Force induced and electron stimulated STM manipulations:
Routes to artificial nanostructures as well as to molecular contacts, engines and switches

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Abstract. Initially invented to image surfaces down to atomic scale, the scanning tunneling microscope (STM) 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 with atomic precision in different manners by using solely the tip-adparticle forces. In this way various artificial structures on nanoscale have been created and in situ characterized with the STM. Such structures as well as single molecules can be investigated by scanning tunnelling spectroscopy (STS) both with respect to their local electronic and even vibrational properties. Modifications of single molecules can be induced by using the tunnelling electron current: Rotations, diffusional jumps, vibrational excitations, desorption, dissociation and even association can be induced in individual molecules, often in a rather precise way by tuning the voltage into the energy levels of specific vibrations or electronic levels. These possibilities give rise to startling new opportunities for physical and chemical experiments on the single atom and single molecule level. Here a brief overview on results obtained with these new techniques is given.

1. Lateral manipulation and build-up of artificial structures
The first laboratories in which artificial structures were built by lateral manipulation on atomic scale with the STM using single atoms and molecules were the IBM Almaden research laboratory [1,2] and the Physics Department of the Free University (FU) in Berlin [3]. Both groups built up first the logos of their institutions with Xe atoms and CO-molecules, respectively. Later quantum corrals of different shape (circles, ellipses, triangles...) were constructed to investigate the electronic properties of the standing waves derived from the surface electronic states on close packed noble metal surfaces in the interior of the corrals [1,2,4-6]. (For films showing the gradual build-up 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). Recently other groups assembled linear metal chains on metal substrates to study the development of 1D-electronic band structures as a function of chain length using STS [7,8].
In lateral manipulation an adparticle at the surface is moved with the tip along the substrate surface to the desired place without loosing contact to the substrate. This is achieved by bringing the tip very close to the adparticle, so that besides the ever present however weak van der Waals interactions also chemical forces between tip and particle are coming into play. These forces can be tuned via the tip-adparticle distance 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 [9]. The different modes can be discerned by recording tip-height curves during manipulation in the STM constant current mode. Upon pulling, the atoms follow 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, 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. Pulling and sliding are usually applied in manipulating metal atoms. In contrast, CO molecules are usually pushed: 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. Nevertheless the build-up of artificial structures in the pushing mode can be successful, if the substrate surface is properly chosen: On Cu(211) CO adsorbs at the upper part of the intrinsic step edges, which act as "railway trails" upon pushing. 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 [10]. 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 [11]. The sole action of tip-particle forces has been proven by measuring threshold curves of current for secure manipulation over a wide range of tunneling voltages [12]. These results were very important for obtaining the goal of automatized build-up of artificial structures as reported very recently [13]. Repulsive forces must usually be applied for the manipulation of large molecules [14] and artificial structures can highly likely be formed with such species even at room temperature [15]. It should be noted that in a recent atomic force microscopy (AFM) manipulation experiment even single atoms were seriously proven to be manipulated at room temperature and an extended artificial structure was built up [16].

2. Vertical manipulation

The deliberate vertical transfer of a particle from the surface to the tip and vice versa is called vertical manipulation. Again the tip is brought close to the particle to be transferred until the force between tip and particle is sufficient 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: This technique might lead to chemical resolution with the STM, a feature which is very much wanted to extend the broad range of STM possibilities: On Cu(111) CO molecules as well as oxygen atoms are imaged as depressions with a tip consisting of metal atoms. If a CO molecule is deliberately picked up by the tip with the technique of vertical manipulation noticeably all CO molecules change in appearance to protrusions whereas the oxygen atoms remain imaged as depressions [17]. It is thus obvious that deliberate functionalization of the tip with different molecules may lead to chemical contrast. This effect could be understood on the basis of theoretical calculations using a Greens function approach, which allows analysis of different electron current paths and their interference [18].

The vertical transfer of CO is interesting because 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. Investigations of the transfer mechanism 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 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 [19].

3. Switching and contacting molecules using lateral manipulation
Manipulation can also be performed into parts of molecules as demonstrated for the case of a TBPP molecule to whose center porphyrin ring there are four TBP legs attached which are perpendicular to the center ring in the gas phase. On Cu(211), however the legs lie flat [20]. 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 open up the possibility of a molecular switch, in which a mechanical action causes switching from conducting to nonconducting behaviour [21]. A related molecule with a long polyaromatic conducting board and the same legs, called lander, has been used to study the problem of contacting molecular wires with atomic precision. It could be shown that upon moving the molecule with the legs parallel towards a step edge, the standing wave pattern of the Cu(111) substrate did not change whereas when the molecule was moved with its legs perpendicular to the step the board connected to the step an electron diffraction pattern characteristic for the contact area and related to an optical diffraction pattern from a slit was observed [22].

4. Molecular shooting: A possible route to molecular engines.
Upon building up artificial structures with the technique of lateral manipulation, one has to rely on the fact, that the particle moved remains located at the site where the tip is withdrawn to the imaging position. It was therefore quite a surprise, when Hla et al. [23] observed in manipulation experiments of the chain like six-carbon ring molecule sexiphenyl on Ag(111), that the molecules went far further than the point of tip withdrawal, whereby the path of the “freely moving” molecule then seems to be influenced by modulations of the surface charge density due to defects on or near the surface. This “shooting effect” was then used in an experiment whereby an artificial nanostructure consisting of two parallel rows of Ag atoms on Ag(111) was used as “gun”: sexiphenyl molecules were brought to one end of the gun and then “shot” towards targets of single Ag atoms located on the other end; the sexiphenyl molecules hitting the Ag atoms enrolled them to form a silver atom-sexiphenyl complex. Manipulation experiments on the complex as well as on the bare molecules pointed to a motion mechanism of the sexiphenyl molecules which bears some reminiscence to a proposition of a molecular engine by Porto et al. [24] who showed on the basis of simple Frenkel-Kontorova like models that in simple adsystems like chains of several particles a unidirectional motion can be induced. Further elucidation of the sexiphenyl shooting effect and experiments aiming for demonstration the molecules can also carry some cargo will obviously be very important towards demonstrating the utility of such molecular engines.

5. Switching molecules employing current effects
Whereas the manipulation procedures discussed up to now mainly relied on the tip-adparticle forces, the mechanism of vertical transfer of CO described in Section 2 indicates that effects can also be due to the interaction of the tunnelling electrons with individual particles on the surface. Such effects can be easily observed by measuring the tunnelling current during electron injection advantageously at fixed electron energies: Abrupt changes in the current indicate changes in the location of the adparticle, its internal conformation or even its breakup into different fragments. The great advantage of the STM is that the resulting situation on the surface can be immediately afterwards observed by normal STM imaging. The ability of the STM to do spectroscopy offers the possibility of further
detailed investigations of the resulting situations. In this way rotations of molecules, (irregular) diffusional jumps as well as dissociation of molecules and even association of reactive species have been observed. A good recent review on these aspects has been given by W. Ho [25]. Very recent investigations of conformational changes in molecules leading to the possibility of local switching can be found in [26,27].

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

Population of an antibonding state as in the case of CO desorption upon vertical manipulation is also important in the preparation of reactants in a full chemical reaction induced by the tip (see Fig.1). In the so called Ullmann reaction which was performed at cryogenic temperatures with individual molecules by Hla et al [28,29], iodine has to be split off from the iodobenzene parent molecules to form the phenyl reactands. Again tunnelling electrons populate temporarily the iodine-phenyl antibonding level thus causing the dissociation step (Fig.1a,b). Both iodine and phenyl fragments are found on the surface. In order to bring two phenyls together (the diffusion step in a chemical reactor), lateral manipulation in the pulling mode is employed (Fig.1c,d). At the low temperatures of the Cu(111) substrate the proximity of the two phenyls is not sufficient to induce their association to biphenyl as was shown very elegantly again by lateral manipulation: 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.1e,f). All these steps were proven to be feasible both with clean metal and functionalized tips. Notice that in Fig.1c,d 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.1g) [29]. 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. It is clear that the appreciable number of different steps necessary to achieve the entire reaction will lead to further detailed investigations of the individual mechanisms of all these steps.

That the final association step in the biphenyl reaction might be associated with the excitation of vibrational modes is probable in view of related results: Local excitation of the scissoring and the OH-stretching modes was 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 [30]. Vibrational modes can be excited by the tunnelling electrons to such a degree that even dissociation of molecules can occur. A particularly nice example of a chemical transformation obtained by exciting a specific C-H vibrational frequency is the hydrogen stripping reaction on trans-2-butene (C\textsubscript{4}H\textsubscript{4}) to transform it into 1,3-butadiene (C\textsubscript{4}H\textsubscript{4}) [31]. Another example of preferential vibrational excitation to induce diffusional jumps or desorption (by exciting the umbrella mode) of NH\textsubscript{3} is provided in [32]. It is clear that the local vibrational spectroscopy possible with STS (STM-IETS, inelastic electron tunnelling spectroscopy) as shown first by the group of Ho [33] constitutes a very important additional method in the STM arsenal.

7. Outlook

The results described above relate to many diverse aspects of physics and chemistry on the atomic and nano-scales. The ability and the mechanisms by which nanostructures in an atom by atom or molecule by molecule way can be built up are thoroughly investigated. Large nanostructures with up to 500 adparticles demonstrating quantum mirages [5] and logical devices using the domino effect in CO complexes (chevrons) [34] were built and their functionality was demonstrated Measuring tip-
Fig.1: 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.
height curves in constant current or current curves in constant height mode during lateral manipulation reveals the mode of motion of atoms but also the internal motion of molecules and thus allows new insights into 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 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. Thus also the build-up of threedimensional nanostructures appears possible, especially by combining lateral and vertical single particle manipulation. The use of artificially created adatom-hole pairs as binary units with writing, reading and rewriting possibilities certainly would yield the utmost possible surface storage density. Artificial structures on the surface built either with native substrate atoms or adsorbed species in a one atom/molecule by one atom/molecule way can be investigated in situ with respect to their physical properties employing STS. Important progress for nanoelectronics can be expected from the ability to modify with the tip internal molecule conformations and to contact molecules with atomic precision to leads [22, 35]. 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 STS. This dream of molecular surgery is certainly one of the most exciting, but also most ambitious challenges for the future. 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; as for sufficiently thin insulator films on metallic substrates the use of the STM is still possible [36, 37]. The recent observation of electron refraction at the edge of an NaCl film on Cu(111), where a surface localized metal state and an interface state localized between metal and ionic film merge [38], even gives rise to speculations on the possibility to build devices based on surface electron optics. Also the possibility to switch the electronic state of single Au atoms lying on a thin NaCl film at will might bear important consequences for electronics with single atoms [39]. It should not be forgotten, that the ability to manipulate individual atoms and molecules also can have important consequences for high precision measurements on surfaces as demonstrated by the experimental determination of the surface state mediated oscillatory interaction between adsorbates [40]. To obtain chemical resolution in STM imaging with deliberately functionalized tips prepared by vertical manipulation also very much deserves further investigations. This holds also for achieving STM images with extremely high resolution. Manipulation possibilities at room temperature as well as on the liquid/solid interface [41] for the build-up of man designed structures constitute further experimental challenges very worthwhile to pursue. Also manipulation with the AFM [16] at low and room temperature remains an important challenge because then also artificial structures built atom by atom on technologically important semiconductor and insulator surfaces will become available.

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