

SCANNING TUNNELING MICROSCOPY MANIPULATION OF COMPLEX ORGANIC MOLECULES ON SOLID SURFACES

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■ **Abstract** Organic molecules adsorbed on solid surfaces display a fascinating variety of new physical and chemical phenomena ranging from self-assembly and molecular recognition to nonlinear optical properties and current rectification. Both the fundamental interest in these systems and the promise of technological applications have motivated a strong research effort in understanding and controlling these properties. Scanning tunneling microscopy (STM) and, in particular, its ability to manipulate individual adsorbed molecules, has become a powerful tool for studying the adsorption geometry and the conformation and dynamics of single molecules and molecular aggregates. Here we review selected case studies demonstrating the enormous capabilities of STM manipulations to explore basic physiochemical properties of adsorbed molecules. In particular, we emphasize the role of STM manipulations in studying the coupling between the multiple degrees of freedom of adsorbed molecules, the phenomenon of molecular molding, and the possibility of creating and breaking individual chemical bonds in a controlled manner, i.e., the concept of single-molecule chemistry.

INTRODUCTION

Our review describes the adsorption of large organic adsorbates on solid surfaces, an area of research that has gained increasing momentum in recent years (1–4). This increase is motivated partly by the fundamental challenge and interest in understanding processes such as self-assembly and molecular recognition down to the single-molecule level, as well as by the possibility of building molecular nanostructures in a bottom-up approach for a broad range of applications, such

as the following: optoelectronic devices (5), molecular electronics (6), nanomechanical biosensors (7), and new, improved, chemically functionalized implantable materials (8).

While the adsorption properties (physisorption, chemisorption, diffusion, desorption, dissociation) of simple adsorbates such as NO, CO, and O₂ on a great number of host surfaces are well-known (for recent reviews, see References 9–11), much less is understood about the physics and chemistry of adsorption of larger organic molecules. The specifics of the adsorption process and ordering of complex organic molecules on single-crystal surfaces are known to depend on both substrate material and surface orientation (1, 3, 4) and are determined by a delicate balance between competing molecule-surface and molecule-molecule interactions [typically noncovalent, e.g., van der Waals (12–14) or hydrogen bonding (4, 15, 16)]. The specificity of the lateral interaction between peripheral functional groups (for example, hydrogen bonding) leads to the self-assembly of molecular species into well-ordered nanostructures and patterns with, e.g., interesting chiral properties (16–18) or a certain degree of specificity in the host-guest interaction with other molecular adsorbates (19–21). Solid surfaces (in particular “open” surfaces such as the 110 fcc) (22–26) also often reconstruct upon organic-molecule adsorption. However, the driving force for these organic adsorbate-induced reconstructions is different than that corresponding to smaller adsorbates. While in the latter case the reconstruction is usually driven by a charge transfer between the substrate and the adsorbate, several examples of organic adsorbate-induced reconstructions caused mainly by noncovalent interactions have already been reported (22–26).

Here we focus on how scanning tunneling microscopy (STM) can be used to characterize and manipulate organic molecules at single-crystal surfaces under clean, well-controlled ultrahigh vacuum conditions. Such systems are often not appropriate for an investigation by means of “traditional” microscopies and spectroscopies (e.g., SEM, UPS and XPS, RAIRS and FTIR, and EELS and HREELS) because organic molecular species are relatively fragile, and electron or radiation doses typically fragment them during measurements. More importantly, these spectroscopic techniques are incapable of yielding any information on individual atoms and molecules because they integrate information obtained over large areas. The high resolution of STM and its ability to manipulate individual atoms and molecules at the nanoscale render it particularly useful for such studies. In particular, operation at low temperatures generally permits STM manipulation of weakly bound molecules with little or no contribution from thermal motion, thus enhancing the ability to position molecules with atomic precision. STM, especially at low temperatures, can also be operated in the spectroscopy mode by acquiring atomically resolved current/voltage (*I/V*) curves, whereby information can be obtained on both the local electronic structure (27) and the local vibrational spectrum (28). The most stable and compact scanning tunneling microscopes can be operated in a fast-scanning dynamic mode, recording time-lapsed STM movies, allowing us to study surface-diffusion processes with atomic or molecular resolution (29–36). These increasingly popular studies have provided new insight into the physics

and chemistry of the adsorption of complex molecules at single-crystal metal substrates, revealing surprising complexities and pointing to special opportunities.

In the first section we briefly describe the methods used for the lateral or vertical manipulation of individual atoms and molecules on solid surfaces with no regard to their internal structure. For large organic molecules, which possess a 3D structure with many configurational and conformational degrees of freedom, STM manipulation studies allow us to probe the coupling between the different degrees of freedom, which is reviewed in the second section. Another important consequence of their 3D molecular structure is the recently discovered phenomenon of molecular molding. This is a particular kind of adsorbate-induced reconstruction related to the accommodation of diffusing adatoms and vacancies in the proximity of adsorbed molecules, which creates nanostructures whose features are determined by the size and shape of the molecules. STM manipulations are fundamental in studying these molecule-induced reconstructions because the nanostructures thus created can only be revealed by gently displacing the molecule. Finally, we discuss the possibility of exciting individual vibrational modes of organic adsorbates by using the inelastic part of the tunneling current. These excitations can lead to the formation or breaking of molecular bonds, which are at the core of single-molecule chemistry.

Before proceeding we briefly mention a few important areas that we unfortunately are not able to discuss in detail owing to space limitations. The first area concerns the study of supramolecular assemblies on single-crystal surfaces. The second area deals with the adsorption of organic molecules on semiconductors, particularly silicon. Many groups have recently devoted significant efforts to these studies because of silicon's importance in the microelectronics industry and the hope that hybrid organic devices can be integrated with existing silicon technology. We refer the interested reader to several recent excellent reviews on this topic (37), as well as a review by Loscutoff & Bent (95) in this volume that deals with the chemical reactivity of group IV semiconductor surfaces. Finally, the investigation of molecules on insulating surfaces is still in its infancy (38–42), and the possibility of performing atomic-scale manipulations by atomic-force microscopy has just recently been explored (42).

MANIPULATION OF ATOMS AND SMALL MOLECULES BY SCANNING TUNNELING MICROSCOPY

The development of STM (43–45) revolutionized the field of surface science because of its ability to image the structure of conducting and semiconductor solid surfaces with atomic resolution and in real space (9, 45, 46). Today this technique and its derivatives [atomic-force microscopy (47) and scanning near-field optical microscopy (48)] have matured significantly and are having a much broader impact on different disciplines, including materials science, electrochemistry, molecular biology, and even medicine.

Soon after the first scanning tunneling microscopes were constructed and operated, it became apparent that the strong interaction between the scanning tunneling microscope tip and the surface (both foreign adsorbates and native substrate atoms) could lead to atomic-scale rearrangements in substrate structure. However, it took nearly a decade until the technique for manipulating matter at the atomic scale in a controlled and reproducible manner was developed and demonstrated (49–51). By operating the scanning tunneling microscopes in different tunneling regimes (i.e., by varying the tunneling current and/or the tunneling voltage, which determine the tip-surface distance, a variation in the tunnel current by one order of magnitude results in a change in distance of 1 Å), it is possible to either enhance the interaction (manipulation mode) or withdraw the tip so that it does not influence the adsorption/diffusion process under observation.

The mechanisms involved in STM manipulation of single atoms and small molecules are presently well understood (52, 53). Because they have been the subject of excellent recent reviews (2, 54, 55), we describe them only briefly. Two main modes of STM manipulation exist: vertical and lateral (Figure 1). In the lateral mode, the interaction between the tip and the sample is used to displace the adsorbate laterally on the substrate (52). This can be achieved either by (a) using the weak attractive tail of the interaction potential between the adsorbate and the tip (56) so that the adatom jumps to a neighboring surface site following the tip's trajectory (pull mode), (b) using the much stronger repulsive interaction between tip and adsorbate (56) so that the adspecies jumps to a neighboring site to escape from the tip's position (push mode, Figure 1b), or (c) the adsorbate can interact with the scanning tunneling microscope tip in such a way that its lateral position follows exactly the trajectory of the tip (slide mode). The three modes can be distinguished, usually a posteriori, by recording the tunneling current as a function of the lateral position of the tip in the constant-height scanning mode (52). Which of the three lateral manipulation modes are chosen and applicable is dictated by the tunneling parameters and the chemical nature of surface, adsorbate, and tip. For instance, for Pb on Cu(211), lateral manipulations can be carried out either by pulling or by sliding, depending on the tunneling conditions (approximately 120 kΩ for the former and 50 kΩ for the latter); Cu adatoms are mainly manipulated in the pulling mode at tunnel for a tunneling gap resistance of 400 kΩ; and finally CO molecules can be manipulated in the pushing mode for gap resistances of 300–600 kΩ.

In the vertical manipulation mode a voltage pulse transfers the adsorbate from the surface to the tip, or vice versa depending on the polarity of the pulse (50). Alternatively, the tip can be approached vertically to the adspecies until a covalent bond is formed and then retracted (57). This second approach, however, is restricted to those cases in which the covalent bond between tip and adsorbate is stronger than the binding between adsorbate and surface. The tip is then repositioned to the point onto which the adsorbate should be transferred, and a new voltage pulse releases it from the tip, transferring the molecule to the desired surface position (Figure 1c).

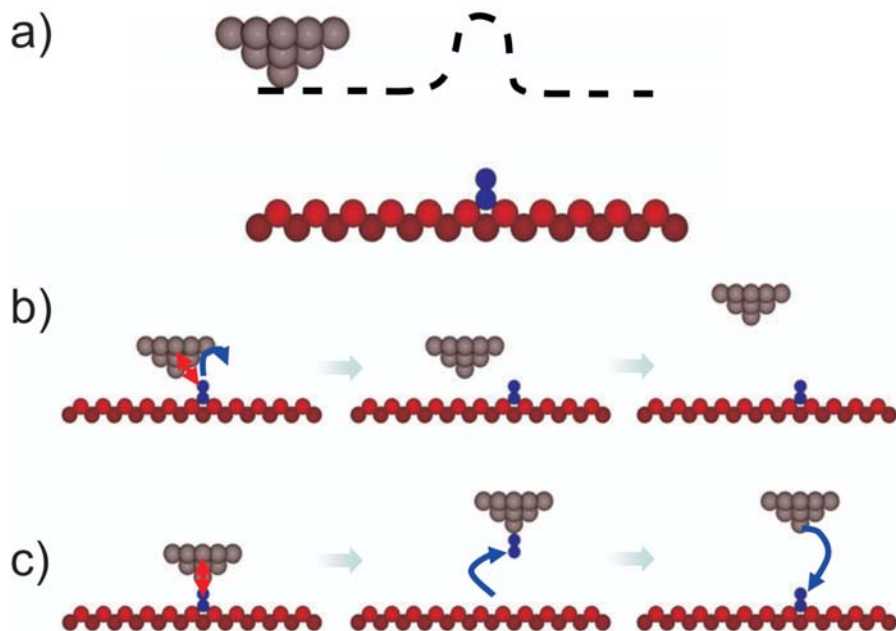


Figure 1 Scheme describing the (a) imaging, (b) lateral manipulation, and (c) vertical manipulation operation modes with a scanning tunneling microscope. In the constant-current imaging mode, the tip's trajectory is adjusted to keep the tunneling intensity at a fixed reference value. The tip's height therefore varies following the surface's topography (a). During a lateral manipulation process, the tip-sample distance is reduced to enhance the lateral interaction between the substrate and the adsorbates, leading to lateral displacement of the adsorbate (b). In the vertical manipulation mode, the tip-adsorbate distance is reduced vertically until the adsorbate is picked up by the tip. The tip will subsequently be repositioned and the adsorbate released, for instance, by means of a voltage pulse.

Besides the direct interaction between tip and sample, there are two other effects that may contribute to the efficiency of the manipulation events. First, "field effects" can be important because the electric field in the region between tip and sample is extremely intense, of the order of $10^9\text{--}10^{10}\text{ Vm}^{-1}$. Indeed, dipolar adsorbates can be repositioned on the surface via application of voltage pulses (58, 59). Second, the excitation of adsorbate vibrational levels by inelastic tunneling electrons can be controlled by the intensity of the tunneling current and the applied bias voltage. Exciting adsorbate vibrational states is somewhat similar to increasing the temperature of the adsorbate locally, which may lead to lateral displacement (60) and, in certain cases, desorption (61). These two effects can influence both the displacement of adsorbates parallel to the surface in lateral manipulation and the transfer of adsorbates between surface and tip in vertical manipulation processes. We use the term mechanical manipulation below to refer to those manipulation

processes mainly caused by the interaction potential between the tip's apex atoms and the molecular adsorbate. The term vibrationally assisted manipulation is accordingly reserved to describe those manipulation events in which the inelastic part of the tunneling current is used to excite vibrational degrees of freedom, which eventually may lead to diffusion, desorption, and selective bond breaking and formation.

A stabler, albeit arguably cruder, method for surface manipulation is to desorb adsorbates (e.g., chemisorbed atomic hydrogen) from a saturated monolayer adsorbed on a surface [e.g., H-passivated Si(111)- 1×1 or 2×1] (61–64). In this way the tip is used as a striker pin to carve the monolayer-covered surface and imprint the desired pattern on it. On passivated Si(111)- 2×1 , the nanopatterns created are stable even at room temperature for several hours. This process has been used to create single vacancies in an otherwise passivated Si(100) surface; these act as single reactive centers to initiate a chain reaction for the growth of 1D molecular structures (65). Alongside the mechanisms described above (mechanical contact, field effects, inelastic tunneling), for tip-induced desorption it has been argued that the injection of electrons into antibonding orbitals might help break the chemisorption bonds. Tip-induced desorption has also been invoked to explain the extraction of Si atoms from the Si(111)- 7×7 surface (66).

The possibility of using atomic manipulation methods to build custom-designed nanostructures in a bottom-up atom-by-atom approach was early recognized. Complex prototype devices capable of performing logic operations have been recently designed by Eigler and coworkers (67) and built with CO molecules positioned one by one on a Cu(111) surface at low temperatures. The basic operation principle of such a nanoscale device is based on the existence of at least two possible configurations for CO trimers on Cu(111), of which one is metastable and decays to the stable configuration in approximately 1 min by displacing the central CO molecule to a nearest-neighbor position (Figure 2*a,b*). By suitably arranging the CO molecules, a chain reaction proceeds, transferring the information of the presence/absence of an initial CO molecule from one end to the other of a molecular chain, in a molecular cascade process (Figure 2*c,d*). For branched structures, the bits of information encoded as the presence or absence of a CO molecule in each one of the input terminals are ingeniously combined to process the input into an output coded in the same way at the exit terminal. In this kind of prototype nanomechanical molecular device, STM manipulation is used not only for constructing the initial diagram of the molecular electronic component, but also for actuating the calculations. Using such techniques in industrial applications is, however, at best a long-term dream and vision, which probably will never be implemented in practice. Problems with the thermal stability of the nanostructures, the necessity of ultrahigh vacuum conditions, and cryogenic temperatures to manipulate the adsorbates in a controlled manner prevent these techniques from being used in an automated manner.

For the structures to be stable at room temperature, the binding between the adsorbate and the surface must be rather strong, which, on the other hand, hinders the possibility of controlled manipulation. In this respect some progress has been

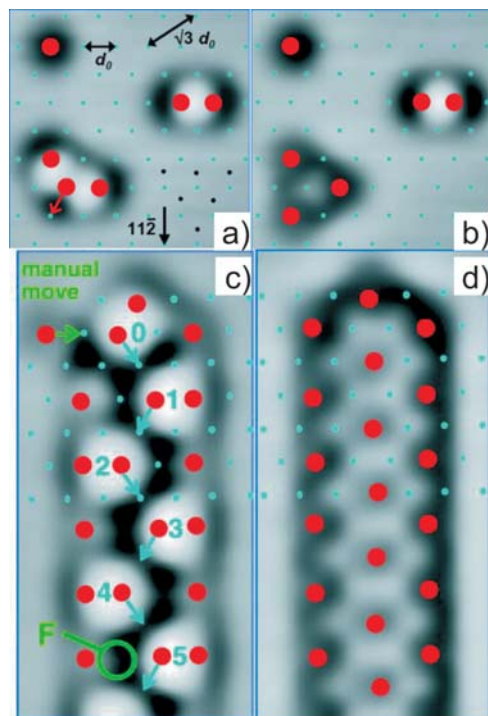


Figure 2 A prototype for a molecular cascade device. CO molecules are deposited on a Cu(111) surface at 4 K. Individual molecules are imaged as depressions (a). The red dots mark adsorption sites for CO molecules, whereas the blue dots represent the lattice positions of Cu atoms. There are two possible geometries for CO trimers: the chevron configuration (*lower left corner* of part a) and the threefold symmetric (*lower left corner* of part b). The chevron trimer is only metastable and decays into the threefold symmetric by displacing the central CO molecule to a nearest-neighbor site (from a to b). By suitably arranging the CO molecules, the decay of one of the trimers into the other one can produce a cascade of events that communicates a bit of information (presence/absence of a CO molecule at a given site) from one end of the chain to the other (c and d). Adapted with permission from Reference 67; copyright 2002 AAAS.

recently made, as single nondiffusing Br atoms have been repositioned at will on a Cu(001) surface at room temperature, thanks to inelastic tunneling excitations that can be controlled by the intensity of the tunneling current (68). Controlled manipulation of large organic molecules has also been demonstrated at room temperature (RT) (60, 69).

Perhaps more significant has been the contribution of molecular manipulation processes to fundamental nano- and surface-science problems. The ability of manipulating and positioning atoms and molecules on a solid surface at will

has opened the possibility to design and build nanometer-scale structures and study their local electronic and mechanical properties. For example, Crommie and coworkers (70) built a circle of 48-Fe atoms on a Cu(111) surface; the surface electrons inside the circle were confined by the scattering potential created by the ring of the Fe adatoms. The electrons formed a standing-wave pattern clearly visible in the low-temperature scanning tunneling microscope images, which directly illustrates in real space the quantum-mechanical wave nature of the electrons. The energies of the quantized states were determined by scanning tunneling spectroscopy. The analysis of these energies provided detailed and interesting atomic-scale information about the scattering properties of individual adatoms that could not have been obtained without the ability for positioning individual adatoms in one of the smallest manmade structures (70). This strategy was subsequently used to design and construct “quantum mirage” motifs, in which the electronic structure of an adatom in a given position can be transferred to a another more distant point by coherent scattering with a manipulation-made confining ellipse of atomic dimensions (Figure 3) (71).

The combination of STM manipulation and imaging has significantly enhanced the capabilities for obtaining atomic-scale information on adsorbate systems. For example, chemical contrast between CO and O₂ molecules adsorbed on Cu(111) has been achieved by functionalizing the scanning tunneling microscope tip with a single CO molecule via vertical manipulation (57). This type of functionalization partially solves one of STM’s limitations, i.e., that of directly distinguishing the chemical nature of adsorbates in STM topography images. By manipulating native Cu atoms from a Cu(110) step edge, the absolute adsorption position of CO, Pb, and C₂H₄ adsorbates was determined (72).

Recently, sliding manipulation experiments for single Co atoms on Cu(111) were used to determine the potential energy surface of the adsorbed Co adatom. When the adatom interacts strongly with the surface, it is attracted to the surface far from the tip, and the change in distance can be recognized by a change in the tunneling intensity (73). The noise in the signal could be interpreted as the signature of the adatom jumping fast between two different adsorption positions. The switching rate shows no significant variation with temperature in between 2 K and 5 K and has been interpreted as resulting from quantum tunneling rather than thermally activated diffusion. A similar mechanism had already been proposed to describe the diffusion of CO molecules on Cu(111) at cryogenic temperatures (67, 73).

MECHANICAL MANIPULATIONS OF LARGE ORGANIC ADSORBATES: ROTATIONAL AND CONFORMATIONAL DEGREES OF FREEDOM

The molecular and atomic adsorbates reviewed above are simple in the sense that, besides vibrational degrees of freedom, the only other degree of freedom relevant to describe their configurational state is the translational one, i.e., the

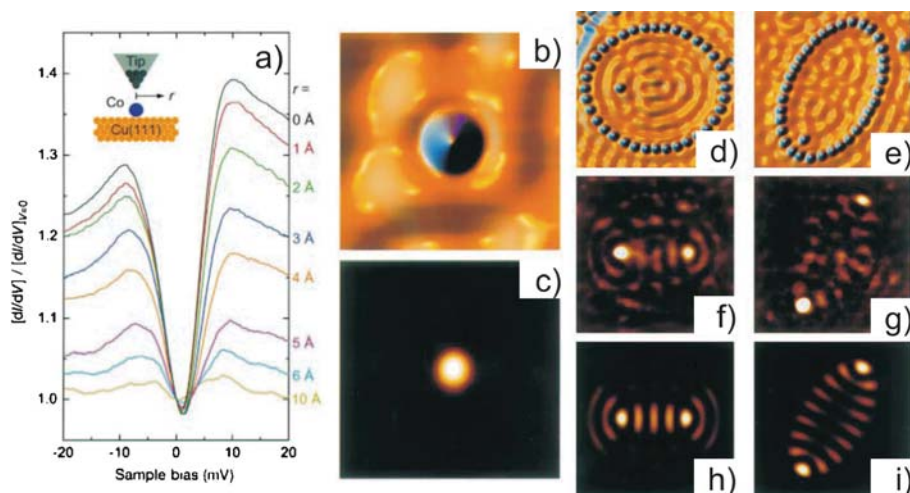


Figure 3 Projection of the electronic structure of a Co adatom sited at the focus of a manmade ellipse to the other focus of the ellipse. The tunneling spectra of individual Co adatoms on a Cu(111) surface shows a depression in the density of states at the Fermi as a result of a Kondo resonance (*a*). This resonance is localized in the immediate surroundings of each individual adatom, as seen by comparing the topography image of an isolated Co adatom (*b*) with the spectroscopic dI/dV map (*c*). Co adatoms also interact with the surface-state electrons of Cu(111) in such a way that electronic standing waves appear in the areas enclosed by scanning tunneling microscope–arranged Co adatoms forming ellipses, such as those shown in parts *d* and *e*. The interaction of a Co adatom placed at one focus of the ellipse with the standing-wave pattern leads to the formation of another Kondo-like resonance in the other focus (*f* and *g*), as shown also by theoretical calculations (*h* and *i*). Adapted from Reference 71.

adsorbate's position with respect to the underlying surface lattice. In contrast, to describe the state of a large organic molecule deposited on a solid substrate, not only the position must be determined, but also its adsorption orientation and its conformation (Figure 4). In this section we discuss a few selected case studies to illustrate how all the nonvibrational degrees of freedom of complex organic adsorbates can be modified at will by mechanical STM manipulations. Moreover, the energy landscape for organic adsorbates turns out to be rather complex, in such a way that the various degrees of freedom are intricately coupled. This fact is of the utmost importance in understanding the dynamics of adsorbed molecules on solid surfaces. STM manipulation is presently the only available technique that allows the study of the complex energy landscape of organic adsorbates at the single-molecule level.

Concerning the translational degrees of freedom, it has been demonstrated that large organic molecules can be manipulated and repositioned by STM following a

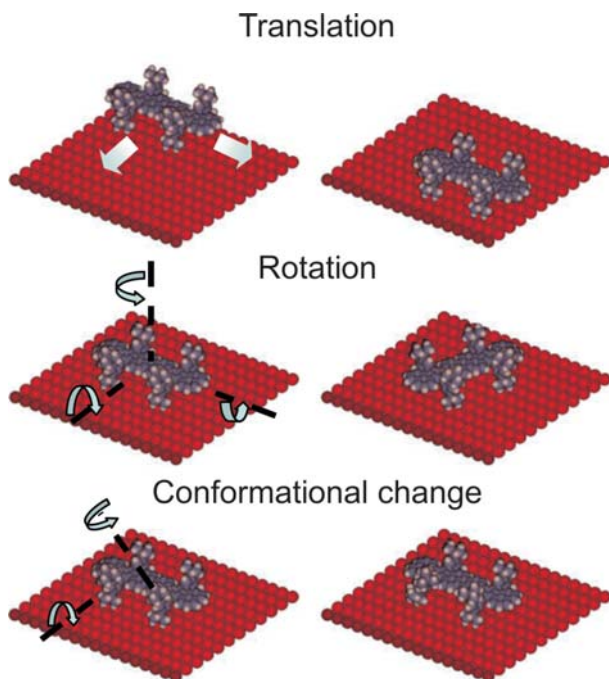


Figure 4 Scheme describing the different translational (*top panel*), rotational (*middle panel*), and conformational (*bottom panel*) degrees of freedom of a complex organic adsorbate [in this case a violet Lander molecule adsorbed on a Cu(110) surface].

similar protocol used for atomic or simple molecular adsorbates (60, 69). In certain cases involving large organic molecules on some metal surfaces, such manipulations can be carried out even at room temperature in a controlled manner (60, 69). The possibility of performing controlled molecular manipulations at RT has been attributed to the interaction strength between the substrate and molecule being in a particular interval; that is, the interaction is sufficiently strong to prevent undesired diffusion events, but weak enough to allow the tip to displace the molecule laterally. However, recent investigations of the diffusion of large organic molecules on surfaces show that the entropy associated with the different molecular orientations plays an important role in determining the diffusivity of complex adsorbates (30, 36). It is expected, therefore, that the absence of molecular diffusion events at room temperature may be a result in some cases of entropic rather than energetic reasons; i.e., the coupling between the molecule and surface phonons may lead more often to the excitation of internal degrees of freedom and other vibrational modes rather than to a displacement of the molecule on the surface. On the contrary, the ability to control the specific interaction between the molecule and the tip in STM manipulation allows the choice of the particular manipulation parameters that would lead to a displacement of the molecule.

It has been repeatedly shown that the lateral displacement of a molecular adsorbate is accompanied by changes in the molecular conformation and/or orientation (74–77). This is observed by recording the tunneling intensity during a lateral manipulation event in the constant- z mode, which we refer to as I- x curve. Along with the periodic signal coming from the substrate periodicity, a superimposed periodic signal can be recognized in many cases. Moresco et al. (75) studied the manipulation of copper porphyrins functionalized with di-*tert*-butyl-phenyl (dTBP) groups that act as spacer legs. They were able to interpret this new feature in the I- x curve, by comparison with molecular-mechanics calculations, as the result of conformational changes in the twisting angle of the legs that occurs during the lateral manipulation of the molecule. Similar conformational changes have been recently reported for sexyphenyl molecules on Ag(111) (76).

Lateral manipulation of large organic molecules can also cause a rotational (rolling) motion of the displaced molecule. It has been recently reported that the I- x curves resulting from lateral manipulation of C_{60} molecules on Si(100)- 2×1 show a periodic sequence of alternative deep and shallow minima (74), consisting of one deep minimum and three shallow minima before the next deep minimum appears. This is consistent with the idea that the effect of the tip is to roll the C_{60} molecule in such a way that the number of broken bonds during the lateral displacement is minimized. This leads to an effective rotation accompanying the movement from one lattice site to a nearest-neighbor site. The rotated molecule is not, however, in the most stable adsorption configuration, which is only restored after three more rolling events, explaining the periodicity of four times the lattice constant. The remaining maxima within each period can be interpreted as each one of the individual rolling events corresponding to the jump of the C_{60} molecule between two nearest-neighbor sites.

Mechanical manipulations in STM have also been used to change the molecule's conformation by selectively acting on a single functional group (26, 78). In the case of the dTBP-functionalized Cu porphyrin, when it is adsorbed on the vicinal Cu(211) surface, two different stable conformations were found from an interplay between STM experiments and elastic scattering quantum chemistry (ESQC) calculations (78, 79): one molecular conformation in which the four dTBP legs are oriented with the phenyl group parallel to the substrate and a different one in which at least one of the dTBP legs is twisted by approximately 60° with respect to the substrate plane. By bringing the apex of the scanning tunneling microscope tip in close contact with one of the dTBP legs, it was possible to switch this particular leg between these two conformations in a controlled manner. The conformational change results in a variation of several orders of magnitude in the tunneling resistance, and the molecule was thus proposed as a prototype for a scanning tunneling-microscope operated single-molecule switch (78). A similar conductance switch associated with a conformational change in adsorbed molecules was reported almost simultaneously (80), but in this case the conformational changes were spontaneous and not precisely controlled by the scanning tunneling microscope tip. The importance of STM as a nanoactuator to operate on

single-molecule electronic devices has been reviewed recently, and we do not discuss it further (2, 3, 6).

We have recently demonstrated that the adsorption orientation of large organic molecules can be modified and controlled by STM manipulations and that the molecular orientation is of utmost importance for the mobility of the molecules (30). The protocol is similar to a lateral manipulation, but the tip's trajectory is adjusted in such a way that it pushes the molecule in an off-centered position.

The molecules studied in these experiments belonged to the Lander family. Molecules from the Lander family are prototype molecules specifically designed to act as "molecular wires" (81). A molecular wire is a long, linear molecule that should have a small HOMO-LUMO gap and a specific organization of molecular energy levels so as to guide tunneling electrons over long distances. Lander molecules have a central, elongated polyaromatic board made of concentric phenyl rings and are endowed with dTBP spacer groups, which are used as separation legs to adapt the height of one extremity of the wire to a metallic step edge to which the molecule may interconnect.

Organic molecules known as violet Landers (VL, $C_{108}H_{104}$) (81) were deposited on a Cu(110) surface. After deposition at room temperature, all the VL molecules were aligned along the close-packed direction of the substrate (12, 24, 30). The surface was then cooled, and manipulations were carried out at 180 K. It was possible to rotate the VL molecules by STM manipulation, but only to another adsorption geometry in which the long direction of the molecular board forms an angle of 70° with respect to the close-packed direction of the substrate (Figure 5*a,b*). For molecules adsorbed on flat terraces, no other adsorption orientation could be stabilized at this temperature. Comparison of the scan lines before and after the manipulation confirms that the molecular conformation remains largely intact.

While the nonrotated molecules do not diffuse even at room temperature, the rotated molecules already diffuse at 150 K with a diffusion coefficient of $D = (4.8 \pm 0.5) \times 10^{-17} \text{ cm}^2/\text{s}$ (Figure 5*c,d*). This implies an increase in the diffusion coefficient of at least two orders of magnitude when the molecule is rotated from its initial orientation parallel to the close-packed direction to the final orientation. The process is fully reversible; in fact the diffusion of a rotated molecule stops when it is flipped back to the nonrotated adsorption geometry (30). From an interplay with molecular-dynamics calculations, this effect was traced back to the different registry between the molecular shape and the atomic corrugation of the substrate: For an adsorption geometry parallel to the close-packed direction, the hydrogen atoms at the bottom of the dTBP legs are in good registry with the fourfold hollow sites of Cu(110), thus locking the molecule in place and hindering its diffusion. On the other hand, for the rotated-adsorption geometry, such a good registry does not exist, and the molecule is free to diffuse. This is referred to as a lock-and-key effect because it depends on the shape complementarity between substrate and adsorbate.

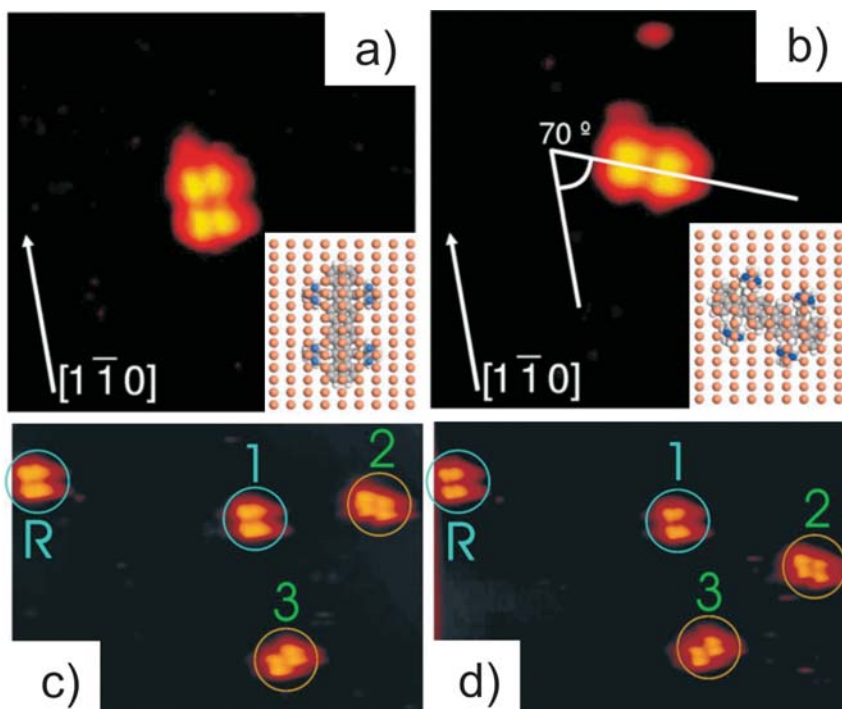


Figure 5 Manipulation-induced rotation of an adsorbed organic molecule (violet Lander, see text) on a Cu(110) and diffusion of the rotated molecules. Violet Lander molecules on metal surfaces are generally imaged with the scanning tunneling microscope as four bumps corresponding to the spacer legs. When deposited at room temperature, all violet Lander molecules are aligned along the close-packed direction of the substrate (a). At 150 K it is possible to rotate the molecules such that their orientation is rotated by 70° (b). Surprisingly, the rotated molecules diffuse at 180 K, whereas the nonrotated ones do not move even at room temperature [c and d; blue circles designate molecules aligned along the close-packed direction of Cu(110), whereas green circles mark rotated molecules.] This effect illustrates the coupling between the rotational and translational degrees of freedom of complex organic adsorbates. Reproduced from Reference 30.

The strong dependence of the linear diffusion coefficient on molecular orientation is another example of the coupling between different degrees of freedom in the dynamics of large organic molecules adsorbed on solid surfaces. Similar to the other case studies described in this section, it would have been impossible to observe without the ability to manipulate individual molecules with the scanning tunneling microscope tip.

MOLECULE-INDUCED SURFACE RESTRUCTURING

In the two sections below, we present selected studies in which single molecules were observed to induce a local restructuring on the metal substrate on which they were adsorbed. More specifically, we discuss STM imaging and manipulation experiments that illustrate how the anchoring of complex molecules on a metal surface may be associated with a local disruption of bonds between the atoms at the uppermost surface layer, just underneath the molecules. In certain cases the surface undergoes a restructuring process so as to accommodate specific molecular geometries (22, 23, 82), subsequently leading to conformational changes within individual molecules (13). Furthermore we describe how individual, fairly large molecules can act as nanoscale molds, reshaping portions of a metallic step edge into characteristic nanostructures adapted to the dimensions of the molecule (23, 24). The restructured surface or step edge provides a preferential adsorption site to which the molecules are effectively anchored (23, 24, 82).

Chiral Restructuring Imprinted by HtBDC Molecules on Cu(110)

The first example describes the adsorption behavior of hexa-*tert*-butyl decacyclene (HtBDC) on Cu(110) at elevated temperature, leading to a surface restructuring process that is actually imprinted by the molecular overlayer. HtBDC molecules consist of a conducting backbone (aromatic π -system) and six spacer groups (*t*-butyl groups, C_4H_9), separating the aromatic part of the molecule from the substrate. The HtBDC molecule is imaged as six bright lobes (82) (see Figure 5*a*), which are arranged in a distorted hexagon with threefold rotational symmetry. Comparison with ESQC shows that each lobe corresponds to tunneling through the *tert*-butyl groups.

Upon molecular deposition at RT, characteristic structures of molecules adsorbed in double rows are observed. The molecules in the rows are held together by weak van der Waals interactions (Figure 6*a*). The molecular rows run along two specific directions of the Cu surface and fluctuate in size, growing and shrinking from the ends where individual molecules may attach or detach. Moreover, at RT the thermal energy is sufficient for individual molecules to diffuse rapidly on clean areas of the Cu surface, also leading to streaks that appear in the STM images (82). All diffusive motion of the molecules can be frozen out by cooling the sample below 150 K (82) (Figure 6*b*).

Schunack and coworkers (82) used the scanning tunneling microscope tip as a tool to manipulate the molecules within this double-row structure. By scanning over the double-row structure with reduced tunneling resistance, it was possible to push away all the adsorbed HtBDC molecules from a certain area of the surface. A clean Cu surface area appears (Figure 6*c,d*) (82). The topmost Cu surface layer, however, reveals a local restructuring at the atomic scale: 14 Cu atoms are removed, and the resulting vacancies are rearranged in two adjacent $[1\bar{1}0]$ rows, forming a

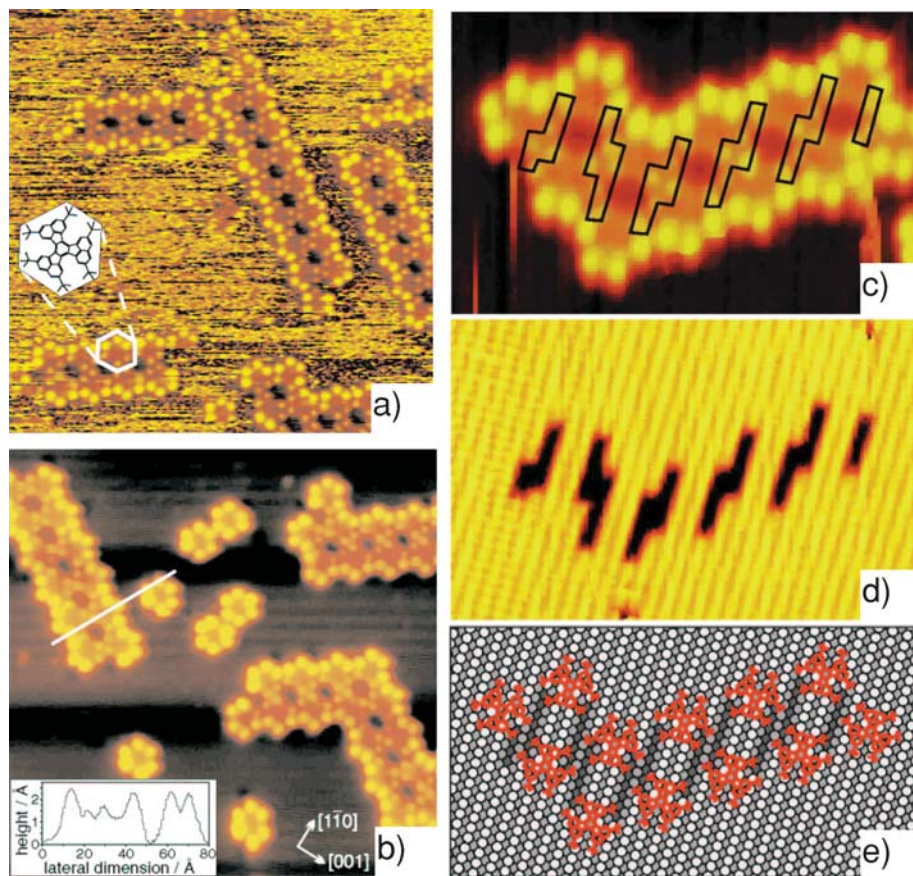


Figure 6 Chiral surface restructuring induced by HtBDC adsorption on Cu(110). HtBDC molecules (inset in Figure 5a) are imaged with the scanning tunneling microscope as six bright lobes corresponding to the *tert*-butyl groups at the molecular periphery. At room temperature there is an equilibrium between diffusing individual HtBDC molecules and the nucleation of double-row islands (a). At lower temperatures, the diffusion of the individual molecules can be frozen out (b). By gently displacing the HtBDC molecules in a double row with the scanning tunneling microscope tip, a chiral hole is revealed underneath the initial position of the molecules (c, d, and e). Adapted from Reference 82.

trench-like base to which the molecules were anchored prior to the manipulation process. The registry of the molecules was determined accurately from atomically resolved images where the molecular double rows and the Cu(110) lattice are resolved simultaneously, inferring that the three more dimly imaged *tert*-butyl lobes of each molecule are positioned on top of Cu vacancy structures (i.e., they are entrenched; see Figure 6e).

Closer inspection reveals that the troughs are chiral (22). In fact, at full coverage every molecule is found to be associated with a chiral hole in the underlying surface. The observed molecule-hole complexes extend homogeneously over the entire surface and segregate spontaneously into enantiomorphic domains upon gentle annealing, thereby creating an ordered, chiral metal surface (22).

The molecular anchoring process on the disrupted surface may have two causes, which can act separately or concurrently. It could be a simple steric effect, i.e., an adaptation of the surface geometry to allow the *tert*-butyl groups to fit into the trenches, which results in a larger interaction area and thus in a larger binding energy. Alternatively, the creation of steps and even kink sites underneath the molecules causes a higher local reactivity and therefore a stronger binding. This is rationalized in terms of a simple correlation between the bonding strength of a molecule and the metal coordination number of the adsorption site (22).

When depositing HtBDC molecules at temperatures below 250 K, the molecular double-row structures do not form. At such reduced temperatures the thermal energy is not sufficient to promote adatom-vacancy formation and diffusion on Cu(110), and therefore the molecules are not able to entrench themselves (22, 82).

These observations show that the adsorption of large organic molecules on a metal surface can locally imprint chiral patterns on the underlying substrate. Because each molecule is associated with one kink site, it is inferred that the molecules are able to transfer specific kink site chirality to the metallic substrate in a chiral imprinting process. This effect may have implications on the asymmetric catalytic behavior of chirally modified surfaces.

Molecular Molding: Lander Molecules on Cu Surfaces

The single Lander (SL) is the parent molecule of the Lander family introduced above. In this section we describe the surprising ability of this family of molecules to act as molecular molds at the nanometer scale, by means of a thermally activated process.

Upon submonolayer deposition of the Lander at RT, molecules adsorb on the surface and diffuse toward step edges, as shown in Figure 7*a* (23). The substrate was then cooled to ~ 150 K, and STM manipulation experiments of isolated molecules were performed to investigate in detail the structural rearrangements associated with anchoring of the molecules to step edges after RT adsorption. By precisely controlling the scanning tunneling microscope tip's position, Rosei et al. (23) pushed away individual molecules selectively, one at a time along a predefined path, leaving the rest of the scan area unperturbed.

Surprisingly, such manipulation of individual Lander molecules anchored at the step edges revealed an underlying restructuring of the monoatomic Cu steps induced by the anchored molecules (23), as depicted from the manipulation sequence shown in Figure 7. A peculiar metal nanostructure appears at the site where the molecules were previously docked (attachment site in Figure 7*b*); a close-up image with atomic resolution is shown in Figure 7*e*.

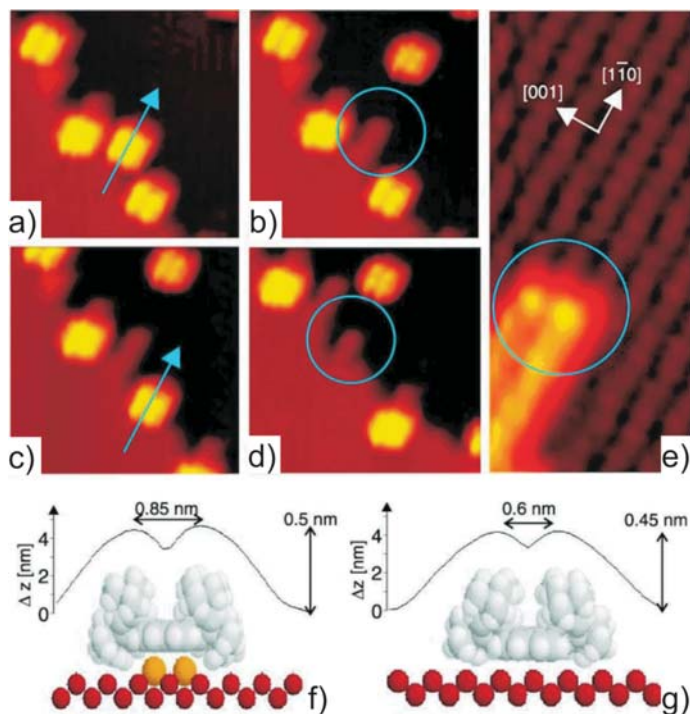


Figure 7 Molding of Cu step edges by single Lander molecules. After deposition at room temperature, single Lander molecules diffuse toward the step edges. By gently pushing the single Lander molecules away from the step edges at 150 K, a nanoscale protrusion is found underneath the initial position of the single Lander molecules (*a–d*). The size of the nanostructure is in good agreement with the molecular dimensions (*e*). Theoretical calculations show that a single Lander molecule adsorbed in such a nanostructure presents a more relaxed conformation than those adsorbed on a flat surface (*f* and *g*). Creating such nanostructures and docking on top is thus energetically favorable for single Lander molecules. Adapted from Reference 23.

The Lander anchors to the nanostructure at a step edge because the total energy required to adsorb the molecule on this structure relative to its adsorption on a flat terrace or to a straight step edge is higher. The molecule's size and shape form a perfect mold for reshaping Cu kink atoms at the step edge, creating a nanostructure that is two Cu atoms wide and seven Cu atoms long, which is exactly the space available under the board and between the legs. It is therefore energetically favorable for the Lander to reshape Cu kink atoms into the observed structure. This adsorption geometry also optimizes the attractive interaction between the molecule's extended π -system and the Cu atoms underneath. At step edges, Cu kink atoms are highly mobile at RT, but this mobility can be

frozen out at low temperatures, allowing the direct visualization of the molded step edge.

Height profiles measured across Lander molecules just before and after displacement indicate that the molecules change conformation during the manipulation process. This shows that the interaction of the central board is optimized when the molecules rest on the nanostructure. ESQC calculations allowed the reason for these conformational changes to be inferred (Figure 6f,g). The molecular central board is strongly attracted to the surface because of the large π -system facing the metal substrate (13, 23). This introduces a severe constraint on the legs when the Lander lies on a flat terrace, which leads to an out-of-plane distortion of each leg-board σ -bond. When the Lander is anchored to the nanostructure, this σ -bond almost restores its planarity relative to the board because its central part is lifted up by more than 0.1 nm relative to the surface (Figure 6g). This effect reduces the steric constraint that acts on the leg-board σ -bond, leading to an increased width (0.83 nm versus 0.63 nm) and height (0.50 nm versus 0.45 nm) of the Lander in the scanning tunneling microscope image, in good agreement with experimental results (23, 83).

The control experiment consisted of adsorbing Lander molecules directly at low temperatures (150 K). Similar to the case of HtBDC, no restructuring of the Cu step edges is observed in this experiment, and the molecules simply anchor to straight step edges. At low temperatures, the mobility of Cu atoms and vacancies (and therefore kink atoms at the step edges) is reduced, effectively hindering the Lander's molding action. It was thus concluded that this process is thermally activated (23).

In general, the intentional separation of a strongly bonding molecular subunit (such as the π -system in the Lander and in HtBDC) from a metal surface is a driving force for a local restructuring of the metallic substrate, so as to regain an optimal interaction and adsorption geometry.

In an attempt to generalize the effect observed for the SL, we exploited the flexibility afforded by synthetic organic chemistry, which allows the preservation of the main design features of a given molecular species yet also allows the modification of specific architectural details. This originally led to the design of the VL Lander (84), which is introduced in the section above on surface diffusion controlled by STM manipulation. The difference between the VL and the SL is the geometry of the board, which is longer for the VL (2.5 nm) than for the SL (1.7 nm) and has a different distribution of phenyl rings with respect to their symmetry axis σ . Similar to the case of the SL, we demonstrated that the VL also reconstructs Cu step edges according to its size and shape (24). The molecules accommodate their aromatic board on the nanostructure created by trapping diffusing Cu kink atoms, whereas the legs rest on the lower terrace. However, the structure reshaped by the VL is always longer and sometimes wider than the corresponding structures created by the SL. This observation demonstrates that appropriate design of molecular size, shape, and functional groups allows imprinting specific patterns on metal surfaces at the atomic scale, generalizing the phenomena observed for HtBDC and the SL.

As in the case of the SL, the formation of the nanostructure and VL's anchoring to it are associated with a measurable change in molecular conformation. This is recognized in the STM images as a decrease in the molecule's height and in the distance between the lobes at each side of the board. A close inspection of the STM images after manipulation reveals that the size of the nanostructures created by the two molecules is different. The nanostructures created by the SL are 7 ± 1 -Cu atoms long and 2-Cu atoms wide, whereas the VL reshapes step edges into structures 9 ± 1 -Cu atoms long and either 2-Cu atoms wide (70%) or 3-Cu atoms wide (30%).

Again, comparison with ESQC calculations allows us to trace the origin of these different molding effects back to the different molecule-substrate interactions arising from the molecules' overall structure. With respect to the length of the nanostructure, the most energetically favorable situation is that in which the length of the metallic nanostructure matches the size of the molecular board because this optimizes the attractive interaction between the extended π -system and the Cu atoms underneath. In particular, this explains the longer nanostructures found in the case of the VL as compared with those observed under the SL because the VL's polyaromatic board is in fact longer. On the other hand, an increase of the width of the nanostructure also increases the attractive interaction between the board and the surface, but at the same time it forces the legs to spread further apart, increasing the stress energy associated with a distortion of the leg-board σ -bond. According to simple effective medium theory calculations (24), in the case of the VL the energy difference between forming a two-row structure as opposed to a three-row structure is only 0.04 eV, which explains why the VL, having a slightly larger board and different arrangement of phenyl rings, may induce both structures, with an overall preference for two-row structures. In conclusion, the different molecular architecture of the SL and the VL is responsible for the differences in the size of the nanostructures they create.

Since our initial studies, surface reconstructions induced by molecules of the Lander family have been observed in a number of cases (25) and have been used to investigate the electronic contact between individual molecules and the reconstructed step edge, which acts similar to a metallic pad (26). These studies further generalize the concept that molecular design may be exploited to imprint predefined patterns on metal surfaces at the atomic scale and illustrate how this can be used, for example, to fabricate suitable nanoscale interconnects for applications in molecular electronics.

VIBRATIONALLY ASSISTED MANIPULATIONS AND SINGLE-MOLECULE CHEMISTRY

In sections above we review the possibility of modifying all the possible degrees of freedom of a large organic adsorbate by mechanical STM manipulations in pushing, pulling, and sliding modes and the information that can be thereby extracted. In the introduction we mention that STM manipulations can also be performed by

exciting particular vibration modes of the molecular adsorbate with the inelastic component of the tunneling current. These vibrationally assisted manipulation processes are not well suited for repositioning individual molecules in a controlled manner because the outcome of such an excitation is to some extent random. However, this kind of manipulation opens the new and exciting possibility of studying chemistry at the single-molecule level (54) because it was shown that particular chemical bonds can be created and broken in a selective manner. In this section we discuss the foundations for these inelastic tunneling effects and some selected examples of single-molecule chemistry induced by vibrationally assisted manipulation processes.

As early as 1966 it was discovered that the tunneling conductance in metal-oxide-metal junctions containing organic molecules showed sharp increases at specific bias voltages corresponding to the energies of the molecular vibrational modes (85). The conductance changes were relatively small (approximately 1%) and were clearly resolved as peaks in the second derivative of the tunneling current versus bias voltage, d^2I/dV^2 . These findings could be understood by assuming that a small fraction of the tunneling electrons can interact inelastically with the molecules in such a way that whenever the bias voltage reaches one of the vibrational modes of the molecule, a new conductance channel opens up, corresponding to the electrons that lose part of their energy in exciting these vibrational modes (Figure 8) (85).

Even though the phenomenon of inelastic tunneling was also expected to take place in the vacuum-tunneling junctions between a scanning tunneling microscope tip and a molecule-covered solid surface, it was not until 1998 that Stipe et al. (28) strikingly demonstrated the possibility of performing vibrational spectroscopy with STM in a well-controlled and reproducible manner. In these experiments, the vibrational levels of acetylene molecules adsorbed on a Cu(100) surface were obtained by recording d^2I/dV^2 as a function of the bias voltage. Not only did the vibrational levels measured correspond well with those obtained from other space-averaged techniques, but the isotopic shift in the deuterated species also agreed well with previously reported values (Figure 9). Since the pioneering work from Ho's group, several other groups have succeeded in applying this technique for the determination of vibrational spectra of adsorbed molecules (86, 87).

The effect of the inelastic electrons is thus to excite the molecule to a high-energy vibrational state, with selectivity over the excited vibration mode. The vibrational energy provided to the molecule may help molecular diffusion on the solid surface (88), molecular desorption (86), or can be redistributed among other degrees of freedom such as rotational (89) or conformational (90). The selectivity in the vibrationally assisted manipulation process described above was recently demonstrated for ammonia molecules on Cu(100) (86). It was observed that simply scanning on top of the molecules at certain voltages led to either lateral displacement or desorption of the molecule, which could be distinguished by subsequent scanning over the same area. The threshold voltages for both processes were different and related to the excitations of the stretch and umbrella vibrational modes for translations and desorption, respectively.

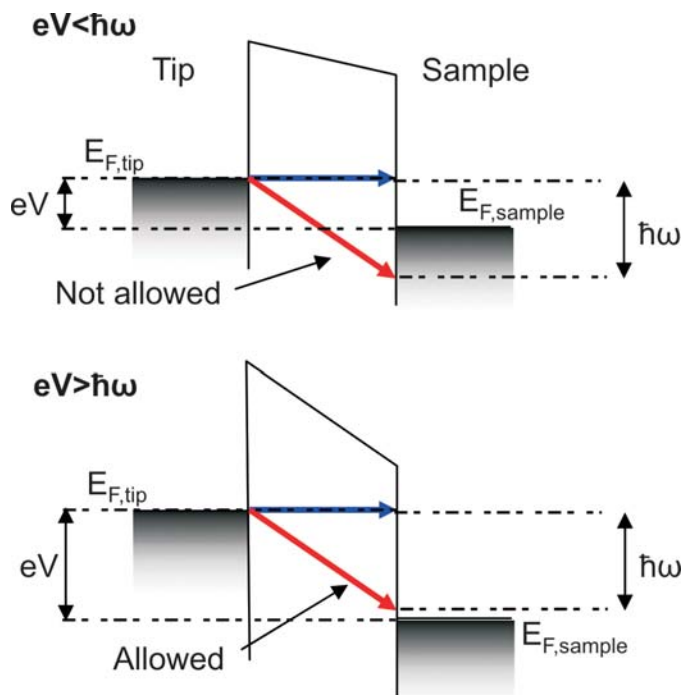


Figure 8 Diagram showing the principle underlying the existence of an inelastic contribution to the tunneling current and the possibility of performing vibrational spectroscopy with scanning tunneling microscopy. An adsorbate has a vibrational level $\hbar\omega$. For voltages below $\hbar\omega$, electrons losing the energy $\hbar\omega$ would acquire an energy below the Fermi level of the opposite electrode, and the tunneling process would thus be forbidden because the final state would be occupied. However, for voltages above $\hbar\omega$, the inelastic tunneling path is allowed because electrons losing this energy would still retain an energy level above the Fermi level of the opposite electrode, and the final state would be empty. Therefore, whenever the voltage crosses one of the adsorbate's vibrational levels, new tunneling channels open up, resulting in an increase in the current slope (peak in the second derivative).

By exciting the stretching mode of linear bonds such as C-H (91), O-O (92), or C-I (93), these bonds can be selectively broken, resulting in the creation of adsorbed free radicals. In some cases, however, abstracting hydrogen from an organic molecule by STM manipulations does not result in a free radical, but in a rearrangement of the electronic structure and the number of single and double bonds, such as in the dehydrogenation of *trans*-2-butene into 1,3-butadiene (87). When these free radicals are moved toward each other, and in some cases excited by inelastic electrons so as to enhance the adsorbate's mobility, new chemical bonds may be created. This is the concept of single-molecule chemistry, i.e., the

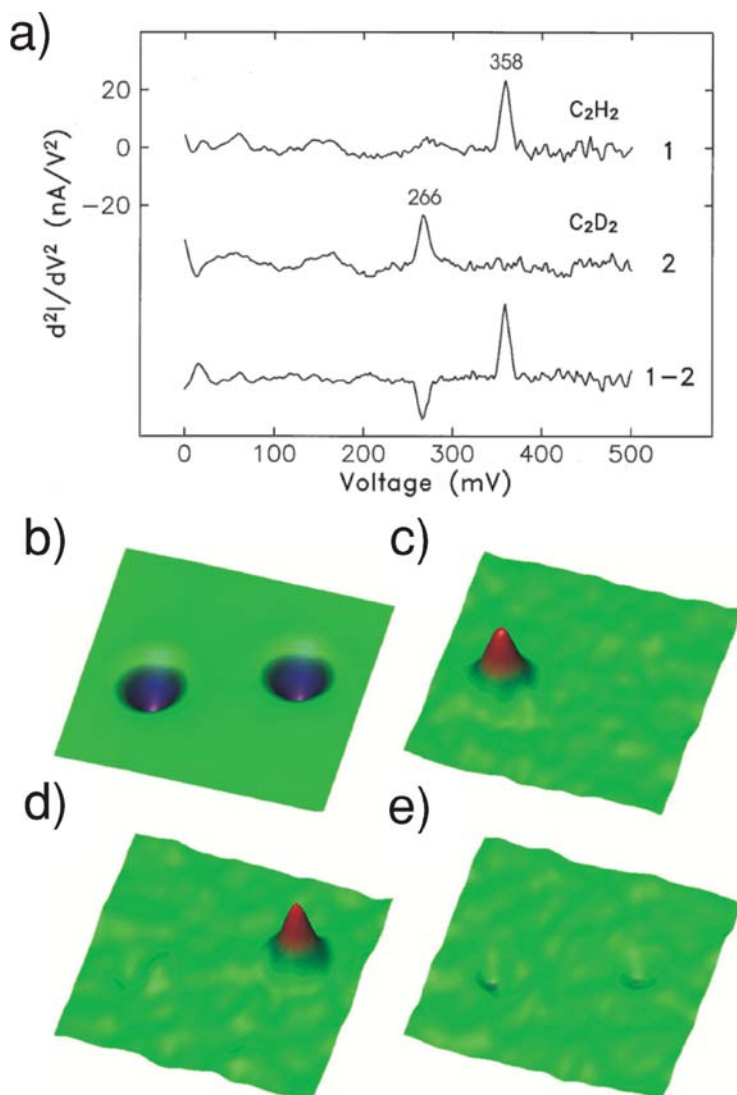


Figure 9 Measuring the vibrational spectrum of molecular adsorbates by scanning tunneling microscopy. Vibrational spectra of acetylene (*curve 1* in part *a*) and deuterated acetylene (*curve 2* in part *a*). The curves have been measured by recording the second derivative d^2I/dV^2 on top of the molecule and subtracting the spectra recorded on top of the substrate. The peaks represent the C-H and C-D vibrational frequencies respectively. The isotopic shift permits us to differentiate between the two chemical species. Whereas the topographic images corresponding to the deuterated and nondeuterated species show no significant difference (*b*), by recording a spectroscopic d^2I/dV^2 map, it is possible to see one of the molecules or the other (*c* and *d*) depending on the applied bias voltage. Adapted from Reference 28.

possibility of creating and breaking bonds between individual molecules, one by one. For instance, Lee & Ho (94) succeeded in synthesizing $\text{Fe}(\text{CO})_2$ complexes from adsorbed Fe atoms and CO molecules, simply by adding CO molecules one at a time to the adsorbed Fe center.

Hla and coworkers (93) were able to induce all elementary steps of an Ullman reaction (synthesis of biphenyl from two iodobenzene molecules catalyzed by Cu) at the single-molecule level with a scanning tunneling microscope tip. They started by tearing apart the iodine group from two iodobenzene molecules adsorbed at the step edges of Cu (111), then dragging the remaining phenyl groups toward each other, and finally applying a current pulse (Figure 10). As a result of this process a single entity could be observed in scanning tunneling microscope images and along the step edge manipulated as a whole. It is argued that a final current pulse is needed to rotate the phenyl groups so that the unpaired electron will not point toward the Cu step edge, but to the unpaired electron of the other molecule, thereby creating a covalent bond. The products of such reactions are usually analyzed by inelastic

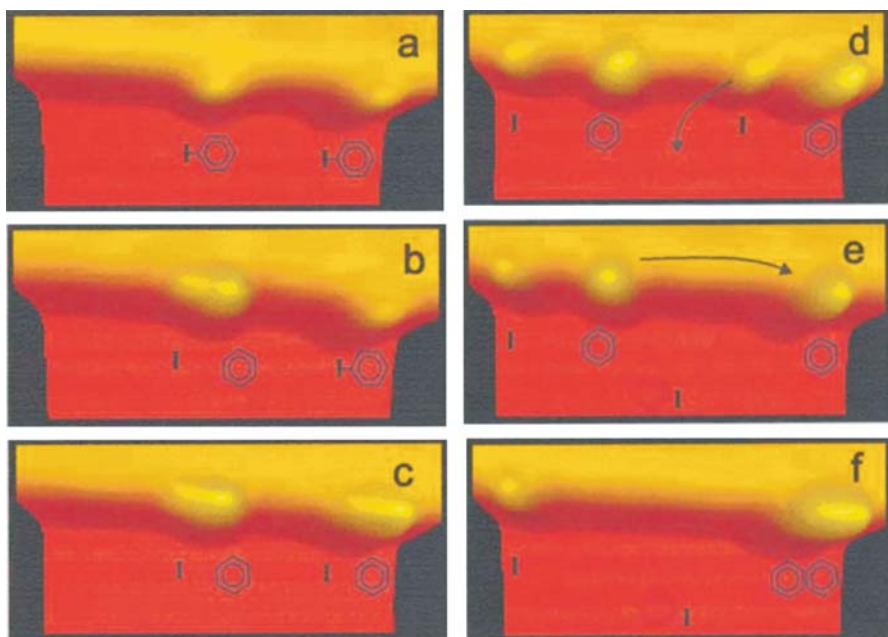


Figure 10 Realization of the concept of single-molecule chemistry. Two iodobenzene molecules are adsorbed at a Cu(111) step edge (*a*). By letting tunneling current flow through the tunneling junction on top of the molecules, they are spliced in two phenyl and two iodine groups (*b* and *c*). One of the iodine groups is removed with the scanning tunneling microscope tip (*d*) and the two phenyl groups are pushed together (*e* and *f*). A subsequent number of voltage pulses leads to the formation of an adsorbed biphenyl molecule. Reprinted from Reference 93; copyright 2000 by the American Physical Society.

electron tunneling spectroscopy. Although suggestive evidence about the formation of covalent bonds by STM manipulation has been discussed in the literature, no conclusive evidence of covalent bonding has been found in the products.

CONCLUSIONS AND PERSPECTIVES

In conclusion, we present in this review selected case studies illustrating the use of STM imaging and manipulations to gain fundamental knowledge on the physics and chemistry of adsorption of large, complex organic molecules on solid surfaces. The information thus gained is in many cases unique, as no other experimental technique could provide similar detailed information at the individual-molecule level. With increasing molecular complexity, a greater role of nonbonding interactions and conformational degrees of freedom in the physico-chemical properties of organic adsorbates is to be expected. The study of these phenomena will require the use of the STM in the manipulation mode, which allows, for example, the selective modification of the adsorption state.

STM manipulations can also be used to fabricate novel nanostructures by arranging individual atomic or molecular building blocks one by one in a bottom-up approach. Current efforts aim at increasing the automatization of the STM-assisted building of nanostructures; we expect significant progress in this area in the near future. Finally, the use of the scanning tunneling microscope tip as a nanoactuator to act on functional, adsorbed molecular devices has already been demonstrated. Progress needs to be made in relaxing the extreme conditions in which these experiments are carried out so as to bring technological applications within reach. Since the first experiments reported by Eigler and coworkers in the early 1990s, this field is more exciting and rich with opportunities, as it leads to unprecedented information on the physical and chemical landscape of surfaces.

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