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Attractive mode manipulation of covalently bound molecules

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Abstract

We have investigated the manipulation of C_{60} molecules on $Si(1\,0\,0)$-2×1 using the tip of a scanning tunnelling microscope. An attractive mode of manipulation has been identified in which molecules hop across the $Si(1\,0\,0)$-2×1 surface in steps of two lattice constants. An abrupt transition to repulsive manipulation occurs as the tip is lowered towards the surface. The attractive interaction is attributed to chemical forces between the tip and molecule.
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Since the scanning tunnelling microscope was first used to position atoms adsorbed on a substrate surface [1] lateral manipulation has been applied to the formation of nanostructures [2,3], and has also been extended to encompass the positioning [4–9] and synthesis [10] of single molecules. In addition both atomic and molecular manipulation have been demonstrated at progressively higher temperatures [4–11] culminating in the recent demonstration of the manipulation of a single adsorbed atom at room temperature [12]. At room temperature a much stronger adsorbate–substrate interaction is required to inhibit spontaneous diffusion, and a correspondingly larger tip–adsorbate force is therefore required to initiate manipulation. All of the examples of controlled room temperature manipulation observed to date

have been attributed to repulsive interactions, since tip–adsorbate potentials of the Lennard-Jones type lead to arbitrarily large repulsive forces.

In this Letter, we describe recent results which show that *attractive* as well as repulsive forces may induce lateral displacement of adsorbates at room temperature. The resulting modes of manipulation may be clearly distinguished and molecules hop in a sequence of steps of one or two lattice constants across the substrate surface. We choose to investigate an adsorbate which is bound to the substrate through a covalent interaction. Molecular manipulation must therefore involve bond breaking and we propose that this is induced by chemical forces between the tip and molecule.

In particular, we have investigated C_{60} molecules adsorbed on a $Si(1\,0\,0)$-2×1 surface, for which repulsive manipulation has been previously demonstrated in a phenomenological study [8]. The $Si(1\,0\,0)$-2×1 surface was prepared in an ultra-high vacuum (UHV) chamber using standard procedures (see for example [6]), and C_{60} was

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sublimed at a rate of ~2 monolayers/hour from a Knudsen cell. The surface was investigated using a scanning tunnelling microscope (STM) operating at room temperature in conjunction with electrochemically etched W tips which were cleaned by annealing in UHV prior to use. For this study we use a home-built controller which facilitates a detailed investigation of the mechanisms underlying manipulation [13].

Fig. 1 inset shows an STM image of the surface. C_{60} molecules are resolved as bright protrusions with an apparent width of ~25 Å and height ~6.5 Å. They are adsorbed in the troughs between the dimer rows which are formed on the Si(1 0 0)-2 × 1 surface [14,15]. These rows are resolved in the inset to Fig. 1 as lines running across the image. The surface and adsorption site are also shown schematically in Fig. 1 inset. In order to initiate manipulation the tip is first placed above a trough (midway between dimer rows) within ~20 Å of a target molecule. The height of the tip above the sample surface is then reduced by adjusting the applied bias, V_s, and target tunnel current, I_t, of the feedback control loop. The tip is then moved along the trough, parallel to the dimer rows, to-

wards the centre of the target molecule in discrete steps (size $\Delta x = 0.14$ Å). After each step the tunnel current is adjusted to its target value using feedback control.

Fig. 1 shows examples of the variation in the tip height during applications of this procedure which result in attractive molecular manipulation. In Fig. 1 (upper curve) the variation of tip height with displacement across the surface acquired with $V_s = -2.4$ V, $I_t = -1.1$ nA (the tip is moved from left to right) reveals that the tip is first retracted from the surface as it encounters and passes over the adsorbed molecule. Then, at the position marked by an arrow, an abrupt change in the tip position is observed which is caused by the molecule hopping from left to right towards the tip. This results in an instantaneous reduction of the effective tip–sample separation and a corresponding rise in current, which, due to the feedback control, results in the retraction of the tip. These data are very similar to those obtained for low temperature attractive manipulation by Bartels et al. [8]. In the example shown in Fig. 1 (upper) two further hops occur. The lower curve in Fig. 1 (acquired with $V_s = -2.9$ V, $I_t = -1.2$ nA) shows a different signature of attractive manipulation in which the molecule hops from right to left before the tip has passed over its centre. In each hopping event in Fig. 1 the molecule moves in steps of two Si lattice constants. Attractive hopping through one or three lattice constants is also observed but represents a small fraction (~10%) of the total observed events. Attractive manipulation is observed for both polarities of applied sample voltage.

An example of the variation of tip height recorded during repulsive manipulation is shown in Fig. 2 ($V_s = 1.25$ V, $I_t = 1.0$ nA). The tip is moved across the surface, responding first to the near-periodic height variation associated with the Si dimers, and then, at the point marked by the arrow in Fig. 2, encounters the target C_{60} molecule. The tip is then retracted by ~1 Å following the molecular profile until the point marked by a second arrow in Fig. 2 at which the molecule hops away from the tip. This results in an increase in the effective tip–sample separation and a feedback induced extension of the tip towards the surface. Further repulsive hops result in a sawtooth
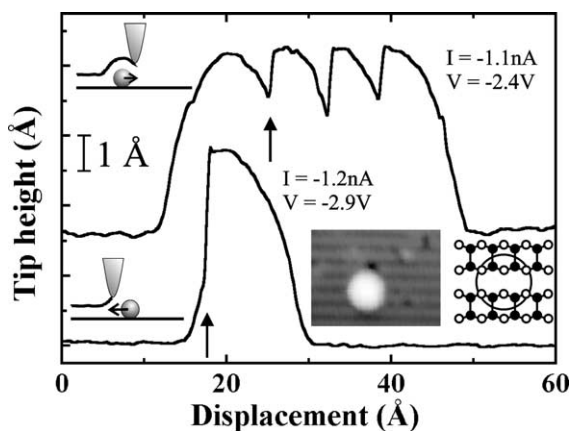

Fig. 1. Line scans showing attractive mode manipulation in which C_{60} hops towards the STM tip either before (lower) or after (upper) the STM tip has passed over the molecule. The inset shows an STM image (75 Å × 55 Å) of C_{60} adsorbed on Si(1 0 0)-2 × 1. Also shown is a schematic of the surface showing the adsorption site of C_{60} in which top and second layer Si atoms are represented as filled and empty circles. The top layer atoms combine to form dimers which in turn form rows. C_{60} is adsorbed in a trough between the rows.
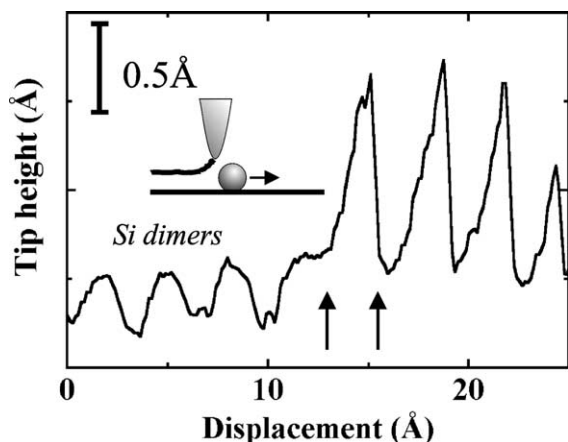
Fig. 2. Line scan showing repulsive mode manipulation. Arrows mark the position where the tip first encounters the C_{60} and the point at which the molecule hops away from the tip.

Fig. 3. Probability of manipulation (ratio of successful manipulations to manipulation attempts expressed as a percentage) versus Δz, the displacement from a common reference position. Statistics for repulsive manipulation based on data for tunnel currents in the range 1.1–1.5 nA. Negative Δz corresponds to displacement towards the surface. Inset shows typical force-distance curve for chemical forces.

response with a period which matches that of the Si dimer separation, showing that the molecule is hopping through one lattice constant between adjacent adsorption sites on the surface. A closely related inverted sawtooth has been observed for low temperature manipulation by Bartels et al. [8].

While the signatures of manipulation in Figs. 1 and 2 have a close resemblance to those reported by Bartels et al. [8] it is important to stress that the processes occurring during manipulation in the present study are fundamentally different, since C_{60} is chemisorbed [16] on Si(1 0 0)-2 × 1 through the formation of covalent bonds [17,18]. In order to initiate manipulation these bonds must be broken. Our results show that there are both attractive and repulsive tip–adsorbate forces which are sufficiently strong to induce bond breaking.

We have investigated the range of parameters over which attractive and repulsive manipulation occur. The fraction of applications of the above procedure which result in manipulation, expressed as a percentage, is plotted versus Δz (the displacement from a common reference position – the tip–surface separation for the voltage and tunnel current used during scanning, −3 V, −0.1 nA) in Fig. 3. The analysis in Fig. 3 is based on ~3500 attempts and ~400 manipulations with currents ranging from −0.1 to −1.5 nA and voltages from −1 to −5 V. Consistent stable operation outside
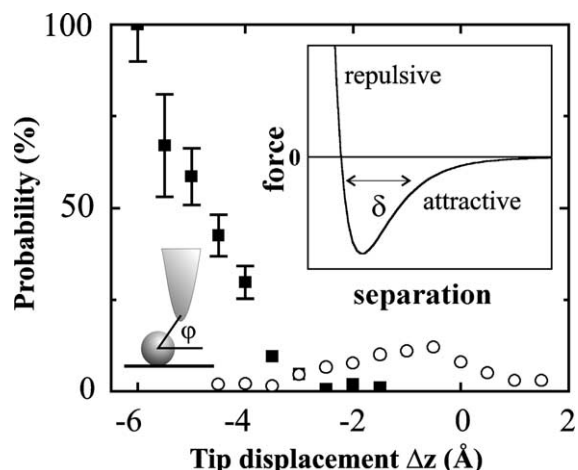
this range was not possible, often resulting in extraction of Si atoms [19,20].

Remarkably we see an abrupt transition from a regime of repulsive to attractive manipulation for $\Delta z = -3$ Å (negative Δz corresponds to displacement towards the surface). The maximum probability for attractive manipulation over the parameter range explored is ~15% while that for repulsive manipulation rises to 100%.

The forces required to initiate manipulation may be estimated by noting that the energy barrier to molecular diffusion, E_B, is lowered in the presence of a force with a component parallel to the surface, $F_\parallel$, by an amount ΔE. The maximum value of $\Delta E \sim F_\parallel a_0/2$, where a_0 (= 3.8 Å) is the surface lattice constant. The barrier lowering leads to a reduced residence time at a particular site, $\tau_{res} = \tau_0 \exp\{(E_B - F_\parallel a_0/2)/kT\}$ (τ_0 is the characteristic vibrational period $\sim 10^{-12}$ s) and results in a dynamic instability against hopping if $\tau_{res} < \tau_{dwell}$ the tip dwell time (~ 1 ms). Thus the molecule may hop if $(E_B - F_\parallel a_0/2)/kT \leqslant \ln(\tau_{dwell}/\tau_0)$, which corresponds to a force $F_\parallel \geqslant 2(E_B - kT \ln(\tau_{dwell}/\tau_0))/a_0$. A value for E_B for C_{60} on Si(1 0 0)-2 × 1 may be estimated as follows. It is known that C_{60} may diffuse

to lower energy adsorption sites on annealing to ~500 °C [14] for times of the order of minutes. This leads to an upper limit for $E_B \sim 2.0$ eV from which we estimate a lateral force $F_\parallel \sim 1.2$ nN assuming room temperature operation.

We attribute the origin of the repulsive interaction to Lennard-Jones type forces, which have no upper bound and so may certainly be greater than the above limit. In determining the origin of the attractive forces we first consider electrostatic and van der Waals interactions and subsequently argue that chemical forces control manipulation. The induced charges on the tip and the molecule, which together form a capacitor, give rise to a force parallel to the surface [21], $F_{cap} \sim 2\pi\gamma\varepsilon_0 V_s^2 \cos\varphi$, where γ is a geometric factor and φ is the angle between the line connecting the centre of the molecule and the tip (see Fig. 3 inset). From our line scans we estimate $\cos\varphi \sim 0.5$–0.7 while, if the tip and molecule are modelled as isolated spheres, $\gamma \sim 1$. Taking $V_s = -2.5$ V, $F_{cap} \sim 0.2$ nN. An alternative electrostatic mechanism, field induced diffusion [22] gives rise to a force estimated to be less than 0.1 nN and will be neglected in this discussion. The characteristic van der Waals interaction for C_{60} (the maximum attractive force between two molecules) ~ 0.2 nN [23] and is lower for a molecule–surface interaction [24]. Thus, both electrostatic and van der Waals interactions are too weak to account for attractive manipulation.

Chemical forces have been discussed widely in the literature in the context of atomic force microscopy (AFM) and arise from the partial formation of bonds between the AFM probe and a surface [21,25–27]. The associated force-distance dependence between an AFM probe and a clean Si surface has now been measured by a number of groups [21,25–27] and has the form shown schematically in Fig. 3 inset. The measured attractive force has a maximum value ~ 2 nN and extends over a length scale $\delta \sim 1$–2 Å [25–28]. During manipulation an adsorbed C_{60} molecule experiences competing chemical forces from the substrate and the STM tip. The dependence of the tip–molecule force on separation would be expected to have the form shown in Fig. 3 inset and a magnitude and range comparable with the values quoted above [26–28]. The maximum attractive

force is thus expected within a few Å of the transition from repulsive to attractive forces. This corresponds closely to the experimentally observed transition from repulsive to maximal attractive manipulation as the tip is retracted from the surface by ~ 2 Å. Thus chemical forces are expected to give rise to a lateral component, $F_\parallel \sim 1$ nN, comparable with the threshold estimated above.

The interactions described above will be determined by the precise atomic configuration of the tip. However the composition and geometry of the tip is generally not well characterised, partly because under operation voltage pulses are applied to optimise scanning resolution, probably resulting in transfer of Si atoms from the substrate to the tip. It is known that C_{60} is chemisorbed on both Si and tungsten [29] although the adsorption energies have not been measured (decomposition occurs at a lower temperature than desorption precluding the possibility of thermally programmed desorption). The adsorption energy for C_{60} adsorbed on Si(1 0 0)-2×1 in a configuration in which four Si–C bonds are formed has been calculated, $E_A = 5.7$ eV [18]. However the equivalent energy minimum resulting from the interaction between C_{60} and a silicon tip will be lower, since bonds would be formed with perhaps only a single Si atom, or at most a nano-facet formed by ~ 3 atoms. Thus, depending on the atomic configuration of the tip, E_A would be expected to lie in the range 1.4–4.2 eV. Combined with a characteristic length scale for covalent bond lengths ~ 1–2 Å gives a characteristic force ~ 1 nN comparable with the values estimated above.

Finally we consider the low probability for successful attractive mode manipulations. Apart from a few exceptional results (such as shown in Fig. 1) we observe single rather than multiple hops with no obvious pattern in the sequence of successful manipulations. The statistical nature of the outcome of manipulation attempts may be a consequence of the process being intrinsically random, or, more likely, a consequence of variations in the tip configuration which result in a variation in the response to manipulation. An explanation of manipulation in terms of partial chemisorption could account for the statistical variations observed in attractive mode manipulation. In particular the tip–molecule force will be sensitive to the micro- or

nano-facets presented at the apex of the tip. The orientation of these facets with respect to the row direction will, in part, determine the magnitude of the component of force along the row leading to a variation in response to manipulation attempts. Note that repulsive manipulation, which results from a force with no upper bound, is likely to be much less sensitive to such tip variations.

Clearly a full description of the manipulation process requires detailed ab initio modelling in conjunction with electrostatics. This may lead to a better understanding of one outstanding issue – the observed hopping through two lattice constants which is presumably related to the geometry of the tip–molecule junction. However for such a large molecule only limited progress has been possible using ab initio methods [18]. Our experimental results show conclusively that the adsorbate–substrate covalent bonds may be broken by an attractive force. The strong attractive interaction is attributed to chemical forces between tip and molecule.

Acknowledgements

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