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Pulling the C_{60} molecule on a Si(001) surface with an STM tip: A theoretical study

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The attractive-regime (pulling) constant-height manipulation of a C_{60} molecule on the Si(001) surface is modeled using density-functional theory with a scanning tunneling microscope tip included explicitly in the calculations. We demonstrate that the structure of the tip and its position with respect to the C_{60} prior to the pulling manipulation process determine its outcome. No translation of the molecule was achieved for some tip trajectories, while for others, the molecule was successfully translated via the pivoting mechanism reported previously [D. L. Keeling *et al.* Phys. Rev. Lett. **94**, 146104 (2005)]. We also find evidence of possible transition between different manipulation modes: the initial mode of manipulation may not necessarily be preserved over the whole tip trajectory, e.g., the pushing mode may go over into the pulling one. Our results agree with the experimentally found relatively low success rate of pulling manipulation and underscore the role of the tip in pulling. The calculated tip forces have a sawtooth pattern that is correlated with the main bond-breaking and bond formation events during the manipulation.

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INTRODUCTION

Manipulation of atoms and molecules using scanning probe microscopy (SPM) is a promising technique for creating nanostructures with desired geometries and properties. The ability to manipulate molecules is important for applications such as molecular electronics and catalysis.[1] Manipulation of several types of molecules has been achieved using scanning tunneling microscopy (STM). Small molecules, such as CO and C_2H_4,[2,3] have been manipulated at low temperatures (4–30 K) on metal surfaces (see Ref. 4 for a review). Manipulation of large molecules has been done as well, for example, porphyrines,[5] Lander molecules,[6] aromatic and polyaromatic molecules on metals,[7–9] and fullerenes on metallic and semiconducting surfaces.[10–13] Typically, the molecules involved in manipulation are physisorbed on metal surfaces, where the adsorption energies are small and the barriers for their translation are low. Manipulation of physisorbed molecules can be done either at low temperatures (7–30 K) (Refs. 2, 3, 7, and 8) or at room temperature.[10–13]

C_{60} on the Si(001) or Si(111) surfaces[11–14] is an example of the system where a molecule is chemisorbed, so that its movement can proceed only via a continuous change of the surface-molecule chemical bonding. The barriers for the movement of the C_{60} on the silicon surface are, therefore, likely to be high. Nevertheless, manipulation of C_{60} on the Si(001) and Si(111) surfaces has been successfully achieved using STM both in the pushing and pulling regimes.[11–14] Notably, features (wave forms) in constant-current scan lines with periodicities of $2a_0$, $3a_0$, and $4a_0$ were observed in the pushing manipulation and those of $2a_0$ and, less frequently, $1a_0$ and $3a_0$, in the pulling manipulation modes[12,13] [$a_0 = 3.84$ Å is the periodicity of the surface, which is equal to the distance between surface dimers along the row on the Si(001) surface].

While there have been several theoretical studies of atomic manipulation[15,16] and the factors responsible for the attractive (pulling) or repulsive (pushing) regime in operation have been identified, such as the tip material, atomic structure, and tip height above the adsorbate, there have been fewer simulations of *molecular* manipulation. The pushing manipulation of large molecules, such as fullerenes[17] and Lander molecules,[6] has been modeled using molecular mechanics. A tip-free diffusionlike movement of the C_{60} molecule on the Si(001) surface[13,18] and its pushing manipulation on the same surface[19,20] have been studied in our group using density-functional theory (DFT) calculations. For this system, the pivoting mechanism was identified, which involves the C_{60}-surface bond breaking, pivoting over the remaining bonds, and the formation of new C_{60}-surface bonds. Most importantly, the bond formation between the tip and C_{60} was demonstrated for the pushing manipulation.[19,20] Pulling manipulation, however, to the best of our knowledge, so far has not been modeled for C_{60} or any other molecule.

Theoretical simulations can provide atomic-scale details of the pulling manipulation and elucidate the differences from the pushing mode. Here, we present the results of our theoretical *ab initio* modeling of the constant-height pulling manipulation of C_{60} on the Si(001) surface with several silicon tip models. We find that only some of the simulations result in displacing the molecule to a new position on the surface. The outcome of the manipulation, therefore, depends very strongly on the strength of the tip-C_{60} bonding, which in turn depends crucially on the structure and position of the tip with respect to the molecule along the manipulation path. We show that the structure of the tip plays a much greater role in pulling than in pushing. We calculate and analyze the forces acting on the tip during pulling. Finally, we compare our theoretical results with the experimental data on the attractive manipulation of C_{60} on the Si(001) surface.

I. METHOD

We use the density-functional code SIESTA,[21] which employs the generalized gradient approximation (Perdew–Burke–Ernzerhof functional[22] for exchange and correlation has been specifically used here), norm-conserving pseudopo-

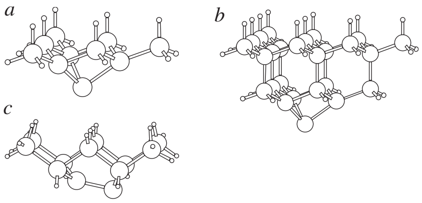

FIG. 1. Tip models: (a) small and (b) large (111)-oriented dangling-bond-terminated tips; (c) two-dangling-bond-terminated (001)-oriented tip.

tentials, and periodic boundary conditions. A localized double-zeta polarized basis set was used to describe the valence electrons, which is composed of 13 orbitals for both carbon and silicon, with maximum orbital radii of 5.5 and 6.9 bohrs, respectively. The mesh cutoff (which indicates the equivalent plane wave cutoff) used was 150 Ry.

Our computational cell contained a C_{60} molecule, a silicon slab consisting of six layers with eight Si dimers in the upper (surface) layer (96 Si atoms altogether, the bottom layer was terminated with H atoms), and a tip with 10–12 Si atoms and 15–20 terminating H atoms. A vacuum gap of 13 Å was present between the top of the C_{60} and the bottom of the periodically repeated silicon slab above it to avoid spurious interaction between the images. The coordinates of the two lowermost layers of Si atoms in the slab, the top layer of Si atoms of the tip, and all terminating H atoms of the slab and the tip were not allowed to relax. The remaining atoms were allowed to relax until the forces on the atoms were smaller than 0.02 eV/Å. Only a single **k** point was used in the calculations due to the large size of the simulation cell. The basis set superposition error (BSSE) correction was accounted for according to the Boys–Bernardi[23] counterpoise method as described in Ref. 24.

Electron density difference plots $\Delta\rho(\mathbf{r})$ for the "C_{60}+tip +Si(001)" system were used for analyzing the detailed changes in chemical bonding in the system along the whole manipulation path. They were calculated by subtracting the electron densities of the isolated C_{60}, tip, and surface from the electron density of the combined system, all in the optimized geometries of the combined system.

II. RESULTS

A. Tip models and tip interaction with C_{60}

We used two different tip models to simulate the pulling manipulation of the C_{60}: (i) the (111)-oriented atomically sharp tips of two sizes terminated with a single dangling bond and (ii) the (001)-oriented tip with two dangling bonds at its apex (see Fig. 1). The tip in Fig. 1(a) has been widely used for modeling SPM imaging and manipulation.[25–29] In particular, we used this tip structure to study the pushing manipulation of C_{60} on the Si(001) surface.[19,20] The tip in Fig. 1(c) was introduced in our simulations of the vertical manipulation of C_{60}.[30] Note that Giessibl and co-workers[26,31] used a (001)-oriented tip to simulate SPM images of the Si(111) surface, but their tip had only a single Si atom at its apex. Another (001)-oriented tip was used in Ref. 32. Since our tip in Fig. 1(c) has two dangling bonds, it is capable of forming two Si—C bonds with C_{60}, and, therefore, strong interaction between C_{60} and the tip can be modeled.

TABLE I. BSSE corrected interaction energies between C_{60} and silicon tips.

Tip position above C_{60}	Binding energy (eV)		
	Dangling-bond-terminated tip		Tip with two dangling bonds
	Small	Large	
2 Å above a C atom	−0.83	−0.78	
2 Å above a hexagon			−1.39
3 Å above a hexagon	0.01		−0.04
2 Å above a C=C bond	−0.42	−0.43	−1.76
3 Å above a C=C bond	0.04		

The interaction of these tips with the isolated C_{60} molecule was studied first, and the interaction energies are summarized in Table I. The tip with a single dangling bond forms chemical bonds with C_{60}, with the Si—C bond lengths of 2.0 Å and binding energies of up to 0.8 eV, depending on the tip position with respect to the molecule. Note that for the Si—C bonds to form, the double and single C—C bonds within C_{60} should be rearranged.

The interaction of the large and small single-dangling-bond-terminated tips with C_{60} was compared for several tip positions above the molecule. The binding energies (Table I) and the electron densities (not shown) for both tips were found to be very similar. Therefore, the large tip was not used in any of our manipulation calculations.

The tip with two dangling bonds forms two Si—C bonds with C_{60}. There are two positions of this tip that are favorable for bonding with C_{60}: Above a C=C bond with a binding energy of 0.88 eV/bond, which is similar to the binding energy for the tip with one dangling bond, and above a hexagon in C_{60} (0.7 eV/bond) when two Si—C bonds are formed at the opposite corners of the hexagon. This smaller (per bond) binding energy is explained by a stronger tip deformation: The Si—Si bond at the tip edge is significantly elongated (2.53 Å rather than 2.33 Å in the isolated tip, cf. 2.38 Å when the tip is above a C=C bond) and there is a significant rearrangement of single and double bonds in the C_{60} itself.

It is worth noting that for some orientations of the two-dangling-bond-terminated tip with respect to C_{60}, such as 30° or 90° rotated tip above the hexagon or the tip placed with its edge Si—Si bond perpendicular (rather than parallel) to the C=C bond of C_{60}, no C_{60}-tip bonding exists. Therefore, the tip-C_{60} bonding is subject to a favorable orientation of the tip with respect to the molecule.

It should be noted that the tips used in STM experiments are typically made of tungsten rather than silicon. However, due to the fact that the tips used in SPM experiments become easily contaminated with the surface material,[28] the usage of silicon tips for modeling the manipulation on the Si(001) surface is justified to ensure a correct description of the tip-molecule interaction.

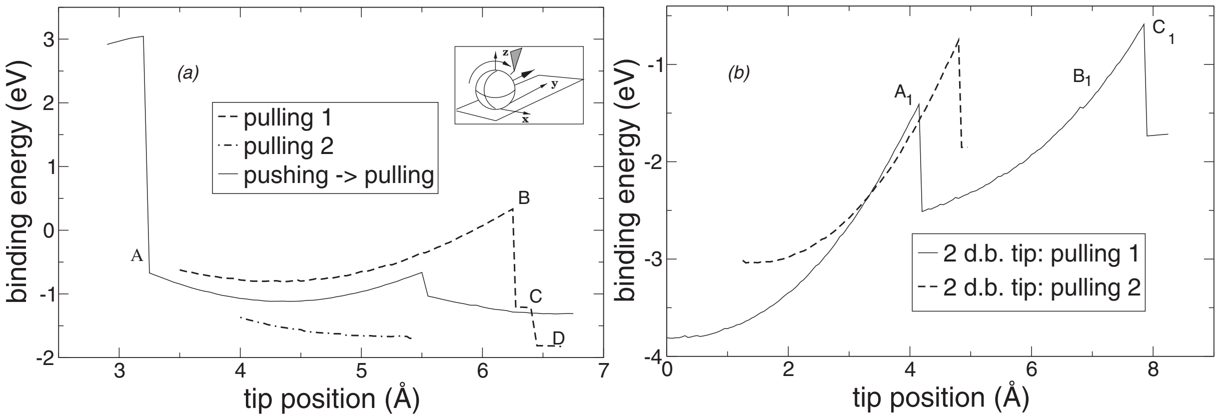

FIG. 2. Binding energies for the lateral pulling of C_{60}: (a) With the single-dangling-bond-terminated tip and (b) with the two-dangling-bond-terminated tip. The BSSE correction of 1.8 and 1.6 eV is included in (a) and (b), respectively. The horizontal coordinate corresponds to the position of the tip measured with respect to the center of mass of C_{60} in the initial equilibrium configuration. The inset shows the direction of axes of the coordinate system.

Our test calculations[35] showed that C_{60} binds to a model tungsten tip with the binding energies of up to 1.5 eV. However, our calculations also showed that the tungsten tip readily interacts with a Si atom, with the binding energies of 3.5–5.5 eV, depending on the number of W—Si bonds formed (one to three bonds). This strong binding energy between the model tungsten tip and Si atoms suggests that the tungsten tips used in experiments are likely to be covered with Si atoms or clusters when these tips are in contact with a silicon surface. Our calculations presented in the next section will show that Si clusters are stable during manipulation. We anticipate in experimental situations that unstable adsorbed clusters will be detached in early stages of experiments, while stable clusters will remain adsorbed and, thus, stable Si-covered tips will be formed.

B. Pulling manipulation of C_{60}

The movement of the C_{60} molecule on the Si(001) surface has been previously modeled in our group as a diffusionlike movement without the SPM tip.[13,18] After that, the pushing manipulation with a tip included explicitly in the calculations has been simulated.[19,20] These calculations showed that the molecule moves in a complex way involving both translational and rotational elements of movement. C_{60} in its stable adsorption configurations forms four Si—C bonds with the surface.[24] The atomic-scale mechanism of the molecule's movement on the surface involves consecutive breaking of the rear two (out of the four) C_{60}-surface bonds, then pivoting over the remaining two front bonds, and forming two new C_{60}-surface bonds. When the tip was included in the calculations,[19,20] an important additional feature emerged, which was the formation of tip-C_{60} bonds and the subsequent rearrangement of these bonds during manipulation.

The formation of tip-molecule chemical bonds during pulling appears to be even more important. Two outcomes of pulling the C_{60} with a tip are possible: (i) Either the C_{60}-surface bonds are too strong and remain intact, while tip-C_{60} bonds break, the molecule remains in its place on the surface, and the tip moves away (the unsuccessful outcome); or (ii) the tip-C_{60} bonds are strong enough and are preserved as the tip moves, while the two rear C_{60}-surface bonds break, facilitating the displacement of the molecule (the successful outcome). Thus, for the pulling manipulation to be successful, the tip should be able to form strong chemical bonds with C_{60}, which should be stronger than a pair of C_{60}-surface bonds. Both tips with one [Fig. 1(a)] and two [Fig. 1(c)] dangling bonds described in Sec. II A appear suitable, as they are able to form one or more bonds with C_{60}.

The starting structure in our simulations of the pulling manipulation was the C_{60} molecule adsorbed on the Si(001) surface above the trough between two dimer rows in the lowest-energy configuration *t*4*c*.[24] The tip was placed next to the molecule and then moved away from it along the trough at a constant height in discrete steps of 0.025 or 0.05 Å. The coordinates of the free atoms (see Sec. I) were relaxed for each tip position.

The binding energies calculated relative to the isolated C_{60}, tip, and the $c(4\times2)$ Si(001) surface (which is the surface ground state[33,29]) for several manipulation runs with the two tip structures are shown in Fig. 2. The values of BSSE were estimated at several points along the manipulation trajectory for both tips and were found to vary by ±0.2 eV around the mean values of 1.8 and 1.6 eV for the tips with one and two dangling bonds, respectively. The variation of the BSSE correction along the path is related to the presence or absence and the strength of the bonding between the tip and C_{60} (the correction is smaller for a weaker tip-molecule bonding). For simplicity and similar to our previous simulations of pushing of C_{60},[19,20] the constant mean values of BSSE were used here for all the energy curves. This assumption leads to a slight inaccuracy in our binding energies which, however, will not affect our conclusions.

The binding energies during simulations of pulling with the single-dangling-bond-terminated tip are shown in Fig. 2(a). Two separate simulations with the tip at two different initial positions with respect to C_{60} were performed. In both cases, the tip was placed ahead of the molecule along the trough with its apex Si atom at the same height as the top of the C_{60} molecule and formed several bonds with C_{60}.

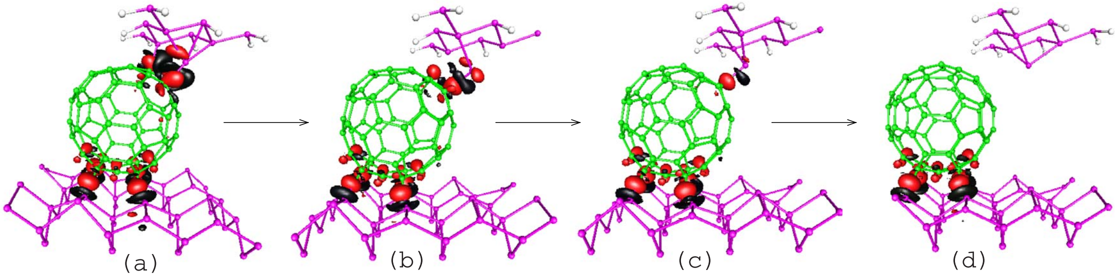

FIG. 3. (Color online) Electron density difference plots for pulling C_{60} with the dangling bond-terminated tip corresponding to the dashed line in Fig. 2(a). Black color denotes the lack, while (dark gray) the excess of electron density in the combined system (isosurfaces at $\pm 0.035e$) as compared to the isolated components. Labels A–D correspond to the bond rearrangement events marked on the energy curve in Fig. 2(a).

In the first of these simulations [the dashed line in Fig. 2(a)], the tip, which was positioned symmetrically above the trough, was only able to pull the C_{60} toward the pivoting point, after that the tip-C_{60} bonds proved to be not strong enough and gradually disappeared, as the tip moved. This is illustrated by the electron density difference plots shown in Fig. 3: The manipulation starts with many tip-C_{60} bonds (a strong redistribution of electron density at point A), the C_{60} moves forward by almost $a_0/2$ (point B), where the binding energy is slightly above zero due to a noticeable deformation of the tip and the molecule, resulting in the tip-C_{60} bonding becoming weaker (illustrated by the smaller electron density differences at points B and C) until it is completely broken, and the molecule returns to its original position [point D in Figs. 3 and 2(a)]. The binding energy at the final point (-1.83 eV) agrees well with that of the C_{60} on the $c(4\times 2)$-reconstructed Si(001) surface in configuration $t4c$ [-1.98 eV Ref. 24], i.e., there is no interaction between the tip and the surface-molecule system. (The slightly smaller binding energy is likely to be caused by the averaged values of the BSSE along the whole manipulation path used in these calculations.)

In the second case [the dot-dashed line in Fig. 2(a)], the tip was initially positioned at the same height as in the previous case, but asymmetrically, i.e., displaced toward one of the dimer rows, which led to a more favorable initial bonding configuration. However, this tip-C_{60} bonding arrangement also did not prove strong enough, as the bonds between C_{60} and the tip gradually disappeared during pulling, without C_{60} moving from its starting position by any appreciable distance.

From the failures of the above simulations, It may sound that the single-dangling-bond-terminated tip is incapable of pulling the molecule along the trough. Indeed, this tip has to break two bonds between the molecule and the surface during rolling, while keeping essentially a single tip-molecule bond. Interestingly, this conclusion about the inability of this tip to pull the molecule turned out to be false, and we discovered this through our studies of *pushing* manipulation. Indeed, one of our simulations of pushing manipulation using the same tip at the same height resulted in the tip first sliding over the C_{60} at the final phase of an elementary translation step $t4c \rightarrow t4g$ (see Ref. 18 for possible sequences of configurations), and then pulling the molecule into the next adsorption configuration $t4b$, as shown by the solid line in Fig. 2(a). Thus, we proved that if the position of the tip is chosen appropriately, even a single dangling bond tip may successfully pull the C_{60} between two equilibrium configurations.

The principal points of this successful pulling manipulation process are illustrated by the electron density plots in Fig. 4, where we show the tip above and slightly behind C_{60} before it slides above the molecule (the starting high-energy structure, the left image), the tip in front of C_{60} after it slid above the molecule (the middle image), and, finally, C_{60} in a different adsorption configuration after the pulling (the right image). Only a single pulling manipulation step took place. After that, upon a further tip displacement, the tip-C_{60} bonds were rearranged and eventually broken.

Notably, there was no pivoting point with only two C_{60}-surface bonds such as that observed in our previous tip-free simulations.[18] Instead, there was a *pivoting interval*, where C_{60} has five bonds to the surface: Two stronger ones in the middle and two rear and one front weaker bonds. The rear C_{60}-surface bonds were then broken, and one more front bond was formed to reach configuration $t4b$. Thus, the movement of the molecule proceeded via a modified pivoting mechanism, with extra C_{60}-surface bonds maintained during the rolling. This is due to the tip height being sufficiently low, which presses the molecule toward the surface.

The results of our simulations dicussed so far clearly prove that the success of the pulling manipulation depends strongly on the tip-C_{60} initial position, which determines the crucial bonding with the molecule. To investigate the effect of the tip structure and the C_{60}-tip bonding further, the two-

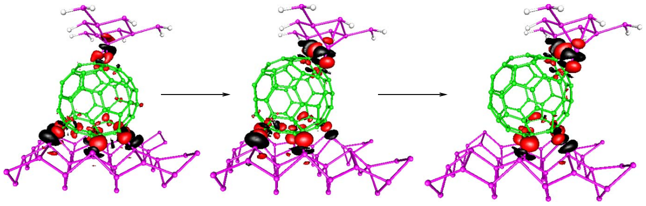

FIG. 4. (Color online) Electron density difference plot for the pulling manipulation of C_{60}, which was a continuation of rolling by pushing. See text for details and the caption to Fig. 3 for the explanation of the color scheme.

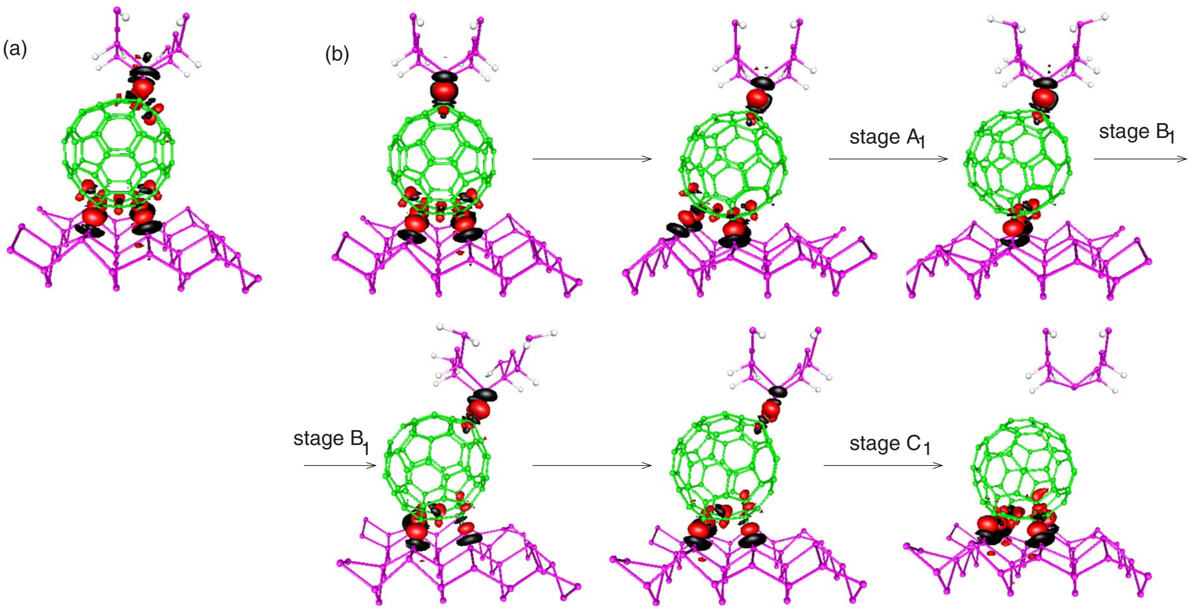

FIG. 5. (Color online) Electron density difference plots for the manipulation processes performed using the two-dangling-bond-terminated tip: (a) the starting configuration for the unsuccessful pulling manipulation and (b) the successful lateral pulling sequence.

dangling-bond-terminated tip of Fig. 1(c) was employed, which has a Si—Si dimer at its apex. The C_{60} in the configuration *t*4*c* has a C═C bond at the hexagon-hexagon junction at the top of the molecule. Two initial positions of the tip with respect to C_{60} were used, both discussed in Sec. II A: (i) The tip dimer aligned exactly with the top C═C double bond of C_{60}, so that the tip-C_{60} bonding produces a Si—C—C—Si four-membered ring [see the first image in the sequence in Fig. 5(b)], and (ii) the tip slightly displaced along the manipulation direction and positioned above the C_{60} hexagon, thus forming two Si—C bonds with two C atoms in the opposite corners of the hexagon [see Fig. 5(a)].

The height of the tip above C_{60} was varied for each of the two tip positions, and the optimum heights that gave the strongest bonding (2 and 1.5 Å above C_{60}, respectively) were used further in our constant-height manipulation simulations.

Of these two tip positions, the one with the tip above the hexagon [the dashed line in Fig. 2(b)] did not lead to a successful pulling manipulation. The possible reason for the relatively weak tip-C_{60} bonding in this case is in the significant elongation of the Si—Si tip apex dimer as a result of the bonding to C_{60}, and extensive single-double bond rearrangement in the C_{60} itself.

The configuration with the tip above a C═C bond, on the other hand, allowed performing a successful pulling manipulation of C_{60}. The principal stages of the manipulation procedure are illustrated by electron density difference plots in Fig. 5(b), while the bindng energy is shown in Fig. 2(b) with a solid curve. At first, after reaching the energy barrier, two rear C_{60}-surface bonds break, bringing an increase in the binding energy (stage A_1). There is a 2.6 Å long pivoting interval, where the molecule has only two bonds to the surface. Then, a new front Si—C bond is formed (stage B_1). Finally, the second front surface-C_{60} bond is formed; however, simultaneously the tip-C_{60} bonds break as well (stage C_1). The final binding energy (−1.72 eV) is close to the adsorption energy of C_{60} in the *t*4*g* configuration [−1.88 eV (Ref. 24)]. Thus, the tip was capable of bringing C_{60} into the next stable four-bond adsorption configuration, but was not able to pull the molecule further; i.e., the manipulation process was terminated after the very first elementary step.

Note that our manipulation simulations proceed at the constant tip height. In the constant-current pulling manipulation (the regime used in the experiment[13]), the tip is lowered by the feedback mechanism during manipulation and then raised after each successful manipulation event. Therefore, we investigated the effect of the feedback mechanism on the ability of the tip to maintain the chemical contact with the molecule after a successful manipulation step. We included the feedback mechanism in an approximate way by considering different tip heights at the final phase of the manipulation step, in order to compare the outcomes of the manipulation processes and to see if the continuation of the manipulation is possible. We found that if the tip is lowered by 1–1.5 Å at the end of the successful manipulation step, the tip-C_{60} bonds are retained. Therefore, we may assume that it should be possible for the tip to continue the manipulation from this new position. Thus, changing the tip height after each manipulation step (as is the case in constant-current experiments) is likely to be an essential factor in maintaining a long-distance pulling manipulation sequence.

The successful manipulation trajectories considered here involved the C_{60} moving from configuration *t*4*c* to *t*4*g* (manipulation with the two-dangling-bond-terminated tip) and from *t*4*g* to *t*4*b* (manipulation with the single-dangling-bond-terminated tip). These are, respectively, the first and second elementary steps in the predicted lowest-energy sequence of adsorption configuirations.[18] The same configurations were obtained in our tip-free[13] and pushing[19,20] simulations. Thus, the sequence of stable adsorption configurations does not depend on the particular bonding between the tip and the molecule, but rather on lowest-energy configurations available to the molecule being manipulated and the lowest barriers between them (corresponding to pivoting), as discussed in Ref. 18.

It is instructive to compare the pulling and the pushing[19,20] manipulation regimes. Note that the binding energies during all the pulling manipulation simulations (Fig. 2) are more negative, indicating a much stronger binding. In addition, unlike the case of the pushing manipulation, the barriers for pulling are much lower and the binding energies during pulling rarely reach positive values: Only one of the curves in Fig. 2 has energy values slightly greater than zero and this corresponds to an unsuccessful manipulation. (Note also that due to an approximate character of the BSSE correction, our binding energies may be about a few tenths of eV in error.) These observations are explained by the different mechanisms of the two manipulation regimes: During pushing, the molecule is trapped between the tip and the surface and is strongly deformed, leading to high barriers and positive binding energies. At the same time, during pulling, the molecule is in a less frustrated configuration: To relieve the strain caused by the pulling tip that is chemically attached to it, the molecule may either follow the tip (successful manipulation) or break bonds with it (unsuccessful). In either case, the deformation of the tip and the molecule never reaches very high values. Therefore, positive binding energies are not likely in pulling. When the binding energy becomes too low, manipulation can be terminated by the tip-molecule bond breaking, so that not all of the pulling manipulation attempts will result in the lateral translation of the molecule. In pushing, the only way for the system to relieve the strain is the forward movement of C_{60}, i.e., by overcoming the barrier for the manipulation.

One more point to note is that there are fewer bond rearrangement events during pulling as compared to pushing. Only C_{60}-surface, but not tip-C_{60}, bond rearrangements were observed. As a consequence, energy curves for pulling manipulation look much simpler and better structured than those for the pushing.[19,20]

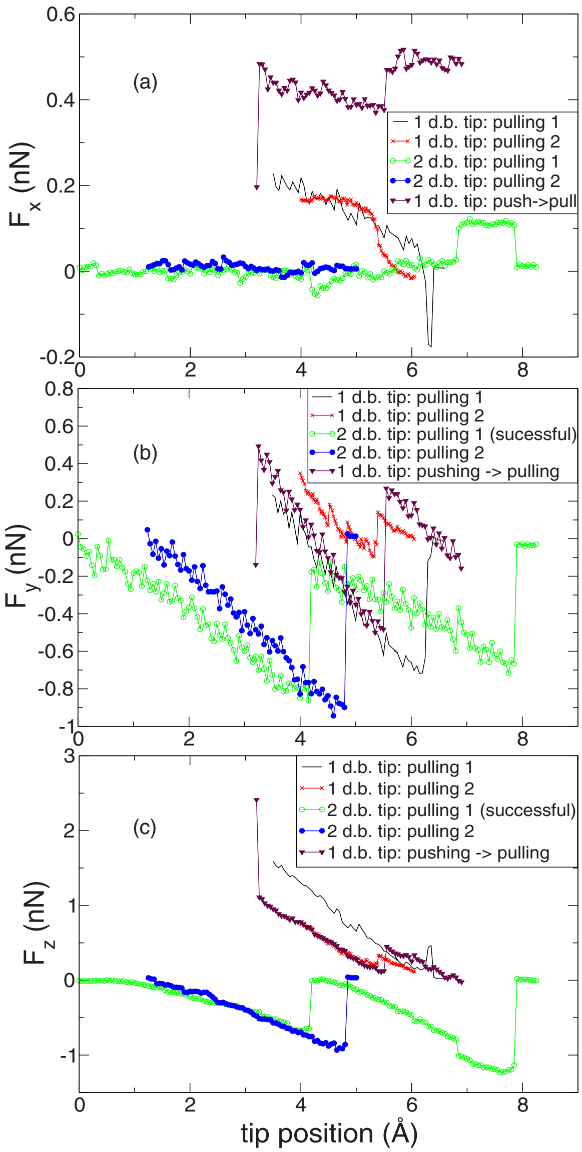

FIG. 6. (Color online) Tip forces F_x, F_y, F_z during pulling manipulations of C_{60}. See the inset of Fig. 2 for the definition of the coordinate axes.

C. Forces on the tip

Forces acting on the tip during manipulation can be obtained in our simulations by summing up the forces on the fixed atoms of the tip. The forces give invaluable information about the manipulation process since these can, in principle, be measured (e.g., Ref. 34). We analyze the forces in this section in order to find regular features typical for the pulling manipulation of molecules and to investigate the differences between the successful and unsuccessful manipulation attempts.

The calculated forces acting during the attractive manipulation of the C_{60} are shown in Fig. 6. These can be compared with the theoretical predictions by Pizzagalli and Baratoff,[16] who considered the tip forces acting during atomic manipulation, and with the calculated forces acting during the repulsive manipulation of C_{60}, which are reported by us elsewhere.[20,35]

It can be seen that F_x, which is the lateral force perpendicular to the manipulation direction, is close to zero in all cases but one, indicating that the molecule is placed symmetrically above the trough. Only in one case (pushing followed by pulling with the single-dangling-bond-terminated tip, triangles in Fig. 6) was the molecule positioned asymmetrically in the trough, resulting in a small nonzero value of the force.

Both F_y, which is the lateral force along the direction of the tip movement, and F_z, which is the vertical force, have a sawtooth shape very similar to that obtained by Pizzagalli and Baratoff for the attractive manipulation of atoms, except that each "tooth" of our molecular manipulation curves corresponds to a single bond rearrangement rather than to the whole manipulation event. The shapes of both F_y and F_z are characteristic of a stick-slip behavior: An abrupt change of the force corresponds to a sudden change in the structure after a long preparation period.[36]

The force F_y for pulling is always negative, i.e., directed toward C_{60}, which is opposite to the direction of the tip movement. Note for comparison that in the case of pushing,[20] the force F_y is also negative, but since the tip is behind the molecule, the tip force is directed away from the molecule. In simple terms, one can imagine that the tip is attached to C_{60} with a spring, which is compressed in the case of pushing and expanded during pulling. In all pulling attempts, the force increases (becomes more negative) and then abruptly decreases to zero or near-zero values when either the tip-C_{60} bonds are broken (unsuccessful manipulation) or the rear C_{60}-surface bonds are broken, and the C_{60} enters the pivoting interval (in the case of successful manipulation). In the case of the successful manipulation with the two-dangling-bond-terminated tip, F_y increases again after the rear C_{60}-surface bonds break and then drops to zero, at the end of the manipulation event, when the new front bonds are formed simultaneously with the tip detaching from C_{60}. The F_y curve for this successful manipulation, thus, has two distinct sections.

The vertical force F_z behaves differently and has different directions during pulling, with the tips terminated with one or two dangling bonds. Recall that the first of these tips was initially located in front of the molecule, with the tip apex at the same height as the top of C_{60}, whereas the second tip was positioned either at 1.5 or 2 Å above the molecule in our simulations. In the case of the unsuccessful pulling with the single dangling bond tip (solid line in Fig. 6), when the tip is not high above the molecule, F_z is initially positive, i.e., the tip is repelled by the molecule. Then the force decreases rapidly to zero as the tip moves forward and its interaction with C_{60} is weakened. The only slight increase of this force occurs when the tip-C_{60} bonds are rearranged before the last bonds are finally broken. In the successful manipulation with this tip (triangles in Fig. 6), F_z first drops from high positivie values, characteristic for the pushing, to almost zero, and then slightly increases to positive (repulsive) values again after one manipulation step is accomplished.

The two-dangling-bond-terminated tip is kept rather high above the molecule, therefore the vertical force F_z is nearly zero at the beginning, but turns to negative values during manipulation. Therefore, the tip is attracted to the molecule and not repelled like in the previous example. The force curve for the successful manipulation (open circles) has a sawtooth shape with two "teeth": (i) From the start of the manipulation until the point where the rear C_{60}-surface bonds are broken, and (ii) until the new front C_{60}-surface bond is formed and the C_{60}-tip bond is ruptured. The event of the first front C_{60}-surface bond formation, which causes a very small (and barely noticeable) change in the binding energy in Fig. 2(b) (at the tip position close to 6.5 Å), can be identified as a small increase of the (negative) force F_z. Finally, when the second front C_{60}-surface bond is formed and the tip is detached from the C_{60}, the force F_z abruptly decreases to zero.

One can notice that both F_y and F_z in Fig. 6 increase less rapidly during successful manipulations than during those, which eventually become unsuccessful. This may point to the reason why some of the manipulation simulations were unsuccessful: The tip-C_{60} system becomes strained very quickly, and the tip-C_{60} bond breaking is the only available bond rearrangement process that can relieve the frustration in this system. This observation may be useful in identifying a successful, as opposite to unsuccessful, manipulation in actual experiments.

By comparing the forces during pulling (Fig. 6) and pushing,[20] we can see that the pattern of forces, especially F_z, is much simpler in the former case. All bond breaking and rearrangement events can be clearly seen in the pulling force curves.

III. DISCUSSION

There are only a few experimental studies of pulling manipulation of molecules with STM, which can be compared with our theoretical results. C_{60} molecules have been manipulated in the pulling as well as pushing regimes.[12,13] Keeling *et al.*[12] obtained tip trajectories of both pushing and pulling and studied the probability of occurrence of each type of manipulation for a range of tip heights. They found that the pushing (repulsive) regime of manipulation takes place predominantly when the tip is low above the surface. When the tip height increases, the probability of pushing manipulation decreases to almost zero, but there is an appreciable probability of pulling manipulation (up to 15%). Altogether, an 8 Å interval of tip heights was investigated in Ref. 12. Pushing was the predominant regime for the lowermost 3 Å. For the next 4–5 Å, the probability of pushing was practically zero, whereas the probability of pulling reached a maximum of 15% and then fell to zero. The importance of the tip height in manipulation was also emphasized in experiments using other molecules.[7–9]

The qualitative experimental findings on C_{60} manipulation can be explained using the results of our calculations. While successful pushing manipulation was modeled with the tip heights of up to 0.5 Å above C_{60},[19,20] successful pulling manipulation was achieved in our calculations when the tip was higher (up to 2.0 Å above C_{60}). The reason for this is clear: If the tip is not sufficiently low, the pushing regime that relies heavily on trapping the molecule between the tip and the surface will not work. At the same time, in the pulling regime, only the bonding between the tip and the molecule is important. The favorable tip heights start from the heights corresponding to pushing. One example is our successful pulling manipulation with the single-dangling-bond-terminated tip, which was a continuation of the interrupted pushing manipulation and involved the tip sliding above the molecule. Thus, we can conclude that there are three intervals of tip heights where either pushing or pulling is the preferred regime: (i) If the tip apex is at the same or lower height than the top of C_{60}, then the manipulation regime is predominantly pushing (corresponds to the first 3 Å of tip heights in the manipulation experiments[12]); (ii) both regimes of manipulation are possible when the tip is approximately at the same height as the top of the molecule (the tip sliding above the molecule that we observed in our simulations is a plausible mechanism of transition from pushing to pulling); (iii) at higher tip positions, pulling is the only possible regime. When the tip is higher than ~2 Å above C_{60}, Si—C bonds between the tip and the molecule do not form and, thus, any tip-induced manipulation becomes unlikely.

Our theoretical studies also showed that only a few of the pulling simulations resulted in a successful manipulation of the C_{60} molecule. This agrees with the observed low success rate for the pulling manipulation experiments.[12] Unlike pushing, which is a very robust procedure that can be terminated only due to a permanent tip deformation or the tip sliding above the adsorbate, pulling relies strongly on the strength of the tip-molecule bonding. This means that the outcome of the pulling manipulation strongly depends both on the tip structure and on the tip position with respect to the molecule. This conclusion is confirmed by our theoretical results. For example, the dangling-bond-terminated tip was able to pull the molecule only in one of our three calculations. The two-dangling-bond-terminated tip is able to form two strong bonds with C_{60} and is, thus, more efficient in pulling the molecule, but the outcome also depends on the details of the tip-C_{60} bonding.

In some experiments, long-distance pulling manipulation sequences where the molecule moved in steps of $2a_0$ or, less frequently, a_0 and $3a_0$ (Ref. 12) have been recorded alongside single manipulation events. The results of our calculations may shed light in understanding how pulling may lead to long periodic manipulation sequences, in spite of the fact that only one pulling manipulation step has been actually achieved in our calculations. To maintain a continuous long-distance manipulation, the tip should preserve the strong bonding with the molecule along the whole path. Since the molecule rolls, this means that tip-C_{60} bonds should be continuously rearranged, which is not helped by the tip maintained at the same height. On the other hand, in the constant-current experiments, the tip height is constantly changing, facilitating the tip-molecule bond formation after each elementary translation. Indeed, after the molecule has jumped toward the tip during pulling, the tip is retracted from the surface by the feedback system and then lowered back to be chemically attached to the molecule again and, thus, to initiate a new elementary translation. Thus, in this case, the problem of rearranging the bonds between the tip and the molecule due to the molecule rolling may be assisted by the feedback system.

Nevertheless, according to Ref. 12, single hops of C_{60} during pulling manipulation are more common than multiple hops (long-distance manipulation). The "statistical nature of the outcome of manipulation attempts"[12] was attributed to the variations in the tip configuration and tip-C_{60} chemical bonding, which is in agreement with the results of our calculations.

While experiments[12] were done at room temperature, our DFT calculations correspond to $T=0$ K. At room temperature, the thermal energy of the molecule will help the molecule to overcome energy barriers for processes like bond rearrangements (both tip-C_{60} and C_{60}-surface bonds). This is expected to result in smoothing out the tip trajectories during manipulation.

We have neglected the effect of the electric current and applied bias voltage in our calculations, since we believe that these factors will have a weak effect on the manipulation process (unless the bias is very strong and changes the electronic structure of the molecule). We believe that the current is used in manipulation experiments solely to control the tip position, and has a small effect on the electronic structure of molecules and, therefore, on manipulation, much smaller than the chemical effect of the tip-C_{60} bond formation. The weak effect of the applied bias voltage is confirmed by the fact that attractive manipulation takes place for both polarities of the bias voltage.[12]

CONCLUSIONS

This paper presents the results of theoretical simulations of the pulling manipulation of a C_{60} molecule on the Si(001) surface with two different types of silicon tips. Two different outcomes were observed: Either manipulation takes place or the tip-molecule bonds are broken and the molecule remains in its original position. When the successful manipulation does happen, the atomic-scale mechanism of the C_{60} translation is based on pivoting, which is in agreement with the earlier tip-free modeling.[13,18] The outcome of each particular manipulation depends on the tip structure and the position relative to the molecule, i.e., eventually on the details of the tip-C_{60} bonding. A transition from pushing to pulling manipulation was also observed: The tip slid above C_{60} and then succeeded in pulling the molecule into the next adsorption configuration.

The forces F_y and F_z acting on the tip during pulling were calculated and were found to have a sawtooth shape, like in the simulations of atomic manipulation,[16] and their structure was found to be much simpler than the forces during the pushing manipulation of C_{60}.[20,35] In the unsuccessful manipulation simulations, the gradient of the forces is greater and the forces reach larger values. This observation may be useful in distinguishing successful and unsuccessful manipulation trajectories in real experiments by recording and comparing the tip forces.

The fact that only a few of our pulling simulations were successful and resulted in a displacement of the molecule into the next adsorption configuration underscores the importance of the tip-C_{60} bonding and the structure of the tip. A suitable tip model is needed to describe each type of the manipulation processes. In particular, pulling manipulation requires a tip that is positioned favorably to the molecule so that it can attach to it strongly.

Based on the experimental results[12] on the success rate of manipulation and on our constant-height theoretical simulations, repulsive (pushing) manipulation can be regarded as a more efficient manipulation approach than pulling (the attractive mode). The pushing manipulation always happens, independent of the tip structure, provided that the tip is kept sufficiently low above C_{60} (otherwise, it will simply pass above the molecule without displacing it). It follows from our calculations that the most likely mechanism for the termination of long pushing manipulation sequences is based on the tip sliding over the molecule with the subsequent rupture of the tip-molecule bonds. In some cases, one or more pulling manipulation elementary steps might be possible after this sliding before the tip is completely detached from the molecule. Attractive manipulation is only possible if there is strong bonding between the tip and the molecule. The outcome of pulling manipulations, therefore, depends strongly on the tip structure and the exact position relative to the molecule, and these are difficult to control in real experiments. A long-range pulling manipulation is difficult to achieve in constant-height manipulation experiments, but it should be greatly facilitated in the constant-current mode.

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