Lateral translation of covalently bound fullerenes

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Abstract
Lateral manipulation of fullerenes on clean silicon surfaces may be induced by
either an attractive or repulsive interaction between adsorbed molecules and the
tip of a scanning probe microscope, and can result in a complex response arising
from molecular rolling. The model for rolling is supported by new results which
show that manipulation is suppressed for adsorbed functionalized fullerenes due
to the presence of phenyl sidegroups. The influence of varying the dwell time
of the tip during manipulation is also reported. By reducing this time to a value
which is less than the response time of the feedback control loop it is possible
to induce manipulation in a quasi-constant height mode which is accompanied
by large increases/decreases in current.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The proximal forces between the tip of a scanning tunnelling microscope (STM) and adsorbates
bound to surfaces have been widely exploited for controlled lateral positioning of atoms
and molecules [1–9]. Much of this work has concentrated on the properties of molecules
adsorbed on metal surfaces and is performed under low temperature operation to suppress the
spontaneous diffusion of these relatively weakly bound adsorbates [1–3, 8, 9]. Over several
years we have investigated the response to STM manipulation of adsorbates which are bound
more strongly, by directional covalent bonds, to a substrate surface [4, 10–14]. In order to
initiate manipulation for such systems the forces between the tip and the adsorbate must be
sufficiently large to break the covalent bonds which bind the molecules to the surface. Much of
our work has focused on fullerenes which are chemisorbed on Si surfaces through the formation
of Si–C covalent bonds [14–20]. The diffusion barriers for these strongly bound adsorbates
are sufficiently large to allow manipulation studies at 300 K and the fullerene/silicon system
remains one of the few to be extensively studied at room temperature.

In this paper we briefly review our previous work and present new results showing that manipulation of fullerenes may be achieved in a quasi-constant height mode of operation. We also show that manipulation is suppressed for fullerenes to which bulky sidegroups are attached. These observations provide further support for our model of fullerene rolling on Si surfaces.

Our initial studies of C_{60} on Si focused on manipulation on the Si(111)-7 × 7 surface leading to the first published demonstration of lateral positioning of molecules at room temperature [4]. Manipulation on the hexagonal Si(111) surface was found to be very difficult to control since the actual trajectory of the molecule was often at an angle to the intended trajectory. For this reason attention was switched to the Si(100)-2 × 1 surface on which rows of dimers are formed. We found that these rows provided enhanced control of the placement of molecules by effectively acting as corrugations along which the molecule could be manipulated. This control is effective only for displacements of the molecule parallel to the rows and a strong anisotropy in response to manipulation was observed with a lower success rate, and very limited directional control, for manipulation across the rows. On the Si(100)-2 × 1 surface it was shown later that other fullerenes such as the azafullerene $C_{59}N$ [12] and endohedral fullerenes [13] could also be manipulated, indicating that this is a general property of this class of cage-like molecules, and is not uniquely related to the detailed electronic structure of any particular fullerene.

Our more recent results have focused on an investigation of the nature of the tip–molecule forces and the dynamical response of molecules which may be deduced by recording the trajectory of the tip during manipulation following the approach of Bartels *et al* [2]. In particular, we have confirmed that manipulation is controlled by a repulsive tip–molecule interaction for the most extreme tunnelling conditions (typically 1 nA, 1 V), but, unexpectedly, an attractive mode of manipulation is also observed for higher gap impedances [11]. For molecules which are sufficiently strongly bound that diffusion is inhibited at room temperature, a large force is required to initiate manipulation. Simple order of magnitude arguments show that these forces must be comparable with the strength of a covalent bond. A repulsive mode of manipulation might be expected since an arbitrarily large repulsive force may be generated between the tip and the adsorbate. This is a consequence of the monotonic increase in repulsive force with reducing tip–sample separation which is expected for a Lennard-Jones intermolecular potential. In contrast, the attractive proximal forces are always limited to some maximum magnitude and it is not obvious, *a priori*, that this magnitude will be sufficiently large to overcome the molecule–substrate bonding as required for manipulation. As we have pointed out previously, the observation of an attractive mode of manipulation for a covalently bound species such as C_{60} implies that an attractive interaction between the tip and the molecule can occur which is comparable in strength to a covalent bond [11]. This interaction may thus be classified as a chemical force although its detailed origin remains unclear. Finally we have recently shown in collaboration with Kantorovich and co-workers [14] that the bond breaking, which must occur in lateral translation of covalently bound molecules, may be coupled with rotation leading to a rolling motion of C_{60} across the Si(100)-2 × 1 surface.

2. Experimental details

Clean Si(100)-2 × 1 surfaces were prepared under ultra-high vacuum (UHV) conditions (base pressure 5×10^{-11} Torr) using standard procedures. Fullerenes were sublimed from a Knudsen cell at a typical rate of ∼2 monolayers hour^{-1}. STM manipulation and imaging were performed at room temperature using electrochemically etched W tips which were cleaned by heating prior to use.

An STM image of the surface following the deposition of 0.02 monolayers of C_{60} is shown in figure 1(a). As previously reported [21, 22], molecules are adsorbed in the troughs between
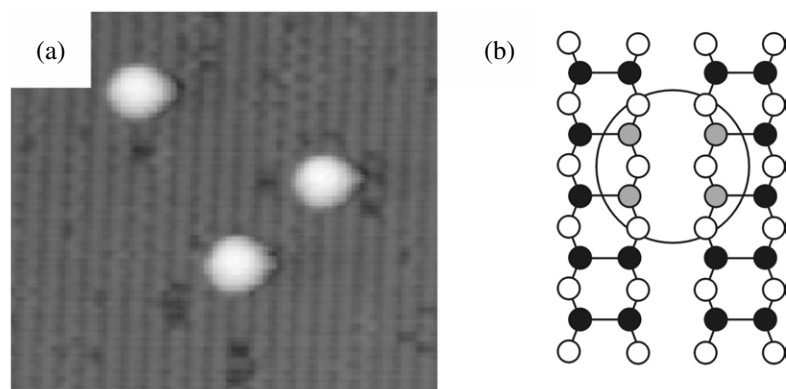
Figure 1. (a) STM image (160 Å × 140 Å) of C_{60} adsorbed on Si(100)-2 × 1; (b) schematic diagram showing Si atoms and adsorbed C_{60} molecules. The Si atoms highlighted are bonded to the fullerene cage.

the dimer rows which are formed on this surface (figure 1(b)) [23]. To perform manipulation experiments a molecule of interest is identified and the tip is then scanned along a single line which runs parallel to the dimer rows and intersects the centre of the molecule. The feedback loop is active during this linescan and, when acquired under standard imaging conditions (3 V, 0.1 nA), the topographic information acquired during this procedure corresponds to a profile of the molecule.

3. Feedback induced manipulation: quasi-constant height mode

In the most common approach to STM induced manipulation, the interaction between the tip and the molecule is controlled by first lowering the tip towards the surface by adjusting the applied voltage and the target tunnel current of the feedback control system. The tip is then displaced across the surface while maintaining feedback control of the tunnel current. Moresco *et al* [24] have shown that, for low temperature operation, manipulation in constant height mode is also possible. We show below that a similar mode of manipulation may also be realized at room temperature for covalently bound molecules. In particular, lateral displacement of molecules may be induced by reducing the dwell time, τ, of the tip at each point to a value which is less than T, the response time of the feedback control system. This leads to a tip trajectory which is intermediate between that observed in constant current and constant height modes of operation. The signature of this type of manipulation may be extracted from the acquisition of a detailed set of data which is similar to that reported in previous low temperature studies [24].

To initiate manipulation the interaction between the tip and the molecule must be increased through a reduction of their separation. There are several parameters which control this separation: (i) sample voltage, V; (ii) target tunnel current, I; (iii) step size between points at which feedback is updated, Δx (note that our control system is digital [25]); (iv) dwell time, τ. The first two parameters determine the tip–surface separation when the tip is positioned over a fixed point on the surface for dwell times which are long, $\tau \gg T$. The measured change in tip–sample separation is approximately constant, 0.1 nm V^{-1}, over a wide range (0.1–1 nA) of tunnel currents.

When scanning with a dwell time which is less than the feedback response time, $\tau < T$, the parameters Δx and τ can also influence the tip–sample separation. Under these conditions
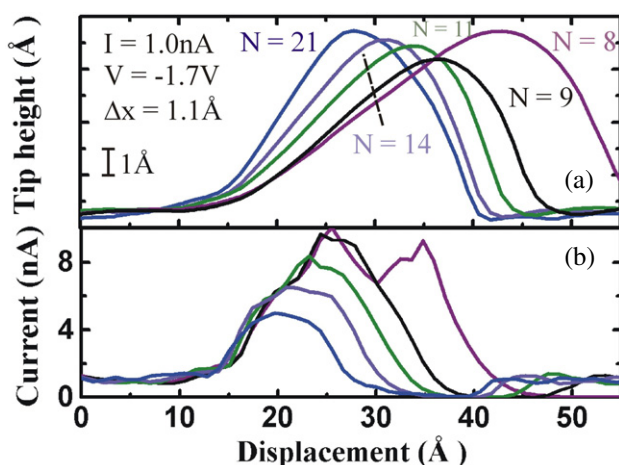
Figure 2. (a) Linescans of a C_{60} molecule acquired with progressively reduced tip dwell times varying from $N = 21$ cycles to $N = 8$ cycles; (b) values of tunnel current acquired simultaneously with the linescans shown in (a). A significant overshoot of current above the target value of 1 nA is observed as the tip encounters the molecule followed by an undershoot in current as the tip passes over the top of the molecule. A manipulation event is observed in the $N = 8$ trace leading to a displacement of the falling edge of the molecular profile and a reduction in the tip current.

the tip does not follow the surface topography and, when approaching an adsorbate such as C_{60}, it is retracted by an amount which is less than that required to reduce the tunnel current to the target value of the feedback control system. This results in an effective reduction of the tip–molecule separation and an overshoot in tunnel current. As the tip is moved through a sequence of points separated by Δx, an accumulation of errors in the tip position occurs and a progressively increasing overshoot in current is observed. Similarly, as the tip moves beyond the centre of the molecule an undershoot in current is expected due to an insufficient extension of the tip towards the surface. In this region the effective tip–sample separation is increased, i.e. is greater than that which results under full feedback control of the tunnel current.

In our previous work we have used values of $\Delta x = 0.14$ Å and $\tau = N\tau_0$ with $N = 101$ ($\tau_0 = 25$ μs is the period of the clock cycle of the digital control system and N is the number of cycles). For these values $\tau > T$, ensuring effective feedback control of the tunnel current. However, for this study we use larger values of Δx (1.1 Å) and smaller values of τ corresponding to $N = 5$–25. Figure 2(a) shows a sequence of profiles acquired as the dwell time is progressively reduced from $N = 21$ to 8 cycles. Figure 2(b) shows the measured tunnel current which is acquired simultaneously with the profiles shown in figure 2(a). The tunnel current is measured over a single digital clock cycle after waiting for a settle time corresponding to $(N-1)$ cycles. The tip is scanned from left to right and the profiles clearly show the expected signature of progressively reduced feedback response.

For the largest value of N, 21, the profile is similar to that previously reported with an apparent height of 7 Å and a width ~25 Å. However, even this profile is asymmetric. As the tip is scanned across the Si prior to encountering the C_{60} (the interval from 0 to 15 Å), the feedback response is satisfactory and the current is within ~10% of the target value, 1 nA. For $N = 21$ the current then rises to ~5 nA as the tip responds to the presence of the molecule and then, having passed over the centre of the molecule, an undershoot in current is clearly observed.

As N is progressively decreased the maxima of the profiles in figure 2(a) are progressively shifted towards the left (large values of displacement) and the gradient of the rising edge
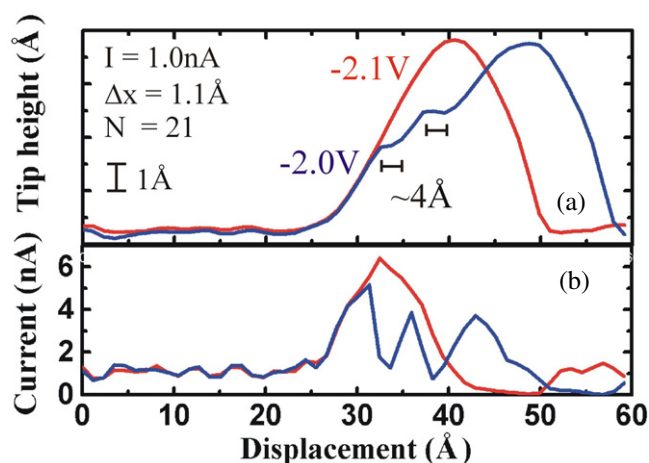
Figure 3. (a) Linescans of molecules with reducing tip–sample voltage; (b) values of tunnel current acquired simultaneously. Two manipulation events occur leading to plateaux in the tip trajectory for the -2.0 V linescan and reduction in tunnel current at displacements of 31 and 36 Å.

(right side) of the profile, where the tip makes initial contact with the molecule, is reduced. The corresponding current overshoot becomes larger and persists over a longer interval. Consequently the height of the tip at the centre of the molecule is progressively reduced and for the final curve in this sequence ($N = 8$) the tip height is 3.5 Å lower than for the initial curve ($N = 21$). For this linescan the increased tip–molecule interaction induced by this reduced separation results in molecular displacement. This is indicated by the shift in the falling edge of the molecular profile and also the drop in tunnel current at a displacement of 25 Å followed by a further rise as the tip encounters the displaced molecule. The displacement is estimated to be 7 Å, corresponding approximately to $2a_0$, where $a_0 = 3.84$ Å is the lattice constant of the Si surface. Since manipulation results in a reduction of tunnel current this event is due to the molecule moving away from the tip, which is consistent with a repulsive mechanism.

Manipulation may also be initiated by reducing the tip–sample separation through adjustment of the sample voltage for a fixed value of N. Figures 3(a) and (b) show successive profiles and tunnel current plots acquired with sample voltages -2.1 and -2.0 V. The profile for -2.1 V has the apparent width and height expected for C_{60} (see above), while the corresponding tunnel current shows an overshoot as discussed above. However, when the sample voltage is set at -2.0 V a more complex profile is observed which is due to the molecule moving through two regular steps of $\sim$4 Å, close to a single lattice constant.

4. Response of non-spherical fullerenes to manipulation

The successful manipulation on Si(100)-2 $\times$ 1 of C_{60}, $C_{59}N$ and La@C_{82} [10–14] indicates that manipulation is a general property of these near-spherical fullerenes. In the light of our recent result showing that C_{60} can be manipulated in a rolling motion across the surface it is of interest to study the adsorption, and response to manipulation, of a non-spherical fullerene on the Si(100)-2 $\times$ 1 surface. For this investigation we have chosen to study phenylated C_{60}, a fullerene with five phenyl sidegroups. In fact we find that manipulation of this species is not possible and we argue that this is a direct consequence of the presence of sidegroups which impede the rolling motion.
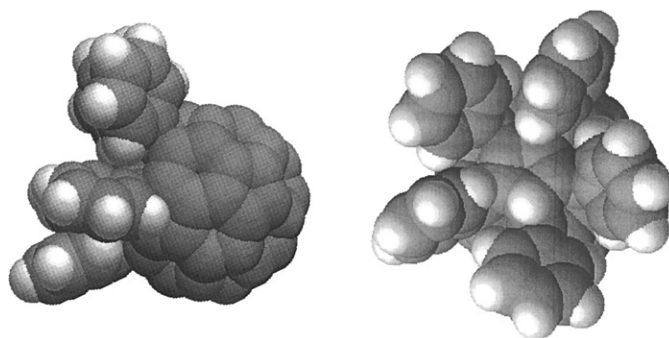
Figure 4. Schematic diagram of pentaphenyl[60]fullerene, $C_{60}Ph_5H$.

Pentaphenyl[60]fullerene, $C_{60}Ph_5H$ is prepared using an established synthetic route [26]. A schematic diagram of the molecule is shown in figure 4. A phenyl group is attached to each of the five C atoms which are bonded to the vertices of one single pentagonal face. The bonds connecting the C atoms to which the phenyl groups are attached and the C atoms in the pentagonal face are converted from double to single bonds in this synthetic process. One of the C atoms of the associated pentagonal face is bonded to a H atom and there are two double bonds between the two remaining pairs of C atoms on this face. The adsorption of $C_{60}Ph_5H$ on the unreactive Ag/Si(111)-$(\sqrt{3} \times \sqrt{3})$R30° surface has been studied previously and the presence of the phenyl groups was found to modify molecular packing, resulting in one-dimensional fullerene chains [27].

Approximately 10 mg of $C_{60}Ph_5H$ was loaded into a tantalum crucible which was placed within the UHV system. On heating to 300–320 °C, sublimation of molecules at a typical rate $\sim$1 monolayer hour^{-1} occurred. In figure 5(a) an STM image acquired following the deposition of 0.01 monolayers of $Ph_5C_{60}H$ on the clean Si(100)-2 × 1 surface is shown. Rows of Si dimers, which run in the $\langle 011 \rangle$ directions, are resolved in the background. As observed for other fullerenes, $Ph_5C_{60}H$ does not diffuse on this surface and the molecules are adsorbed randomly, with no evidence of clustering. Higher resolution images (figure 6) reveal that different molecules present different topographic features which are assumed to be dependent on their orientation. The molecules have apparent heights ranging between 7 and 9 Å and their apparent widths lie between 20 and 29 Å. Analysis of $\sim$200 molecules indicates that three distinct orientational configurations predominate, as illustrated in figure 6. The approximate position of the phenyl groups and their orientation are identified in figure 6, with a precision which is limited by the resolution of the STM.

Configuration A (see figure 6) has an axis of symmetry parallel to the dimer rows. The cage is centred in a trough midway between dimer rows, as observed for C_{60}. The fraction of molecules adsorbed in this configuration is 23%. An alternative configuration, B, in which the phenyl groups are at an angle to the dimer rows, whilst the cage remains in a trough site, is found for 40% of molecules. For both A and B the phenyl groups and the cage have approximately the same height, $\sim$7 Å, which is close to the value observed for C_{60} [21, 22]. This indicates that the axis of the molecule (the line running from the cage centre to the centre of the pentagonal face around which the phenyl groups are bonded) is approximately parallel to the surface. A significant fraction (33%) of molecules are observed in a third orientation, C, with larger topographic heights (9 Å) and a symmetrical appearance, suggesting that the phenyl groups are facing upwards (see figure 6). Some of these molecules are not centred on the trough between the dimer rows. A small fraction of molecules (4%) cannot be attributed to any of the
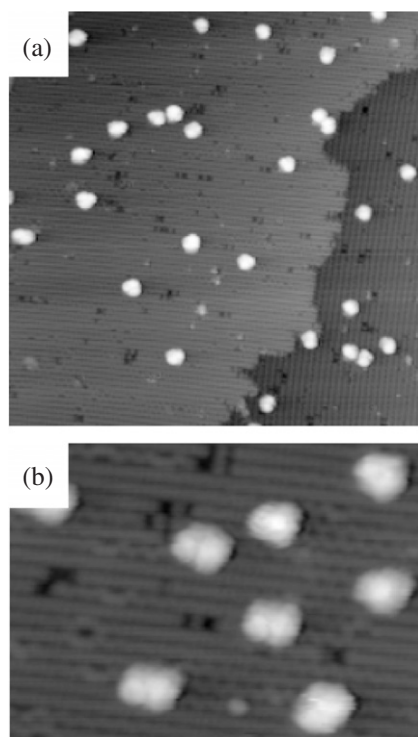
Figure 5. (a) STM image showing a low coverage of $Ph_5C_{60}H$ molecules on Si(100)-2 × 1 (600 Å × 600 Å, −3.5 V, 0.2 nA); (b) higher resolution image revealing molecular structure and Si dimer rows (200 Å × 200 Å, −3.5 V, 0.2 nA).

above configurations. Overall a fraction of 95% of molecules have the C_{60} cage sub-unit of the molecule sitting within the trough between the dimer rows.

The response of these molecules to attempts at manipulation has been investigated using a procedure similar to those described above, but using steps of length $\Delta x = 6$ Å and effective feedback control, i.e. $\tau > T$. The presence of sidegroups on $C_{60}Ph_5H$ strongly inhibits manipulation. A loss of tip resolution frequently occurs, often accompanied by imaging artefacts such as doubling. In many cases molecules are removed from the surface or appear to be fragmented due to the tip interaction. In figure 7 the outcome of a manipulation attempt where the resolution remains the same after breaking a molecule adsorbed in a 'C' configuration is shown. Part of the molecule, possibly the phenyl groups, remains on the surface after manipulation, whilst the rest of the molecule is no longer present, probably due to transfer onto the tip. A similar response to that observed for C_{60}, $C_{59}N$ and $La@C_{82}$, in which fullerenes may be readily be displaced over distances >100 Å, was never observed for this molecule.

5. Discussion

The new results discussed in this paper provide further evidence that fullerene manipulation occurs through a rolling mechanism. This process has recently been used to design molecules which undergo directional diffusion across a surface [28]. The presence of the phenyl sidegroups impedes manipulation and the response to attempts to manipulate these molecules is in strong contrast to other fullerenes with varying geometries and chemical/electronic
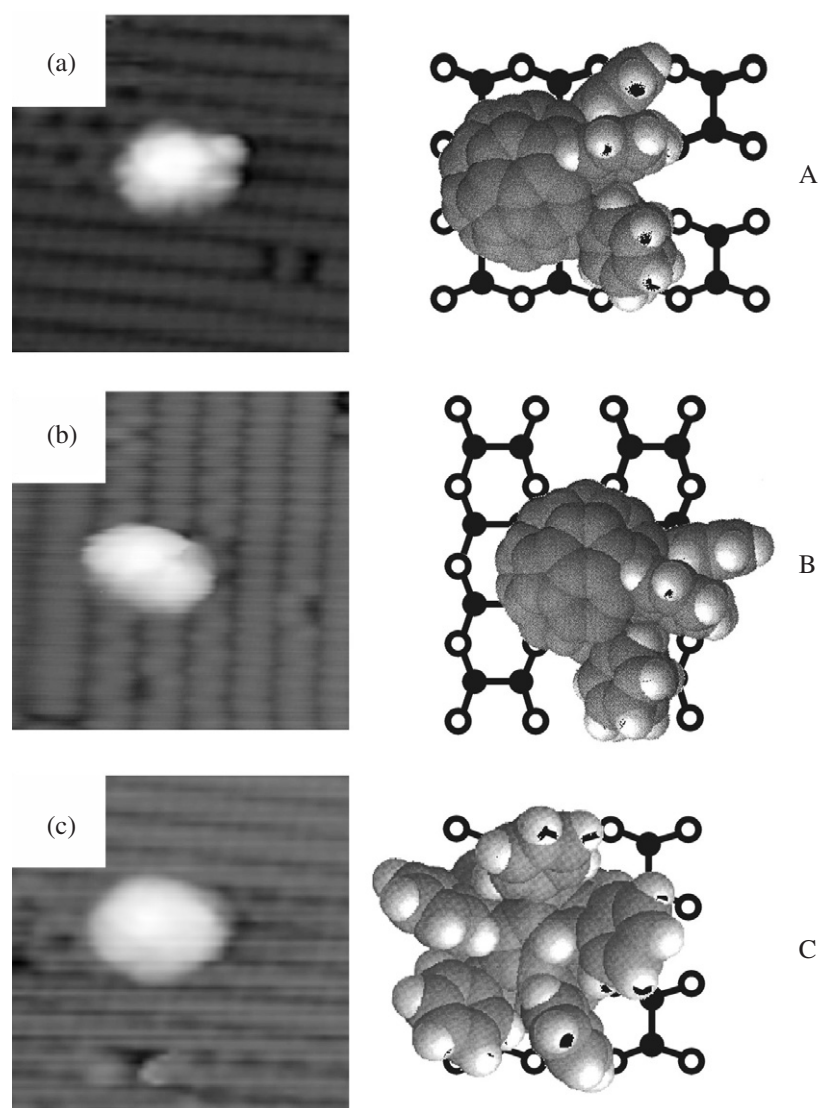
Figure 6. The most commonly observed orientations of $Ph_5C_{60}H$ molecules on Si(100)-2 $\times$ 1 (80 Å $\times$ 80 Å, -3.5 V, 0.2 nA).

properties, but no attached sidegroups. The demonstration that lateral positioning of fullerenes can be initiated in a quasi-constant height mode confirms that there is a wide variation of experimental conditions which may generate manipulation. Taken together with previous results we have observed manipulation with tunnel currents and voltages varying by more than one order of magnitude 0.2–5 nA and 0.3–3 V. This confirms that manipulation of fullerenes bound covalently to a substrate surface is not driven either by local heating or electrostatic effects alone. Interestingly this indicates that proximal forces alone may be used to generate lateral translation of molecules, leading to the possibility of using atomic force microscopy for the type of lateral manipulation discussed in this paper. This is likely to prove a fruitful area for future research.
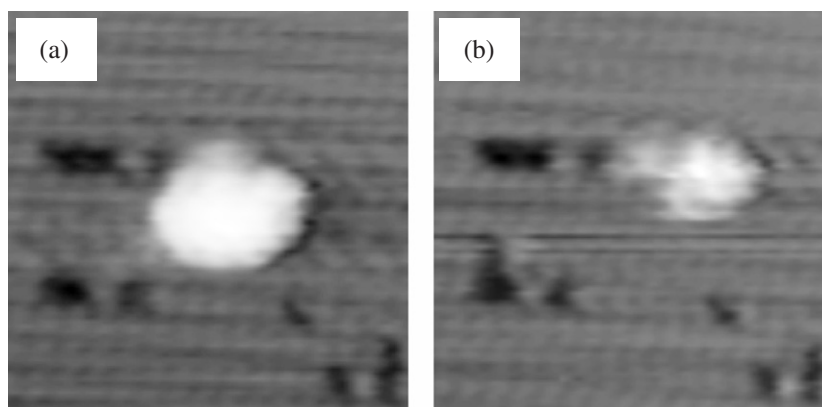
Figure 7. STM images showing a manipulation attempt on a $Ph_5C_{60}H$ molecule. The molecule is significantly modified by the interaction with the tip (100 Å × 100 Å; manipulation parameters −1.0 V, 1.0 nA, scanning parameters −3.2 V, 0.4 nA).

Acknowledgments

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