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MANIPULATION OF ATOMS, MOLECULES AND CLUSTERS FOR CONSTRUCTION OF NANOSYSTEMS

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Controlled manipulations with the scanning tunneling microscope (STM) down to the scale of small molecules and single atoms allow to built molecular and atomic nanosystems, leading to the fascinating possibility of creating manmade structures on atomic scale. Here we present a short review on atomic scale manipulation investigations. Upon soft lateral manipulation of adsorbed species, in which only tip/particle forces are used, three different manipulation modes (pushing, pulling, sliding) can be discerned. We show that even the manipulation of highly coordinated native substrate atoms is possible and we demonstrate how this can be applied as local analytic and synthetic chemistry tools, with important consequences on surface structure research. Vertical manipulation of Xe and CO is demonstrated, leading to improved imaging with functionalized tips. With CO deliberately transferred to the tip, we have also succeeded 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. Finally, we have extended the manipulation techniques to large specially designed molecules by performing lateral manipulation in constant height and realizing the principle of a conformational molecular switch.

Keywords: low temperature scanning tunneling microscope, atomic and molecular manipulation, nanosystems
PACC: 0779

I. INTRODUCTION

The scanning tunneling microscope (STM) was initially intended for imaging surfaces and has proven its unique abilities in producing images down to atomic resolution. Soon it was realized that, due to its close proximity to the surface atoms, the STM tip often influences and modifies the surface. This obvious disadvantage for imaging was however readily turned into a positive prospect by realizing that the tip-substrate interaction can be used to manipulate the surface in a wanted way. Pertinent studies showed that the STM indeed offers startling possibilities to modify surfaces down to the nm- and even to the atomic scale.[1−3] Thus, the longstanding dream of building up man-designed 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.[2] Nevertheless, although field and current effects can be used for manipulation, reliable precision on atomic scale is achieved by "soft manipulation", where mainly the tip-substrate forces are employed. These forces can be tuned by changing the distance between the tip and the manipulated particle. On 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 place without loosing contact to the substrate (Fig.1), while in the latter mode a particle is deliberately picked up to the tip and then released back to the surface (Fig.2).

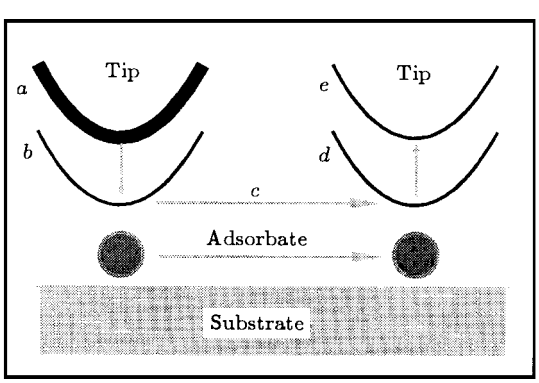


Fig.1. Sketch of the pulling procedure in lateral manipulation of single atoms or molecules on a Cu(211) surface (lateral manipulation).

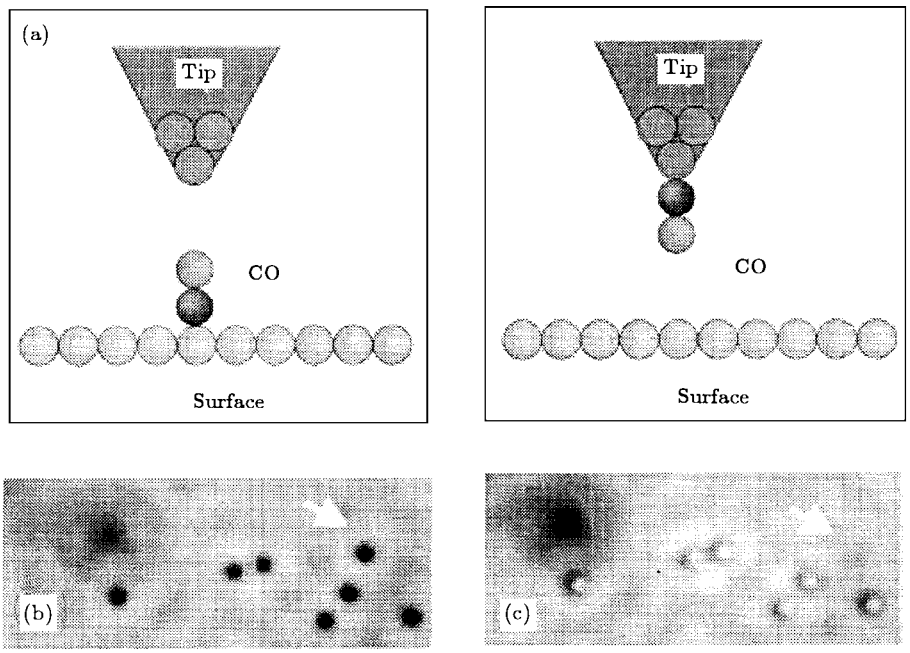


Fig.2. (a) Schematic picture demonstrating the flipping of a CO molecule upon vertical transfer from the substrate to the tip. (b) and (c) Demonstration that chemical contrast is obtained for CO-molecules with a CO-tip, whereas oxygen remains unaffected. The white arrow denotes the CO-molecule, which was transferred deliberately towards the tip.

II. 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.[4]. As substrates for the manipulation experiments here described 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 UHV by several cycles of sputtering with Ne-ions and annealing at about 700K. Very low coverages of gaseous adsorbates were prepared by dosing through a very fine hole to 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.

III. LATERAL MANIPULATION

In Fig.3 we show our ability to create 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 15K. At this temperature, the molecules are frozen in to a sufficient degree, so that precise working is possible with a rather large number of particles and the artificial structure remains stable for a long time. An impression concerning different stages of the buildup work of an artificial structure is given in Fig.4.

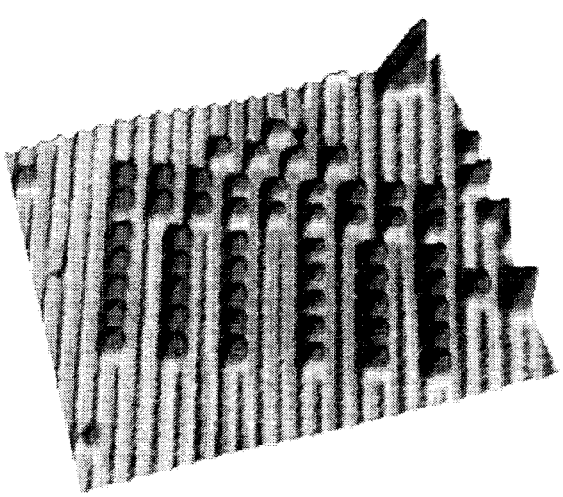


Fig.3. STM images of the Brandenburg Gate, as a very recent example of lateral manipulation. CO-molecules deposited on Cu(211) were used. The substrate temperature was 15K.

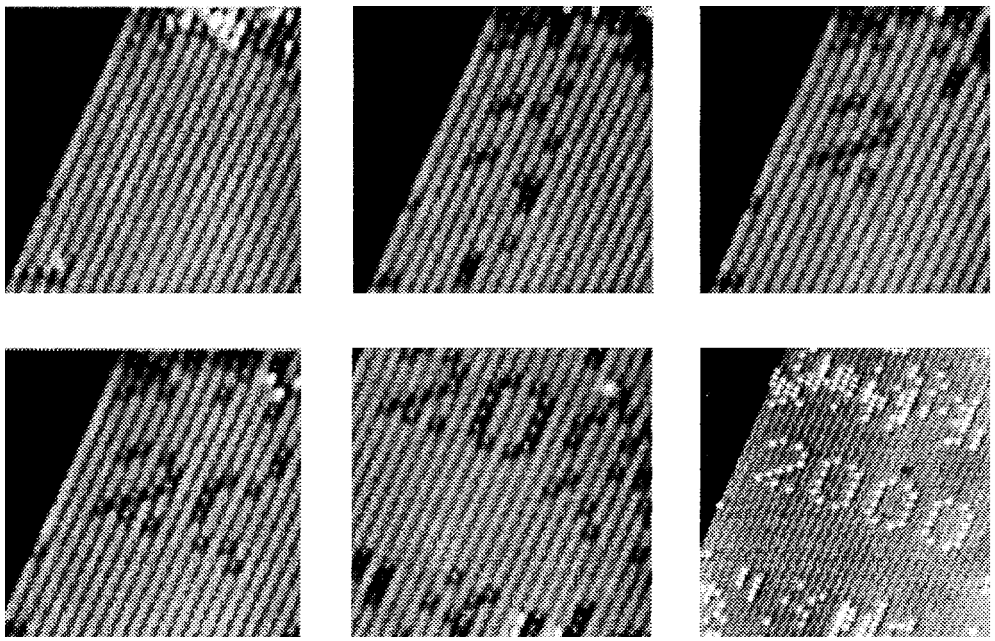


Fig.4. Sequence of STM pictures showing the gradual build-up of the symbol "2000" with CO-molecules on a Cu(211) substrate. Notice that an area free from any CO-molecules had to be prepared at the beginning.

After having successfully manipulated small molecules like CO and C_2H_4, we experimented the manipulation of atoms like Pb and Cu.[3] In these cases we have observed that increasing forces have to be applied in the respective order. With still increasing forces, we showed on Cu(211) that it is also possible to release native substrate atoms from sixfold coordinated kink sites (Fig.5(a)–(c)) and even from sevenfold co-ordinated regular step-edge sites (Fig.5(d)–(f)).[5] This important result opens the way for structuring the surface itself with the promising prospect that also deeper lying substrate layers may be included in the build-up of artificial prototype structures. We could also show that vacancies at step edges of regularly stepped surfaces like Cu(211) can be healed out by manipulating single atoms into them; interestingly, a larger force is required for this purpose than for manipulation along defect free step edges.[6] Manipulation of Cu atoms perpendicular to the step edges on Cu(211) can also lead to particle exchange at the steps.[7]

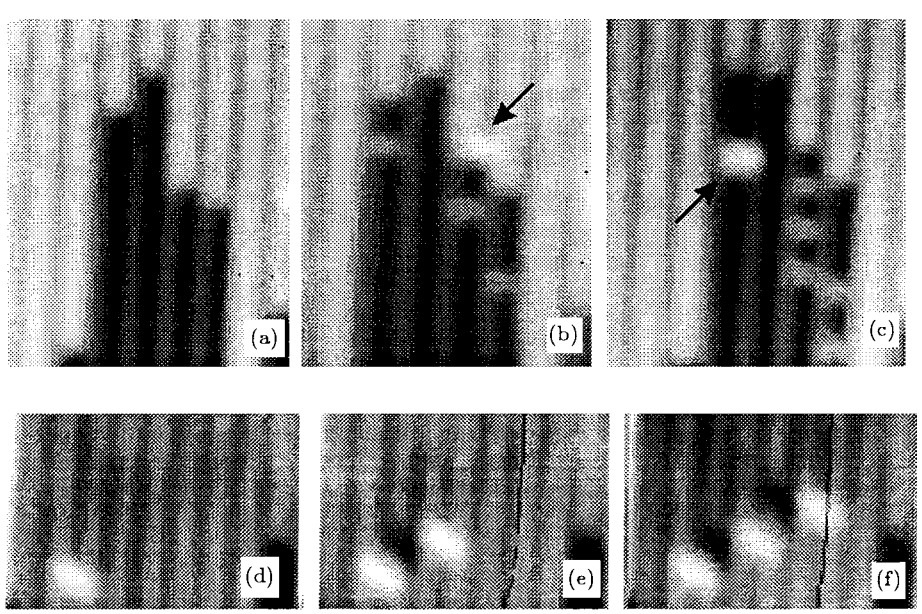


Fig.5. Manipulation of native Cu-atoms from six-fold coordinated kink sites at defect steps (a)–(c) and from seven-fold coordinated regular step sites (d)–(f) on Cu(211). Notice the appearance of adatom/vacancy pairs in the latter case.

The structure presented in Fig.6 shows the formation of a quantum corral by lateral manipulation of Ag atoms on a Ag(111) surface, similar to the ones first created in Eigler's group. The atoms have been positioned in a circular geometry 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.[8,9] 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 put in one focus shows up as a mirage at the other focus via its magnetic Kondo signature.[10]

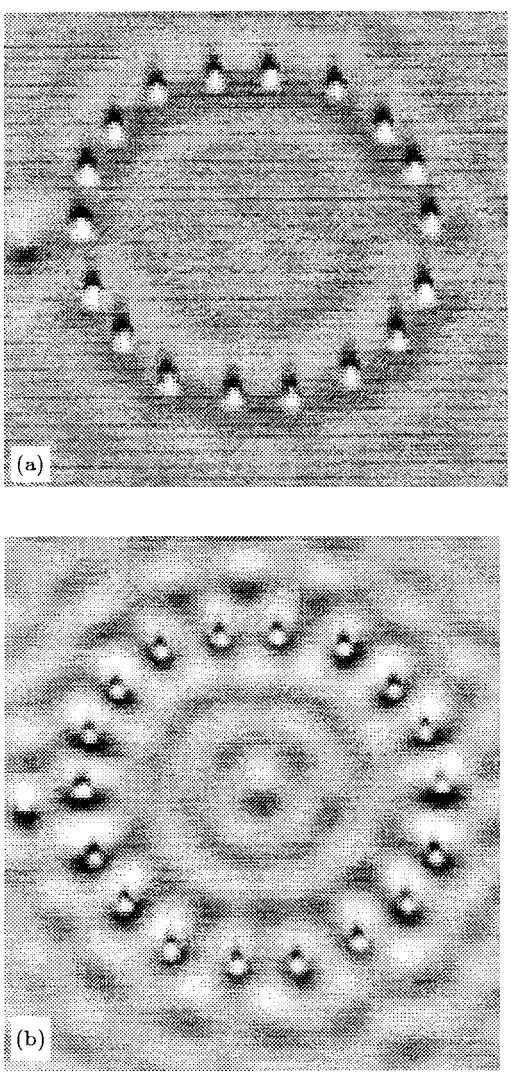


Fig.6. Formation of a quantum corral by lateral manipulation of Ag atoms on a Ag(111) surface. The diameter of the circular structure is 22nm. Sample voltage: (a) –45mV (b) 19mV.

IV. 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, depending on the applied tip-particle force (qualitatively measured by the tunneling resistance). These manipulation modes are shown in Fig.7. Pb- (and also Cu-) atoms could be manipulated via attractive tip-adatom interactions in a way in which they follow the tip discontinuously by hopping from one adsite to the next (pulling mode, Fig.7(a)). Upon application of larger forces than for pulling, Pb-atoms could also be manipulated attractively in a continuous way (sliding mode,

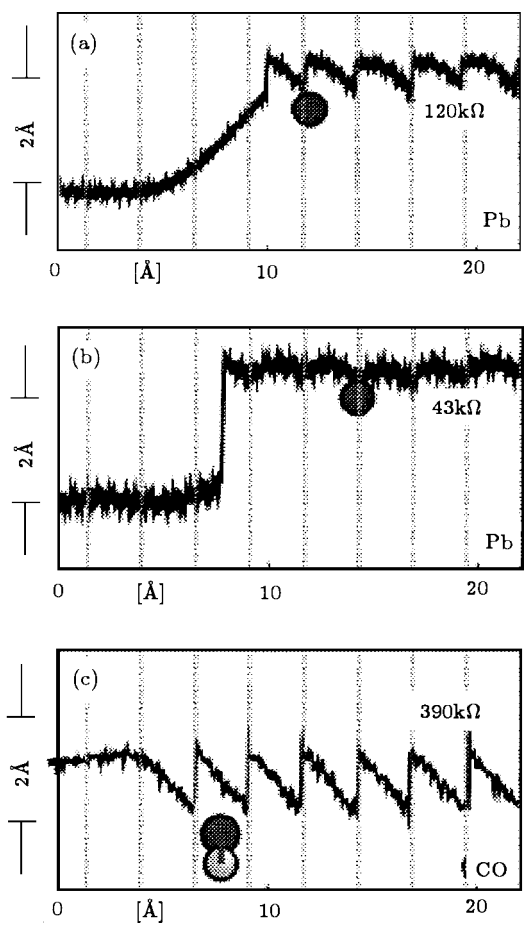


Fig.7. Tip height curves during manipulation of (a) and (b) a Pb-atom and (c) a CO-molecule along step edges on Cu(211). The tip is moved from left to right and respective tunneling resistancies are indicated. The vertical dotted lines correspond to fcc sites next to the step edge. The initial sites 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 particle performs hops away from the tip.

Fig.7(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 still strong enough to keep the particle on the substrate. Finally, single CO-molecules as well as rows of several CO-molecules could to be reliably manipulated via repulsive interaction (pushing mode, Fig.7(c)), whereby the intrinsic step edges, on top of which the CO-molecules are bound, act as railway trails.[11]

V. VERTICAL MANIPULATION

Vertical manipulation was first observed by Eigler, who demonstrated an atomic switch by transferring repeatedly a Xe atom from the surface to the tip and vice versa. In our experiments with Xe we chose another way to prove successful transfer of Xe to the tip: we picked up a Xe on the tip apex and we used it for imaging the same area as before with the bare tip. We noted a markedly improved resolution, showing that the single Xe atom "sharpens" the tip.

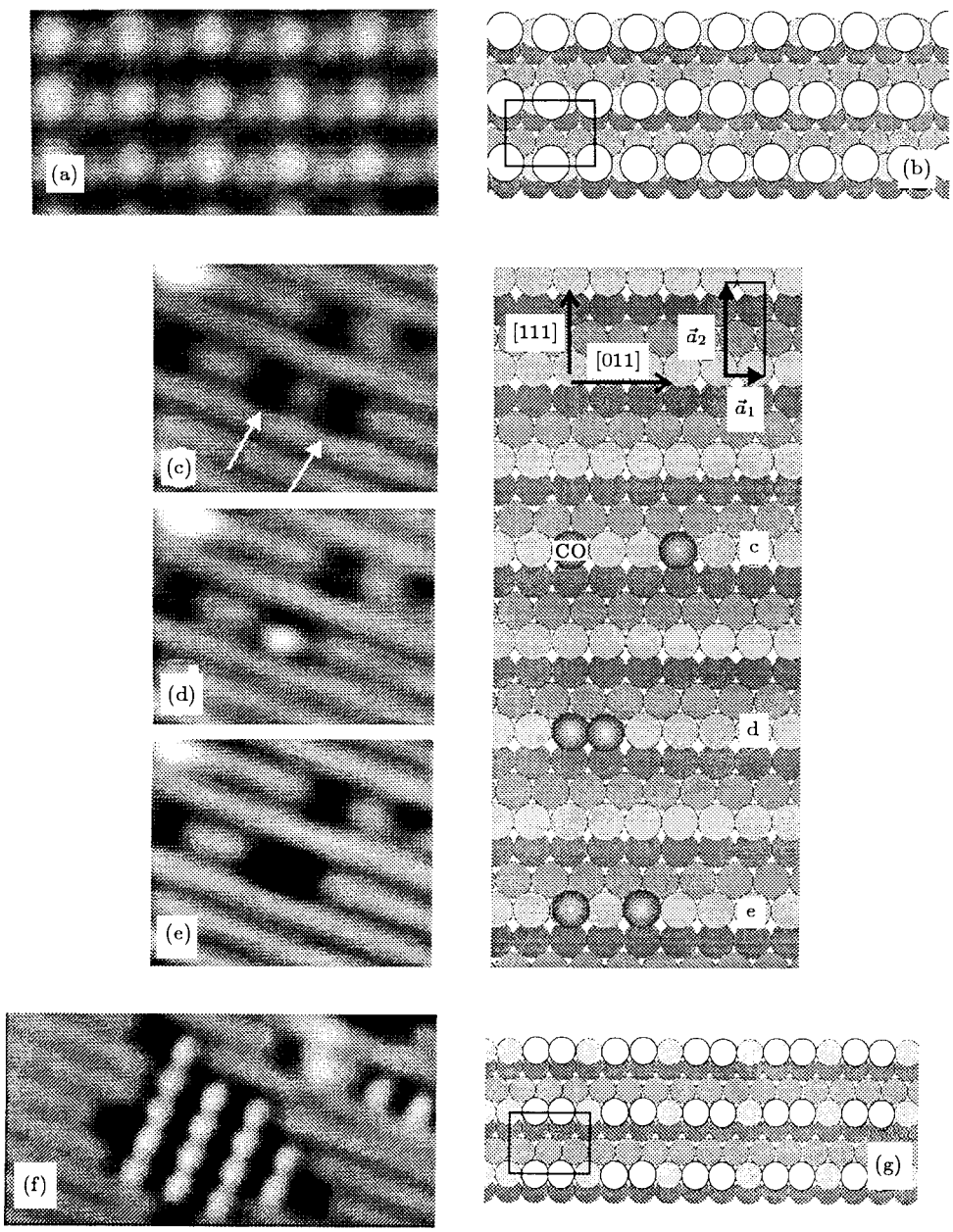


Fig.8. (a) STM image of a ragular adlayer of CO on Cu(211) with (3×1) periodicity. The coverage is 2/3 of a monolayer. (b) Naive model of the (3×1) structure. The CO molecules occupy on-top and bridge sites. (c)–(e) STM images and corresponding sphere models of the manipulation of two CO molecules to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

After having proven also vertical manipulation of C_3H_6, we concentrated on the pick-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 has consequently to turn around (Fig.2(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 simultaneous decrease of the tip-CO distance.[12]

An advantageous byproduct of the ability to deliberately transfer CO to the tip is demonstrated in Fig.2(b) and (c). As one can see in Fig.2(b), all species imaged with a clean metal tip appear as depressions. When a CO-molecule (denoted in this case by the white arrow) is transferred to the tip apex, all CO molecules change their appearance to protrusions (Fig.2(c)), whereas the oxygen atom in the upper left part of Figs.2(b) and (c) retains its appearance.[12] Thus, we can achieve chemical contrast in STM imaging, a phenomenon very useful for the analytic abilities of the STM.

The dependence of STM images on parameters like the chemical constitution of the tip or the density of adsorbed species on the surface is, however, still an open problem, as can be realized from Fig.8.[13] In Fig.8a we show a regular adlayer of CO on Cu(211) with (3×1) periodicity. With the knowledge that the coverage is 2/3 of a monolayer, a structural model like the one illustrated in Fig.8b, where CO molecules occupy on-top and bridge sites thus maximizing their mutual distance, appears plausible. In Fig.8(c)–(e) we show, however, that laterally manipulating together two CO molecules 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 changes to the initial shape. Using the lateral manipulation technique we can form also an extended domain of the (3×1) structure (Fig.8(f)) leading to the conclusion that the model depicted in Fig.8(g) is the proper one and has to replace that of Fig.8(b). It is worthwhile 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.

VI. VIBRATIONAL SPECTROSCOPY WITH THE STM

Whereas spectroscopy of electronic states employing the STM is used since more then 10 years, vibrational spectroscopy was pioneered only in 1998, when the group of Ho[14] 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[15] as well as the internal stretching mode were observed on Cu(100) and Cu(110).[16] After having transferred 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.[17]

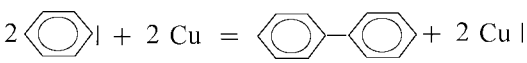
VII. EFFECTS DUE TO ELECTRON CURRENT

A detailed analysis of the vertical transfer mechanism of CO-molecules on Cu(111)[18] showed that a minimum tunneling bias of 2.4V 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 known from 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 to induce a hop of a CO molecule depends on the applied bias and has a value below 10^{-10}, if the bias does not exceed 3V. 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 5×10^{-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.[18] Thus, the CO-transfer depends on an effect induced by the electrons provided by the tunneling current. The approach of the tip in the pick-up procedure just increases the probability, that the molecule is "caught" at or near the tip apex.[12]

VIII. INDUCING A CHEMICAL REACTION WITH THE STM TIP

By combining all hitherto known 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 low temperature, at which the reaction would not proceed naturally. Specifically, all elementary steps of a century old basic aromatic ring coupling mechanism known as the Ullmann reaction[19] has been induced on single molecules using the STM tip at 20K on a Cu(111) substrate. The synthesis of biphenyl out of iodobenzene on copper



essentially consists of three steps: dissociation of iodobenzene (C_6H_5I) to phenyl (C_6H_5) and iodine, diffusion of phenyl to find another phenyl as a reaction partner and their chemical association to form biphenyl ($C_{12}H_{10}$). Fig.9 shows the steps of the reaction sequence. First, the iodine atoms originating from two C_6H_5I molecules adsorbed at a Cu(111) step (Fig.9(a)) have been separated from the parent molecules by injecting 1.5eV energy tunneling electrons from the tip (Fig.9(b)). The iodine (smaller hills) and phenyl (larger hills) are further separated with the tip (Fig.(9)c). Then, the iodine atom placed between the two phenyls has been removed to the lower terrace by using lateral manipulation (Fig.9(d)). The left phenyl is then repositioned close to the right phenyl by pulling with the tip and then the injection tunneling electrons with an energy of 500 meV is 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.[20] In this image sequence, the top and bottom images exactly represent the left and right side of the Ullmann equation, showing that we have been able for the first time to reproduce a whole chemical equation and all its elementary reaction steps.

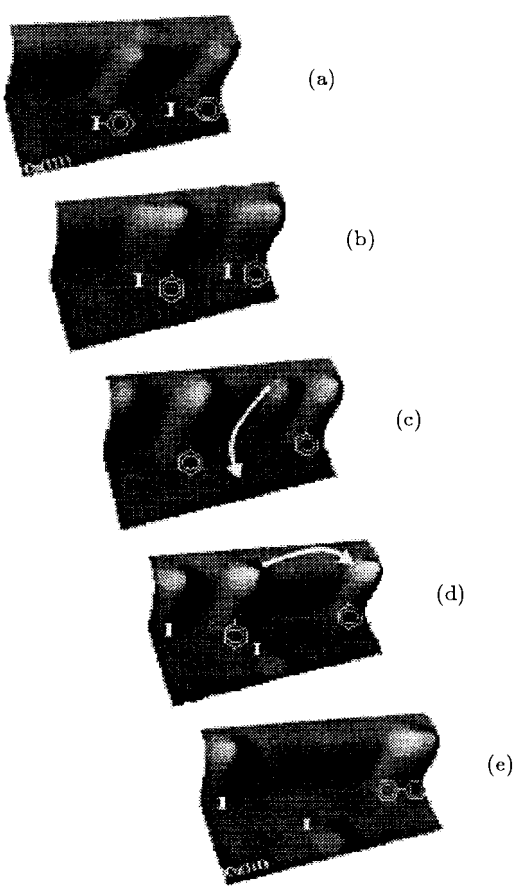


Fig.9. STM-tip induced single-molecule-Ullmann reaction sequence on a Cu(111) substrate at 20K.

IX. MANIPULATION OF LARGE MOLECULES

The technique of single atom manipulations by means of the scanning tunnelling microscope can now be applied to the controlled displacement of large molecules. Single Cu-TBPP molecules deposited on Cu substrates were manipulated at low temperatures by means of the interaction between the molecule and the tip.

Due to the complicated structure of the molecules and their high conductance, we have explored the possibilities of performing controlled lateral manipulation at constant height.[21] In the more conventional constant current mode of manipulation, the tip apex distance to the surface increases as the tip approaches the molecule, minimising the mechanical interactions between tip apex and molecule. On the contrary, a constant height mode reinforces the tip apex to molecule interaction and provides the molecule enough intramolecular deformations to overcome the surface barriers.

Constant height manipulation processes performed on a Cu-TBPP molecule deposited on Cu(111) are presented in Fig.10(a) and (b) together with the current signal recorded during the manipulation (Fig.10(c)). The exact path of the tip during each manipulation is represented by arrows. The tip height was reduced to a distance z=0.4nm relative to the point contact position and a voltage V=–50mV was applied. As one can see, the result of the manipulation is a translation of the molecule associated by a rotation. The position on the molecule where the tip-leg contact takes place is indicated by a X in Fig.10(a)–(b) (left images). This position corresponds (on the right images) to the point where the tip leaves the

molecule after the manipulation and indicates that the tip interacts with the molecule through a single leg during the entire process. In its final orientation, the molecule is 120° rotated with respect to its initial position. The current signal recorded during the lateral manipulation (Fig.10(c)) shows several jumps, not identical in form and length. The current behavior is more complex than expected from a simple translational movement and can be explained by the superposition of the translational movement with a rotational one.

The manipulation at low temperature of Cu-TBPP molecules on Cu(211) offers the possibility of realizing the principle of a conformational molecular switch.[22] Lateral and vertical manipulation were used to selectively modify the molecular conformation, by rotating single legs around their σ-bond, in and out the porphyrin plane. STM images of the molecule in the two different configurations is shown in Fig.11, together with a schematic representation of the molecule in the two cases. The interaction between tip and molecule has been quantitatively investigated by recording the $I(z)$ curves on different positions on the molecule. We have been able to demonstrate that the tunneling current through one leg strongly depends on the extend of its rotation. Molecular mechanics calculations[22] showed that a rotation of 90° induces a change in resistance of over six orders of magnitude.

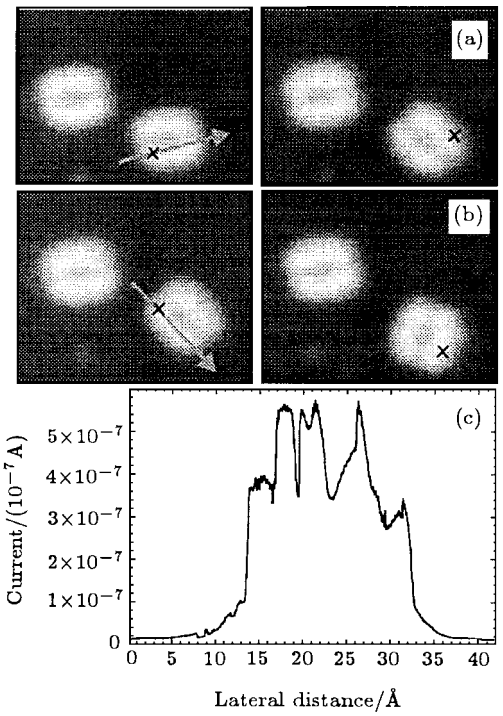


Fig.10. (a)(b) STM images showing the result of the manipulation in constant height mode, recorded at a tunneling current of 400 pA and a bias voltage of 300mV. The images on the left indicate the position of the molecule before the process and the images on the right show the result of the manipulation. The arrows indicate the path of the tip during the manipulation. The tip interacts with the molecule through a single leg, in the position labelled by X. (c) Current signal recorded during the manipulation in (b).

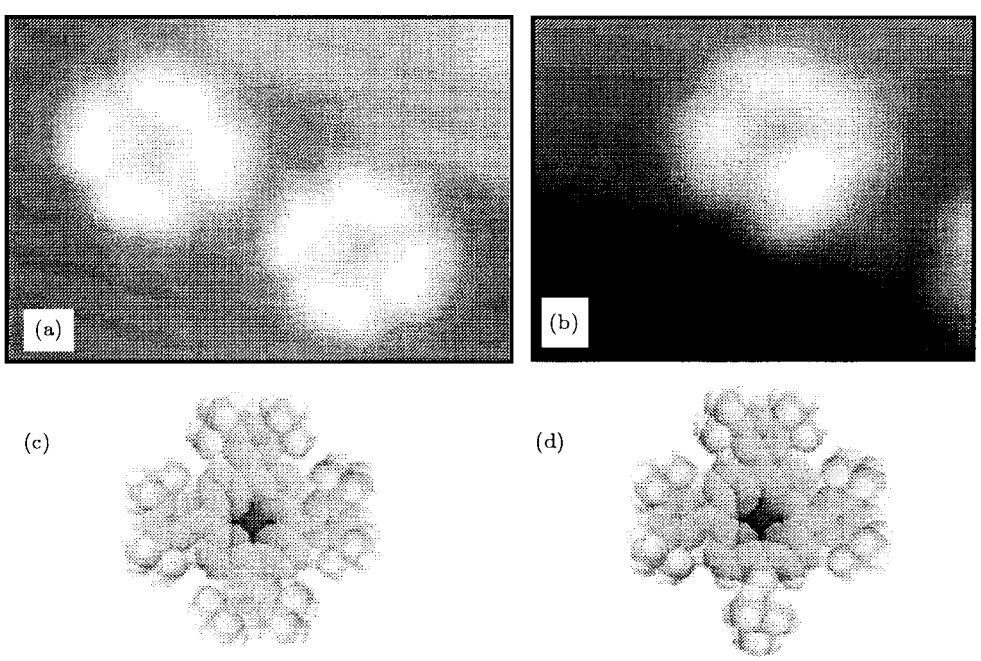


Fig.11. (a) STM image of a Cu-TBPP molecule on Cu(211) lying flat on the surface and oriented parallel to the intrinsic step edges. (b) STM image of a Cu-TBPP molecule on Cu(211) showing one leg rotated out of the porphyrin plane. (c) and (d) Sketch of the approximate molecular conformation for (a) and (b).

X. SUMMARY

In this review, we discussed manipulation of atoms and molecules on metallic surfaces with the technique of "soft manipulation", in which basically only tip-particle forces are employed. Detailed vertical manipulation experiments show that beside tip/particle forces also electronic effects are important for the transfer of particles like CO and Xe from substrate to the tip and vice versa. Electric current effects play also dominant roles in STM-induced chemical modifications of molecules like dissociation.[2] A combination of all parameters (forces, current, field) is required to associate several species and to yield new chemical entities. Moreover, manipulation of single large molecules opens the route to the creation of electronic devices at the nanoscale and to the ability of controlling the internal mechanics of a molecule by the STM tip. Engineering with single molecules and single atoms, i.e. the ability making novel manmade functional structures appears no longer to be a mere utopia.

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