Si-based infrastructure.[4] According to recent experimental[1–4] and theoretical[5–7] studies, the reaction between such cyclic hydrocarbons and Si(001) is facilitated by the interaction of the π bond of unsaturated hydrocarbons with the dangling bonds of a Si dimer. This so-called $[2+2]$ cycloaddition reaction is facile even at room temperature.[1–3]

For adsorbed 1,4-cyclohexadiene molecules on Si(001) low-energy electron diffraction[2] (LEED) showed a sharp (2 ×1) pattern at saturation coverage, indicating that the (2 ×1) dimer structure is maintained upon adsorption. At saturation coverage photoelectron spectroscopy[2] (PES) also found that (*i*) almost all the Si dangling bonds are reacted with adsorbed molecules and (*ii*) only one of the two π bonds in 1,4-cyclohexadiene reacts with the Si dimer. Based on these experimental observations, Hamaguchi *et al.*[2] proposed the upright structural model [Fig. 1(c)] where the 1,4-cyclohexadiene molecules adsorb on top of all the Si dimers by forming two σ bonds between C and Si atoms, with the unreacted C=C bond protruded out into the vacuum side. The PES study[2] further showed that the π orbital in the unreacted C=C bond has components parallel ([110] direction) and perpendicular (p_z) to the Si surface, implying to the authors that the molecular plane is inclined from the [001] direction (but equally consistent with buckling).

In this article we present our first-principles calculation results for the geometric and energetic properties of 1,4-cyclohexadiene molecules adsorbed on the Si(001) surface. Based on past studies of the adsorption structures of cyclohydrocarbons,[2,3] we consider two structural models: one is termed the pedestal model [Fig. 1(a)] and the other is the upright model [Fig. 1(b)]. For half coverage we find that the pedestal model is more stable than the upright model by 1.23 eV in adsorption energy. More importantly, we also find that one doubly bonded pedestal molecule plus one free molecule are lower in energy than two singly bonded upright molecules by 0.68 eV. As proposed for the reactions of several unsaturated hydrocarbons with Si(001),[5–7] we study the reaction path for the upright structure via the so-called ''three-atom'' intermediate state. We further study the reaction path from the upright structure to the pedestal one, where an energy barrier of ~0.95 eV is calculated, indicating a reaction rate of about 0.01 s^{-1} at room temperature. Thus, assuming an adsorption rate more rapid than this, the second bonding site required for the pedestal structure would be blocked, consistent with the recent low-energy electron diffraction and photoelectron spectroscopy experiments.[2] The geometry of adsorbed 1,4-cyclohexadiene in the upright model shows buckling of the molecular plane, in accord with the PES analysis.[2] Finally, our scanning tunneling microscopy (STM) simulation shows the disparate features in the filled-state images between the pedestal and the upright models. This result will be useful for future STM studies to identify the adsorption structure of 1,4-cyclohexadiene on Si(001).

The rest of the text is organized as follows. In Sec. II the calculational method is described. In Sec. III we determine the adsorption structure of 1,4-cyclohexadiene on Si(001) within the pedestal and the upright models. Here, the results
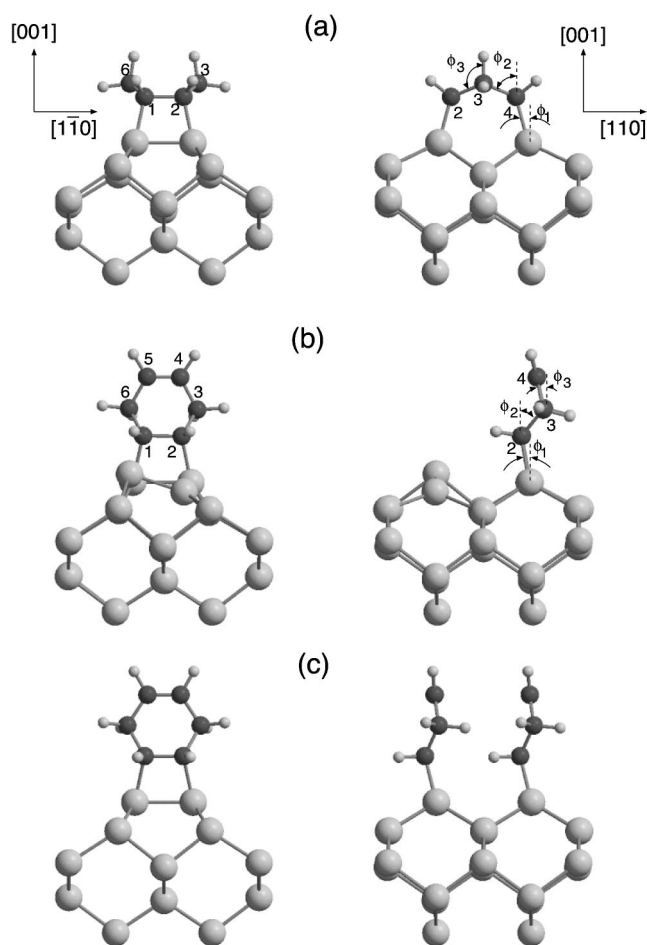
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FIG. 1. Side views of the optimized geometry of adsorbed 1,4-cyclohexadiene on Si(001): (a) the pedestal model, (b) the upright model ($\theta=0.5$ ML), and (c) the upright model ($\theta=1$ ML). The two side views are obtained from the [110] and [1$\bar{1}$0] directions. The buckling angles (ϕ_1, ϕ_2, and ϕ_3) are defined by the projection angle of the corresponding bond relative to the (110) plane. The large, medium, and small circles represent Si, C, and H atoms, respectively.

of the reaction path, the lateral interaction of adsorbed molecules, and the STM simulation are presented. Finally a summary is given in Sec. IV.

II. CALCULATIONAL METHOD

The total-energy and force calculations were performed by using first-principles density-functional theory[8] within the generalized-gradient approximation (GGA). We used the exchange-correlation functional of Perdew, Burke, and Ernzerhof[9] for the GGA. The norm-conserving pseudopotentials of Si and H atoms were constructed by the scheme of Troullier and Martins[10,11] in the separable form of Kleinman and Bylander.[12] For carbon whose $2s$ and $2p$ valence orbitals are strongly localized, we used the Vanderbilt ultrasoft pseudopotential.[13,14] We employed a periodic slab geometry with 12 Si atomic layers and adsorbed 1,4-cyclohexadiene molecules on both sides of the slab. The vacuum region between these slabs is about 9 Å. The electronic wave functions were expanded in a plane-wave basis set using a cutoff energy of 25 Ry, and the electron density was obtained from the wave functions at eight and four **k** points in the surface Brillouin zone of the (2×1) and (2×2) unit cells, respectively. The two central planes of Si were taken at their calculated bulk separations of $a/4=1.369$ Å. All other atoms were allowed to relax along the calculated Hellmann–Feynman forces until all the residual force components were less than 1 mRy/bohr. These calculation parameters have been successfully applied for the adsorption of unsaturated hydrocarbon molecules (such as acetylene,[15] ethylene,[15] and cyclopentene[7]) on Si(001).

III. RESULTS

We determine the atomic structure of adsorbed 1,4-cyclohexadiene on Si(001) for the coverage of $\theta=0.5$ ML (1 ML is defined as one molecule adsorption per Si dimer) within the pedestal and upright models. The optimized structures for both models are shown in Figs. 1(a) and 1(b), respectively. The calculated adsorption energy (E_{ads}) and structural parameters such as the bond lengths and the angles ϕ (defined in Fig. 1) are given in Table I. The pedestal model is found to be more stable than the upright model by $\Delta E_{\text{ads}} = 1.23$ eV. The reduced stability of the upright model can be attributed to the existence of the unreacted π bond on the molecule as well as the π bond on the neighboring Si dimer whose electronic states are energetically unstable compared to those of the reacted ones. Here, the unreacted C=C bond length ($d_{\text{C}_4-\text{C}_5}$) of 1.35 Å is identical to the double bond length in a free 1,4-cyclohexadiene molecule (see Table I), whereas the reacted C=C bond length increases to $d_{\text{C}_1-\text{C}_2} = 1.57$ Å because of its single bond character. Note that there are two different C–C single bond lengths in the upright

TABLE I. Calculated adsorption energy (eV/molecule), bond lengths (Å), and buckling angles (degrees) of adsorbed 1,4-cyclohexadiene molecules on Si(001) within both the pedestal and upright models. For comparison, the bond lengths of a free 1,4-cyclohexadiene molecule are also given. The bond length $d_{\text{C}=\text{C}}$ denotes the length of the double bond in a free C_5H_8 molecule, whereas $d_{\text{C-C}}$ is the single bond length. For the definition of the buckling angles, see Fig. 1. For the calculation of the adsorption energy (defined as the difference in the total energy of the 1,4-cyclohexadiene/Si(001) system from its separated limit), the total energy of the clean Si(001) surface is obtained from the $p(2\times2)$ reconstructed surface.

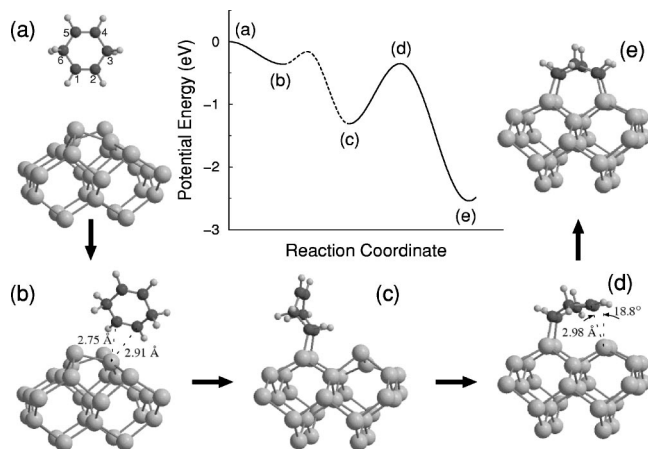| Model	Coverage	E_{ads}	$d_{\text{C}_1=\text{C}_2}$	$d_{\text{C}_4=\text{C}_5}$	$D_{\text{C}_2-\text{C}_3}$	$d_{\text{C}_3-\text{C}_4}$	$d_{\text{C-Si}}$	ϕ_1	ϕ_2	ϕ_3
Free C_5H_8			1.35	1.35	1.50	1.50				
Pedestal [Fig. 1(a)]	0.5 ML	2.54	1.58	1.58	1.55	1.55	1.97	14.9	67.6	112.3
Upright [Fig. 1(b)]	0.5 ML	1.31	1.57	1.35	1.54	1.51	1.96	9.7	39.7	11.4
Upright [Fig. 1(c)]	1 ML	0.93	1.57	1.35	1.54	1.51	1.97	13.5	23.9	7.3

FIG. 2. Calculated energy profile for the reaction process of 1,4-cyclohexadiene on Si(001) and the atomic geometries at five representative points: (a) the gas state, (b) the three-atom intermediate state, (c) the upright structure, (d) the transition state, and (e) the pedestal structure.

model: $d_{C_2-C_3} = d_{C_1-C_6} = 1.54$ Å and $d_{C_3-C_4} = d_{C_5-C_6} = 1.51$ Å. On the other hand, in the pedestal model both the reacted C=C bond lengths become $d_{C_1-C_2} = d_{C_4-C_5} = 1.58$ Å, while all the C–C bond lengths are identical to one another (1.55 Å). The C–C single bond lengths in both the pedestal and upright models tend to increase compared to the corresponding one in a free 1,4-cyclohexadiene molecule, as a consequence of the adsorption on Si(001) where the Si–Si bond length is larger than the C–C one. The buckling angles ϕ_1, ϕ_2, and ϕ_3 in the pedestal (upright) model are 14.9 (9.7), 67.6 (39.7), and 112.3 (11.4) degrees, respectively; that is, upon adsorption the planar geometry of a free 1,4-cyclohexadiene molecule changes into the buckled geometry, in accord with the implication derived from the PES analysis.[2]

In organic chemistry the [2+2] cycloaddition reactions (e.g., the reaction of two ethylene molecules to form cyclobutane) are extremely slow because of symmetry conditions in the involved molecular orbitals.[16,17] However, it is known that the analogous reaction of unsaturated hydrocarbons such as acetylene,[5] ethylene,[6] cyclopentene,[1] 1,4-cyclohexadiene,[2] and 1,5-cyclooctadiene[3] with Si(001) is facile even at room temperature. Recently, a "three-atom" intermediate state which is composed of a three-membered ring with the two C atoms and the down Si atom (in a Si dimer) was proposed for the initial reaction stage of unsaturated hydrocarbon molecules on Si(001).[5–7] For adsorbed 1,4-cyclohexadiene we also find the three-atom intermediate state which is stabilized over the gas state by 0.36 eV in adsorption energy [see Figs. 2(a) and 2(b)]. The bond lengths of the three-membered ring in Fig. 2(b) are $d_{C_1-Si} = 2.75$ Å and $d_{C_2-Si} = 2.91$ Å. We note that these bond lengths are somewhat larger than those calculated for 1,3-cyclohexadiene ($d_{C_1-Si} = 2.54$ Å and $d_{C_2-Si} = 2.66$ Å).[18,19] This difference may be due to the different locations of the unsaturated C=C bonds between the 1,3- and 1,4-cyclohexadiene molecules, although some of the difference could be due to differences between cluster[18] and surface

calculations. Note that in the 1,3(4)-cyclohexadiene the two C=C bonds are composed of carbon atoms 1,2 and 3,4 (1,2 and 4,5); see Fig. 2(a). Since there is energetically favored hybridization between the π bonding state of unsaturated hydrocarbons and the empty dangling-bond state of the down Si atom, the three-atom intermediate state can be reached from the gas state without an adsorption barrier. However, the energy barrier from the three-atom intermediate state to the upright structure was reported in the other unsaturated hydrocarbons such as acetylene[5] ($\Delta E_b = 0.01–0.20$ eV) and 1,3-cyclohexadiene[18] ($\Delta E_b = 0.17–0.34$ eV). This small energy barrier leads to the upright structure by thermal activation, forming two new σ bonds between C and Si atoms. Similarly, we believe that for adsorbed 1,4-cyclohexadiene on Si(001) the upright structure is easily formed via the three-atom intermediate state, supporting recent LEED and PES experiments.[2]

In order to investigate the reaction path from the upright structure to the pedestal one, we calculate the energy profile of the optimized structures by varying both the distance of two new σ bonds (between the C and the Si dimer atoms) and the angle ϕ_1 in the pedestal structure [see Fig. 2(d)]. Here, we assume that the directions of the Si dimer and the $C_4=C_5$ bond are kept parallel for simplicity. The energy barrier from the upright structure to the pedestal one is obtained to be about 0.95 eV.[20] Using an Arrhenius-type activation process with a typical value[21] ($\sim 10^{14}$ Hz) for the preexponential factor the reaction rate is estimated as $\sim 1.1 \times 10^{-2}$ s^{-1} which corresponds to a half-life of about 63 s.[22] This should be sufficient time for nearly complete coverage of the surface to occur, effectively blocking the formation of the pedestal structure.

From the valence-band ultraviolet PES spectra Hamaguchi *et al.*[2] observed that the Si dangling bond states completely disappear after the saturated adsorption of 1,4-cyclohexadiene, leading to the saturation coverage $\theta = 1$ ML. This saturation coverage of adsorbed 1,4-cyclohexadiene is similar to the cases of adsorbed acetylene and ethylene.[23–26] Using core-level x-ray photoemission, Rochet *et al.*[26] found that the adsorption of ethylene on Si(100) occurs easily with the sticking coefficient of nearly unity up to $\theta = 0.5$ ML after which the adsorption rate decreases strongly, but the completion of 1 ML is allowed if the surface is exposed to large dose of ~ 2330 Langmirs (L) (1 L $= 10^{-6}$ Torr s). We found a similar behavior for the adsorption of ethylene with respect to coverage. We found that this is due to the repulsive H–H interaction between the neighboring adsorbed ethylene molecules.[15] We expect a relatively larger repulsive H–H interaction between adsorbed 1,4-cyclohexadiene molecules, because the molecular geometry in the upright model is buckled with the C–H bonds pointing toward the direction of the Si dimer row. In order to estimate this steric interaction, we consider a small unit cell of $p(2 \times 1)$ in which the 1,4-cyclohexadiene molecules adsorb on top of every Si dimer. The optimized structure of $p(2 \times 1)$ with $\theta = 1$ ML is given in Fig. 1(c). As expected, the adsorption energy for $\theta = 1$ ML is found to be below that for $\theta = 0.5$ ML by $\Delta E_{ads} = 0.38$ eV (see Table I). We note that the buckling angles ϕ_2 and ϕ_3 become smaller at $\theta = 1$ ML
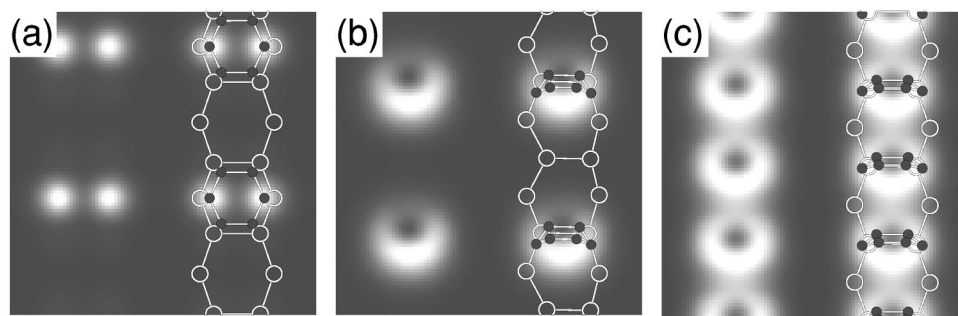
FIG. 3. Simulated filled-state STM images of adsorbed 1,4-cyclohexadiene on Si(001): (a) the pedestal model, (b) the upright model ($\theta=0.5$ ML), and (c) the upright model ($\theta=1$ ML). The filled-state images were obtained by integrating the charge from occupied states within 3 eV of the highest occupied state. The images were taken at 2.2 Å above the outermost C atom. The small dark and large open circles represent the positions of the C and the first and second Si layer atoms, respectively.

compared to $\theta=0.5$ ML (see Table I), implying the presence of some steric interactions between the neighboring 1,4-cyclohexadiene molecules. This repulsive intermolecular interaction should affect the energy profile for the reaction process in Fig. 2, which is obtained from the $p(2\times2)$ unit cell (with $\theta=0.5$ ML). Our previous study[7] for adsorbed cyclopentene on Si(001) found that for high coverage above 0.5 ML the reaction barrier from the gas state to the three-atom intermediate state was $E_b=0.22$ eV. Assuming that such reaction barrier for the adsorption of cyclopentene would be similar to the present 1,4-cyclohexadiene case, we expect that even above $\theta=0.5$ ML the [2+2] reaction of 1,4-cyclohexadiene at room temperature is probable with a relatively large reaction rate ($\sim2\times10^{10}$ s^{-1}), leading to the saturated upright structure [Fig. 1(c)] as observed in the PES study.[2]

STM is very useful for providing a direct view of adsorbed organic molecules on Si(001).[4] To our knowledge there is no STM study for adsorbed 1,4-cyclohexadiene on Si(001). For future STM study we simulate the filled-state STM images for the pedestal and upright models. As shown in Fig. 3, we find disparate features in the simulated STM images between the two models. For the upright model with $\theta=0.5$ ML [Fig. 3(b)] and 1 ML [Fig. 3(c)] the bright image represents the π orbital of the unreacted C=C bond whose photoemission peak was observed at -3.8 eV below the Fermi energy.[2] Despite the mirror symmetry of the π orbital about the unreacted C=C bond, the STM images of the upright model show different brightness in the upper and the lower sides (on top view in Fig. 3). This can be ascribed to the buckling (ϕ_3) of the molecular plane. As a matter of fact, the angle ϕ_3 of $\theta=0.5$ ML is larger than the value of $\theta=1$ ML (see Table I) and therefore the asymmetric pattern in Fig. 2(b) is more dominant than in Fig. 2(c). On the other hand, in the pedestal model the image shows the two bright spots in the center region between two Si dimers, related to the outermost C–H bonding.

IV. SUMMARY AND CONCLUSIONS

We have performed first-principles calculations for the adsorption of 1,4-cyclohexadiene on Si(001). We found that the pedestal model with $\theta=0.5$ ML is thermodynamically favored over the upright model with $\theta=1$ ML by 0.68 eV per 2×2 surface unit cell. However, the upright structure is easily formed by the kinetics compared to the pedestal struc-

ture and thus can block the formation of the pedestal structure, consistent with the proposed structural model from recent LEED and PES experiments.[2] Our calculated half life of 63 s for an unblocked upright molecule indicates that some pedestal molecules should be present, the exact amount depending on the pressure of the cyclohexadiene gas during adsorption. (Neither the pressure nor the Langmirs of exposure were given in Ref. 2.) This we do not believe is inconsistent with the experimental data. The PES data shows the presence of upright molecules but not the absence of pedestal molecules, while the LEED data does not seem to be of sufficient quality to preclude the presence of some pedestal molecules. Be that as it may, what is required is additional experimental data taken as a function of exposure pressure and time. In particular, what is required are STM studies which should easily be able to distinguish between the disparate features of the upright and pedestal structures which are seen in our simulated STM images.

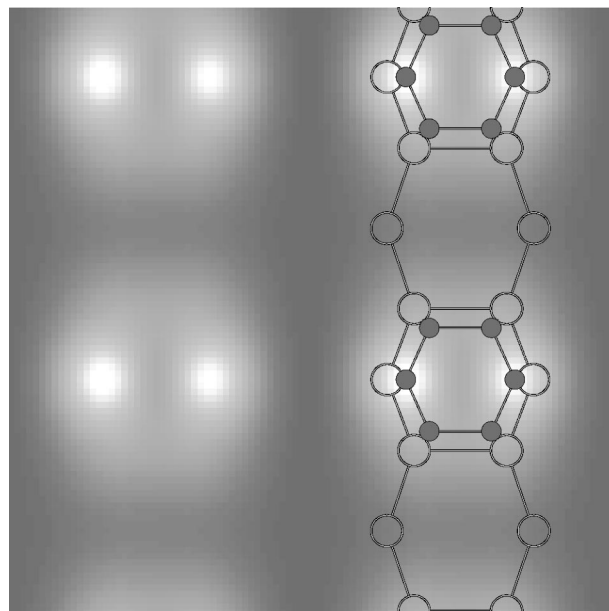*Note added*: Long after this article was first submitted

FIG. 4. Simulated empty-state STM image of adsorbed 1,4-cyclohexadiene on Si(001) for the pedestal model. This image was obtained by integrating the charge from unoccupied states within 1.3 eV of the highest occupied state. The images were taken at 2.2 Å above the outermost C atom. The small dark and large open circles represent the positions of the C and the first and second Si layer atoms, respectively.

for publication we were made aware of the recent STM data of Hamaguchi *et al.*[27] on Si(001) sparsely covered with 1,4-cyclohexadiene. They interpret their data as consistent with the upright structure when clearly it is more consistent with the pedestal structure. In Fig. 4 we display our pedestal unoccupied state STM simulation which looks essentially the same as the occupied state simulation in Fig. 3(a). Since the data was taken on boron-doped *p*-type Si and the sample bias was 1.3 V, we integrated the charge density upward 1.3 eV from the top of the valence bands at a point 2.2 Å above the highest carbon atoms. Because the figures are virtually unaffected by the voltage chosen, we did not replot Fig. 3 at the experimental sample bias but we did note that the higher the tunneling tip, the more diffuse the bright spots. For both simulations the bright spots are exactly midway between the Si dimers as they are in the experimental images. Hamaguchi *et al.* attribute this to the upright molecules being tilted, but our calculation indicates the upright molecules are buckled rather than tilted and although their STM images are displaced from the Si dimer to which they are bonded, this displacement is much less than half way to the next Si dimer. It is physically unrealistic to believe that the molecule would tilt half way to the next dimer without falling over and forming the pedestal structure. The unoccupied state tip height plot in Ref. 27 shows two distinct peaks which are separated by about 2.6 Å. The points of maximum brightness in the two bright spots in Fig. 4 are separated by 2.54 Å. The occupied state tip height plot also shows two peaks, but these are extremely broad which is the only aspect of the experimental results which is not completely consistent with our simulations. Since the tunneling current was fixed at 0.1 A in both cases but the density of states below E_F is much greater than that above, it is quite possible that this broadening was caused by using a much larger tip height for the occupied state tunneling. We note that our simulations do not take account of the relative conductivity of the various states from or into which the tunneling occurs. Thus exact agreement between theory and experiment cannot be expected but the overall agreement of the STM data with the pedestal structure as compared with the upright structure is clear.

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