Investigation of CO on Pt(111) with STM and AFM and of PTCDA and CuPc with LFM



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1. Introduction

The invention of the scanning tunneling microscope $(STM)^1$ in 1982 by G. Binnig and H. Rohrer enabled atomic resolution in real space of electronically conducting surfaces [1]. The STM led to advances in research areas such as on-surface chemistry [2–4], material science [5–7], and biology [8]. The atomic force microscope (AFM) was invented by G. Binnig, C.F. Quate, and Ch. Gerber in 1986 and allowed the investigation of electronically non-conducting surfaces but in a destructive manner [9]. A tip at the end of a flexibel cantilever was slid in contact with the surface over the surface and the tip and the sample were exposed to wear and erosion. Non-contact AFM with atomic resolution utilizing a frequency-modulation detection was achieved in 1994 by F. Giessibl [10]. There, an oscillating piezolever was used and the attractive and repulsive interaction with the surface led to a frequency shift of the piezolever oscillation frequency. In the year 1998 a quartz tuning fork was used as a sensor [11] with which true atomic resolution of Si(111)- (7×7) was achieved in the year 2000 [12]. The fixation of one tuning fork prong to the sensor substrate led to the development of the qPlus sensor which enables combined FM-AFM and STM measurements.

Crucial for the imaging resolution and the reproducibility of measurements of STM and FM-AFM is the atomic configuration of the tip apex. In ultra-high vacuum and at low temperatures one method to identify the atomic tip apex configuration is the 'carbon monoxide front atom identification' (COFI) [13–16]. There, a carbon monoxide (CO) molecule is adsorbed vertically on the Cu(111) surface and by scanning very close over the CO molecule where short-range forces are present the number and configuration of the frontmost atoms of the tip can be individually resolved in the FM-AFM image but not in the STM image. On Cu(111) the CO appears as a wide trough whereas on Pt(111) the CO appears as narrow peak in the conductance. Therefore the question arose are the frontmost atoms of the tip the tip can be the tip the tip the conductance.

¹In this thesis the abreviation 'STM' is used depending on the context for 'scanning tunneling microscope' or 'scanning tunneling microscopy'.

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maybe also visible in the STM image on Pt(111)? If yes, what are the physical reasons for the high spatial STM resolution? The vertically adsorbed CO molecule acts as a torsional spring with a higher lateral stiffness on Pt(111) compared to Cu(111). Is the increased lateral stiffness of the CO molecule on Pt(111) the reason for the increased STM resolution?

In 'normal' FM-AFM² the tip oscillates vertically to the surface and the FM-AFM sensor is sensitive to vertical long-range forces as electrostatic forces or van der Waals forces or vertical short-range forces as Pauli repulsion. In lateral force microscopy (LFM) the sensor is rotated by 90° and the tip oscillates parallel to the surface. This method is highly sensitive to short-range forces and long-range forces with large vertical components do not contribute to the frequency shift signal making it highly sensitive to height differences of the potential energy landscape of e.g. an adsorbate [17]. 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and copper(II) phthalocyanine (CuPc) are well investigated organic semiconductors [18-21] and form mixed phases with different stoichiometries on Ag(111) [22]. So far it was not clear how the adsorption geometry of PTCDA and CuPc changes within the different mixed phases or how the relative conductance close to the Fermi energy of the molecules changes. Or, are there mixed phases which were not observed so far? On Cu(111) isolated CuPc can switch between two states by rotation in the presence of inelastically tunneling electrons [23, 24] or by the proximity of the tip [17]. When the CuPc molecule is adsorbed close to different numbers of PTCDA molecules can the PTCDA molecules lock the CuPc molecule in different rotation states? And how do the PTCDA molecules affect the adsorption geometry and the electronic structure (near the Fermi energy) of the CuPc molecule?

In chapter 2 the basics of STM and FM-AFM are explained as well as the special case of LFM. Force deconvolution methods to calculate forces and energies from frequency shift data are mentioned and a modification of the probe particle model is discussed to simulate LFM images.

In chapter 3 the experimental setup is described. The ultra-high vacuum and low temperature microscope is explained and a self-built molecular evaporator is discussed which was used for the experiments in chapter 7 and 8. Next, the Cu(111), Ag(111), and Pt(111) sample preparation methods are explained and the qPlus

²When in the following the term 'normal FM-AFM' is used, the case is meant where the tip oscillates vertically to the surface.

sensor as well as a modified sensor hold for LFM measurements. Then, a method to calculate the stiffness of a LFM sensor including the tip is presented and a comparison of the method with a static bending experiment is carried out. Finally, tip preparation methods and the tip functionalization with a CO molecule is explained.

In chapter 4 a method to determine the amplitude and tilt of an LFM sensor is presented. The influence of the sensor tilt on the frequency shift data is demonstrated for normal FM-AFM and LFM as well as the effect of the amplitude and tilt on the STM data for LFM. To determine the amplitude and tilt of the sensor a 2D current map method is discussed as well as a fitting algorithm.

In chapter 5 a method to identify the atomic configuration of the metallic tip apex using STM and normal FM-AFM on Pt(111) is presented. The difference of the STM images of CO on Cu(111) and Pt(111) are discussed and the ratio of the 2D to the 3D density of states of Cu(111) is calculated. Then normal FM-AFM and STM images of metallic single, two, and three-atom tips are investigated and compared to Cu(111). The influence of CO bending on the STM images is analyzed and the STM images for a two and three-atom tip are modeled.

In chapter 6 the STM and normal FM-AFM images of CO on Pt(111) recorded with a CO tip are discussed. To demonstrate the influence of CO bending on the STM contrast a probe particle simulation of a group of 5 CO molecules is performed and bending angles of the probe particle were extracted and compared with an STM image of a group of 5 CO's. Then, conductance z spectra at different lateral positions of an isolated CO are discussed and a hard sphere and tight binding model is introduced to simulate the conductance z spectra. In addition, conductance z spectra calculated by density functional theory are compared with the experimental data.

In chapter 7 a literature review of PTCDA and CuPc as well as of mixed phases of PTCDA and CuPc are given. Next, the adsorption geometry, the rotation direction of isolated CuPc relative to the Ag(111) atomic surface lattice and the adsorption site are investigated. Then, LFM and STM images of CuPc and PTCDA mixed phases with different stoichiometries on Ag(111) are analyzed, especially the adsorption geometry and the conductance close to the Fermi energy of CuPc and PTCDA. Moreover, LFM and STM images of a single CuPc adsorbed next to different numbers of PTCDA molecules on Cu(111) are discussed as well as the rotation direction of the CuPc relative to the Cu(111) atomic surface lattice are investigated. Finally, the influence of different numbers of PTCDA molecules on

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the STM topography images of a single CuPc at different bias voltages (100 mV to 1500 mV) are discussed.

In chapter 8 the energy dissipation with LFM and a CO terminated tip is investigated. First, the energy dissipation model of Ref. [25] is explained. Then, the excitation data recorded between a hydrogen atom of one PTCDA and an oxygen atom of another PTCDA is discussed as well as the excitation data recorded at the CuPc lobe and between the oxygen side of a PTCDA and a hydrogen atom of CuPc lobe are investigated. Then, the maximum energy dissipation data as a function of the height is analyzed and compared and the influence of different CO tips is discussed.

In appendix A two python programs to log and plot the pressure values of the microscope are explained as well as a LabView program to log the temperature values are described.

2. Scanning tunneling and frequency-modulation atomic force microscopy

2.1. Scanning tunneling microscopy

The scanning tunneling microscope $(STM)^1$ was realized first in 1982 by Binnig et al. [27]. It utilizes the quantum mechanical electron tunneling effect, which is caused by the wave nature of the electrons in the quantum mechanical picture. In the classical picture electrons could not pass a classical forbidden barrier [28]. Figure 2.1(a) shows a sketch of the working principle. A conductive tip is at height z_T above a conductive sample. At the sample a voltage U is applied and the tip is connected to ground.

An applied bias voltage on the sample leads to a shift of the Fermi energy $E_{F,S}$ by V = eU relative to the Fermi energy $E_{F,T}$ of the tip as shown in Fig. 2.1(b). Thus, electrons can tunnel from occupied surface states of the sample into empty tip states [27, 28].

The z dependence of the tunneling current between the tip and the sample can be modeled by the solution of the one dimensional Schrödinger equation for a potential barrier [28]:

$$I = I_0 \exp\left(-2\kappa z\right) \tag{2.1}$$

 I_0 is current at point contact and κ is the material dependent decay rate:

$$\kappa = \sqrt{\frac{2m_e\Phi}{\hbar^2}} \tag{2.2}$$

¹In this thesis the abbreviation 'STM' is used for 'scanning tunneling microscopy' and for 'scanning tunneling microscope'.



Figure 2.1.: (a) Sketch of a STM tip at a height z_T above a sample with an applied bias voltage U. (b) Shift of the Fermi energy $E_{F,S}$ relative to $E_{F,T}$ by the energy V = eU with U is the bias voltage. The tip and the sample are separated by a vacuum gap of width z_T . E_V is the vacuum energy and Φ_S the work function of the sample. Figures adapted from Ref. [26].

 m_e is the electron mass, \hbar is the reduced Plank constant, and Φ is the average material-dependent work function of the tip and the sample [28]. The work function is also dependent on the crystal orientation. For e.g. Cu(111): $\Phi = 4.94 \text{ eV}$ [29]. This yields for Cu(111) a decay rate of $\kappa = 1.14 \times 10^{10} \text{ m}^{-1}$. A height change of 100 pm results in a change of the tunneling current approximately by a factor of 10. This is the reason for the high spatial resolution of the STM. For instance, if there would be just one atom standing out at a relatively blunt tip, most of the tunneling current would flow through this single atom resulting in a very high spatial resolution [26].

The density of states is not included in the solution of the one dimensional Schrödinger equation. This is considered by the Bardeen formalism and described by the equation:

$$I = \frac{4\pi e}{\hbar^2} \int_0^{eV} \rho_S(E_F - eV - \epsilon)\rho_T(E_F + \epsilon)|M|^2 d\epsilon$$
(2.3)

e is the electron charge, ρ_S is the density of states of the sample, ρ_T is the density of states of the tip, and M contains the tunneling matrix elements [30]. M has the dimension of energy and describes the energy lowering due to the overlap of states [28].

If the radius of the tip is considered and it is assumed that the states of the tip

are only s waves, the tunneling current mainly represents the Gaussian smoothed density of states of the surface (Tersoff and Hamann approximation) [28, 31].

2.2. Frequency-modulation atomic force microscopy

For non-conducting samples the STM is not applicable and it is difficult to measure the forces between the tip and the sample [26]. By measuring the forces between the tip and the sample friction on the atomic scale can be investigated [25, 32, 33] or chemical bonds can be studied [34, 35]. A microscope to probe non-conducting samples and which is sensitive to the interatomic forces was invented by Binnig et al. in 1986 and is called the atomic force microscope (AFM) [9]. In AFM, a very hard and sharp tip at the end of a cantilever is scanned over a surface. The interaction forces between the tip and the sample lead to a deflection of the cantilever. Binnig et al. realised the deflection measurement with an STM sitting on top of the cantilever. Atomic resolution with this setup was reached in 1992 on potassium bromide by Giessibl and Binnig [36] but this imaging method was not very reliable.

Measuring the static deflection of the cantilever also brought some problems. A lower stiffness of the cantilever leads to a larger deflection, but if the stiffness is too low, e.g. $15 \,\mathrm{N}\,\mathrm{m}^{-1}$, then it is possible that the tip makes contact with the sample and remains at the sample because the restoring force of the cantilever is too low (jump-to-contact). If the stiffness of the cantilever is high e.g. $1500 \,\mathrm{N}\,\mathrm{m}^{-1}$, a force of $1.5 \,\mathrm{nN}$ would lead to a deflection of $\Delta z = \frac{F}{k} = 1 \,\mathrm{pm}$, which is not easy to measure.

A solution to this problems is dynamic AFM where the cantilever is driven to oscillate. There are two main modes: one is amplitude modulation AFM (AM-AFM), where the cantilever is driven to oscillate by a fixed drive signal at a constant frequency and the frequency of the drive signal is close to the resonance frequency of the cantilever. The interaction with the surface leads to a change of the recorded amplitude and phase relative to the drive signal amplitude and frequency. It is however hard to extract the forces out of the signal and a nonsinusoidal tip motion is possible (tapping-mode).

The second dynamic AFM mode is frequency-modulation AFM (FM-AFM). There, a cantilever is driven at its resonance frequency with constant amplitude A and with mainly attractive interaction with the surface (non-contact mode). The



Figure 2.2.: (a) Equivalent spring model of the oscillating cantilever and tip with stiffness k and effective mass m^* . The interaction with the sample can be considered as an additional spring with stiffness k_{TS} . (b) Oscillating cantilever with tip above the surface. A is the amplitude. Figures adapted from Ref. [26]

interaction with the sample leads to a change of the resonance frequency Δf of which the atomic forces and energies can be extracted. Note that FM-AFM needs two control loops one for the oscillation amplitude and one for the oscillation frequency. From now on, the abbreviation 'AFM' refers to FM-AFM.

2.2.1. Frequency shift, forces and energies

If there is no interaction with the surface the oscillating cantilever can be described by a driven damped harmonic oscillator with resonance frequency f_0 [26]:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}$$
(2.4)

k is the stiffness of the cantilever and m^* the effective mass of the cantilever and the tip. If the interaction with the surface is considered (e.g. attractive forces), it can be modeled by an additional spring with stiffness k_{TS} as shown by Fig 2.2(a). k_{TS} is the force gradient $k_{TS} = -\frac{\partial F_{TS}}{\partial z}$ with F_{TS} being the force between the tip and the sample, and $F_{TS} = -\frac{\partial E_{TS}}{\partial z}$ with E_{TS} is the potential energy between the tip and sample. This leads to the equations

$$f = \frac{1}{2\pi} \sqrt{\frac{k + k_{TS}}{m^*}}$$
(2.5)

$$= f_0 \sqrt{1 + \frac{k_{TS}}{k}}.$$
 (2.6)

If it is considered that $k_{TS} \ll k$ and Eq. 2.6 is expanded in a Taylor series, the frequency shift $\Delta f = f - f_0$ can be calculated by

$$\Delta f = \frac{f_0}{2k} k_{TS},\tag{2.7}$$

where k_{TS} is constant within the oscillation cycle (small amplitude approximation) [26].

Usually, k_{TS} is not constant within an oscillation cycle and the frequency shift cannot be calculated by Eq. 2.7 and the oscillation amplitude has to be taken into account. In Ref. [26] the Hamilton-Jacobi method is used to calculate the frequency shift by

$$\Delta f = -\frac{f_0}{kA^2} \langle F_{TS} z' \rangle, \qquad (2.8)$$

where z' is the position of the tip in an oscillation cycle. The brackets indicate the average over an oscillation cycle. This equation can be transformed into a function of the force gradient k_{TS} :

$$\Delta f(z) = \frac{f_0}{2k} \langle k_{TS}(z) \rangle \tag{2.9}$$

with

$$\langle k_{TS}(z) \rangle = \frac{1}{\frac{\pi}{2}A^2} \int_{-A}^{A} k_{TS}(z-z')\sqrt{A^2 - z'^2} dz'.$$
 (2.10)

By comparing Eq. 2.9 with Eq. 2.7 it can be seen that by considering the amplitude, k_{TS} becomes replaced by the averaged $\langle k_{TS} \rangle$ with a weighting function. The weighting function is a semicircle with radius A divided by the area of the semicircle $(\frac{\pi A^2}{2})$. Changing the amplitude A enables tuning the sensitivity of the FM-AFM measurement. For small amplitudes short range forces contribute strongly to the frequency shift, because they have large force gradients over a short range. For large amplitudes long range forces contribute to the frequency shift, because they have small force gradients over a larger range [26].

Typical long range forces between the tip and sample in vacuum are electrostatic, magnetic, and van der Waals forces. Typical short range forces come from Pauli repulsion and covalent bonds. The electrostatic and magentic forces can be eliminated by an inverse electric or magnetic potential. The van der Waals forces cannot be avoided [26]. Lateral force microscopy has the advantage of being not sensitive to vertical long range forces [37].

The oscillating cantilever has an intrinsic energy loss per cycle of $\Delta E_{Prong} = 2\pi \frac{E}{Q}$, where $E = \frac{1}{2}kA^2$. A is the amplitude and k the stiffness of the oscillating cantilever. Q is the quality factor. Further energy loss ΔE_{TS} can happen when dissipative forces between tip and sample occur (see chapter 8). The energy loss per cycle ΔE_{TS} can be calculated from the drive signal A'_{drive} [26]:

$$\Delta E_{TS} = 2\pi \frac{E}{Q} \left(\frac{|A'_{drive}|}{|A_{drive}|} - 1 \right)$$
(2.11)

 A_{drive} is the drive signal of the sensor far away from the sample.

2.2.2. Lateral force microscopy

First frequency-modulation lateral force microscopy (LFM) experiments were performed in 2002 by Pfeiffer and co-workers [32]. There, a silicon cantilever was excited to oscillate in the torsional eigenmode and forces near step edges and impurities on Cu(100) could be determined. In the same year Giessibl et al. made use of the qPlus sensor to perform LFM measurements [33]. A detailed description of the qPlus sensor will follow in section 3.4. In 'normal' FM-AFM the qPlus sensor is oriented parallel to the surface and the tip vertically as shown in Fig. 2.3(a). In LFM the qPlus sensor is rotated by 90° and the tip is glued along the long cantilever axis as shown 2.3(b).

2.2.3. Force deconvolution

The frequency shift is a result of the force gradient as it can be seen by Eq. 2.9. For small amplitudes Δf is directly proportional to k_{TS} , for larger amplitudes



Figure 2.3.: Sketches of qPlus sensors in (a) normal AFM orientation, where the tip oscillates in z direction and (b) rotated 90° in LFM orientation, where the tip oscillates in x direction. Also shown is a sketch of an adsorbed CO molecule on the surface.

Eq. 2.10 has to be considered and a weighting takes place. The weighting of the force gradient means that a convolution occurs². To calculate the forces from the Δf signal a deconvolution is necessary³.

Two popular deconvolution methods are the matrix inversion method by Giessibl [38] and the Laplace integration method by Sader and Jarvis [39]. The Sader-Jarvis method is used to calculate forces and energies in chapter 5. These deconvolution methods are sensitive to the inflection points in the Δf data and can be ill-posed such that the deconvolution does not reproduce the forces and energies correctly [40]. The Δf signal of LFM measurements usually exhibits many inflection points and the Matrix and Sader-Jarvis force deconvolution methods can be unreliable for LFM [41].

More reliable for LFM measurements is the Fourier method developed by Seeholzer and co-workers [41]. It makes use of the periodic property of certain Δf LFM measurements. Periodic means that the interaction with a CO molecule on Pt(111), for instance, produces zero frequency shift from a certain distance on the side of the CO molecule. This can be approximated by a periodic potential. A detailed explanation of the Fourier method can be found in Ref. [41, 42]. The

²A convolution is function h, which is the result of two other functions h = (f * g).

³A deconvolution is an inversion problem: calculating f from h when g is known.

2. Scanning tunneling and frequency-modulation atomic force microscopy



Figure 2.4.: Sketch of the probe particle attached to a tip base atom positioned above an adsorbate or surface atoms. At the probe particle the acting forces vectors are shown. Figure adapted from Ref. [43].

Fourier method is used to calculate energies of parts of molecules in chapter 7.

2.2.4. Simulating LFM images with the probe particle model

Functionalizing the tip with a CO molecule enhances the spatial resolution of AFM and STM measurements [34, 44–46]. The CO molecule adsorbs vertically on the tip. It is flexible and comparable to a torsional spring, which has significant influence on the contrast formation of AFM and STM images [43, 47, 48]. The probe particle model is an efficient program to simulate AFM and STM images considering the flexibility of the CO tip.

The probe particle model was introduced by Hapala and co-workers in 2014 [43]. It uses classical forces from Lennard-Jones (LJ) potentials to calculate the relaxation of a CO tip during interaction with surface atoms/molecules. Fig. 2.4 shows the probe particle which is bound to the tip base by a LJ force $F_{\text{Tip,r}}$ and a linear restoring force $F_{\text{Tip,xy}}$. F_{Surf} is calculated by summing up all LJ forces acting between the probe particle and the adsorbate or surface atoms. The probe particle is allowed to relax until the total force $F_{\text{Tip,r}} + F_{\text{Tip,xy}} + F_{\text{Surf}}$ is smaller than $10 \times 10^{-6} \text{ eV Å}^{-1}$ or $1.6 \times 10^{-14} \text{ N}$. (This values is set by default in probe particle model and is a good compromise between computation accuracy and computation time). The tip base and the adsorbate or surface atoms are kept fixed. Then, if the CO is relaxed, F_z is calculated by a projection of F_{Surf} onto the z axis and the Δf signal is calculated by Eq. 2.8. By applying this method for various (x, y, z)positions over the adsorbate AFM images can be generated.

To generate LFM images the oscillation in x/y direction has to be simulated. Therefore, the probe particle model code was modified to output the lateral forces F_x and F_y . Line number 2 and 3 were added right after line number 1 in the file 'relaxed_scan.py':

```
GU.save_scal_field( dirname+'/OutFz', Fs[:,:,2], lvecScan,
1
                                     data_format=data_format )
  GU.save_scal_field( dirname+'/OutFx', Fs[:,:,:,0], lvecScan,
\mathbf{2}
                                     data_format=data_format )
  GU.save_scal_field( dirname+'/OutFy', Fs[:,:,1], lvecScan,
3
                                     data_format=data_format )
```

These added code lines generate the files OutFx.xsf and OutFy.xsf with the lateral forces for every point (x, y, z). Then the lateral force files were loaded in MATLAB and Δf images were calculated.

Depending in which direction ϕ the lateral oscillation should be simulated from $F_x(x, y, z)$ and $F_y(x, y, z)$ the resulting force $F_{res}(x, y, z)$ can be calculated by:

$$F_{res}(x, y, z) = F_x(x, y, z)\cos\phi + F_y(x, y, z)\sin\phi$$
(2.12)

From $F_{res}(x, y, z)$ the frequency shift can be calculated by [26]:

$$\Delta f(x, y, z) = -\frac{f_0^2}{kA} \int_0^T F_{res}(x') \cos(2\pi f_0 \tau) d\tau$$
(2.13)

With f_0 being the oscillation frequency of the sensor, A the oscillation amplitude, k the sensor stiffness, T the oscillation periode, and x' the oscillation path.

Alternatively, Δf can be calculated by [26]:

$$\Delta f(x, y, z) = \frac{f_0}{\pi k A^2} \int_{-A}^{A} k_{TS}(x') \sqrt{A^2 - x'^2} dx'$$
(2.14)

with $k_{TS} = -\frac{\partial F_{res}(x,y,z)}{\partial x}$, where x is in the oscillation direction as defined by Eq.2.12. Equation 2.13 and 2.14 yield similar results.

To compare the numeric calculation of Eq. 2.13 and Eq. 2.14 Δf images of copper(II) phthalocyanine (CuPc) were calculated. A ball-and-stick model of CuPc is shown in Fig. 7.1(b). The Δf image in Fig. 2.5(a) was calculated by Eq. 2.13 and in Fig. 2.5(b) by Eq. 2.14. The differences are marginal. Since Eq. 2.14 requires



Figure 2.5.: Δf images of Copper(II) phthalocyanine (CuPc) calculated with (a) Eq. 2.13 and (b) Eq. 2.14.

a differentiation of $F_{res}(x, y, z)$ the Δf values have abrupt jumps due to numeric processing. In Fig. 2.5(b) the Δf values were cropped for a better comparison.

3. Experimental setup

In this chapter the experimental setup will be explained. A self-built molecular evaporator will be described (section 3.2) and the sample preparation procedure is discussed (section 3.3) as well as a modified sensor holder for LFM measurements (section 3.4). To calculate the stiffness of a LFM sensor with a tip an Euler–Bernoulli beam theory calculation is presented and experimental results of stiffness measurements are discussed and compared with the Euler–Bernoulli theory calculation (section 3.5). Finally the tip preparation and functionalization will be described (section 3.6). The description of the pressure and temperature logging programs can be found in appendix A.

3.1. Ultra-high vacuum and low temperature microscope

All experiments mentioned in this thesis were performed with a low temperature (LT) and ultra-high vacuum (UHV) microscope from CreaTec Fischer & Co. GmbH, Berlin, Germany. Figure 3.1 shows a photograph with marked parts of the system. Most important is the analysis chamber (marked dark blue) and the preparation chamber (marked green).

In the preparation chamber samples can be prepared by e.g. argon ion sputtering or annealing. The sample preparation processes for the different kinds of samples will be explained in section 3.3 in more detail. Evaporation of molecules with the molecular evaporator is also executed in this chamber. A detailed explanation of the molecular evaporator will be given in section 3.2. To measure the deposition rate of evaporated molecules, a quartz crystal microbalance was installed in the preparation chamber.

On the left of the preparation chamber sits the analysis chamber (marked blue in Fig 3.1). Both are connected by a gate valve. In the analysis chamber sits the microscope. To reduce mechanical vibrations the microscope is spring loaded

3. Experimental setup



Figure 3.1.: Components of the LT-UHV microscope.

and an eddy current damping mechanism is integrated. The microscope is located within a radiation shield to reduce warming. Mounted to the analysis chamber is also a needle valve which is used for dosing carbon monoxide molecules into the microscope.

The bath cryostat marked red in Fig. 3.1 consists of an outer liquid nitrogen tank (14 liters) and an inner liquid helium tank (4.2 liters). By this configuration a cooling temperature of 5.6 K and a cooling time of 72 h can be achieved. Measurements at 5.6 K have the advantage of very low thermal noise ($k_BT = 0.5 \text{ meV}$), lower thermal diffusion, and lower thermal drift. This enables very stable and slow measurements for days and weeks without almost any disturbances of the measurement system. The temperature is measured by two temperature diodes. One close to the cryostat and one within the microscope head. To log the temperature values over time a logging program was written (see appendix A.1).

Below the analysis chamber is the ion getter and titanium sublimation pump (marked yellow in Fig 3.1). There is also another ion getter and titanium sublimation pump below the preparation chamber. Once a pressure of 1×10^{-8} mbar is achieved by pumping the system with a turbo pump and a scroll pump and a bake-

out for 48 hours at 150 °C, the ion pump takes over the vacuum pumping. Thereby a pressure of 1×10^{-10} mbar to 1×10^{-11} mbar is reachable. Within the shields the pressure is even lower because most of the residual gas adsorbs on the cold shield in a process called cryopumping. The ultra-low vacuum prevents contaminations and allow for atomically-precise measurements on a well-defined and clean sample surface. The pressure of the analysis and preparation chamber, and load lock is measured by ion gauges. A program to log the pressure values is explained in appendix A.2.

Samples and sensors can be transferred into the preparation chamber through the load lock (marked light blue in Fig. 3.1). It is connected to a turbo pump and to the preparation chamber by a gate valve and can be pumped separately by the turbo pump. Samples and sensors can be transferred to the analysis chamber by the xyz manipulator marked pink in Fig. 3.1.

3.2. Molecular evaporator

For the experiments discussed in chapters 7 and 8 the evaporation of molecules in the vacuum onto the samples was necessary. Therefore a molecular evaporator was developed. Molecules, which are in a in a solid state as a crystalline powder at room temperature are heated in a crucible and undergo sublimation into the gas state because of the very low pressure in the preparation chamber.

Figure 3.2(a) shows the assembled evaporator. The evaporator consists basically of two parts: the evaporator head and a cluster flange with a rotary feedthrough. In Fig. 3.2(b) the self-built evaporator head is shown. The CAD drawing was done by Anja Merkel from the group of the author and the metal parts were fabricated by the in-house workshop. The evaporator head encapsulates the crucibles and directs the hot molecular gas in one direction. As a heating filament a tungsten wire was wound around the crucibles. In the base of the evaporator head are the isolation washers made of macor for the current connections. The metal housing acts as an electrical ground for the return currents. Figure 3.2(c) shows the filled crucibles with PTCDA (red powder) and CuPc (blue powder). PTCDA and CuPc were bought from Sigma-Aldrich¹. A more in detailed explanation of the molecules is given in chapter 7.

The second part of the evaporator is the cluster flange. The cluster flange can

¹Merck KGaA, Darmstadt, Germany





Figure 3.2.: (a) The molecular evaporator without the cap and the shutter mounted on a cluster flange. (b) CAD drawing of the evaporator head (by Anja Merkel from group of the author). (c) Head of the molecular evaporator with the crucibles filled with two different molecules (PTCDA red, CuPc blue).



Figure 3.3.: Quartz crystal microbalance oscillation frequency as function of time t in minutes.

be seen at the bottom of Fig. 3.2(a). To the cluster flange a rotary feedthrough is mounted. It was bought from Hositrad Holland B.V. The rotary feedthrough is connected by a rod to the shutter which is on top of the evaporator head and covers or opens the holes for the molecular beam. By opening and closing the shutter the molecular beam can be turned on or off. To the cluster flange are two BNC feedthroughs mounted for the current supply. The other two CF16 flanges were closed with blank flanges.

3.2.1. Calibration and test

To demonstrate a calibration of the molecular evaporator the frequency change over time of the quartz crystal microbalance was determined².

The quartz crystal microbalance works by measuring the oscillation frequency of an oscillating quartz crystal. By depositing very small amounts of molecules on a quartz plate the oscillation frequency changes. By determining the frequency difference δf for a time interval δt the rate $R = \frac{\delta f}{\delta t}$ can be obtained. This rate is

²Before the first use the evaporator was degassed. Degassing is an operation of the device for several hours with intermediate power to remove any contaminations and water within the molecule powder.

3. Experimental setup



Figure 3.4.: Constant current STM image of individual CuPc molecules on Cu(111). The image was line flattened.

proportional to the deposition rate of the molecules.

Figure 3.3 shows the oscillation frequency of the quartz microbalance as a function of the time in minutes. The evaporator was warmed up with a filament current of 1.41 A for 10 min. Then the current was increased to 1.51 A and the frequency recording was started. This yielded for $R = 0.0083 \,\text{Hz s}^{-1}$.

However, during the tests the following problems appeared:

- R is dependent on the pre-heating time and pre-heating current
- R increases non-linearly with the current

Therefore, to calibrate the evaporator several depositions were conducted and checked by STM measurments to determine the optimal deposition parameters. Figure 3.4 displays a constant current STM image of individual CuPc molecules (bright fourfold-symmetric features) evaporated with 1.51 A for 1.5 min. The preheating time was 7 min with 1.41 A and 3 min with 1.51 A. This yielded a reproducible deposition rate of $0.0125 \,\mathrm{CuPc/nm^2}$.

The monitoring of the evaporation parameters could be improved by installing thermocouple elements close to the crucibles.



Figure 3.5.: (a) Cleaned Cu(111) surface with an L shaped step edge. (b) Cleaned Ag(111) surface (c) Cleaned Pt(111) surface with carbon atoms in the surface (dark spots) and carbon monoxide molecules (bright spots)

3.3. Cu(111), Ag(111), and Pt(111) sample preparation

The measurements performed in this thesis were carried out on the single crystal metallic surfaces Cu(111), Ag(111), and Pt(111). All three crystals exhibit the face-centered cubic (fcc) crystal structure.

The cleaning of the surfaces is performed in the preparation chamber by repeated sputtering with Ar ions and annealing. To sputter the sample the valve to the ion pump has to be closed and the valve to the turbo pump has to be opened. Ar gas has to be introduced with a needle value to a pressure of 1×10^{-7} mbar in the preparation chamber. The Ar gas is ionized and accelerated by a sputtering gun towards the sample. Then, the Ar gas and the sputtered material are pumped off by the turbo pump (flow-through sputtering). The accelerated Ar ions remove the first few atomic layers from the sample and therefore any adsorbates, defects or contaminations. A typical acceleration voltage is 1.0 kV with a typical ion current of 2µA. This forms many craters on the surface which can be healed by heating up the sample for e.g. Cu(111) to $600 \,^{\circ}C$ or Ag(111) to $500 \,^{\circ}C$. Due to the high temperature edge atoms become mobilized and fill up the craters. During the annealing many natural contaminations can diffuse from the crystal bulk to the surface. Therefore the sputter and annealing cycles are usually repeated 1 - 2times. Samples newly transferred into the microscope have to be cleaned with 8 -10 cycles. Figure 3.5(a) shows the topography of a cleaned Cu(111) surface with an L shaped step edge. Also visible are some defects (dark spots). Figure 3.5(b)

shows the topography of a cleaned Ag(111) surface with many surface steps visible in the right top of the image. In the center of the image a screw dislocation is visible.

Pt(111) requires more cleaning cycles and a higher annealing temperature (1000 °C) because of its high reactivity and its higher melting point. Also a higher acceleration voltage of 1.2 kV for the sputtering was used. To obtain the higher annealing temperature a combination of radiative and electron beam heating was used. First, the sample was heated with the tungsten filament to 800 °C. Then a high voltage (800 V) was applied between the sample and the heating filament. This accelerates the 'hot' electrons towards the sample and heats it up due to the kinetic energy of the electrons leading to a temperature of $1000 \,^{\circ}$ C. Pt(111) requires usually 6 -8 cleaning cycles. To avoid any melting of the contacts on the xyz manipulator it has to be cooled with liquid nitrogen during the annealing cycles. To reduce the diffusion of carbon atoms from the bulk to the surface the last annealing cycle is performed with 800 °C. Figure 3.5(c) shows the topography of a cleaned Pt(111)surface. The dark spots are most probably carbon atoms which diffused from the bulk to the surface. Carbon is a natural contamination of Pt. The bright spots are CO molecules adsorbed on the Pt(111) surface after CO gas was dosed in to the analysis chamber by the needle value (see section 3.1).

3.4. qPlus sensor and sensor holder

The qPlus sensor was developed by Giessibl in 1998 [11]. The original design was based on a quartz tuning fork with a tip glued to one prong. However, for the tuning fork sensors used until then the additional mass of the tip on the prong led to a break down of the quality factor (Q factor) [26, 49]. The reason for this is that the two prongs can be considered as a coupled oscillator. An additional mass on one prong breaks the symmetry of the coupled oscillator and the Q factor breaks down. Therefore, in the qPlus configuration one prong was fixed to a substrate, whereas the other one could freely oscillate (with the attached tip) [50]. This setup is a single oscillator and does not have the problem of the Q factor break down. That is where the name 'qPlus' comes from. The qPlus sensor enables AFM and STM at the same time when the tip material is conductive.

Figure 3.6(a) shows a qPlus sensor glued on a sensor body (white substrate). 1 and 3 are the AFM contacts to sense the oscillation. 2 is the STM contact,



Figure 3.6.: (a) qPlus sensor in LFM configuration glued on the sensor body (white substrate) (1,3) mark the AFM contacts (2) the STM contact. (b) Modfied sensor body with diagonal cut. Source: Anja Merkel

which goes to the tip. The tip is glued along the long axis of the prong and the qPlus sensor is orientated that the tip oscillates in horizontal direction [compare Fig. 2.3(b)]. This is the LFM configuration that is used for the most experiments in this thesis, except the experiments in chapters 5 and 6. The experiments in chapters 5 and 6 were performed with a normal AFM sensor where the qPlus sensor is rotated 90° and the tip oscillates vertically to the surface [compare Fig. 2.3(a)].

The qPlus sensor can be driven to oscillation using a piezoelectric shaker element, mechanically connected to the sensor. By applying an alternating voltage on the piezoelectric shaker element with the frequency equal to the resonance frequency of the qPlus sensor, the qPlus sensor is excited. The oscillation of the qPlus sensor is sensed using the piezoelectric effect of the quartz of which the qPlus sensor is made. A deformation of the material induces an electric field in the material. The electric field induces charges in the electrodes, which are on the side of the prong. This leads to a current, which is amplified and converted to a voltage with an transimpedance amplifier. An oscillating prong leads to an alternating voltage signal. From this alternating voltage signal the oscillation frequency and amplitude can be determined. A method to determine the amplitude of a qPlus sensor in LFM configuration can be found in chapter 4.

Different tip materials can be used depending on the measurements. For in-

stance, Pielmeier et al. showed by using a magnetic tip that magnetic spin resolution can be achieved without an external magnetic field [51]. Another example is sapphire which reduces the interaction with liquids due to its hydrophobic property under ambient conditions [52]. For experiments in this thesis tungsten tips were used because they have to be conducting and stiff.

The qPlus sensor is glued on a holder which establishes the electric and mechanical connection to the microscope head. A detailed description of how to build a sensor can be found in Ref. [42]. For LFM a specific sensor holder was designed which offers a large surface for gluing the qPlus sensor in vertical orientation and also allows a good view to the sensor, when it is in the microscope head. Figure 3.6(b) shows a CAD drawing of the designed sensor body. The CAD drawing was done by Anja Merkel from the group of the author.

The proximity of the STM and AFM electrodes on the prong can cause problems. For instance under certain conditions electromagnetic coupling can occur from the STM electrode to the AFM electrode (cross-talk) [53, 54]. In all measurements for this PHD thesis cross-talk was reduced by measuring with low currents and AFM images at different bias voltages were compared to exclude any influence of cross-talk.

3.5. LFM sensor stiffness calculation

Another unique challenge of an LFM sensor is the determination of the stiffness k. The calculation of forces, energies and dissipative energies require the knowledge of k [26, 55]. For normal AFM with a sufficiently small tip attached perpendicular to the end of the prong, k does not change significantly from the stiffness of the bare prong [56–58]. This is because the tip is vertically very stiff and therefore applied forces are transferred directly – with a minimum of mechanical deformation – to the cantilever. In case of LFM, where forces act perpendicular on the tip, bending of the tip can occur. Even without any bending, an additional LFM tip changes the length of the tine, which leads to significant change of the sensor stiffness. In this section the Euler–Bernoulli beam theory is used to calculate the LFM sensor stiffness.



Figure 3.7.: LFM sensor parameterization: w is the thickness of the cantilever, t the width, L_q the length. L is the length including the cantilever and the tip, R is the radius of the tip, and F the applied force at the end of the tip. ω represents the total deflection of the combined beam.

3.5.1. Derivation

Figure 3.7 shows a simplified LFM sensor as a rectangular cantilever and an attached cylindrical tip at the end, ignoring the glue and the conical ending of the tip. We begin with the static bending equation for a point like force F applied at x = L [59]:

$$\frac{d^2\omega}{dx^2} = \frac{F(L-x)}{E(x)I(x)} \tag{3.1}$$

with I(x) the second moment of area and the E(x) the Young's modulus. ω is the deflection in z direction (see Fig. 3.7). For a rectangular cross section of the cantilever and a circular cross section of the tip, I(x) can be written as [59]:

$$I(x) = \begin{cases} I_q = \frac{1}{12}wt^3, & 0 \le x \le L_q \\ I_t = \frac{1}{4}\pi R^4, & L_q < x \le L \end{cases}$$
(3.2)

w, t, and R are defined as shown in Fig. 3.7.

The Young's modulus E(x) is also piecewise defined considering the different materials of the cantilever and the tip:

$$E(x) = \begin{cases} E_q, & 0 \le x \le L_q \\ E_t, & L_q < x \le L. \end{cases}$$
(3.3)

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 E_q is the Young's modulus of the cantilever (quartz) and E_t of the tip (tungsten). The first derivative of ω can be calculated by integrating Eq. 3.1:

$$\frac{d\omega(x)}{dx} = \begin{cases}
\int_{0}^{x} \frac{F(L-l)}{E_{q}I_{q}} dl, & 0 \leq x \leq L_{q} \\
\int_{0}^{L_{q}} \frac{F(L-l)}{E_{q}I_{q}} dl + \int_{L_{q}}^{x} \frac{F(L-l)}{E_{t}I_{t}} dl, & L_{q} < x \leq L. \end{cases}$$

$$= \begin{cases}
\frac{F}{E_{q}I_{q}} (Lx - \frac{1}{2}x^{2}), \\
\frac{F}{E_{q}I_{q}} (LL_{q} - \frac{1}{2}L_{q}^{2}) + \frac{F}{E_{t}I_{t}} (Lx - \frac{1}{2}x^{2} - LL_{q} + \frac{1}{2}L_{q}^{2}) + C_{1},
\end{cases}$$
(3.4)

where C_1 is a integration constant. The values for x of Eq. 3.4 are also valid for Eq. 3.5. C_1 has to be determined to fulfil the continuity conditions:

$$\left. \frac{d\omega}{dx} \right|_{x=0} = 0 \tag{3.6}$$

$$\left. \frac{d\omega}{dx} \right|_{x=L_q}$$
, continuous (3.7)

Equation 3.6 is fulfilled. Condition 3.7 leads to

$$C_1 = 0 \tag{3.8}$$

 $\omega(x)$ can be calculated by integrating equation 3.5 one more time:

$$\omega(x) = \begin{cases} \int_{0}^{x} \frac{F}{E_{q}I_{q}} (Ll - \frac{1}{2}l^{2}) dl, & 0 \le x \le L_{q} \\ \int_{L_{q}}^{x} \left(\frac{F}{E_{q}I_{q}} (LL_{q} - \frac{1}{2}L_{q}^{2}) \right) dl & (3.9) \\ + \int_{L_{q}}^{x} \left(\frac{F}{E_{t}I_{t}} (Ll - \frac{1}{2}l^{2} - LL_{q} + \frac{1}{2}L_{q}^{2}) \right) dl, & L_{q} < x \le L \\ & = \begin{cases} \frac{F}{E_{q}I_{q}} \left(\frac{1}{2}Lx^{2} - \frac{1}{6}x^{3} \right), & 0 \le x \le L_{q} \\ F \left(\frac{1}{E_{q}I_{q}} - \frac{1}{E_{t}I_{t}} \right) \left(LL_{q} - \frac{1}{2}L_{q}^{2} \right) (x - L_{q}) & (3.10) \\ + \frac{F}{E_{t}I_{t}} \left(\frac{1}{2}Lx^{2} - \frac{1}{6}x^{3} - \frac{1}{2}LL_{q}^{2} + \frac{1}{6}L_{q}^{3} \right) + C_{2}, & L_{q} < x \le L \end{cases}$$

Note that in Eq. 3.9 and 3.10 the second and third line belongs together. Since

Parameter	Value
L	$2.33 \mathrm{mm} (440 \mathrm{\mu m} \mathrm{tip} \mathrm{length})$
R	$25.0\mu\mathrm{m}$
t	$0.214\mathrm{mm}$
w	$0.127\mathrm{mm}$
L_q	$1.89\mathrm{mm}$
E_q	$78.7\mathrm{GPa}$
I_q	$1.037203073 \times 10^{-16}\mathrm{m}^4$
E_T	$400\mathrm{GPa}$
I_T	$3.067961575 \times 10^{-19}\mathrm{m}^4$
k	$1343 \mathrm{N}\mathrm{m}^{-1}$

Table 3.1.: LFM sensor parameters

 $\omega(x)$ has to be continuous at $x = L_q$ the integration constant can be determined to be:

$$C_2 = \frac{F}{E_q I_q} \left(\frac{1}{2} L L_q^2 - \frac{1}{6} L_q^3 \right)$$
(3.11)

Using Hook's law the stiffness can be calculated by

$$k = \frac{F}{\omega(L)} \tag{3.12}$$

3.5.2. Stiffness calculation with real values

Table 3.1 shows the values for the stiffness calculation of an LFM sensor used for the experiments in this thesis. With these values a stiffness of $k = 1343 \text{ N m}^{-1}$ was obtained. Figure 3.8 shows the plot of $\omega(x)$ from 0 to L.

3.5.3. Static bending measurements

To validate the Euler-Bernoulli theory calculations presented in the section above, static bending measurements on a S1.0 Statek qPlus sensor with a tip in LFM configuration were performed. The tip was a tungsten wire with diameter $125 \,\mu\text{m}$ and length $2.0 \,\text{mm}$.

Figure 3.9 shows the setup of the experiment. A qPlus sensor with a tip was glued on a aluminum block and a weight was attached at different positions dL at the tip. This led to a bending dz of the prong and the tip, which was measured with



Figure 3.8.: Plot of $\omega(x)$ from 0 to L



Figure 3.9.: Static bending experiment. A mass m was attached at different positions on the tip at position dL. This led to the deflection dz which was measured by an optical microscope.



Figure 3.10.: Blue dots show measured stiffness for various tip length or points of mass. Orange dots are calculated stiffness values with the Euler-Bernoulli theory considering a circular tungsten tip. The green dots are the calculated stiffness using the approximation $k = k_q \frac{L_q^3}{(L_q + \Delta L)^3}$, where k_q is the stiffness of the prong without a tip and ΔL is the length of the tip.

an optical microscope (Keyence VHX-600³). The stiffness k was then calculated by $k = \frac{F}{dz} = \frac{mg}{dz}$, where $g = 9.81 \text{ m/s}^2$. A small screw with weight m = 0.500 g was used as the mass, which was hung on the tip with a small gold wire with diameter 25 µm. The additional mass of the gold wire was not measurable with the precision scale Sartorius Basic⁴ (precision $\pm 1 \text{ µg}$). The gold wire loop around the mass was closed by gluing the ends together.

Figure 3.10 shows the measured stiffness for different positions of the weight on the tip (blue dots). For these positions the theoretical value was calculated with Eq. 3.10 and Eq. 3.12 shown by the orange dots, which considers a circular tungsten tip attached to the cantilever. The position of the mass in the experiment was considered as the tip length in the calculation. The absolute error of the optical microscope was estimated to be $\pm 1 \,\mu\text{m}$. At small dL the bending was only 6.48 µm which leads to a relative error of 15.4%. For larger dL the relative error is smaller. This can be seen in the decreasing error bars with increasing dL. The calculated values are in good agreement with the experimental ones for $dL > 1.200 \,\text{mm}$. In most cases the calculated values are within the error bars. Only

³Keyence Deutschland GmbH, Siemenstr. 1, 63263 Neu-Isenburg

⁴Sartorius AG, Otto-Brenner-Str. 20, 37079 Goettingen, Germany

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for small dL < 0.8 mm they lay outside of the error bars. One reason is the limited accuracy of the optical microscope to measure such small bendings. Another is an overestimation of k by the Euler-Bernoulli theory. In the calculation the end of the cantilever is considered to be fixed. This is not the case in a qPlus sensor were a deformation of the quartz happens already before the base of the prong [60]. Also the connection of the tip and the cantilever is considered to be infinitely stiff in the model, which is not the case in a real configuration due to the gluing of the tip.

Another way to approximate the stiffness of sensor with a tip is by the formula

$$k = k_q \frac{L_q^3}{(L_q + \Delta L)^3}$$
(3.13)

where k_q is the stiffness of the cantilever without a tip and ΔL is the length of the tip [26]. This approximation assumes a tip with the same cross section and the same material as the cantilever. A comparison of this approximation formula with the Euler-Bernoulli theory calculation will be done next. The calculated values are shown in Fig. 3.10 by the green dots. All values lie above the values calculated with Euler-Bernoulli theory. The difference of the approximation to the Euler-Bernoulli calculation increases as function of dL.

In this experiment a tungsten tip with diameter $125 \,\mu\text{m}$ was used because a higher weight could be attached on the tip without an irreversible plastic deformation of the tip. For a typical LFM sensors a tip with 50 μ m diameter is usually used. The approximation formula considers a 'tip' made of quartz with the cross section of the cantilever. Therefore, a higher difference between the stiffness calculated with the Euler-Bernoulli and the approximation formula is expected, when a tip with a diameter of 50 μ m is used.

In summary the Euler-Bernoulli theory calculation which considers the extent of a rectangular cantilever with a circular tungsten tip is a good estimate of the total stiffness of a LFM sensor and superior to the approximation formula for thin tips. Increased accuracy of the static bending experiment, especially for short tip lengths, could be achieved by using an interferometer.

3.6. Tip preparation and tip functionalization

A well-defined single-atom tip is important for the reproducibility of measurements and tip functionalization. There are three ways to manipulate the tip apex. The


Figure 3.11.: (a) COFI LFM Δf image of a single atom metal tip. The image was filtered by a 6 × 6 pixels Gauss filter to increase the contrast. The oscillation is in horizontal direction. (b) COFI LFM Δf image of a CO terminated tip. The oscillation is in horizontal direction.

first manipulation happens when the sensor is built. A tungsten tip as they are used throughout this work gets sharpened by electro-chemical etching. Once the sensor is in the microscope, the tip can be shaped by poking or a field emission.

In field emission a bias voltage of 100 V is applied between the tip and sample and a current of around $5 \,\mu\text{A}$ is set to flow using the z feedback loop. The current leads to a warm up of the tip apex and a re-ordering of the front atoms, which can be observed in the change of z of the feedback control. When a new sensor is transferred into the microscope a field emission of the tip is also necessary. In the electro-chemical etching process of the tungsten tip, during the sensor manufacturing, an oxide layer forms at the tip which is non-conducting. Note that the oxide layer can be also removed by poking the tip a few nanometers into the sample. The field emission method is, however, more effective and yields stable tip conditions faster than the initial poking.

For precise and controlled shaping the tip can be poked. Poking is the controlled drive of the tip a few hundred picometers or a few nanometers into the sample surface. By this either atoms from the surface were picked up and reshape the tip apex or atoms from the tip are dropped on the surface.

After the tip is poked into the surface, its sharpness can be initially judged

by scanning the surface in feedback mode (bias voltage of 10 mV and a current of 100 pA) and looking at the depth of single CO molecules in the topographic line profile. If the depth of the topographic line profile of a CO is around 50 pm most likely a single atom tip persists [61, 62]. If this method indicates a reasonably sharp tip, the tip apex can be characterized in more detail. A lower depth indicates usually a blunter tip. Note that this method works only on Cu(111).

For normal AFM, where the tip oscillates vertically to the surface, the frequency shift can be used as a measure for the tip geometry [61, 62]. If the frequency shift in the STM feedback mode with a bias voltage of 10 mV and a current 100 pA is almost zero, a single atom is most likely present. If the frequency shift is lower a blunt tip persists. A blunt tip has increased attractive van-der-Waals forces due to the larger area on which attractive forces can act.

To identify if the tip apex is terminated with a single-atom tip the CO molecule can serve as a probe to scan the tip apex. This method is called 'carbon monoxide front atom identification' (COFI) [13–16]. In a COFI image the number and position of visible features corresponds to the number and position of the atoms at the tip apex. A detailed explanation of this method on Pt(111) can be found in chapter 5. Figure 3.11(a) shows a LFM COFI image of a single atom metal tip. The image was filtered by a 6×6 pixels Gaussian filter to reduce noise. The oscillation is in horizontal direction. An explanation of the Δf contrast can be found in chapter 4.

When a single-atom tip was identified, it can be functionalized with a CO molecule. The method to functionalize the tip with a CO molecule was introduced by Bartels et al. [63, 64]. To functionalize the tip with a CO molecule the tip has to be positioned above the CO molecule using the STM image. Then with 'feedback on' a bias voltage of 1.0 V and a current of 1.0 nA have to be set. Note that the voltage is positive because the bias voltage in the microscope is applied at the sample. Next, the feedback controller is turned off and the bias voltage is increased in 0.1 V steps and the current signal should be observed. At a bias voltage between 2.3 V to 3.3 V a decrease of the current should be visible. This indicates a jump of the CO to the tip. If the current increases, this indicates that the CO has been laterally manipulated away from the tip-sample junction. A successful transfer of the CO molecule to the tip can be verified by scanning other COs. On Cu(111), in the STM image COs with a CO tip exhibit a bump in the middle (see inset in Fig. 4.7(a)). Or the Δf image can be used to verify a CO tip. Figure 3.11(b) shows a LFM Δf image of a CO on Cu(111) recorded with a CO tip [48]. The oscillation is in horizontal direction. A discussion of normal AFM Δf images of CO on Pt(111) recorded with a CO tip can be found in chapter 6. Normal AFM Δf images of CO on Cu(111) recorded with a CO tip can be found in Ref.[65].

4. Determining amplitude and tilt of a lateral force microscopy sensor

Most of the work presented in this chapter is published in Beilstein Journal of Nanotechnology [66]. Parts of the following text are identical to the publication. The co-authors contributed to the analysis, experimental measurements and writing of the publication.

4.1. Introduction

Frequency modulation atomic force microscopy (AFM) is a non-contact atomic force microscopy technique where the frequency shift (Δf) of an oscillating tip is detected [67]. The frequency shift is a measure of the total force gradient acting on the tip, which includes both long-range and short-range contributions. A typical experimental setup is to study an isolated surface feature, e.g. a defect or an adsorbate, on a flat terrace. In case of "normal" AFM, where the tip oscillates perpendicular to the surface, long-range forces including electrostatic and van der Waals forces contribute to the measured Δf signal, which have to be subtracted in order to isolate the short-range contributions from the surface feature [68]. If the cantilever is rotated by 90° [as illustrated in Fig. 4.1(a)] so that the tip oscillates lateral to the surface, long-range forces with large vertical components do not contribute to the Δf signal [37]. This microscopy technique is called lateral force microscopy (LFM).

One advantage to LFM is that it is highly sensitive to short-range interactions. A drawback is that it is not a suitable technique for approaching a sample or determining the sample tilt. Here a complementary technique such as STM (used in our setup) or biaxial AFM with normal force detection is required.

Experimentally, there are several methods for performing frequency-modulation lateral force microscopy, what is referred to as LFM in this chapter. In 2002 Pfeiffer



Figure 4.1.: (a) Sketch of the qPlus sensor in LFM orientation with amplitude A and the sensor tilt θ . (b) Photograph of a qPlus sensor glued perpendicular on a sensor holder shown by the white substrate.

and co-workers excited a silicon cantilever in the first torsional mode [32]. This has been used to achieve atomic resolution of a sample that is laterally stiff and vertically soft [69]. It has also been used in ultra-high vacuum conditions [70] as well as in liquid to yield atomic resolution [71]. Also in 2002, Giessibl and co-workers performed LFM using a qPlus sensor as shown in Fig. 4.1(b) [33]. In our group, the method is used to quantify molecular stiffness at low temperature [48] and to evaluate the potential energy landscape above a molecule at room temperature [55]. More recently, LFM is used with a CO-terminated tip to investigate the internal structure of a molecular adsorbate [17, 25]. Moreover, other methods include using a long tip on a qPlus sensor that oscillates laterally at a higher flexural mode are also possible [72].

In LFM or normal AFM, the recorded frequency shift Δf is related to the force gradient k_{ts} in the direction of the tip oscillation. For a sensor oscillating in the xdirection, $k_{ts} = -\frac{\partial F}{\partial x} = \frac{\partial^2 U}{\partial x^2}$, where F is the component of force in the x direction and U is the potential energy. In general, the relevant force gradient at a spatial coordinate (x, z) for a tip oscillating at an angle θ with respect to the x direction is:

$$k_{ts}(x,z) = \frac{\partial^2 U(x,z)}{\partial x^2} \cos^2 \theta + \frac{\partial^2 U(x,z)}{\partial z^2} \sin^2 \theta \tag{4.1}$$

The frequency shift is related to the sensor parameters and the weighted average of the force gradient over the tip oscillation, $\langle k_{ts} \rangle (x_0, z_0)$, where x_0 and z_0 define

the average tip position over one oscillation cycle [26]:

$$\Delta f(x_0, z_0) = \frac{f_0}{2k} \langle k_{ts} \rangle (x_0, z_0).$$
(4.2)

 f_0 is the resonance frequency of the sensor away from the surface and k the stiffness of the sensor. The weighted average must also take into account the direction of the tip oscillation:

$$\langle k_{ts} \rangle (x_0, z_0) = \frac{2}{\pi A^2} \int_{-A}^{A} k_{ts} (x_0 - q \cos \theta, z_0 - q \sin \theta) \sqrt{A^2 - q^2} dq,$$
 (4.3)

where A is the oscillation amplitude. Extracting force and potential energy from the measured Δf is a complex inversion problem requiring deconvolution. Several deconvolution methods include a matrix inversion method developed by Giessibl [38], a Laplace transform method developed by Sader and Jarvis [39] and a Fourier method developed by Seeholzer and co-workers [41]. All of these methods require the knowldedge of oscillation amplitude A of the cantilever.

Amplitude determination means determining a calibration factor which relates the recorded amplitude signal of the oscillation in volts to the real oscillation amplitude in meters. At room temperature the thermal excitation of the sensor can be used to calibrate the amplitude [73]. For low temperatures another method has to be used, since the thermal energy to excite the sensor is very small and mechanical vibrations can dominate the excitation [74]. For low temperature LFM the lattice of the substrate can be used to calibrate the amplitude if the periodicity of the lateral features is known [75]. For electrically excited piezoelectric-based sensors, the energy input required to maintain the oscillation amplitude constant can be measured to calculate the calibration factor [76]. Besides these experimental methods, the amplitude can be also calibrated by calculating the electro-mechanical properties of the cantilever [77]. This theoretical method, however, does not take the real geometry of the sensor and electrodes into account. At low temperatures, the most common method is to use STM to calibrate the amplitude, assuming that STM is available and that the sample is conducting. This method is often used for normal AFM, where the cantilever oscillates vertically to the surface, and the current is related to the vertical position z of the tip above the sample, via $I = I_0 \exp(-2\kappa z)$, where I_0 is the current at z = 0 m and κ is the decay constant [78]. For non-conducting surfaces Δf spectra with different oscillation amplitudes can be used [78].

4.1.1. Comparing the effect of tilt on normal versus lateral force microscopy

In addition to the amplitude, the tilt θ of a LFM sensor is of great importance. Usually, θ is ignored in normal AFM experiments because it has a smaller effect on the observed Δf . This can be seen by modelling $\langle k_{ts} \rangle$ of a normal AFM sensor and comparing it to the signal of a LFM sensor. The position of the tip at time tas it oscillates around a point x_0, z_0 is given by

$$x(t, x_0) = A\cos\left(2\pi f t\right)\cos\theta + x_0 \tag{4.4}$$

$$z(t, z_0) = A\cos\left(2\pi f t\right)\sin\theta + z_0 \tag{4.5}$$

where t is the time, θ the tilt of the sensor as defined above and $f = f_0 + \Delta f$. We model the interaction between the tip and a surface feature as a Morse potential:

$$U(r) = E_B\left(\exp\left(-2\frac{r-\sigma}{\lambda}\right) - 2\exp\left(-\frac{r-\sigma}{\lambda}\right)\right),\tag{4.6}$$

where E_B is the binding energy, σ is the equilibrium distance and λ is the decay length. The position of the tip x and z yield the distance to the surface feature $r = \sqrt{x^2 + z^2}$ (i.e. the feature sits at (0, 0)).

We used the following parameters for the Morse potential: $E_B = 100 \text{ meV}$, $\sigma = 500 \text{ pm}$ and $\lambda = 50 \text{ pm}$.

We first calculated the z dependence of $\langle k_{ts} \rangle$ for a tip with no tilt oscillating vertically above the center of the adsorbate. For θ as defined in Fig 4.1(a), being 90°, the calculated $\langle k_{ts} \rangle$ is shown in Fig. 4.2(a) (red dashed curve).

We also calculated $\langle k_{ts} \rangle$ with a small tilt from the vertical so that $\theta = 86^{\circ}$ shown in Fig. 4.2(a) by the blue solid curve. The similarity of the two curves shows that the tilt has little influence on normal AFM data.

We then calculated the x dependence of $\langle k_{ts} \rangle$ for a LFM tip with no tilt, where $\theta = 0^{\circ}$, shown in Fig. 4.2(b) by the red dashed curve at $z_0 = 560$ pm, and contrasted it to the LFM signal with a tilt of $\theta = 4^{\circ}$ shown in Fig. 4.2(b) by the blue solid curve. The tilted LFM signal is strongly asymmetric with one local minimum lower and the other higher. Also the peak at x = 0 pm is slightly shifted.

Figure 4.2(c) shows a vertically oscillating tip following the tip path of the lat-



Figure 4.2.: Simulated Morse potential interaction for LFM setup and comparison to normal AFM. θ is defined by Eq. 4.1 in the main text. (a) Simulated force gradient $\langle k_{ts} \rangle$ of a vertical oscillating tip above an atom with $\theta = 86^{\circ}$ shown by the blue solid curve and without tilt ($\theta = 90^{\circ}$) shown by the red dashed curve. The atom was simulated by a Morse potential. (b) $\langle k_{ts} \rangle$ of a laterally oscillating tip above an atom with sensor tilt $\theta = 4^{\circ}$ shown by the blue solid curve and without ($\theta = 0^{\circ}$) shown by the red dashed curve at height $z_0 = 560$ pm. The height z_0 is defined according to Eq. 4.5. The ratio of the difference between the minima of the curve with tilt and without tilt to the overall curve without tilt is 14.2%. (c) $\langle k_{ts} \rangle$ of a vertically oscillating tip following the path of the lateral oscillating tip at the same height with a tilt ($\theta = 86^{\circ}$, blue solid curve) and without a tilt ($\theta = 90^{\circ}$, red dashed curve). The ratio of the difference between the minima of the curve with tilt and without tilt to the overall curve with tilt and without tilt is 3.3%.

erally oscillating tip from Fig. 4.2(b) at the same height with $\theta = 90^{\circ}$ displayed by the red dashed curve and with $\theta = 86^{\circ}$ displayed by the blue solid curve. The ratio of the difference between the minima of the curve with tilt and without tilt to the overall curve without tilt is 3.3%, in contrast to the ratio of the LFM curves in Fig. 4.2(b) which is 14.2%. This larger difference between the LFM curves shows that sensor tilt is more visible in LFM data.

4.1.2. Effect of amplitude and tilt on the STM signal in LFM

In the following the influence of the tip oscillation and tip tilt on the current signal is demonstrated for LFM. Due to the bandwidth of the STM channel, the recorded signal $\langle I \rangle$ is the average of the current over the motion of the tip [79]:

$$\langle I \rangle (x_0, z_0) = \frac{1}{T} \int_0^T I(x(\tau, x_0), z(\tau, z_0)) d\tau,$$
 (4.7)



Figure 4.3.: Simulating the effect of a laterally oscillating tip with different amplitudes and tilt angles on the STM signal. (a) With no oscillation.
(b) With an amplitude of 500 pm and θ = 0° shown by the blue solid curve, θ = 1° shown by the green dotted curve, and θ = 2° shown by the dashed red curve. With increasing oscillation amplitude two peaks evolve which differ in height in dependence of the tilt angles.
(c) With an amplitude of 900 pm and θ = 0° displayed by the blue solid curve, θ = 1° displayed by the green dotted curve, and θ = 2° displayed by the red dashed curve. With a higher oscillation amplitude the difference of the two peaks increase.

where $T = \frac{1}{f}$ is the period. I(x, z) is the tunneling current at time τ at coordinates x and z of the tip described by Equation 4.4 and 4.5. Consider a surface feature which appears with no oscillation as a Gaussian curve as shown in Figure 4.3(a). With large oscillation amplitudes $(A > \sigma)$ the current curve becomes wider with two maxima, as shown by the blue solid curve in Fig. 4.3(b) for an oscillation amplitude of A = 500 pm. With an amplitude of 900 pm the distance between the maxima increases as shown by the blue solid curve in Figure 4.3(c). If θ is varied and set e.g. to $\theta = 1^{\circ}$ the two local maxima become vertically shifted, one higher and the other one lower as depicted by the green dotted curve in Fig. 4.3(b) and in Fig. 4.3(c). With a tilt of $\theta = 2^{\circ}$ the two local maxima become even more separated as illustrated by the red dashed curve in Fig. 4.3(b) and (c). The differences in current of the local maxima are related to the tilt of the sensor and the horizontal distance depends on the oscillation amplitude.

In this chapter a method is presented to calibrate the amplitude and determine the tilt of the LFM sensor. The method is based on collecting STM data of a surface feature both without and with tip oscillation, as was proposed in Ref [75]. The data without oscillation is used as input to a simulation that calculates expected STM data with oscillation as a function of A and θ . A and θ are then determined by fitting the calculated data to the experimental data. It uses a two-dimensional



Figure 4.4.: Two-dimensional (2D) current map without oscillation and calculated and recorded curve with oscillation. (a) Sketch of the tip taking a 2D dataset of a surface feature (red circle) in different heights z_i . (b) 2D current map of an iron adatom on Cu(111) taken with a metal tip. The dashed white line indicates the current line at z_0 at which the 2D current map is used to calculate the curve with oscillation. The inset shows a constant current STM image of an iron adatom on Cu(111), which is used for the 2D current map. (c) Line profile of a constant height scan of an iron adatom on Cu(111) with oscillation shown by the red solid curve. The fit uses the 2D current map yielding an amplitude $A = 1050 \text{ pm} \pm 2\%$ and sensor tilt of $\theta = 1.59^{\circ} \pm 2\%$ shown by the blue dashed curve.

current map.

4.2. Experimental setup

Measurements were performed with a low-temperature STM/AFM system (CreaTec Fischer GmbH, Berlin, Germany) operating in ultra-high vacuum at 5.6 K equipped with a qPlus sensor [11]. The sensor was equipped with an etched tungsten tip which was repeatedly poked into a Cu(111) surface to generate well-defined tip apex configurations. Cu(111) was cleaned by standard sputtering and anneal cyles. Single iron adatoms were evaporated with home built evaporator onto the cold sample. Carbon monoxide (CO) was leaked in at a partial pressure of 5×10^{-8} mbar for 5 min.

4.3. Determining A and θ with a 2D current map

In the following a method to determine A and θ is presented. As shown before, A and θ influence the shape of the average current signal, $\langle I \rangle$. Initially, the current I above a surface feature is recorded without oscillation, as sketched in Fig. 4.4(a).

In the next step current data acquired with oscillation can be simulated at a given height z_0 , $\langle I \rangle_{A,\theta,z_0,x_{\text{off}}}^{\text{calc}}$ using Eq. 4.7, with A,θ , and x_{offset} as parameters. By varying z_0 , A, θ , and x_{offset} , $\langle I \rangle_{A,\theta,z_0,x_{\text{off}}}^{\text{calc}}$ is fit to the measured $\langle I \rangle$ to determine the amplitude and tilt.

To do this first a full two-dimensional current map without oscillation is acquired, as sketched in Fig. 4.4(a), to measure I(x, z). Figure 4.4b shows I(x, z) above a single iron adatom on Cu(111) taken with a metal tip. The similarity with the simulated curves shown in Fig. 4.3 can be seen. However small discrepancies are visible. The reason for the discrepancies are Cu(111) surface states and nearby COs, which were caputured in the data. The inset in Fig. 4.4(b) shows an STM image of a single iron adatom [13]. The red solid curve in Fig. 4.4(c) shows the current profile $\langle I \rangle$ along a line in x direction over a single iron adatom on Cu(111) with tip oscillation. The blue dashed curve is the fitted $\langle I \rangle_{A,\theta,z_0,x_{\text{off}}}^{\text{calc}}$ yielding for $A = 1050 \,\text{pm} \pm 2\%$ and $\theta = 1.59^{\circ} \pm 2\%$. The difference between $\langle I \rangle$ and $\langle I \rangle_{A,\theta,z_0,x_{\text{off}}}^{\text{calc}}$ was 0.48%.

The tip tilt angle is defined by the tilt relative to the flat sample, as shown in Fig. 4.1(a). Different regions on the sample can have different sample tilts, which would change the relative tip tilt. To account for this, the sample tilt must be accounted for before measuring.

To efficiently determine the best-fit parameters, an automated fitting algorithm was programmed. This algorithm minimizes the least square error between the calculated curve and the recorded curve with oscillation. A common problem when determining the least squares error is to find the global minimum (best fit). Tests with different starting values revealed that the error landscape has many local minima. These local minima have higher least square errors than the global minimum, which can be fitted to a much lower least square error. By defining a low enough error limit e_{LIM} many of local minima with higher least square error can be ruled out. A good start is an $e_{\text{LIM}} = 0.5\%$. To find parameters that can then be used as starting parameters for further runs of the software, for which e_{LIM} can be reduced by 0.1% for each run until an acceptable fit is found. Note that the program will not converge to a solution if e_{LIM} is too small because of noise and factors like drift.

Another problem is the choice of starting values. To try different combinations with equal probability random starting values within a definable interval were generated. Care has to be taken at the definition of the intervals. Our tests showed



Figure 4.5.: Structure of the fitting algorithm to avoid a local minimum: random starting values within definable interval are used to start the first iteration to minimize the least square error for z_0 , A, θ , and offset until the total error $e_{\text{FIT}} < e_{\text{LIM}}$.

that these intervals have to cover the final fitted values for A, θ , and z_0 to find the best fit. Therefore reasonable chosen starting values are necessary. An estimate of the amplitude can be made by considering data with oscillation of a single feature, as sketched in Fig. 4.3. The data will show the feature spread by a lateral extent of approximately 2A. The relative heights of the feature are indicative of the tilt, which can be estimated by comparing to Fig. 4.3(b) and (c).

Fig. 4.5 shows the structure of the fitting algorithm. The outer *while* loop starts the fitting with the random starting parameters as long as the fitted error $e_{\text{FIT}} > e_{\text{LIM}}$.

The parameters are changed in the direction in which the least square error gets smaller. The order in which the parameters are changed has significant impact on the convergence of the error. The x_{offset} parameter is the lateral offset of the calculated curve to the data taken with oscillation. Since a variation of z_0 leads to a higher variation of the least squares error than A or θ or the x_{offset} , z_0 is determined first, then A, θ , and then x_{offset} as it is shown in Fig. 4.5. After this iteration the whole loop is started over again with a higher precision and e_{FIT} is calculated.

The numeric implementation requires a discretization of the oscillation cycle dividing the period T into a number of points. Lower errors can be obtained with a higher number of discretization points up to a certain limit. Our tests showed that a discretization point number of 250 is a good compromise between fitting



Figure 4.6.: Error as a function of A and θ. (a) The blue circles show the calculated error for varying amplitudes. The other parameters such as θ, z₀, and x_{offset} were kept constant. The red curve shows a parabolic fit through the points to estimate the uncertainty of the fitted A and yielded a value of 0.002 pm. (b) The calculated error for varying θ shown by the blue circles. The other parameters as A, z₀, and x_{offset} were kept constant. The red curve shows a parabolic fit through the points to estimate the uncertainty of the fitted a value of 0.002 pm. (b) The calculated error for varying θ shown by the blue circles. The other parameters as A, z₀, and x_{offset} were kept constant. The red curve shows a parabolic fit through the points to estimate the uncertainty of the fitted θ and yielded a value of 0.001°. (c) Amplitude as a function of the drive signal.

accuracy and computation time.

The fitting algorithm yields a very high repetitive accuracy if e_{LIM} is low enough. To test how robust our algorithm is, five fits using starting values is performed in a range of $\pm 30\%$ of the actual values. This led to almost equal values determined by the algorithm for A and θ , depending on the set error. In the case of our fits, $e_{\text{LIM}} = 0.1\%$ is used, which resulted in a spread of A of 0.2%.

To estimate the uncertainty of the fitted A and θ the error is calculated as a function of A and θ as shown by the blue circles in Fig. 4.6(a) and (b). In Fig. 4.6(a) the error as function of the amplitude is shown. The other parameters such as θ , z_0 , and x_{offset} were kept constant. The fitted amplitude value of 1050 pm is indeed a minimum, since the error around this value increases. To calculate the uncertainty a parabolic function is fitted according to $E(A) = a(A-b)^2 + c$ to the data points. a, b and c are the fitting parameters of the parabola. b represents the location of the minimum. The Matlab function "fit" outputs the variation of the fitting parameters with confidence bounds of 95%. From this confidence bounds the uncertainty for b was calculated yielding a very small value of 0.002 pm for the amplitude.

The same procedure was applied to estimate the uncertainty for θ . The blue circles in Fig. 4.6(b) show the calculated error as function of θ . The other parameters as A, z_0 , and x_{offset} were kept constant. The error increases around the fitted



Figure 4.7.: Two-dimensional (2D) current map without oscillation and calculated and recorded curve with oscillation. (a) 2D current map of a carbon monoxide molecule (CO) on Cu(111) taken with a CO adsorbed on the tip (CO tip). The dashed white line indicates the current line at z_0 at which the 2D current map is used to calculate the curve with oscillation. The inset shows a constant current STM image of a CO on Cu(111), which is used for the 2D current map. (b) Line profile of a constant height scan of a CO on Cu(111) with a CO tip with oscillation shown by the red solid curve. The fit uses the 2D current map yielding an amplitude $A = 890 \text{ pm} \pm 2\%$ and sensor tilt of $\theta = 2.00^{\circ} \pm 2\%$ shown by the blue dashed curve.

minimum of 1.59°. The red curve shows a parabolic fit according to the equation $E(\theta) = g(\theta - h)^2 + i$. This yielded also a very small uncertainty for h of 0.001°.

The method inherently yields a very small uncertainty for both the amplitude and tilt. However, it relies upon the x, y calibration of the microscope, which is proposed to be the be the largest source of uncertainty. The position calibration typically has a precision on the order of a few percent, which is why an uncertaincy of 2% is proposed. A similar argument for accuracy holds for the tilt estimate. It relies on the x, y, z and sample tilt calibration and an uncertainty of 2% is estimated.

Figure 4.6(c) shows the amplitude of the oscillation as a function of the drive signal. It is linear, meaning that the calibration amplitude determined for large amplitudes on the order of 1 nm is also valid for amplitudes under 100 pm, where typically high-resolution data is acquired.

To demonstrate that this method can be applied to more complex systems, calibration data was taken of a CO molecule on Cu(111) with a CO tip. When lateral forces act on the CO on the tip and the surface, they tend to act as a

torsional spring and bend [65, 80]. While this makes the signal more complex than that over the Fe adatom [compare Fig. 4.7(b) to Fig. 4.4(c)], the CO bending does not affect the measurements. In general, if CO bending occurs, it is present in the data both with oscillation and without as the CO bends faster than the cantilever moves. At the heights where the amplitude calibration is performed, a LFM signal is not observed, meaning that the lateral forces were anyway insignificant. Also, the excitation frequency of the frustrated translational mode is in the THz range [81, 82] and are not excited by the tip which oscillates in the kHz range.

Fig. 4.7(a) shows the I(x, z) current map without oscillation. In the inset an STM image of a CO with a CO tip is shown [63]. The red solid curve in Fig. 4.7(b) shows the current profile $\langle I \rangle$ along a line in x direction over a CO molecule on Cu(111) with a CO tip. The dashed blue curve in Fig. 4.7(b) is $\langle I \rangle_{A,\theta,z_0,x_{\text{off}}}^{\text{calc}}$ and yielded for $A = 890 \text{ pm} \pm 2\%$ and for $\theta = 2.00^{\circ} \pm 2\%$.

4.4. Conclusion

A method of determining the oscillation amplitude and tilt of a LFM sensor was presented by analyzing the tunneling current above a surface feature. The method requires a 2D current map without tip oscillation and an isolated line profile with oscillation. It fits a calculated averaged current curve, which considers the tip oscillation to a constant height current curve with oscillation to determine A and θ . The method can be applied in principle to any surface feature like e.g. a commonly used PTCDA molecule or a surface defect. The fitting of the parameters for the 2D current map method was done by a fitting algorithm written in MATLAB, and details of the algorithm were explained. MATLAB files are included in the supplemental.

5. CO on Pt(111) investigation with normal AFM

Most of the work presented in this chapter is published in Physical Review Research [16]. Parts of the following text are identical to the publication. The coauthors contributed to the analysis, experimental measurements and writing of the publication.

5.1. Introduction

Single carbon monoxide (CO) molecules have been used widely as tip terminations in high spatial resolution scanning tunneling microscopy (STM) [63] and particularly in atomic force microscopy (AFM) [83]. Picking up a single CO molecule at the end of a metal tip (forming a CO-tip) has enabled submolecular resolution with frequency-modulation atomic force microscopy (FM-AFM). CO-tips have also been used in STM to achieve intramolecular resolution [84, 85].

Conversely, when single CO molecules are adsorbed on a metal surface, they can be used to identify the number, configuration and, with limitations, the chemical species of front atoms at the tip apex [13, 14, 86, 87]. This technique is called carbon monoxide front atom identification (COFI) [13, 14, 86]. Understanding the apex of the probe tip is essential to interpreting high resolution images and comparing observations to simulation in STM, inelastic electron tunneling spectroscopy [88] and FM-AFM [89].

In the first publication about COFI by Welker et al. in 2012, a single CO molecule on Cu(111) imaged a metal tip [14] and the attractive features separated by several Angstroms in the FM-AFM image were initially interpreted as a reflection of the crystal orientation of a single atom at the tip apex [14]. In a follow-up article using COFI, Hofmann et al. analyzed force-distance curves and showed that a Cu front atom at the apex could be clearly discriminated from a W or Fe

front atom [87]. In 2014, Gao et al. and Schwarz et al. investigated CO adsorbed on NiO(100), asserting that multiple features separated by several Angstroms indicated a tip that terminated in multiple atoms, where each feature represented an atom at the apex [90, 91]. In 2015, Emmrich et al. imaged both small iron clusters on Cu(111) with a CO tip and the inverse system, concluding that the multiple attractive features in the FM-AFM channel indicate tip apexes ending with multiple atoms [13] and correcting the initial interpretation of a correspondence of multiple extrema to the crystallographic orientation of tip's front atom in Ref. [14]. Our current understanding is that when an adsorbed CO molecule is imaged with FM-AFM, the small and sharp CO molecule (the O atom has only 40% of the diameter of a typical metal atom) probes the number and configuration of atoms at the apex of a metal tip. The dangling bonds of the adatoms of Si(111)-(7×7) have also shown to create similar images of multi-atom metal tips as CO/Cu(111) [86].

If COFI is performed on CO adsorbed to Cu(111), single Cu or Fe atom tips appear in FM-AFM images as attractive features with a repulsive ring around them, while e.g. Si tip atoms would appear as single repulsions [35]. Individual atoms at the tip apex can be directly observed in the raw FM-AFM image, but not in the raw STM images [14, 87].

5.1.1. STM of CO on Cu(111) vs Pt(111)

Figures 5.1(a) and (b) compare STM images of a CO adsorbed on Cu(111) and Pt(111). On Cu, a wide trough in the conductance over the adsorbate is observable, whereas on Pt a narrow peak in the conductance appears over the adsorbed CO. For the data shown in Figs. 5.1(a) and (b), the full width at half maximum of the trough on Cu(111) is 555 pm, shown in Fig. 5.1(c), and the peak on Pt(111) is 365 pm, shown in Fig. 5.1(d). It is suggested that the stark difference of the STM contrast of CO on Cu(111) versus Pt(111) is due to the presence of a surface state with a high density of states on Cu(111) [92]. A simple estimate shows that the density of states of the surface state at the Fermi energy reaches 119% of the bulk value for Cu(111), while Pt(111) has an empty surface state [93].

In STM, the tunneling matrix element contains the density of states of the tip and the density of states of the sample. If the sample has an occupied surface state at the Fermi energy as in Cu(111), the density of states at the Fermi level, E_F , of the bulk states and the surface states have to be considered. Figure 5.1(e) shows a sketch of the density of states for Cu of the bulk (3D) and of the surface states (2D). Generally, the density of states of a three-dimensional electron gas as a function of energy, $D_{3D}(E)$, and of a two-dimensional electron gas, $D_{2D}(E)$, can be written as follows [94]:

$$D_{3D}(E) = \frac{(2m_{3D}^*)^{3/2}}{2\pi^2\hbar^3}\sqrt{E}$$
(5.1)

$$D_{2D}(E) = \frac{m_{2D}^*}{\pi \hbar^2 L_z}$$
(5.2)

where m_{2D}^* denotes the effective mass of the electrons in the surface state and m_{3D}^* is the effective mass for the bulk electrons. L_z is the thickness of the surface state, yielding the same unit for both $D_{3D}(E)$ and $D_{2D}(E)$ of number of states per volume (m³) and energy (J).

The thickness of the surface state can be estimated by its vertical decay length $\lambda = 1/\kappa$, via the work function, ϕ : $L_z \approx \lambda = 1/\kappa = \hbar/\sqrt{2m_e\phi}$. $D_{2D}(E)$ can then be written:

$$D_{2D}(E) = \frac{m_{2D}^* \sqrt{2\phi m_e}}{\pi \hbar^3}$$
(5.3)

If the ratio of the density of states at the Fermi level (which is significant for STM at low bias voltages) is calculated, $D_{2D}(E_F)/D_{3D}(E_F)$, yields:

$$\frac{D_{2D}(E_F)}{D_{3D}(E_F)} = \pi \frac{m_{2D}^* \sqrt{m_e}}{(m_{3D}^*)^{3/2}} \left(\frac{\phi}{E_F}\right)^{1/2}.$$
(5.4)

In the case of Cu(111) $m_{2D}^* = 0.46 m_e$ [96], $m_{3D}^* = 1.01 m_e$ [97], $\phi = 4.94 \text{ eV}$ [29], and $E_F = 7.04 \text{ eV}$ [94]. In absolute numbers, the bulk density of states are $D_{3D}(E_F) = 1.16 \times 10^{47} \text{ states}/(\text{m}^3\text{J})$ or 0.22 states per atom and eV. The absolute surface density of states is $D_{2D}(E_F) = 1.38 \times 10^{47} \text{ states}/(\text{m}^3\text{J})$ or 0.26 states per atom and eV. Surprisingly, the density of states at the Fermi level for Cu is larger for the surface state than for the bulk states with a ratio of $D_{2D}/D_{3D} = 1.19$. Therefore, the surface states provide a larger contribution to the STM images of bare Cu(111) at low bias than the bulk states, giving rise to the typical standing wave images [98]. On Cu(111) an adsorbed CO molecule apparently repels the surface state, leading to the wide trough in the STM image [99]. For some tips, the CO molecule in the center of the trough even shows up as a small local peak (see Fig. 1E in Ref. [100]). The through-molecule current on Cu(111) can sometimes



Figure 5.1.: Constant-height STM images of CO on Cu(111) with bias 10 mV (a) and Pt(111) (b) with bias 1 mV. Corresponding line profiles of (a) and (b) are plotted in (c) and (d), indicating the evaluated full-width at half maximum as an estimate of the feature width. (e) Schematic plot of the density of states (DOS) for Cu bulk (see, e.g., fig. 6 in [95]) and for the surface states of Cu(111) (2D). The bulk DOS of Cu relates nicely to the electronic states of the free Cu atom. The valence shell configuration of Cu is given by $3d^{10}4s^1$, and the large DOS from about 1.3 eV to about 4.6 eV below the Fermi level are due to the ten 3d electrons per atom that constitute the 3d bands, while the conduction band that ends at the Fermi level originate from atomic 4s states. The 3d-states are included in this sketch for completeness, although they are fully occupied and do not affect the density of states at the Fermi level. The surface state provides 0.26 states per surface atom and eV, while the 4s-conduction band bulk states only provide 0.22 states per atom and eV.

be made visible by Laplace filtering the current data (see Figs. 2A,C and E in Ref. [14]).

On Pt(111), the through molecule tunneling dominates and the conductance is higher over a CO molecule than over the bare Pt(111) surface. [101]

As on Cu(111) on Cu(110) an adsorbed CO appears as a trough in the STM image. Some metal tips do show surface states and some tips do not [102]. The ratio of the density of surface states to the density of bulk states on Cu(110) is $D_{2D}/D_{3D} = 0.66$ with $\phi = 4.48 \text{ eV}$ [29], and $m_{2D}^* = 0.27 m_e$ [103]. Therefore the density of states is lower at the surface than in the Cu bulk near E_F , indicating a suppression of more bulk states than surface states by an adsorbed CO.

Here, simultaneous STM and FM-AFM is used to image isolated CO molecules adsorbed on the Pt(111) surface with metal tips. For certain tips several attractive features in the FM-AFM images are observed, which is associated to multiple atoms at the apex, as on Cu(111) [13].

Surprisingly, also corresponding high-conductance features in the STM images are observed which are assigned to the individual atoms of the apex. These highconductance STM features can be reproduced by approximating the tunneling current by *s*-waves at the position of each tip atom. This finding opens the possibility of characterizing tips at the atomic scale with STM using CO molecules adsorbed on Pt(111).

5.2. Experimental setup

Measurements were performed with a combined low temperature UHV FM-AFM and STM (CreaTec Fischer GmbH, Berlin, Germany) operating at 5.6 K in ultrahigh vacuum equipped with a qPlus sensor [11] (spring constant k = 3627 N/m, frequency $f_0 = 35\,813.6$ Hz and quality factor $Q = 29\,439$). All experiments were performed with an amplitude of A = 50 pm. The sensor was equipped with a tungsten tip which was repeatedly poked into the Pt(111) surface to generate different tip apex configurations.

The Pt(111) surface was cleaned by several sputtering (Ar-ions at 1.2 keV) and annealing (1300 K) cycles. The final anneal cycle was performed at 1070 K to reduce the diffusion of natural contaminations like carbon from the bulk to the surface. CO was leaked in at a partial pressure of 5×10^{-8} mbar for 5 min.

After a tip apex of interest was identified, three-dimensional frequency shift Δf

and current I datasets were collected by acquiring sets of constant-height images. First, an isolated CO adsorbate was identified. Then the molecule is approached in 10 pm steps until the CO laterally moved. Subsequently, the tip was retracted 10 pm and the closest scan was acquired.

After each image, the tip-sample distance was increased by 10 pm until no Δf contrast was detected. From the three-dimensional Δf datasets, the normal force F_z was evaluated using the method introduced by Sader and Jarvis [39].

5.3. Experimental results and discussion

Figures 5.2(a-f) show I and F_z images at z = 340 pm, 220 pm, and 150 pm for a single-atom tip. Figure 5.2s is a sketch of a single-atom tip and a CO. The zero point z = 0 pm is defined by the tunneling conductance at point contact of $(12906 \Omega)^{-1}$ at the lower turnaround point of the tip [104].

In Fig. 5.2(a), at $z = 340 \,\mathrm{pm}$, the CO molecule appears as a single circular attractive feature. Closer to the surface at $z = 220 \,\mathrm{pm}$, the attractive features increase in intensity: The force minimum decreases to -150 pN. On the left side of the force minimum, a repulsive feature with a magnitude of $+22 \,\mathrm{pN}$ emerges. At further distance reduction to $z = 150 \,\mathrm{pm}$, shown in Fig. 5.2(c), the force image for the single atom tip becomes quite complex. A new repulsive feature emerges at the center, and the repulsive feature on the left-hand side appears as a crescent. The complex shape of single metal adatoms adsorbed on Cu(111) has recently been explained by Huber et al., who acquired data of a single Si-, Cu- and Fe adatoms on Cu(111) with a CO-tip [35] and found that for the metal adatoms, strong hybridization between CO and the metal adatoms can occur. They report similar data to Fig. 5.2(c): A repulsive ring, surrounding an attractive inner ring and a repulsive feature in the center. The ring turns into a crescent when the tip is slightly tilted, as explained in the context of Fig. S6 in Ref. [35]. DFT calculations show that the repulsive ring with an attractive center is a complex phenomenon: Pauli repulsion between the CO tip and the Cu adatom prevails at the circumference, while for a CO tip that is exactly above the Cu adatom, hybridization occurs that leads initially to attraction, followed by Pauli repulsion for even smaller distances (see Fig. S3 in [35]).

The STM images for the single-atom tip shown in Figs. 5.2(d,e,f) are much easier to interprete. For all three heights a single feature of higher conductance can be



Figure 5.2.: (a-f): COFI of a single-atom tip at three different heights on Pt(111). F_z at (a) z = 340 pm, (b) z = 220 pm, (c) z = 150 pm. I at (d) z = 340 pm, (e) z = 220 pm, (f) z = 150 pm with bias voltage 1 mV. COFI of (g-l) a two-atom tip and (m-t) a three-atom tip: F_z at (g) z = 340 pm, (h) z = 220 pm, (i) z = 150 pm. I at (j) z = 340 pm, (k) z = 220 pm, (l) z = 150 pm with bias voltage 2 mV. F_z at (m) z = 340 pm, (n) z = 220 pm, (o) z = 150 pm. I at (p) z = 340 pm, (q) z = 220 pm, (r) z = 150 pm with bias voltage 2 mV. The bottom row is a schematic view of the CO on the surface and the single (s) -, two (t)- and three (u) - atom tips.

seen, with almost identical lateral sizes. A discussion of the line profiles far and close to the CO will be done later.

Figure 5.2(g-r) shows I and F_z images of tips ending in two and three atoms. Figures 5.2(s), (t) and (u) show schematic views of single-, two- and three-atom tips. At a height of z = 340 pm, the two-atom tip appears as a single elongated attractive feature, shown in Fig. 5.2(g). At z = 220 pm, in Fig. 5.2(h), two distinct attractive features can be observed. Finally, at the closest approach, these two features are separated by a repulsive force ridge of 70 pN, shown in Fig. 5.2(i). As discussed previously, these two features indicate a two-atom tip [13, 14, 90]. The STM images of the two-atom tip can be seen in Fig. 5.2(j-l). Here the two features at z = 150 pm can be clearly made out.

Figures 5.2(m-o) show F_z images of a three-atom tip. The vertical forces show a similar progression upon approach: At z = 340 pm (Fig. 5.2(m)), a single attractive feature is observed and at z = 220 pm (Fig. 5.2(n)), three distinct features start to emerge, which are more distinct at z = 150 pm (Fig. 5.2(o)).

Figures 5.2(p-r) display the tunneling current image of the three-atom tip. At the closest distance in Fig. 5.2(r), three distinct features can be identified. The STM images in Figs. 5.2(l) and (r) are markedly different from data of CO molecules adsorbed on Cu(111) reported in Ref. [14]. On Cu(111), at low bias, STM images of CO molecules with a metal tip do not reveal individual atoms of the tip apex. The STM data must first be processed (e.g. by subtracting a Gaussian fit to the large depression as done in Fig. 2 of [14] before atomic features can be seen. On Pt(111), the number and orientation of the atoms at the tip apex can be identified in both the FM-AFM and STM channels when scanning a metal tip over a single CO molecule.

Comparing the I and F_z data at closest approach for the two-atom tip (Fig. 5.2(i) and (l)) and three-atom tip (Fig. 5.2(o) and (r)), it can be seen that the atomic features with a greater attractive force do not necessarily correspond to one with higher conductance. The two attractive features in Fig. 5.2(i), each corresponding to one of the two atoms at the tip apex, have slightly different minima, with the one on the left having greater attraction. Similarly, the STM image at the same height (Fig. 5.2(l)) shows that the atom on the left has higher conductance. This pattern is not observed for the three-atom tip, where the lower-left atom has the least attraction, as can be seen in Fig. 5.2(o), and yet the highest conductance, shown in Fig. 5.2(r). Indeed, there are further datasets of mutiple-atom tips, which



Figure 5.3.: A second two-atom tip dataset (a) STM image with a bias voltage of 4 mV. (b) Line profiles of the conductance and vertical force. (c) Corresponding vertical force image. The global maximum of the conductance line profile does not lie on top of the global maximum of the vertical force line profile.

do not show this trend.

A second two-atom tip apex is shown in Fig. 5.3. A line profile through the current and force is plotted in Fig. 5.3(b). There are two local minima in the force curve: Over the global minimum, the current is not maximal. The current reaches its global maximum over the second local minimum. To conclude the atomic features do show a local maximum in I and local minimum in F_z , but that the intensity is a function of the tip shape and the higher-lying atomic layers, which are not accessible.

In order to check for possible cross talk between current and force, two data sets at the same height were compared. In Fig. 5.4 where the voltage and thus the current is doubled on the right column to 2 mV and about 3.6 nA with respect to the left column from 1 mV and about 3.5 nA respectively, showing similar COFI images in both the FM-AFM channels (top row) and STM channel.

The focus is now on the major difference between our STM data and previously published data of a CO adsorbed on Cu(111): The atomic resolution visible in the raw I images. Why is each atom clearly resolved when scanning over a single CO molecule on the Pt(111) surface, while this is not possible on Cu(111)? Possible reasons include the higher lateral stiffness of CO on Pt(111) or a different orbital electron tunneling contribution of the CO.



Figure 5.4.: Comparison of frequency shift Δf (top row) and constant height STM current (bottom row) of two different one-atom tips at a bias voltage of 1 mV (left column) and 2 mV bias (right column).

5.4. Influence of CO bending

It is well-known that the flexibility of the CO molecule can affect FM-AFM images [43, 83]. Persson previously presented the idea of considering the frustrated translational mode as the CO moving like a torsional spring[105]. Modelling the CO as a torsional spring has been an important component in understanding FM-AFM data with a functionalized tip [14, 34, 48, 106]. The frustrated translational mode of CO is 5.94 meV[107, 108] on Pt(111) compared to 4.2 meV[81] on Cu(111). This results in an effective lateral stiffness of a single CO molecule of 3.6 N/m on Pt(111) versus 1.7 N/m on Cu(111) as it can be shown by the following calculation.

CO adsorbed on Pt(111) or Cu(111) can be described by a torsional spring constant D and bending angle ϕ and the following differential equation as referenced in Ref [14] supplemental:

$$(m_C(r_{Cu} + r_C)^2 + m_O(r_{Cu} + 2r_C + r_O)^2)\ddot{\phi} = -D\phi, \qquad (5.5)$$

where r_{Cu} , r_C , and r_O are the covalent bonding radii of Cu, C and O (128, 77 and 66 pm) [14]. By using the energies of the frustrated translational modes ($E_{Pt} =$



Figure 5.5.: (a) Force line profiles of single atom tips at heights with equal force minimum. (b) Line profiles of the current before (blue curve) and after (red curve) correction of lateral distortion

5.94 meV and $E_{Cu} = 4.2 \text{ meV}$ [81, 107, 108]), $\omega = E/\hbar$, as well as the relation for the lateral stiffness $k_{CO} = \frac{D}{(l_{CO})^2}$ [48], where l_{CO} is the distance between the center of the surface atom and the oxygen atom of the CO, the lateral stiffness k_{CO} can then be calculated by

$$k_{CO} = \frac{\omega (m_C (r_{Cu} + r_C)^2 + m_O l_{CO}^2)}{l_{CO}^2}$$
(5.6)

which results in values of 3.6 N/m on Pt(111) and 1.7 N/m on Cu(111).

One method to investigate the effect of CO bending on the FM-AFM data is to compare linescans of force of a single atom tip between a CO adsorbed on Cu(111) and on Pt(111), shown in Fig. 5.5(a). As expected, given the larger stiffness of CO on Pt(111), the width of the line profile is smaller than for the force profile on Cu(111).

5.4.1. Influence of CO bending on the STM image

To characterize the effect of bending of the CO molecule on the STM data, the lateral forces from the FM-AFM data with a method utilized in [100] were extracted. For the two-atom tip, the maximum lateral force is 79 pN, which corresponds to a lateral displacement (with the lateral spring constant of 3.6 N/m) of 22 pm. For the three-atom tip shown in Fig. 5.2(o), the maximum lateral force is 93 pN, which corresponds to a lateral displacement of 26 pm.



Figure 5.6.: (a) the raw two-atom STM image, (b) the corrected STM image and (c) the vector field of the lateral forces.

To quantitatively study the influence of CO bending during the acquisition of the STM images, every pixel in the STM image according to the lateral displacement vector, calculated by the lateral forces and the CO stiffness were extracted.

Therefore, every pixel (x,y) in the STM image was displaced by a displacement vector $\vec{X}(x,y)$. Using the lateral forces $F_x(x,y)$, $F_y(x,y)$, the stiffness k_{CO} , and Hook's law, the displacement vector $\vec{X}(x,y)$ can be calculated by

$$\vec{X}(x,y) = \frac{1}{k_{CO}} \begin{pmatrix} F_x(x,y) \\ F_y(x,y) \end{pmatrix} = \begin{pmatrix} q_1(x,y) \\ q_2(x,y) \end{pmatrix}.$$
(5.7)

 F_x , F_y were calculated by taking the derivatives $-\partial U/\partial x, y$ of the deconvoluted potential energy U(x, y) at z = 150 pm. $k_{CO} = 3.6$ N/m as calculated for CO on Pt(111) in the beginning of chapter 5.4. For e.g. a two-atom tip each pixel at (x, y) of the STM image (Fig. 5.6(a)) was displaced by (q_1, q_2) and a new image was generated as depicted in Fig. 5.6(b). The differences are marginal and the STM image became more fuzzy. However the overall shape remains unchanged. By plotting the lateral forces F_x and F_y as a vector field, the magnitude and directions of the lateral forces can be seen (Fig. 5.6(c)). The highest lateral forces do not lie above the current maxima.

Figure 5.5(b) displays a linescan of the STM data of the two-atom tip of both the raw data and the data corrected for the lateral displacement. The distance between the maxima is reduced from 225 pm to 211 pm, but the overall change to the profile is minimal.

A second demonstration that CO bending has a minimal effect on the STM signal is to compare the normalized current profile of a single atom tip far from the



Figure 5.7.: Normalized line profiles of the STM images of a single-atom tip from Fig. 5.2(d)-(f).

surface, where the bending is negligible, to the current profile close to the surface.

The similarity of the two current profiles (shown in Fig. 5.7) shows that CO bending does not affect the STM image significantly.

Is it, however, possible that the softer CO on Cu(111) "smoothes out" the STM image of two-atom or three-atom tip, thus preventing atomic resolution in the raw STM image? The short answer is no: The raw data of two- and three-atom tips from Ref. [14] was analyzed and maximum lateral forces of 41 pN for the two-atom tip and 52 pN for the three-atom tip were found. With a lateral stiffness of CO on Cu(111) of 1.7 N/m, these lateral forces correspond to a lateral displacement of 24 and 31 pm, respectively, which are quite similar to the case of CO on Pt(111). Hence, they do not significantly alter the STM channel. This can also be seen in Ref. [14], Fig. 1 in which constant-height STM images are presented at various tip-sample distances. At further distances, the lateral forces are negligible, and yet the STM images do not drastically change.

Therefore the resolution in the STM images on Pt(111) is not a result of a stiffer CO, but rather is due to more localized electron tunneling.

5.5. Through molecule current

In order to demonstrate the through molecule current contribution, the STM images of a two- and three-atom tip were modelled, and it was assumed that the tunneling through each atom is dominated by s-waves.

To do this, the tunneling current can be modelled by a sum of s-states[28]:

$$I(x, y, z) \propto \sum_{i} \frac{1}{\kappa r_i} e^{-\kappa r_i}$$
(5.8)

where *i* represents each atom at the tip, κ is the tunneling decay rate over the CO. The length of the vector from the surface to the tip atoms is given by $r_i = \sqrt{(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2}$, where x_i and y_i indicate the positions of the individual atoms evaluated from the STM images in Figs. 5.2(1) and (r). The height z_1 was set to 0 pm and images were evaluated at z = 150, 220, and 340 pm describing the height of the metal tip above the CO molecule. This is a larger tip-sample distance than determined by the quantum point contact method but yielded better agreement with the data. The decay rate κ was determined by fitting $I(z) \propto \exp(-2\kappa z)$ at the position of the current maxima for each tip in the closest STM image. For the two-, and three-atom tip this yielded values for κ of $1.15 \times 10^{10} \,\mathrm{m}^{-1}$ and $1.25 \times 10^{10} \,\mathrm{m}^{-1}$, respectively.

The resulting modelled images for the two-atom tip are shown in Fig. 5.8(a-c). Here the atomic resolution at the closest image can clearly be seen. The intensity difference between the atoms is included in this model, by setting the height of the second atom to $z_2 = z_1 + 12$ pm. At a larger distance, the two distinct features are no longer distinguishable as evident in Figs. 5.8(a) and (b).

Also the STM images for the three-atom tip were modelled, shown in Figs. 5.8(df). Here, the atomically resolved features at the closest image can be observed (Fig. 5.8(f)). The intensity difference could again be reproduced by a 12 pm offset of the positions of z_2 and z_3 relative to z_1 . For greater tip-sample distances, the atomic features become less distinct as shown in Figs. 5.8(d) and (e). Although this model does not take the tunneling into the surface into account, it nonetheless reproduces the STM contrast shown in Fig. 5.2(1) and (r).

5.6. Conclusion

In conclusion, it was shown that the atomic structure of the tip can be revealed by STM when probing CO/Pt(111) in contrast to CO/Cu(111), where AFM is needed to clearly resolve the tip apex. This feature rests on the highly localized conductance through the adsorbed molecule that in the case of CO/Pt(111), and

5.6. Conclusion



Figure 5.8.: Calculated STM images at three different heights 340, 220, and 150 pm (left to right). (a - c) Calculated STM images of a two-atom tip. (d - f) Calculated STM images of a three-atom tip. Values are normalized and relative to the maximum of the measured STM images.

the increased stiffness of the CO on Pt(111) is not the origin of the higher STM resolution. On Cu(111), an adsorbed CO appparently repels the surface states, which leads to a wide trough in the STM image. The higher density of states of the surface states at Fermi level on Cu(111) compared to the bulk states (ratio of $D_{2D}/D_{3D} = 1.19$) illustrate the dominating contribution of the surface state to the STM image. By simulating STM images on Pt(111), it was able to show that the images of two-atom and three-atom tip apexes could be reproduced by considering *s*-waves at the position of each tip atom. In this system, the number and orientation of atoms at the apex of a metal tip can be quantified in raw STM images, allowing straightforward characterization of the tip apex in SPM experiments.

6. CO on Pt(111) investigated with a CO terminated tip

In the last chapter CO on Pt(111) with a metal tip was investigated. In this chapter CO on Pt(111) with a CO terminated tip will be discussed. The method to terminate the tip apex with a CO molecule was first introduced by Bartels et al. in 1997 [63] leading to higher spatial resolution 12 years later and enabling the resolution of the chemical structure of a molecule with normal AFM¹ [83]. CO tips can be also used to probe molecular bonds by inelastic electron tunneling [84], or it can be used to discriminate bond orders [34]. In 2009 Sun and co-workers studied an individual CO on Cu(111) with a CO tip, coming to the conclusion that at close distances the CO's bend away from each other due to Pauli repulsion [80].

The conductance of a CO on Cu(111) with a CO tip at different heights is very characteristic: At far distances a depression with a small protrusion in the center is visible (Fig. 5(a) in Ref. [65]). At intermediate distances the protrusion is increased with a dark ring around it, and at close distances a deformed ring shape with two dark spots at the center can be seen, where one spot is larger than the other. On Pt(111) CO appears as a protrusion instead as a depression in STM. Further, the CO on Pt(111) has a higher lateral stiffness than the CO on Cu(111) (see Ch. 5). This results in different STM images of a CO on the Pt(111) surface with a CO tip compared to Cu(111).

In this chapter the STM and normal AFM images of CO on Pt(111) recorded with a CO tip will be investigated as well as the potential energy between the CO's [see Fig. 6.1]. To demonstrate the influence of CO bending on the STM contrast an STM image of a group of 5 CO's on Pt(111) is discussed and a probe particle simulation is performed from which the bending angles of the tip CO are calculated (see section 6.1). Then, conductance spectra at different lateral positions of an individual CO are discussed (see section 6.2). To explain these spectra a combined

¹Normal AFM is when the tip oscillates vertically to the surface (see Ch. 2).

hard sphere (HS) and tight binding (TB) model will be introduced and conductance spectra were simulated (see section 6.3). The model takes into account CO bending and assumes the conductance to be determined by the geometry of s and p orbitals. The model showed qualitatively a good agreement with the data, but does not consider the change of the density of states (DOS) of the CO's when they interact, nor the change of the DOS of the metallic surface or tip atom, when the CO's bend. Therefore, density functional theory (DFT) calculations were performed and the structure relaxation constraints are discussed and the conductance curves, which did not show a good agreement with the data (see section 6.4). Therefore, geometries were generated using a Morse potential as described in Ref. [48] for the CO-CO interaction. These conductance calculations are currently the subject of further investigation.

In the following the STM and AFM images will be discussed, but to relate the height of the images to a reference point the potential energy curve will be discussed first. Figure 6.1(a) shows the potential energy E_{Pot} between the CO's as a function of the height². E_{Pot} was calculated with the Sader-Jarvis method [39]. $\Delta z = 0$ refers to the height at the energy minimum of the CO's. The next two rows in Fig. 6.1 show STM and normal AFM images of a CO on Pt(111) with a CO tip at different heights. The left column Fig. 6.1(b,c,d) is far from the surface at $\Delta z = 100$ pm. The second column Fig. 6.1(e,f,g) is at $\Delta z = 0$ pm, the next column Fig. 6.1(h,i,j) is at $\Delta z = -100$ pm, and the last column Fig. 6.1(k,l,m) is at the closest height at $\Delta z = -200$ pm. The STM and AFM images are parts of a 3D dataset. A 3D dataset is series of images with height differences of 10 pm. The bias voltage was 10 mV. The oscillation amplitude was 50 pm. The images were smoothed by a 2.5 × 2.5 pixels Gaussian filter to reduce the noise.

Figure 6.1(b) shows the conductance at $\Delta z = 100$ pm. A circular increase can be seen. Figure 6.1(c) shows the corresponding Δf image. A small attractive feature is visible with a slightly visible repulsive crescent on the left side of the attractive feature.

At $\Delta z = 100 \text{ pm } E_{\text{Pot}}$ is negative [see Fig. 6.1(a)] indicating an attractive interaction of the CO's. The attractive interaction between the CO's leads to a vertical alignment as shown in Fig. 6.1(d). On Cu(111) the STM image at a height where the frequency shift shows an attractive feature is different: the conductance has a

²The x, y position of potential energy calculation was the maximum of repulsive feature in the Δf image shown by the blue cross in Fig. 6.1(l)



Figure 6.1.: (a) E_{Pot} as function of the height. Next two rows: STM and normal AFM images at different heights. Frist left column (b,c,d) at $\Delta z = 100 \text{ pm}$, second column (e,f,g): $\Delta z = 0 \text{ pm}$, third column (h,i,j): $\Delta z = -100 \text{ pm}$, fourth column (k,l,m): $\Delta z = -200 \text{ pm}$. $\Delta z = 0 \text{ pm}$ is set to the energy minimum between the CO's [shown in (a)]. Top row: STM images of a CO on Pt(111) with a CO tip and at a bias voltage of 10 mV. Second row: Corresponding normal AFM images with an oscillation amplitude of 50 pm. Third row: Interaction model of the CO's. Oxygen is represented as red and carbon as dark gray atoms. The colored dots in (k) show the positions where the conductance spectra were taken. The Δx values are given in the top right box. $\Delta x = 0 \text{ pm}$ refers to the minimum of the reduced conductance feature in (k). The blue cross in (l) indicates the position where the potential energy spectrum was calculated.

depression above the CO's (Fig. 5(a) in Ref. [65]).

Figure 6.1(e) shows the conductance at $\Delta z = 0$. Still, a circular increase is visible. The Δf image is shown in Fig. 6.1(f) and is more complex. A repulsive center with an attractive crescent on the right side and a repulsive crescent on the left side is visible. The potential energy between the CO's at $\Delta z = 0$ is negative [see Fig. 6.1(a)]. This indicates a vertical alignment of the CO's as shown by Fig. 6.1(g). The origin of the attractive and repulsive crescent [shown in Fig. 6.1(f)] is most likely due to a tilted CO tip. If the CO on the tip would not be tilted this would lead to an attractive ring surrounded by a repulsive ring. The repulsive center surrounded by an attractive and repulsive ring gives also indications for a hybridization of the CO's similar as shown in Ref. [35]. In Ref. [35] they acquired Δf images of a individual Cu-, and Fe adatoms on Cu(111) with a CO tip and found that weak hybridization can occur between the CO and the metal adatom. As explained in the context of Fig. S6 in Ref. [35] they observed a repulsive ring, surrounding an attractive inner ring and a repulsive center.

Figure 6.1(h) shows the conductance at $\Delta z = -100 \text{ pm}$. A ring shape can be made out. The inside of the ring shows a lower conductance, when compared to the conductance over the surface. Also the outside of the ring exhibits a reduced conductance relative to the surface conductance. In Fig. 6.1(i) the corresponding normal AFM image is shown. A large repulsive ring with an attractive crescent on the right side is visible. The center exhibits a lower frequency shift than the ring. The asymmetry of ring structure is most likely caused by a tilted CO tip as stated above. The Δf image is similar to CO on Cu(111) with a CO tip as shown by Fig. 5(f) in Ref. [65]: A repulsive ring, with an attractive center and crescent. E_{Pot} at $\Delta z = -100 \text{ pm}$ is positive as it can be seen in Fig. 6.1(a). This indicates repulsive interaction of the CO's as shown by Fig. 6.1(j).

Figure 6.1(k) shows the conductance at closest approach ($\Delta z = -200 \text{ pm}$). A distinct reduced conductance in the center of a ring can be made out. The hexagonal structure of the Pt(111) surface is visible by bright dots. The colored dots and the magenta colored square are positions where conductance spectra were taken. These will be discussed later. The normal AFM image is shown in Fig. 6.1(1). The repulsive ring is more extended and the attractive center became more pronounced. On the left and right side of the repulsive ring attractive crescents can be seen. The potential energy between the CO's at this height is even more positive (40 meV) indicating a even stronger repulsion of the CO's as indicated in Fig 6.1(m).


Figure 6.2.: (a) STM image of an island of 5 CO's on Pt(111) imaged with a CO tip. (b) 2D plot of CO bending angles simulated by the probe particle model of a CO island. The bending angles were inverted for a better comparison with the experimental data.

6.1. CO island

To demonstrate the relation of the conductance with the bending angle of the CO at the tip, a group of 5 CO molecules on Pt(111) was investigated. Figure 6.2(a) shows a STM image (constant height) of a group of 5 CO's on Pt(111) imaged with a CO tip. The bias voltage was 10 mV and the image is part of a 3D dataset. Spots with lower conductance above the center of CO's compared to the surface conductance can be made out. Between the CO's dark lines can be seen.

To investigate the origin of the dark lines a probe particle simulation was performed [43]. The 5 CO's were positioned on the top sites of a hexagonal metal surface as extracted from the STM image. Then the relaxed probe positions $x_{CO}(x, y)$ and $y_{CO}(x, y)$ were used to calculate the bending angle $\alpha(x, y)$ at each tip position (x, y) for a CO tip with length $l_{CO} = 4$ Å [43].

$$\alpha(x,y) = \arcsin\frac{r_{\rm CO}(x,y)}{l_{\rm CO}},\tag{6.1}$$

with $r_{CO}(x, y)$ is the absolute value of the x/y position vector of the probe:

$$r_{\rm CO}(x,y) = \sqrt{x_{\rm CO}(x,y)^2 + y_{\rm CO}(x,y)^2}$$
(6.2)

Fig. 6.2(b) shows the bending angles $\alpha(x, y)$ for a island of 5 CO's. The bending



Figure 6.3.: Conductance spectra as a function of the height Δz at different Δx positions. $\Delta z = 0 \,\mathrm{pm}$ refers to the height of the energy minimum between the CO's [see Fig. 6.1(a)]. The positions were the conductance spectra were taken are shown by the colored dots in Fig. 6.1(k). $\Delta x = 0 \,\mathrm{pm}$ refers to the center of the low conductance feature in Fig. 6.1(k).

angles were inverted for a better comparison with the experimental data. As it can be seen dark spots at center of the CO's are visible indication a high CO bending. Further, dark lines between the CO's can be observed and indicate an origin of the dark lines in the STM image due to CO bending.

6.2. Conductance z spectra

In the last section it was shown that the conductance of the CO-CO system relates to CO bending. In this section conductance spectra at different lateral positions indicated in Fig. 6.1(k) by the colored dots are discussed and a hard sphere (HS) and tight binding (TB) model to simulate these spectra is introduced in the next section. The model considers the bending of the tip CO by HS interaction. Figure 6.3 shows I(z) at different Δx positions. $\Delta x = 0 \,\mathrm{pm}$ refers to the center of the low conductance feature in Fig. 6.1(k). The vertical axis of Fig. 6.3 is the base 10 logarithm of the conductance G divided by G_0 . G_0 is the quantum point conductance ($G_0 = \frac{2e^2}{h} = 7.748\,091\,696 \times 10^{-5}\,\mathrm{S}$). The red curve shows I(z) directly above the CO ($\Delta x = 0 \,\mathrm{pm}$). The conductance in the region at $\Delta z = 200 \,\mathrm{pm}$ to 500 pm is greater than the conductance of the bare surface (magenta curve). The decay rate κ above the CO at this height range is $\kappa_{\rm CO} = (1.26 \pm 0.03) \text{ Å}^{-1}$. The decay rate was determined by fitting $I(z) \propto \exp(-2\kappa_{\rm CO}z)$. At $\Delta z = 30 \,\mathrm{pm}$ the red curve crosses the conductance of the bare surface (magenta curve) and remains less than the bare surface conductance. The other curves (blue, green, and cyan) have a similar trend, but the difference to the bare surface conductance (magenta curve) became less in this order. The cyan curve is almost indentical with the bare surface conductance. For $\Delta z > 50 \,\mathrm{pm}$ these conductance curves are greater than the bare surface conductance curve and for $\Delta z < 50 \,\mathrm{pm}$ these conductance curves are smaller than the bare surface conductance curve. The decay rate of the bare surface conductance $\kappa_{\rm Surf}$ was determined to be $\kappa_{\rm Surf} = (1.19 \pm 0.01) \text{ Å}^{-1}$ and is close to $\kappa_{\rm CO}$. A possible reason for the different κ values could be the different density of states of the surface CO vs. the metal surface density of states which get involved in the tunneling process.

6.3. Hard sphere and tight binding model

In this section a HS and TB model will be introduced to simulate the conductance curves shown in section 6.2. The hard spheres describe the deflection of the tip CO as modeled by a torsional spring. The TB model is used to calculate the conductance. This model was proposed by Prokop Hapala³ and the model coefficients were adjusted by the author to yield the best agreement with the data.

The relaxed geometry of the CO-CO system is modeled by considering hard spheres at the position of the oxygen atoms of the tip CO and surface CO. Figure 6.4 shows the hard spheres by the gray balls. The upper sphere is flexible and it can bend away with a moment arm with length L. The moment arm is fixed at a vertical position z and at a lateral position x. This simulates the bending of the CO at the tip. The lower sphere is fixed, and represents an infinite stiffness of the surface CO⁴. Both spheres have radius R/2. The angle θ is defined between the z axis and the line that connects the centers of the spheres⁵. Therefore, θ can be

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⁴In Ref. [48] it was found that the stiffness of the CO on the tip is approximately 6.7 times lower than of the CO on the surface. At the beginning in the model also a flexible HS on the surface was used, but a fixed HS on the surface yielded better results.

⁵In Ch. 4 θ was defined as the tilt of the LFM sensor. In this chapter θ is defined as the angle between the HS's with respect to the z axis.



Figure 6.4.: The hard sphere model. The oxygen atom of the tip CO is represented by a flexible hard sphere with moment arm \vec{L} . The oxygen atom of the surface CO is represented by a static hard sphere. Source: Prokop Hapala

calculated as a function of x and z. The calculated θ values will then be used as an input for the conductance calculation.

The method to calculate the conductance was introduced in Ref. [43] and was modified by Prokop Hapala for the CO-CO on Pt(111) system. It starts with the Landauer formula $J = G/G_0 = \sum_i |T_i|^2$, where G is the conductance, G_0 the quantum point conductance, and T_i is the transmission coefficient of the individual channels [109, 110]. The channels are considered to be independent and add up linearly. The transmission coefficients can be also considered as tunneling probabilities [111].

The conductance of the CO's was modeled by two channels

$$J_{\rm CO} = \gamma T_{\rm Bg1}^2 + T_{\rm Hybrid}^2, \tag{6.3}$$

where γ adjusts the contribution of the T_{Bg1} channel and is a fitting parameter. T_{Bg1} is a background tunneling channel and is defined by

$$T_{\text{Bg1}} = \exp(-\kappa_{\text{Surf}}z). \tag{6.4}$$

 κ_{Surf} is the tunneling decay rate over the surface, and z is the height. In Fig. 6.3 it can be seen that the conductance over the CO's (red curve) is lower than the

surface conductance (pink curve at z = -200 pm) close to the surface. This can be modeled by destructive interference between tunneling channels, where one channel has to be negative. The resulting conductance over the CO's is therefore

$$T_{\rm Hybrid} = \delta T_{\rm CO} + T_{\rm Bg2}, \tag{6.5}$$

where $T_{\rm CO}$ is the tunneling through the CO's and can be negative, and $T_{\rm Bg2}$ is a second background channel. δ adjusts the contribution of the channel and is a fitting paramter. The second background channel is defined by

$$T_{\rm Bg2} = \beta \exp(-\kappa_{\rm Surf} z), \tag{6.6}$$

where β is a fitting paramter.

The bare surface conductance is composed by the two background channels:

$$J_{\rm Surf} = T_{\rm Bg1}^2 + T_{\rm Bg2}^2. \tag{6.7}$$

To calculate the tunneling through the CO's $T_{\rm CO}$ is decomposed in tunneling between individual orbitals. This method is similar to orbital hopping as it is used as in the TB theory [112]. In the TB theory the atomic orbitals are localized at the atomic sites and electronic properties are approximated by a superposition of the atomic orbitals [linear combination of atomic orbitals (LCAO)]. The orbitals can overlap which can lead to a hopping of electrons from one atomic site to the next one. In the TB theory the electron hopping is calculated by an integral of the wave function on one atomic site and the wave function on the next atomic site. In the orbital hopping method presented here, the electron hopping is approximated by the orientation of the orbitals on the oxygen atom of the tip relative to the orbitals of the oxygen atom on the surface. This method was introduced by Slater and Koster [113]. The hopping between the orbitals considers s, p_x , and, p_z orbitals, since a CO tip can also exhibit p-wave character [44].

Figure 6.5(a) shows the orientation of a p_x orbital localized at the oxygen atom of the CO at the tip and a *s* orbital localized at the static oxygen atom of the surface CO for $\theta = 0^{\circ}$ and $\theta = 90^{\circ}$. The direction of the p_x orbital defines the *x* direction. The colors represent the phase of the orbitals/lobes. Red is positive and blue is negative. θ is the angle between the hard spheres as introduced in the beginning of this section. Before sphere contact the angle between the HS's is



Figure 6.5.: Orientation of s, p_x , and p_z orbitals for $\theta = 0^\circ$ and $\theta = 90^\circ$: (a) The p_x orbital is at the oxygen atom of the tip CO and the s orbital is at the oxygen atom of the surface CO. (b) The p_z orbital is at the oxygen atom of the tip CO and the s orbital is at the oxygen atom of the surface CO. (c) On both oxygen atoms of the CO's are s orbitals. (d) On both oxygen atoms of the CO's are p_z orbitals. The coordinate system shown in (a) is also valid for (b,c,d).

 $\theta = 0^{\circ}$. For this case the orbital hopping is zero as it follows from $E_{s,x} = \sin \theta C_{sp_x}$, where θ is the angle between the p_x orbital and the line which connects the p_x and s orbital [113]. For $\theta = 90^{\circ}$ the orbital hopping is positive. The signs of $E_{s,x}$ are also depicted in Fig. 1-11 in Ref. [114]. C_{sp_x} is the hopping constant and is a fitting parameter. The exponential decay of the orbital can be considered by $\exp(-\kappa_{\rm CO}r)$, where $\kappa_{\rm CO}$ is the tunneling decay rate and is a fitting parameter, and r is the distance between the centers of the HS's. This results in the electron hopping function $T_{sp_x} = C_{sp_x} \sin \theta \exp(-\kappa_{\rm CO}r)$ for $s - p_x$ hopping.

Figure 6.5(b) shows the orientation of a p_z orbital localized at the oxygen atom at the tip CO relative to a *s* orbital localized at the oxygen atom of the surface CO for for $\theta = 0^{\circ}$ and $\theta = 90^{\circ}$. The direction of the p_z orbital defines the direction of the z axis. For $\theta = 0^{\circ}$ the p_z orbital is aligned on the z axis with the s orbital and the electron hopping is positive. For $\theta = 90^{\circ}$ the electron hopping is zero since the lobes of the p_z orbital are perpendicular to the connecting line between the p_z and s orbital. This follows from $E_{s,z} = \cos \theta C_{sp_z}$ [113]. The electron hopping function for $s - p_z$ hopping is therefore $T_{sp_z} = C_{sp_z} \cos \theta \exp(-\kappa_{\rm CO} r)$ with C_{sp_x} is a hopping constant and a fitting parameter.

Figure 6.5(c) shows the case for s - s electron hopping. Due to the symmetry of the *s* orbitals the electron hopping is independent of θ . The s - s orbital hopping is negative as can be seen from Tab. 2-3 in Ref. [114]. The electron hopping function can be written as $T_{ss} = -C_{ss} \exp(-\kappa_{\rm CO} r)$. $C_{\rm ss}$ is the hopping constant and is a fitting parameter.

Figure 6.5(d) shows the case for $p_z - p_z$ orbital hopping. For $\theta = 0^\circ$ the p_z orbitals are on top of each other and for $\theta = 90^\circ$ the p_z orbitals are side by side. According to Slater and Koster the $p_z - p_z$ orbital hopping can be approximated by $E_{z,z} = \cos^2 \theta V_{pp\sigma} + (1 - \cos^2 \theta) V_{pp\pi}$ [113]. $V_{pp\sigma}$ is the hopping constant for $\theta = 0^\circ$ when the p_z orbitals are on top of each other and 'form' a σ bond. $V_{pp\pi}$ is the hopping constant for $\theta = 90^\circ$ when the p_z orbitals are side by side and 'form' a π bond. As it can be seen in Tab. 2-3 in Ref. [114] $V_{pp\sigma}$ is positive and $V_{pp\pi}$ is negative and have usually different magnitudes. In this model it is approximated that $V_{pp\sigma}$ and $V_{pp\pi}$ have the same magnitude. This results in the electron hopping function $T_{p_z p_z} = -C_{p_z p_z}(1 - 2\cos^2 \theta) \exp(-\kappa_{\rm CO} r)$. $C_{p_z p_z}$ is the hopping constant and is a fitting parameter.

The hopping processes between the different orbitals at the CO's are considered to be independent. T_{CO} can then be expressed by

$$T_{\rm CO} = \left[-C_{ss} + C_{sp_z}\cos\theta + C_{sp_x}\sin\theta - C_{p_zp_z}(1 - 2\cos^2\theta)\right]\exp(-\kappa_{\rm CO}r) \qquad (6.8)$$

To show the mechanism of destructive interference of $T_{\rm CO}$ and $T_{\rm Bg2}$ as given by Eq. 6.5 the square of $T_{\rm Hybrid}$, $T_{\rm CO}$, and $T_{\rm Bg2}$ were plotted. Figure 6.6 shows the base 10 logarithm of the channels. The constant C_{ss} was set to 1.0 and because of the minus before C_{ss} in Eq. 6.8 the contribution is negative. All other hopping constants were set to 0. Further, the following parameters were used $\kappa_{\rm Surf} = 1.19 \,\text{\AA}^{-1}$, $\kappa_{\rm CO} = 1.42 \,\text{\AA}^{-1}$, and $\beta = 0.7$. The values of the parameters were determined by manual fitting of J_{CO} to the data shown in Fig. 6.3. Further, for the HS model the following parameters were used: $R = 2 \times 1.66 \,\text{\AA}$ [115] and $L = 4.0 \,\text{\AA}$ [43]. $T_{\rm Bg2}^2$



Figure 6.6.: T_{Hybrid}^2 channel (gray curve), T_{CO}^2 channel (pink curve), and T_{Bg2}^2 channel (cyan curve).

shows the conductance of the second background channel and $T_{\rm CO}^2$ (magenta curve) is the conductance through the CO's. For z = 7.4 Å to 12 Å T_{CO}^2 is a straight line due to the exponential distance dependence of the conductance. For z < 7.4 Å the HS's get in contact and the conductance is constant, since the distance of the spheres stay constant. The gray curve shows $T_{\rm Hybrid}^2$ which is the difference of the $T_{\rm CO}$ and $T_{\rm Bg2}$ (Eq. 6.5) since $-C_{ss}$ is negative. When the magenta and the cyan curve intersect the difference becomes 0 and the logarithm of $T_{\rm Hybrid}^2$ becomes minus infinity as it can be seen by the pole⁶ at around z = 5 Å. On the left side of the pole $T_{\rm Hybrid}^2$ asymptotically approches $T_{\rm Bg2}^2$. This is the mechanism leading to a conductance greater than the surface conductance before sphere contact and a conductance smaller than the surface conductance after sphere contact. To maintain a lower conductance after sphere contact the parameter γ was introduced in Eq. 6.3.

6.3.1. Conductance calculations

In the following the conductance spectra will be discussed calculated with the model as introduced in the section before at different x positions and with different hopping constants. For the calculations the following parameters were used:

⁶Due to the discrete numeric calculation of the plot the gray curve does not go down to minus infinity at this point.



Figure 6.7.: Conductance curves at different x positions and with different orbital hopping coefficients: (a) $C_{ss} = 1.0$ and $C_{sp_z} = -1.0$. The other hopping constants were set to 0. Here, no harmonic weighting was used. (b) $C_{ss} = 1.0$ and $C_{sp_z} = -1.0$ with harmonic weighting. The other hopping constants were set to 0. (c) $C_{sp_x} = 1.0$ with harmonic weighting. The other hopping constants were set to zero. (d) $C_{sp_x} = -1.0$ with harmonic weighting. The other hopping constants were set to zero.

 $\kappa_{\text{Surf}} = 1.19 \text{ Å}^{-1}$, $\kappa_{\text{CO}} = 1.42 \text{ Å}^{-1}$, $\beta = 0.7$, and $\gamma = 0.0025$. These parameters were determined by manual fitting of the conductance curve to the data shown in Fig. 6.3. Further, for the HS model the following parameters were used: $R = 2 \times 1.66 \text{ Å} [115]$ and L = 4.0 Å [43].

Figure 6.7(a) shows the calculated conductance at different x positions (magenta, cyan, yellow, and blue curve) and the bare surface conductance (gray curve) as a function of z. The hopping constants were set to $C_{ss} = 1.0$ and $C_{sp_z} = -1.0$. The other hopping constants were set to zero. These choice of hopping constants yielded the best agreement with the data. For distances z > 7 Å all four colored curves are above the bare surface conductance curve and the conductance decrease

as x increases. This trend is in qualitative agreement with the data as shown in Fig. 6.3. At sphere contact around z = 7 Å a kink in the magenta, cyan, and yellow curve can be seen. On the left side of the kink poles⁷ can be made out, which result from the destructive interference of $T_{\rm CO}$ and $T_{\rm Bg2}$. On the left side of the poles the conductance approaches the surface conductance from below and maintain a distance as it is in qualitative agreement with the data as shown in Fig. 6.3. However, in the data [Fig. 6.3] for $\Delta x = 0 \,\mathrm{pm}$ (red curve) the conductance is almost a half order of magnitude lower than the bare surface conductance (magenta curve) close to the surface. In the model the difference is lower. One reason may be, that the model does not take into account the change of the local DOS of the CO's when they are in contact. The AFM image in Fig. 6.1(f) showed indications of weak hybridization and it can be expected that the DOS of the CO's changess. The model also does not consider the change of the local DOS of the surface atom on which the surface CO is adsorbed when the surface CO bends. The kink in the magenta, cyan, and yellow curve shown in Fig. 6.7(a) is caused by the HS model, when the spheres get in contact. If Lennard-Jones or Morse potential interaction would be considered between the CO's, it would be a smooth transition. Another mechanism which would lead to a smooth transition is the vertical oscillation of the tip, which averages the current over the range of the oscillation amplitude. To consider the vertical oscillation of the tip conductance averaging according to Eq. 4.7 was incorporated.

In Fig. 6.7(b) the conductance curves at different x positions with the same parameters as in Fig. 6.7(a) are shown, but with harmonic averaging. The oscillation amplitude was A = 50 pm as it was used for collecting the data. The overall characteristic in comparison to Fig. 6.7(a) is preserved. However the transition region at sphere contact is smooth. The harmonic averaging reproduces the smooth transition of the curves from above the surface conductance to below the surface conductance as shown in the data [Fig. 6.3].

On Cu(111) the p_x and p_y orbitals of the CO mainly contribute to the tunneling current, which leads to the reduced conductance at the center of the CO [65, 99]. Therefore, a conductance calculation with $s - p_x$ orbital hopping was performed to demonstrate the difference to the choice of hopping coefficients discussed in the paragraphs before. C_{sp_x} was set to 1.0. The other hopping constants were set to

⁷Due to the discrete numeric calculation of the plot the curve does not go down to minus infinity at this point.

zero. The conductance was averaged by the harmonic function (Eq. 4.7) to consider the vertical oscillation of the tip. Figure 6.7(c) shows the conductance curves at the different x positions. In a distance range of z = 8.5 Å to 12 Å the magenta curve (x = 0 pm) is below the surface conductance (gray curve) and goes above at z = 8.5 Å. At z = 4.5 Å the magenta curve goes below the surface conductance again and remains below it. The other conductance curves (cyan, yellow, and blue) are above the surface conductance at z = 12 Å but have equal conductance (overlapped). At z = 8 Å the blue curve slightly separate from the vellow and cyan curve, but the cyan and yellow curve remain almost at the same conductance. The blue, cyan, and yellow curve go below the surface conductance z = 4.5 Å and remain below the surface conductance. These conductance curves are not qualitatively in agreement with the data shown in Fig. 6.3 especially in the range z = 8 Å to 12 Å. To demonstrate the $s - p_x$ orbital hopping with a different sign of the C_{sp_x} orbital hopping constant C_{sp_x} was set to -1.0. Figure 6.7(d) shows the conductance curves at the different x positions (magenta, cyan, yellow, and blue curve). At far distances (z = 12 Å) all curves are below the surface conductance (gray curve). The cyan and yellow curve cross the bare surface conductance at z = 9.5 Å and go below the surface conductance z = 6.1 Å.

Both conductance curves calculated with $C_{sp_x} = 1.0$ [Fig. 6.7(c)] and $C_{sp_x} = -1.0$ [Fig. 6.7(d)] are qualitatively not in agreement with the data shown in Fig. 6.3 and indicate that the s-s and $s-p_z$ orbital hopping to reproduce the data are required. The contribution of the p_x and p_y orbital to the tunneling current could be too low to be measurable in the experiment. In a theoretical investigation of CO on Pt(111) in Ref. [101] it was found that on Pt(111) the p_x and p_y orbitals of the CO have almost zero contribution to the tunneling current. The main contribution to the tunneling current of the CO on Pt(111) would come from the HOMO 5σ and 3σ orbitals.

6.3.2. Conclusion

A HS model in combination with a TB model was introduced and conductance curves were calculated at different x positions and with different orbital hopping constants. The model does not take the change of the DOS of CO's into account, when they get in contact. The AFM image in Fig. 6.1(f) showed indications of weak hybridization. Therefore it could be assumed that the DOS of CO's change when they are in contact. The model does also not consider the change of the DOS of the metallic surface and tip atom, when the CO's bend, but it qualitatively reproduces the data. The smooth transition of the conductance in the data from above the surface conductance to below the surface conductance could be reproduced by considering the vertical oscillation of the tip and destructive interference of the CO tunneling channel and a background tunneling channel. A calculation with $s - p_x$ orbital hopping, which would consider the orbital configuration of the CO on Cu(111) did qualitatively not reproduce the data. Qualitative good agreement could be obtained by considering s - s and $s - p_z$ orbital hopping.

6.4. Density functional theory calculations

To consider the change of the DOS of the CO's when they interact, DFT calculations were performed by Vladislav Pokorný⁸ who gives the following details about the calculations:

All DFT calculations were performed utilizing the Turbomole 7.1 package. We used the def2-SV(P) (double-zeta) basis and GGA(PBE) exchange-correlation functional for the geometry optimization step as well as for the final results. The transmission calculations were performed using our home-brew NEGF code⁹ based on the method described in Arnold et al. [116].

As already mentioned in Ch. 5 a CO adsorbs on the top site on Pt(111). Within this simulation, the relaxation of the structure, however, led to a wrong adsorption site of the CO on the Pt(111) surface. Also the CO at the tip did not stay at the front metal atom. Therefore the carbon atoms were fixed in position and only the oxygen atoms were allowed to relax. Figure 6.8 shows the fully relaxed structure within these constraints at a specific height which was used for the conductance calculation. Gray balls indicate Pt atoms (metallic tip and surface atoms), brown carbon atoms, and red oxygen atoms.

Figure 6.9 shows the conductance calculations at a bias voltage of 0 V as function of the distance d, which is defined as the distance between the center of the lowest metallic tip atom to the center of the metallic surface atom. The black dots represent the conductance to the surface. The red dots show the conductance through the CO's. As it can be seen the red curve does not fall below the surface conductance and does not reproduce the data shown in Fig. 6.3 ($\Delta x = 0$ pm, red

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⁹Yangon, github.com/pokornyv/Yangon



Figure 6.8.: CO-CO junction on Pt. Gray balls are Pt atoms, brown carbon atoms, and red oxygen atoms. Source: Vladislav Pokorný

curve). The reason for this is most likely the fixed carbon atoms of the CO's, which does not lead to a change of the local DOS of the surface and metallic tip atoms, when the CO's interact. Most likely because the relative orientation of the carbon atom orbitals and the metallic surface/tip atom orbitals do not change. Besides, a direct comparison with Fig. 6.3 (red curve) is difficult since it is unknown at which height the energy minimum in the calculation is.

To take into account the change of the DOS of the metallic surface and metallic tip atom a Morse potential interaction model of CO molecules was used as presented in Ref. [48] to calculate the bending angle of the CO's as function of the distance. These bending angles were then used to generate new geometries for several distances. Figure 6.10 shows the generated geometry of CO-CO junction with the bending angles extracted from the Morse potential interaction. The CO at the tip bends stronger than the surface CO, since the stiffness used in the Morse



Figure 6.9.: Conductance calculation as a function of the distance at zero bias voltage. Black dots display the conductance over the surface. Red dots show the conductance through the CO's. Source: Vladislav Pokorný

potential calculation for the tip CO is lower than the stiffness of the surface CO. The carbon atoms do not sit directly above the metallic surface or tip atom anymore. The bonding distances of the carbon and oxygen atoms were taken from the Turbomole calculation result and were kept constant as well as the positions of the surface and metal tip atoms. This geometry can then be used for the conductance calculations as performed for the old geometry. These calculations are currently subject of further investigation.

6.5. Conclusion and outlook

STM and normal AFM images of a CO on Pt(111) with a CO tip were discussed as well as the interaction of the CO's by considering the potential energy. The AFM image at the height where the potential energy has a minimum shows indications of hybridization of the CO's as reported for individual Fe, and Cu adatoms on Cu(111) [35]. The STM images show increased conductance at far distances (relative to the surface conductance) and a ring shape with reduced conductance in the center at close distances.

To demonstrate the relation of the bending of the CO tip to the conductance a



Figure 6.10.: CO-CO junction on Pt using the bending angles of the surface and tip CO extracted from a Morse potential interaction from Ref. [48]. The surface and the metallic tip atoms are Pt atoms. Dark gray atoms are carbon and red oxygen atoms.

STM image of a group of 5 CO's on Pt(111) were discussed and a probe particle simulation was performed. From the x and y positions of the relaxed probe the bending angles were calculated and an image was generated. The dark centers and lines between the CO's in the STM image were reproduced indicating a strong relation of the conductance features to CO bending.

Conductance z spectra of an individual CO at different Δx positions in the STM image [Fig. 6.1(k)] were investigated. At the center of the CO's the conductance is higher than the surface conductance at far distances and goes below the surface conductance in a smooth transition at close distances. The conductance z spectra were modeled by a combined HS and TB model. The orbital hopping functions were explained by the orbital hopping approximations by Slater and Koster [113]. To simulate the transition of the conductance from above to below the surface conductance, interference of tunneling channels was demonstrated. Calculated conductance curves at different x positions were discussed. Due to the HS interaction a kink in the conductance curves was visible. This could be smoothed by taking the vertical oscillation of the tip into account by harmonic averaging of the conductance curves. Considering s - s and $s - p_z$ orbital hopping showed qualitatively a good agreement with the experimental data. s - s and $s - p_z$ orbital hopping is also legitimated by a theoretical investigation of CO on Pt(111), where mainly the 5σ and 3σ orbital of CO contribute to the tunneling current [101]. $s - p_x$ orbital hopping as it would consider the orbital contribution to the tunneling current of CO on Cu(111) [65, 99] did not show a qualitative agreement with the experimental data.

The HS / TB model does not consider the change of DOS of the CO's when they get in contact, nor the change of DOS of the metallic surface and tip atom when the CO's bend. Therefore, DFT calculations were performed. However, geometry optimizations led to wrong adsorption site of the CO on the surface and the tip. To account for this, the carbon atoms were kept fixed in position during the geometry optimization. The resulting conductance curve did not show an agreement with the data, most likely because of the fixed carbon atoms. Density functional calculations are still problematic and adsorption site calculations are still challenging [117, 118]. To improve the calculations bending angles of the CO at the tip and surface was extracted from a Morse potential interaction model from Ref. [48] and geometries were generated. These calculations are currently subject of further investigation.

As an outlook the HS / TB model to simulate the conductance could be improved by using Lennard-Jones or Morse potential interaction instead of HS's as demonstrated in Ref. [43] or in Ref. [48]. This would avoid a kink in the conductance curves. In addition, the orbital hopping functions could be improved by considering the rotation of the tip orbitals with θ as demonstrated in the supplemental in Ref. [43]. So that the tip orbital rotates with the moment arm as shown in Fig. 6.11 and does not maintain the orientation in space. Figure 6.11 shows a p_z orbital at the oxygen atom of the tip and a *s* orbital at the oxygen atom of the surface CO for $\theta = 0^{\circ}$ and $\theta = 45^{\circ}$. \vec{L} is the moment arm of the tip CO. As it can be seen the p_z orbital at the tip rotates with the moment arm. This would simulate the orbital hopping more accurately.



Figure 6.11.: Rotation of the tip p_z orbital with θ . \vec{L} is the moment arm of the tip CO. The *s* orbital is at the oxygen atom of the surface CO.

7. PTCDA and CuPC investigation with LFM

7.1. Introduction and literature review

Organic semiconductors like 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and copper(II) phthalocyanine (CuPc) are of great research interest because of their application in organic field effect transistors or organic light emitting diodes [119].

PTCDA and CuPc form mixed phases with different stoichiometries on Ag(111). So far it is not clear how the adsorption geometry of CuPc and PTCDA changes within the mixed phases for different stoichiometries and also how the electronic structure near the Fermi energy of CuPc and PTCDA changes within the mixed phases. Or, are there mixed phases which were not observed so far? How is the situation on Cu(111)? On Cu(111) mixed phases were not observed in the experiments and CuPc adsorbs at the boundary of PTCDA islands. Therefore the question arose how do different numbers of close PTCDA molecules influence the adsorption geometry and electronic structure near the Fermi energy of a CuPc molecule. Isolated CuPc on Cu(111) adsorbs aligned to a high-symmetry direction of the Cu(111) surface and in a $\pm 7^{\circ}$ rotated state in the presence of inelastically tunneling electrons or a strong tip sample potential. Single CuPc molecules close to different numbers of PTCDA molecules can adsorbed aligned to a high-symmetry direction of the atomic surface lattice or rotated with a small angle similar as the reported $\pm 7^{\circ}$ relative to a high-symmetry direction (rotated position). How do close PTCDA molecules influence the rotation of a CuPc molecule?

Lateral force microscopy is very sensitive to height differences below 10 pm [25] making it ideal to image geometric height differences of individual molecules in different local environments as it will be investigated on Cu(111) or in mixed phases with different stoichiometries of PTCDA and CuPc on Ag(111). The simultaneously acquired STM data additionally enables studies of the electronic structure of



Figure 7.1.: Stick and ball models of molecules: (a) perylenetetracarboxylic dianhydride (PTCDA) (b) copper(II) phthalocyanine (CuPc)

the molecules.

In section 7.1.1 and 7.1.2 an overview of the research progress of PTCDA and CuPc adsorbed on Ag(111) and Cu(111) will be given. In section 7.1.3 mixed phases will be discussed, where PTCDA and CuPc form heteromolecular monolayers with different stoichiometries. In section 7.2 geometric and electronic changes of individual CuPc and PTCDA molecules within a mixed phase on Ag(111) will be investigated. A new P₄C₂ mixed phase was observed, where four PTCDA's and two CuPc molecules are within a unit cell. On Cu(111) (section 7.3) the geometric and electronic structure of individual CuPc adsorbed next to one, two, and three PTCDA molecules will be studied. It will be shown that nearby PTCDA's allow the CuPc to adsorb in the $\pm 7^{\circ}$ rotated state. In section 7.3.4 the influence of close PTCDA molecules on the STM topography of the CuPc will be studied with higher bias voltages.

When in the following the term 'monolayer' is used an alomst full single layer coverage of the metal surface with molecules is meant.

7.1.1. 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA)

Figure 7.1(a) shows a stick-and-ball model of a PTCDA molecule. This molecule consists of a perylene core (central five benzol rings), which has three oxygen atoms on the short side (red) and 4 hydrogen atoms on the long side (white). The mid oxygen atom is also called the anhydride oxygen and the outer two are called carboxylic oxygen [120]. The carboxylic oxygens have a double bond to the



Figure 7.2.: STM topography of a PTCDA molecule island in herringbone configuration adsorbed on Cu(111). Set point: 100 mV and 50 pA. Ball-andstick models of PTCDA molecules are overlaid. In the right top corner is the Cu(111) surface visible.

carbon atom and the anhydride oxygen is bound with a single bond to two carbon atoms. The perylene core forms a π -conjugated system, which leads to delocalized π -electrons [21, 121].

At submonolayer coverage and when PTCDA is deposited at room temperature on Cu(111) or Ag(111) PTCDA assembles in a flat and compact structure and is well suitable for AFM and STM measurements. Figure 7.2 shows an STM topography image in constant current mode (set point: 100 mV and 50 pA) of a PTCDA domain in herringbone configuration on Cu(111). The oxygen side of the PTCDA faces the hydrogen side with an offset to the outer hydrogen atoms. The partly positively charged hydrogens get attracted by the negatively charged oxygens, which leads to weak hydrogen bonds [122] and a stabilization of the molecular network. When PTCDA is deposited at low temperatures (below 150 K) on Ag(111) irregular molecular structures can be observed [121].

LFM images of PTCDA on Cu(111) show that PTCDA does not adsorb totally flat, meaning that it adsorbs with a small tilt along the long axis of the molecule. On Ag(111) the LFM images of PTCDA do not show such a tilt and PTCDA appears rather flat. These observations could be reproduced by probe particle model simulations [123].

Density functional theory calculations showed that the adsorption height of PTCDA varies with the atomic species of the metal surface. On Au(111) the carbon back bone of the PTCDA adsorbs at 3.34 Å, on Ag(111) at 2.98 Å, and on Cu(111) the adsorption height is the lowest with 2.89 Å [120]. The oxygen atoms of the PTCDA change their relative height to the carbon plane on different metal surfaces. On Ag(111) the carboxylic atoms of PTCDA bend towards the surface. On Cu(111) the position of the oxygen atoms is still under debate. Some measurement indicate that they bend above the carbon plane of the PTCDA [124], whereas other findings indicate that they bend below the carbon plane [120].

Organic/metal systems e.g. PTCDA on Ag(111) exhibit an interface state which lies above the Shockley surface state Fermi energy of bare Ag(111). The Shockley surface state is a state which is localized at the transition region from the metal to the vacuum [125]. The Shockley surface state gets modified by the π conjugated perylene core of an adsorbed PTCDA molecule by applying a potential to the Shockley surface state. This leads to interface states. The energies of the interface states are related to the adsorption height of PTCDA molecules on Ag(111). By increasing the temperature of the sample the adsorption height of the PTCDA molecules changes and the interface state was measured by scanning tunneling spectroscopy. The adsorption height was measured by x-ray standing wave experiments. The change of the interface state with the adsorption height could be well reproduced by an analytical one-dimensional model with the carbon metal atom distance as the only adjustable parameter [126].

In addition to the surface state a charge transfer from the metal surface into the lowest unoccupied molecular orbital (LUMO) of the PTCDA on Ag(111) occurs. PTCDA binds on Ag(111) by chemisorption where the carbon backbone is involved as well as the carboxylic oxygen atoms [21, 127].

7.1.2. Copper(II) phthalocyanine (CuPc)

Another interesting organic molecule is copper(II) phthalocyanine (CuPc). Figure 7.1(b) shows a stick-and-ball model of a CuPc molecule. It consists of a central copper atom (orange), surrounded by 4 nitrogen atoms (blue). At these nitrogen atoms 4 identical lobes are attached consisting of a benzol ring (gray) saturated with hydrogen atoms (white) [128]. These benzol rings exhibit a π conjugated



Figure 7.3.: (a) LFM image of CuPc adsorbed on Cu(111). The oscillation amplitude is 50 pm. The oscillation is in horizontal direction. (b) Corresponding STM image with a bias voltage of 1 mV.

electron system [129].

CuPc does not form domains and repels each other when adsorbed on metal surfaces [17, 22, 130–132]. At low coverage and with an increase of the coverage the distance between the CuPc molecules decreases without forming regular structures on Ag(111) [132]. At high coverage (> 0.76 monolayer on Cu(111) and > 0.89 monolayer on Ag(111)) commensurate structures can be observed on Cu(111) and Ag(111) [133, 134]. In gas phase CuPc exhibits fourfold symmetry with degenerate highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). CuPc has also a single occupied molecular orbital (SOMO), which lies between the LUMO and the HOMO [19, 135]. The fourfold symmetry of the molecule becomes broken, when it is adsorbed on Cu(111) [17, 24, 128, 130].

Figure 7.3(a) shows an LFM image of CuPc on Cu(111). The oscillation path of the tip is in horizontal direction. Two opposite lobes are clearly raised as it can be seen by the increased Δf contrast, whereas two perpendicular lying lobes have lower Δf contrast. Figure 7.3(b) shows the corresponding STM image (constant height) with a bias voltage with 1 mV. The higher lying lobes have clearly higher conductance as it can be seen by the bright features. These features are not so well visible in the lower lying lobes. When CuPc is adsorbed on Ag(111) the interaction with the surface is weaker and the CuPc molecule remains relatively flat [17].

On Ag(111) CuPc shows physisorption whereas on Cu(111) CuPc shows chemisorption [136]. Chemisorption describes the hybridization of electronic orbitals of

molecule and surface upon adsorption and physiosorption is induced by van der Waals forces. CuPc interacts with the surface by electron donation/back-donation, where charge is transferred from a former HOMO to the surface (donation) and is transferred back into a LUMO (back-donation). The former LUMO becomes partly occupied. This mechanism contributes to the repulsive interaction of CuPc molecules on metal surfaces [131, 132, 134].

On Cu(111) and at bias voltages above 100 mV CuPc can undergo frustrated rotations induced by inelastically tunneling electrons [17, 23, 24, 137]. The molecule switches quickly between the aligned state, where the CuPc lobes are aligned in a high-symmetry direction of the hexagonal Cu(111) surface and a $\pm 7^{\circ}$ rotated state. With the switching process the geometry of CuPc molecule changes, meaning the lower lying lobes become the higher lobes and vice versa. The switching of the CuPc can also be thermally induced and the potential energy landscape of the molecule is changed by the proximity of a tip. At close tip distances the potential energy landscape changes from the aligned state as a preferred state to the rotated state as preferred state. This tip induced frustrated rotation does not occur on Ag(111) [17].

7.1.3. PTCDA and CuPc mixed phases

Mixed phases are heteromolecular structures where different numbers of CuPc and PTCDA molecules are in a unit cell. On Ag(111) depending on the deposition ratio of CuPc and PTCDA mixed phases with different stoichiometries can coexist as well as individual CuPc molecules [22, 138]. A detailed phase diagram for PTCDA and CuPc in the submonolayer regime can be found in Fig. 4 in Ref. [22].

On Ag(111) the observed mixed phases so far encompass the P₂C mixed phase, where two PTCDA's and one CuPc are in the unit cell, the PC mixed phase, where one PTCDA and one CuPc are in the unit cell, and the PC₂ mixed phase with one PTCDA and two CuPc molecules are in the unit cell [20, 22] (see Fig. 1 in Ref. [22]). When the coverage of CuPc is increased further a PC₂ mixed phase can be observed [138], where one PTCDA molecule and two CuPc molecules are in the unit cell (see Fig. 1 in Ref. [138]). On Cu(111) a P₂C mixed phase was observed after the sample preparation was annealed to 400 K [139]. In the mixed phase experiments performed for this thesis no mixed phases could be observed on Cu(111) after annealing the sample.

The occurrence of the mixed phases P_2C , PC, and PC₂ on Ag(111) can be

explained by attractive intermolecular interaction. The interaction is caused by attractive electrostatic forces between the negatively charged oxygen atoms of the PTCDA and the partly positively charged hydrogen atoms of the CuPc molecule and van der Waals forces [138].

On Ag(111) the P₂C mixed phase shows a counter-intuitive behavior regarding the adsorption heights and chemical interactions: one would expect that a higher adsorption height (relative to the surface atoms) of a molecule corresponds to a lower bonding energy. In the P₂C mixed phase on Ag(111) the opposite can be observed which is mediated by the metal surface. Both species mutually increase their charge-donating and -accepting character [20]. In the P₂C mixed phase the adsorption heights of CuPc and PTCDA equalize: the adsorption height of CuPc reduces, whereas the adsorption height of PTCDA increases [20].

7.2. CuPc and PTCDA on Ag(111)

7.2.1. Individual CuPC

To be able to investigate the influence of nearby PTCDA molecules on the geometric and electronic structure of CuPc, isolated CuPc on Ag(111) will be studied first. Also the alignment of the molecule relative to the hexagonal surface and their adsorption site will be investigated.

Figure 7.4(a) shows a LFM image of CuPc adsorbed on Ag(111) recorded with a CO terminated tip. The tip oscillates in horizontal direction and the oscillation amplitude was 50 pm. The contrast of the four lobes is very similar indicating a flat geometry. Although the four lobes show similar contrast, a slight asymmetry especially between the left and right horizontal lobe can be seen. This is most likely caused by a tilt of the CO at the tip, since this is not visible in another dataset. Figure 7.4(b) shows an LFM image of a CuPc molecule recorded with a different CO tip (taken from Ref. [17]). The asymmetry of the lobes is reduced and the geometry of the molecule appears flat. A LFM probe particle simulation (see section 2.2.4) of a CuPc molecule confirms this finding [17, 43]. Figure 7.4(c) shows a simulated LFM image of a isolated CuPc molecule with a flat geometry (taken from Ref. [17]). The similarity to Fig. 7.4(b) can be seen, confirming the flat geometry of CuPc on Ag(111).

The interpretation of a flat adsorption geometry of CuPc on Ag(111) is further



Figure 7.4.: CuPc on Ag(111) (a) LFM image recorded with a CO tip. The tip oscillates in horizontal direction and the oscillation amplitude was 50 pm.
(b) LFM image of another CuPc recorded with a different CO tip. The tip oscillates in horizontal direction and the oscillation amplitude was 50 pm. Taken from Ref. [17]. (c) Probe particle simulation of CuPc with flat geometry. Taken from Ref. [17]. (d) Corresponding STM image to (a) with a bias voltage of 1 mV. (e) Adsorption direction of the CuPc molecule in (a) relative to the surface atomic lattice.

corroborated when comparing the LFM images recorded of isolated CuPc molecules adsorbed on Cu(111) [Fig. 7.3(a)] and Ag(111) [Fig. 7.4(a),(b)], respectively. While the image recorded on Ag(111) shows a fourfold rotational symmetry where all lobes show a similar Δf contrast, the image recorded on Cu(111) only shows twofold rotational symmetry, as the Δf contrast is significantly higher above two lobes of the CuPc molecule.

In Fig. 7.4(d) the corresponding STM image to Fig. 7.4(a) measured with a bias voltage of 1 mV is shown. The molecule appears fourfold symmetric with similarly high conductance features around the center. The small asymmetry of the left and right lobe is most likely caused by a tilted CO tip in analogy to the small asymmetry in the LFM image shown in Fig. 7.4(a). This is different from CuPc on Cu(111) where two lobes exhibit higher conductance and two lower as shown in Fig. 7.3(b).

Figure 7.4(e) shows the alignment of the CuPc molecule shown in Fig. 7.4(a) relative to the Ag(111) lattice. The Ag(111) lattice was resolved in constant current mode with a set point of 5 mV and 2 nA with a CO tip. The alignment of the CuPc molecule is indicated by the white cross. The Ag(111) lattice is highlighted by the green circles with one of its high-symmetry directions by the black dashed line. This demonstrates the alignment of the CuPc in the high-symmetry direction of the hexagonal surface. While on Cu(111) the CuPc molecule can switch to a $\pm 7^{\circ}$ rotated state at close tip-sample distances, such a switching behavior was not the observed on Ag(111) [17].

To make a statistical statement of the adorption direction of CuPc on Ag(111) the alignment of several molecules was investigated in a STM topography image (set point 10 mV and 100 pA). Fig 7.5(a) shows the alignment of different CuPc molecules indicated by black crosses relative to the high-symmetry direction of the Ag(111) surface (dashed white lines). The high-symmetry directions of the atomic surface lattice were identified in Fig. 7.4(e). All molecules are aligned to the high-symmetry direction allowing the conclusion that this state is the preferred state of CuPc on Ag(111). This finding is new and was not reported so far.

Interestingly, in Fig 7.5(a) also a step edge is shown at which several CuPc molecules are adsorbed. Since the CuPc molecules repel each other on a flat terrace on Ag(111), the step edge acts as a diffusion barrier at which the molecules adsorb and overcome their repulsive interaction. The step edge has a increased reactivity and increased electrostatic force where the electrostatic attraction of the CuPc



Figure 7.5.: (a) STM topography image (set point 10 mV, 100 pA) of individual CuPc molecules on Ag(111) showing the alignment (black crosses) relative to the surface high-symmetry directions (dashed white lines). The high-symmetry directions of the atomic surface lattice were identified in Fig. 7.4(e). Also shown are CuPc molecules adsorbed at a step edge.
(b) Constant current STM image at different set points (upper part and lower part). Green circles show an extrapolation of the surface lattice. The black cross shows the center of the CuPc molecule indicating the adsorption site of the central copper atom at a bridge site.

with the step edge is stronger then repulsive interaction of the CuPc molecules.

On Cu(111) the central copper atom of the CuPc molecule adsorbs on a bridge site [23, 24]. To investigate the adsorption site of CuPc on Ag(111) a constant current image with different set points was taken. This resolves the silver lattice and the position of the molecule in one image. By extrapolating the surface lattice the adsorption site of the CuPc can be determined. Figure 7.5(b) shows the extrapolated atomic surface lattice by the green circles. The center of the molecule is indicated by the black cross. This indicates the adsorption site of CuPc on Ag(111) to be on a bridge site.

7.2.2. CuPc and PTCDA mixed phases

Mixed phases of CuPc and PTCDA were grown on Ag(111) by successive evaporation of PTCDA and CuPc with a home-built molecular evaporator. A detailed description of the evaporator can be found in section 3.2. The Ag(111) surface was cleaned by two sputtering and annealing cycles as described in section 3.3. PTCDA was deposited with a submonolayer coverage first and CuPc was added afterwards with a submonolayer coverage on the Ag(111) sample at room temperature. Initial scans, however, showed a too low coverage of PTCDA and more PTCDA was added. This procedure yielded mixed phases with different stoichiometries as it will be shown later. In Ref. [138] it is discussed that mixed phases are energetically favored when CuPc is added first and PTCDA is added second. When CuPc is added first the molecules have relatively large intermolecular distances, where PTCDA's can easily squeeze in between. Forming a mixed phase is energetically more favorable than a formation of separate phases. If PTCDA is deposited first the compact domain structure is energetically more favorable than a mixed phase, since it costs energy to remove a PTCDA molecule from the domain structure. In this order mixed phases are unlikely without annealing the sample after the deposition of the molecules [138].

The following STM and AFM images of the mixed phases are part of a 3D dataset (except the STM topography images of section 7.3.4). A 3D dataset consists of a series of (usually 20 to 30) constant-height images with a vertical spacing of 10 pm between each other (if not stated otherwise). For the closest distance a height with a set point of 10 mV and current 50 pA over the bare metal surface was set. Then the STM feedback controller was switched off, the bias voltage was changed and constant-height images were recorded with increasing tip-sample distance. From the 3D dataset an image was chosen at a height were just no energy dissipation was visible anymore and the Δf contrast was not distorted by the energy dissipation of the CO (see Ch. 8). This image showed the highest Δf contrast of the 3D dataset.

Frequency shift data gives information about relative adsorption heights and molecular geometries. For normal AFM the (short-range) frequency shift minimum for the same kind of atoms is a function of the atomic positions of an adsorbate [140]. LFM is mainly sensitive to short-range forces and the Δf signal strength gives information about the adsorption height and the geometry of a molecule [17]. Furthermore, the lobes of CuPc molecule and the PTCDA perylene core consist of carbon atoms where it could be assumed to have a similar interaction potential with the CO tip.



Figure 7.6.: (a) Molecular model of the P₂C mixed phase. The green vectors span the unit cell. (b) Δf image of the P₂C mixed phase on Ag(111) taken with a CO tip. The oscillation is in horizontal direction and the amplitude was 50 pm. The image was smoothed by a 2 × 2 Gaussian filter. (c) Corresponding STM image at a bias voltage of 1 mV. (d-e) Δf line profiles at positions marked by the colored lines in (a).

P_2C mixed phase on Ag(111)

The P₂C mixed phase consists of two PTCDA and one CuPc molecule in the unit cell. Figure 7.6(a) shows the unit cell with ball-and-stick models of the molecules. The unit cell vectors are spanned by the green arrows of length $a_{P_2C} = 1.8$ nm and $b_{P_2C} = 2.8$ nm. The angle between these vectors is 73°. The area of this unit cell is $A_{P_2C} = 4.9$ nm². The model of the mixed phase was derived from the LFM image discussed next.

Figure. 7.6(b) shows the LFM image taken with a CO tip and an amplitude of 50 pm. The oscillation direction is in horizontal direction. Some CuPc and PTCDA molecules are overlaid to guide the eye of the reader. Linear chains of CuPc and PTCDA molecules can be made out. At the position of the PTCDA molecules the perylene core is well pronounced in the frequency shift. The structure of the CuPc can be made out, too. In comparison with the LFM image of the individual CuPc shown in Fig. 7.4(a) a smililar contrast can be observed with the left lobe having a higher contrast than the right lobe. This trend is also visible at the PTCDA molecules. The left side of the perylene core exhibits an increased Δf contrast compared to the right side. This asymmetry is most likely caused by a tilted CO tip. The overall contrast of the PTCDA's and CuPc's is very similar as it will be shown by a comparison of line profiles, later.

Figure. 7.6(c) shows the corresponding STM image measured at a bias voltage of 1 mV. Features with increased conductance can be observed at the perylene core of the PTCDA molecules. At the CuPc's features with increased conductance around the molecule center can be observed. The relative conductance difference between the CuPc's and PTCDA's in the middle of the image appear to be small, except for CuPc's in the left top and right bottom corner, which show an increased conductance. The lower right CuPc's are located at the boundary of a mixed phase island.

To compare the relative contrast of CuPc's and PTCDA's in the LFM image [shown in Fig. 7.6(b)] line profiles are compared. To account for the influence of a tilted CO tip, a line profile on the left side of a CuPc is compared with a line profile on the left side of a PTCDA. The same comparison was done on the right side of the molecules. Figure 7.6(d) shows line profiles on the right lobe of a CuPc marked in the LFM image by a blue line and on the right side of a PTCDA molecule marked in the LFM image by a orange line. The dashed blue curve and the orange curve have a similar minimum of roughly -3 Hz. Figure 7.6(e) shows line profiles



Figure 7.7.: STM topography of the PC mixed phase on Ag(111) (setpoint: 100 mV and 50 pA). Ball-and-stick models of the PTCDA and CuPc are overlaid.

at the left lobe of a CuPc marked in the LFM image by purple line and on the left side of a PTCDA molecule marked in the LFM image by a green line. The dotted purple curve and the green curve have a similar minimum around -4.5 Hz.

This indicates similar adsorption heights of the CuPc and PTCDA molecule in the P₂C mixed phase. This can be concluded since the line profiles were taken at positions where the same atomic species are present (at CuPc and PTCDA) and a CO tip was used where it can be assumed that a similar distance dependence for short-range interaction persists. But there could be still a contribution of a different bond order [34], a different angle of the bonds relative to the oscillation direction, and a contribution from the neighboring molecules, which could influence the Δf signale. The appearance of equal adsorption heights of PTCDA and CuPc in the P₂C mixed phase is also corroborated by the literature. In Ref. [20] it was shown that CuPc and PTCDA equalize their adsorption heights in the P₂C mixed phase.

PC mixed phase on Ag(111)

In Ref. [22] the reported mixed phases encompass the P_2C , PC, and PC₂ mixed phases. The P_2C mixed phase was just discussed. During the measurements the PC mixed phase was observed as well. Figure 7.7 shows the STM topography of a PC mixed phase island. Ball-and-stick models of the PTCDA and CuPc are overlaid. A unit cell consisting of one PTCDA and one CuPc molecule can be seen. However, when the PC island shown in Fig. 7.7 was found, the CO tip was unstable and a preparation of a new CO tip was necessary and no LFM data could be acquired.

PC_2 mixed phase on Ag(111)

The PC_2 mixed phase was not observed in the experiments most probably because the CuPc coverage in the preparation was not high enough.

P_4C_2 mixed phase on Ag(111)

Besides the mentioned mixed phases a P_4C_2 mixed phase was observed, which was not reported so far. Figure 7.8(a) shows the molecular model of the P_4C_2 mixed phase. The molecular model was derived from the LFM image discussed later. The unit cell consists of four PTCDA and two CuPc molecules. The unit cell is spanned by the green vectors of length $a_{P_4C_2} = 3.3$ nm and $b_{P_4C_2} = 3.5$ nm, which are larger than the unit cell vectors of the P_2C mixed phase. The angle between the unit cell vectors of 69° is smaller when compared to the P_2C mixed phase (73°). The area of this unit cell is $A_{P_4C_2} = 10.1$ nm² and is more than twice the area of the P_2C mixed phase ($A_{P_2C} = 4.9$ nm²) and consists of twice the number of molecules. Interestingly, a void between the molecules can be observed.

Figure 7.8(b) shows the Δf image taken with a CO tip and an amplitude of 50 pm. The oscillation direction is in horizontal direction. The image was smoothed by a 2 × 2 Gaussian filter to reduce noise. Ball-and-stick models of PTCDA and CuPc are overlaid at the left top corner. Two rows of CuPc molecules can be observed, where one lobe is always higher than the opposite in alternating order (see cyan arrows). Since the order of the lobe with increased Δf contrast alternates a contribution to this contrast from a tilted CO tip can be ruled out. Between the CuPc, PTCDA molecules can be made out, where two are facing with the oxygen side to each other (yellow arrow). This region appears with a higher Δf contrast, indicating that these sides of the PTCDA's are raised. Also visible are CO molecules near the PTCDA molecules indicated by the red arrows.

In order to determine differences in the adsorption height of the individual molecules within one unit cell Δf line profiles were taken. Figures 7.8(c-d) show line profiles at positions marked by the colored lines in the Δf image. The blue line is at the right side and the orange line at the left side of a PTCDA molecule. As it can be seen by the line profiles in Fig. 7.8(c) the dashed blue curve has lower minimum than the orange curve, indicating that the right side of the PTCDA is higher than the left side. Figure 7.8(d) shows line profiles of the lobes of a CuPc molecule. The dashed magenta curve is on the right lobe and the green curve



Figure 7.8.: (a) Molecular model of the P_4C_2 mixed phase. The green vectors span the unit cell. (b) Δf image of the P_4C_2 mixed phase on Ag(111) taken with a CO tip and an amplitude of 50 pm. The image was smoothed by a 2×2 Gaussian filter. Also visible are CO molecules near the PTCDA molecules (red arrows). Ball-and-stick models of PTCDA and CuPc are overlaid. (c-d) Δf line profiles at positions marked by the colored lines in the LFM image. (e) Corresponding STM image to (b) at a bias voltage of 5 mV.

on the left lobe. The magenta curve has a lower minimum than the green curve indicating that the right lobe is higher than the left lobe.

This trend can be also observed in the STM image shown in Fig. 7.8(e). The bias voltage was 5 mV. The two PTCDA molecules which face the oxygen side to each other have features with increased conductance at this side [see yellow arrows in Fig. 7.8(e)]. At the CuPc molecules one of the horizontal lobes has increased conductance in alternating order [see cyan arrows in Fig. 7.8(e)]. The lobes with a higher conductance feature correspond to lobes in the LFM image with increased Δf contrast [see cyan arrows in Fig 7.8(b)]. This indicates that the increased conductance features of the lobes are caused by the geometry of the molecule.

Another interesting property of this mixed phase is the relative conductance of the CuPc's and the PTCDA's. The overall conductance of the CuPc's in Fig. 7.8(e) is higher than the conductance of the PTCDA's near the Fermi energy as the CuPc molecules appear brighter than the PTCDA molecules. This is different in comparison to the P_2C mixed phase, where both molecules have almost equal relative conductance. A possible reason for this could be a different adsorption height of the PTCDA and the CuPc in the P_4C_2 mixed phase. This can be analyzed by comparing the Δf line profiles shown in Fig. 7.8(c-d). If the right side of CuPc [dashed purple curve in Fig. 7.8(d)] is compared with the right side of the PTCDA [dashed blue curve in Fig. 7.8(c)] it can be seen that the CuPc lobe exhibits a lower frequency shift minimum compared to the PTCDA (-3.5 Hz vs - 2 Hz). The same comparison can be done for the left sides: The left side of the CuPc has a Δf minimum of -2 Hz. The left side of the PTCDA a minimum of around -1 Hz. Since both Δf minima of the CuPc are lower than the Δf minima of the PTCDA, it can be concluded that the CuPc has a higher average adsorption height than PTCDA. The equalization of the adsorption heights in the P_2C mixed phase reported in Ref. [20] is obviously suppressed in the P_4C_2 mixed phase. A possible cause could be the void within the unit cell and a reduced intermolecular interaction and interaction with the surface. In the P_2C mixed phase one CuPc molecule is surrounded by three PTCDA molecules on average [see Fig. 7.6(a)]. In the P_4C_2 mixed phase one CuPc molecule is surrounded by two PTCDA molecules on average [see Fig. 7.8(b)] and has therefore a decreased interaction with PTCDA molecules. Moreover, Ref. [20] reports that charge transfer of the PTCDA and CuPc with the surface occurs, which alters the electronic structure of both molecules. A general influence of the electronic structure on the conductance of PTCDA and CuPc shown in Fig 7.8(e) cannot be excluded.

PTCDA and CuPc mixed structure on Ag(111)

In this section a non-periodic structure of PTCDA's and CuPc's will be discussed. This structure was observed in course of the same preparation as mentioned in section 7.2.2. Figure 7.9(a) shows a constant height STM image at a bias voltage of 1 mV recorded with a CO tip. Four CuPc molecules marked by A, B, C, and D surround a single PTCDA molecule. These CuPc's are integrated into a PTCDA island. CuPc A and B are located at the edge of the molecular island. The current range of the STM image was cropped to increase the contrast. In the left bottom corner high currents occured at a PTCDA molecule, which appears very bright. A possible cause could be an abnormal adsorption geometry. The LFM image [Fig. 7.9(b)] does show an increased Δf contrast at the right hand side of this PTCDA molecule, but it is unclear how this leads to the increased conductance of the whole PTCDA molecule. In the STM image in Fig. 7.9(a) the CuPc molecules A and B, which sit at the boundary of the island, have an increased conductance compared to CuPc C and D, which sit inside of the island. To determine whether this is a geometric or an electronic effect, the adsorption heights of the CuPc molecules will be again analyzed based on the Δf contrast in a constant-height LFM image.

Figure 7.9(b) shows the corresponding Δf image taken with an amplitude of 50 pm. The oscillation is in horizontal direction. The image was smoothed by a 2×2 Gaussian filter to reduce noise. Colored lines indicate positions where line profiles were taken [see Fig. 7.9(c-d)].

In the STM image CuPc A has the highest conductance and CuPc C the lowest. To account for an geometric cause for the conductance difference, these two molecules are compared. Figure 7.9(c) shows line profiles on the right lobe of CuPc A (blue dashed curve) and on the right lobe of CuPc C (orange curve). The minimum of the blue curve is lower than the minimum of the orange curve (-2.5 Hz vs. -2 Hz). This indicates the right lobe of CuPc A is higher than the right lobe of CuPc C. Figure 7.9(d) shows line profiles on the left lobe of CuPc A (purple dashed curve) and on the left lobe of CuPc C (green curve). The minimum of purple curve is higher than the minimum of the green curve (-2 Hz vs. -2.5 Hz), showing a higher lobe of CuPc C. In conclusion no evidence of a higher adsorption height of CuPc A can be seen, indicating the increased conductance of CuPc A as


Figure 7.9.: (a) STM constant height image taken with a CO tip at a bias voltage of 1 mV of four CuPc's surrounding one PTCDA on Ag(111). The current range was cropped to increase the contrast. (b) Corresponding Δf image recorded with an amplitude of 50 pm. The oscillation is in horizontal direction. The image was smoothed by a 2 × 2 Gaussian filter. (c-d) Δf line profiles taken at positions marked by the colored lines in (b).

an electronic effect.

Conclusion and outlook

Different mixed phases of CuPc and PTCDA on Ag(111) were discussed. STM and LFM images of the P_2C mixed phase were investigated. The LFM image showed similar contrast and flat geometries of the PTCDA's and the CuPc's in the P_2C mixed phase. In the STM image both molecules showed similar conductance. In the P_4C_2 mixed phase CuPc's showed an increased conductance relative to the PTCDA's. Furthermore, non-flat geometries of both molecules could be observed in the LFM image. The origin of the increased conductance of CuPc's is most likely caused by a higher adsorption height of the CuPc's relative to the PTCDA's. Lobes with increased height in the LFM image showed also an increased conductance in the STM image. In a non-periodic mixed structure of CuPc's and PTCDA's an analysis of the LFM contrast indicated that the increased conductance of a CuPc at the island boundary is not a result of a higher adsorption height but most likely an electronic effect.

The P_4C_2 mixed phase exhibits remarkable cavities in the unit cell. The cavities in this mixed phase could be used to host guest adsorbates. A more advanced experiment would be to evaporate e.g. Fe adatoms on the P_4C_2 mixed phase and investigate their occupation of the cavities. A similar experiment was done with dicarbonitrile pentaphenyl molecules on Cu(111), which form a honeycomb network with relatively large cavities. Evaporated iron adatoms adsorb mostly in the center of the cavities [141]. In addition, to investigate the structure of the P_4C_2 mixed phase more deeply, Lennard-Jones potential calculations could be performed as described in Ref. [136, 138]. This could answer the question if the cavities of the P_4C_2 mixed phase structure can be reproduced by considering only molecular interactions or if the surface has to be taken into account, which would, however, require density functional theory calculations.

7.3. PTCDA and CuPc on Cu(111)

In the previous section, different mixed phases of PTCDA and CuPc on Ag(111) have been discussed. Similarly, Ref. [139] reports a mixed phase of these two molecular species on the Cu(111) surface. Analogously, a Cu(111) sample with PTCDA and CuPc adsorbates was prepared with the goal to reproduce this mixed

phase. However, no evidence for a mixed phase was found, here. Instead, CuPc molecules adsorbed at the edge of PTCDA islands. The sample was prepared by, first, evaporation of CuPc, followed by evaporation of PTCDA and finally annealing the sample to 200 °C as given in the preparation details in Ref. [139]. Possible reasons that no mixed phases were observed are maybe that in Ref. [139] the sample was annealed with a different real temperature or a different coverage of CuPc and PTCDA for the preparation was used.

In this section CuPc molecules adsorbed next to different numbers of PTCDA molecules are investigated with LFM and STM. The influence of the nearby PTCDA's on the geometric and electronic structure of the CuPc molecule will be analyzed. For instance, CuPc close to one, two, and three PTCDA molecules will be investigated. The potential energy is calculated and the alignment of the CuPc relative to the Cu(111) surface is determined.

7.3.1. CuPc close to one PTCDA

Figure 7.10(a) shows the Δf image recorded with a CO tip of a CuPc molecule close to one PTCDA on Cu(111). The oscillation of the LFM sensor is in horizontal direction and the amplitude is 50 pm. On the right side of the image a part of a PTCDA island can be seen. The boundaries of the individual molecules are better distinguishable in the STM image shown in Fig 7.10(b). The single CuPc next to a PTCDA and the PTCDA's of a PTCDA island can be seen. In the LFM image in Fig. 7.10(a) CuPc appears relatively flat compared to an isolated CuPc molecule adsorbed on Cu(111), which is shown in Fig. 7.3(a). Note that, while the horizontal lobes and the lower lobe have similar contrast, the upper lobe has a slightly increased contrast. This indicates that three lobes have a lower adsorption height and one lobe a higher adsorption height. Isolated CuPc on Cu(111) shows two lobes raised and two lowered as it can be seen in Fig. 7.3(a).

The perylene cores of the PTCDA molecules are well pronounced in the LFM image showing a higher contrast relative to the CuPc molecule. To investigate the relative adsorption heights of PTCDA and the CuPc, line profiles were taken at positions marked by the colored lines in Fig. 7.10(a). Figure 7.10(c) shows line profiles at the horizontal lobes of the CuPc. Both minima are between -3 Hz to -2 Hz. Figure 7.10(d) shows line profiles at the PTCDA next to the CuPc. Both minima are at -4 Hz. This indicates a higher adsorption height of the PTCDA. To quantify the height difference between the CuPc and the PTCDA line profiles at



Figure 7.10.: (a) Δf image of CuPc close to a PTCDA molecule. The oscillation is in horizontal direction and the amplitude was 50 pm. (b) Corresponding STM image with bias voltage of 1 mV. (c) Δf line profiles at the horizontal CuPc lobes marked by the blue and orange line in (a). (d) Δf line profiles at the PTCDA marked by the green and purple line in (a). (e) Δf line profiles at the same positions at the PTCDA marked by the green and purple line in (a) in an LFM image 35 pm heigher than (a). (f) Potential energy map of a part of the CuPc marked by the black dashed box in (a). (g) CuPc rotation relative to the Cu(111) atomic surface lattice. The blue cross indicates the CuPc orientation relative to the a high-symmetry direction of the Cu(111) atomic surface lattice (black dashed line).

a higher height at the PTCDA were compared. The LFM image in Fig. 7.10(a) is part of a 3D dataset. The height difference of the images in the 3D dataset is 5 pm. By picking an LFM image at a height where the Δf line profile minima of PTCDA equals the the Δf line profile minima of the CuPc, the relative height difference can be estimated. Figure 7.10(e) shows Δf line profiles of an LFM image 35 pm higher than the LFM image shown in Fig. 7.10(a). The line profiles in Fig. 7.10(e) have minima between -3 Hz to -2 Hz. This is in the same range as the Δf line profile minima of the CuPc (-3 Hz to -2 Hz). The height difference between the CuPc and the PTCDA can be estimated to be 35 pm.

On Cu(111) the average adsorption height of the perylene core of PTCDA (in a PTCDA domain) is very similar to the average adsorption height of the carbon atoms of individual CuPc (2.66 Å [124] vs 2.64 Å [136] (at 300 K)). Interestingly, this is not the case in this configuration, where both molecules changed their relative adsorption height. A possible explanation for the height difference could be a charge transfer between the PTCDA and the CuPc through the metal surface as it occurs on Ag(111) which leads to an equalization of the adsorption heights of PTCDA and CuPc [20]. A similar mechanism could be expected on Cu(111) which would lead to a descrease of the adsorption height of the CuPc.

Figure 7.10(b) shows the constant height STM image with a bias voltage of 1 mV. The vertical lobes of the CuPc have features with higher conductance than the horizontal lobes, whereas the top lobe has a feature with the highest conductance. The horizontal lobe facing the PTCDA molecule has the lowest conductance in the STM image. To investigate whether this is a geometric or electronic effect, Δf line profiles are compared. The line profiles were taken at the left and right horizontal lobes [blue and orange line in Fig. 7.10(a)]. Fig. 7.10(c) shows the line profiles. The minimum of the orange curve (right lobe) is higher than the minimum of the dashed blue curve (left lobe). This indicates that the right horizontal lobe facing the PTCDA molecule is lower than the left horizontal lobe. Therefore, the lower conductance of the right horizontal lobe observed in the STM image is most likely caused by the adsorption geometry of the CuPc and is not an electronic effect.

Next, the tip-sample interaction potential above the CuPc will be investigated. To calculate the potential energy the Fourier method was used [41]. It requires the frequency shift to be zero at the boundaries. Therefore only a part of the CuPc, which does not have any other molecules directly on the side could be used for the calculation [see dashed black box in Fig. 7.10(a)]. Note that for the potential energy calculations of the rest of this chapter the LFM sensor stiffness $k = 1950 \text{ N m}^{-1}$ was used as estimated in Ref. [142] and not the stiffness as estimated by the Euler-Bernoulli method in section 3.5.2. Therefore the absolute value of the potential energy is overestimated by 45%. Nevertheless, this allows a comparison with the data presented in Ref. [17], where the same sensor was used with the (too high) stiffness of $k = 1950 \text{ N m}^{-1}$.

Figure 7.10(f) shows the calculated potential energy. The values range from -72 meV to 16 meV. When compared to the potential energy of an individual CuPc on Cu(111) as shown in Fig. 4(e) in Ref. [17] (-115 meV to 15 meV), the potential energy is lower. A possible reason is that the energy could only be calculated from a part of the CuPc, which does not include the molecule center, where the energy would be lower. Another reason would be a different tip height. An estimate of the tip height in Ref. [17] was not possible, since the data was recorded with a bias voltage of 0 mV. Another 3D dataset of an isolated CuPc with a bias voltage of 10 mV showed at the same bare surface conductance as of Fig. 7.10(b) rotations of the CuPc and the energies could not be extracted.

Last, the alignment of the CuPc relative to the high-symmetry direction of the Cu(111) atomic surface lattice will be discussed. Figure 7.10(g) shows the CuPc rotation (blue cross and blue line) relative to the Cu(111) atomic surface lattice (yellow circles)¹. The high-symmetry direction of the hexagonal lattice is indicated by the black dashed line. The rotation of the CuPc molecule relative to the high-symmetry direction of the atomic surface lattice is $\pm 8^{\circ}$. As mentioned in the introduction of this chapter CuPc can undergo frustrated rotations of $\pm 7^{\circ}$ induced by inelastically tunneling electrons [23, 24] or by the proximity of the tip [17]. In the absence of a tip or tunneling electrons CuPc is aligned in a high-symmetry direction of the atomic surface lattice. Figure 7.10(g) shows that a close PTCDA molecule can lock the CuPc molecule in a rotated position. This shows that the alignment of a CuPc molecule can not only be influenced by inelastically tunneling electrons or the proximity of the tip but also by the local molecular environment.

7.3.2. CuPc close to two PTCDA's

In this section the data of CuPc close to two PTCDA molecules will be discussed. Figure 7.11(a) shows the Δf image of a CuPc molecule close to two PTCDA

 $^{^1\}mathrm{The}$ copper lattice was resolved with a CO tip, set point $5\,\mathrm{mV}$ and $2\,\mathrm{nA}.$



Figure 7.11.: (a) Δf image of a CuPc molecule next to two PTCDA molecules. The oscillation is in horizontal direction and the amplitude was 50 pm. (b) STM image recorded with a bias voltage of 1 mV. (c) Potential energy map of a part of the CuPc molecule marked by the black dashed box in (a). (d) CuPc rotation relative to the Cu(111) surface. The blue cross indicates the orientation of the CuPc molecule relative to a high-symmetry direction of the Cu(111) atomic surface lattice (black dashed line). molecules. The oscillation of the LFM sensor is in horizontal direction and the amplitude was 50 pm. The oxygen sides of the PTCDA molecules face the lower vertical lobe with an angle of approximately 45°. The boundaries of the individual molecules are better distinguishable in the STM image shown in Fig 7.11(b) (bias voltage 1 mV). In the LFM image the horizontal lobes of the CuPc exhibit a higher Δf contrast than the vertical lobes. This is similar to an isolated CuPc molecule on Cu(111) shown in Fig. 7.3(a). In the STM image the horizontal lobes show a higher conductance than the vertical lobes. The lower vertical lobe, which faces the PTCDA's, exhibits the lowest conductance.

Figure 7.11(c) shows the deconvoluted potential energies of the dashed black area in Fig. 7.11(a). The values ranges from -84 meV to 30 meV. This is close to the potential energy of a CuPc close to one PTCDA shown in Fig. 7.10(f) (-72 meV to 16 meV). The negative potential energy is higher than the negative potential energy of an individual CuPc on Cu(111) as shown in Fig. 4(e) in Ref. [17] (-115 meV). A possible reason for the discrepancy is probably a different tip height and that only a part of the CuPc could be used for the energy calculation in Fig. 7.11(c).

Figure 7.11(d) shows the orientation of the CuPc molecule (blue cross and blue line) relative to the Cu(111) atomic surface lattice (yellow circles). The high-symmetry direction of the hexagonal surface is indicated by the dashed black line. The CuPc is aligned in a high-symmetry direction of the surface lattices.

Interestingly, while a CuPc molecule adsorbed close to only one PTCDA molecule is locked in the rotated position $(\pm 7^{\circ})$ (compare section 7.3.1), the molecule is locked and aligned to the high-symmetry direction when it is adsorbed next to two PTCDA molecules. Isolated CuPc remains aligned to the surface high-symmetry direction only in the absence of inelastic tunneling electrons and where the long range attraction of the tip is weak [17, 24, 137]. This demonstrates that nearby PTCDA molecules can also inhibit the rotation of the CuPc to the rotated position in the presence of the tip and tunneling electrons.

7.3.3. CuPc close to three PTCDA's

The previous sections have shown that the number of PTCDA molecules adsorbed adjacent to a CuPc molecule determines whether the latter adsorbs in an aligned or a rotated position with respect to the copper surface lattice. Moreover, the intermolecular interaction locks the molecule in its adsorption geometry and hinders a rotation of the molecule due to inelastically tunneling electrons or the tip-molecule



Figure 7.12.: (a) Δf image CuPc next to two PTCDA molecules. The oscillation is in horizontal direction and the amplitude was 50 pm. (b) STM image with a bias voltage of 1 mV. (c) Δf line profiles at CuPc lobes A and C marked by the colored lines in (a). (d) Δf line profiles at the PTCDA marked by the colored lines in (a). (e) Potential energy map of a part of the CuPc marked by the black dashed box in (a). (f) CuPc rotation relative to the Cu(111) surface. The blue cross indicated the CuPc orientation (blue cross) relative to a high-symmetry direction of the Cu(111) atomic surface lattice (black dashed line). interaction previously observed for an isolated CuPc molecule adsorbed on Cu(111).

In this section the data of CuPc molecule close to three PTCDA molecules will be discussed. Figure 7.12(a) shows the Δf image of a CuPc molecule close to three PTCDA molecules. The oscillation of the LFM sensor is in the horizontal direction and the amplitude was 50 pm. The CuPc lobes are marked by A, B, C, and D. The boundaries of the individual molecules are better distinguishable in the STM image shown in Fig 7.11(b) (bias voltage 1 mV). In the STM image the CuPc lobe A exhibits a higher conductance than e.g CuPc lobe C. Whether this is an geometric or electronic effect can be investigated by comparing line profiles at these lobes. Figure 7.12(c) shows Δf line profiles at CuPc lobe A (orange curve) and at CuPc lobe C (blue dashed curve). The exact positions where the line profiles were taken are shown by the colored lines in Fig. 7.12(a). Both line profiles exhibit the same minimum of -2.6 Hz. This indicates an equal height of lobe A and C. The reason for the increased conductance of lobe A in Fig. 7.12(b) is most likely an electronic effect and not caused by different heights of the lobes.

In Fig. 7.12(a) the overall contrast of the CuPc appears to be lower than the contrast of the close PTCDA's. To investigate an adsorption height difference line profiles at a PTCDA were taken. Fig. 7.12(d) shows Δf line profiles at the right side of a PTCDA (purple dotted curve) and on the left side of a PTCDA (green curve). Both Δf minima are in the range of -4 Hz to -3 Hz. This is lower than the minima of the CuPc lobes which are at -2.6 Hz and shows the increased adsorption height of the PTCDA relative to the CuPc molecule. In addition, the Δf minimum on the right side of the PTCDA is lower than the minimum on the left side. From this observation it can be concluded that the side of the PTCDA molecule facing the CuPc molecule has a higher adsorption height than its left side.

Next, the potential energy map is calculated for an area shown by the black dashed box in Fig. 7.12(a). Figure 7.12(e) shows the potential energy map. Only a small part of the CuPc could be used for the energy deconvolution. The values range from -35 meV to 11 meV. The minimum is significantly higher when compared to the potential energy minimum of an individual CuPC in Fig. 4(e) in Ref. [17] (-115 meV). A reason for the higher minimum is that only a small part of the CuPc was used for the energy calculation and probably a different tip height.

Last, the alignment of the CuPc will be discussed. Figure 7.12(f) shows the rotation of the CuPc (blue cross and blue line) relative to the Cu(111) atomic surface lattice (yellow circles). A high-symmetry direction of the surface is shown

by the black dashed line. The rotation angle measures 8° showing that the CuPc molecule adsorbs in the rotated position. In the Ref. [24] it is discussed that there is still a height difference between the 'vertical' and 'horizontal' lobes for an isolated CuPc molecule adsorbed in the rotated state on Cu(111). This height difference is not visible in Fig. 7.12(a) at the CuPc which is close to three PTCDA's and is in the rotated position. This observation indicates that the intermolecular interaction between the PTCDA molecules and the CuPc molecule or the charge transfer between the PTCDA and CuPc molecule through the surface can change the adsorption geometry of the CuPc molecule with respect to the geometry of an isolated adsorbate.

7.3.4. Conductance at different bias voltages

In the section before it was already shown that close PTCDA's have an influence on the geometric and electronic structure close to the Fermi level of the CuPc. The following investigation considers influence of close PTCDA's on the STM topography images of CuPc at higher bias voltages. In this section the differences in the STM topography images of CuPc close to one, two, and three PTCDA's with different bias voltage will be investigated. The images were taken with a CO terminated tip. Note that the STM topography images were taken with constant current $I_{set} = 50$ pA and the tip was not close enough to the molecules to achieve a Δf contrast. In constant current mode conductance differences are measured as height differences as the STM feedback loop keeps the current constant.

Figure 7.13 shows STM topography images of CuPC close to different numbers of PTCDA molecules. Each row represents a different bias voltage from 100 mV (top row), 500 mV (second row), 1.0 V (third row), and 1.5 V (last row). In the first column CuPc is close to one PTCDA, in the second column CuPc is close to two PTCDA's, and in the third column CuPc is close to three PTCDA's.

Figure 7.13(a) shows a STM topography image of CuPc close to one PTCDA molecule at a bias voltage of 100 mV. Two lobes of the CuPc appear with increased intensity, whereas the two perpendicular lobes appear with reduced height. The same pattern can be seen in Fig. 7.13(b), where CuPc close to two PTCDA's at bias voltage of 100 mV is shown. However, the intensity difference between the lobes appears to be smaller as compared to the image recorded of a CuPc molecule adsorbed next to only one PTCDA molecule. Note that the left lobe of the CuPc molecule shows a slightly stronger STM signal than the right lobe. In Fig. 7.13(c)



Figure 7.13.: STM images at different bias voltages in constant current mode (I = 50 pA) of CuPc adsorbed close to different numbers of PTCDA molecules: row-wise (a-c) at U = 100 mV, (d-f) at U = 500 mV, (g-i) at U = 1.0 V, and (j-l) at U = 1.5 V. Column-wise (left) CuPc adsorbed to one PTCDA molecule, (center column) CuPc adsorbed to two PTCDA molecules, and (right column) CuPc adsorbed to three PTCDA molecules.

CuPc close to three PTCDA's at bias voltage of 100 mV is shown. An intensity difference between the lobes is visible as well. In all three images of the row two lobes have higher intensity and two lobes have lower intensity. Additionally, submolecular features can be identified in the center of the CuPc molecules.

Figures 7.13(d-f) show the corresponding STM topography images of CuPc next to one, two, and three PTCDA molecules at a bias voltage of 500 mV. While all three images show qualitatively the same pattern as the images recorded at 100 mV [Fig. 7.13(a-c)], the relative contrast between the horizontal and vertical lobes is decreased as compared to the images recorded at lower bias voltage. Additionally, no [Fig. 7.13(d,e)] or only faint [Fig. 7.13(f)] submolecular features can be recognized in the images.

For higher bias voltages [1.0 V, Fig. 7.13(g-i) and [1.5 V, Fig. 7.13(j-l)] the images show similar trend that the STM contrast reduces with increasing bias voltage. Submolecular features are not visible anymore most likely due to the increased tip-sample distance with higher bias voltages.

To conclude, close PTCDA molecules have no visible influence on the STM topography images of a CuPc molecule in the voltage range of 100 mV to 1500 mV.

7.3.5. Conclusion and outlook

The combined STM and LFM measurements presented in this section show that PTCDA's adsorbed close to CuPc can affect the geometric and electronic structure (near the Fermi level) of CuPc on Cu(111). An isolated CuPc molecule on Cu(111) adsorbs in the aligned state and can switch to the rotated state in the presence of inelastically tunneling electrons and a strong tip-sample potential. Close PTCDA's can lock the CuPc in a rotated position (relative to the high-symmetry direction of the atomic surface lattice), where CuPc appears relatively flat [Fig. 7.10(a)], which is different from the geometry of isolated CuPc molecules adsorbed on Cu(111)[Fig. 7.3(a)] where two lobes are bent downwards and two upwards. In contrast CuPc close to two PTCDA's can be locked and aligned to the high-symmetry direction of the atomic surface lattice and two lobes show increased Δf contrast and two lobes show reduced Δf contrast [Fig. 7.11(a)]. This is similar to individual CuPc on Cu(111) [Fig. 7.3(a)]. CuPc close to three PTCDA's appears flat as well where one lobe shows an increased conductance [Fig. 7.12(b)] although the Δf line profiles do not show an increased height and indicate an electronic effect. At higher bias voltages no differences in the STM topography of the CuPc close to different

7. PTCDA and CuPC investigation with LFM

numbers of PTCDA's are visible.

The physical reason of the flat geometry of CuPc when adsorbed in the rotated position close to three PTCDA molecules could be investigated with density functional theory calculations as performed for individual CuPc on Cu(111) [24]. This could answer the question if the flat geometry of CuPc is caused by a charge transfer between the CuPc and PTCDA through the Cu surface as on Ag(111) [20] or by intermolecular long-range van der Waals interaction or electrostatic interaction. Furthermore, the change of the density of states of the CuPc close to different numbers of PTCDA's could be investigated in more detail by scanning tunneling spectroscopy.

8. Energy dissipation with LFM

Building on the result that CO terminated tips yield intramolecular resolution [83, 84], it was shown that the apex CO molecule can snap over chemical bonds using an LFM sensor [25]. In LFM the tip oscillates parallel to the surface. The CO molecule at the tip acts as a torsional spring [48, 80] and when it oscillates over a chemical bond e.g. a C-C bond of the perylene core of a PTCDA it can bend away or towards the bond depending on the position of the CO relative to the bond [see Fig. 8.1(a), (adapted from Ref. [25])]. When it bends away or towards the bond the CO gets loaded like a torsional spring and it can release the energy by snapping over the bond at another point in the oscillation path of the tip. Figure 8.1(b)shows the bending angle θ of the CO as a function of the distance from the bond¹. The blue curve represents the forward, the red curve the backward oscillation path. As it can be seen at certain positions the CO snaps from a negative bending angle to a positive and vice versa. This rapid change of the bending angle is related to a change of the direction of the force between the bond and the CO. Figure 8.1(c)shows the lateral force between the bond and CO for the forward (blue) as well for the backward path (red) of the oscillation. At x positions where the CO snaps over the bond the force changes its sign. The area encapsulated between the forward and backward force curves is the dissipated energy E_{diss} .

So far the energy dissipation E_{diss} was observed at locations where a chemical bond exists. A ball-and-stick model of a PTCDA molecule is shown in the inset in Fig. 8.1(a). The gray atoms are carbon, red oxygen, and white hydrogen. Figure 8.1(d) shows the dissipated energy at the perylene core of a PTCDA molecule. The carbon ring structure of the perylene core is mostly reproduced by the E_{diss} signal. At the top right and the bottom left in Fig. 8.1(d) no E_{diss} signal can be seen. This was also observed in other E_{diss} data of the PTCDA perylene core. The reason for this could be the complex potential energy landscape of the PTCDA

 $^{^{1}\}mathrm{In}$ chapter 4 and 6 θ was defined differently. In this chapter θ is the bending angle to the vertical of the tip CO.



Figure 8.1.: (a) (Inset, right) Sketch of a PTCDA molecule. (Main) Moving the CO tip over a bond at x = z = 0 m causes the CO to tilt, but it cannot reach the universal low energy position. The background grayscale shows the potential energy (in meV) of the O atom as acted upon by the two C atoms, modeled with Morse potentials. As the tip passes from left to right (*i* to *ii*), the CO cocks over the bond (*iii*) until it snaps down (*iv*). (b) The angle that the CO makes with the vertical as a function of the x position of the metal tip apex. (c) The lateral force on the apex makes a hysteresis loop around the snap. The area of this loop is the dissipated energy E_{diss} . (d) Excitation image of a single PTCDA molecule and (e) corresponding LFM image. The scale bar for both (d) and (e) is shown in (d). The direction of oscillation is horizontal. Figures and caption adapted from Ref. [25].



Figure 8.2.: (a) The maximum energy dissipation above a bond as a function of the height of the tip. Black dots are experimental values, red circles are the model output. The blue line is an exponential fit to the data from z = 5 pm to 15 pm. The green line is a linear fit to the data from z = 0 pm to 2 pm. (b) The six atoms that were included in this model are shown darker than the others. Figure and caption adapted from Ref. [25].

molecule. The perylene core is reproduced in the Δf image shown in Fig. 8.1(e).

The E_{diss} signal is only detectable in a small height range. This can be seen in Fig. 8.2(a) (taken from Ref. [25]). It shows the maximum of the excitation signal as a function of the tip height z (black dots). The dashed blue curve shows an exponential fit to the data. The characteristic decay length can be determined by fitting an exponential curve $[y_1 = b_1 \exp(-z/\lambda)]$ to the data, where λ is the characteristic decay length. This yielded for λ a value of 4 pm at a PTCDA C-C bond. The experimental data [black dots in Fig. 8.2(a)] shows a linear region in the range z = 0 pm to 2 pm. The slope of the linear region can be determined by fitting a linear function $[y_2 = sz + b_2]$ to the data in this region, where s is the slope of the linear fit. In this case the linear function was fit by eye. This yields a slope of 1 meV/cycle/pm at a PTCDA C-C bond.

The red dots in Fig. 8.2(a) show the output of the model described in Ref. [25]. The model considers Lennard-Jones or Morse potential interaction between the oxygen atom of the CO at the tip and the 6 C atoms of a PTCDA molecule, highlighted in Fig. 8.2(b). The C atoms of the PTCDA molecule are static and are not allowed to relax. Due to the mirror symmetry of the C atoms to the x, z plane [Fig. 8.2(b)] the CO molecule is only allowed to relax in this plane. The CO molecule is modeled as a torsional spring with a moment arm of 300 pm and a spring constant of 0.5 N m^{-1} . The dissipated energy over one cycle is calculated by $W(x) = -E_{\text{diss,model}}(x) = \int_{-A}^{A} F_{\text{fwd}}(x-q)dq + \int_{A}^{-A} F_{\text{bwd}}(x-q)dq$, where F_{fwd} is the lateral force on the forward path of the tip and F_{bwd} is the lateral force on the backward path of the tip. A is the oscillation amplitude.

The data presented in this chapter were taken with different CO tips. When the CO molecule is adsorbed on the tip, the lateral stiffness of the CO k_{CO} can have different values depending on the configuration of the second and third atomic layers of the metallic tip apex. When the tip is poked into the surface to yield a single atom tip, the configuration of the second and third atomic layers can change. In Ref. [48], k_{CO} was determined to be $0.24 \,\mathrm{N}\,\mathrm{m}^{-1}$ and is lower than the stiffness of a CO adsorbed on a Cu(111) surface. Density functional theory calculations showed that k_{CO} can vary from $0.3 \,\mathrm{N}\,\mathrm{m}^{-1}$ to $1.3 \,\mathrm{N}\,\mathrm{m}^{-1}$ depending on the atomic configuration of the metal tip.

In this chapter excitation images will be discussed where the excitation signal was recorded between PTCDA molecules where no chemical bonds exist. It can be expected that between the PTCDA molecules hydrogen bonds exist, although they could be rather weak [122, 143]. Further, excitation data was recorded at the CuPc lobe and between the lobe of a CuPc molecule and a PTCDA molecule. Then the maxima of E_{diss} as a function of z will be analyzed of the mentioned molecular positions and at a PTCDA C-C bond. From these data the exponential characteristic decay length and slope of the linear region are determined and compared. Last, the influence of the CO stiffness on the magnitude of the energy dissipation maxima is demonstrated by comparing different datasets.

8.1. Intermolecular and intramolecular energy dissipation

In this section excitation images will be discussed where the excitation signal was recorded between PTCDA molecules as well as excitation data recorded at the CuPc lobe and between the lobe of a CuPc molecule and a PTCDA molecule. The excitation signals recorder between PTCDA's and between the CuPc lobe and a



Figure 8.3.: STM images, excitation images, and overlaying molecule models. Oscillation direction in all images is in horizontal direction. (a) In the background: STM image of PTCDA molecules on Cu(111) with a CO tip. On top: ball-and-stick models of PTCDA and between an exitation image, where the signal was measured. The excitation data as a function of z was collected along the yellow line. (b) Excitation image of a CuPC molecule on Cu(111) with a CO tip. On top a ball-and-stick model of CuPc is overlaid. The exitation data as a function of z was collected along the yellow line. (c) In the background: STM image of CuPC next to a PTCDA island on Cu(111) with a CO tip. On top a ball-and-stick model of CuPC and PTCDA. The excitation data as function of z was taken along a horizontal line in the center of the yellow box. PTCDA molecule are unexpected as no chemical bonds exist here.

Figure 8.3(a) shows in the background a constant height STM image of PTCDA molecules on Cu(111). As it was explained in chapter 7 PTCDA's form domains on metal surfaces. Ball-and-stick models of PTCDA molecules are overlaid and scaled to the image size. Between the molecules an excitation signal was measured and overlaid at the position where it was recorded (green box). The oscillation direction is in horizontal direction with an amplitude of A = 50 pm. The excitation signal between the PTCDA molecules has a rectangular shape with a smaller lateral thickness in the middle. The excitation signal goes probably from the oxygen atom of one PTCDA to the hydrogen atom of the other PTCDA. The yellow line indicates where excitation data (line profiles) at different heights were taken (will be discussed later in section 8.2).

Figure 8.3(b) shows an excitation image at the lobe of a CuPc molecule on Cu(111) recorded with a CO tip. The oscillation direction is in horizontal direction with an amplitude of A = 50 pm. A ball-and-stick model of the CuPc lobe is overlaid. An excitation signal is visible at the C-C bonds at the CuPc C₆ ring. The excitation signal is only visible at the left side of the CuPc lobe. The reason for this is probably a height difference of the carbon atoms of the lobe. In the Δf image of individual CuPc on Cu(111) in chapter 7 in Fig. 7.3(a) it could be observed that the CuPc lobes curve upward and the geometry of CuPc is not flat. The yellow line indicates where excitation data at different heights was taken (will be discussed in section 8.2).

Figure 8.3(c) shows an STM image of a CuPC molecule next to a PTCDA of a PTCDA island on Cu(111). Overlayed are ball-and-stick models of the molecules. In the center a smaller constant height STM image is visible after which the molecule models are aligned (dark region). The oscillation direction is in horizontal direction with an amplitude of A = 50 pm. In the yellow box an excitation image is shown² of an area between the CuPc and PTCDA. The excitation shape is similar like in the case of two PTCDAs: a rectangular shape which is laterally thinner in the middle.

 $^{^{2}}$ Due to the drift of the microscope a part of an older excitation image is visible on the side.

8.2. $E_{\rm diss}$ as a function of z

In this section the exponential characteristic decay length and the linear slope of E_{diss} data recorded at different intra and intermolecular positions will be compared. These data were taken with different CO tips and it will be shown that the exponential characteristic decay length and the linear slope of the data are equal within uncertainty for different CO tips.

In this chapter E_{diss} was calculated from the excitation data by Eq. 2.11. We will first discuss E_{diss} data taken at a C-C bond of a PTCDA with CO tip A and compare it to Ref. [25]. Figure 8.4(a) shows the maxima of E_{diss} as a function of z (blue dots). The C-C bond at which the excitation data was taken is marked by a green oval at the ball-and-stick model of the PTCDA. z = 0 pm refers to the closest approach. As the tip approaches the surface at $z = 30 \text{ pm} E_{\text{diss}}$ increases exponentially as can be seen by the exponential fit (right black curve) until it reaches a maximum of 24 meV/cycle. The determined characteristic decay length at the exponential increase is $(5 \pm 2) \text{ pm}$. In Ref. [25] the reported characteristic decay length is 4 pm and is equal within uncertainty to the measurement. After the maximum E_{diss} decreases linearly as it can be seen by the linear fit [left black curve in Fig. 8.4(a)]. The linear fit yielded a slope of $(0.7 \pm 0.3) \text{ meV/cycle/pm}$. In comparison to the slope of the linear region in Fig. 8.2(a) (slope 1 meV/cycle/pm) the determined slope is equal within uncertainty to the data in Ref [25].

It is supposed that the linear decrease of $E_{\rm diss}$ is caused by a vertical movement of the adsorbate on the surface, which was not considered in the model in Ref. [25], yet. In case of the energy dissipation at a C-C bond of a PTCDA one could imagine that the CO pushes the PTCDA down which would reduce the energy dissipation. This is currently subject of further investigations with density functional theory calculations.

Next, E_{diss} data taken at the H-O position between two PTCDA molecules with CO tip B will be discussed. In Fig. 8.4(b) the position where the data was taken is indicated by the green oval at the ball-and-stick model. The blue dots show the maxima of E_{diss} as a function of z. As for the energy dissipation of the PTCDA C-C bond E_{diss} increases exponentially until it passes a maximum and decreases linearly. The maximum reaches 14 meV/cycle and is lower than the maximum at the PTCDA C-C bond shown in Fig. 8.4(a). The exponential fit yielded a characteristic decay length of (6 ± 1) pm and is equal to the decay length



Figure 8.4.: E_{diss} as a function of z (blue dots) and exponential and linear fits (black curves). The positions where the excitation data was taken is marked by the green oval at the ball-and-stick models. (a) at the C-C bond of a PTCDA molecule. (b) Between an oxygen and a hydrogen atom of two PTCDA molecules. (c) At the C-C bond of a CuPc lobe. (d) Between a PTCDA molecule and a CuPc lobe.

of the C-C bond $[(5 \pm 2) \text{ pm}]$ within uncertainty. The linear fit yielded a slope of $(1.0 \pm 0.2) \text{ meV/cycle/pm}$, which is equal within uncertainty to the slope of the linear region at the C-C bond $[(0.7 \pm 0.3) \text{ meV/cycle/pm}]$.

The energy dissipation signal between the PTCDA molecules is unexpected because no chemical bonds exist between the PTCDA molecules. It is assumed that weak hydrogen bonds exist between the molecules [122, 143]. A contribution of the hydrogen bonds is probably too low to explain the observed pattern, because they are believed to be too low to be accessible by the oxygen atom of the CO tip, which is usually located 300 pm higher [144]. The energy dissipation signal is most probably caused by Pauli repulsion with the local atoms as demonstrated in Ref. [25]. Furthermore in Ref. [25] it was shown that six C atoms of the PTCDA perylene core instead of two C atoms have to be considered in the simulation in order reproduce the experimental data. This indicates an interaction of the CO with the second and third neighbouring atoms. Another contribution to the energy dissipation signal could come from an electrostatic interaction. In Ref. [145] it was demonstrated that electrostatic forces play a substantial role in the imaging mechanism with a CO tip.

It is now continued with the discussion of the energy dissipation data recorded at the C₆ ring of the CuPc lobe with CO tip C. The exact position is marked by the green oval at the ball-and-stick model in Fig. 8.4(c). In Fig. 8.4(c) the blue dots shows the maxima of E_{diss} as a function of z. The signal exhibits a similar trend: Far away it increases exponentially until a maximum of 21 meV/cycle is reached and afterwards decreases linearly. The maximum (21 meV/cycle) is close to the maximum of the PTCDA C-C bond (24 meV/cycle). The exponential fit is shown by the right black curve and yielded a value of (7 ± 2) pm and is equal to the decay rates (within uncertainty) at the C-C bond of a PTCDA [(5 ± 2) pm] and H-O between two PTCDAs [(6 ± 1) pm]. The linear fit (left black curve) yielded a slope of (0.9 ± 0.2) meV/cycle/pm as equal within uncertainty to the linear slope of E_{diss} of the PTCDA C-C bond [(0.7 ± 0.3) meV/cycle/pm] and the H-O between the PTCDA molecules [(1.0 ± 0.2) meV/cycle/pm].

Figure 8.4(d) shows E_{diss} recorded between the CuPC lobe and the oxygen side of a PTCDA molecule with CO tip C. The position is marked by the green oval in Fig. 8.4(d) at the ball-and-stick models. The top ball-and-stick model is a part of the CuPc lobe and the lower is a part of a PTCDA molecule. In Fig. 8.4(d) the blue dots show the maxima of E_{diss} as a function of z. The energy dissipation signal has also an exponential increase and reaches a maximum of 11 meV/cycle and is lower than the energy dissipation maxima of the other cases. The characteristic decay length is (4 ± 2) pm and is equal within uncertainty as in the other cases. The linear fit in the region z = 9 pm to 14 pm yielded a slope of $(1.6 \pm 0.6) \text{ meV/cycle/pm}$ and is equal within uncertainty as in the other cases.

The energy dissipation signal between the CuPc lobe and the oxygen side of a PTCDA caused by hydrogen bonds is unlikely. In Ref. [20] it was investigated by DFT calculations that on Ag(111) the formation of a hydrogen bond network between the CuPc and PTCDA is unlikely in the P₂C mixed phase. A possible cause of the energy dissipation signal could be Pauli repulsion interaction of the CO tip with the molecules and an electrostatic interaction.

The equal values (within uncertainty) of the characteristic decay length of the exponential region and the slope of the linear region show that different CO tips do not have an influence on the exponential decay length and the slope of the linear region. This indicates that the interaction potential of different CO tips is constant. However, in the next section it will be shown that different CO tips have an influence on the magnitude of E_{diss} which is most likely caused by a different lateral stiffness of different CO tips.

8.3. CO stiffness influence

In the last section it was shown that different CO tips have no influence on the characteristic decay length of the exponential region and the slope of the linear region of $E_{\rm diss}$. In this section it will be shown that different CO tips have an influence on the magnitude of $E_{\rm diss}$. This will be demonstrated by scaling all the data taken with one CO tip with the same scaling factor and comparing it to the data which was taken with another CO tip. For instance, energy dissipation data were taken at the C-C bond of a PTCDA molecule and at the H-O position between two PTCDA's with CO tip B. The magnitudes of these data differs from data taken with another CO tip D at equivalent molecular positions³. By scaling the energy dissipation data which was recorded with CO tip B with the same scaling factor (1.5) the magnitudes are almost equal to the energy dissipation data which was recorded with another CO tip D. This is most likely caused by a variation of the

³For different CO tips the energy dissipation data was not taken exactly at the same molecule, but at the same position of an identical molecule with the same orientation.



Figure 8.5.: Dissipated energy as a function of z with different CO tips. (a) Red dots: at PTCDA C-C bond with CO tip B and scaled by 1.5. Blue dots: between PTCDA molecules with CO tip B and scaled by 1.5. Black dots: at a PTCDA C-C bond with CO tip D. Blue circles: between PTCDA molecules with CO tip D. (b) Green dots: at a PTCDA C-C bond with CO tip A. Red circles: between PTCDA molecules with CO tip A. Red circles: between PTCDA molecules with CO tip B. Blue dots: between PTCDA molecules with CO tip D. C-C bond with CO tip B. Blue dots: between PTCDA molecules with CO tip B. Blue dots: between PTCDA molecules with CO tip B. Blue dots: between PTCDA molecules with CO tip B. Blue dots: between PTCDA molecules with CO tip B. The datasets were shifted along the z axis for a better comparison.

lateral stiffness $k_{\rm CO}$ of the CO at the tip, since the interaction of the CO with the adsorbate can be considered to be constant as it was shown in the section before. Further, in Ref. [34] it was shown by DFT calculations that the $k_{\rm CO}$ can vary for different configurations of the metal atoms of the tip. However, by comparing the data which was recorded with CO tip B with data which was record with a third CO tip A, the magnitudes are almost equal without a scaling factor which shows that $k_{\rm CO}$ can also remain equal for different CO tips.

Figure 8.5(a) shows the maxima of E_{diss} as a function of z with two different CO tips. The datasets were shifted along the z axis to align the E_{diss} maxima for a better comparison. The red dots show E_{diss} at a C-C bond of a PTCDA molecule and the blue dots show E_{diss} at the H-O position between two PTCDA molecules. Both datasets were taken with CO tip B and were scaled by 1.5. The black dots also show E_{diss} at a C-C bond of a PTCDA molecule and the blue circles show E_{diss} at the H-O position between two PTCDA molecules. Both datasets were taken with CO tip D. As it can be seen the maxima and trend of the datasets taken with CO tip D are in agreement with the datasets taken with CO tip B after a scaling. The small discrepancy of the maxima of the red dots is probably caused by the instability of the CO at the tip. Since the atomic interaction of the CO with the adsorbate atoms can be considered to be constant, a scaling factor indicates a variation of k_{CO} .

Now it will be shown that the magnitude and trend of the energy dissipation datasets are almost equal for different CO tips. Figure 8.5(b) shows the maxima of $E_{\rm diss}$ as a function of z. The datasets were shifted along z axis for a better comparison of the magnitudes. The green dots show $E_{\rm diss}$ at a C-C bond of a PTCDA molecule and the red circles show $E_{\rm diss}$ at the H-O position between two PTCDA molecules. Both datasets were taken with CO tip A and the they were not rescaled. The red dots also show $E_{\rm diss}$ at a C-C bond of a PTCDA molecules at the H-O position between two PTCDA molecules. Both datasets were taken with CO tip A and the they were not rescaled. The red dots also show $E_{\rm diss}$ at a C-C bond of a PTCDA molecules. Both datasets were taken with CO tip B. The magnitudes and the trend of the datasets taken with two different CO tips agree very well without a rescaling of one of the datasets. This demonstrates that k_{CO} of different CO tips can remain equal.

8.4. Conclusion and outlook

The maximum energy dissipation as a function of z was investigated at the C-C bond of a PTCDA, at the H-O position between two PTCDA's, at the C-C bond of a CuPc lobe, and between a CuPc lobe and the oxygen side of a PTCDA molecule. In all cases, when the tip approaches the adsorbate $E_{\rm diss}$ increases exponentially and decreases linearly afterwards. The exponential characteristic decay rates were determined and are equal within uncertainty. The slopes of the linear region are equal within uncertainty as well and show that the interaction of different CO tips with the adsorbate can be considered to be constant. Different CO tips, however, have an influence on the magnitudes of $E_{\rm diss}$. The stiffness of the CO at the tip can vary due to a variation of the atomic configuration of the metal atoms at the tip as it was shown by DFT calculations [34]. By comparing datasets taken with two different CO tips (B and C) the trend and the maxima agreed very well after a scaling of all the data taken with CO tip B. Another comparison of datasets recorded with CO tip B and CO tip A showed that the magnitudes and trend of the datasets are in agreement without a rescaling.

As already mentioned in section 8.2 the linear decrease of E_{diss} could be caused by a push down of the adsorbate(s) by the CO tip which could lead to a decrease of $E_{\rm diss}$. This is currently subject of further investigation with density functional theory calculations.

9. Summary

This thesis presented high-precision normal atomic force microscopy, scanning tunneling microscopy, and lateral force microscopy measurements of organic molecules on metal surfaces with CO terminated tips and metal tips. The interaction mechanism which is responsible for the AFM and STM contrast formation was analyzed in detail for different tip-sample distances.

In section 2.2.4 a modification of the probe particle model to simulate LFM images was presented, which supported the interpretation of LFM images.

In section 3.2 a self-built molecular evaporated was described, which was required to deposite PTCDA and CuPc molecules on the samples.

The tip of an LFM sensor has a significant influence on the total stiffness of an LFM sensor and the precise determination of the stiffness is necessary for an accurate force and energy deconvolution and for calculating the energy dissipation. Therefore, in section 3.5 an Euler-Bernoulli theory method was described to calculate the stiffness of an LFM sensor with a simplified tip. The Euler-Bernoulli method was compared to the results of a static bending experiment and to a method which approximates a tip by the same cross section as the cantilever and by the same material as the cantilever. Both methods showed good agreement with the experimental data, but the Euler-Bernoulli theory method was superior to the other approximation method, because it considers the real cross section and the material of the tip.

In chapter 4 a method to determine the amplitude and tilt of an LFM sensor was presented. Existing amplitude calibration methods are not applicable for mechanically excited LFM sensors at low temperature. Knowing the oscillation amplitude is important for calculating the energy dissipation and for the force and energy deconvolution. Furthermore, the tilt of the LFM sensor has a significant influence on the frequency shift data. To determine the amplitude and tilt the STM channel was used and data of a local surface feature without and with oscillation was acquired. A full two-dimensional current map of the STM data without oscillation was used to simulate data for a given amplitude and tilt. Finally, the amplitude and tilt were determined by fitting the simulation output to the data with oscillation. A fitting algorithm and the accuracy of the method were discussed as well.

In chapter 5 the atomic configuration of the tip apex of metal tips is investigated using normal AFM and STM with CO on Pt(111). When scanning very close over a CO molecule, the frontmost atoms of the tip can be individually resolved in both the AFM image and in the STM image. This is in contrast to previous work where CO was adsorbed on a different substrate: Cu(111). In this previous study, individual atoms could not be observed in the raw STM image but only in AFM. The the mechanisms behind the higher spatial resolution in STM is discussed. On Cu(111), the occupied surface state plays a large role in STM images near the Fermi level, and as adsorbed CO repels the surface state, it appears as a wide trough in STM images. In contrast, Pt(111) lacks an occupied surface state and an adsorbed CO molecule appears as a peak. It was investigated if CO bending strongly influences the STM images, concluding that the atomic resolution of the tip over Pt(111) is due to highly localized through-molecule tunneling and CO bending is insignificant for contrast formation. Modeling the current between the CO and front atoms of the tip supported the findings.

In chapter 6 an isolated CO on Pt(111) with a CO terminated tip is investigated with normal AFM and STM. AFM and LFM images were discussed as well as the potential energy between the surface and tip CO. The correlation between conductance features in the STM image of a group of 5 CO molecules and the CO bending of the CO tip was demonstrated by a probe particle simulation from which a map of bending angles of the probe particle was calculated. Then the conductance zspectra of an isolated CO at different lateral positions were discussed which are very characteristic: above the CO at far tip-sample distances the conductance is greater than the bare surface conductance and at close tip-sample distances the conductance is smaller than the bare surface conductance. As the lateral distance to the center of the surface CO increases the conductance z spectra undergo a smooth transition to the bare surface conductance z spectrum. These conductance spectra were simulated by a combined hard sphere and tight binding model. The tight binding theory model considers orbital hopping between the s, p_x , and p_z orbital to calculate the conductance. A qualitative good agreement with the experimental data was achieved by considering s and p_z orbital hopping. p_x orbital hopping which would consider the contribution of the p_x and p_y orbitals to the conductance of CO on Cu(111) did not show a qualitative good agreement with the experimental data. The AFM image of an isolated CO recorded with a CO tip at the energy minimum [Fig. 6.1(f)] shows weak indications of hybridization which is not considered in the hard sphere and tight binding theory model. Moreover, the model does not consider the change of the density of states of the metallic surface and metallic tip atom when the CO's bend. Therefore, density functional theory calculations were performed by Vladislav Pokorn y^1 . The full relaxation of the structure led to a wrong adsorption site of the CO on the surface and to a displacement of the CO at the metal tip. Therefore the carbon atoms of the CO's were fixed in position. The calculated conductance as a function of z did not show a qualitative good agreement with the experimental data, most likely because of the fixed carbon atoms which did not lead to change of the density of states of the metallic surface and metallic tip atom when the CO's bend. As a consequence the CO-CO interaction was calculated by a Morse potential as demonstrated in Ref. [48]. These conductance calculations are currently subject of further investigation.

In chapter 7 the adsorption geometry and conductance near the Fermi energy of CuPc and PTCDA molecules in mixed phases with different stoichiometries on Ag(111) were investigated with LFM and STM as well as a single CuPc molecule close to different numbers of PTCDA molecules on Cu(111). On Ag(111) in the P_2C mixed phase the LFM image indicates a flat adsorption geometry of the CuPc and PTCDA molecules and in the STM image the molecules showed similar relative conductance. This findings are in agreement with the literature. In Ref. [20] it was shown that CuPc and PTCDA equalize their adsorption heights in the P_2C mixed phase. In the P_4C_2 mixed phase the CuPc molecules exhibit an increased conductance relative to the PTCDA molecules. The analysis of the LFM images showed that the increased conductance of the CuPc is most likely caused by an increased adsorption height of the CuPc molecules relative to the PTCDA molecules. The P_4C_2 mixed phase was not reported so far and the unit cell exhibits remarkable cavities. A possible reason for the increased adsorption height of the CuPc molecules could be a reduced interaction with PTCDA molecules when compared to the P₂C mixed phase by charge transfer through the surface or intermolecular interaction. In the P_4C_2 mixed phase one CuPc molecule is surrounded by two PTCDA molecules on average [see Fig. 7.8(b)] whereas in the P₂C mixed phase one CuPc

¹Institute of Physics, Czech Academy of Sciences, Praha, Czech Republic

molecule is surrounded by three PTCDA molecules on average [see Fig. 7.6(a)]. In a non-periodic mixed structure of CuPc and PTCDA molecules a CuPc molecule at the edge of the structure showed an increased conductance compared to the other CuPc molecules within the structure which was not caused by a higher adsorption height but is an electronic effect. Furthermore, the influence of close PTCDA molecules on the adsorption geometry and conductance of single CuPc molecules on Cu(111) were analyzed as well as the rotation direction of CuPc relative to the Cu(111) atomic surface lattice. An isolated CuPc molecule on Cu(111) shows a non-flat adsorption geometry (two lobes up and two lobes down) and adsorbs in the aligned state where the axes of the CuPc lobes are aligned to the high-symmetry direction of the atomic surface lattice. In the presence of inelastically tunneling electrons or a strong tip-sample potential the CuPc can rotate to the $\pm 7^{\circ}$ rotated state, where the adsorption geometry changes in that way that the higher lobes become the lower and the lower lobes become the higher. When CuPc is adsorbed close to different numbers of PTCDA molecules they can lock the rotation direction of the CuPc molecule and influence the adsorption geometry. When CuPc is adsorbed close to one PTCDA molecule the adsorption geometry of the CuPc molecule appears relatively flat and it is locked with a rotation angle similar as the reported $\pm 7^{\circ}$ relative to the high-symmetry direction of the Cu(111) surface (rotated position). The analysis of Δf line profiles indicated also a 35 pm lower adsorption height of the CuPc molecule relative to the close PTCDA molecule. When CuPc is adsorbed close to two PTCDA molecules the adsorption geometry of the CuPc molecule appears similar when compared to the isolated CuPc (two lobes up and two lobes down) and it is locked by the close PTCDA molecules with the lobes being aligned to the high-symmetry direction of the Cu(111) surface. When CuPc is adsorbed close to three PTCDA molecules the adsorption geometry of the CuPc molecule appears relatively flat. In the STM image one lobe exhibited an increased conductance near the Fermi energy. The analysis of Δf line profiles indicated that the increased conductance of this lobe is caused by an electronic effect. The close three PTCDA molecules locked the CuPc in the rotated position. These observations indicate that the intermolecular interactions between the PTCDA molecules and the CuPc or the charge transfer between the PTCDA molecules and the CuPc through the surface can change the adsorption geometry of the single CuPc with respect to the adsorption geometry of an isolated CuPc. At higher bias voltages $(100 \,\mathrm{mV} \text{ to } 1500 \,\mathrm{mV})$ the STM topography images of a CuPc molecule close to one, two, and three PTCDA molecules did not show significant differences.

In chapter 8 the energy dissipation at PTCDA and CuPc molecules was investigated with a CO terminated tip. The dissipated energy of the CO tip at the C-C bond of a PTCDA molecule is explained by a model described in Ref. [25]. Excitation images taken between PTCDA molecules, at the CuPc lobe, and between a PTCDA and CuPc molecule were shown. The maximum energy dissipation as a function of z was analyzed for different CO tips at the C-C bond of a PTCDA molecule, between the hydrogen atom of one PTCDA and the oxygen atom of another PTCDA, at the C-C bond of the CuPc lobe, and between the oyxgen side of a PTCDA molecule and a CuPc lobe. In all cases when the tip approaches the sample the energy dissipation increases exponentially until it reaches a maximum and decreases linearly afterwards. The characteristic decay lengths of the exponential regions and the slopes of the linear regions were determined and are equal within uncertainty for different CO tips, which shows that for different CO tips the interaction potential does not change. Different CO tips, however, have an influence on the magnitudes of the energy dissipation. The stiffness of the CO at the tip can vary due to a variation of the atomic configuration of the metal atoms at the tip. By comparing datasets taken with two different CO tips (B and C) the trend and the maxima agreed very well after a scaling of all the data taken with CO tip B. Another comparison of datasets recorded with CO tip B with datasets taken with CO tip A showed that the magnitudes and trend of the energy dissipation are in agreement without a rescaling. This demonstrates the reproducibility of the energy dissipation data with certain CO tips as well as the influence of the CO stiffness on the energy dissipation magnitudes. The energy dissipation recorded between the PTCDA molecules and between a PTCDA and a CuPc molecule are unexpected since no chemical bonds between the molecules exist. A possible cause could be Pauli repulsion and electrostatic interaction of the CO tip with the adsorbates. The linear decrease of the energy dissipation could be caused by a push down of the adsorbate(s) by the CO tip which could lead to a decrease of the energy dissipation and is currently subject of further investigations with density functional theory calculations.

A. Appendix

A.1. Temperature logging

In this section it is explained how the temperature logging for the microscope was realized. In the microscope are two silicon diodes – one is close to the cryostat and one is close to the sample. (There is also a third one at the xyz manipulator, but this temperature value will not be logged.) The temperature is determined by feeding a current of 10 µA through the diodes and measuring the voltage at the diodes. By using a look-up table the temperature can be determined. Figure A.1 shows the voltage as a function of the temperature for a DT-670 silicon diode, which is used in the microscope. The slope of the curve is higher for temperatures lower than 25 K indicating a higher sensitivity below this temperature. This makes this diode very appropriate for measuring low temperatures, but it can be also used for temperatures up to 500 K.

Logging of the temperature is useful for monitoring reasons, but also for problem finding. Logging means that the date, time and temperature values are written to a text file every minute. At the beginning of the project an electronic circuit to read the temperature diode was designed with Christoph Setescak from the group of the author using a microcontroller which is connected to a PC. However, the read out electronic circuit was buggy and another solution was found.

The control software of the microscope bases on LabView. This means that the whole scan and experiment control software is written in LabView. LabView is a visual programming language from National Instruments. The manufacturer of the electronics and developer of the software is SPECS Surface Nano Analysis GmbH. The control electronics and software is called Nanonis. SPECS offers a LabView programming interface for the microscope control software (Nanonis programming interface). This means that custom LabView programs can be written to control or read almost all parameters of the microscope.

Therefore a LabView program was written to read the temperature diode values



Figure A.1.: Voltage-temperature dependence of the DT-670 silicon diode. Source: www.lakeshore.com

and write them to a text file. Figure A.2 shows the block diagram of the LabView program. The basic structure of the program is a while-loop (gray frame) which contains the program blocks. Marked with (1) are the temperature read blocks from the Nanonis programming interface. They return the temperatures of the sample and cryostat as a float value. Then, marked with (2), the temperature values were converted to a string value to prepare them to be written to a text file. Marked with (3) is a LabView function to get the current date and time. After this block the date and time value is reformatted in the order year, month, day, hour, minute, second. (4) generates a concatenated string including the date, time, and the temperature values. At (5) the string is written to a text file. Then the program waits 60 seconds and starts over again.

Figure A.3 shows the graphical user interface of the LabView program. In the lower text field the location of the text file can be specified and the temperature values are displayed. The upper text field can be used to save only the current temperatures to a file. It should be noted that once the LabView program was stopped e.g. because of a Windows update, a new file name has to be specified. The program cannot append the values to an existing file which could be improved


Figure A.2.: Block diagram of the LabView program to log the temperature values.

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Figure A.3.: Graphical user interface of the LabView programm.

in future by using another file writing block.

A.2. Pressure logging

In this section it is explained how the pressure logging of the microscope is realized. There are three ion gauges in the UHV system. One is in the analysis chamber, one is in the preparation chamber, and one is in the load lock. The manufacturer of the ion gauges and the control electronics is VACOM Vakuum Komponenten & Messtechnik GmbH.

The working principle of an ion gauge is as follows: A hot filament serves as a source for free electrons. These free electrons collide with residual gas molecules and ionize them. The ionized molecules are accelerated towards a collector by an acceleration grid. This leads to a current in the collector. By measuring the current at the collector the pressure can be determined.

Logging the pressure values over time helps for identifying problems or a better overview of the progress of the pressure after a bake out. Therefore a pressure logging program was implemented with Python which communicates with the control electronics of the ion gauges via a serial port. The program does basically the following: it initializes the serial communication to the control electronics, generates a byte block according to the VACOM protocol, sends the byte array, receives the pressure value and stores them in a text file. The full code can be seen in section A.2.1. To plot the pressure values as a function of time another Python



string (mbar)

Figure A.4.: The VACOM serial communication protocol [146].

program was written using a graphical plotting library. The full code can be seen in the section A.2.2.

To communicate with the control electronics the data had to be sent in a specific order. Figure A.4 shows the content of a byte block. The first four hex numbers are a fixed value, which has to be at the beginning of every send block. The next two hex values are the command in this case the value is 20 10 for requesting the actual value (pressure in mbar). The next 16 hex values are the command parameters. Here, the value is 05 00 (...) for pressure channel 5. The last two hex values are the checksum of the previous values. In the Python program the byte block is generated by writing the values to a byte array as shown by line numbers 14-32 in section A.2.1 for e.g. the preparation chamber pressure value. A detailed description of the available commands and parameters can be found in Ref. [146].

The end of the byte block needs a valid checksum value which has to be calculated once. The checksum calculation was done using a CRC calculation tool from the website www.sunshine2k.de/coding/javascript/crc/crc_js.html. Figure A.5 shows a screenshot of the tool from the website and the used settings. To use the correct algorithm the following settings had to be done: CRC width: CRC-16, CRC parametrization: CRC16-MODBUS. For the bytes shown in Fig. A.5 the checksum 0xED7E was calculated. This has to be attached to the end of the byte block in reverse direction as it can be seen in line number 103 - 104 of the code in section A.2.1 for reading the analysis chamber pressure value. Then the byte block is sent to the control electronics (line 107) and the response is read (line 108). Line 111 - 121 is for error handling. If the ion gauge is turned off for some reasons the received value is 'NaN' (not a number), which would usually cause the program to crash since it expects a float and not a string. Therefore the response value is catched and checked for float (line number 41-43). Otherwise the response value is truncated (line number 45- 46 in section A.2.1).

	CRC
CRC width	
RadioButton: 🔘 CRC-8 🖲 CRC-16 🔘 CRC-32	
- CRC parametrization	
Predefined CRC16_MODBUS	
CRC detailed parameters	
Input reflected: 🗹 Result reflected: 🗹	
Polynomial: 0x8005	
Initial Value: 0xFFFF	
Final Xor Value: 0x0	
- CRC Input Data	
String Bytes	
A5500000201003000000000000000000000000000	
Show reflected lookup table: 🔲 (This option does not affect the CRC calcul	ation, o
Calculate CRC!	

Result CRC value: 0xED7E

Figure A.5.: Checksum calculation with a tool from the website: www.sunshine2k. de/coding/javascript/crc/crc_js.html



Figure A.6.: Graphical user interface of the Python program to plot the pressure values.

Since every ion gauge has a different channel number the whole communication routine was written for every channel as a Python function. The function returns the pressure value. The main routine of the program is an infinitely repeating while-loop (line number 123 - 145 in section A.2.1), which executes the functions for each channel, appends the pressure values to a text file with a time stamp and waits 60 sec.

To plot the different pressure values as a function of time another Python program was written which uses the Python library 'pyqtgraph'. The program reads the text file with the pressure values (line number 18 - 20 in section A.2.2). Then it stores the pressure values in separate arrays (line number 22 - 46 in section A.2.2). Finally, the plots were generated (line number 48 - 54 in section A.2.2). The resulting graphical user interface can be seen in Fig. A.6. It is interactive meaning that the graphs can be moved and scaled with the mouse.

A.2.1. Pressure logging Python program

```
import serial
1
2
     import time
3
     import datetime
4
     #import matplotlib.pyplot as plt
5
6
     ser = serial.Serial('COM1', 19200, bytesize=8, parity='N',
                                      stopbits=1, timeout=1)
\overline{7}
     print(ser.name)
8
     print("Reading pressure channel VAX CH1, CH2 & CH3")
9
     print("...")
10
11
     #Preperation Chamber
12
     def readCh1():
13
     #Channel 1
     lenght = bytes(24)
14
15
     barray = bytearray(lenght)
16
     # construct example array: request pressure value mbar
17
     # Startblock
18
     barray[0] = 0xa5
19
     barray[1] = 0x50
     barray[2] = 0x00
20
21
     barray[3] = 0x00
22
     #Commando + Subcommando
23
     barray[4] = 0x20
24
     barray[5] = 0x10
25
     #Parameter uebergabe
26
     barray[6] = 0x01
27
     #Checksumme
28
     barray[22] = 0xff
     barray[23] = 0x8c
29
30
31
     #print("Request")
32
     req0 = bytes(barray)
33
     ser.write(req0)
34
     s = ser.read(24)
35
    #catch error
     #convert and trancate
36
    b1 = str(s)
37
38
     c = b1[20:-19]
39
     i = 1
40
     while True:
```

```
41
     try:
42
     d = float(c)
43
     break
44
     except ValueError:
45
     c = b1[20:-19-i]
     i += 1
46
     return str(d)
47
48
     def readCh2():
49
     #Channel 2, LoadLock Pressure
50
     lenght3 = bytes(24)
51
52
     barray3 = bytearray(lenght3)
53
     # construct example array: request pressure value mbar
54
     # Startblock
     barray3[0] = 0xa5
55
56
     barray3[1] = 0x50
57
     barray3[2] = 0x00
     barray3[3] = 0x00
58
     #Commando + Subcommando
59
60
     barray3[4] = 0x20
61
     barray3[5] = 0x10
62
     #Parameter uebergabe
63
     barray3[6] = 0x02
64
     #Checksumme
65
     barray3[22] = 0xbf
66
     barray3[23] = 0x7d
67
68
     req3 = bytes(barray3)
69
     ser.write(req3)
70
     s3 = ser.read(24)
     #catch error
71
     #convert and trancate
72
73
     b3 = str(s3)
74
     c3 = b3[20:-19]
     k = 1
75
76
     while True:
77
     try:
     d3 = float(c3)
78
79
     break
     except ValueError:
80
81
     c3 = b3[20:-19-k]
82
     k += 1
```

```
83
      return str(d3)
84
85
86
      #STM Chamber
87
     def readCh3():
88
      #Channel 3
      lenght2 = bytes(24)
89
90
      barray2 = bytearray(lenght2)
91
      # construct example array: request pressure value mbar
      # Startblock
92
      barray2[0] = 0xa5
93
94
      barray2[1] = 0x50
95
      barray2[2] = 0x00
96
      barray2[3] = 0x00
97
      #Commando + Subcommando
98
      barray2[4] = 0x20
99
      barray2[5] = 0x10
100
      #Parameter uebergabe
101
     barray2[6] = 0x03
102
      #Checksumme
103
      barray2[22] = 0x7e
104
      barray2[23] = 0xed
105
106
     req1 = bytes(barray2)
107
     ser.write(req1)
108
     s2 = ser.read(24)
109
     #catch error
110
     #convert and trancate
111
     b2 = str(s2)
112
     c2 = b2[20:-19]
113
     j = 1
114
     while True:
115
     try:
    d2 = float(c2)
116
117
     break
118
     except ValueError:
119
    c2 = b2[20:-19-j]
120
     j += 1
121
     return str(d2)
122
123
     while True:
124
     stm_press = readCh1()
```

```
125
      prep_press = readCh3()
126
      ll_press = readCh2()
127
128
      #write log file and append data
      fout = open("C:\\Users\\LocalAdmin\\Documents\\Logging\\
129
                                        pressure_value.txt", 'a')
130
      fout_temp = open("C:\\Users\\LocalAdmin\\Documents\\Logging\\
                                        current_pressure.txt", 'w+')
131
      fout.write(f"{datetime.datetime.now():%Y-\%m-\%d_\%H:\%M:\%S"+'\t')
132
133
        fout.write(stm_press +'\t')
134
        fout.write(prep_press +'\t')
135
        fout.write(ll_press +'\n')
136
        fout.close()
137
138
        fout_temp.write(f"{datetime.datetime.now():%Y-%m-%d_%H:%M:%S}"
                                        +'\n')
139
          fout_temp.write(stm_press +'\n')
140
          fout_temp.write(prep_press +'\n')
141
          fout_temp.write(ll_press +'\n')
142
          fout_temp.close()
143
144
          #time sleep sec
145
          time.sleep(60)
146
```

A.2.2. Plotting pressure values Python program

```
1
          from pyqtgraph.Qt import QtGui, QtCore
2
          import numpy as np
3
          import pyqtgraph as pg
4
          #QtGui.QApplication.setGraphicsSystem('raster')
5
6
          app = QtGui.QApplication([])
\overline{7}
          #mw = QtGui.QMainWindow()
8
          #mw.resize(800,800)
9
10
          win = pg.GraphicsWindow(title="Basic plotting examples")
11
          win.resize(1000,600)
          win.setWindowTitle('LT3 Homes Pressure Graphs')
12
13
```

```
14
          # Enable antialiasing for prettier plots
15
          pg.setConfigOptions(antialias=True)
16
17
          # Initialize the pressure data
          fin = open('C:\\Users\\LocalAdmin\\Documents\\Logging\\
18
                                       pressure_value.txt', 'r')
19
          lines = fin.readlines()
20
          fin.close()
21
22
          x1 = []
23
          y1 = []
          y2 = []
24
25
          y3 = []
26
27
          for line in lines:
          p = line.split()
28
29
         x1.append(str(p[0]))
30
          y1.append(float(p[1]))
31
          y2.append(float(p[2]))
          y3.append(float(p[3]))
32
33
34
35
          # Time and date
36
          xv = np.array(x1)
37
          # STM chamber
38
          # yv = np.array(np.log10(y1))
39
          yv = np.array(y1)
40
41
          # Prep chamber
42
          #yx = np.array(np.log10(y2))
43
          yx = np.array(y2)
44
          # Load lock
45
          #yz = np.array(np.log10(y3))
         yz = np.array(y3)
46
47
         p1 = win.addPlot(title="Pressure STM chamber in mbar", y=yv,
48
                                        pen=(255,0,0))
         p1.showGrid(x=True, y=True)
49
50
          win.nextRow()
          p2 = win.addPlot(title="Pressure Prep chamber in mbar", y=yx
51
                                       , pen=(0,255,0))
52
         p2.showGrid(x=True, y=True)
```

```
53
         p3 = win.addPlot(title="Pressure Load Lock in mbar", y=yz,
                                     pen=(0,0,255))
         p3.showGrid(x=True, y=True)
54
55
56
         ## Start Qt event loop unless running in interactive mode or
                                       using pyside.
         if __name__ == '__main__':
57
58
         import sys
         if (sys.flags.interactive != 1) or not hasattr(QtCore, '
59
                                     PYQT_VERSION'):
60
         QtGui.QApplication.instance().exec_()
61
```

List of Publications

The following list shows all publications to which the author of this thesis contributed as first or co-author.

- T. Seeholzer, O. Gretz, F. J. Giessibl, and A. J. Weymouth, A Fourier method for estimating potential energy and lateral forces from frequency-modulation lateral force microscopy data, New Journal of Physics **21**, 083007 (2019).
- A. J. Weymouth, E. Riegel, O. Gretz, and F. J. Giessibl, *Strumming a Single Chemical Bond*, Physical Review Letters, **124**, 196101, (2020).
- O. Gretz, A. J. Weymouth, and F. J. Giessibl, *Identifying the atomic configuration of the tip apex using STM and frequency-modulation AFM with CO on Pt(111)*, Physical Review Research, **2**, 33094, (2020).
- A. J. Weymouth, E. Riegel, B. Simmet, O. Gretz, and F. J. Giessibl. Lateral Force Microscopy Reveals the Energy Barrier of a Molecular Switch, ACS Nano, 15, 3264–3271, (2021).
- O. Gretz, A. J. Weymouth, T. Holzmann, K. Pürckhauer, and F. J. Giessibl, Determining amplitude and tilt of a lateral force microscopy sensor, Beilstein Journal of Nanotechnology, 12, 517–524, (2021).

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