

Chapter 3

Cyclopentadienyl Molecules on Ag (111)

Introduction

The room temperature STM built up in this work with its optimized stability was constructed with the aim to perform atomic and molecular manipulation. Manipulation of atoms, small molecules and big molecules has been achieved with the scanning tunneling microscope at low temperature, for a review see e.g. [1]. However, more interesting and promising for future directions is the manipulation of atoms and molecules at room temperature. Here only a few examples have been published. For molecular manipulation at room temperature several conditions need to be fulfilled: Low thermal mobility of the molecule, strong intramolecular bonding and a delicate bonding of the molecule to the surface. One molecule which satisfies these conditions is the cyclopentadienyl C_5H_5 (cp) radical. Tip induced diffusion has been demonstrated on Ag(100) [5]. The Ag(111) surface is more interesting since the surface state electrons are expected to open up exciting possibilities for artificial atomic/molecular structures [7]. The fivefold symmetry of the C_5H_5 radical gives rise to a pronounced

anisotropy as observed in the STM images. Furthermore this anisotropy leads to a preferred direction of the molecule-molecule interaction resulting in molecular lines as imaged in this work for the first time. The underlying mechanism will be discussed. Attempts for the manipulation of C_5H_5 radical will be shown.

The cyclopentadienyl radical can be found in so called metallocenes. In chemistry, and in particular, in organometallic chemistry, a metallocene is a compound consisting of an aromatic organic ligand bound to a metal. A key feature of metallocenes are planar aromatic organic ligands in which the carbon atoms in the ring form equivalent metal-carbon bonds. The prototypical metallocene is ferrocene, consisting of two cyclopentadienyl rings bound on opposite sides of a central iron atom (*Fig.1*), forming an *organometallic sandwich compound*. In the case of ferrocene, for instance, the length and strength and bond angles of the metal-carbon bonds are identical. The nature of the bonding of the organic ligand to the metal is referred to as its "hapticity" and is indicated by the Greek letter η . The equivalent bonding of all 5 carbon atoms of each cyclopentadienyl ring in ferrocene is denoted as η -5. The systematic name of ferrocene is, therefore, bis(η -5-cyclopentadienyl)iron. The discovery of ferrocene in 1951 and its structural elucidation by two separate research groups in the following year marked the birth of contemporary organometallic chemistry. This revolutionary advance in organometallic chemistry was recognized with a Nobel Prize in Chemistry in 1973 (Prof. Ernst Otto Fischer (TU München) and Prof. Geoffrey Wilkinson (Imperial College London) for their pioneering work on the chemistry of the organometallic, so called sandwich compounds).

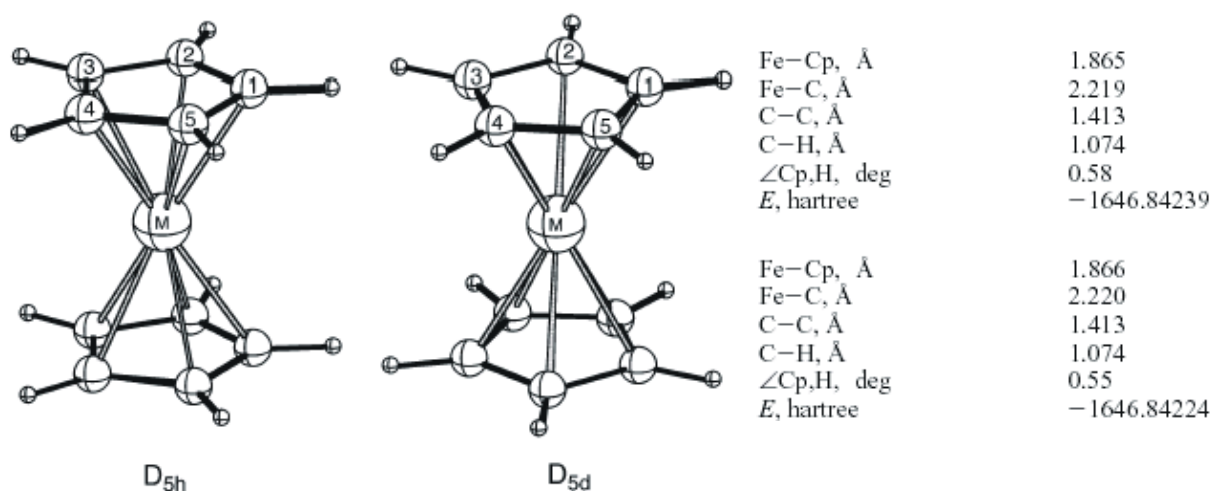


Fig.1

A Ferrocene molecule consists of two cyclopentadienyl rings bound on opposite sides of a central iron atom (sandwich structure) which can form the eclipsed and staggered configuration. The results from HF calculations are taken from [2].

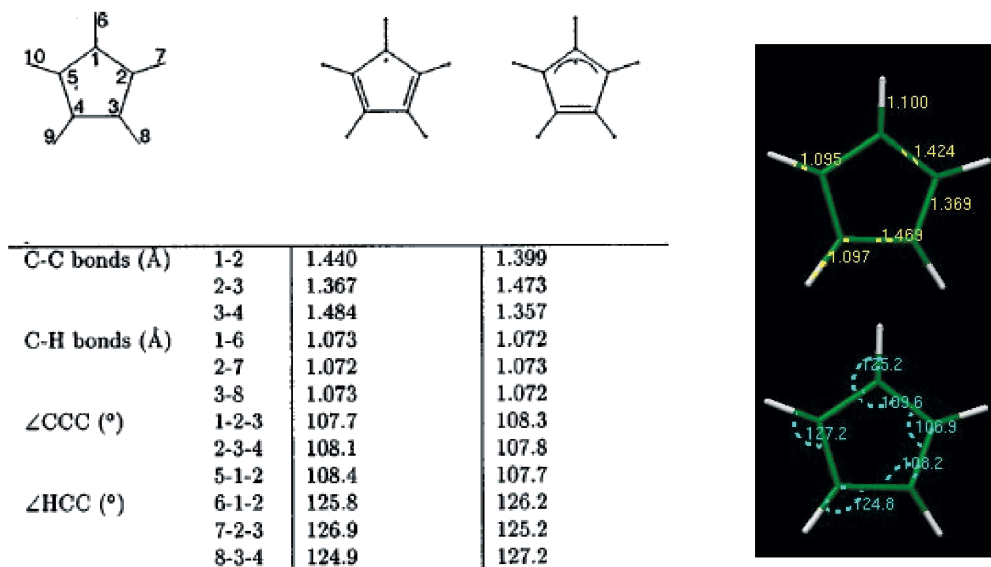


Fig.2

Left: The free cp radical does not have a C_5 symmetry and exists in two possible configurations in its ground state [3]. Right: Relaxed LDA calculation of the right state[4].

For the free C_5H_5 radical there are two electronic configurations which give rise to the A2 and B1 state under the C_{2V} point group, which have the same ground state energy. The free C_5H_5 radicals in Ferrocene are strongly bonded (ferrocene is stable up to 400 degrees C) and have a C_5 symmetry along the molecules axis. C_5H_5 radicals cannot be brought directly on the surface, but only as part of ferrocene [5], as after fragmentation only the C_5H_5 radical is left on the surface. The molecular ferrocene adsorbed on Ag(100) is very weakly bonded, desorbing at about 250 K. It can be fragmented with synchrotron light, whereas the fragments are far more strongly chemisorbed [6].

Appearance and adsorption site

Ferrocene molecules were deposited on the Ag (111) surface at liquid nitrogen temperatures through a standard leak valve. Due to their high vapour pressure they cannot be kept in the UHV of the preparation chamber. Instead they are kept in an evacuated line and are dosed from there into the UHV system. Normal deposition was done by exposure for 10 min at $1 \cdot 10^{-6}$ mbar. After the deposition the sample was warmed up to room temperature. Upon warming most of the ferrocene molecules desorb as intact molecules, only few of them fragmentize. The C_5H_5 radicals are then left on the Ag (111) surface. The appearance of the C_5H_5 radicals on the surface is rather tip dependent, a number of typical images are shown *in Fig.3, Fig. 4, and Fig.5.*

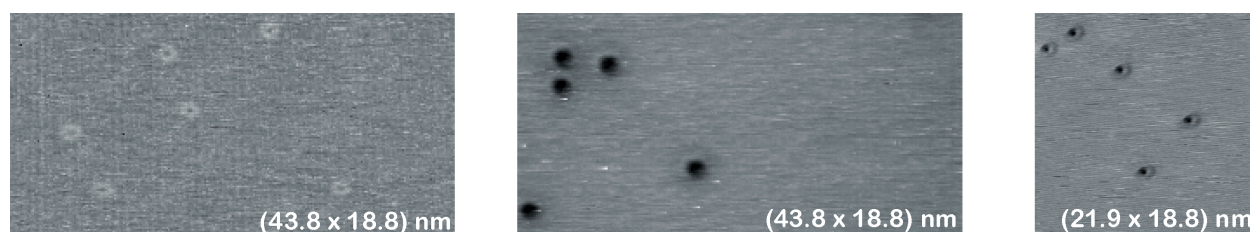


Fig.3a

(21.9 x 18.8) nm and (43.8 x 18.8) nm images show the different appearance of the C_5H_5 radicals on Ag(111) substrate. The appearance is strongly dependent on the state of the PtIr tip which was used in this experiment.

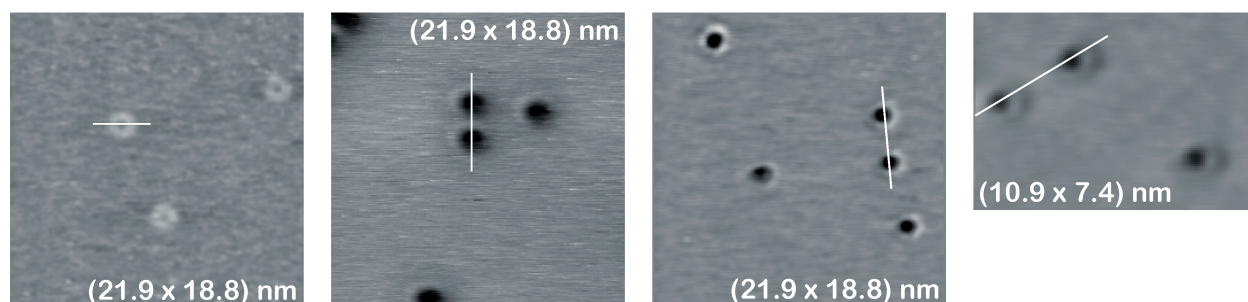


Fig.3b

C_5H_5 radicals can appear as circles or as half-rings of 0.4 - 1.1 nm size, while the real size of the radical is 0.4 nm [3] (the reason of the increase in size of the radical is strong electronic screening).

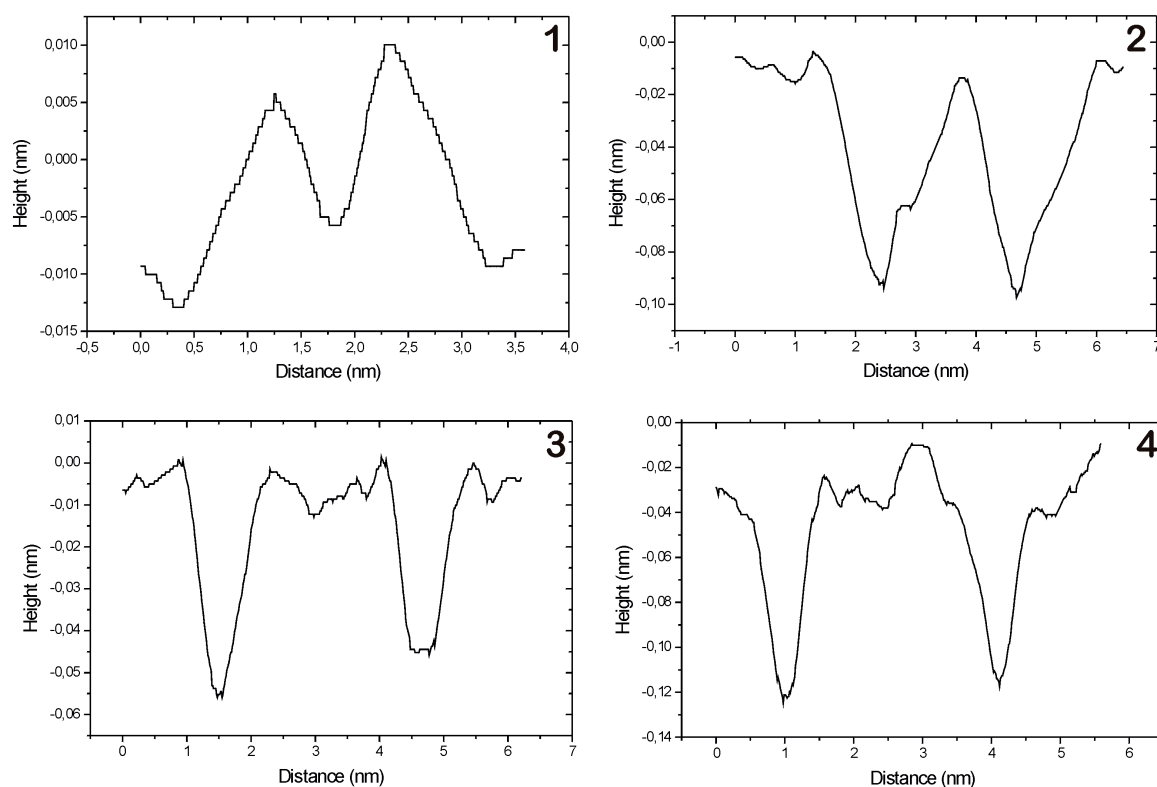


Fig.3c

Linescans corresponding to the topography images of Fig.3b.

So there are actually two major types of the tip state: The state where the C_5H_5 radical is imaged as a white ring and a state where the C_5H_5 radical is measured as a protrusion. In *Fig.4* one can see the two images of C_5H_5 radicals taken one after another with a tip change between the images. So the same C_5H_5 radicals are first imaged as white rings and then as protrusions.

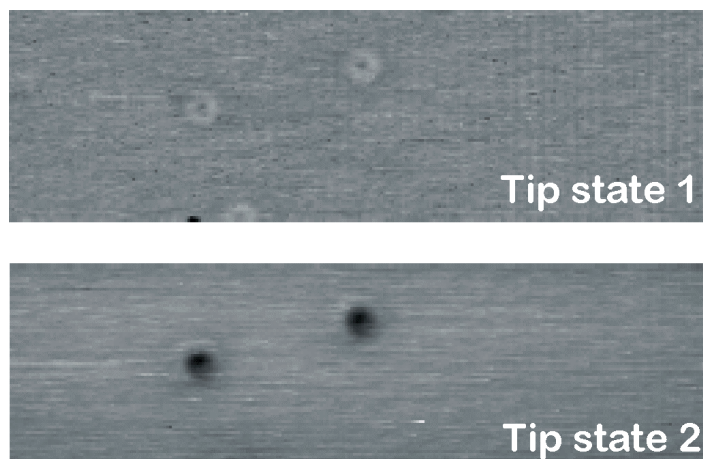
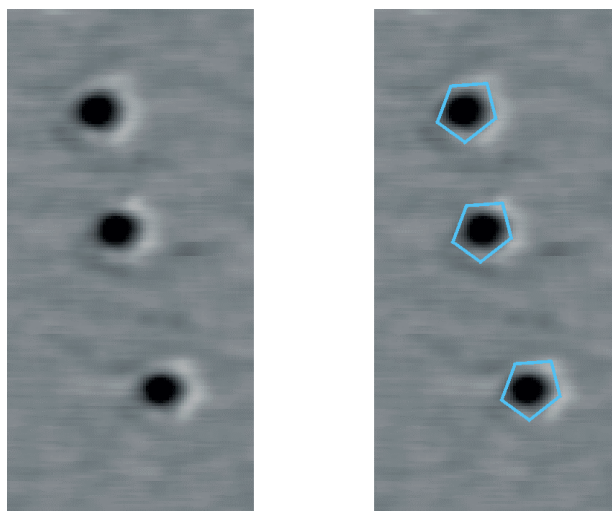


Fig.4

Two types of the possible tip states. With the tip in state 1 it is possible to observe the C_5H_5 radicals as white rings. With a tip in state 2 C_5H_5 radicals are observed as depressions. The diameter of a protrusion completely covers the white ring.

In most of the cases the C_5H_5 radical is observed as a ring with an anisotropy. The detailed image in *Fig.5* clearly reveals a fivefold structure with a twofold mirror symmetry along its long axis.

*Fig.5*

A fivefold structure of C_5H_5 radicals.

More information one can obtain from the STM images where C_5H_5 radicals and the atomically resolved Ag (111) surface are visible together. This is possible to achieve only with a special kind of a tip. With such a tip the C_5H_5 radicals are imaged as depressions.

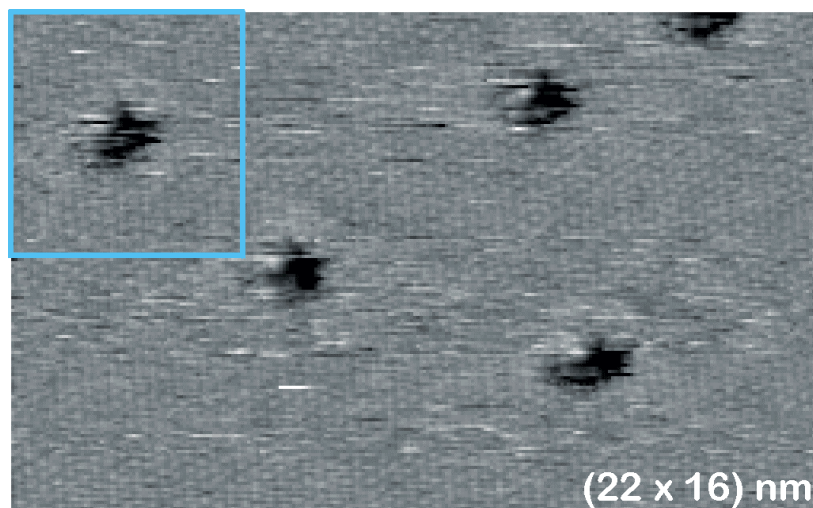


Fig.6

Ag(111) atomically resolved terrace together with C_5H_5 radicals.

From *Fig.6* one can clearly see that C_5H_5 radicals have a certain orientation on the Ag (111) surface. With the help of atomically resolved Ag(111) images (see also Room Temperature STM instrumental Chapter) it is possible to determine the orientation of the C_5H_5 radical on the Ag (111) surface. For this we will consider the area marked with a blue square in *Fig.6*.

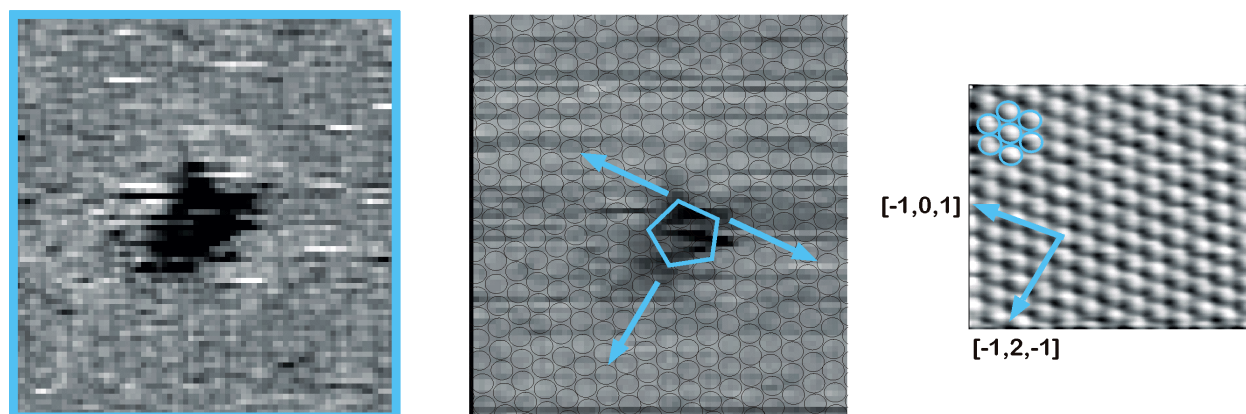


Fig.7

Left: C_5H_5 radical on Ag (111) surface.

Middle: Same image with Ag (111) lattice marked with black circles. The C_5H_5 pentagon is marked and the directions of the `basis` of the pentagon and the direction `top` of the pentagon are shown.

Right: Atomically resolved Ag (111) image with the crystallographic directions.

From the analysis of *Fig.7* one can clearly see that all the C_5H_5 radicals point in the $\left[\bar{1}2\bar{1} \right]$ direction and are aligned parallel to the $\left[\bar{1}01 \right]$ direction. It is not possible to mark intuitively the C_5H_5 radical with a pentagon of the correct size because the size in which the C_5H_5 radical is imaged depends drastically on the state of the tip. One can obtain more information from the C_5H_5 radical appearance in the STM image calculations which are shown below.

The measured diameter of the C_5H_5 radical amounts to 0.4 - 1nm. This value is larger than the diameter of a circle around the hydrogen atoms of the C_5H_5 radicals in the ferrocene (*Fig.1*) which is itself larger than the diameter for the free C_5H_5 ring (*Fig.1*). In [5] the discrepancy was explained by the screening of the molecule by surface electrons; the authors suggested that it is this screening pattern which is actually imaged. In STM structural and electronic effects both contribute to the image, hence calculations within LDA are useful [4,8]. Calculations of a C_5H_5 radical on a three layer 3x3-Ag(111) slab were performed and the results after relaxation are shown in *Fig.8*.

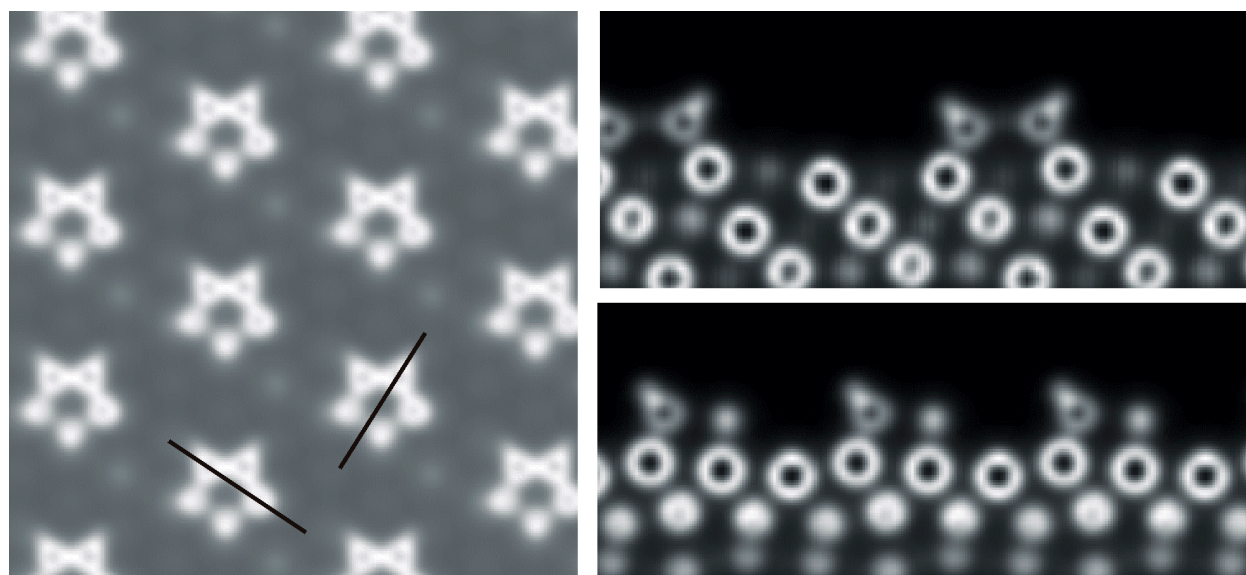


Fig.8

LDA calculations, planes of the total charge density. Left: Surface plane showing C_5H_5 radicals adsorbed on a three layer 3x3-Ag (111) slab. Right: The two planes perpendicular to the surface as indicated in the left image.

The calculations demonstrate that as the most pronounced effect, the hydrogen atoms shift away from the surface, therefore the molecule is not planar anymore. Ab initio calculations for C_6H_6 on a Pd (110) show that the C-H bonds bend away from the surface [9]. Additionally the twofold symmetry as observed in the experiment is reproduced. The cuts perpendicular to the surface do not show a screening which could explain the observed appearance of the molecule. Therefore the measurement process itself is responsible for the appearance. It can be caused by an anisotropy of the conductance which is therefore much larger at the outside of the C_5H_5 ring. The surface state is not fully developed in the three layer Ag(111) slab, but it is not at all present on the Ag(100) surface where the C_5H_5 ring amounts to the same diameter. Furthermore the center of the molecule is shifted away from the ontop position in agreement with the atomically resolved image in *Fig.7*.

Molecule orientation and line formation

Remarkably in one surface area only one orientation of the C_5H_5 radical is observed although six orientations are expected on the six-fold Ag(111) surface. Two orientations have been found, but never together in one surface area. As the C_5H_5 radical is immobile at room temperature, this adsorption site is therefore determined from the low temperature site of the ferrocene. This site preference may be caused by an ordered layer of ferrocene molecules. Due to the lattice mismatch the ferrocene is adsorbed only on selected adsorption sites where it becomes fragmented. The rotational domains then cause the C_5H_5 radical orientation in other areas.

Additionally the C_5H_5 radicals form almost straight atomic lines parallel to the step edges which run in the close packed direction. The lines are usually observed close to the step, sometimes even a second less dense line is found (*Fig.9*). Here the molecule-step interaction becomes important. It can be caused either by the standing wave pattern of the surface electrons or by an elastic interaction through the lattice. The latter one is usually short-ranged and unlikely to cause effects over the observed 8 nm distance between the lines of *Fig.10*. On the other hand the Fermi wave length of the surface state is 7.6 nm, therefore the line distance would create a resonance of the second harmonic.

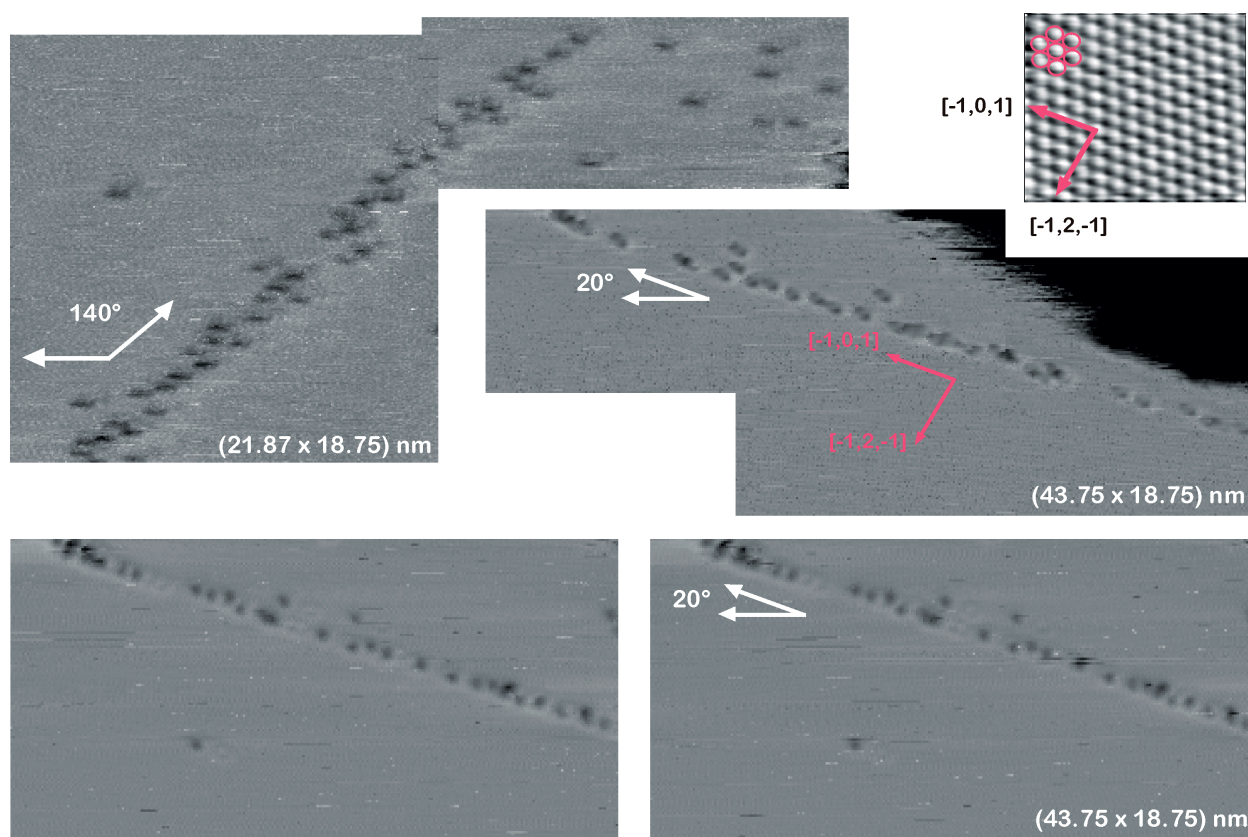


Fig.9

Atomic lines of the ferrocene radicals

Upper left: Two (21.87 x 18.75) images showing the lines of C_5H_5 radicals

Upper right: Two (43.75 x 18.75) images showing the lines of C_5H_5 radicals

The insert in the right upper corner indicates the surface orientations according to the atomically resolved STM picture.

Lower left and right: Forward and backward (43.75 x 18.75) nm images rather perfect straight lines of the C_5H_5 radicals. Both forward and backward images are presented to prove that the straightness of the line is not a tip effect.

The angle between the observed lines of C_5H_5 radicals is exactly 120° . The third possible direction was not observed due to a limited set of measurements. The radicals within a line are pointing parallel to each other (the direction of the C_5H_5 radical orientation is marked with red arrows in *Fig.9*). In *Fig.10* the analysis of the relative distances between the two lines of C_5H_5 radicals and a step edge is presented. The five corresponding linescans are shifted relative to each other to make it possible to observe the step edge at the same distance. The

first C_5H_5 radical row is observed at a relative distance of 4 nm from the step edge. The second row of C_5H_5 radicals is observed at a relative distance of 12 nm from the step edge, so it is 3 times further away from the step edge in comparison with the first C_5H_5 radical row.

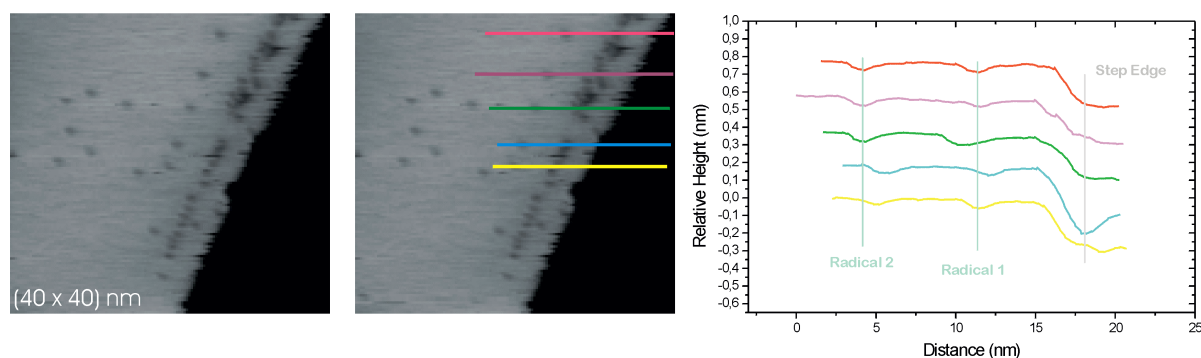


Fig.10

Left: (87.2 x 40) nm image showing two rows of C_5H_5 radicals running parallel to the step edge. Middle: Five linescans made along C_5H_5 radicals of both first and second rows and a step edge. Right: Graph contains five linescans shifted relatively to each other in a way that a step edge appears in the same position. The linescans are also artificially separated one from another in height to make all of them clearly visible.

On the terraces far from the step edges C_5H_5 radicals do not show any kind of ordering and are distributed randomly.

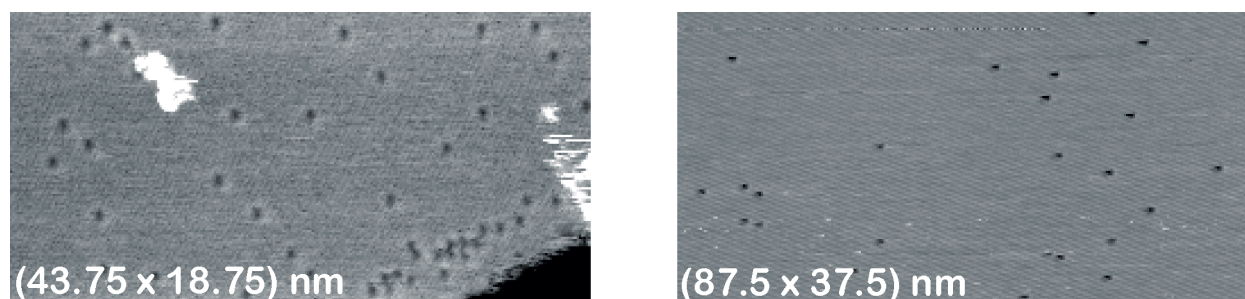


Fig.11

Random distribution of the C_5H_5 radicals on the terrace.

Manipulation of C_5H_5 radicals

One of the main goals of the STM studies of the C_5H_5 radicals at room temperatures was to investigate the possibilities of performing lateral and vertical molecular manipulation [7]. An example of building an artificial atomic structure consisting of 98 Ag atoms on a Ag (111) substrate performed with the low temperature STM at 5 K is shown in *Fig.12*. This manipulation was part of this work to get acquainted with manipulation techniques. The Ag atoms were deposited insitu at 5 K and the formation of the specially designed structure took 3 days.

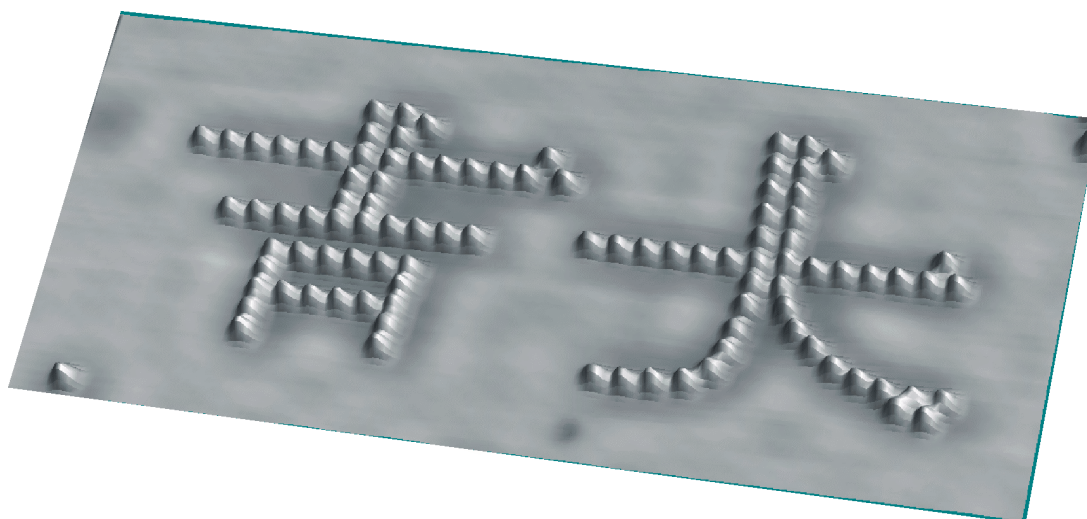


Fig.12

98 Ag atoms on Ag (111) substrate forming the two chinese letters: Ji Jing (the name of a University in China).

In comparison with the manipulation at liquid helium temperature, several difficulties arise at room temperature. These are the thermal drift and instability of the tip. The main problem with a thermal drift is that one actually cannot be completely sure where exactly is the molecule in the specific moment. But it is possible to estimate the speed of the thermal drift to make the manipulation task easier. In *Fig.13* two images of the same area taken one after another are presented. The distances between C_5H_5 radical and the border of the image were measured for both images and then the speed of the thermal drift was calculated.

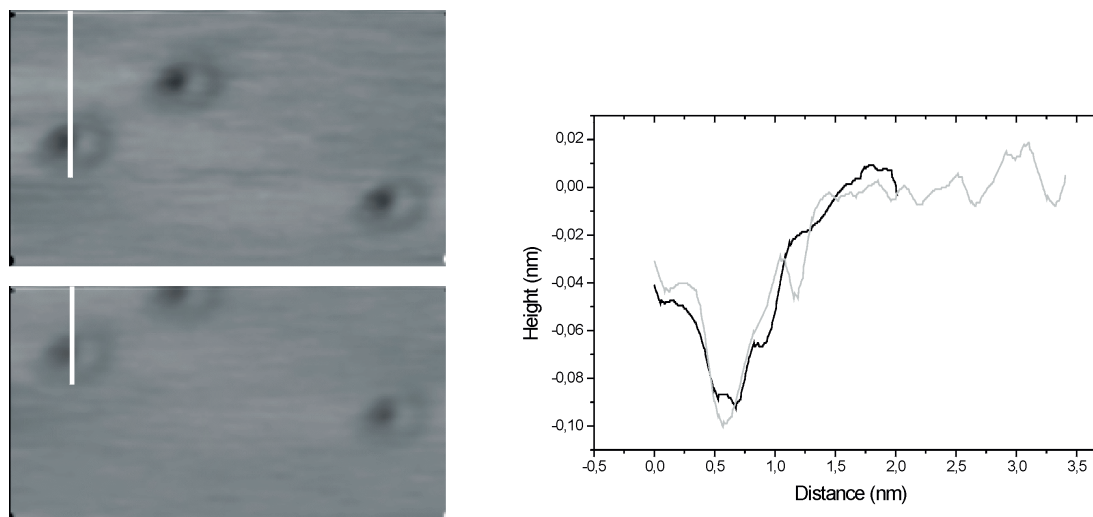
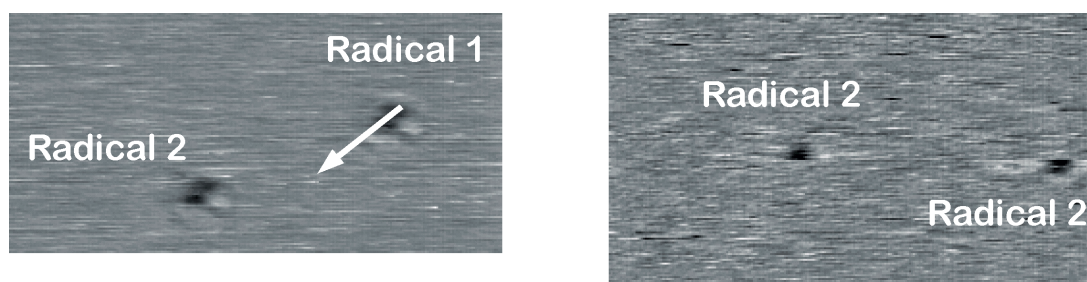


Fig.13

Two images showing the thermal drift at room temperature and the corresponding linescans which are measuring the distance between the C_5H_5 radical and the border of the image.

Thus, from the linescans of *Fig.13* it was calculated that the C_5H_5 radical drifted by 1.36 nm in 39 seconds or equivalent 0.035 nm per second. Such sort of a thermal drift correction is required prior to a controlled manipulation experiment on atomic scale. The thermal drift as was determined here is caused by the cold sample holder after sample preparation and is much lower in thermal equilibrium after a few hours of operation.

On the Ag(100) surface the C_5H_5 radical was moved by tip induced diffusion [5], while on Ag(111) it was found to be stable under all imaging conditions (± 1.5 V, 0.3-10 nA). In this work we were trying to perform controlled lateral manipulation [7] where the molecule could be pushed in front of or pulled after the tip. Again, the molecule showed to be more stable than the tip and did not move. Often the manipulation procedure provoked a tip crash and destroyed the whole area. Sometimes the molecule was picked up to the tip or desorbed in such an attempt. Two examples of the manipulation of C_5H_5 radicals are shown in *Fig.14*.



*Fig.14**Manipulation of C_5H_5 Radical 1 and Radical 2.*

The manipulation was performed with 0.12 nA and 1.3 V. In the left image one can see the C_5H_5 Radical 1 on the initial place and the desired tip path during manipulation (white line, already corrected for drift). In the right image one can see that the C_5H_5 Radical 1 disappeared. Therefore the C_5H_5 Radical 1 was picked up by the tip (manipulated vertically). Additionally in the right image Radical 2 was picked up by the tip during scanning and dragged to the right. To conclude from the manipulation experiment the C_5H_5 radical appears to be more strongly bound on Ag(111) than on Ag(100). Hence the controlled lateral manipulation of molecules at room temperatures and the building of artificial molecular structures still remains one of the open challenges of future room temperature STM experiments.

Conclusion

In view of extending the temperature range of controlled atomic and molecular manipulation to room temperature the system of cyclopentadienyl molecules adsorbed on a Ag(111) surface was investigated with a room temperature STM for the first time. The radicals are adsorbed at low temperature as part of ferrocene molecules which fragmentize below room temperature and leave the chemisorbed radicals on the surface. The radicals appear as ringlike protrusions or depressions dependent on the tip state. The ring has a larger diameter than the diameter of the free radical and shows a 2-fold symmetry. With the help of calculations the imaging mechanism was elucidated, showing that the highest conductance is located at the outer brim of the molecule. Atomically resolved images reveal a shift of the center away from the ontop position in accordance with the calculations. Imaging under a wide range of conditions and manipulation experiments show that the radical is usually more strongly bound to the surface than the tip apex atom, allowing therefore only a vertical manipulation of this molecule adsorbed on the Ag (111) surface. Surprisingly the radicals are all oriented in one of the close packed directions in the same area. Furthermore they form straight lines extending over more than 100 nm in the close packed direction due to the molecule-molecule interaction.

These lines are located close and parallel to step edges, indicating a strong interaction between the molecules and the steps.

References

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