

STM as an operative tool: physics and chemistry with single atoms and molecules

K.H. Rieder¹, G. Meyer², K.F. Braun¹, S.W. Hla³, F. Moresco¹,
K. Morgenstern¹, J. Repp², S. Foelsch⁴, L. Bartels⁵

¹ Fachbereich Physik, Freie Universität Berlin, Germany

² IBM Zurich Research Laboratory, Rueschlikon, Switzerland

³ Ohio University, Athens, USA

⁴ Paul-Drude-Institute, Berlin

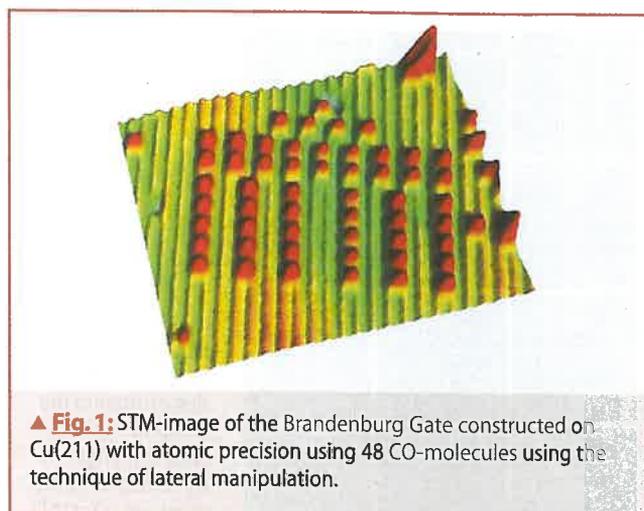
⁵ UC Riverside, USA

The scanning tunneling microscope, initially invented to image surfaces down to atomic scale, has been further developed in the last few years to an operative tool, with which atoms and molecules can be manipulated at low substrate temperatures at will in different manners to create and investigate artificial structures. These possibilities give rise to startling new opportunities for physical and chemical experiments on the single atom and single molecule level. Here we provide a short overview on recent results obtained with the new techniques.

Lateral manipulation and build-up of artificial structures

Fig. 1 shows a first example of an artificial structure on atomic scale. The Brandenburg gate has been formed with 48 CO molecules by laterally manipulating them into the proper positions with atomic accuracy [1].

In lateral manipulation an adparticle at the surface is moved with the tip along the substrate surface to the desired place without losing contact to the substrate. This is achieved by bringing the tip very close to the adparticle, so that besides the ever present van der Waals interactions also chemical forces between tip and particle are coming into play. These forces can be tuned to be large enough to surmount the surface diffusion barriers, so that the adparticle comes along with the tip, if the tip is moved parallel to the surface to the desired end point. It is fascinating that even at the level of the very atoms, a distinction can be made between different manipulation modes, namely pulling, pushing and sliding [2]. Fig. 2 shows tip height curves obtained in the STM constant current mode during manipulation of metal atoms and CO-molecules. Fig. 2a displays the pulling behaviour of a metal adatom: The atom follows the tip in regular jumps from one adsorption site to the next due to attractive tip-particle forces. Applying larger forces (measured by smaller tunneling resistivities) a sliding motion is induced (Fig. 2b), in which the adparticle is trapped under the tip and follows the tip motion continuously, so that the tip height curve yields a picture of the substrate corrugation. In contrast to metal adatoms, CO molecules are usually pushed (Fig. 2c): The molecules move discontinuously in front of the tip due to repulsive forces. On close packed surfaces like Cu(111), pushing is not very reliable, as the particles tend to move to the side of the tip and get lost. That the buildup of artificial structures like that in Fig. 1 is successful at all is due to the

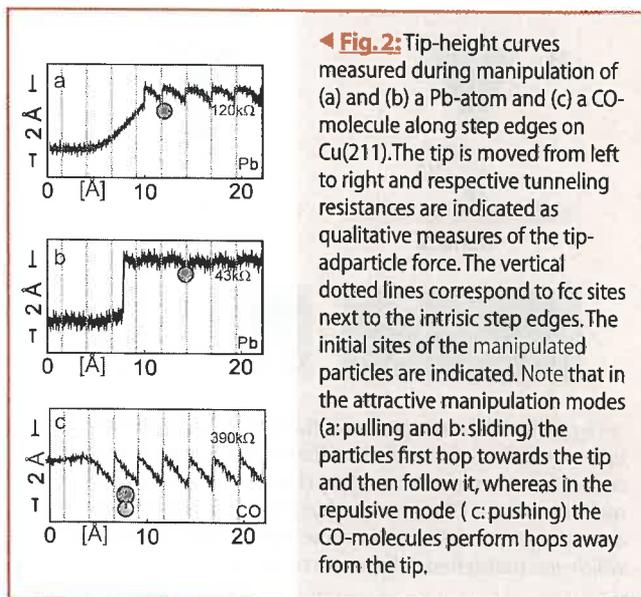


▲ Fig. 1: STM-image of the Brandenburg Gate constructed on Cu(211) with atomic precision using 48 CO-molecules using the technique of lateral manipulation.

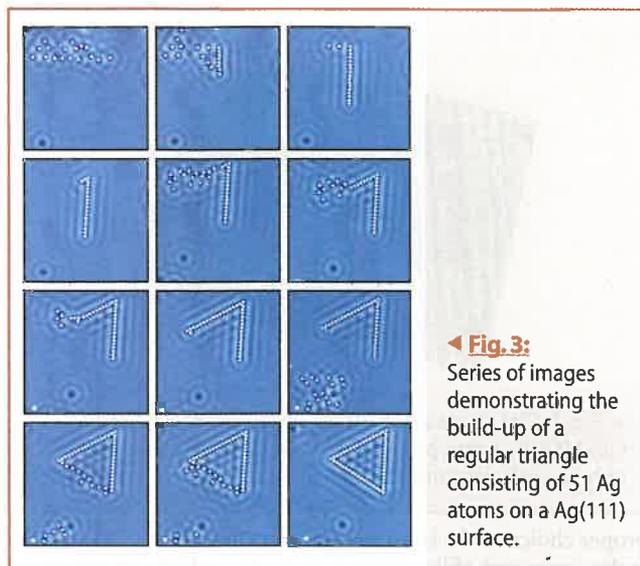
proper choice of the substrate surface: On Cu(211) CO adsorbs at the upper part of the intrinsic step edges, which act as “railway trails” upon pushing. The artificially created regular triangle whose buildup is shown in Fig. 3 has been made by pulling Ag atoms on a Ag(111) surface. With sufficiently stable and nevertheless sharp tips it is even possible to remove native substrate atoms from highly coordinated defect step sites and even from regular step sites of high index surfaces in a one by one manner [2]. This ability was used in analytic chemistry on the atomic scale by investigating the monolayer structure formed on Cu(211) upon Pb-evaporation at room temperature: Atom by atom removal from an island edge revealed that a surface Cu-Pb lead alloy had formed although the two metals do not mix in the bulk.

Vertical manipulation

A different kind of manipulation concerns the deliberate vertical transfer of a particle from the surface to the tip and vice versa. Fig. 4 shows the principle together with an example [3]. Again the tip is brought close to the particle to be transferred until the force between tip and particle is sufficiently strong, so that the particle can go with the tip upon its withdrawal. Here electron current effects can help to transfer the particle in the wanted direction: The polarity should be chosen such, that the electrons flow in the transfer direction.



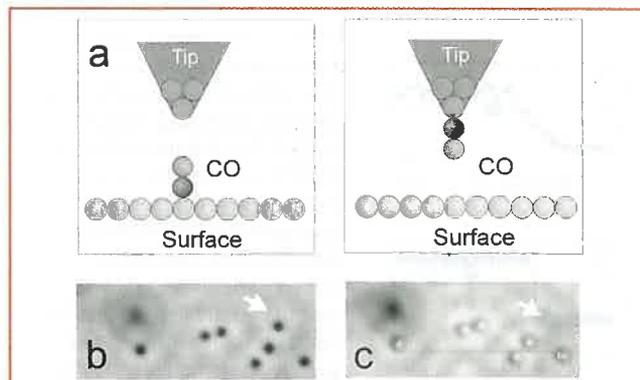
◀ Fig. 2: Tip-height curves measured during manipulation of (a) and (b) a Pb-atom and (c) a CO-molecule along step edges on Cu(211). The tip is moved from left to right and respective tunneling resistances are indicated as qualitative measures of the tip-adparticle force. The vertical dotted lines correspond to fcc sites next to the intrinsic step edges. The initial sites of the manipulated particles are indicated. Note 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 CO-molecules perform hops away from the tip.



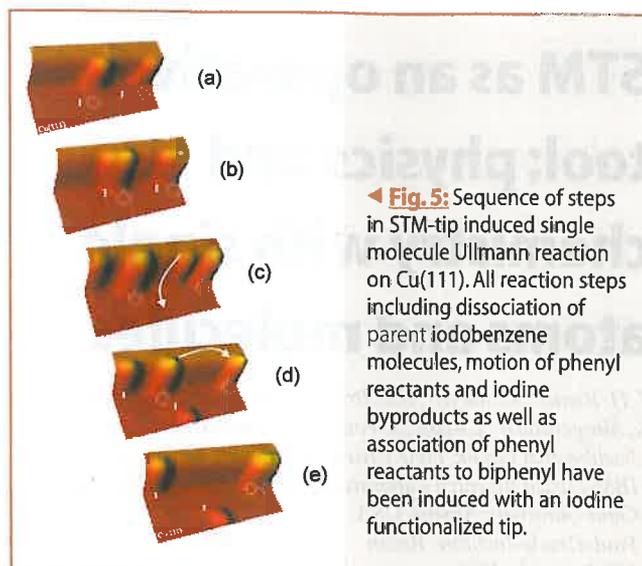
◀ **Fig. 3:** Series of images demonstrating the build-up of a regular triangle consisting of 51 Ag atoms on a Ag(111) surface.

The STM pictures in Fig. 4b refer to an image of Cu(111) with several CO molecules and one oxygen atom in the upper left corner. All species are imaged as depressions with a tip consisting of metal atoms. The CO molecule designated by an arrow is then picked up with the technique of vertical manipulation and the same area is imaged again. Noticeably all CO molecules have changed in appearance to protrusions whereas the oxygen atom remains imaged as a depression. It is obvious that deliberate functionalization of the tip with different molecules may lead to chemical contrast, a feature very much desired in STM.

The vertical transfer of CO is interesting due to the fact, that CO stands upright on metal surfaces with the carbon atom binding to the substrate. Upon transfer to the tip, the molecule consequently has to turn around. A reliable experimental procedure for transferring single CO molecules was found to require ramping of the tunneling voltage and simultaneous decrease of the tip-molecule distance. The transfer mechanism was investigated in great detail and yielded the following picture. Voltage ramping supplies the minimum tunneling bias of 2.4 eV required to populate the CO antibonding $2\pi^*$ level. As the CO hopping rate depends linearly on the tunneling current, a one electron process is responsible for the excitation. Although only 0.5% of



▲ **Fig. 4:** (a) Schematic picture of the flipping of a CO molecule upon vertical manipulation from the surface to the tip apex. (b) and (c) Demonstration of imaging changes obtained for CO-molecules with a CO-tip; notice that the image of the oxygen atom is unaffected. The white arrow denotes the CO-molecule which was transferred deliberately to the tip.



◀ **Fig. 5:** Sequence of steps in STM-tip induced single molecule Ullmann reaction on Cu(111). All reaction steps including dissociation of parent iodobenzene molecules, motion of phenyl reactants and iodine byproducts as well as association of phenyl reactants to biphenyl have been induced with an iodine functionalized tip.

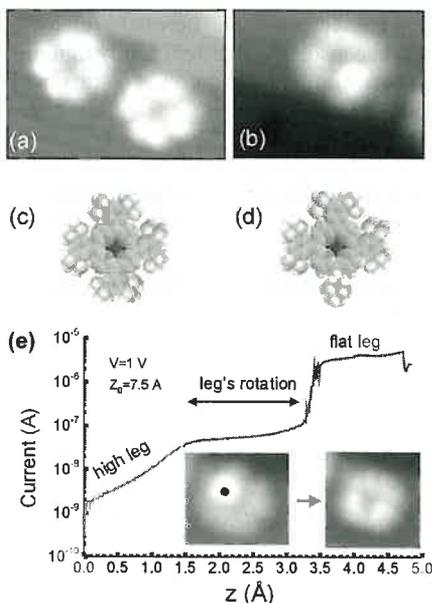
the tunneling current pass through the $2\pi^*$ orbital and the lifetime of the electrons in this antibonding level is only of the order of femtoseconds, the continuous supply of tunneling electrons eventually causes release of the CO from the surface. The approach of the tip in the pickup procedure just increases the probability that the molecule is “caught” at or near the tip apex upon desorption [3].

Chemistry with the STM-tip: Inducing all steps of a chemical reaction

Population of an antibonding state is also important in the preparation of reactants in a full chemical reaction induced by the tip [4]. In the so called Ullmann reaction, iodine has to be split off from the iodobenzene parent molecules to form the phenyl reactants. Again tunneling electrons populate temporarily the iodine-phenyl antibonding level thus causing the dissociation step (Fig. 5a, b). Both iodine and phenyl fragments are found on the surface. To induce the diffusion step to bring two phenyls together lateral manipulation in the pulling mode is employed (Fig. 5c). At the low temperatures of the Cu(111) substrate the proximity of the two phenyls is not sufficient to induce the association to biphenyl: If a pulling procedure is applied to the phenyl couple from one end, the phenyl on the rear does not go along. Only after injection of electrons the synthesis step is performed, which can be proven by pulling the product from one end and realizing that the entire molecule follows the tip (Fig. 5d). Notice that in Fig. 5c one of the iodine atoms was transferred deliberately to the tip after dissociation of the iodobenzene and all the following steps were performed with the iodine functionalized tip. The iodine was finally put back on the surface (Fig. 5f). The synthesis of the two phenyls to biphenyl is probably connected with local excitation of vibrational modes in the phenyl groups enabling the two open bonds to find the proper relative orientation for bond formation. Local excitation of the scissoring and the OH-stretching modes was indeed observed to be responsible in tip-induced diffusion of water molecules adsorbed on Cu(111). Furthermore, hydrogen bonds can be formed and broken and thus ice clusters can be crystallized via the same mechanism.

A possible molecular switch realized by STM-manipulation

Manipulation can also be performed into parts of molecules as shown in Fig. 6 The chemical structure of a TBPP molecule is

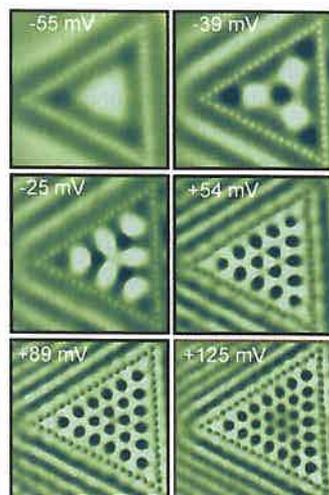


▲ **Fig. 6:** (a) STM image of a Cu-TBPP molecule on Cu(211) with its legs lying flat on the surface. (b) Image of the same molecule after one of its legs has been moved up to a conformation almost perpendicular to the substrate by manipulation with the tip. (c) and (d) show models of the two conformations in (a) and (b). The observation that at the same tip height the current through the leg is different by orders of magnitudes in the two conformations can be used to realize the principle of a molecular switch. (e) shows the measured change in tunneling current upon pushing the leg with the tip from the vertical to the parallel conformation.

shown in Fig. 6a. To the center porphyrin ring there are four legs attached which are perpendicular to the center ring in the gas phase. On Cu(211), however the legs lie flat (Fig. 6b). Using lateral manipulation, a single leg can be transformed into an almost perpendicular conformation and the leg can be pushed back into the flat position with the tip again. As the perpendicular and parallel conformations exhibit orders of magnitude different conductivities these experiments point to the possibility of a molecular switch, in which a mechanical action causes switching from conducting to nonconducting behaviour [5].

Physics with artificial structures: Measuring electron lifetimes inside a quantum corral

Adparticles arranged in a closed geometry act as partial confinement for electrons and can be used to determine the electron lifetime [6]. By means of lateral manipulation 51 Ag atoms have been precisely positioned at distances of 5 times the nearest neighbour distance to form a triangle with a base length of 245 Å as shown in Fig. 3. The electrons of the surface state present on the Ag(111) surface are scattered by these Ag adatoms, resulting in a complex interference pattern. Energy resolved data as shown in Fig. 7 were taken in the spectroscopic dI/dV-mode. The energies in Fig. 7 correspond to energies where the wavelength of the electrons is in resonance with the triangle resulting in a strong enhancement of the intensity. Calculations of the wave pattern have been performed based on a multiple scattering approach taking into account the phase-relaxation lengths of the electrons, which reflect scattering events inside the triangle influencing their phase coherence and can directly be converted into electron life-

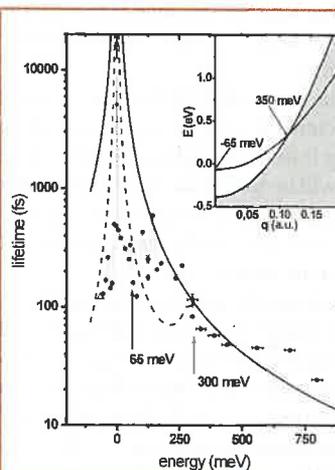


◀ **Fig. 7:** Spectroscopic dI/dV maps measured with the triangle of Fig. 3 displaying the local density of states at energies where the wavelength of the electrons are in resonance with the triangular quantum corral.

times. Inside of the triangle electron-electron and electron-phonon scattering determine the electron lifetime and the spatial decay of the interference pattern which has been measured here. Fig. 8 depicts the result of the evaluations for the electron lifetimes as function of energy. The measurements clearly show a sharp maximum at the Fermi energy in accordance with Fermi liquid theory for a 2DEG due to a decreased phase-space for electron-electron and electron-phonon scattering. Furthermore two pronounced edge-like features show up in the data at +65 meV and +300 meV as indicated in Fig. 8. The latter can be attributed to the transition of the surface state into a surface resonance. The former can be interpreted by a change of the scattering probability as the electron energy becomes smaller than the surface state binding energy of 65 meV. Finally, additional finestructure can be observed which has to be attributed to the geometrical influence of the triangle.

Outlook

The results described above relate to many diverse aspects of physics and chemistry on the atomic and nano-scales. Measuring tip-height curves in constant current or current curves in constant height mode during lateral manipulation reveals internal motion of the entities and thus refers to nanomechanics. The fact that small structures can be assembled or taken apart yields important routes to synthetic and analytic chemistry on the atomic scale. The possibility to take atoms out of the substrate



◀ **Fig. 8:** The full circles connected by straight lines denote the measured electron lifetimes in the triangle of Figs. 3 and 7. The open triangle is a measured value on a defect free terrace and the solid line represents an extrapolation of measurements above 1 eV. The dashed line is an adaptation to theoretical calculations for Cu(111).

features

FEATURES

from defect or intrinsic surface steps can be used to structure the surface itself with the possibility to include also layers deeper than the topmost one. The use of artificially created adatom-hole pairs as binary units with writing, reading and rewriting possibilities certainly would give rise to the utmost possible storage density. Artificial structures on the surface can be built either with native substrate atoms or adsorbed species and their properties can be investigated with spectroscopic methods. Important progress for nanoelectronics can be expected from the ability to modify with the tip internal molecule conformations. The successful induction of all steps of a complex chemical reaction using force, current and field effects raises the hope that new molecules can be built by taking different parent molecules apart and welding dissociation products together at will to synthesize new molecules, whose properties can be investigated again by tunneling spectroscopy. As controlled atomic manipulation allows the design of arbitrary scattering geometries, on the basis of a deeper understanding of the electron lifetimes it should become possible to even engineer these lifetimes, which are a key quantity in quantum computing

and quantum transportation. A further important present goal is to transfer all possibilities outlined here to technologically important substrates like insulators; for sufficiently thin insulator films on metallic substrates the use of the STM is still possible.

References

- [1] For films showing the gradual buildup of several artificial surface structures in an atom by atom way by lateral manipulation see the homepage of the authors: <http://www.physik.fu-berlin.de/~ag-rieder/index.html>.
- [2] L. Bartels *et al.*, *Phys. Rev. Lett.* 79, 697 (1997); G. Meyer *et al.*, *ibid.* 77, 2133 (1996)
- [3] L. Bartels *et al.*, *Appl. Phys. Lett.* 71, 213 (1997) and *Phys. Rev. Lett.* 80, 2004 (1998)
- [4] Saw Wai Hla *et al.*, *Phys. Rev. Lett.* 85, 2777 (2000)
- [5] F. Moresco *et al.*, *Phys. Rev. Lett.* 86, 672 (2001) and *ibid.* 87, 88302 (2001)
- [6] K.F. Braun and K.H. Rieder, *Phys. Rev. Lett.* 88, 096801 (2002)