

Bond Breaking Coupled with Translation in Rolling of Covalently Bound Molecules

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The response of a C_{60} molecule to manipulation across a surface displays a long range periodicity which corresponds to a rolling motion. A period of three or four lattice constants is observed and is accompanied by complex subharmonic structure due to molecular hops through a regular, repeating sequence of adsorption states. Combining experimental data and *ab initio* calculations, we show that this response corresponds to a rolling motion in which two of the four Si- C_{60} covalent bonds act as a pivot over which the molecule rotates while moving through one lattice constant and identify a sequence of C_{60} bonding configurations that accounts for the periodic structure.

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Since the original demonstration that atoms and molecules may be laterally translated using the tip of a scanning tunneling microscope (STM) [1], there has been great progress in understanding molecular manipulation. Attractive, repulsive, and sliding modes of lateral translation may be identified [2], while more recently, STM induced changes in the internal conformation of large molecules, such as the Landers, have been demonstrated [3,4]. Many of these advances have been focused on relatively weakly bound adsorbates using an STM operating under low temperature conditions [5–9]. However, for manipulation under room temperature conditions [10–12], many adsorbates of interest are bound by strong covalent bonds [10], and the mechanisms of manipulation, particularly the role of bond breaking, are not well understood. Here we report the measurement of a complex tip trajectory which, combined with *ab initio* density functional (DFT) calculations, provides new insights into the dynamical response of covalently bound molecules to manipulation. In particular, we show that the sequential breaking and reforming of highly directional covalent bonds results in a dynamical molecular response in which bond breaking, rotation, and translation are intimately coupled in a rolling motion.

Molecular rolling is characterized by an STM tip trajectory which has a long range periodicity and a complex subharmonic structure. We have observed these trajectories in a study of the model system of C_{60} on Si(100)-(2 × 1) [13–15]. For our experiments we prepare a Si(100)-(2 × 1) surface under ultrahigh vacuum conditions (UHV) by annealing (1200 °C for 1 min) a 4 × 7 mm² piece of a *p*-type wafer. Submonolayer coverages of C_{60} were deposited by sublimation. Images of the surface were acquired using an STM operating at room temperature which was housed within the UHV system. Electrochemically etched tungsten tips, which were cleaned by electron beam heating, were used for both imaging and manipulation.

A typical STM image of C_{60} adsorbed on Si(100)-(2 × 1) is shown in the inset to Fig. 1. The (2 × 1) reconstruc-

tion of Si(100) results in the formation of rows of Si dimers which are resolved in the STM image as bright horizontal lines [16]. C_{60} is chemisorbed at the center of the trough between dimer rows (see Fig. 2) through the formation of Si-C covalent bonds as shown by STM [17,18] photoelectron spectroscopy [19,20] and confirmed by *ab initio* calculations [21–23] (see also below).

We have previously shown that C_{60} may be manipulated along the troughs through either an attractive or a repulsive

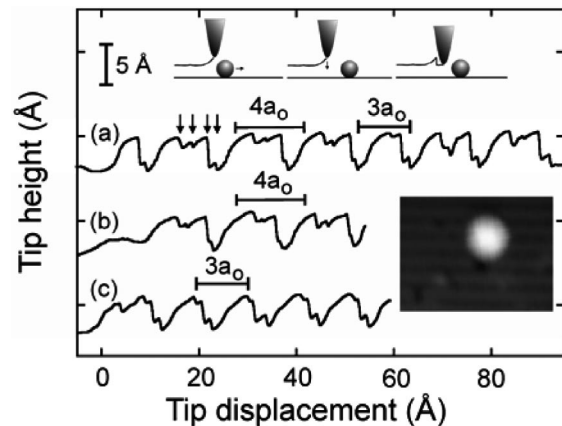


FIG. 1. Measured tip trajectories acquired during repulsive manipulation. Curve (a) shows clear periodic structure with a period of $4a_0$ apart from a short section of length $3a_0$ between ~ 55 and ~ 65 Å. The waveform shows clear subharmonic structure and provides clear evidence that the translational manipulation of the molecule is coupled with a change in rotational configuration. Curve (b) also shows a periodic response with a period of $4a_0$ and a waveform which is very similar to curve (a). Curve (c) shows a response with a period of $3a_0$. Note the similarity between this waveform and the $3a_0$ section identified in curve (a) indicating that the $3a_0$ response is a modified $4a_0$ response. The upper inset shows a schematic of the sawtooth tip response during repulsive manipulation [2], and the lower inset shows an STM image of C_{60} on Si(100)-(2 × 1). Sample voltage and tunnel current for these traces were (a) -1.9 V, 1.3 nA; (b) -1.7 V, 1.1 nA; (c) -1.6 V, 1.1 nA.

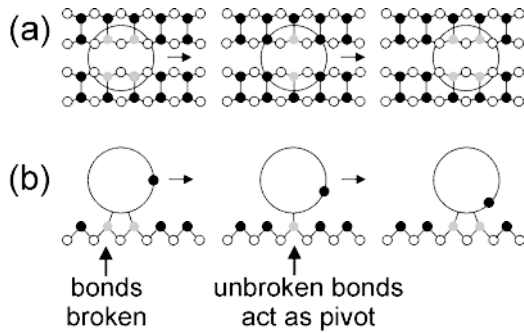


FIG. 2. Schematic diagram of the proposed rolling mechanism for C_{60} manipulation. (a) and (b) are, respectively, top and side views of the rolling. Filled and empty circles represent, respectively, top- and second-layer Si atoms, and the Si atoms to which C_{60} is bonded are shaded in gray. The stable adsorption site for C_{60} is centered midway between four Si dimers. The approximate position of the atom constrained in the simulations is highlighted in (b).

mode of manipulation [13,14]. In order to manipulate molecules, the tip is positioned above a trough between dimer rows close to, but not directly above, a target molecule. The tip-sample separation is reduced by adjusting the tip current and sample voltage and the tip is then moved along the trough in steps of $\Delta x (= 0.14 \text{ \AA})$ towards the target molecule (see inset to Fig. 1). In common with previous work, feedback control of the STM tip is maintained during manipulation by adjusting the tip height after each step. The dwell time of the tip after moving through each step of length Δx was typically 1–5 ms and the movement in discrete steps was continued while manipulating molecules. For an appropriate choice of tunnel current and sample voltage, typically $\sim 1 \text{ nA}$ and $\pm 1 \text{ V}$, respectively, the molecule is manipulated by the tip along the trough.

The tip height is recorded during this procedure and Fig. 1 shows a series of measured trajectories, which, as we demonstrate below, are characteristic of molecular *rolling*. Repeating sequences are clearly observed in all curves. In curve (a), the molecule is displaced over $\sim 100 \text{ \AA}$ while the tip follows a trajectory in which the dominant periodicity is equal to $4a_0$ ($a_0 = 3.84 \text{ \AA}$ is the surface lattice constant, i.e., a lateral separation of Si dimers). Curve (b) shows another tip trajectory which also displays a periodicity of $4a_0$ and has a periodic waveform very similar to that observed in curve (a). There is also a clear repeating waveform in curve (c); however, in this case the period is $3a_0$. Many other traces showing similar periodic responses have been acquired. We have observed some variation in the subharmonic structure of the waveforms, but the only periodicities clearly observed are $3a_0$ and $4a_0$. Similar traces are observed using tunnel currents and bias voltages down to 0.05 nA and 0.1 V, respectively.

The abrupt variations in tip height in the curves in Fig. 1 are characteristic of repulsive manipulation [2] (see sche-

matic inset to Fig. 1). The points at which the molecule is manipulated are marked by arrows for the first periodic sequence in curve (a). The subharmonic features in the $4a_0$ periodic waveform are attributed to four hops, each through a single lattice constant. Similarly, the $3a_0$ periodic waveform is composed of three hops through a single lattice constant.

The subharmonic structure in Fig. 1 shows that there is a periodic variation of the tip height at the point where manipulation occurs. This indicates that the molecule sequentially adopts nonequivalent adsorption states and must move through as many as four translational steps, each of a single lattice constant, before returning to an equivalent configuration. Most importantly, the periodic traces in Fig. 1 provide direct experimental evidence that a common mechanism must be responsible for lateral translation and the change in adsorption configuration. We attribute the configurational change to a sequence of different molecular orientations and propose a model for manipulation based on a rolling motion in which two of the four Si-C bonds linking C_{60} to the Si(100)-(2 \times 1) surface act as a pivot around which the molecule rotates.

A schematic of the proposed rolling mechanism, in which a displacement of one lattice constant is accompanied by a change in orientation, is shown in Fig. 2. Consider Fig. 2(a) (far left), which shows a C_{60} molecule in a four dimer site. Si-C bonds are formed between the molecule and one Si atom from each of the four dimers above which it is adsorbed [highlighted atoms in Fig. 2(a)]. Figure 2(b) shows a side view. As the molecule is displaced from left to right, the leftmost two bonds are broken while those to the right remain intact and act as a “pivot” over which the molecule rolls. This process minimizes the number of broken bonds during manipulation and is expected to lead to a minimum energy barrier for translation.

The pivoting of the molecule over two unbroken bonds leads to a coupling of rotation and translation and is the central hypothesis of our model. To determine the validity of this hypothesis, and to determine candidate sequences of adsorption states which satisfy the observed periodicities, we have undertaken extensive *ab initio* DFT calculations. We use periodic boundary conditions, the generalized gradient approximation, norm-conserving pseudopotentials, and a localized numerical basis set as implemented in the SIESTA package [24]. Computational details are similar to those used in our previous study of this system [23]. Nine stable orientations of C_{60} between four dimers in the Si(001) trench have been identified (including four previously reported [21,22]) with adsorption energies between 3 and 4 eV due to four Si-C bonds formed between the molecule and the Si surface as discussed above.

We focus on the most stable configuration *t4c* (see the top right image in Fig. 3; the nomenclature is chosen for consistency with previous work) and use a constrained minimization technique to move the molecule along the

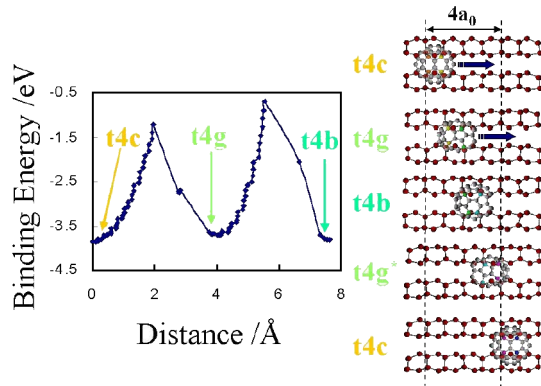


FIG. 3 (color online). The variation of calculated energy with center of mass of the C_{60} molecule as it moves through the first two elementary steps of the $4a_0$ sequence of C_{60} rolling: $t4c \rightarrow t4g \rightarrow t4b$. The actual relaxed geometries of the stable configurations (top view) are also shown on the right-hand side. Note that only lower C atoms of the fullerene cage are actually shown for clarity. All pivoting C atoms have different colors, which they preserve as the molecule rolls. Other C atoms directly facing the surface are shown in gray. The full sequence of adsorption states in the $4a_0$ periodic trace are shown: $t4c \rightarrow t4g \rightarrow t4b \rightarrow t4g^* \rightarrow t4b$.

trench. In this method one atom of the fullerene cage, the approximate position of which is shown in Fig. 2, is displaced along the trough (taken as the x direction for convenience) by 0.05 \AA . The x coordinate of the atom is then fixed, while its y and z coordinates, all coordinates of the other 59 atoms of the C_{60} molecule, as well as the coordinates of all the atoms in the upper four layers of the Si slab simulating the Si(001) surface, were allowed to relax until the forces on all atoms are smaller than 0.04 eV/\AA . This process is performed repeatedly and serves to move the C_{60} molecule along the silicon trench in small quasistatic steps. Note that the diffusion barriers calculated using this approach are upper bounds.

As the molecule is displaced, the leftmost two bonds are stretched resulting in a decrease of the binding energy. The variation of binding energy with position of the center of mass of the C_{60} molecule is shown in Fig. 3. On displacing the molecule through $\sim 2.0 \text{ \AA}$ the binding energy is reduced by $\sim 2.6 \text{ eV}$ after which it increases by over 1.5 eV as the two stretched bonds are finally broken. (Note that in successive points in Fig. 3 the constrained atom in the C_{60} cage is displaced in regular steps of 0.05 \AA ; the large displacement of the center of mass accompanying the decrease in total energy is a consequence of the relaxation of the C_{60} cage distortion following the breaking of the Si-C bonds.) The molecule then adopts an intermediate state in which it is attached to the surface by only two Si-C covalent bonds. The intermediate state is highly unstable to any lateral displacement and the proposed pivoting action is evident as the molecule undergoes a transition to a new configuration in which two new bonds are formed with a

different hexagon-pentagon face of the cage. Note that in this configuration there are also four Si-C bonds, two of which are unbroken during this elemental rolling step. Although the starting configuration is highly symmetrical, our calculations demonstrate that C_{60} arrives at an asymmetric state $t4g$ (see Fig. 3). This is a consequence of the dimer buckling which breaks the surface symmetry.

A continuation of the *ab initio* calculations to determine the binding energy variation during a further hop of the molecule shows (see Fig. 3) a second abrupt increase in binding energy as the leftmost bonds of the $t4g$ configuration are broken and the molecule undergoes a transition to the symmetrical $t4b$ state, Fig. 3. As in the first hop, two of the bonds in the $t4g$ configuration remain unbroken in this transition.

The results from the *ab initio* calculations confirm our basic hypothesis: in undergoing a translational step of a_0 the molecule pivots over two unbroken bonds. The coupling of rotation and translation through the bond pivot model determines the possible transitions between rotational configurations of the molecule. Because of the symmetry of configurations $t4c$ and $t4b$ it is possible to identify a sequence of stable configurations that has an overall periodicity of $4a_0$: $t4c \rightarrow t4g \rightarrow t4b \rightarrow t4g^* \rightarrow t4c$ ($t4g^*$ is obtained from $t4g$ by a reflection through a plane perpendicular to both the surface and the dimer rows, and the ground states of these two configurations are therefore physically equivalent). Thus the molecule returns to a $t4c$ configuration after four translation steps of a_0 and a 180° rotation; see Fig. 3.

We have investigated many other molecular configurations and it is possible to identify other sequences which satisfy the constraints of bond pivoting and also give a periodicity of $4a_0$ [25]. In the sequence identified above, the molecule undergoes transitions between the three most stable adsorption configurations.

The model of pivoting over unbroken bonds successfully accounts for the $4a_0$ periodic data. However, there is no sequence with $3a_0$ periodicity which combines translation and rotation in a similar rolling motion. In fact, we propose that the $3a_0$ periodic sequence is a variant of the $4a_0$ sequence in which an alternative change in configuration occurs in one of the translational steps. This conclusion may be drawn from sections of the data in Fig. 1 where there is a switch from $4a_0$ to $3a_0$ periodicity. In particular, in curve (a) there is a section of length $3a_0$ (from ~ 55 – 65 \AA) embedded between two extended sections with $4a_0$ periodicity. The close similarity between the subharmonic structure in the $4a_0$ periodic sequences before and after this section provides direct evidence that following this section of $3a_0$ the molecule is in an identical configuration to that which recurs after a $4a_0$ periodic sequence. Furthermore, analysis of this section shows that it is composed of subsections of the $4a_0$ periodic waveform, indicating that over this interval the molecule

has a modified response in which two out of the three translational steps conform to the bond pivot model described above. In the remaining single translational step a more complex transition occurs in which the change in configuration is equivalent to two rotations. There are many complex trajectories through configurational space which combine translation with rotations about axes parallel and perpendicular to the surface and would result in the breaking of three or even all four Si-C bonds. For example, the high symmetry of the C_{60} molecule allows a direct transition from $t4g$ to a configuration equivalent to $t4g^*$ by allowing three bonds to be broken. In this case, a $3a_0$ waveform is recovered.

In light of the discussion we therefore conclude that the $3a_0$ section identified in curve (a) is a signature for a sequence in which a molecular rotation of 180° is combined with three translational steps. We note the very close similarity between this section and the subharmonic structure in curve (c), Fig. 1. From this we conclude that the $3a_0$ periodic structure is a repeating sequence of 180° rotations combined with three translations, i.e., a modified $4a_0$ periodic sequence.

We have observed several other traces in which there is an apparent switch between the $4a_0$ and the $3a_0$ periodic response. In addition, we have observed traces in which either the $3a_0$ or the $4a_0$ periodicity is observed but the relative weights of the peaks within the repeating waveform are slightly different to those in Fig. 1. In a small number of cases we observe that the relative heights of the peaks within the repeating waveform vary in a regular manner during a manipulation sequence. We attribute these differences to unavoidable variations in both the initial tip position and also the orientation of the tip trajectory relative to the dimer rows.

Our results show that motion induced by the STM for covalently bound molecules is controlled by bond breaking. The highly directional nature of covalent bonds constrains the possible trajectories of molecules and can lead to a complex sequence of coupled rotational and translational dynamics. The methodology and results we have presented will underpin further advances in the handling, manipulation, and bond breaking of covalently bound systems.

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