

## Manipulation of Atoms and Molecules with the Low-Temperature Scanning Tunneling Microscope

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The controlled manipulation with a scanning tunneling microscope (STM) down to the scale of small molecules and single atoms allows the buildup of molecular and atomic nanostructures. In the case of the lateral manipulation of adsorbed species, in which only tip/particle forces are used, three different manipulation modes (pushing, pulling, sliding) can be discerned. Vertical manipulation of Xe and CO is demonstrated, leading to the formation of functionalized tips, which can be used for improved imaging and even to perform vibrational spectroscopy on single molecules. Furthermore, we describe how we have reproduced a full chemical reaction with single molecules, whereby all basic steps, namely, preparation of the reactants, diffusion and association, are induced with the STM tip.

**KEYWORDS:** Low-temperature scanning tunneling microscope, atomic and molecular manipulation, vibrational spectroscopy, nanostructures, carbon monoxide

### 1. Introduction

The scanning tunneling microscope (STM) was initially intended for imaging surfaces and has proven its unique abilities in producing images with down to atomic resolution, but it has been realized that, due to its close proximity to the surface atoms, the STM tip often influences and modifies the surface. However, the obvious disadvantage for imaging became a positive prospect with the realization that the tip-substrate interaction can be used to manipulate on the surface in a controlled manner. Pertinent studies have shown that the STM offers startling possibilities for modifying surfaces down to nm- and even atomic scale.<sup>1–3</sup> Thus, the longheld dream of fabricating functional nanostructures and to create new material combinations or even new materials in an atom-by-atom manner appears to have come into realistic reach.

To modify a surface by means of a STM tip, one can use three different parameters: the electrical field between tip and substrate, the tunneling current, and the forces between tip and surface.<sup>2</sup> Effects of the electrical field and electronic/vibrational excitation by inelastic tunneling have been exploited for manipulation on semiconductor surfaces, because of the high binding forces involved, in a variety of ways to extract or deposit atoms.<sup>4,5</sup> Reliable precision for lateral

manipulation on the atomic scale on flat metal surfaces can be achieved by using mainly the tip-substrate forces. Compared to the electrical field and current effects, these forces are very localized and can be easily tuned by changing the distance between the tip and the manipulated particle. Through working with single atoms and molecules, we distinguish lateral and vertical manipulation modes. In the former mode, a particle on the surface is moved along the surface to the desired location without losing contact with the substrate (Fig. 1), while in the latter mode a particle is deliberately picked up by the tip and then released back onto the surface (Fig. 7).

### 2. Experimental

In our experiments we used three different self-built STM machines, capable of operation between 8 and 300 K. A detailed description of the first self-built instrument can be found in ref. 6. As substrates for the manipulation experiments described here we used Cu(111), Ag(111), Cu(100) and Cu(211), a regularly stepped surface consisting of (111)-nanofacets separated by (100)-steps of monoatomic height. The crystals were prepared in ultra high vacuum (UHV) by several cycles of sputtering with Ne-ions and annealing at about 700 K. Very low coverages of gaseous adsorbates were prepared by dosing through a very fine hole onto the sample located in the STM in the first system and in a separate preparation chamber in the newer setup. Metals and molecules were evaporated from Knudsen cells in analogous ways.

### 3. Lateral Manipulation

In Fig. 2 we demonstrate the creation of artificial structures by lateral manipulation. The Brandenburg Gate of Berlin is perfectly reproduced on the atomic scale. The structure was built by manipulating CO molecules laterally on Cu(211). The experiment was performed at 15 K. At this temperature, the molecules are frozen to a sufficient degree, so that precise working is possible with a large number of particles and the artificial structure remains stable for a long time. An outline of the different stages of the buildup process of an artificial structure is given in Fig. 3.

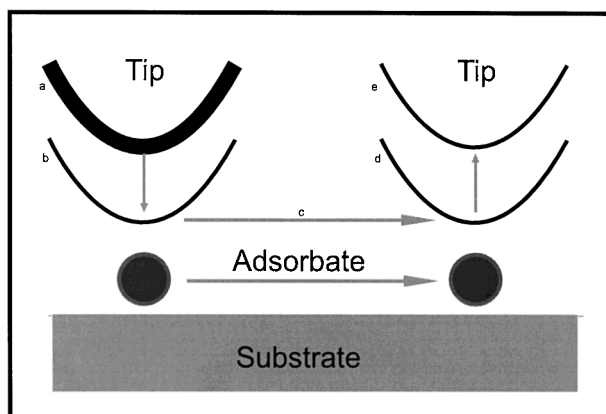


Fig. 1. Sketch of the pulling procedure in the lateral manipulation of single atoms or molecules on a Cu(211) surface (lateral manipulation).

After successfully manipulating small molecules such as CO and C<sub>2</sub>H<sub>4</sub>, we experimented with the manipulation of atoms such as Pb and Cu.<sup>7)</sup> Applying higher forces, we demonstrated on Cu(211) that it is also possible to release na-

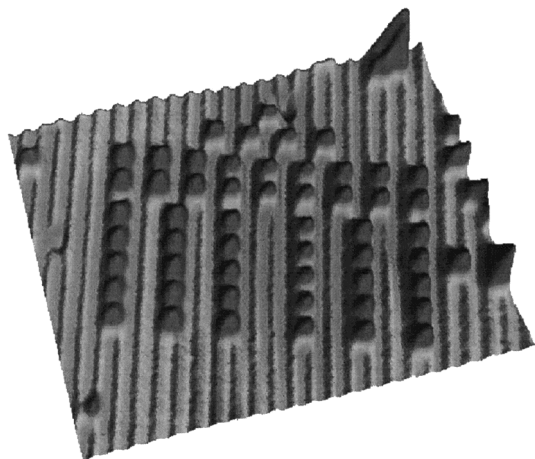


Fig. 2. (a) STM image of the Brandenburg Gate, as a very recent example of lateral manipulation. CO molecules deposited on Cu(211) were used. The substrate temperature was 15 K.

tive substrate atoms from sixfold coordinated kink sites (Figs. 4(a)–4(c)) and even from sevenfold co-ordinated regular step-edge sites (Figs. 4(d)–4(g)).<sup>8)</sup> This important result opens the way for the structuring of the surface itself, with the additional prospect that deeper lying substrate layers may also be included in the buildup of artificial prototype structures. We have also shown that vacancies at the step edges of regularly stepped surfaces such as Cu(211) can be filled by manipulating single atoms into them; interestingly, a larger force is required for this purpose than for manipulation along defect-free step edges.<sup>8)</sup>

The structure presented in Fig. 5 shows the formation of a quantum corral by the lateral manipulation of Ag atoms on a Ag(111) surface, similar to those first created in Eigler's group. The atoms have been positioned in a circle with a diameter of 22 nm. The electrons in the surface state are scattered by the Ag atoms resulting in a circular interference pattern. The observed standing wave pattern becomes highly sensitive to the phase relaxation length of the electrons if the diameter of the corral is of comparable size.<sup>9)</sup> In this context these corrals may be thought of as nanoscale quantum laboratories. Manoharan *et al.* have shown that in an elliptical corral, a magnetic atom placed in one focus is seen as a mirage at the other focus via its magnetic Kondo signature.<sup>10)</sup>

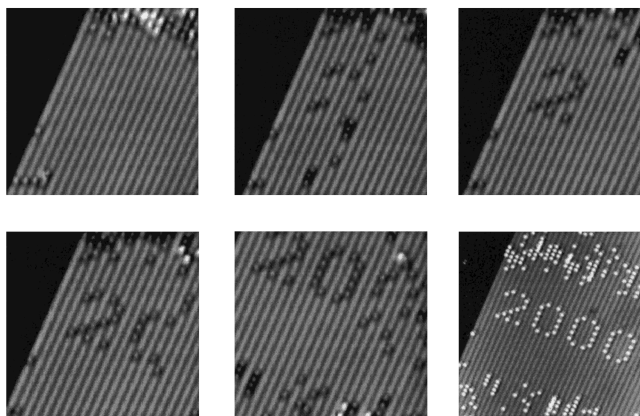


Fig. 3. Sequence of STM micrographs showing the gradual build-up of the symbol "2000" with CO molecules on a Cu(211) substrate. Notice that an area completely free from CO molecules had to be prepared at the beginning.

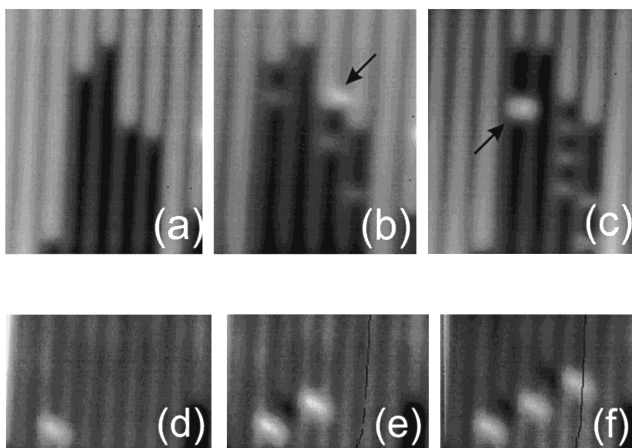


Fig. 4. Manipulation of native Cu atoms from six fold coordinated kink sites at defect steps ((a)-(c)) and from seven-fold coordinated regular step sites ((d)-(f)) on Cu(211). Notice the appearance of adatom/vacancy pairs in the latter case.

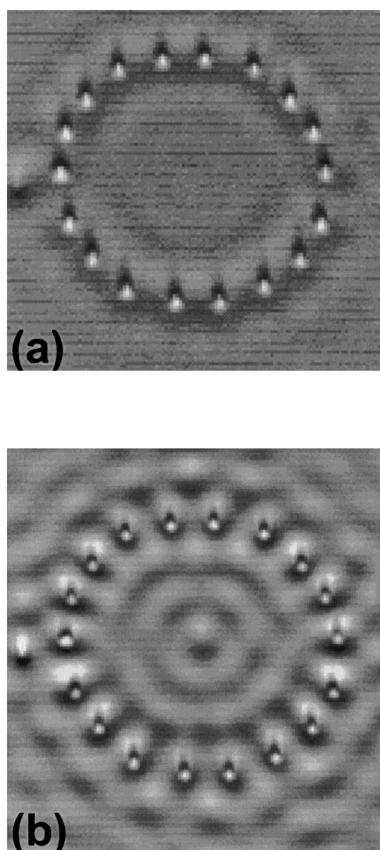


Fig. 5. Formation of a quantum corral by lateral manipulation of Ag atoms on a Ag(111) surface. The diameter of the circular structure is 22 nm. Sample voltage: (a)  $-45$  mV (b) 19 mV.

#### 4. Pulling, Pushing and Sliding of Atoms and Molecules

In manipulation experiments performed with Cu atoms, Pb atoms and CO molecules on Cu(211) we could distinguish different manipulation modes. These manipulation modes are shown in Fig. 6. Pb (and also Cu) atoms could be manipulated via attractive tip-atom interactions in such a way, that they follow the tip discontinuously by hopping from one adsite to the next (pulling mode, Fig. 6(a)). Upon application of larger force than that for pulling, Pb atoms could also be manipulated attractively in a completely continuous way (sliding mode, Fig. 6(b)); in this mode the tip-particle interaction is increased so strongly that the tip-particle system scans the corrugation of the substrate, while the particle-substrate interaction is sufficiently strong enough to keep the particle on the substrate. The transition from pulling mode to sliding mode evolves continuously with decreasing the tunneling resistance as evidenced by the magnitude of the discontinuity in tip height signal. Finally, single CO molecules as well as rows of several CO molecules could be reliably manipulated via repulsive interaction (pushing mode, Fig. 6(c)), whereby the intrinsic step edges, on top of which the CO-molecules are bound, act as railway tracks.<sup>11)</sup>

#### 5. Vertical Manipulation

Vertical manipulation was first observed by Eigler, who demonstrated an atomic switch by repeatedly transferring a Xe atom from the surface to the tip and vice versa. In our experiments with Xe we chose another way to prove the suc-

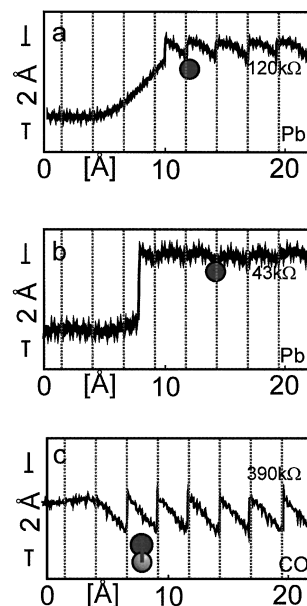


Fig. 6. Tip height curves during manipulation of (a) and (b) a Pb atom and (c) a CO molecule along step edges on Cu(211). The tip is moved from left to right and respective tunneling resistances are indicated. The vertical dotted lines correspond to fcc sites adjacent to the step edge. The initial sites of the manipulated particles are indicated. Notice that in the attractive manipulation modes (a: pulling and b: sliding) the particles first hop towards the tip and then follow it, whereas in the repulsive mode (c: pushing) the particles hops away from the tip.

cessful transfer of Xe to the tip: we picked up a Xe atom on the tip apex and we used it to image the same area as before with the bare tip. We noted a markedly improved resolution, showing that the single Xe atom “sharpen” the tip.

After also proving the vertical manipulation of  $C_3H_6$ , we concentrated on the picking up of CO. This process is interesting, as it is well known that CO stands upright on Cu with the carbon atom binding to the substrate. Upon transfer to the tip, the molecule must consequently to turn around (Fig. 7(a)). A reliable experimental procedure for transferring single CO molecules to the tip apex and back to the surface was found to require ramping of the tunneling voltage and the simultaneous decrease of the tip-CO distance.<sup>12)</sup>

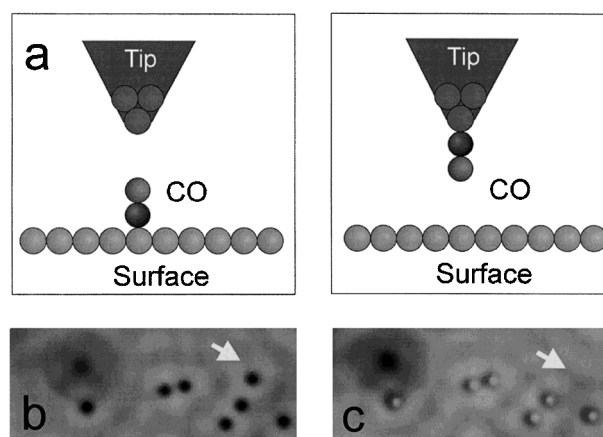


Fig. 7. (a) Schematic demonstrating the flipping of a CO molecule upon vertical transfer from the substrate to the tip. ((b) and (c)) Demonstration that chemical contrast is obtained for CO molecules with a CO tip, whereas oxygen remains unaffected. The white arrow indicates the CO molecule which was transferred deliberately towards the tip.

An advantageous byproduct of the ability to deliberately transfer CO to the tip is demonstrated in Figs. 7(b) and 7(c). As evident in Fig. 7(b), all species imaged with a clean metal tip appear as depressions. When a CO molecule (indicated in this case by the white arrow) is transferred to the tip apex, all CO molecules change their appearance to protrusions (Fig. 7(c)), whereas the oxygen atom in the upper left parts of Figs. 7(b) and 7(c) retains its appearance.<sup>12)</sup> Thus, we can achieve chemical contrast in STM imaging, a phenomenon very useful for the analytic application of the STM.

The dependence of STM images on parameters such as the chemical constitution of the tip and the density of adsorbed species on the surface is, however, still an open problem, as can be realized from Fig. 8.<sup>13)</sup> In Fig. 8(a) we show a regular adlayer of CO on Cu(211) with  $(3 \times 1)$  periodicity. With the knowledge that the coverage is  $2/3$  of a monolayer, a structural model such as that illustrated in Fig. 8(b), where CO molecules occupy on-top and bridge sites thus maximizing the distance between them, appears plausible. In Figs. 8(c)–8(e) we show, however, that laterally manipulating two

CO molecules together into adjacent on-top sites changes the image from two minima into one maximum located between the two on-top sites. Thus, upon formation of a CO “dimer”, a dramatic change in the appearance of the two CO molecules has occurred (Fig. 8(d)). By separating the two CO molecules, their appearance returns to their initial shape. Using the lateral manipulation technique we can also form an extended domain of the  $(3 \times 1)$  structure (Fig. 8(f)) leading to the conclusion that the model depicted in Fig. 8(g) is the accurate one and should thus replace that shown in Fig. 8(b). It is worth noting that the formation of a domain of a regular adlayer of a foreign species in a particle-by-particle manner can be regarded as a first example of chemical synthesis on atomic scale.

## 6. Vibrational Spectroscopy with the STM

While spectroscopy of electronic states employing the STM has been used for more than ten years, vibrational spectroscopy was pioneered only in 1998, when Stipe *et al.*<sup>14)</sup> showed that the C–H stretch mode could be observed on single  $C_2H_2$  molecules adsorbed on a Cu(111) surface. Later the CO frustrated translational and rotational modes<sup>15)</sup> as well as the internal stretching mode were observed on Cu(100) and Cu(110).<sup>16)</sup> After transferring a single CO molecule on the tip by vertical manipulation, we could also observe the frustrated rotational and vibrational modes of CO on Cu(211) with energies at 5.8 and 35.9 meV, respectively.<sup>17)</sup>

## 7. Effects Due to Electron Current

A detailed analysis of the vertical transfer mechanism of CO molecules on Cu(111)<sup>18)</sup> showed that a minimum tunneling bias of 2.4 V is required to excite a molecule. This corresponds to the onset of the CO derived  $2\pi^*$ -level of the CO/Cu(111) system as found by two photon photoelectron spectroscopy (2PPE). The hopping rate depends linearly on the tunneling current, which indicates that a one electron process is the basis of the excitation mechanism. The probability per tunneling electron of inducing a hop of a CO molecule depends on the applied bias and has a value below  $10^{-10}$  if the bias does not exceed 3 V. A strong isotope effect for the quantum yield of the hopping process can be found using  $^{12}C^{16}O$  and  $^{13}C^{18}O$ . Within the framework of the Menzel-Gomer-Redhead model, this isotope effect can be used to estimate a per excitation probability for a hop of a CO molecule of  $5 \times 10^{-9}$  and a fraction of 0.5% of the electrons making up the tunneling current passing through the  $2\pi^*$ -level of the CO-molecules; the lifetime of the electrons in the antibonding  $2\pi^*$ -level is as short as 0.8–5 femtoseconds.<sup>18)</sup> Thus, the CO-transfer depends on the effect induced by the electrons provided by the tunneling current. The approach of the tip during the pick-up procedure simply increases the probability that the molecule is “caught” at or near the tip apex.<sup>12)</sup>

## 8. Inducing a Chemical Reaction with the STM Tip

By combining all previously established techniques of working with single atoms and molecules, we were recently able to induce all steps of a complex chemical reaction with the STM tip at a low temperature at which the reaction would not proceed naturally. Specifically, all of the elementary steps

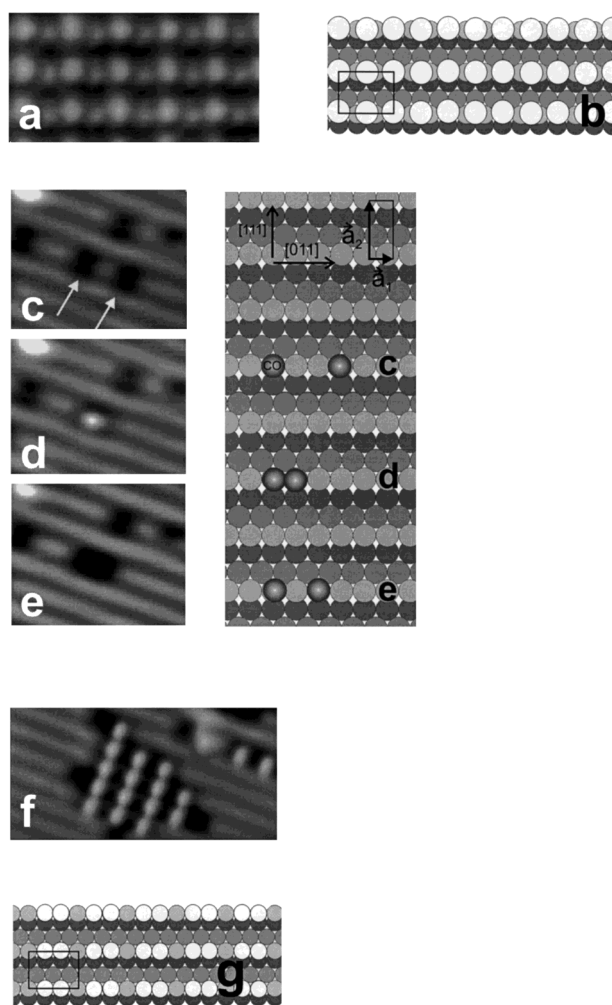
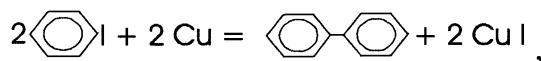


Fig. 8. (a) STM image of a regular adlayer of CO on Cu(211) with  $(3 \times 1)$  periodicity. The coverage is  $2/3$  of a monolayer. (b) Naive model of the  $(3 \times 1)$  structure. The CO molecules occupy on-top and bridge sites. (c)–(e) STM images and corresponding sphere models of the manipulation of two CO molecules to the shortest lateral distance and apart again. Notice that a dramatic change in the appearance of the two CO molecules occurs when the distance between them changes. (f) Local  $CO(3 \times 1)$  domain formed by lateral manipulation. (g) Accurate model of the  $CO(3 \times 1)$  structure.

of an almost 100 years old basic aromatic ring coupling mechanism known as the Ullmann reaction<sup>19)</sup> have been induced on single molecules using the STM tip at 20 K on a Cu(111) substrate. The synthesis of biphenyl out of iodobenzene on copper,



essentially consists of three steps: dissociation of iodobenzene ( $\text{C}_6\text{H}_5\text{I}$ ) to phenyl ( $\text{C}_6\text{H}_5$ ) and iodine, diffusion of phenyl to locate another phenyl as a reaction partner and their chemical association to form biphenyl ( $\text{C}_{12}\text{H}_{10}$ ). Figure 9 shows the steps of the reaction sequence. First, the iodine atoms originating from two  $\text{C}_6\text{H}_5\text{I}$  molecules adsorbed at a Cu(111) step (Fig. 9(a)) were separated from the parent molecules by injecting 1.5 eV energy tunneling electrons from the tip (Fig. 9(b)). The iodine (smaller hills) and phenyl (larger hills) are further separated by means of the tip (Fig. 9(c)). Then, the iodine atom placed between the two phenyls is removed to the lower terrace by lateral manipulation (Fig. 9(d)). The left-hand phenyl is then repositioned close to the right-hand

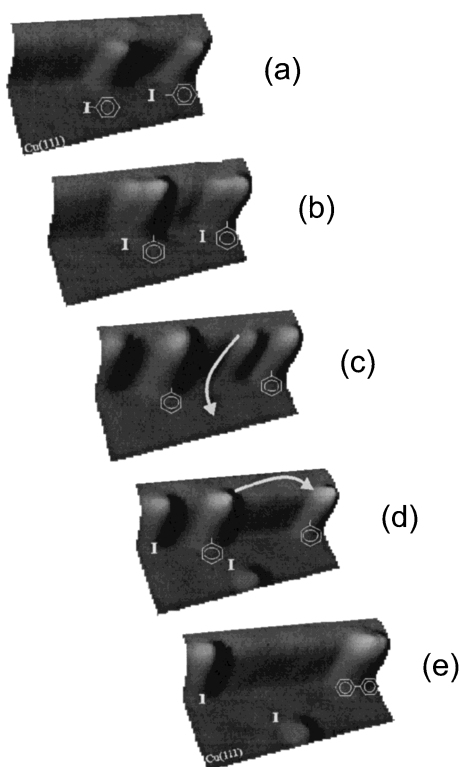


Fig. 9. STM-tip-induced single-molecule-Ullmann reaction sequence on a Cu(111) substrate at 20 K.

phenyl by pulling with the tip, and then the injection tunneling electrons with the energy of 500 meV are needed for the chemical association of the phenyl couple (Fig. 9(e)). The formation of biphenyl is verified by pulling the synthesized molecule from its front end with the tip.<sup>20)</sup> In this image sequence, the top and bottom images exactly represent the left-hand and right-hand side of the Ullmann equation, showing that we have been able to reproduce an entire chemical equation and all of its elementary reaction steps for the first time.

## 9. Summary

In this review, we discussed the manipulation of atoms and molecules on metallic surfaces by a technique in which primarily only tip-particle forces are employed. Detailed vertical manipulation experiments show that in addition to tip/particle forces, electronic effects are also important for the transfer of particles, such as CO and Xe from the substrate to the tip and vice versa. Electric current effects also play dominant roles in STM-induced chemical modifications of molecules such as dissociation. A combination of all parameters (forces, current, field) is required to associate several species and to yield new chemical entities. Engineering with single molecules and single atoms, i.e., the ability to fabricate novel functional structures no longer appears to be a mere dream.

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