Chapter 6

Tip-induced isomerization of an azobenzene derivative on Au(111)

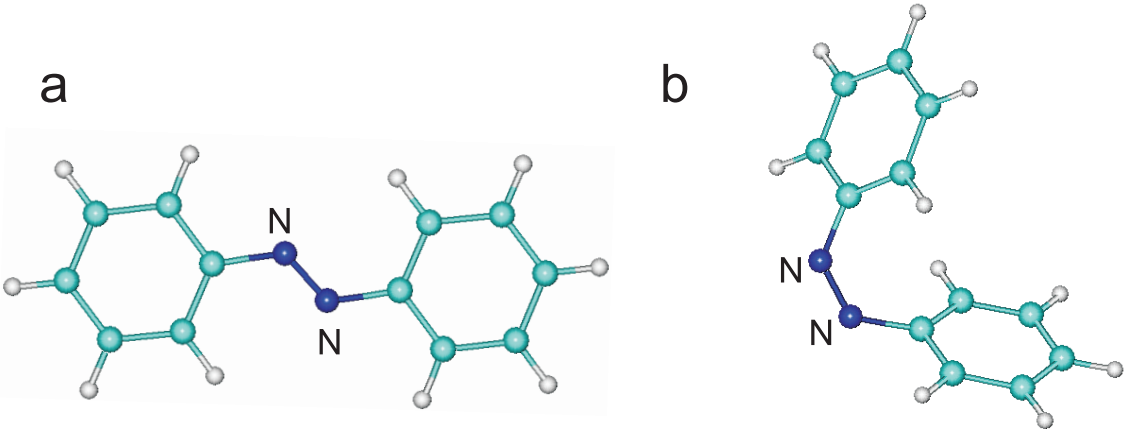

Figure 6.1: Azobenzene molecule: (a) nearly planar *trans*-form and (b) 3-dimensional *cis*- form. In the structural models larger spheres represent carbon atoms, while smaller ones hydrogen atoms. The nitrogen atoms (which form a double bond) are represented in blue.

Understanding and controlling conformational changes of single molecules adsorbed on a surface is currently one of the most actively pursued goals because it could help in the development of molecular electronics. For example, a geometrical modification of a molecule could be used to perform the function of a nano-mechanical device, or be related to a change in the molecular conductance, thus realizing a molecular switch [15].

Recent experiments have shown that conformational changes within a porphyrin molecule can be mechanically induced by the STM tip [20]. By approaching the tip vertically, a very high reliability of intramolecular manipulation of the Lander molecule was obtained [133]. Moreover, it has been demonstrated that molecular rotation between stable

states can be controlled by electronically exciting molecules with tunneling electrons [23].

Looking for molecules suitable for application in molecular electronics, the current research interest is focusing on molecular switches [134, 135]. A molecular switch undergoes a reversible transformation between at least two distinct stable or metastable states, usually geometrical or valence isomers, associated with different physicochemical properties (for example absorption spectrum, dipole moment, refractive index) based on a change in molecular geometry and/or electronic distribution [134].

The azobenzene molecule represents a very interesting example of such a molecular switch [134, 136] and its operating mechanism based on a *trans-cis* isomerization of a double bond is conceptually related to the basic principle of vision in the human eye [137]. The reversible switching of azobenzene can be induced by photo-isomerization [138]. The thermally induced *cis*$\longrightarrow$*trans* isomerization is also possible in the ground state [139, 140].

The aim of the experiment described in this chapter is to translate this well-known molecular switch into a solid state device setting. The molecule used for this goal is composed of an azobenzene core equipped with four lateral groups. Similarly to the case of the Lander molecule (see Chapter 4), the lateral groups act as legs which elevate the central azobenzene core and decouple it electronically from the surface and therefore facilitate the lateral manipulation with the STM tip. In this Chapter, the study of the *trans-cis* isomerization of an azobenzene derivative on Au(111) using the STM tip is reported. A number of different manipulation techniques are employed in order to investigate the driving mechanism of the isomerization process.

6.1 A molecular switch: azobenzene molecule

The azobenzene molecule itself ($C_6H_5N{=}NC_6H_5$) is composed of two phenyl rings connected by two nitrogen atoms (Fig. 6.1(a)). The nitrogen atoms form a double bond which is oriented 120° with respect to the N-C bond.

In the electronic ground state, azobenzene adopts two different conformations [141, 142]: a nearly planar *trans*- (Fig. 6.1(a)) and a non-planar, three-dimensional *cis*- form (Fig. 6.1(b)). The total energy of the *trans*- conformation is 0.6 eV lower than that of the *cis*- form, and the two configurations are separated by a barrier of about 1.6 eV (isomerization from *trans*- to *cis*-) [139]. They undergo a reversible photoinduced isomerization,

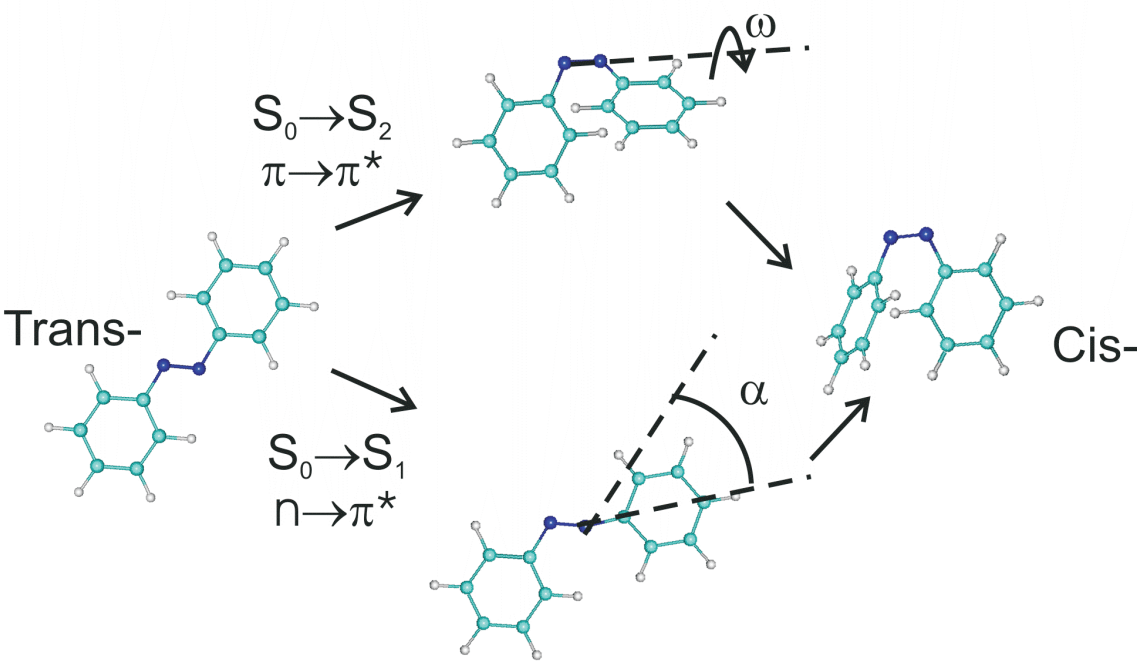

Figure 6.2: Schematics of photo-isomerization: inversion and rotation paths are shown. Relevant conformation coordinates are the angle ω for the rotation mechanism (rotational axis is the N=N bond), and the angle α for the inversion (rotational axis perpendicular to the drawing plane).

well understood in solution and in gas phase [143–149]. The photon energy needed to switch from *trans*- to *cis*- isomer is 3.40 eV (λ_1=365 nm), while in the opposite direction it is 2.95 eV (λ_2=420 nm).

It is well established that the photo-isomerization occurs on an excited state potential energy surface, through a conical intersection with the ground state potential energy surface [143–149]. Two different pathways have been theoretically proposed for the photo-isomerization (see Fig. 6.2): the so-called rotation mechanism [144], which is a twisting around the N-N bond (change of angle ω), and an in-plane rotation of the C-N-N (α angle), known as inversion path [143]. The rotation pathway has been associated with a $S_0 \longrightarrow S_2$ excitation ($\pi \longrightarrow \pi*$), while the inversion with a $S_0 \longrightarrow S_1$ excitation (n$\longrightarrow \pi*$). In particular the $S_0 \longrightarrow S_1$ transition is dominated by a HOMO$\longrightarrow$LUMO excitation, while the $S_0 \longrightarrow S_2$ transition is essentially a HOMO-1$\longrightarrow$LUMO excitation.

Azobenzene has potential applications in a molecular device set-up as the conductance of the two isomers has been predicted to differ strongly [150]. However, its application as

a switch for electronic or mechanical molecular devices needs its adsorption on surfaces. In contrast to the cases of azobenzene in the gas phase and solution, studies of azobenzene molecules adsorbed on surfaces are just recently emerging and the isomerization mechanism on surfaces is under discussion. In particular, the isomerization process on a surface (if it occurs) may be different from those in solution or gas phase, as for example here the degrees of freedom of the molecule are reduced. Moreover when the molecules are adsorbed on metal surfaces, new channels for dissipation of the excitations are present as well as changes on the electronic structures of the two isomers due to the coupling with the substrate may occur. Understanding the most important parameters for the isomerization of azobenzene on a surface (for instance with respect to the molecule-substrate interaction) is therefore of great interest for its application in molecular electronics.

The adsorption of azobenzene on surfaces has been recently studied by STM [151–153]. Also the investigation by STM of the light induced isomerization of azobenzene molecules embedded in a *n*-dodecanethiol (C_{12}) self-assembled monolayer formed on Au(111) have been reported [154]. However, a new perspective is to use the STM tip instead of light to induce the isomerization of azobenzene on the molecular scale. Using manipulation techniques, it has been shown that the azobenzene molecule can be moved laterally on Au(111) with the STM tip [155]. Furthermore, in the case of an azobenzene derivative (Dimetacyanoazobenzene), the rotation around a N-C bond of a phenyl ring can be controlled by STM [156]. Very recent experiments have also reported the isomerization of azobenzene [157] and of an azobenzene derivative (Disperse Orange 3) [158, 159] on Au(111) by STM. In both cases the mechanism is induced using tunneling electrons, as will be discussed in detail in Sec. 6.7.4.

6.2 The Au(111) surface

The Au(111) surface is used as substrate in this investigation because of its inert character. A strong molecule-substrate interaction could hinder molecular movements and thus the isomerization process.

Gold is a fcc metal with a lattice constant of a = 4.08 Å. The Au(111) is the close-packed face of the Au crystal, with a nearest neighbor distance of $a/\sqrt{2} = 2.88$ Å and a step height of $a/\sqrt{3} = 2.36$ Å. An atomically resolved STM image of the Au(111) surface is shown in Fig. 6.3(a).

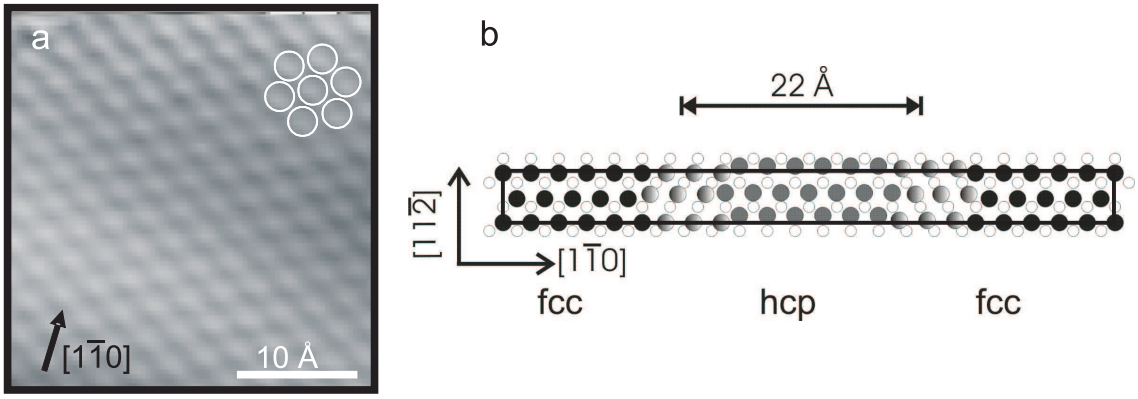

Figure 6.3: (a) Atomically resolved STM image of Au(111). The positions of the atoms are indicated in the image. STM parameters: U = 0.1 V, I = 2 nA; Image dimensions = (24×24) Å^2. (b) Schematic of the unit cell of the reconstructed Au(111) surface. White circles indicate the atoms in the second atomic layer, black circles correspond to atoms with fcc stacking, gray ones to hcp stacking, while shadow atoms represent the atoms in the transition regions.

The Au(111) surface exhibits a long-range surface reconstruction with a (22 $\times\sqrt{3}$) rectangular unit cell [160]. In the topmost-layer 23 Au surface atoms along the [1$\bar{1}$0] direction sit on 22 bulk lattice sites. This contraction leads to an alternation of regions with top-layer atoms in fcc bulk sites and hcp sites (see Fig. 6.3(b)). At the domain boundary between hcp and fcc stacking the atoms are squeezed out from their position and form two ridges per unit cell. These ridges run parallel and at domains boundaries (about every 250 Å) bend by $\pm 120^\circ$ giving rise to a zig-zag pattern (so-called herringbone reconstruction).

6.3 TBA molecule

The 3,3',5,5'-tetra-*tert*-butyl-azobenzene (TBA) is an azobenzene molecule carrying four lateral *tert*-butyl groups (Fig. 6.4). TBA was synthesized by S. Hecht and M. V. Peters at the Max-Planck-Institut für Kohlenforschung in Mühlheim an der Ruhr. There are several distinct advantages of the particular substitution pattern used: (i) it does not significantly alter the electronics of the azobenzene chromophore, (ii) it does not impart steric hindrance upon the isomerization process, (iii) it increases the separation between surface and the azobenzene π-system thereby leading to an increased surface mobility and potentially a lower electronic coupling, and (iv) its set of four symmetrically placed labels facilitates conformational analysis.

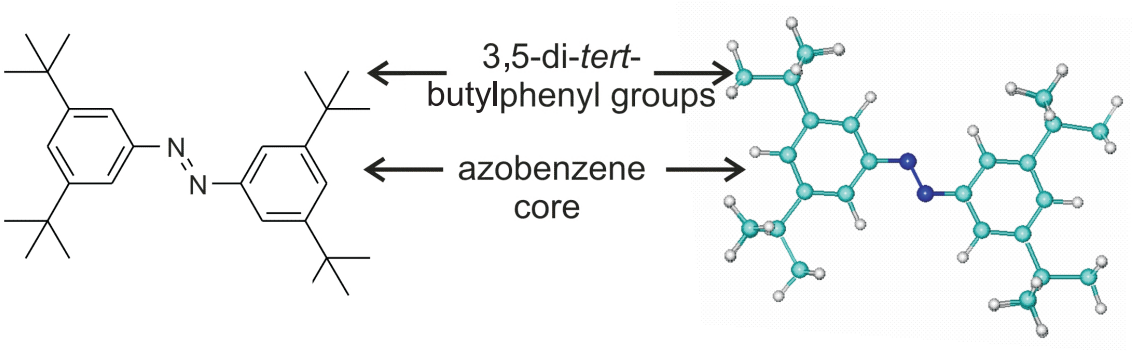

Figure 6.4: 3,3',5,5'-tetra-*tert*-butyl-azobenzene (TBA): chemical structure (left) and sphere model (right). The molecule is composed of an azobenzene part which is equipped with spacer *tert*-butyl- groups.

After the synthesis, S. Hecht and M. V. Peters have proven by absorption spectroscopy that the molecules exhibit in solution the photochemical and thermal isomerization behavior typical for azobenzene derivatives. Photo-isomerization in both *trans*$\longrightarrow$*cis* and *cis*$\longrightarrow$*trans* directions was carried out in cyclohexane using appropriate excitation wavelengths (Fig. 6.5(a) and (b)). The *trans*$\longrightarrow$*cis* photo-isomerization was executed repeatedly (Fig. 6.5(c)). In Fig. 6.5(d) the thermal *cis*$\longrightarrow$*trans* is shown. The isomerization was carried out at elevated temperatures (50° C).

6.4 Adsorption of TBA on Au(111)

TBA molecules were deposited by evaporation from a Knudsen cell at about 370 K. The dosage was monitored via a quartz crystal microbalance. During the deposition of the molecules the sample was kept at room temperature.

An overview STM image of TBA molecules on Au(111) is shown in Fig. 6.6. The Au(111) herringbone reconstruction can be seen in the image as parallel pairs of ridges. After adsorption at room temperature, the molecules are mobile, as they cover step edges and form islands, but a few are also found isolated on terraces. Notice that the herringbone reconstruction is slightly visible also underneath the ordered island at the center, indicating that the adsorbed molecules do not lift the reconstruction of the covered Au(111) surface.

All observed molecules are in the same planar configuration, assigned to the *trans*-isomer (Fig. 6.4). This finding is actually very reasonable since, already after the syn-

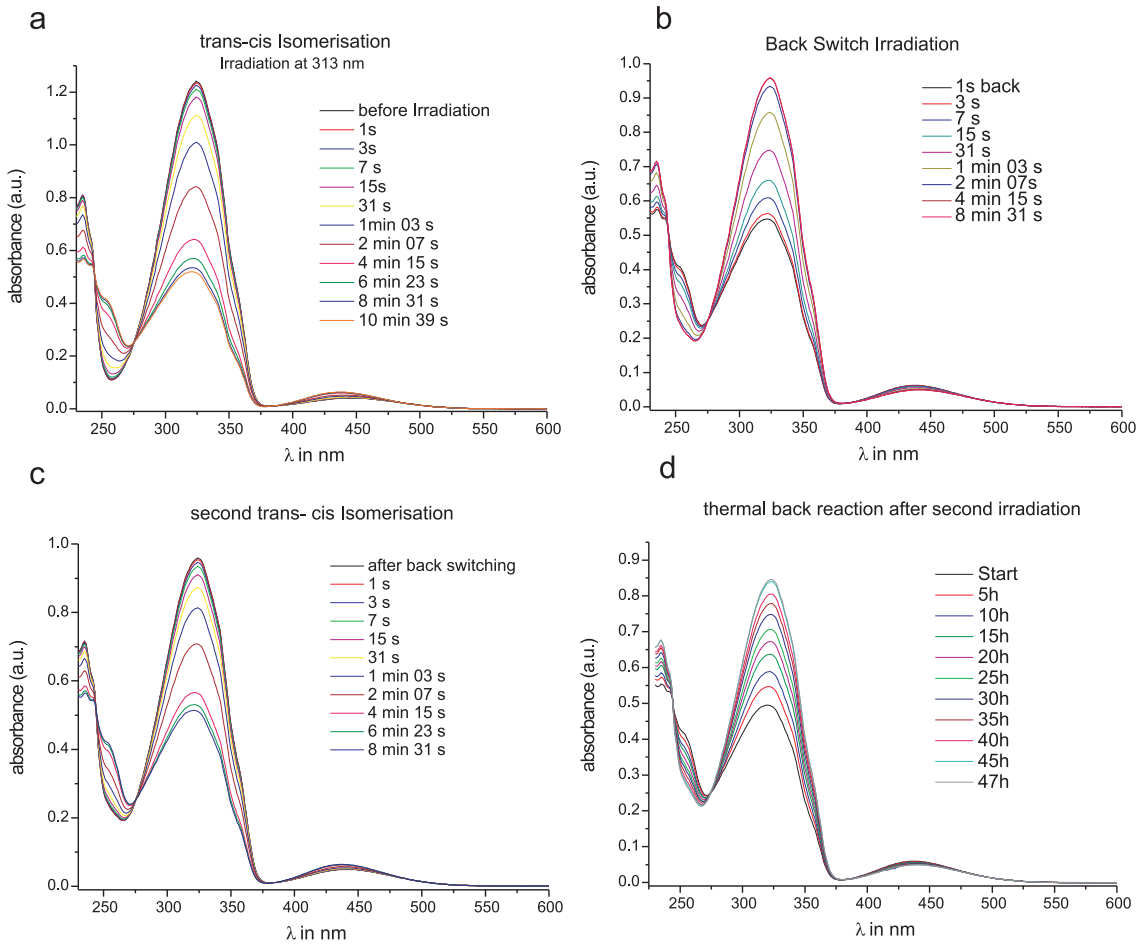

Figure 6.5: Photochemical and thermal *trans-cis* isomerization of TBA in cyclohexane at 25° C. In the spectra the time evolution of the absorption peak characteristic of the *trans*- isomer (at about 325 nm) upon radiation is clearly visible. (a) Photochemical *trans*⟶*cis* isomerization of TBA. 1000 W XBO light source equipped with interference filter $\lambda_{\text{max T}}$ = 313 nm (11% T, Full-Width Half-Maximum (FWHM) = 10 nm). (b) Photochemical *cis*⟶*trans* isomerization with a 1000 W XBO light source equipped with cut-off filter $\lambda_{10\%\text{ T}}$ = 377 nm and $\lambda_{50\%\text{ T}}$ = 398 nm. (c) Photochemical *trans*⟶*cis* isomerization after the 1st switching cycle (irradiation conditions as in (a)). (d) Thermal *cis*⟶*trans* isomerization of TBA in cyclohexane at 50° C.

thesis, 97% of the molecules are in the *trans*- isomer, which is the energetically favored state in the gas phase. Moreover, any heating process increases the fraction of the *trans*-isomers to the expense of the *cis*- molecules [139, 140]. The complete missing of *cis*- isomers on the surface is therefore expected, because the molecular substance is heated up to 370 K for deposition. Notice that after preparation the sample is only shortly exposed to the ordinary laboratory light until it is inserted into the STM (where the sample receives

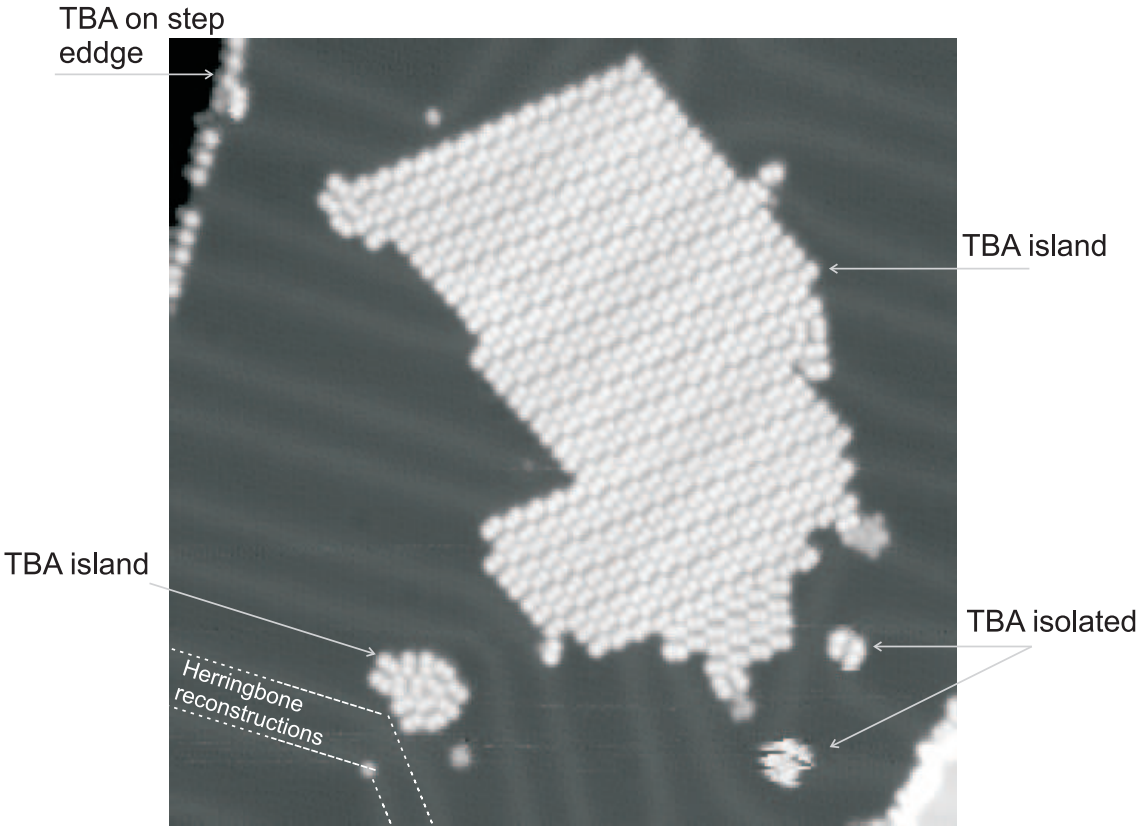

Figure 6.6: Overview STM image of TBA adsorption on Au(111). A large ordered island of molecules and a disordered island (bottom left) of molecules are visible. Two isolated molecules (bottom right) are found at the elbows of the Au(111) reconstruction. Notice that one isolated molecule is not stable in the image since it rotates during scanning. The step edges are covered by molecules. STM parameters: U =1 V, I = 0.1 nA, T =5 K; Image dimensions = (390$\times$390) Å^2.

no light radiation), so that isomerization by light is unlikely.

6.4.1 Isolated molecules

Single molecules appear as four lobes with an apparent average height of 2.7$\pm$0.1 Å arranged in a rhombic shape (Fig. 6.7(a)). The dimensions of the sides of the rhomboidal, measured between intensity maxima are a = 4.9$\pm$0.4 Å and b = 10.5$\pm$0.6 Å, while the angle between two sides is ϕ = 80°$\pm$3°. According to the dimensions of the molecule in the gas phase (a = 5.5 Å, b = 9 Å and ϕ = 85°), the lobes can be assigned to the *tert*-butyl groups in accordance to their large spatial extension. The central azobenzene part is typically not visible. Only in a few cases a visible contribution at the molecular center has been detected (Fig. 6.7(a)), due to a very sharp tip. No change in the STM images is observed by varying the sample voltage in the range from $-$2 V to +2 V.

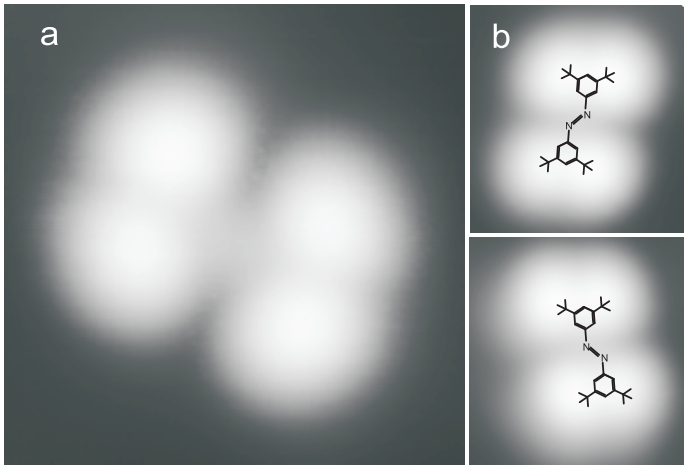

Figure 6.7: (a) Isolated TBA molecule ((50×50) Å^2). (b) Determination of the chirality of TBA molecules on the surface. We found molecules of different chirality adsorbed on the surface as shown by the structural models. STM parameters for all images: U = 1 V, I = 0.1 nA, T =5 K.

Two different shapes of isolated molecules, one the mirror image of the other, have been distinguished on Au(111). This observation is related to the concept of chirality. The term chirality was first indicated by Lord Kelvin (1893), who said: "I call any geometrical figure, or group of points, chiral, and say it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself".

In the same way the molecules visible in Fig. 6.7(b), which are mirror images of each other, cannot be brought to coincide with itself, and therefore show chirality. Actually, TBA molecules are not chiral in three dimensions, but may become chiral upon adsorption on a surface due to the reduced symmetry, as observed for other kinds of molecules [161, 162].

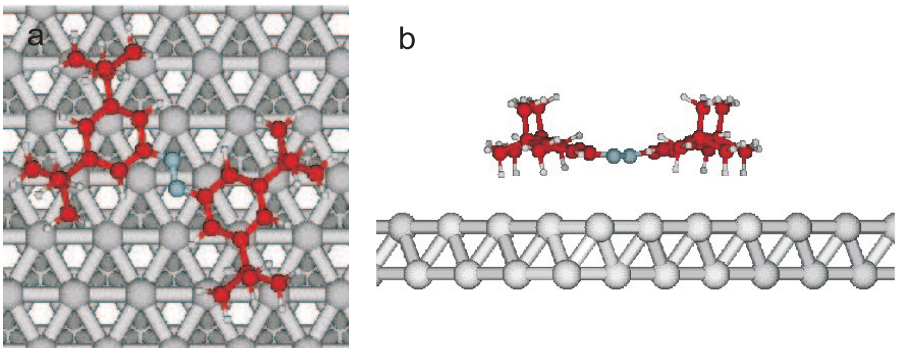

Figure 6.8: MM optimization of the adsorption conformation of the *trans*- isomer, (a) top view and (b) side view.

Christian Joachim and collaborators (CEMES-CNRS, Toulouse) have calculated with MM (see Chapter 2) the conformation of the *trans*- isomer on Au(111). The result of the molecular structure optimization is shown in Fig. 6.8. The planar adsorption of the phenyl rings is found to correspond to a physisorption structure where the molecule remains quasi planar and where the *tert*-butyl- groups avoid the mixing of π orbitals with the metal.

As one can see in Fig. 6.9(a), isolated molecules on terraces are always positioned at the elbows of the Au(111) herringbone reconstruction, which act as nucleation centers. They are oriented with their long molecular axis parallel to the close-packed directions of the substrate. The isolated molecules easily rotate under the influence of the tip at normal tunneling conditions (I = 1 nA, U = 1 V) revealing a rather weak interaction with the substrate.

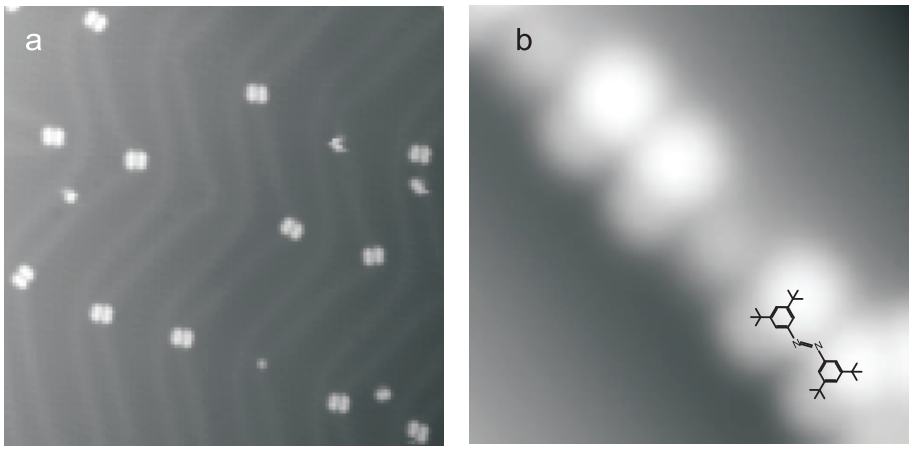

Figure 6.9: Adsorption of isolated molecules. (a) Several isolated molecules at elbows of herringbone reconstruction (390×390) Å^2. STM parameters: U = 1 V, I = 0.1 nA; (b) Molecular adsorption at step edges. In the image ((45×45) Å^2) two molecules are found absorbed at a step edge. The adsorption geometry is indicated by a model superimposed on one molecule. STM parameters: U = 1.3 V, I = 0.04 nA, T =5 K.

Molecules are also found adsorbed on step edges. The STM image in Fig. 6.9(b) shows two molecules adsorbed on a step edge. The adsorption geometry, deduced from their appearance, is indicated: two legs of the molecule lie on the upper terrace and two on the lower. The azobenzene part is parallel to the direction of the step edge.

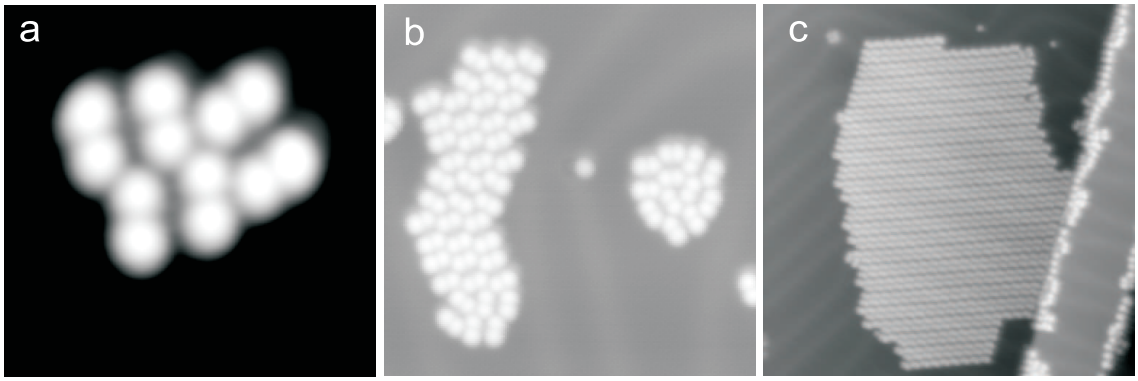

Figure 6.10: Islands of TBA molecules. As the number of molecules increases, the ordering of the islands increases. (a) Island formed by three TBA molecules ((50×50) Å^2). (b) Two disordered islands ((150×150) Å^2. Notice how the island on the left follows the herringbone reconstruction. (c) Large, highly ordered island of about 400 TBA molecules ((410×410) Å^2). STM parameters for all images: U = 1 V, I = 0.1 nA.

6.4.2 Islands

When TBA molecules are adsorbed on the substrate kept at room temperature, they diffuse and form islands. It turns out that islands formed by less than about 40 molecules are disordered, i.e. the molecules are not equally oriented, while larger islands show a high order (and a well defined periodicity). In Fig. 6.10 three STM images are shown: in the first image (a) three TBA molecules are imaged. Each molecule appears as four lobes and is oriented with the long axis parallel to one of the Au(111) close-packed directions. In the second STM image (b) there are two disordered islands of TBA. The one on the right is grown at an elbow of the Au(111) reconstruction. This behavior is always observed for small islands and shows that nucleation starts to form at these sites. The island in the left part of the image follows the direction of the herringbone reconstruction, indicating the influence of the substrate on the growth mechanism. In the third image (c), a large island is shown. It has a high degree of order which extends over several hundred Ångstroms.

The degree of order increases with the number of molecules. This observation can be explained by considering that for small islands the molecule-substrate interaction determines the adsorption geometry while, as the number of molecules increases, the intermolecular interaction prevails, leading to ordered islands. The position and orientation of individual molecules inside ordered islands is shown in Fig. 6.11. For discerning the position of individual molecules, the corners of an island are used as reference, as shown

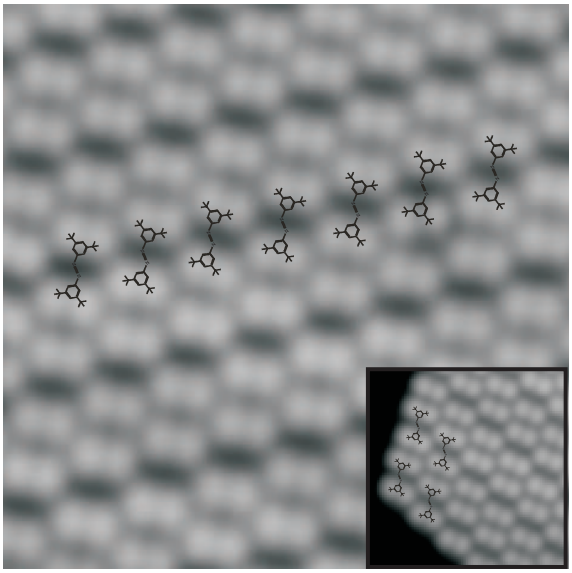

Figure 6.11: Part of a molecular island (= (90×90) Å^2) where it is possible to observe the long range ordering of the molecules. (inset) Corner of an ordered island ((60×60) Å^2) which is used to determine the molecular adsorption geometry is determined as indicated by the structural model inserted in the image. STM parameters for both images: U = 1 V, I = 0.1 nA.

in the inset of Fig. 6.11. The molecules form parallel rows, which run in an angle of $\pm(5^\circ \pm 2^\circ)$ with respect to the close-packed directions of the substrate. The long axis of the molecules is always parallel to one of the close-packed directions of the substrate. Inside a row, it is possible to observe that each molecule is arranged in such a way that one of its legs points through the center part of the next molecule. This comes probably from hydrogen bond like or van der Waals interactions between the molecules. The interaction between rows is of van der Waals type, since in this case no hydrogen-like bond can be formed as only saturated hydrogen atoms of *tert*-butyl- groups are directly interacting.

The chirality of molecules within islands is not observed, indicating that the shift between pairs of legs is slightly distorted when the molecules interact with each other.

6.5 Tip-induced isomerization of TBA

Manipulation experiments were performed by positioning the STM tip at a fixed height above a molecule with the feedback loop switched off and applying a voltage pulse U_m to the sample for a time t_{pulse}.

In Fig. 6.12 an example of such a switching experiment in a molecular island is shown. Subsequent voltage pulses (each 20 seconds long) with U_m= 2 V have been applied with the STM tip always at the same position above the island of TBA in the *trans*- state (Fig. 6.12(a)). After each pulse an STM image was recorded. In Fig. 6.12(b)-(d) the STM images after 9, 18, 27 of such equivalent pulses are shown. The complete sequence is shown in the Appendix. As one can see, many molecules have changed their appearance, showing a larger height (4.1$\pm$0.3 Å) then *trans*- molecules (2.7$\pm$0.1 Å). The bright molecules are stable and to let them return to their initial appearance one has to apply a further pulse. The number of bright molecules increases with the number of pulses, and when a sufficient number of them is present in the island, the bright lobes return to their initial intensity and the *trans*- form is exactly restored, as indicated in Fig. 6.12(b) and (c) by circles. The reversibility of the experiment and its high reproducibility (the switching experiments has been reproduced several hundred times) exclude molecular dissociation or the presence of any contamination as cause for the observed change of the molecular appearance and let one conclude that the observed changes are due to the isomerization of single molecules from the *trans*- form to the *cis*- form, and back to the *trans*- form.

The reversibility of the switching process is shown in Fig. 6.13. A detail of a molecular island of TBA molecules where one molecule has been switched to the *cis*- form, is shown. As one can see, the isomerization process has no effect on the neighboring *trans*- molecules, which remain unchanged. After the application of a voltage pulse, the *trans*-isomer is exactly the same after a *trans*$\rightarrow$*cis*$\rightarrow$*trans* isomerization step.

Notice that also an other conformational change of the molecule could show reversibility. However, the only possible conformational change of the TBA molecule, which would lead to an enhanced apparent height in the STM image, is a rotation of one phenyl ring around the N$-$C bond. It has been shown for the phenyl "legs" of TBPP molecules [20] that it is possible, using repulsive chemical forces between the STM tip and molecule, to rotate a leg of the molecule from an orientation perpendicular to the surface to that of a

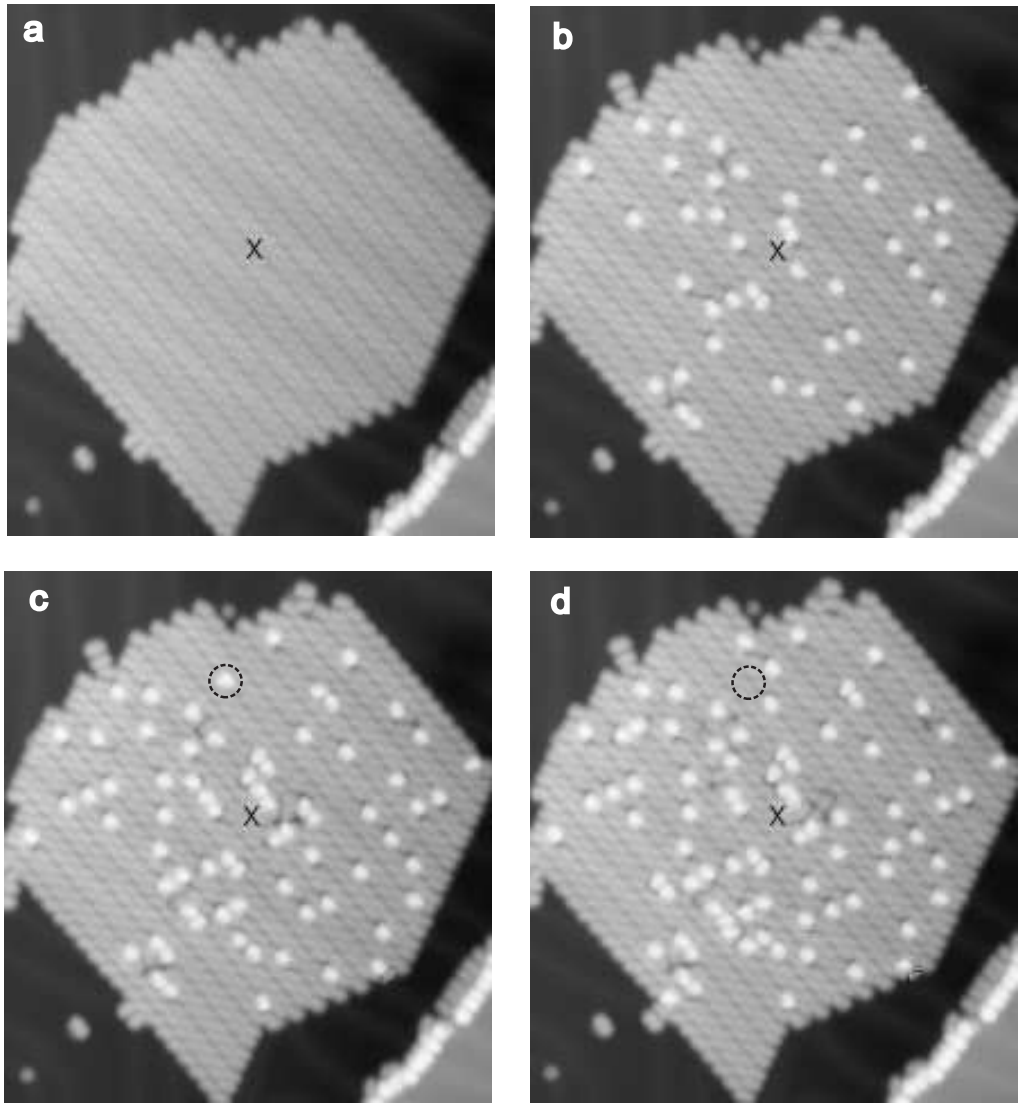

Figure 6.12: (a) A molecular island of 3,3',5,5'-tetra-tert-butyl-azobenzene molecules with about 400 molecules. Subsequent voltage pulses (20 seconds each) with U_m = 2 V and the tip 6 Å above the surface are applied at the position indicated by the cross and after each pulse an STM image is recorded. The complete experiment is shown in the Appendix. (b) STM image after nine pulses: it can be seen that after the pulses 43 molecules in the island have been isomerized to the *cis*-form and appear brighter. (c) STM image after 18 pulses. (d) STM image after 27 pulses. Note that during the pulses in (b) and (c) the *cis*⟶*trans* isomerization occurs as well: bright lobes return to their initial intensity (an example is indicated by the dashed circles in the images c-d). Notice that in principle this process happens also at step (b), but the number of isomerized molecules which return before the end of the pulse, can not be determined. STM parameters for all images: U = 1 V, I = 0.1 nA, T =5 K. For all the images the dimensions are (330×360) $Å^2$.

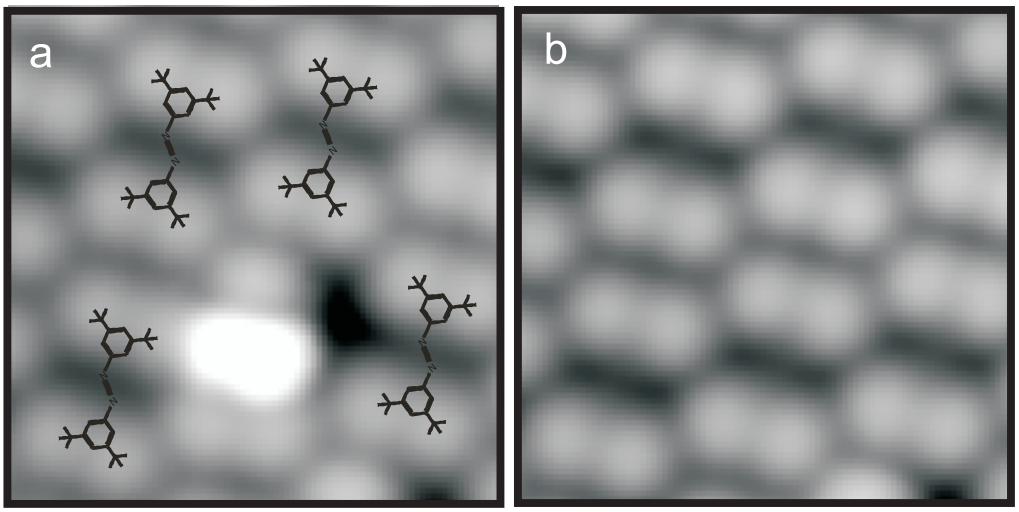

Figure 6.13: (a) STM image showing a detail (35×35 Å^2) of a molecular island where one molecule has been previously switched to the *cis*- conformation (bright lobe), while the other molecules are in the *trans*- form, as indicated by the structural models. (b) After applying a voltage pulse U_m =1.5 V for t_{pulse} = 5 s at tip height = 5 Å above the bright lobe, the molecule is switched back to the *trans*- conformation and the *trans*- form is exactly restored .

flat adsorption geometry. The "leg" of TBPP is composed of a phenyl ring with *tert*-butyl groups as in the TBA. Thus, if the bright lobe observed for of TBA would arise from a rotation of a phenyl ring, it is expected to be restorable by pushing with the STM tip.

An example of a manipulation experiment with TBA using chemical forces is shown in Fig. 6.14. The STM images before and after the manipulation are shown in the inserts, where a *cis*- isomer appears brighter than the other molecules. After having disabled the feedback loop, the tip (which has been positioned direct above the *cis*- isomer) is moved from its initial position vertically towards the surface (tip height z is linearly decreased with time) and retracted again. During this motion, the current signal was recorded. As characterized for I(z) curves with C_{60} molecules [21] different regimes are observable in the curve in Fig. 6.14: between 6.6 Å and about 4 Å, the tunneling current shows the typical behavior as the tip approaches the molecule (i.e. log(I(z)) has a linear dependence on the tip height z). At about 4 Å the tip has reached the van der Waals contact with the molecule. Van der Waals contact (also called mechanical contact) occurs at a tip molecule distance where the van der Waals and the repulsive forces are balanced [21]. Afterwards, the tip push the molecule vertically until the electrical contact is reached. Electrical contact occurs after mechanical contact, when the orbitals of molecule and tip

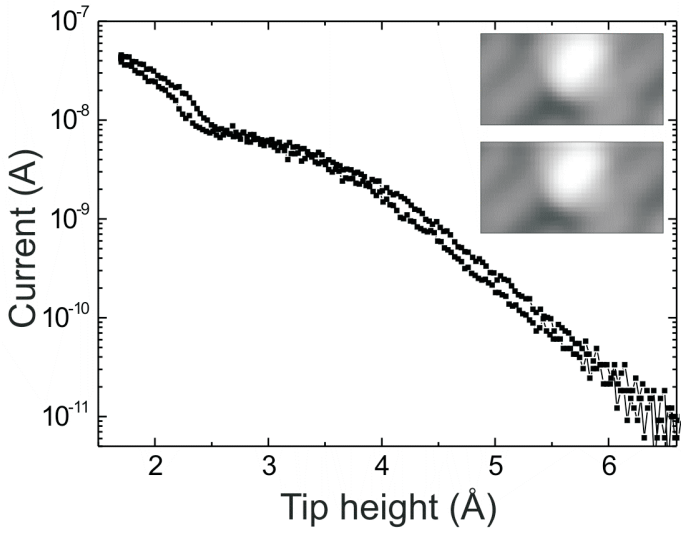

Figure 6.14: Manipulation experiment where chemical forces are used for pushing a *cis*- isomer with the STM tip. (left) STM images before (top) and after the manipulation (bottom). The *cis*-isomer remained unchanged after the manipulation. (right) Current measured during the manipulation versus tip height plotted in a logarithmic scale. During the approaching of the tip towards the molecule, the logarithm of the tunneling current depends linearly on the tip height. When the tip is in electronic contact with the molecule the curves has a change in slope. The plot shows both curves of the tunneling current recorded during approaching and retracting of the tip. Parameters during the manipulations: the tip height is decreased from 6 Å to 2.4 Å, U = 0.05 V.

mix.

Notice that in the curve in Fig. 6.14 the current signals for both the toward and backward tip movement have been recorded (the curve for the backward direction is the one with slightly lower current value). Unlike the case of a metal-tip contact [163], no characteristic signature of irreversibility is visible in the curves. Instead the curves are equivalent showing that the process is reversible.

The STM image taken after the manipulation is completely equivalent to the previous one, demonstrating that it is not possible to switch the molecule to its initial *trans*-conformation by using chemical forces. This result supports the interpretation of an isomerization process, because it points against a simple rotation of one phenyl ring.

The switching of isolated molecules on terraces is very rare because, under the effect of a voltage pulse, the molecule can move or rotate thereby efficiently competing with the isomerization process. This effect is avoided in islands in which the molecules are

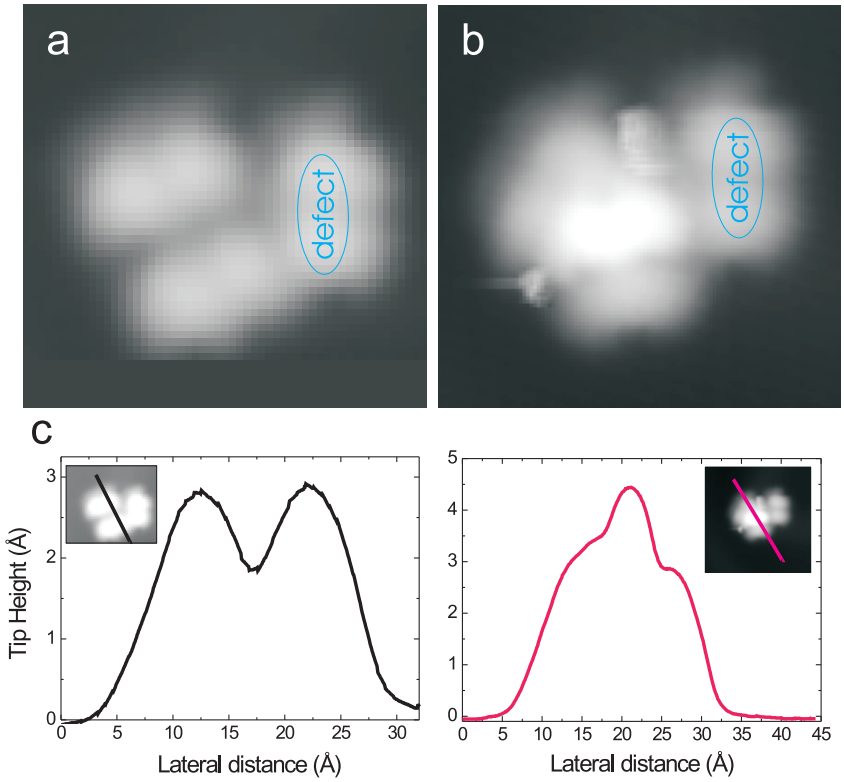

Figure 6.15: (a) STM image of a *trans*- isomer, before the manipulation. Notice that the molecule is attached at a defect, which stabilizes the molecule. (b) Image of a *cis*- isomer, switched after having applied a voltage pulse in which U was varied from -0.2 V to 1.8 V within 60 s. (c) Line scans over *trans*- and *cis*- isomers. The line over the molecules in the insets indicates the path where the line scans are performed. STM parameters: U = 1 V, I = 0.1 nA; Image dimensions =(35×35) Å^2.

stabilized by each other or in isolated molecule attached to defects. Such an example is shown in Fig. 6.15, where a voltage pulse in which U was varied from -0.2 V to 1.8 V within 60 s was applied. The surface defect is indicated in the image for clarity. Also in this case of isolated molecules the *cis*- isomer is not planar (Fig. 6.15(b)), as indicated by the line scans over the molecule before and after the manipulation in Fig. 6.15(c).

6.6 Model for the *cis*-isomer

In an STM image all *cis*- isomers in the molecular islands have the same appearance. As can be clearly seen in Fig. 6.13(a), the *cis*- form shows a bright central intensity maximum, while three lateral lobes in a triangular shape can be resolved. The STM images show that the *cis*- conformation is completely different from the planar *trans*- conformation.

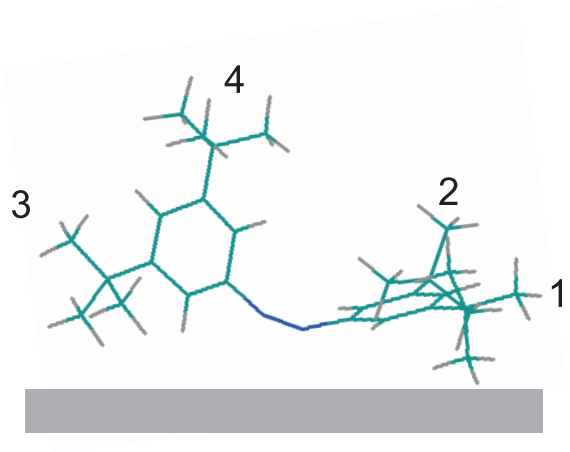

Figure 6.16: Proposed model of the *cis*- isomer in a side view. One phenyl ring remains on the surface, while the second one is out of plane. Similarly to the gas phase the *cis*- isomer is not planar.

A model proposed for the conformation of the *cis*- isomer adsorbed on Au(111) is shown in Fig. 6.16. In the model one phenyl moiety remains on the surface in a similar geometry as in the *trans*- conformation, while the azo (N=N) part of the molecule together with the second phenyl ring are oriented upwards.

In the STM images (see Fig. 6.13) the three lateral lobes with approximately the same intensity are assigned to the three legs of the molecule indicated in the model in Fig. 6.16 with 1,2,3, while assigning the central intensity maximum to the leg 4 pointing upwards.

It turns out that the *cis*- isomer is not planar, in agreement with the molecular conformation in the gas phase [145] and as observed by STM [157] for azobenzene molecules on Au(111).

6.7 Study of the isomerization mechanism

In order to understand the isomerization mechanism of TBA, a detailed study of the process has been performed by varying the relevant STM parameters. As it has been described in Section 2.5, by tuning the STM parameters during a manipulation one can investigate different interaction between tip and adsorbate as well as select different driving mechanisms to induce a process. For example, by changing the voltage applied between tip and sample, one controls the energy of the tunneling electrons and by modifying the tip-surface distance one changes the number of electrons inserted into the system as well as the electric field in the STM junction.

6.7.1 Dependence of the isomerization process on the sample voltage and on the tip height

It turns out that it is possible to induce the switching process only by applying a voltage above a certain minimum value (threshold voltage U_{th}). Its values has been determined at normal scanning conditions to be U_{th} = (1.6$\pm$0.1) V for the *trans*$\longrightarrow$*cis* switching and U_{th} = (1.2$\pm$0.1) V for the *cis*$\longrightarrow$*trans* process. Moreover, it has been found that switching is possible with both positive and negative voltage polarities.

In order to understand the underlying mechanism of the switching process, it is important to study the threshold voltage for different tip-surface distances and tunneling currents. Different behaviors as a function of the tip-surface distances are expected to be found for different mechanisms (see Section 2.5). Also the dependence of the threshold voltage on the tip height for both polarities and both isomerization processes has been investigated in detail (see Fig. 6.17 and Fig. 6.18).

The experimental points have been measured by fixing the tip height and applying a voltage pulse for a fixed time t_{pulse} = 30 sec. Starting from U = 0, the voltage is increased by 0.1 V steps until a switched molecule is observed in a lateral area of 80$\times$80 Å^2 from the tip position. Each sequence was repeated 10 times. The error bars have been obtained from the statistical analysis of the 10 measurements.

In order to determine the tip height, I(z) curves have been first recorded by approaching the tip on the bare gold surface until a characteristic plateau in the log I(z) curves is observed, which corresponds to the formation of a point contact of atomic dimensions [164].

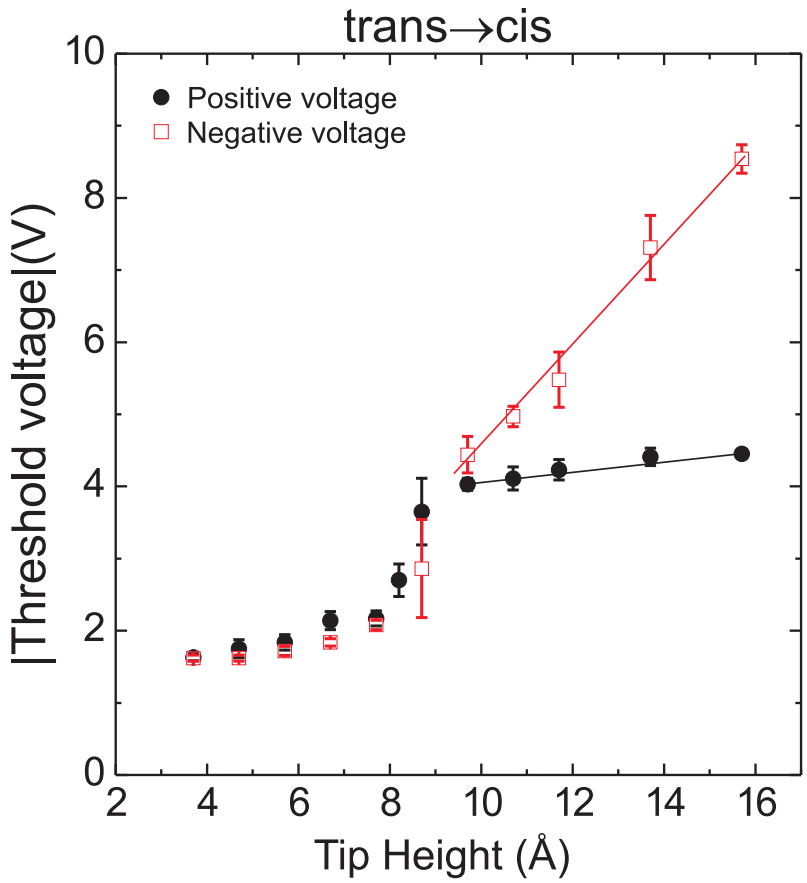

Figure 6.17: Plot of the threshold voltage versus tip height for the *trans→cis* isomerization for positive (electric field points towards the STM tip) and negative polarities. The experimental points have been measured by fixing the tip at a specific height (referred to the bare Au(111) surface and calibrated by recording I(z) curves) and applying a voltage pulse for a fixed time t = 30 s. Starting from V = 0, the voltage is increased by increments of 0.1 V until a switching event is observed in a lateral area of 80×80 Å^2 from the tip position. Each sequence was repeated 10 times. The tunneling current is (7±1) nA at a tip height of 3.7 Å and (52±6) pA at 6.7 Å tip height.

Before each manipulation sequence, the height of the tip is the same (i.e. constant tunneling parameters). After disabling the feedback loop, the tip is moved from this position to the desired height for a switching experiment. The tip height calibrated in this way refers to the bare gold surface.

As one can see in the plots in Fig. 6.17 and Fig. 6.18, the threshold voltage for the isomerization clearly increases (at large tip heights) when retracting the tip for both iso-

merization processes (*trans*⟶*cis* and *cis*⟶*trans*). This rules out a process induced by electron resonant tunneling, which is characterized by a tip height independent threshold voltage. Surprisingly, the isomerization process occurs also at very large tip distances where pragmatically no tunneling current is flowing.

Notice that at tip heights of about 14 Å the tunneling current is in the order of magnitude of 10^{-18} A. Notably, even in the extreme case when the tip is 36 Å above the surface, TBA molecules have been switched from *trans*- to *cis*- by applying a voltage pulse of 6.8 V.

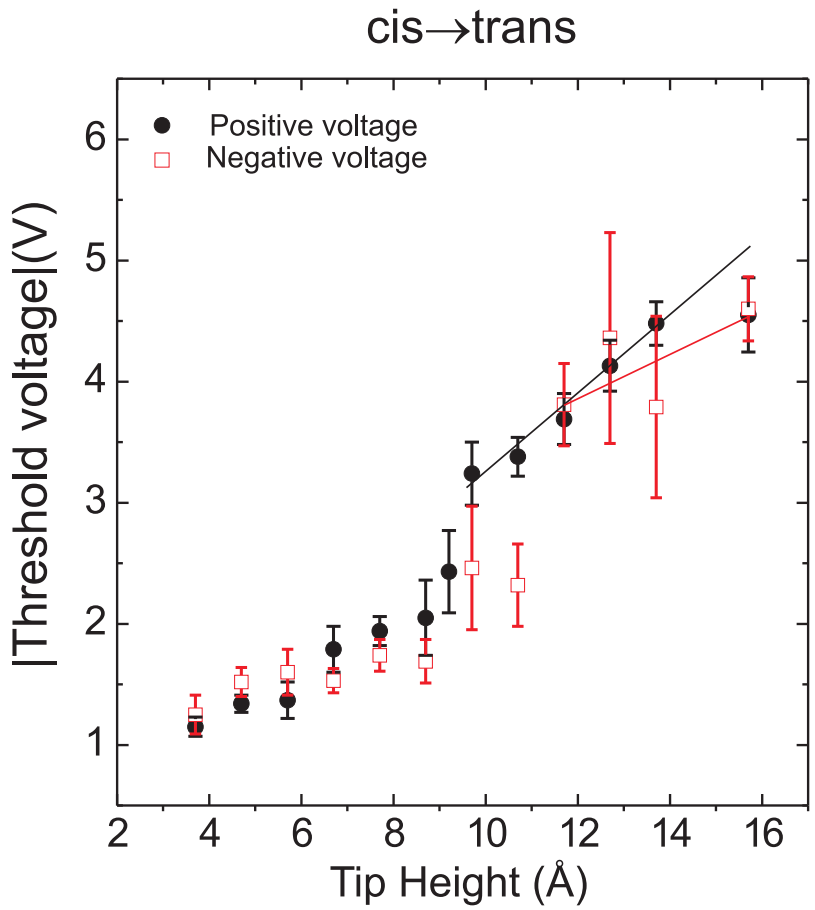

Figure 6.18: Plot of the threshold voltage versus tip height for the *cis*→*trans* isomerization for positive (electric field points towards the STM tip) and negative polarities. The experimental points have been measured by fixing the tip at a specific height (referred to the bare Au(111) surface and calibrated by recording I(z) curves) and applying a voltage pulse for a fixed time t = 30 s. Starting from V = 0, the voltage is increased by increments of 0.1 V until a switching event is observed in a lateral area of 80×80Å^2 from the tip position. Each sequence was repeated 10 times. The tunneling current is (8±1) nA at a tip height of 3.7 Å and (67±6) pA at 6.7 Å tip height.

6.7.2 Lateral distribution of the switching process

Typically, the application of a single voltage pulse causes the switching of several molecules in a radius up to 500 Å around the position of the tip. Processes induced by tunneling of electrons from the STM tip into molecules are very localized near the position of the STM tip, as described in Section 2.5.2. Therefore, to explain the observed extended range of switching with an electronic process, a propagation of the electronic excitations must be considered.

It has been suggested that the photo-isomerization of bistilbene molecules adsorbed on Ag/Ge(111)-($\sqrt{3}\times\sqrt{3}$) [165] is assisted by the creation of excitons (strongly correlated electron-hole pairs) which in turn migrate to neighboring molecules within an island.

However, we observed that it is possible to isomerize TBA molecules inside an island when the tip is positioned above the bare surface nearby the island. This finding excludes the possibility that switching happens through the migration of excited excitons, because they cannot be created on the bare metal.

It is important to note that during the application of a voltage pulse on top of a *cis*-isomer, the *cis*$\longrightarrow$*trans* switching of the molecule directly underneath the tip is always induced. Interestingly this is not the case for the *trans*$\longrightarrow$*cis* isomerization.

6.7.3 Switching by electric field in the STM junction

All the observations presented in Section 6.7.1 and in Section 6.7.2 let one conclude that the isomerization of TBA molecules on Au(111) is driven by the electric field in the STM junction. In fact, this mechanism (*i*) does not involve tunneling of electrons and is therefore operable at very large tip to sample distances, (*ii*) exhibits a linear dependence of the threshold voltage on the tip height (which is in a first approximation expected in the case of an electrostatic driving force), (*iii*) is operable at both polarities and (*iv*) has a large lateral extension, i.e. is not limited to the molecule directly underneath the tip but enables also to isomerize molecules in an extended area. This last finding reflects the weaker dependence of the electric field on the tip-sample distance compared to electronically induced processes: while the first one depends on V/d, the latter one exhibits an exponential behavior on the distance. On the other hand, it is well known that, while only the small tip apex contributes to the tunneling process, the end of the STM tip has a much larger

curvature with radii of typically several tens of nanometers.

An electric field induced isomerization was never experimentally observed so far, but it has been recently proposed by Peter Saalfrank and collaborators (University of Potsdam) that it is possible to induce the isomerization of azobenzene and of TBA in the gas phase by an electric field [166]. To estimate these effect, they considered in the calculations an homogeneous electric field. Neglecting any other field components, inhomogeneities, and high-order polarizabilities, they have calculated with DFT method the effective molecular potential as in Eq. 2.25.

In the presence of an electric field, the potential energy surface related to a reaction path can be deformed, thus leading to an effective lowering of the isomerization barrier. This effect, based on the (de-)stabilization of certain molecular configurations, depends on the presence and orientation of an intrinsic dipole moment, but also on the polarizability of the molecule, as already explained in Section 2.5.3.

In Fig. 6.19 the calculations of the energy shifts for the two isomer of TBA, as well as the energy barrier changes are shown. Taking into account that in the STM experiments the *trans*- isomer lies flat on the surface, in the calculations the N=N axis and the phenyl rings of the *trans*- isomer are assumed to be perpendicular to the electric field. Two different models are considered for the *cis*- isomer. In the model A the intrinsic and induced dipole moments of the *cis*- isomer are considered aligned to the electric field (i.e. in the STM experiment, they are perpendicular to the surface). In the model B the intrinsic dipole moment is considered perpendicular to the electric field, while the induced dipole moment has a component parallel to the electric field. Intrinsic dipole moments are characteristic in intensity and orientation of the two isomers, as well as the polarizabilities. In the calculations of Peter Saalfrank [166] the intrinsic dipole moment parallel to the field is μ_t=0 for the *trans*- isomer, μ_c=3.6 Db for the *cis*- isomer (model A) and μ_c=0 Db for model B. The calculated values of the polarizabilities in the direction of the electric filed of the two isomers (zz- element of the diagonalyzed polarizability tensor) are (in atomic unit) 231.4 a.u. for the *trans*- form, 352.5 a.u. for the *cis*- isomer in model A and 300.1 a.u. in model B. One can note that for model A there is an asymmetry in the absolute voltages needed to switch the molecule by changing the sign of the electric field. This means that the orientation of the molecular intrinsic dipole moment with respect to the

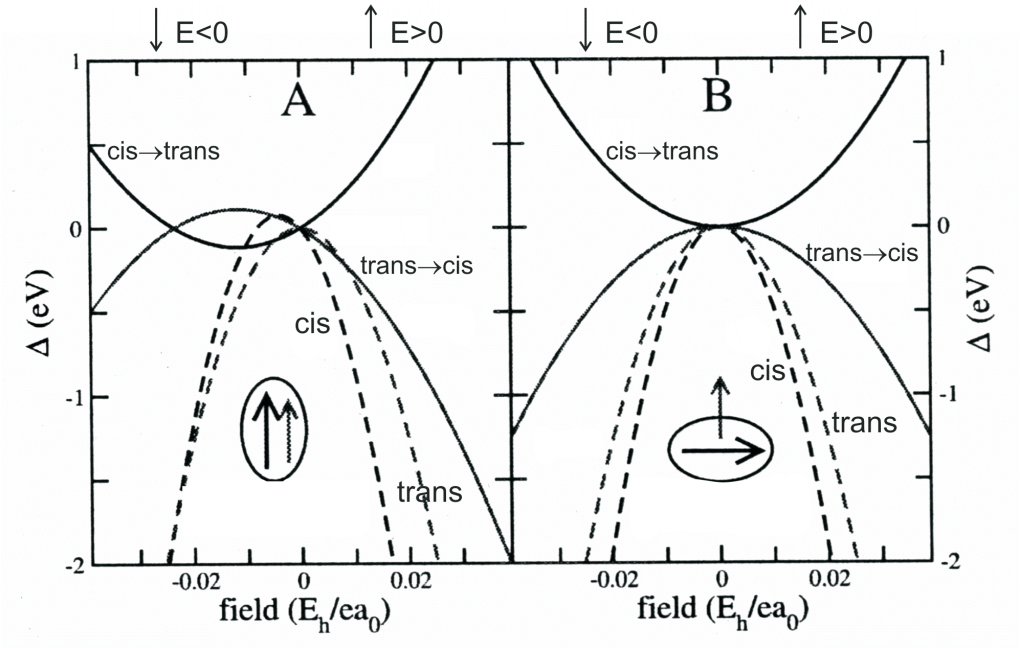

Figure 6.19: Image modified from Ref. [166]: Calculations of the energy barrier change (solid lines) and the energy shifts (dashed lines) for the *cis*- and *trans*- isomers. In the calculation two different model are considered. In model A, the permanent molecular dipole (thick arrow) and the induced dipole moment (thinner arrow) are aligned with the electric field. In model B, the intrinsic dipole moment is perpendicular to the electric field. The energies are given in eV, while the strength of the electric fields in atomic units. Note that 0.01 E_h/ea_0 corresponds to 0.5 V/Å.

electric field leads to variation of the field needed for the isomerization by changing the sign of the electric field. In contrast, for the model B the system is symmetric.

By performing a linear regression of the data in figures 6.17 and 6.18 in the large tip height regime, it has been found that the threshold voltage varies with the distance, for the *trans*⟶*cis* isomerization, as 0.1 V/Å (V>0) and 0.7 V/Å (V<0), while for the *cis*⟶*trans* as 0.3 V/Å (V>0) and 0.2 V/Å (V<0). Small tip heights are not included in the analysis because in this region there is a change in slope, which could be related to electronic effects that come into play at small tip heights (i.e. large currents), as will be discussed in the next section. By approximating the slopes of the curves, V_{th} vs. tip height, with the values of the electric field for switching TBA molecules, one finds that these value are smaller than that calculated in the gas phase for model A (more similar to experiments), which is about 1.5 V/Å.

The difference between the calculated and the experimentally determined threshold

electric field is probably due to the assumption of the theory that the molecule is in the gas phase. This simplifies the calculations, but on the other hand does not account for the influence of the metallic surface on the intrinsic and induced dipole moments of the molecule. As a result, the potential energy of the two isomers or an intermediate molecular configuration change and the reaction path can be modified. Additionally, the exact variation of these parameters along the reaction path was not included in the model. The different slopes for positive and negative voltages in the case of *trans*⟶*cis* isomerization as compared to the *cis*⟶*trans* process (Fig. 6.17 and 6.18) are not explained by the calculations, where it results that either a difference for positive and negative sample bias is observed for both processes (model A) or not (model B). The different slopes are probably due to the delicate balance between the intrinsic dipole moment of the molecule and its polarizability for the different adsorption geometries and reaction paths on the surface. In particular, it turns out that for the *cis*⟶*trans* isomerization the polarization is mostly influencing the process (quadratic term), while in the *trans*⟶*cis* case the intrinsic dipole moment is important. As a result, the sign of the electric field does not play a role in the first case (similar slopes), but becomes important in the latter one (the two slopes differ).

Notice that from the STM studies presented here it is not possible to determine whether the isomerization happens via rotation or inversion mechanism [143, 144].

6.7.4 cis→trans isomerization for small tip heights

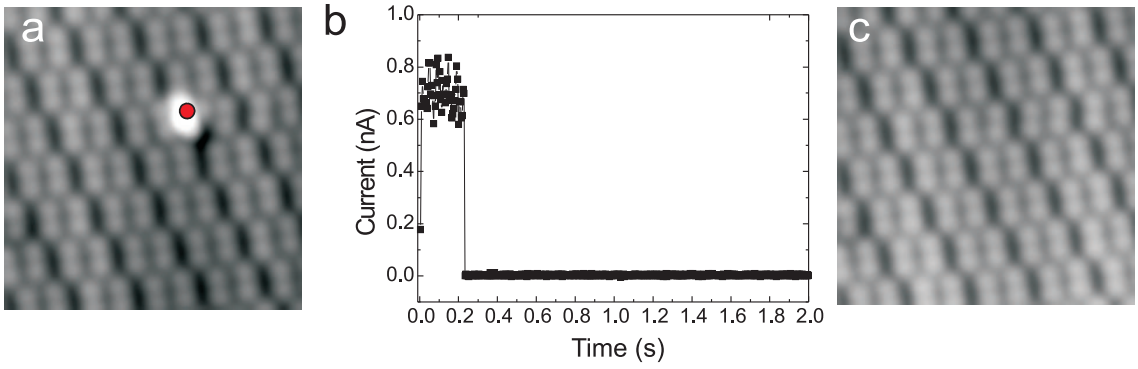

Figure 6.20: Manipulation experiment for *cis*⟶*trans* isomerization (T =5 K). A voltage pulse 2 s long with U_m = +1.6 V and the tip at about 6 Å above the surface has been applied. (a) STM image before the manipulation. The circle indicates the position of the tip during the pulse. (b) Manipulation signal. The tunneling current has a sharp drop at the time at about 0.2 s when the molecule switches from the *cis*- to *trans*- form. (c) STM image after the manipulation.

At small tip heights, where tunneling of electrons could play a role, the *cis*⟶*trans* switching has been analyzed in detail by studying the manipulation signal. It was not possible to study the *trans*⟶*cis* process in the same way, because as already mentioned the molecule below the tip is not likely to switch.

As explained in Chapter 2.5.2, the manipulation signal contains important information on the manipulation mechanism. During the application of the voltage pulses the tunneling current has been recorded as a function of time. In this way, one directly detects the time at which switching happens. An example of such a measurement is shown in Fig. 6.20. The images before and after the manipulation are shown in (a) and (c), while the manipulation curve is reported in (b).

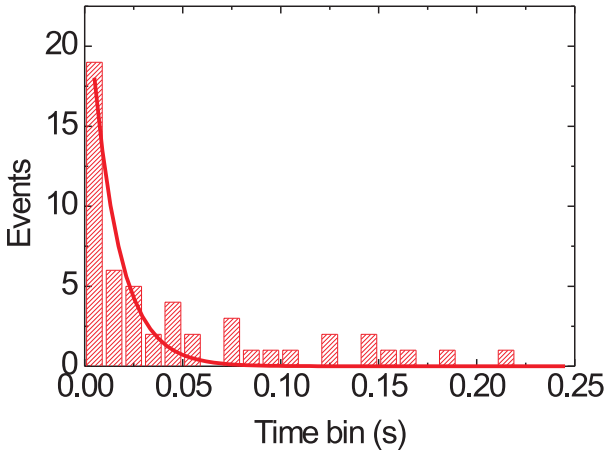

Figure 6.21: Distribution of the time needed to switch the molecule from *trans*- to *cis*- when voltage pulses with U_m = +1.6 V and tip height = 5 Å are applied. The current was I = 1 nA. The exponential fit in shown (R_{switch} = (72±10) s^{-1}).

By repeating such a measurement on many individual molecules, for a fixed tip height and a fixed sample voltage, one determines the distribution of the time the molecules stay in the *cis*- state before the switching. In Fig. 6.21 an example is shown. In this case, the distribution is obtained considering the number of molecules which have switched in a time interval dt, where dt = 10 ms by applying U_m = +1.6 V with the tip at 5 Å above the surface. The distribution of switching times follows an exponential law, as shown in Fig. 6.21. A fit of the curve gives the average value of the switching rate R_{switch} for the chosen tip height and voltage.

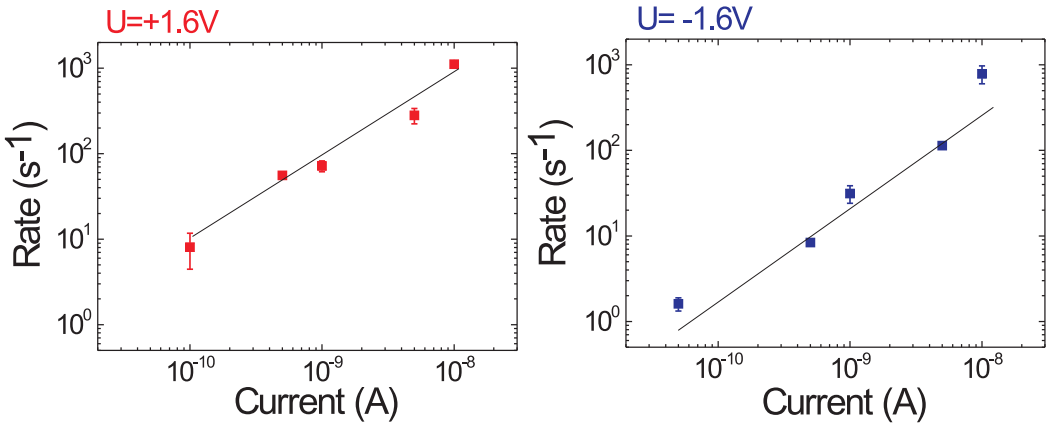

Figure 6.22: Switching rate as a function of current for $U_m = \pm 1.6$ V. The solid lines are fits to the data and correspond to power laws, $R_{switch} \sim I^N$ with $N = 1.0 \pm 0.2$ for U = +1.6 V and $N = 1.1 \pm 0.3$ for $U = -1.6$ V

The dependence of the switching rate on the tunneling current has been obtained by repeating the described measurements for different tip heights.

The results for $U = \pm 1.6$ V are shown in Fig. 6.22.

It has been already demonstrated [22] that for an electronic induced process the switching rate follows a power law of the type $R_{switch} \sim I^N$ where N is the number of electrons needed for this process. Notice that this is not expected for a process induced by the electric field. By performing a linear regression of the data in Fig. 6.22 ($\log R_{switch} = A + N \log I$, where A is a constant value) it came out that $N(+1.6\text{ V}) = 1.0 \pm 0.2$ and $N(-1.6\text{ V}) = 1.1 \pm 0.3$. These values are in agreement with a one electron process.

The mechanisms, which could cause the isomerization of azobenzene molecules by means of tunneling of electrons from the tip of an STM, include two diverse scenarios:

(*i*) Excitation of vibrational modes with tunneling electrons. As shown by a schematic in Fig. 6.23, the potential barrier is overcame by ladder climbing of vibrational states excited by electrons which tunnel inelastically into the molecule. This mechanism has been suggested to drive the isomerization of Disperse Orange 3 molecules on Au(111) [158, 159].

(*ii*) On the other hand, the switching could be caused through the formation of a negative (positive) ion resonance state by transferring of a tunneling electron (or hole) into an unoccupied (occupied) electronic state of the molecule, as proposed in the case of

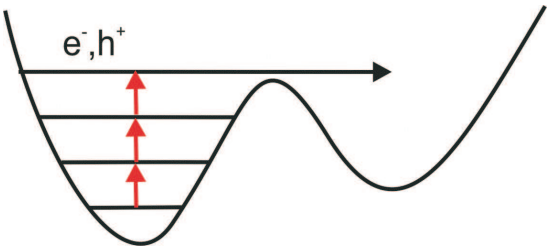

Figure 6.23: Schematic of the isomerization mechanism through vibrational excitations. Inelastic tunneling of electrons or holes excites vibrational modes and the potential barrier between *trans*- and *cis*-stable conformations is overcame by ladder climbing.

bare azobenzene on Au(111) [157] and described theoretically [167]. This mechanism is schematized in Fig. 6.24.

Interestingly, it has been recently shown by quantum chemical calculations that the formation of a molecular anionic state (transient state) by tunneling of electrons into a molecular orbital of azobenzene, strongly lowers the barrier for the isomerization compared to the ground state [166] and in particular the overcoming of the barrier becomes spontaneous for the *cis*⟶*trans* isomerization.

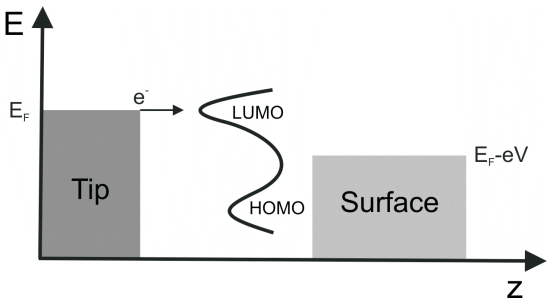

Figure 6.24: Schematic of the electronic-excitation mechanism via tunneling into electronic molecular orbitals. The transfer of a tunneling electron to molecular orbitals (LUMO in the scheme) creating a charged molecular state, induces the isomerization process.

Since the energy needed for the switching, in the case of *cis*⟶*trans* isomerization of TBA at small tip height (about 1.3 eV for positive voltages and about 1.5 eV for negative voltages), is likely too high to be related to the excitation of a vibrational mode, electrons (holes) are probably tunneling in molecular states, forming a charged state which allows the isomerization process. To better understand this mechanism at low tip height, we have performed scanning tunneling spectroscopy (STS) measurements for both isomers.

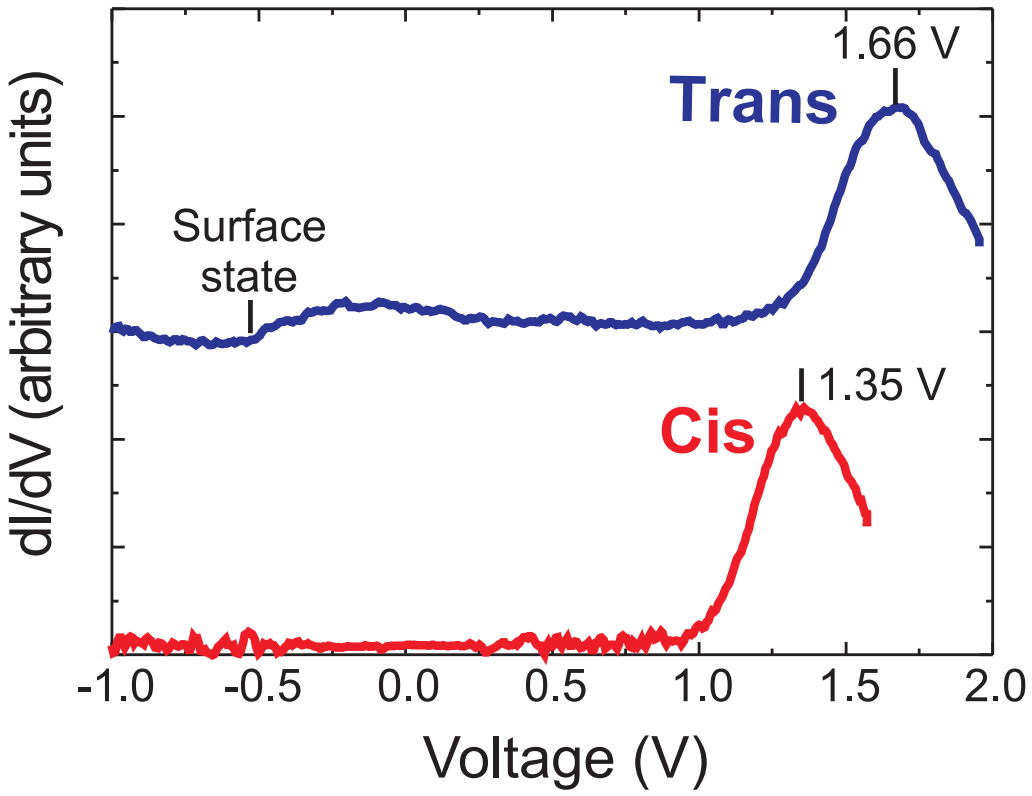

Figure 6.25: dI/dV spectra of the molecule in the *trans*- and the *cis* - configurations (recorded at the molecular center) for positive sample voltage. The dI/dV curves have been recorded using a lock-in amplifier with frequency 640 Hz and a voltage modulation of 20 mV. The peaks observed at 1.67 V and 1.35 V are attributed to the LUMO of the molecules. A shift of the LUMO peak is observed between the two isomers.

6.7.5 Scanning tunneling spectroscopy

dI/dV spectra have been recorded by positioning the tip above the center of the *trans*- and *cis*- isomers respectively. As it has been explained in Section 2.3, the dI/dV signal is proportional to the LDOS of the sample at the position of the tip at a given energy in the approximation that the tip has a constant density of states. The quality of the tip for spectroscopy studies has been analyzed by recording STS spectra on the bare Au(111). In this way one can exclude a strong influence of the tip electronic structure on the measurements using tips with featureless electronic structures in the considered energy range. On the other hand, the sensibility of the measurements is checked using the feature arising from the surface state of Au(111), as it has been already shown in Section 3.9.

The observed dI/dV spectra for sample voltages between -1 V and +2 V for *trans*-

and *cis*- isomers are shown in Fig. 6.25.

For positive energy values (corresponding to tunneling into molecular unoccupied states), an intense feature is visible for both *cis*- and *trans*- isomers. Such peaks can be assigned to the LUMO of the molecules, because no peaks are present at lower (positive) voltages. Their positions are (1.67$\pm$0.1) V for the *trans*- and (1.35$\pm$0.1) V for the *cis*- configuration.

One should note that in general the energy of molecular orbitals is known to be influenced by several factors, like the adsorption geometry of the molecule, the presence of lateral groups, and the superposition of the orbitals with the metallic surface. We found that there is a shift in energy of the LUMO for the two isomers of about 0.3 eV which is a fingerprint of the two isomers. Upon a further isomerization back to the *trans*- form, the initial spectrum can be precisely restored. As an isomerization process modifies the electronic structure of the molecule, a change in the local density of states is expected.

Notice that the characteristic feature of the Au(111) surface state is visible in the *trans*- isomer spectra, but not in the *cis*- one. This is probably due to the fact that when the tip is positioned above a *cis*- isomer (which is three dimensional), its distance from the surface is larger than in the case of the *trans*- isomer and thus the intensity of the current signal for the surface state is lower.

In the range of negative voltages, we did not observe clear peaks and only by comparing the spectra on the bare surface and on the molecules we found an indication of a molecular orbital, which corresponds to the HOMO of the two isomers. In the upper spectra of Fig. 6.26, the dI/dV signals for a *trans*- isomer and for the bare gold substrate are shown. As one can see, in the range between about -0.2 V and -1.7 V, the spectra are very similar, as they show the same features at the same energy positions. In both spectra the characteristic feature of the surface state of Au(111) is visible. However, at about -1.8 V for the *trans*- isomer an enhancement of the dI/dV signal on the molecules with respect to the signal on the bare gold substrate is observed. Such effect is probably related to the existence at these energies of molecular electronic states. A similar situation is observed in the bottom spectra of Fig. 6.26: at about -1.4 V the signal for the *cis*- isomer becomes much more intense in comparison with that of the substrate.

The spectroscopic results are in agreement with the interpretation of the *cis*$\longrightarrow$*trans*

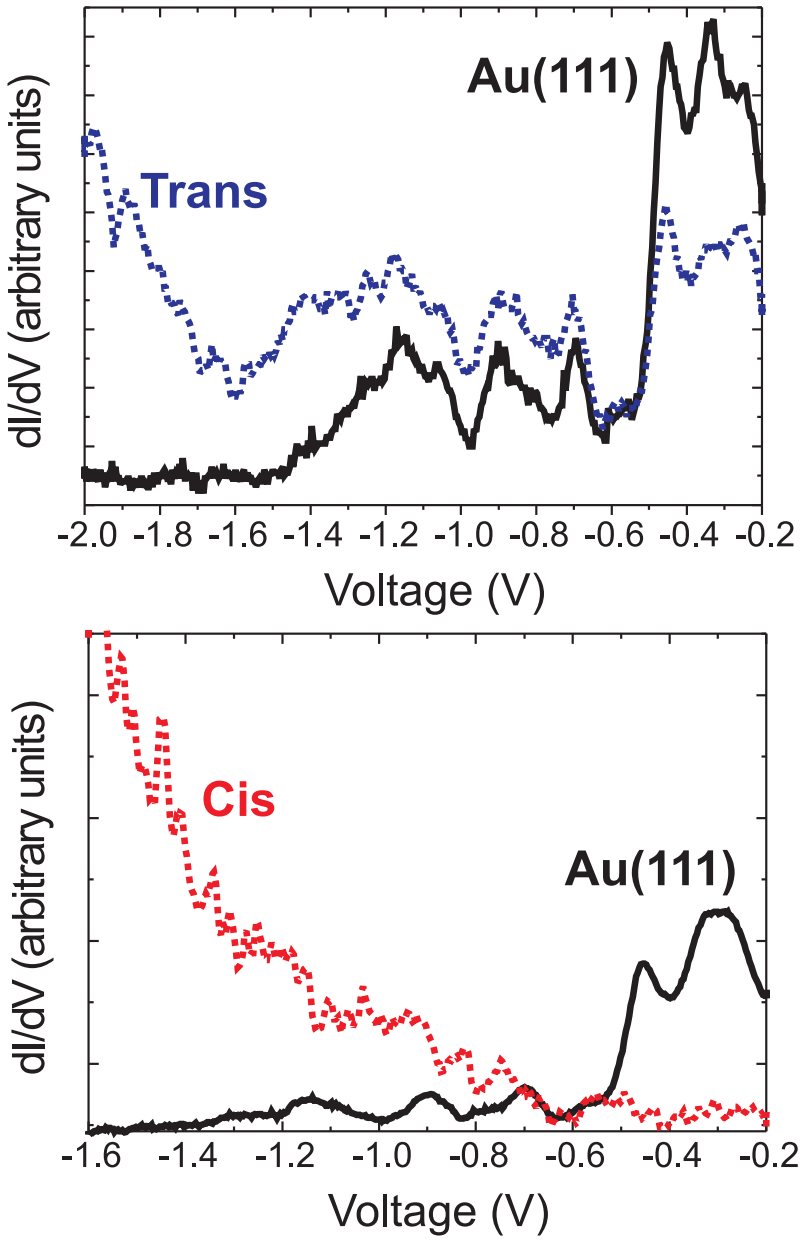

Figure 6.26: dI/dV spectra of the molecule in the *trans*- and the *cis*- configurations for negative sample voltages (dashed line) and as a reference the spectra on the gold substrate (solid lines). The dI/dV curves have been recorded using a lock-in amplifier with frequency 620 Hz and a voltage modulation of 16 mV.

isomerization at small tip heights by means of tunneling of one electron (hole) into molecular states forming a negative (positive) charged resonance state. In fact, at the voltage needed for the isomerization (about +1.3 V for positive voltages and about -1.5 V for negative voltages) the existence of a molecular electronic states is measured (at about +1.3 V for positive voltages and about -1.4 V for negative voltages).

Recently, the electronic states of TBA adsorbed on Ag(111) have been studied by one-photon and two-photon photoemission spectroscopy by P. Tegeder *et al*. [168]. While the value of the HOMO level of TBA adsorbed on Ag(111) corresponds to the value measured in the present study, the authors found that the LUMO energy is 0.66 meV lower than on Au, finding it on Ag(111) at 1 eV above the Fermi energy. This finding has been explained by considering the difference in work functions between Au and Ag. Assuming that the electron affinity of TBA is not strongly modified by adsorption on Au or Ag, one would expect the LUMO state for TBA to lie closer to the Fermi level for Ag than for Au by a value comparable to the Au-Ag-work function difference (which is indeed 990 mV).

Notice that the lower sensibility of the spectra at negative sample voltages arises from the fact that the dominant contribution to the tunneling current comes from the unoccupied states near the Fermi energy of the negatively biased electrode. In fact, the further an occupied state is below the Fermi energy, the larger is the effective barrier for that state. In particular one can show that each eV a state lies further below the Fermi energy, corresponds approximately to one order of magnitude in the tunneling probability [169]. As a consequence the investigation of occupied sample states is more delicate and sensitive to the electronic structure of the tip's empty states.

As a further comment, notice that for the *trans*-isomer is very critical to obtain dI/dV spectra, because during the recording of the spectra the molecules can switch. To overcome this problem the spectra were recorded when the tip is retracted from the surface with respect to normal scanning conditions, thus lowering the signal intensity.

6.8 Conclusion

In this chapter, the investigation of the *trans-cis* isomerization of TBA molecules on Au(111) has been described. TBA molecules were specially synthesized for studying the isomerization of azobenzene on a surface.

First, the study of the molecular adsorption was characterized yielding the exact molecular conformation upon adsorption: After deposition on Au(111), all the molecules are in the *trans*- form, which corresponds to a planar adsorption geometry. Molecules are either isolated at the elbow of the herringbone reconstruction of Au(111), or adsorb in large highly ordered islands.

By applying voltage pulses with the STM tip the *trans-cis* isomerization of TBA has

been induced in a reversible way. The configuration of the *cis*- isomer on Au(111) has been determined: As in the gas phase it corresponds to a three-dimensional conformation.

It turned out that the stabilization of the molecules in islands facilitates the isomerization process allowing to exactly reproduce the switching process several hundred times. Due to this high reproducibility it was possible to study the switching mechanism in detail. By tuning the STM parameters during a manipulation, different driving mechanisms to induce a process were successfully selected. The threshold voltage for inducing the isomerization has been determined and its dependence on the tip height has been measured. We found that the threshold voltage is not a constant value, but increases (linearly) when retracting the tip. Furthermore, the isomerization process is operable also at the zero current limit. These results demonstrate 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. This finding is of high interest for the present research of molecular switches in general, since the realization of the switching of azobenzene molecules by electric field was never observed experimentally so far, neither in solution nor on a surface. A theoretical model by Peter Saalfrank and collaborators, which explains the isomerization of TBA molecule in the gas phase by electric fields, has been discussed.

Additionally, for small tip heights when the tunneling of electrons plays a role, the *cis*$\longrightarrow$*trans* isomerization was investigated by studying the signal during the manipulation. The dependence of the switching rate on the tunneling current is characterized. It shows the characteristic behavior of a one electron process. Spectroscopy measurements allowed to determine the energies of the molecular orbitals (HOMO and LUMO) and thus to conclude that tunneling of an electron (hole) into molecular orbitals drives the *cis*$\longrightarrow$*trans* switching mechanism at small tip heights.