

## Chapter 7

### Conclusions and outlook

In this thesis, a low temperature STM working at 5 K is used to study the adsorption and manipulation of organic molecules on metal and oxide surfaces. The studied molecules are model systems for future applications in molecular electronics. Three different molecules have been investigated: the Lander molecule, specially designed to study single molecular wires on metallic surfaces, an azobenzene derivative, interesting example of a molecular switch in the gas phase and in solution, and pentacene, a linear hydrocarbon molecule used as a prototype for studying the molecular electronic decoupling from a metal surface.

In Chapter 4, the manipulation of the Lander molecule on Cu(211) is performed. First, the study of the molecular adsorption has been carried out: The exact molecular conformations upon adsorption on Cu(211) have been extracted by the interplay between experimental STM images and theoretical calculations.

The technique of lateral manipulation in constant tip height is used to position the molecules on the surface in a well controlled way and to form a molecular chain. 304 manipulations attempts have been performed, in which it was possible to exactly determine the molecular conformations and orientations before and after the manipulation. From a statistical analysis of the experiments, it came out that the intrinsic steps of the surface act as rails for manipulations.

The manipulation perpendicular to the intrinsic steps of the Cu(211) surface is possible too, but unfavored because of the high diffusion potential barrier.

The study of the manipulation signal has shown that only in the case of manipulation parallel to the step edges the signal is regular and very reproducible. Its periodicity shows

that the molecule jumps from an adsorption site to the next in the direction of the surface steps, as it is pushed by the STM tip. Furthermore, the comparison of the experimental manipulation signal with theoretical calculations has allowed to gain detailed information on the internal mechanics of the molecule during its manipulation. Small intramolecular deformations have been extracted in real time. The manipulation signal provides information on the mechanical motions of molecular parts that are not directly in interaction with the tip apex during the manipulation sequence. This is due to the fact that the intramolecular deformation induced by the manipulation opens an additional tunneling path through the molecular board, even if the tip apex pushes and is in close contact with a leg (*tert*-butyl-phenyl group) of the molecule.

In Chapter 5, the study of the formation of thin vanadium oxide films on  $\text{Cu}_3\text{Au}(100)$  has been performed. The growth of thin vanadium oxide films on single-crystal metal surfaces is very interesting because it allows to fabricate uncontaminated vanadium oxide surfaces, which are of considerable interest in terms of technological applications. Vanadium oxide films have been obtained on  $\text{Cu}_3\text{Au}(100)$  by first oxidizing the metal surface and afterward depositing vanadium. By controlling the vanadium amount, the oxygen quantity, and the substrate temperature, new oxide phases have been formed that exhibit novel, non-bulk-like structures. The thin vanadium oxide films have been used to electronically decouple pentacene molecules, from the metallic substrate. To approach the very complex system of pentacene on thin vanadium oxide films, the molecular adsorption has been first studied on the bare metal  $\text{Cu}_3\text{Au}(100)$  surface, on the oxidized  $\text{Cu}_3\text{Au}(100)$  and finally on the oxide films. The effect of decoupling of the film has allowed the imaging of the unperturbed molecular HOMO orbital.

In Chapter 6, the possibility of inducing a *trans-cis* isomerization of an azobenzene derivative (TBA) with the STM tip, has been explored on  $\text{Au}(111)$ . The study of the molecular adsorption allowed a very precise control of the environment conditions, in contrast to studies of the isomerization of azobenzene in the gas phase and solution. After deposition onto  $\text{Au}(111)$ , the molecules are either isolated at the elbows of the herringbone reconstruction of  $\text{Au}(111)$ , or adsorb in highly ordered islands. All TBA molecules are in the *trans*- form, which is the energetically favored configuration in the gas phase.

The reversible switching of TBA from the *trans*- state to the *cis*- and back, which

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plays a key role for a possible application of azobenzene as a molecular switch, has been realized by applying voltage pulses with the STM tip. Switching is facilitated when the molecules are stabilized in molecular islands, where the interaction between molecules hinders molecular rotation upon the application of voltage pulses and thus allows the isomerization process.

The conformations of the two isomers on Au(111) have been extracted. The *trans*- isomer corresponds to a planar adsorption geometry. The *cis*- isomer is completely different from the *trans*- isomer as it is not planar, in agreement with the molecular configuration in the gas phase. Diverse values of conductance of the two isomers when located between two electrodes are expected and well predicted by theory.

The use of the STM tip instead of light for inducing the process has not only allowed to induce a switching process at the single molecular scale, but furthermore to gain a basis understanding on the isomerization mechanism on surfaces. In fact, by tuning the STM manipulation parameters different driving mechanisms have been proven. To allow such a detailed study of the isomerization mechanism, switching of molecules in islands has been exactly reproduced several hundred times. The values of the threshold voltage (for both polarities) to induce the isomerization for both *trans*  $\rightarrow$  *cis* and *cis*  $\rightarrow$  *trans* process have been determined. Furthermore, the dependence of the threshold voltage on the tip height has been measured.

In all cases, the threshold voltage is not a constant value, but increases (linearly) when retracting the tip. Moreover, the isomerization process was operable also when the tip is positioned at very large tip heights (36 Å) from the surface, demonstrating that the switching process is induced by the electric field between the STM tip and the sample surface. As a result, the switching process is not limited to the molecule directly under the tip apex, but applies to many molecules within an island. Since the realization of the switching of azobenzene molecules by electric field has never been observed experimentally so far, neither in solution nor on a surface, this finding is of high interest for the present research of molecular switches in general.

Additionally, for small tip heights, when the tunneling of electrons become important, the *cis*  $\rightarrow$  *trans* isomerization is investigated by studying the current signal during the manipulation. The dependence of the switching rate on the tunneling current shows

the characteristic behavior of a one electron process. Spectroscopy measurements allowed to prove the energy position of the molecular orbitals (HOMO and LUMO) and thus to conclude that tunneling of an electron (hole) into the molecular orbitals, drives the *cis*→*trans* switching mechanism at small tip heights.

The fundamental studies performed in this thesis open interesting perspectives for future experiments. In the case of Lander molecule, it is now possible to explore the chemical synthesis at the molecular level, using STM manipulation for connecting several Lander-type molecules and allowing longer distance electron transport.

The experiment with pentacene molecule can be further developed using the LT-STM manipulation to electronically contact a single pentacene molecule to a metallic atomic scale electrode in a planar configuration and in ultra-clean conditions. This would lead to quantitatively characterize the charge transport through a molecular unit. Oxide films can be further used to electronically decouple the molecule from a metal substrate, allowing conductivity measurements through a single molecule with the metal step edge acting as one electrode and having the STM tip as a second electrode.

The experiment with azobenzene opens the possibility to investigate the influence of the molecule-substrate interaction on the isomerization process, by adsorbing the molecules on different substrates. Moreover it can be studied how changes in the substitution pattern of the molecules affect the switching process. In future experiments, electron transport measurements by STM for the two isomers of TBA are of great interest.