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Translation, rotation and removal of C_{60} on $Si(100)-2 \times 1$ using anisotropic molecular manipulation

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Abstract

We have investigated the interactions of C_{60} molecules adsorbed on $Si(100)-(2 \times 1)$ through their response to manipulation induced by a scanning tunneling microscope operating at room temperature. Intramolecular features are resolved which vary as a molecule is displaced showing that C_{60} undergoes rotation during tip-induced displacement. For translation to and from certain bonding sites, the apparent size of a molecule may change following lateral manipulation. Furthermore, reversible changes in dimer buckling are observed as a molecule is moved across the surface. Our experimental observations show that the $C_{60}/Si(100)-(2 \times 1)$ interaction is dominant over the $C_{60}-C_{60}$ interaction and attempts to move a molecular pair result in the transfer of one molecule across a dimer row due to barrier lowering by the intermolecular interaction. We also show that transfer of a molecule from sample to tip (or vice versa) changes both the imaging and manipulation properties of the tip. © 1998 Elsevier Science B.V. All rights reserved.

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Lateral translation of adsorbates on solid surfaces using a scanning tunneling microscope (STM) enables the atom-by-atom assembly of pre-defined nanostructures [1]. The structural and electronic properties of the atomic or molecular arrangements thus formed may, in turn, be probed using the STM [2]. In addition, adsorbate–adsorbate and adsorbate–substrate interactions may be investigated using controlled and precise positioning of atoms and molecules with the STM tip [3–5]. While STM manipulation of adsorbates at low temperature was demonstrated some time ago [1], the extension of this work to room temperature operation requires a much larger diffusion barrier and, therefore, a much stronger adsorbate–sub-

strate interaction. Progress towards this goal has been limited due to the difficulty of initiating manipulation of strongly adsorbed molecules. In a number of recent papers the controlled manipulation of molecules at room temperature has now been reported [6–9]. However, progress to date has encompassed only the placement of adsorbates.

In this paper we discuss the results of a series of room temperature manipulation experiments in which the STM has been used to change the position, bonding site and orientation of individual adsorbed molecules. In addition, the effect of C_{60} adsorption and manipulation on the underlying Si surface reconstruction has been examined and we have used molecular manipulation to investigate the intermolecular and molecule–surface interactions of C_{60} adsorbed on the $Si(100)-2 \times 1$ surface. The role of the microscopic structure of the

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STM tip in the manipulation process is discussed and we demonstrate the changes in resolution and the response to manipulation that occur following the adsorption of a C_{60} molecule on the tip.

The experiments were performed using an ultra-high vacuum (UHV) STM [10] operating at room temperature. For both STM imaging and manipulation, tungsten tips prepared by electrochemical etching and heating by electron bombardment in vacuum were used. The Si(100) samples were degassed at 750°C overnight, flash-annealed at 1200°C for 20 s and then held at 800°C for 3 min. before cooling to room temperature. This annealing results in a (2×1) reconstructed Si(100) surface with a low defect density. C_{60} was sublimed from a Knudsen cell operating at 320°C, with a 10 s exposure resulting in a coverage of 0.01 ML.

The reconstruction of Si(100) results in a highly anisotropic surface structure formed by rows of Si dimers. Fig. 1a shows an STM image in which C_{60} molecules appear as circular features and the rows of the Si(100)- (2×1) reconstruction run up the image. The Si(100)- (2×1) surface and the adsorption site for C_{60} are shown schematically in Fig. 2. For adsorption of C_{60} at room temperature we find that C_{60} is adsorbed in the troughs between the dimer rows at the four-dimer site (labelled A in Fig. 2) in agreement with previous studies [11,12]. Note that the rows on the Si(100)- (2×1) surface arise from the dimerization of top layer atoms [13].

The lateral translation of an adsorbate on a surface was first demonstrated by Eigler et al. [1] at low temperature and we have previously demonstrated that a closely related type of manipulation may be realized at room temperature [6,7]. Further demonstrations have been published more recently [8,9]. The tip-sample separation is first decreased by reducing the gap resistance to a value ~ 1 G Ω . The tip is then moved a predetermined distance (3 nm in the experiments below) in steps of 0.6 nm either parallel or perpendicular to the dimer rows. The tunnel current is controlled by a digital feedback loop which is updated after each step. The tip is then retracted by increasing the gap resistance to ~ 30 – 40 G Ω and returned to its original position. We do not observe a dependence of manipulation on bias voltage polarity.

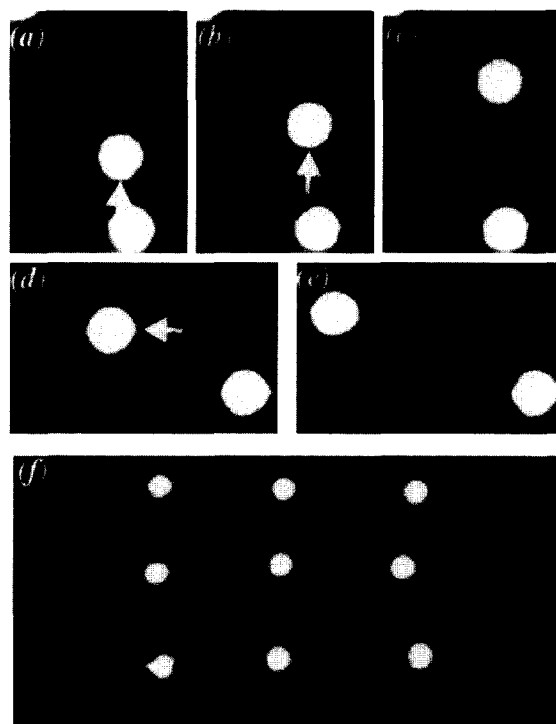


Fig. 1. Demonstration of molecular manipulation: (a)–(c) parallel to the Si(100)- (2×1) dimer rows, scan area 7.5×10 nm²; (d)–(e) across dimer rows, scan area 10×6.3 nm². The arrows indicate the direction of tip displacement. (f) A 3×3 array of C_{60} molecules, scan area 40.5×19.7 nm². For (a)–(f): scan parameters -3.5 V, 0.1 nA; manipulation parameters -1.0 V, 1.0 nA.

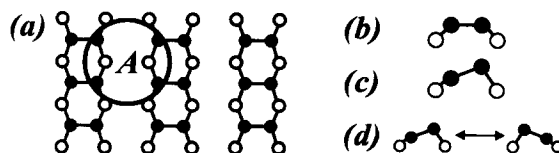


Fig. 2. (a) Schematic of the Si(100)- (2×1) surface and the adsorption site for C_{60} labelled A; (b) symmetric; (c) buckled Si dimers; (d) hopping between buckled states which occurs at 300 K. Solid circles are top layer, open circles second layer Si atoms.

The response of C_{60} to STM manipulation is highly anisotropic. Fig. 1 shows examples of manipulation where the tip moves either parallel (a–c) or perpendicular (d, e) to the dimer rows. Two successive 3 nm displacements of the tip induced the displacements in Fig. 1a–c. Between the acquisition of Fig. 1d and e five parallel lines

separated by 6 \AA were swept out forming an area of $3 \times 3 \text{ nm}^2$. Although manipulation perpendicular to the rows is possible, we have found a success rate for this direction of only $\sim 15\%$, compared with $\sim 95\%$ for motion parallel to the dimer rows. Identical parameters were used for sweeping in both directions. In our work on Si(111)- 7×7 a much lower gap impedance ($\sim 100 \text{ M}\Omega$) was required to initiate manipulation and the C_{60} generally moved at an angle to the tip displacement [6,7] with a fairly low success rate (10–50%). The response of molecules to manipulation across the dimer rows on Si(100)- 2×1 bears many similarities to the Si(111)- 7×7 case. In particular the molecule does not move in a direction which is exactly parallel to the tip direction. This is clearly revealed in Fig. 1d and e where some movement of the molecule along the dimer row is evident. However, for displacement parallel to the rows on Si(100)-(2×1) the molecule is guided along the troughs facilitating more precise and controllable placement. A simple pattern is shown in Fig. 1f.

To distinguish whether manipulation results from a repulsive or attractive interaction we have applied a modified procedure, in which the tip is not retracted before returning to its original position. We have found that the C_{60} remains at the extreme of the tip excursion implying that the manipulation in Fig. 1 results from a repulsive interaction.

We have used STM manipulation to investigate a model for C_{60} adsorption on Si(100)-(2×1) which has recently been proposed [14]. Within this model molecules are confined to the centre of troughs between dimer rows due to a strong molecule–surface interaction. However, the component of forces parallel to the dimer rows due to the molecule–surface interaction is taken to be negligible and the position of molecules along the rows is determined by interactions with other adsorbed molecules. The molecules are assumed to be physisorbed and they interact via van der Waals' forces [15,16] with an equilibrium intermolecular separation $d_0 = 1.005 \text{ nm}$. Fig. 3a and b shows the result of an attempt to reduce the separation of a C_{60} pair by moving the lower molecule along the trough towards the upper molecule. The initial position of the tip was chosen to ensure that it did

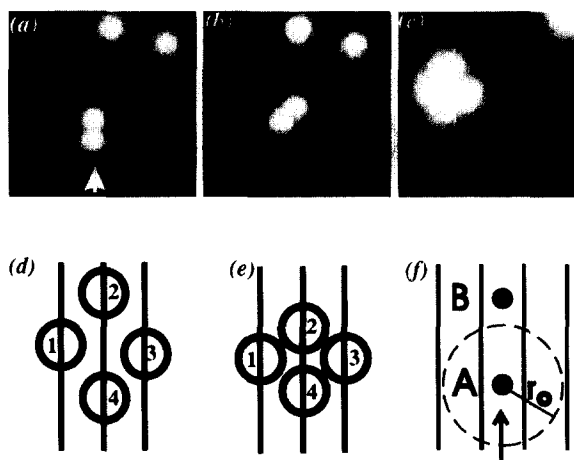


Fig. 3. A pair of C_{60} molecules ($d = 1.15 \text{ nm}$) prior to manipulation. The result of an attempt to reduce the intermolecular separation by moving the lower molecule towards the upper molecule is shown in (b). The arrow in (a) indicates the direction of tip displacement. Manipulation parameters: -1.0 V , 1.5 nA . (c) A molecular cluster assembled using the STM tip. (d) schematic diagram showing the position of the molecules in (c). Solid lines represent the minima of the troughs. (e) $c(4 \times 3)$ arrangement. According to a recent theory the cluster shown in (c) and (d) should spontaneously relax to the configuration in (e), however, this is not observed. (f) Schematic illustrating the barrier lowering for transfer across a dimer row due to the interaction between molecules A and B.

not interact directly with the upper molecule. This means that it is sufficiently far away from the upper molecule so that no manipulation would result in the absence of the lower molecule. Prior to manipulation, the separation, d , of the C_{60} pair is $1.15 \pm 0.02 \text{ nm}$ [equal to $3a$, where $a (= 0.384 \text{ nm})$ is the surface lattice constant]. The manipulation causes the upper molecule of the pair to move across a dimer row into an adjacent trough, reducing the molecular separation to $1.09 \pm 0.02 \text{ nm}$. In addition, both molecules move “up” the image by $\sim 0.8 \text{ nm}$.

We have repeated this experiment many times. For the majority of molecular pairs the upper molecule is transferred, as in Fig. 3b, although in some cases the lower molecule moves across a row. The minimum separation of molecules along a trough that we can attain is $1.15 \pm 0.02 \text{ nm}$, a result which is inconsistent with ref. [14], in which a value equal to the intermolecular separation d_0 is predicted. We have also assembled molecular clus-

ters. According to the model described above the cluster in Fig. 3c should relax to an ordered [local $c(4 \times 3)$] arrangement, but this is inconsistent with our data (see Fig. 3d and e).

We consider two possible explanations for these differences. First, the molecules are not physisorbed, but chemisorbed, and the resulting charge exchange between adsorbate and substrate modifies the intermolecular potential leading to a different equilibrium separation. A second possibility (and on the basis of our STM results more likely) is that the positions of the molecules along the trough are determined by the molecule–surface interaction rather than intermolecular forces. Both explanations imply a much stronger interaction between C_{60} and Si(100)– 2×1 than is consistent with physisorption. This is confirmed by recent photoemission studies which show that C_{60} is chemisorbed on Si(100)– 2×1 [17].

We now consider the hopping of molecules across dimer rows which results from attempts at manipulation of molecular pairs. Note that in the experiments in Fig. 3a and b the initial tip position is chosen so that there is no direct interaction with the upper molecule. It is, therefore, the intermolecular interaction which forces the upper molecule to move in Fig. 3 rather than the direct tip/adsorbate interaction as is usually the case for STM manipulation. It is possible to account for the response of the upper molecule using a simple model. We characterize the potential landscape for a C_{60} on Si(100)– 2×1 by two energy barriers, Δ_{\perp} and Δ_{\parallel} , which must be overcome for displacement parallel and perpendicular to the rows. These are given as follows:

$$\Delta_{\perp} = \Delta_{\perp}^0 + \Delta_{\perp}^1,$$

$$\Delta_{\parallel} = \Delta_{\parallel}^0 + \Delta_{\parallel}^1,$$

where Δ_{\perp}^0 and Δ_{\parallel}^0 are the barriers experienced by an isolated molecule and Δ_{\perp}^1 and Δ_{\parallel}^1 are the changes induced due to the presence of a neighbouring molecule. The response to manipulation of isolated C_{60} implies $\Delta_{\perp}^0 > \Delta_{\parallel}^0$. Consider the case shown in Fig. 3f in which molecule A is moved towards molecule B. As the intermolecular separation, r , is reduced to a value less than the equilibrium separation, r_0 , the potential energy of B is increased. For

a short range potential the intermolecular interaction will have a negligible effect on the barrier for motion along the dimer row. However, molecule B can jump across a dimer row while maintaining equilibrium contact with molecule A. The barrier for motion across rows is, therefore, lowered by E_B (the minimum value of the C_{60} – C_{60} potential for molecules adsorbed on Si(100)– 2×1) at the intersection of a circle of radius r_0 centred on molecule A and the dimer row (Fig. 3f). To first order, therefore, $\Delta_{\perp}^1 \sim -E_B$ and $\Delta_{\parallel}^1 \sim 0$. Our experimental results imply that $\Delta_{\perp} > \Delta_{\parallel}$, which implies in turn $(\Delta_{\perp}^0 - \Delta_{\parallel}^0) < E_B$. The van der Waals' potential [15, 16] gives $E_B = 0.28$ eV, however, use of this potential is not strictly valid since there is charge transfer between adsorbate and substrate. The highest order correction will be due to dipole–dipole repulsion. The dipole magnitude, p , may be estimated from calculated values for charge transfer ($p \sim 8 \times 10^{-29}$ Cm) [18]. However, a more recent calculation based on an ab initio method. Jones [26] gives a lower dipole ($p \sim 3.5 \times 10^{-29}$ Cm). Taking account of screening by the Si the dipole–dipole interaction ($\propto p^2$) decreases the binding energy by ~ 10 meV which is small compared with the estimate for E_B above.

We now consider changes in orientation of the molecule which may be induced by manipulation. Fig. 4a shows an STM image in which clear variations in contrast are observed within C_{60} each molecule. Note that the pattern of internal features varies from molecule to molecule. The intramolecular contrast, therefore, does not arise from a tip artifact [19] such as an “inverse” imaging of the tip structure by a C_{60} molecule on the Si(100) surface. As we discuss below, the chemical structure, and thus local density of states, of the tip may play a role in determining the precise form of the observed intramolecular contrast.

Intramolecular contrast has previously been observed for C_{60} on Si(100) [11, 12, 19] and has also been investigated theoretically [20]. A close inspection of Fig. 4a indicates that the internal structure visible in the adsorbed C_{60} molecules consists predominantly of curved “stripes” with the direction of curvature varying from molecule to molecule. The detail of the internal structure is quite different from that previously observed

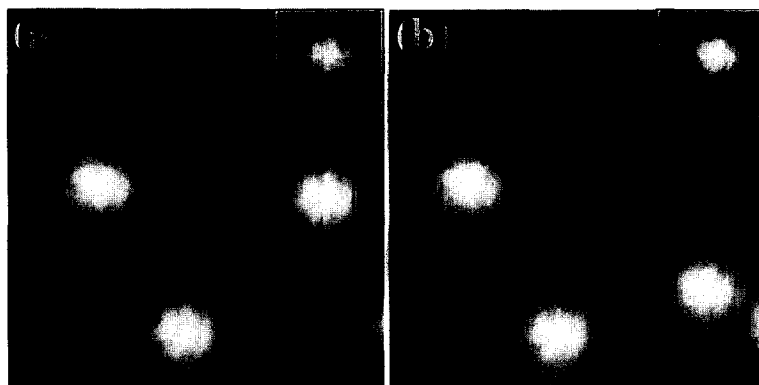


Fig. 4. Tip-induced rotation of an individual adsorbed C_{60} molecule. Intramolecular features appearing as curved stripes are visible within the three molecules shown in both (a) and (b) (6.8×6.8 nm constant current scans, -3.5 V bias, 0.1 nA setpoint current). Translation of the molecule visible in the right of (a) between equivalent bonding sites results in a distinct change in intramolecular contrast, as seen in (b). The insets to (a) and (b) are zooms of the manipulated molecule to highlight the changes in internal features induced by manipulation. Note that although the preferred bonding site for C_{60} on $Si(100)-(2 \times 1)$ at room temperature is in the trough between the dimer rows (see Fig. 2), the centres of the molecules shown in (a), (b) and (c) do not appear directly above the troughs. This results from a particular type of tip artifact that has previously been discussed by Chen and Sarid [10] and may be identified from a comparison of the positions of molecules adsorbed on the orthogonal (2×1) and (1×2) domains of the $Si(100)$ surface.

[12,19] and it is difficult to draw a close comparison between the intramolecular features and the C_{60} cage structure. Intramolecular features resembling curved “stripes” (similar to those in Fig. 4a) were reported by Wang et al. [21], although in that case C_{60} was adsorbed on $Si(111)-(7 \times 7)$.

The molecule on the right hand side of Fig. 4a has been moved along a trough “down” the image by approximately 1.9 nm using room temperature molecular manipulation as described above. Fig. 4b shows the position of the molecule following the tip-induced translation. Analysis of the position of the displaced C_{60} with respect to the underlying dimers of the (2×1) reconstruction indicates that the molecule moves from one four-dimer site (the adsorption site illustrated in Fig. 2) site to an *equivalent* four-dimer site. While the internal features of the molecules that have not been manipulated are identical to those observed in Fig. 4a, the displaced molecule exhibits a distinct change in intramolecular structure. Both the direction of curvature and the fine structure of the internal “stripes” have changed – compare the high magnification images of the molecule before and after manipulation shown in the insets to Fig. 4a and b, respectively.

A comparison of the $Si(100)$ surface structure before and after the translation of the C_{60} molecule (Fig. 4a and b) shows that both the original and final bonding sites are free of defects. The difference between molecules displaying striped features (as observed in this and earlier work [12]) and cage-like features [19] cannot, therefore, be explained in terms of adsorption at defects. The molecule in Fig. 4 is moved along a trough from one bonding site to an equivalent (four-dimer) site and, therefore, the difference in intramolecular contrast observed before and after manipulation must arise from *a change in molecular orientation* with respect to the surface. A change in molecular orientation following manipulation directly implies that the fullerene molecule rotates or “rolls” as a result of being pushed by the STM tip.

Unfortunately, it is not possible to determine the exact C_{60} orientation from intramolecular structure alone. The “stripe” features observed for the molecules in Fig. 2 bear no resemblance to the calculated local density of states of a free C_{60} molecule [22]. While our results clearly show that a C_{60} molecule may rotate as it is translated by the STM tip, the C_{60} -Si interaction significantly affects the intramolecular structure we observe

[20]. Furthermore, as discussed below, changes in the structure and density states of the tip produce strong variations in the patterns of internal structure.

We now consider differences in molecular appearance which occur for molecules that are moved to and from *inequivalent* bonding sites. As noted above, C_{60} molecules deposited at room temperature on Si(100)-(2×1) reside in the troughs between dimer rows. It has been demonstrated that following annealing of the Si(100) substrate at 600°C, C_{60} molecules are no longer found exclusively in the troughs but may bond directly on top of the dimer rows [11,19]. After annealing the Si(100) substrate at approximately 500°C we observe C_{60} bonded both between and on top of the dimer rows (see molecules labelled A and B in Fig. 5a).

A modified version of the manipulation procedure was used to move the molecules shown in Fig. 5a. Instead of sweeping a single line with the tip (as was the case for the translation of the molecule shown in Fig. 1) 10 parallel lines separated by 0.6 nm were used to induce molecular movement [6]. For each line the cycle of tip movements was as follows: (i) the gap resistance was first decreased to 1.6 GΩ to move the tip closer to the surface; (ii) the tip was moved from left to right 6 nm across the surface with the feedback loop updated every 0.6 nm; (iii) the gap resistance was increased to that used for scanning (30 GΩ); and (iv) the tip was returned to its original position at the start of the line. In this case the advantage of “sweeping” an area (as opposed to a single line) with the tip is that we can attempt to move molecules bonded at inequivalent surface sites under identical manipulation conditions. Differences in the response of individual molecules to manipulation may then be associated with variations in molecule–surface bonding.

Following acquisition of the image shown in Fig. 5a the manipulation procedure described above was carried out a number of times over a 6×6 nm area encompassing both molecules A and B. In each case only molecule A was displaced. For example, Fig. 5b illustrates the translation of molecule A by approximately 2 nm while molecule

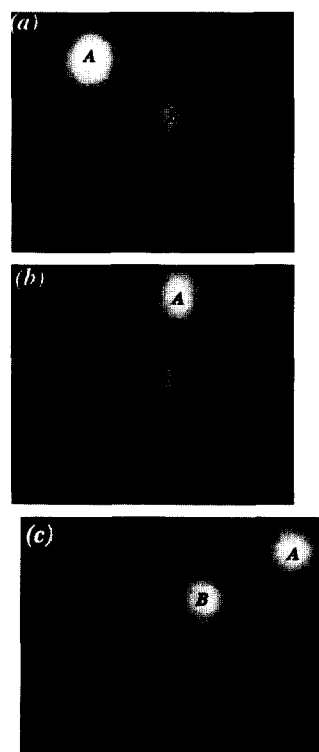


Fig. 5. (a) Following annealing of $C_{60}/Si(100)-(2\times 1)$ at 500°C, molecules bond both in the troughs between dimer rows (labelled A) (as observed following room temperature adsorption), but also directly on top of the dimer rows (molecule labelled B). (b) Application of the manipulation procedure over a 6×6 nm area encompassing both molecules and with a gap resistance of 1.6 GΩ induces movement of only molecule A. (c) A gap resistance of 1 GΩ was required to move molecule B from its bonding site directly above a dimer row to a trough site.

B remains undisturbed. To induce movement of molecule B it was necessary to reduce the gap resistance during the manipulation process to 1 GΩ (0.6 GΩ lower than that used to displace molecule A alone). The lowering of the gap resistance leads to a smaller tip–sample separation, a greater molecule–tip interaction and, correspondingly, displacement of *both* molecules A and B (compare Fig. 5b and c). Importantly, molecule B is moved from a bonding site on top of a Si dimer row to occupy a site in a trough between rows. In addition, both the apparent width (FWHM) and height of the molecule increase (from 1.22 to 1.55 nm and 0.47 to 0.75 nm, respectively) following manipulation.

The lower gap resistance required to move mole-

cule B from its bonding site above the dimer row would suggest that a stronger C_{60} -surface interaction exists for molecules bonded above dimers (as compared to those adsorbed in trough sites). It has been proposed [11,19] that, for room temperature adsorption, C_{60} molecules are physisorbed, but that annealing promotes the formation of covalent bonds between the fullerene molecules and the substrate. Although our molecular manipulation and photoelectron spectroscopy data [17] show that, even at room temperature, C_{60} is chemisorbed on Si(100)-(2×1), the results of Fig. 5 indicate that stronger C_{60} -Si(100) bonding is associated with molecules adsorbed on top of dimer rows. However, as noted above, a small (approximately factor of two) change in gap resistance from that used to manipulate molecule A is required to translate molecule B. This factor of two should be compared with the order of magnitude difference in gap resistance required for manipulation of C_{60} on Si(111)-(7×7) [6]. It strongly suggests that there is only a relatively small difference in the C_{60} -Si(100) bond strength before and after annealing. The change in apparent size of molecule B following manipulation may be explained in terms of differences in the C_{60} local density of states (in particular, a reduction in the LDOS of the highest occupied molecular orbital) for adsorption above, compared to between dimer rows [11].

In addition to the variations in intramolecular contrast and molecular appearance induced by STM manipulation we have observed changes in the *substrate* structure following the translation of molecules across the surface. It should be emphasized, however, that these changes do not result from a corruption of the surface (via the production of vacancies or other defects) following application of the manipulation procedure. Instead, reversible variations in the buckling of Si dimers [see Ref. [23] for a description of dimer buckling on Si(100)-(2×1)] are produced as a C_{60} molecule is moved across the surface.

Fig. 6 illustrates the appearance and removal of dimer buckling due to the presence or absence of a fullerene molecule. Prior to manipulation of the C_{60} molecule shown in the centre of Fig. 6a, the region highlighted by a white box is free of

buckled dimers. Following movement of the molecule, buckling of the dimers, giving rise to the “zig-zag” pattern along the dimer rows highlighted in Fig. 6b, is observed. An additional translation of the molecule (Fig. 6c) leads to the disappearance of buckling in the region highlighted in Fig. 6b. However, buckling now appears along the dimer rows either side of the trough in which the C_{60} molecule is adsorbed. Chen and Sarid [11] have suggested that C_{60} adsorption induces “zig-zag”, that is, $c(4 \times 2)$, ordering of buckled dimers. The results shown in Fig. 6 support this conclusion. However, we note that translation of a molecule to a particular site has occasionally resulted in the *removal* of buckling around that site. Note that we have carried out a number of control experiments to eliminate the possibility that the structural changes in the surface are related to the STM alone as opposed to the movement of a C_{60} molecule. In these experiments the manipulation procedure was applied to clean (i.e. molecule free) regions of Si(100)-(2×1), but no changes in surface structure or dimer buckling were observed.

During the course of manipulation experiments similar to those described above we have occasionally observed transfer of C_{60} molecules between the STM tip and the sample surface. Unlike lateral molecular manipulation, tip-surface transfer of C_{60} molecules is an unpredictable and irreproducible process and occurs for approximately 0.2% of lateral manipulation attempts. Fig. 7a–c illustrate changes in image resolution that result from the adsorption and desorption of a single C_{60} molecule. Following acquisition of the image shown in Fig. 7a, the manipulation procedure (covering an area of $3 \times 3 \text{ nm}^2$) was applied to the highlighted molecule. Instead of translating the highlighted C_{60} across the Si(100) substrate, the manipulation procedure resulted in the removal of the molecule from the surface (as shown in Fig. 7b). A comparison of Fig. 7a and b also clearly shows that the transfer of the C_{60} molecule to the tip has resulted in a considerable enhancement in resolution. The peak-to-valley corrugations measured from line profiles across the dimer rows in the images shown in Fig. 7a and b are 0.015 and 0.035 nm, respectively. A second application of the manipulation procedure in the area highlighted in Fig. 7b resulted in the

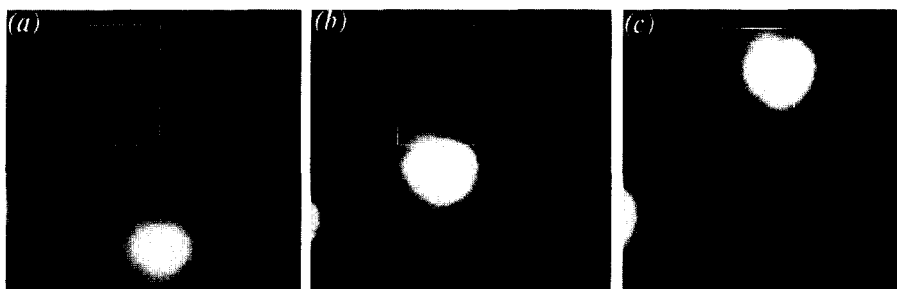


Fig. 6. (a) The white rectangle highlights a region of the Si(100) surface that is free of buckled dimers. (b) The C_{60} molecule observed at the bottom of (a) has been moved to a new bonding site adjacent to the highlighted region. Buckling of dimers is induced by the adsorbed molecule. (c) Following translation of the molecule to a new bonding site the dimer buckling within the highlighted region disappears. However, buckled dimers are now visible in the dimer rows adjacent to the trough in which the molecule is adsorbed. (For all images; scan size: 7.2×7.2 nm; bias: -3.5 V; setpoint current: 0.1 nA).

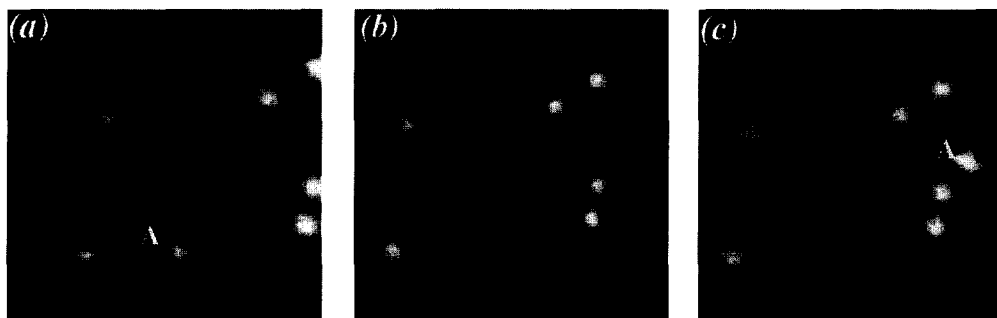


Fig. 7. (a) An attempt to translate the molecule labelled A results in its adsorption on the tip, leading to enhanced image resolution as shown in (b). (c) A subsequent attempt at translation of an adsorbed C_{60} results in the deposition of the molecule labelled A. (Scan size: 21×21 nm for all images, bias voltages and setpoints for scanning are the same as for Fig. 4).

desorption of the adsorbed C_{60} molecule from the tip and its re-adsorption on the Si(100) surface (see Fig. 7c). Accompanying the desorption of C_{60} from the tip is a return to the poor image resolution observed in Fig. 5a. Similar surface–tip molecular transfer has been observed, though with a higher frequency of occurrence, during scanning with relatively low bias voltages (≤ 1.5 V) and relatively high currents (≥ 1 nA) [24].

In the sequence of images shown in Fig. 7 C_{60} transfer to the tip results in enhanced resolution. Fig. 8a and b illustrate that molecule transfer to the STM tip may also result in image artifacts. In this case, the C_{60} visible in the centre of Fig. 8a has been adsorbed on the tip resulting in the remaining molecules appearing “doubled” in Fig. 8b. This effect is due to the presence of an additional tunneling centre following the adsorption of the C_{60} molecule on the STM tip.

For the majority of manipulation and imaging

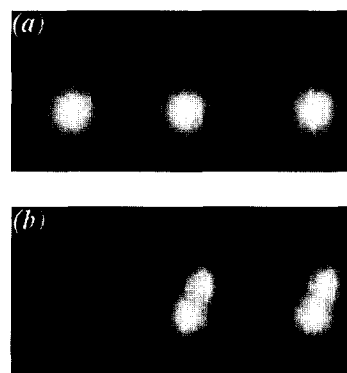


Fig. 8. (a) Adsorption of the molecule shown in the left of (a) on the STM tip, leads to clear image artifacts, as shown in (b), where the remaining two molecules now appear “doubled”.

experiments we could not obtain high resolution images of the internal structure of the adsorbed C_{60} molecules. That is, a specific tip configuration is required to resolve the intramolecular structure

shown in Fig. 2. It is, therefore, necessary to consider the electronic structure of both the adsorbed molecule and the tip (and the overlap of their wavefunctions) in understanding the intramolecular features observed in this work and previous studies.

Finally, while enhanced imaging resolution has previously been reported for C_{60} -covered STM tips [25], we also observe changes in the manipulation capability of the tip following adsorption of C_{60} . In general the transfer of a fullerene molecule affects the success rates for manipulation both parallel and perpendicular to the Si(100) surface dimer rows. For the case of the tip structure that produced the image shown in Fig. 8b the success rate for manipulation perpendicular to the rows increased to approximately 33%. The most plausible explanation for this increase is that the transfer of one (or more) C_{60} molecule(s) will lead to an asymmetric tip cross-section leading to an enhanced probability for manipulation perpendicular to the rows.

In conclusion, we have exploited an anisotropic surface reconstruction to investigate the interactions experienced by an adsorbed molecule on a solid surface. Our results imply that C_{60} is chemisorbed on Si(100) and this is confirmed by recent photoemission studies. Changes in intramolecular contrast consistent with molecular rotation have been observed and the apparent size of an adsorbed molecule has been found to change following manipulation. We have demonstrated that individual molecules may be transferred between a Si surface and an STM tip at room temperature and observed enhanced image resolution following adsorption of an individual molecule on the tip. Of particular importance to the development of STM manipulation both as a probe of adsorbate–adsorbate and adsorbate–substrate interactions and as a method of producing molecular nanostructures, we have shown that transfer of a single molecule to the tip strongly modifies the response of an adsorbed species to manipulation.

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References

- [1] D.M. Eigler, E.K. Schweizer, *Nature* 344 (1990) 524.
- [2] M.F. Crommie, C.P. Lutz, D. Eigler, *Science* 262 (1993) 218.
- [3] G. Meyer, S. Zöphel, K.H. Rieder, *Phys. Rev. Lett.* 77 (1996) 2113.
- [4] G. Meyer, S. Zöphel, K.H. Rieder, *Appl. Phys. Lett.* 69 (1996) 3185.
- [5] D.M. Eigler, in: Ph. Avouris (Ed.), *Atomic and Nanometre-scale Modification of Materials: Fundamentals and Applications*. NATO ASI series, Kluwer Academic, Dordrecht, 1993.
- [6] P.H. Beton, A.W. Dunn, P. Moriarty, *Appl. Phys. Lett.* 67 (1995) 1075.
- [7] A.W. Dunn, P.H. Beton, P. Moriarty, *J. Vac. Sci. Technol.* B14 (1996) 943.
- [8] T.A. Jung, R.R. Schlitter, J.K. Gimzewski, H. Tang, C. Joachim, *Science* 271 (1996) 181.
- [9] M.T. Cuberes, R.R. Schlitter, J.K. Gimzewski, *Appl. Phys. Lett.* 69 (1996) 3016.
- [10] Oxford Instruments SPM Group, formerly WA Technology, Cambridge, UK.
- [11] D. Chen, D. Sarid, *Surf. Sci.* 318 (1994) 74.
- [12] T. Hashizume, X.D. Wang, Y. Nishina, H. Shinohara, Y. Saito, Y. Kuk, T. Sakurai, *Jpn J. Appl. Phys.* 31 (1992) L881.
- [13] R.M. Tromp, R.J. Hamers, J.E. Demuth, *Phys. Rev. Lett.* 55 (1985) 1303.
- [14] D. Klyachko, D.M. Chen, *Phys. Rev. Lett.* 75 (1995) 3693.
- [15] L.A. Girifalco, *J. Phys. Chem.* 96 (1992) 858.
- [16] Ch. Girard, Ph. Lambin, A. Dereux, A.A. Lucas, *Phys. Rev.* B49 (1994) 11425.
- [17] P. Moriarty, M.D. Upward, A.W. Dunn, Y.R. Ma, P.H. Beton, D. Teehan, *Phys. Rev. B* 57 (1998) 362.
- [18] T. Yamaguchi, *J. Vac. Sci. Technol.* B12 (1994) 1932.
- [19] X. Yao, T.G. Ruskell, R.K. Workman, D. Sarid, D. Chen, *Surf. Sci.* 366 (1996) L743.
- [20] A. Yajima, M. Tsukada, *Surf. Sci.* 366 (1996) L715.
- [21] X.D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, T. Sakurai, *Jpn J. Appl. Phys.* 31 (1992) L983.
- [22] N. Troullier, J.L. Martins, *Phys. Rev.* B46 (1992) 1754.
- [23] R.A. Wolkow, *Phys. Rev. Lett.* 68 (1992) 2636.
- [24] P. Moriarty, Y.R. Ma, P.H. Beton, In preparation.
- [25] K.F. Kelly, D. Sarkar, G.D. Hale, S.J. Oldenburg, N.J. Halas, *Science* 273 (1996) 1371.
- [26] R. Jones, Private communication, Department of Physics, University of Exeter.