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Preparation and Interpretation of Kelvin Probe Force Microscopy Experiments on Bulk Insulators

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To my family

A mi familia

” *The night is darkest just before the dawn. And I
promise you, the dawn is coming.*

— Harvey Dent, *The Dark Knight*

Contents

1	Introduction	1
2	Scanning Probe Microscopy Techniques	5
2.1	Introduction	5
2.2	Scanning Tunnelling Microscopy	6
2.3	Atomic Force Microscopy	7
2.3.1	Frequency-Modulation Atomic Force Microscopy	7
2.4	Kelvin Probe Force Microscopy	9
2.4.1	Introduction	9
2.4.2	The Kantorovich Equation	13
2.4.3	Frequency-Modulation Kelvin Probe Force Microscopy	15
3	Equipment	19
3.1	Omicron VT AFM/STM XA	19
3.2	MATRIX Control Unit and Software	21
3.3	HF2 Lock-In Amplifier	26
3.4	Atom-Tracking System	26
3.5	Connections of the Equipment	27
4	Substrates	29
4.1	Au(111)	29
4.2	Calcite (10.4)	31
5	KPFM Measurements: from Theory to Experiments	33
5.1	Introduction	33
5.2	Transfer Functions	35
5.2.1	Transfer Function of the PLL	35
5.2.2	Transfer Function of the Experimental System	38
5.3	Distance-Dependent Measurements	43
5.3.1	Amplitude Calibration	44
5.3.2	Static Deflection	45
5.3.3	Preparation of Metal-Coated AFM Tips	45
5.4	Use of Atom-Tracking System	46
5.5	Summary	46

6	KPFM Experiments: Preparation of Metal-Coated Silicon AFM Tips	49
6.1	Introduction	49
6.2	Preparation of the Metallic Substrate Au(111)	50
6.3	KPFM Feedback: Error Channel and Noise	56
6.4	Preparation of Metal-Coated Silicon AFM Tips	69
6.5	Stability of Au-Coated Silicon AFM Tips	102
6.6	Summary	109
7	KPFM Experiments: Calcite (10.4) and 2,5-DHBA on Calcite (10.4)	111
7.1	Introduction	111
7.2	Experiments on Calcite (10.4)	112
7.3	Experiments on 2,5-DHBA Deposited on Calcite (10.4)	133
7.4	Information About the Au-Coated Tips Used	154
7.5	Summary	156
8	Summary	159
	Bibliography	161
A	Temperature Calibration Curve of Heating Stage	171
B	Data Analysis	173
C	KPFM Experiments on Au(111): Part 1	177
D	KPFM Experiments on Au(111): Part 2	185
E	KPFM Experiments on Au(111): Part 3	197
F	KPFM Distance-Dependent Measurements on Calcite (10.4)	203
	List of Acronyms	215
	Talks & Poster Presentations	217

Introduction

Molecular electronics is a promising field in nanotechnology. It is motivated by the idea of building up miniaturized electronic devices. To construct these devices, small building blocks are needed. These building blocks could be individual molecules or molecular structures. However, before individual molecules or molecular structures can be used for building up electronic devices, it is necessary to understand all different aspects that influence the formation of the different molecular structures. Only then we can design devices whose components are based on molecular structures with specific functions, such as switches, transistors or rectifiers.

Molecular self-assembly is the field of study of the different structures that molecules can form by interacting with each other. For molecular electronics, it is necessary that the molecular structures are arranged on a surface. These structures can be islands [1, 2], molecular nanowires [2–5], dimers [6] or trimers [7], for example. The stability of these structures depends on the substrate-molecule and molecule-molecule interactions. These interactions can be hydrogen bonds [6, 8, 9], van der Waals [10] or electrostatics forces [11, 12]. Understanding molecular self-assembly requires understanding the factors that influence the substrate-molecule and molecule-molecule interaction. In order to obtain local information about the molecular structures, we use scanning probe microscopy (SPM) techniques. However, for molecular electronics, we need to create molecular structures which are electronically decoupled from the substrate. Because of this, we work on insulating substrates. Hence, we need to use atomic force microscopy (AFM), which does not require a conducting substrate as scanning tunnelling microscopy (STM) does.

Among several interactions, electrostatics is important in understanding molecular self-assembly [7, 13, 14]. Therefore, we have to use a technique capable of probing charges. Kelvin probe force microscopy (KPFM) is an AFM mode, which allows to map the charge distribution on the sample surface simultaneously with AFM measurements. It has been used to study insulating substrate surfaces [15, 16]. KPFM experiments have also been performed on different molecular structures on insulators [12, 17–20]. Furthermore, it has even been employed for mapping the charge distribution within a single molecule [21, 22]. Additionally, it has been utilized to study different species after manipulating its charge state. These species are metal atoms [23, 24] or clusters [25], single molecules [26] or molecular islands

[27, 28] on insulating substrates. For long time, no precise model that explains the KPFM signal has been proposed. Most known models of the tip-sample interaction [29–32] do not consider the contribution of localized point charges to the KPFM signal. Furthermore, some investigations on thin insulating films [33–35] refer to the KPFM signal as contact potential difference. This can be also found in studies of molecules deposited on insulators [17, 18]. In all these investigations, the existence of the insulating substrate is ignored. There was not a general theory that explains KPFM for all types of samples.

Recently, using an existing model of the tip-sample electrostatic interaction [36], theory describing the meaning of the KPFM signal for the different modes has been presented [37, 38]. This theory predicts that the KPFM signal has two type of contributions: the contact potential difference between the metallic tip and the metallic sample (or metallic counter-electrode) and all point charges between tip and sample [37, 38]. Furthermore, the theory states that, in the presence of point charges between tip and sample, the KPFM signal depends on the tip-sample distance. Experimental evidence of the KPFM distance-dependence has been provided [22, 37, 39, 40]. Thus, no quantitative statements must be done only from KPFM images: distance-dependent measurements are required. This has not been considered in numerous investigations [12, 15, 16, 18, 19, 25, 33–35, 41–53]. Furthermore, this model states that all point charges between tip and sample contribute to the KPFM signal. Thus, localized point charges on the tip apex also contribute to the KPFM signal. In order to perform quantitative KPFM measurements, metal-coated tips free of localized point charges must be employed. Although the tip preparation is a common procedure, no evidence of the absence of localized point charges on the tip is provided [12, 15, 17–19, 33–35, 39, 41–51, 54–58]. For long time, a general theory that explains KPFM for all type of samples was missing.

The goal of this thesis is to conduct a systematic investigation on the meaning of the KPFM signal on insulators in ultra-high vacuum (UHV). I put the focus in the influence of using tips with localized point charges in the KPFM signal. The results of my experiments show a procedure to prepare and test the metal-coated tips before and after performing experiments on molecules deposited on bulk insulators.

This work is structured as follows. In chapter 2, the theory necessary to understand the used technique is explained, covering scanning tunnelling microscopy (STM), atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM). The technical aspects of the experimental system employed are described in chapter 3. The two substrates used in this work, Au(111) and calcite, are described in chapter 4. In chapter 5, I will show which parameters influence the KPFM signal and which procedures should be followed in order to obtain reliable KPFM data.

The experimental results are discussed in chapters 6 and 7. The preparation of metal-coated silicon AFM tips is described in chapter 6. Furthermore, a detailed interpretation of the KPFM data obtained during the experiments performed on a test metallic sample is extensively discussed. Finally, the experiments on calcite (10.4) and on 2,5-dihydroxybenzoic acid (2,5-DHBA) deposited on calcite are discussed in chapter 7.

Scanning Probe Microscopy Techniques

Contents

2.1	Introduction	5
2.2	Scanning Tunnelling Microscopy	6
2.3	Atomic Force Microscopy	7
2.3.1	Frequency-Modulation Atomic Force Microscopy	7
2.4	Kelvin Probe Force Microscopy	9
2.4.1	Introduction	9
2.4.2	The Kantorovich Equation	13
2.4.3	Frequency-Modulation Kelvin Probe Force Microscopy	15

2.1 Introduction

Scanning probe microscopy (SPM) refers to a group of techniques used in surface science to perform local studies with nanometre resolution. The common principle is the use of a probe, commonly a very sharp tip, brought close to the sample surface. The probe or the sample are mounted on a piezoelectric tube which can move in X, Y or Z-directions when high voltage is applied (piezo-tube scanner). By monitoring the tip-sample interaction, properties of the sample surface can be investigated. Furthermore, by scanning the tip in X and Y-direction, images of the properties of the sample surface can be acquired. One of these properties commonly studied is the shape of the sample surface, *i.e.*, the features of the surface, such as kinks or steps edges. I will refer to these features as the topology of the sample surface. Furthermore, by using feedback loops to keep constant one or several parameters of the tip-sample interaction, it is possible to access other properties. The feedback loop which is common to all these techniques is the distance feedback loop, which consist of a feedback which moves the piezo-tube scanner in Z-direction. The property which results of this feedback loop operation is the topography¹: an image of the sample surface topology. It must be noted that topology and topograhly are not

¹In many investigations, the authors refer to *topography images*. However, since the suffix -graphy already refers to a drawn or image, I consider it redundant. In this thesis, I will refer always to topography and not topography image(s).

equivalent: the topography is a convolution of the properties of the sample surface and the tip.

2.2 Scanning Tunnelling Microscopy

In 1982, scanning tunnelling microscopy (STM) was invented by Binnig and Rohrer [59]. This is the first technique in the family of the scanning probe microscopy and it is based on the quantum tunnelling effect: a particle with energy E can go through a potential barrier U , with $E < U$: this is forbidden according to classical mechanics. In the classical forbidden region, the particle can be expressed as the decaying wave function:

$$\psi(z) = \psi(0) \cdot \exp\left(-\frac{\sqrt{2m(U-E)}z}{\hbar}\right) \quad (2.1)$$

where m is the mass of the particle, z the distance covered by the electron in the forbidden region and $\hbar$ is the reduced Planck constant.

The STM consist of a metallic tip brought close to the surface of a conducting sample. The classical forbidden region is the vacuum, air or even liquid gap between tip and sample. When the tip is close enough to the sample surface, the orbitals of the atoms of the tip overlap with the orbitals of the atoms of the surface, and current can flow between them. This current can be expressed as:

$$I_T \propto V \cdot \rho_s(E_F) \cdot \exp\left(-2\frac{\sqrt{2m(\Phi-E)}z_{ts}}{\hbar}\right) \quad (2.2)$$

where I_T is the tunnelling current, V is the voltage applied between tip and sample, $\rho_s(E_F)$ is the local density of states (LDOS) at the Fermi level, Φ is the height of the barrier and z_{ts} the distance between the atom of the tip and the atom of the sample. A more detailed description of the tunnelling current can be found in [60–62].

Equation (2.2) shows the exponential dependence of the tunnelling current on the distance between the apex of the tip and the sample surface: a change of 1 Å in the tip-sample distance implies a change of one order of magnitude in the tunnelling current. This behaviour provides a remarkable accuracy to STM and makes it a tool for surface science.

By using a distance feedback loop to keep constant the tunnelling current between tip and sample (*constant-current mode*) and scanning the tip in X and Y directions, topography images of the sample surface can be acquired. As explained before, the topography is not an exact image of the sample surface topology: in STM, it is

a convolution of the topology and electronic properties of the sample and the tip. Furthermore, it is possible to disentangle the topological and electronic properties of the sample. This can be achieved by disabling the distance feedback loop and recording the tunnelling current while varying the piezo-tube scanner position in Z-direction or the bias voltage V_{bias} [59, 63, 64].

2.3 Atomic Force Microscopy

In 1986, Gerd Binnig invented the atomic force microscopy (AFM) [65]. It consists of a very sharp tip mounted at the end of a cantilever. When the tip is brought close to the sample surface, the forces between tip and sample bend the cantilever in normal or lateral direction.

In order to study the movement of the cantilever due to the interaction with the sample surface, a laser is pointed on the backside of the cantilever, and the reflection is collected by a position sensitive photo-diode (PSPD) (see figure 2.1). The PSPD can consist of two or four quadrants. In microscopes with a PSPD with two quadrants, by subtracting the two voltages in the appropriate way, the normal position of the laser beam reflection is tracked and, thus, the normal deflection of the cantilever. In microscopes with four quadrants, the lateral deflection of the cantilever can also be tracked. There exists a wide variety of the measuring modes: a more detailed description of the different modes can be found in Morita *et al.* [66] and Söngen *et al.* [67]. In this work, only the Frequency-modulation AFM (FM-AFM) mode has been employed, which will be explained in the next section.

2.3.1 Frequency-Modulation Atomic Force Microscopy

Frequency-modulation atomic force microscopy (FM-AFM) [68] is a dynamic AFM mode, in which the cantilever is excited with an external force $F_{\text{exc}} = F_0 \cos(2\pi\nu_{\text{exc}}t)$, where F_0 is the excitation force amplitude and ν_{exc} the excitation frequency. The deflection q of the cantilever (for FM-AFM, lateral deflection is not considered, so the deflection q only refers to the deflection in normal direction) is an oscillation which, within the *harmonic approximation* [67], is described by:

$$q = q_s + A \cos(2\pi\nu_{\text{exc}}t + \phi) \quad (2.3)$$

where q_s is the static deflection of the cantilever, A is the amplitude of the oscillation and ϕ is the phase shift between the external force and the deflection of the cantilever. For a fixed external force amplitude F_0 , the maximum amplitude A is achieved when

the cantilever is excited with an excitation frequency $\nu_{\text{exc}} = \nu_e$, with ν_e as the eigenfrequency of the cantilever, and the phase shift $\phi = -\pi/2$.

When the tip is brought close to the sample, we can define the tip-sample distance z_{ts} as the position of the tip apex with respect to the sample surface as:

$$z_{\text{ts}} = z_c + A \cos(2\pi\nu_{\text{exc}}t + \phi) \quad (2.4)$$

where z_c is the center position of the cantilever. The amplitude A and phase shift ϕ can vary due to the tip-sample interaction. From the tip-sample force F_{ts} , we can define the tip-sample force gradient k_{ts} :

$$k_{\text{ts}}(z_{\text{ts}}, \dot{z}_{\text{ts}}) = \frac{\partial F_{\text{ts}}(z_{\text{ts}}, \dot{z}_{\text{ts}})}{\partial z_{\text{ts}}} \quad (2.5)$$

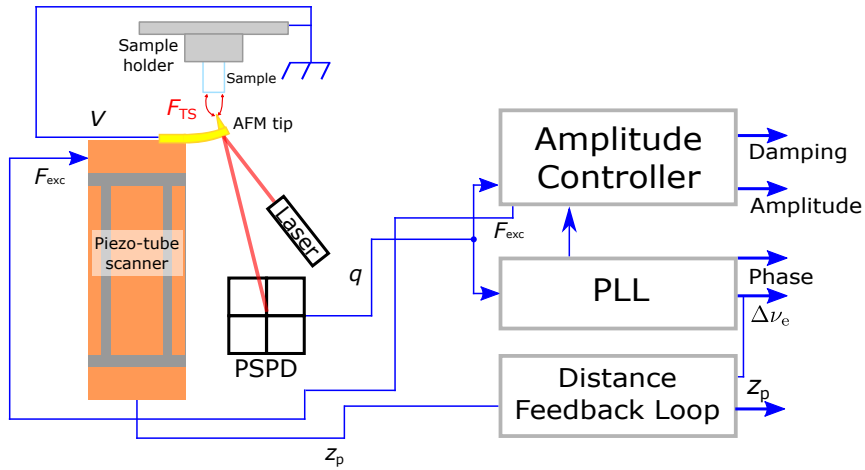


Figure 2.1.: Scheme of atomic force microscopy (AFM) in frequency modulation (FM) operation. On the left of the image, the main physical components are indicated. On the right, the electronic devices which process the signals proceeding from the the PSPD.

In FM-AFM, in order to keep the amplitude A constant, a feedback loop is used, commonly known as amplitude controller. Furthermore, a phase-locked loop (PLL) is used. This device demodulates the deflection signal from the PSPD and, by another feedback loop, changes the excitation frequency ν_{exc} so the phase shift ϕ is constant (usually at $-\pi/2$). The PLL produces another signal, named as *frequency shift* or *detuning* $\Delta\nu_e$:

$$\Delta\nu_e = \nu_e - \nu_{\text{exc}} \quad (2.6)$$

The relation between the excitation frequency ν_{exc} and the tip-sample force gradient k_{ts} is given by the equation:

$$\langle k_{\text{ts}}(z_{\text{ts}}, \dot{z}_{\text{ts}}) \rangle_{\cap} = k \left(1 - \left(\frac{\nu_{\text{exc}}}{\nu_e} \right)^2 \right) - \frac{F_0}{A} \cos(\phi) \quad (2.7)$$

The tip-sample force gradient k_{ts} is averaged over the cantilever oscillation with the 'cap' averaged, defined as [67]:

$$\langle f \rangle_{\cap} = \int_{-A}^A dz f(z_c + z) w_{\cap}(z), \quad \text{with} \quad w_{\cap} = \frac{2}{\pi A^2} \sqrt{A^2 - z^2} \quad (2.8)$$

When the phase shift ϕ is kept constant at $-\pi/2$, the second term on the right side of equation (2.7) vanishes. Considering $\Delta\nu_e \ll \nu_e$, we can rewrite equation (2.7) as:

$$\Delta\nu_e = \frac{\langle k_{ts}(z_{ts}, \dot{z}_{ts}) \rangle_{\cap}}{2k} \nu_e \quad (2.9)$$

In FM-AFM, in order to obtain the topography, the distance feedback loop is feed with the frequency shift $\Delta\nu_e$ signal. The distance feedback loop regulates the z-piezo position z_p so the frequency shift $\Delta\nu_e$ remains constant (*constant-frequency shift mode*).

2.4 Kelvin Probe Force Microscopy

2.4.1 Introduction

Since it was invented in 1986 by N. Nonnenmacher [69], Kelvin probe force microscopy (KPFM) has been used to study the tip-sample electrostatic interaction. The possibility of performing simultaneous AFM and KPFM measurements makes the combination of both techniques a powerful surface science technique which allows to relate the sample surface features with its charge distribution.

The simplest electrostatic model for the tip-sample system is a capacitor. In this model, assuming both tip and sample as conductors, the electrostatic force F_{es} acting on the tip can be expressed as [56]:

$$F_{es} = -\frac{1}{2} \frac{\partial C}{\partial z_{ts}} V^2 \quad (2.10)$$

where C is the capacitance of the tip-sample system and V the voltage applied between them. If an alternating voltage of the form $V_{AC} \sin(\omega t)$, where V_{AC} is the magnitude of the alternating signal and ω is the frequency, is applied between tip and sample, the electrostatic force can be expressed in three spectral components:

$$F_{dc} = -\frac{\partial C}{\partial z_{ts}} \left(\frac{1}{2} (V_{DC} - V_{CPD})^2 + \frac{1}{4} V_{AC}^2 \right) \quad (2.11)$$

$$F_{\omega} = -\frac{\partial C}{\partial z_{ts}} (V_{DC} - V_{CPD}) V_{AC} \sin(\omega t) \quad (2.12)$$

$$F_{2\omega} = \frac{\partial C}{\partial z_{ts}} \frac{V_{AC}^2}{4} \cos(2\omega t) \quad (2.13)$$

V_{DC} is the direct or static voltage and V_{CPD} is the contact potential difference between tip and sample. The contact potential difference V_{CPD} is defined as the difference of work functions of tip and sample divided by the elementary charge e [69]. Tracking the ' ω ' component with a lock-in amplifier and using a feedback loop to nullify this spectral component, the V_{CPD} can be measured. At first, KPFM was used to characterize the work function of metals in ambient conditions [69]. However, the work function can vary due to the presence of adsorbates on the surface [70]. In 1998, KPFM was implemented in ultra-high vacuum (UHV) by Kitamura *et al.* [71], showing the different V_{CPD} on two different samples, Au on Si(111) and Ag on Si(111).

In 1995, Hudlet *et al.* [29] modelled the case of a metallic tip on top of a semiconducting surface with total charge of the semiconductor Q_S as:

$$F_{es} = -\frac{Q_S^2}{2\varepsilon_0} \quad (2.14)$$

Three years later, they considered the tip-sample system as a metallic sphere in front of an metallic infinite flat surface [31]. The expression for the electrostatic force is then:

$$F_{es} = \pi\varepsilon_0 \left[\frac{R^2}{z(z+R)} \right] V^2 \quad (2.15)$$

Equations (2.15) and (2.14) have been probed to match experimental results when the tip is metallic and the sample is a metal or a semiconductor, respectively.

KPFM has been used to study more complex samples. Different studies on semiconductors using KPFM show potential drops across pn-junctions [49], band bending at individual grain boundaries [48], defects [47] and surface photovoltage [44, 47]. Furthermore, KPFM has also been used to study self-assembled molecular structures on metals [45] and on highly oriented pyrolytic graphite (HOPG) [39, 58, 72–74]. In some of these works, the authors study the influence of compensating the electrostatic interaction on the apparent height of the measured nanostructures [53, 72, 74].

At first, KPFM has been performed in two main ways that have been used: amplitude-modulation KPFM (AM-KPFM) and frequency-modulation KPFM (FM-KPFM). In both methods, as previously described, the cantilever is excited with an oscillating voltage. In AM-KPFM, the effect of the oscillating applied voltage in the tip-sample interaction is checked in the deflection of the cantilever at the $\omega/2\pi$ frequency: the electrostatic interaction induced an oscillation of the cantilever at this frequency.

However, in FM-KPFM, the effect of the oscillating voltage is checked in the spectra of the excitation frequency ν_{es} of the cantilever [34, 56].

Sadewasser *et al.* [49] modelled the AFM tip as a staircase, a combination of disks stacked on top of each other, whose radius is reducing successively, following the shape of a cone ended in a sphere. They compared the simulations with the results of amplitude modulation KPFM (AM-KPFM) experiments of a GaP pn-junction. The simulations and experimental results match for small tip-sample distances, but diverge for large, indicating the limitation of the model.

Zerweck *et al.* [34] modelled cantilever and tip as a large disk and a cone with an opening angle α ended by a sphere of radius R . They computed the electrostatic energy of the system by integrating the total electric field energy between tip and sample. They repeated the procedure for different tip-sample distances. They calculated the first and second derivative of the obtained values in order to get the tip-sample force and force gradient. They used this simulations to compare with experiments performed on submonolayers of KBr deposited on Au(111) substrate. They concluded that the model presents a higher accuracy for frequency-modulation KPFM (FM-KPFM) than for AM-KPFM experiments.

C. Barth and C. R. Henry [52] showed that the surfaces of insulating substrates prepared in UHV conditions are charged due to the cleavage. The voltage applied between tip and counter-electrode necessary to minimize the electrostatic interaction decreased after several days. They attribute this change to the rearrangement of charge defects. By annealing the crystals, their ionic conductivity increased and the charges dissipated in a shorter time. After this, they studied gold nanoclusters deposited on alkali halide surfaces with KPFM [25]. Since the clusters were deposited as neutral, the KPFM images should show no difference between them and the alkali halide surfaces, but they did. The authors suggest that the gold nanoclusters got charged from defects on the substrate surfaces.

In 2007, they presented a study about defects localized in step edges and kinks [15]. They presents KPFM images with different signal in specific spots in step edges and defects and in the terraces. They compare these results with constant height frequency shift images recorded on step edges. This is an indication of the influence of this charge spots in the total tip-sample interaction. One year later, they presented their work on Suzuki precipitates [16], showing the difference in KPFM signal between two different species: the substrate and the Suzuki precipitates.

In 2008, Bocquet *et al.* [75] presented an analytical model to explain the atomic contrast in KPFM images recorded on (001) ionic surfaces. They considered the tip-sample electrostatic interaction as the sum of three different contributions. Each

of these contributions corresponds to the interaction of a specific part of the tip with the sample: mesoscopic, microscopic (apex) and an asperity (or mini-tip). The electrostatic potential distribution of the ions on the surface was assumed as the Madelung potential. The ionic KPFM contrast was explained as a consequence of the displacement of the ions due to the electric field between tip and counter-electrode. In 2009, Nony *et al.* [76] confirmed this explanation by simulating the polarization of conductors and displacement of atoms depending on the voltage applied between tip and counter-electrode.

In order to get some understanding in the role of electric charge in the molecular self-assembly on insulating substrates, different studies have been performed [12, 18, 19, 37, 51, 77]. Furthermore, two recent works [27, 28] even after charging the islands of molecules with the very same cantilever and studying them using KPFM: these experiments are a clear signature that KPFM is sensitive to charges.

Lately, *static FM-KPFM*² has become in a common method of studying the charge distribution on a sample surface at low temperature. It is based in sweeping the bias voltage applied between tip and sample. This results in the $\Delta\nu_e(V)$ parabolas. The position of the maxima of the $\Delta\nu_e(V)$ parabolas (in both vertical and horizontal axis) is directly related with the position of the charge distribution within the tip sample system. Recently, it has been used in the study of single metallic adatoms before and after charging them [23] and in the charge transfer between AFM tip and single molecules [26]. The transfer of electrons between these species and the AFM tip resulted in changes of the position of the maxima of the $\Delta\nu_e(V)$ parabolas recorded.

Recently, in order to increase the lateral resolution in AFM measurements, some research groups functionalized the AFM tips with single molecules or atoms adsorbed in the tip apex. This tip functionalization has also been extended to KPFM experiments, mapping the charge distribution within single molecules [21, 78]. The tips were functionalized with a CO and NO molecules and Br, Xe or Kr atoms.

Later experiments [22, 79, 80] using the same experimental procedure studied the dependence of the KPFM signal on the distance between the molecule adsorbed on the apex of the tip and the molecule deposited on the substrate (the last one compared the KPFM results with tunnelling current measurements). A model to explain the KPFM signal measured with functionalized tips was proposed by Gross *et al.* [40].

²This method will be explain in detail in following sections.

All previous works mentioned in this section helped in our understanding of KPFM: the technical aspects, tip modelling, resolution enhancement by attaching molecules to the tip apex or the influence of trapped charges in bulk insulators in AFM and KPFM measurements. Nevertheless, none of this works presented a model that explains the tip sample interaction for the experiments we wanted to perform: non-uniform distribution of point charges deposited on a dielectric substrate mounted on a metallic counter-electrode and probed with an AFM tip. However, the model explained in the following section fits our requirements.

2.4.2 The Kantorovich Equation

In Kantorovich *et al.* [36], the authors introduce a model, which describes the interaction between m finite metallic conductors with static point charges q_i distributed in the space between them with coordinates r_i . External batteries keep each of the conductors at a corresponding fixed potential Φ_m upon moving any of the conductors. A complete derivation of the electrostatic energy of the system, including the effect of the batteries, can be found in the original publication [36]. The simplification of the system for metallic conductors, *i.e.*, tip and metallic sample or counter-electrode (see figure 2.2), is included in the chapters written by H. Söngen and P. Rahe for the book "Kelvin Probe Force Microscopy - From Single Charge Detection to Device Characterization" [81].

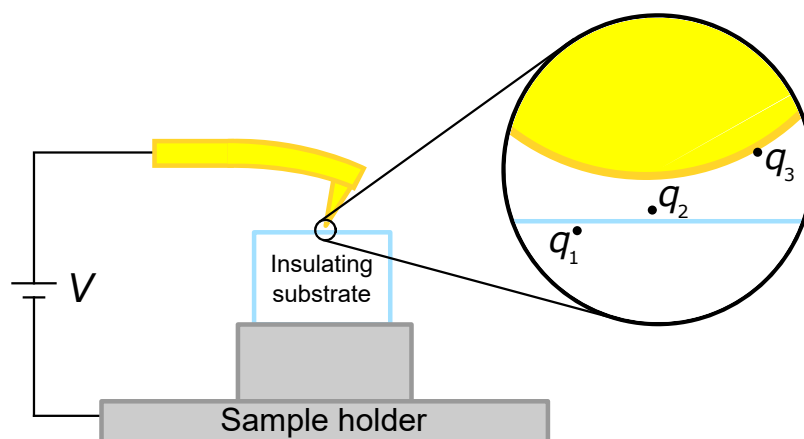


Figure 2.2.: Scheme of tip and sample with point charges in between. The AFM tip is in the close proximity of an insulating substrate, which is mounted on a metallic sample holder. The tip and the metallic sample holder are connected to a battery which applies a voltage V between them. In the zoom, it is possible to observe three point charges.

The total electrostatic energy U_{es} can be expressed as four different contributions:

$$U_{\text{es}} = U_{\text{C}} + U_{\text{q-C}} + U_{\text{q-q}} + U_{\text{im}} \quad (2.16)$$

The first term correspond to the energy stored between the conductors:

$$U_{\text{C}} = -\frac{1}{2}C_{\text{void}}V^2 \quad (2.17)$$

where C_{void} is the capacitance of the equivalent tip-sample system with no point charges in between. From now on, I will refer to this term as the capacitance of the void tip-sample system. The second term include the energy of each individual point charge due to their interaction with the tip-sample system:

$$U_{\text{q-C}} = \sum_{i=1} q_i \Phi_{\text{void}}(\mathbf{r}_i) \quad (2.18)$$

where $\Phi_{\text{void}}(\mathbf{r}_i)$ is the electrostatic potential in the point of space $\mathbf{r}_i$ between the conductors. As it scales with the potential applied between tip and sample, it is possible to define the normalized electrostatic potential $\hat{\Phi}_{\text{void}}(\mathbf{r}_i)$ and rewrite equation (2.18) as:

$$U_{\text{q-C}} = \sum_{i=1} q_i \hat{\Phi}_{\text{void}}(\mathbf{r}_i) \cdot V \quad (2.19)$$

The third term of equation (2.16) corresponds to the pairwise Coulomb interaction between all point charges:

$$U_{\text{q-q}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_i \sum_{j, i \neq j} q_i q_j \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.20)$$

The fourth term is the image energy:

$$U_{\text{im}} = \frac{1}{2} \sum_i q_i \Phi_{\text{im}}(\mathbf{r}_i) \quad (2.21)$$

which corresponds to the interaction of each of the point charges q_i with the image potential:

$$\Phi_{\text{im}}(\mathbf{r}_i) = \sum_j q_j \Phi_{\text{ind}}(\mathbf{r}_i, \mathbf{r}_j) \quad (2.22)$$

Here, $\Phi_{\text{ind}}(\mathbf{r}_i, \mathbf{r}_j)$ is the potential at a position $\mathbf{r}$ due to the image charges produced by a charge q_j located at the position $\mathbf{r}_j$.

The normal components of the electrostatic force and force gradient, F_{es} and k_{es} respectively, can be computed by deriving the electrostatic energy in the form:

$$F_{\text{es}}(z_{\text{ts}}, V) = -\frac{\partial U_{\text{es}}(z_{\text{ts}}, V)}{\partial z_{\text{ts}}} \quad (2.23)$$

$$k_{\text{es}}(z_{\text{ts}}, V) = -\frac{\partial^2 U_{\text{es}}(z_{\text{ts}}, V)}{\partial z_{\text{ts}}^2} \quad (2.24)$$

That results in:

$$F_{\text{es}}(z_{\text{ts}}, V) = \frac{1}{2} \frac{\partial C_{\text{void}}}{\partial z_{\text{ts}}} \cdot V^2 - \sum_{i=1}^N q_i \frac{\partial \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}}(\mathbf{r}_i) \cdot V - \sum_{i=1}^N \sum_{j=1}^N q_i q_j \frac{\partial \Phi_{\text{ind}}}{\partial z_{\text{ts}}}(\mathbf{r}_i, \mathbf{r}_j) \quad (2.25)$$

$$k_{\text{es}}(z_{\text{ts}}, V) = \frac{1}{2} \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} \cdot V^2 - \sum_{i=1}^N q_i \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i) \cdot V - \sum_{i=1}^N \sum_{j=1}^N q_i q_j \frac{\partial^2 \Phi_{\text{ind}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i, \mathbf{r}_j) \quad (2.26)$$

Both equations (2.25) and (2.26) consist of three terms and present parabolic dependence with V . The equation for the electrostatic force (equation (2.25)) includes the first derivatives of the capacitance C_{void} and the normalized electrostatic potential $\hat{\Phi}_{\text{void}}$, while the equation for the electrostatic force gradient (equation (2.26)) includes the second derivatives.

2.4.3 Frequency-Modulation Kelvin Probe Force Microscopy

In this thesis, only frequency-modulation Kelvin probe force microscopy (FM-KPFM) [56] measurements have been performed in two modes: static FM-KPFM and closed-loop KPFM. A more detailed description of the different KPFM modes, the physical implications and meaning of the signals measured, can be found in the chapter written by H. Söngen and P. Rahe [81].

Static FM-KPFM

In static FM-KPFM, the voltage applied between tip and metallic sample (or metallic counter-electrode) is only static: $V = V_{\text{bias}}$. The combination of equations (2.6), (2.7) and (2.26) show a parabolic dependence of $\Delta\nu_e$ on the voltage V_{bias} . The maximum of this parabola, thus, fulfills the conditions:

$$\frac{\partial \mathcal{F}[\Delta\nu_e](\nu_{\text{es}})}{\partial V_{\text{bias}}} = 0 \quad \Rightarrow \quad \frac{\partial \langle k_{\text{es}} \rangle_{\cap}}{\partial V_{\text{bias}}} = 0 \quad \text{for} \quad V_{\text{bias}} = V_{\text{FM}} \quad (2.27)$$

and the form of the applied voltage is:

$$V_{\text{FM}} = -V_{\text{CPD}} + \sum_{i=1}^N q_i \frac{\left\langle \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i) \right\rangle_{\cap}}{\left\langle \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} \right\rangle_{\cap}} \quad (2.28)$$

From equation (2.28) it follows that the KPFM signal has two contributions. The first contribution corresponds to the contact potential difference V_{CPD} between tip and sample or metallic counter-electrode (when the studied sample is an insulator). The second contribution is the weighted sum over all point charges between tip and sample or metallic counter-electrode. The magnitude of the point charges is weighted by the ratio of the weighted average over the cantilever oscillation of two quantities: the second derivatives of the normalized electrostatic potential of the void tip-sample system $\hat{\Phi}_{\text{void}}$ and the capacitance of the void tip-sample system C_{void} . Hence, the contribution of each point charge to the total V_{FM} signal depends on its magnitude but also on its position, since the value of the normalized electrostatic potential $\hat{\Phi}_{\text{void}}$ is not constant between tip and sample. Furthermore, since both capacitance C_{void} and normalized electrostatic potential $\hat{\Phi}_{\text{void}}$ depend on the tip geometry, the V_{FM} signal also depends on it. Finally, both quantities $\hat{\Phi}_{\text{void}}$ and C_{void} depend on the tip-sample distance z_{ts} , the value of the V_{FM} signal is distance-dependent. Equation (2.28) provides support to the experiments described in the introduction of this chapter [21–23, 26, 78–80] by relating the value V_{FM} with the position and magnitude of the charges.

Closed-loop FM-KPFM

In FM-KPFM, the voltage V applied between tip and sample is a combination of direct and alternating voltage:

$$V = -V_{\text{CPD}} + V_{\text{bias}} + V_{\text{es}} \cos(2\pi\nu_{\text{es}}t) \quad (2.29)$$

V_{es} and ν_{es} are the electrostatic excitation amplitude and frequency, respectively. Thus, the frequency shift $\Delta\nu_e$ presents three spectral components. These spectral components are the weighted average over the whole oscillation of the cantilever (as defined in equation (2.8)). The three spectral components of the electrostatic force gradient k_{es} are:

$$\begin{aligned} k_{\text{es,a}} = & \frac{1}{2} \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} \left((V_{\text{bias}} - V_{\text{CPD}})^2 + \frac{1}{2} V_{\text{es}}^2 \right) \\ & - (V_{\text{bias}} - V_{\text{CPD}}) \sum_{i=1}^N q_i \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i) \cdot V_{\text{bias}} \\ & - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N q_i q_j \frac{\partial^2 \Phi_{\text{ind}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i, \mathbf{r}_j) \end{aligned} \quad (2.30)$$

$$k_{\text{es,b}} = \left(\frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} (V_{\text{bias}} - V_{\text{CPD}}) - \sum_{i=1}^N q_i \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i) \right) V_{\text{es}} \quad (2.31)$$

$$k_{\text{es,c}} = \frac{1}{4} \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} V_{\text{es}}^2 \quad (2.32)$$

Only the second spectral component can be completely nullify by applying an specific V_{bias} , so the condition is:

$$\mathcal{F}[\Delta\nu_e](\pm\nu_{\text{es}}) = 0 \quad \Rightarrow \quad \langle k_{\text{es,b}} \rangle_{\square} = 0 \quad \text{for} \quad V_{\text{bias}} = V_{\text{FM}} \quad (2.33)$$

and the form of the applied voltage is:

$$V_{\text{FM}} = -V_{\text{CPD}} + \sum_{i=1}^N q_i \frac{\left\langle \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i) \right\rangle_{\square}}{\left\langle \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} \right\rangle_{\square}} \quad (2.34)$$

Note that both equations (2.28) and (2.34) contain the same information: according to the theoretical model, both methods static and closed-loop FM-KPFM provide the same information about the charge distribution on the sample surface.

The weight-function for charges

Both equations (2.28) and (2.34) show that the contribution of each one of the charges to the Kelvin V_{FM} signal is weighted by the ratio of the averaged second derivatives of the capacitance C_{void} and the normalized electrostatic potential $\hat{\Phi}_{\text{void}}$. It is possible to define this ratio as the *FM weight function for charges* W_{FM} :

$$W_{\text{FM}}(\mathbf{r}) = \frac{\left\langle \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}) \right\rangle_{\square}}{\left\langle \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} \right\rangle_{\square}} \quad (2.35)$$

and rewrite equations (2.28) and (2.34) as:

$$V_{\text{FM}} = -V_{\text{CPD}} + \sum_{i=1}^N q_i W_{\text{FM}}(\mathbf{r}_i) \quad (2.36)$$

All weight functions for charges (in the chapter written by H. Söngen and P. Rahe [81], the description includes all KPFM weight functions for all modes) depend on the quantities C_{void} and the normalized electrostatic potential $\hat{\Phi}_{\text{void}}$, which, in turn, depend on the shape of the apex of the tip. Sadeghi *et al.* [82] introduced a model similar to the one presented by Zerweck *et al.* [34]: the tip-cantilever system modelled as a large disk and a cone with an opening angle α ended by a sphere of radius R was used to compute both quantities by a finite elements method (FEM) method. Neff *et al.* [37] used this method to simulate the AM and FM-KPFM signals due to a single charge on the surface of a thick insulator.

A later work, Sadeghi *et al.* [83] presented another way to compute these quantities: solving the electrostatic problem of the sphere in front of a metallic infinite plate using the method of image charges. This method was used by Söngen *et al.* [38] to study the weight functions in AM and FM-KPFM on metallic and insulating samples. The sign of the KPFM weight functions defines the sign of the contribution of each point charge between tip and sample. If a point charge q_i is weighted by the KPFM weight function with positive value at the coordinates of the point charge r_i , its contribution to the total KPFM signal has the same sign as the value of the point charge; however, if the value of the KPFM weight function is negative, the contribution of the point charge to the total KPFM signal has opposite sign as the value of the point charge. In this work only FM-KPFM experiments on metallic and insulating substrates in vacuum (case relative permittivity $\varepsilon_r > 1$), what means that positive (negative) charges contribute positively (negatively) to the K V_{FM} signal. This conclusion is essential for understanding KPFM experiments.

Equipment

Contents

3.1	Omicron VT AFM/STM XA	19
3.2	MATRIX Control Unit and Software	21
3.3	HF2 Lock-In Amplifier	26
3.4	Atom-Tracking System	26
3.5	Connections of the Equipment	27

3.1 Omicron VT AFM/STM XA

All experiments have been performed with the commercial UHV system Omicron VT XA (Scienta Omicron, Taunusstein, Germany). The system consists of three chambers: the load-lock, the preparation (or analysis) chamber and the variable temperature or VT chamber. The base pressure of the system is p typically better than $1 \cdot 10^{-10}$ mbar.

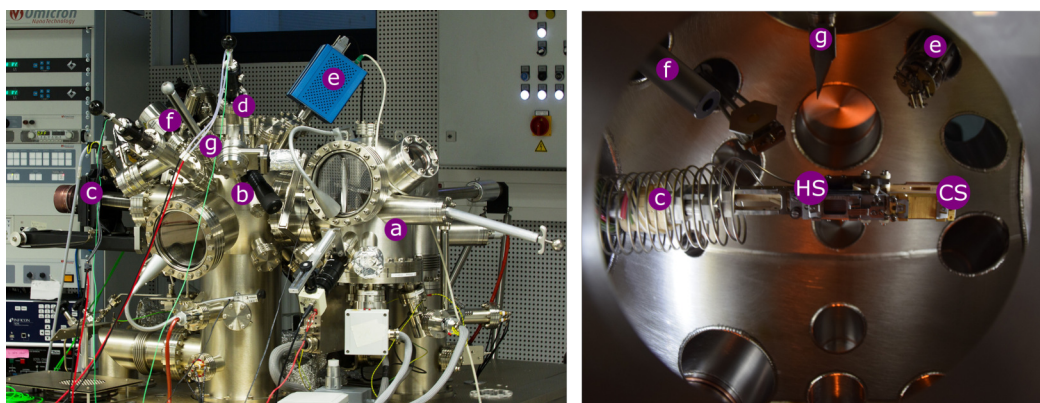


Figure 3.1.: The UHV chamber composed of the VT chamber (a) and the preparation chamber (b). The load-lock is not visible in the images: is located in the back side of the preparatio chamber. Left image courtesy of Holger Adam.

The load-lock is a small chamber designed to lock-in and extract tips and samples into the UHV system. The preparation chamber is the largest of the three chambers. AFM tips and samples are prepared in this chamber. Figure 3.1 shows the different elements attached to the preparation chamber:

- A manipulator (c), in which tips and samples are transferred from the load-lock. There are two stages to place tips and samples: the *cooling stage* (CS), which allows to cool down samples, and the *heating stage* (HS), where samples can be heated.
- Two molecule sublimators (one is indicated by (d)) used to deposit molecules on the sample surface. They are equipped with a Knudsen cell, shown and explained in figure 3.2. The Knudsen cell consists of a glass crucible filled with molecules and closed with glass wool. Two thermocouple wires are attached to the closed end of the crucible and a tantalum wire (in figure 3.2, referred to as Ta-wire) is coiled around the crucible. To heat up the molecules, a current flow through the tantalum wire is adjusted until the desired temperature, checked with the thermocouple, is reached.

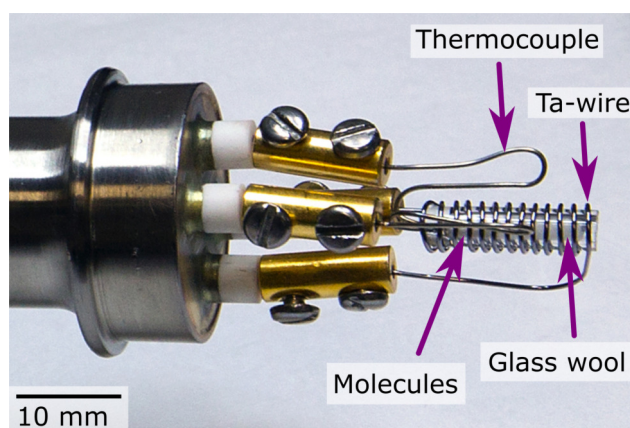


Figure 3.2.: Knudsen cell mounted on a molecule sublimator. Image courtesy of Holger Adam.

- A quadrupole mass spectrometer e-Vision+ (MKS Instruments, Andover MA USA) (e) is used to analyse the background gas and check the quality of the vacuum and the Ar (argon) line.
- The sputter gun (f) is used to sputter tips and samples with Ar^+ ions. During this work, two different sputter guns have been used: the ISE 5 and ISE 10 (Scienta Omicron, Taunusstein, Germany).
- The cleaver (g) is used for *in-situ* crystal cleavage [84].

The SPM scanhead is in the VT chamber (figure 3.1 (a)). The sample stage is grounded and the sample surfaces point downwards. With this system, it is possible to perform individual AFM or STM measurements, but also simultaneous AFM/STM (qPlus) measurements, just by exchanging the tip holder. Figure 3.3 shows the

system prepared for AFM experiments. The cantilever points upwards (to the sample surface) and is attached to a chip (b), which is glued to a tip holder (c). The tip holder is on top of the piezo-tube scanner (d). Different electrodes connected to the piezo-tube scanner in different positions and geometries allow to move it in different coordinates: the electrode marked by (f) is one of the two which elongate the piezo in Z direction, while the electrode marked by (e) is one of the four which move it in the XY plane.

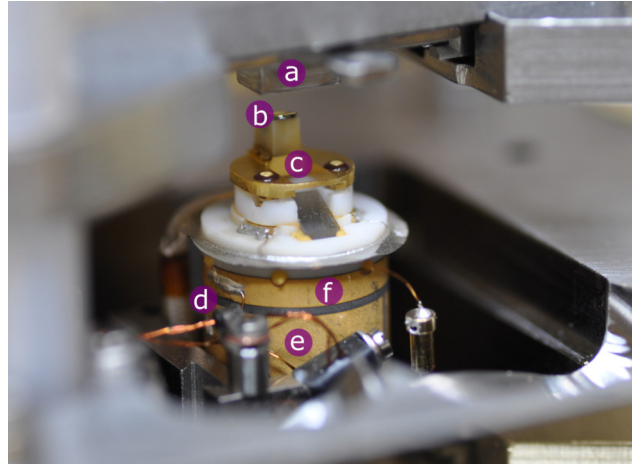


Figure 3.3.: VT SPM XA scanhead and sample stage. Image courtesy of Holger Adam.

3.2 MATRIX Control Unit and Software

The SPM is operated by the controller called MATRIX Control Unit (CU) V.2 and the software MATRIX (Scienta Omicron, Taunusstein, Germany). During this work, versions 3.1 and 3.3 have been used. The software offers different measurement tools, some of them for specific experiments: only STM imaging, both STM imaging and spectroscopy curves,... These measurement tools are called *experiments*. The *experiments* used in this thesis are *STM spectroscopy*, *Non-Contact AFM* and *Custom* (based on the *Non-Contact AFM* experiment).

In the software, the labelling of the frequency shift $\Delta\nu_e$ is different from the name given in chapter 2, even between different windows or settings in the software. In the software is referred to as Df or Δf . From now on, I will refer to this quantity as $\Delta\nu_e$.

The MATRIX CU includes an internal Amplitude Controller and PLL. Both are operated in the software in the window *PLL*. All experiments have been performed in the *Const. Amplitude* (constant amplitude) mode:

- The Amplitude Controller is operated in the section *Amplitude Control*. It is operated by the proportional (P) and integral (I) gains, labelled in the software as *Amplitude P-Gain* and *Amplitude I-Gain* and the amplitude setpoint *A-vib*. Note that *A-vib* refers to the peak-to-peak amplitude. The Amplitude Controller produces the channels *Damping* and *Amplitude*, which correspond to the external force amplitude F_0 and the amplitude A defined in section 2.3.1.
- The PLL is also controlled by P and I gains, labelled in the software as *P-Part* and *I-Part*. The value of the gains are linked to the bandwidth¹ of the PLL: the maximum value of *P-Part* implies the maximum value of the PLL bandwidth. The PLL produces the channels *Phase* and $\Delta\nu_e$, which correspond to the phase shift ϕ and the frequency shift $\Delta\nu_e$ defined in section 2.3.1.

The *distance feedback loop* is controlled in the window *Z-Regulation*. A display in the upper left corner part of this window shows the current position of the piezo-tube scanner in Z direction. A button next to it allows to enable or disable the *distance feedback loop*. When the feedback is disabled, it is possible to approach the tip to the sample or retract it by introducing an offset in the box labelled as ΔZ , in the part called *Z-Offset*.

The experiments *Non-Contact AFM* and *Custom* include the *Twin* option. This option allows to choose between operating in STM mode (in the *Z-Regulation* window, *STM*) or FM-AFM mode (in the *Z-Regulation* window, *AFM NonContact*):

- The *AFM NonContact* feedback is operated by an I gain, labelled as *Loop Gain I* and the frequency shift setpoint labelled as $\Delta\nu_e$ -Setpoint.
- The *STM* feedback is operated by an I gain, labelled as *Loop Gain I*, the tunnelling current setpoint *I-Setpoint* and the *I-Range*. This last parameter changes the maximum current from 3.3 nA to 333 nA.

The *distance feedback loop* produces the channel Z, which corresponds to the piezo position z_p . The connections between the three feedback loops are indicated in figure 3.4.

¹There are several definitions of bandwidth. In this work, the bandwidth of an electronic device is the range of frequencies for which the magnitude of the ratio of the output and input signal is larger or equal than $1/\sqrt{2} = 0.707$. The frequencies at which the ratio is equal to $1/\sqrt{2}$ are called cutoff frequencies. For a low-pass filter or a PLL, the bandwidth is given by the range of frequencies between DC and the cutoff frequency.

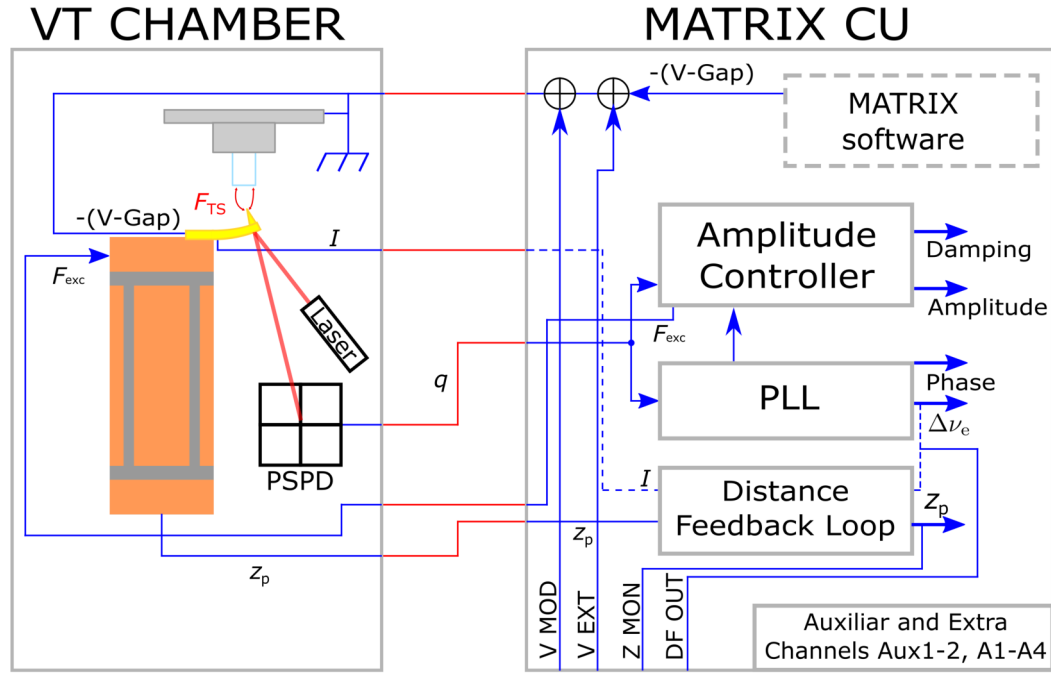


Figure 3.4.: Block diagram of the equipment connections for standard STM or FM-AFM imaging. The main connections inside the VT chamber and the MATRIX CU are indicated (in blue colour). The connections between the VT and MATRIX CU are indicated in red colour. The feedback loop in the MATRIX CU are represented by boxes. Inside each box corresponding the names of the parameters corresponding to each feedback loop are included. The dashed lines connected to the distance feedback loop correspond to the quantities tunneling current I and frequency shift $\Delta\nu_e$: the user can change from one feedback loop to another, but not operate both at the same time. The channels recorded are indicated by arrows pointing to the right.

The voltage applied to the SPM tip is the combination of a DC voltage set via Software and external BNC inputs to the MATRIX CU. They are added internally. These different voltage sources are labelled in different ways in the software and the front panel of the MATRIX CU. Furthermore, for future explanations, I have defined physical quantities assigned to these voltages. The relation of the names each voltage is shown in table 3.1.

Software	External Input in MATRIX CU	Defined Quantity
V-Gap	—	V_{Gap}
V-Ext	V EXT	V_{Ext}
V-Mod	V MOD	V_{Mod}

Table 3.1.: Relation of the different voltages names. As the voltage V-Gap is set in the software, there is no external input.

The DC voltage is referred to V-Gap in the software. Its range is ± 10 V and its sign is inverted by the MATRIX CU. The MATRIX CU has additional BNC inputs for external voltage sources. Only two of them are available in the experiments used in the present work, labelled in the front panel of the MATRIX CU as V EXT and V MOD. These two inputs (both of them are AC) can be enabled or disabled independently from each other via software, in the window labelled as *External Inputs*. The transfer function of both inputs have been measured by setting V-Gap = 0 and only enabling the corresponding input in the software. An oscillating signal with 1 V amplitude was connected to the inputs and the output voltage amplitude and phase shift were measured by sweeping the frequency from 100 mHz to 500 kHz. Figure 3.5 (a) and (b) show the transfer function of the V EXT and V MOD inputs, respectively. The bandwidth of the both inputs is shown in table table 3.2.

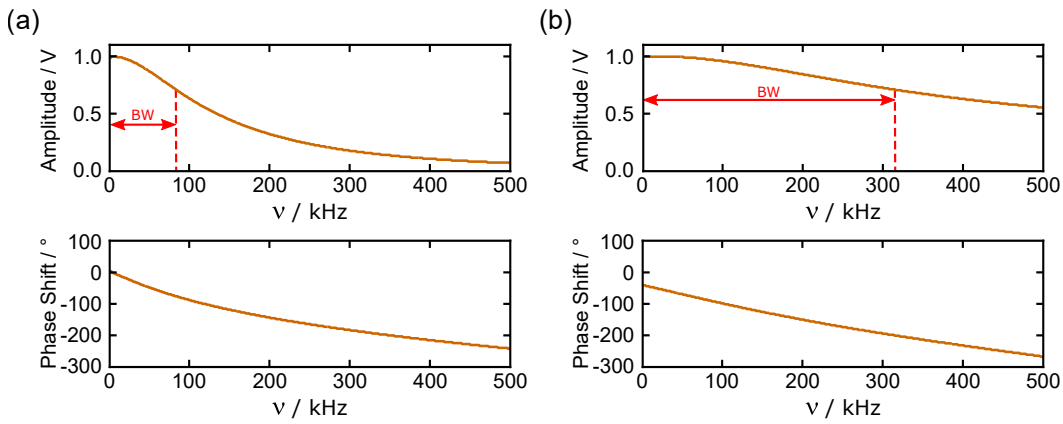


Figure 3.5.: Transfer function of the external voltage inputs V EXT ((a) and (c)) and V MOD ((b) and (d)). BW states for bandwidth.

Voltage Input	Bandwidth / kHz
V EXT	82.2
V MOD	313.9

Table 3.2.: Bandwidth of the external voltage inputs.

When both external inputs V-Ext and V-Mod are disabled, the voltage applied to the tip is:

$$V = -V_{\text{Gap}} \quad (3.1)$$

In the case of both external inputs V-Ext and V-Mod enabled, the voltage input at V EXT is added to the voltage V-Gap and then filtered as set in the software. In this work, no filter has been selected. Additionally, the voltage input at V MOD is added. Thus, the total voltage applied to the tip V is:

$$V = -V_{\text{Gap}} + V_{\text{Ext}} + V_{\text{Mod}} \quad (3.2)$$

The *experiments* of the software named before allow to collect data upon varying the voltage applied between tip and sample and upon varying the z -piezo position z_p . These modes are controlled in the window *Spectroscopy*. Note that the term *Spectroscopy* refers to the study of a sample upon varying the energy of an incident beam of electromagnetic radiation. For example, Thus, it is not suitable to name the processes described before. From now on, I will refer to these processes as distance-dependent curves and voltage-dependent curves. When performing the curves, it is possible to choose sweeping from smaller to larger as well as from larger to smaller values. It can be set to perform both kind of sweeps and select which one is done in first place. In the next chapters, I will refer to this kind of different sweeps as explained in the following:

- For voltage-dependent curves, the curves recorded by sweeping the voltage from smaller to larger values will be referred as positive sweep voltage curves. For the curves recorded by sweeping from larger to smaller voltage values, the name assigned is negative sweep voltage curves.
- For distance-dependent curves, it is possible to distinguish between approach (varying the z -piezo position z_p towards the sample) and retract curves (varying the z -piezo position z_p away from the sample). However, for large z_p variations, the piezo creep becomes relevant. Neff [20] showed the hysteresis between the approach and retract $\Delta\nu_e$ curves upon varying z_p by tens of nanometres. For this reason, only retract curves are presented in this work and there is no need for distinction.

The MATRIX CU presents another two BNC outputs of importance for this work:

- The BNC output labelled as DF OUT can output the Damping signal or the difference between the frequency shift ν_e and the $\Delta\nu_e$ -Setpoint.
- The BNC output labelled Z MON produces a voltage proportional to the z -piezo position z_p .

The standard MATRIX CU V2 presents two auxiliary inputs. This connections can be used for recording extra channels produced in external devices. These two inputs are labelled in the MATRIX CU as Aux In 1 and Aux In 2. In the software, they are named Aux 1 and Aux 2. Moreover, the MATRIX CU employed in this work features four extra inputs, labelled in both the MATRIX CU and the software as A1 to A4. These extra inputs are only available in the *Custom* experiment.

3.3 HF2 Lock-In Amplifier

The HF2 lock-in amplifier (Zurich Instruments AG, Zürich, Switzerland) is a digital lock-in amplifier. In this work, the software used to operate the HF2 lock-in amplifier is *ziControl* [85]. The software presents several tools to analyze the signals tracked at specific frequencies. The ones used in the present work are:

- The *FFT* tool shows the Fast Fourier Transform of a signal at a specific frequency range. For example, this tool can be used to visualize the spectral components of the frequency shift $\Delta\nu_e$.
- The *Sweeper* displays the magnitude R and the phase Θ of a specific signal at one of the *Signal Inputs* with respect of one of the *Signal Outputs* upon varying one parameter related with any of the two signals. For example, it was used to measure the transfer function of the external inputs V_{EXT} and V_{MOD} in the MATRIX CU (figure 3.5), upon varying the frequency ν of the AC voltage.
- The *PID tabs* are PID (proportional-integral-derivative) feedback loops. In this thesis, the *PID tabs* have been used for closed-loop FM-KPFM.

From now on, the HF2 lock-in amplifier will be referred to as HF2 LIA or HF2. A more detailed description of the HF2 and the software *ziControl* can be found in the HF2 User Manual - *ziControl* Edition [85].

3.4 Atom-Tracking System

The atom-tracking system we have in our research group is described in detail in [86, 87]. In our group, it has been used for drift compensation: in X, Y and Z-direction in 3D mapping experiments [88–90] and, as for the present work, only for drift compensation in Z-direction [37].

The atom-tracking system analyses the position of the piezo-tube scanner z_p as function of time. If the z-piezo position z_p is linear with time, these z_p values can be fitted to a line. The slope of the line provides the drift velocity in Z-direction. The device produces a voltage proportional to the drift velocity in Z-direction. This voltage is added to the voltage produced by the SPM controller and applied to the piezo-tube scanner. This process is repeated until the drift velocity is minimized.

3.5 Connections of the Equipment

In order to perform proper FM-KPFM measurements, the HF2 lock-in Amplifier and the atom-tracking system have been connected to the MATRIX CU and between MATRIX CU and the VT chamber, respectively. Figure 3.6 shows the connections between the VT chamber, the MATRIX CU; the atom-tracking system and the HF2.

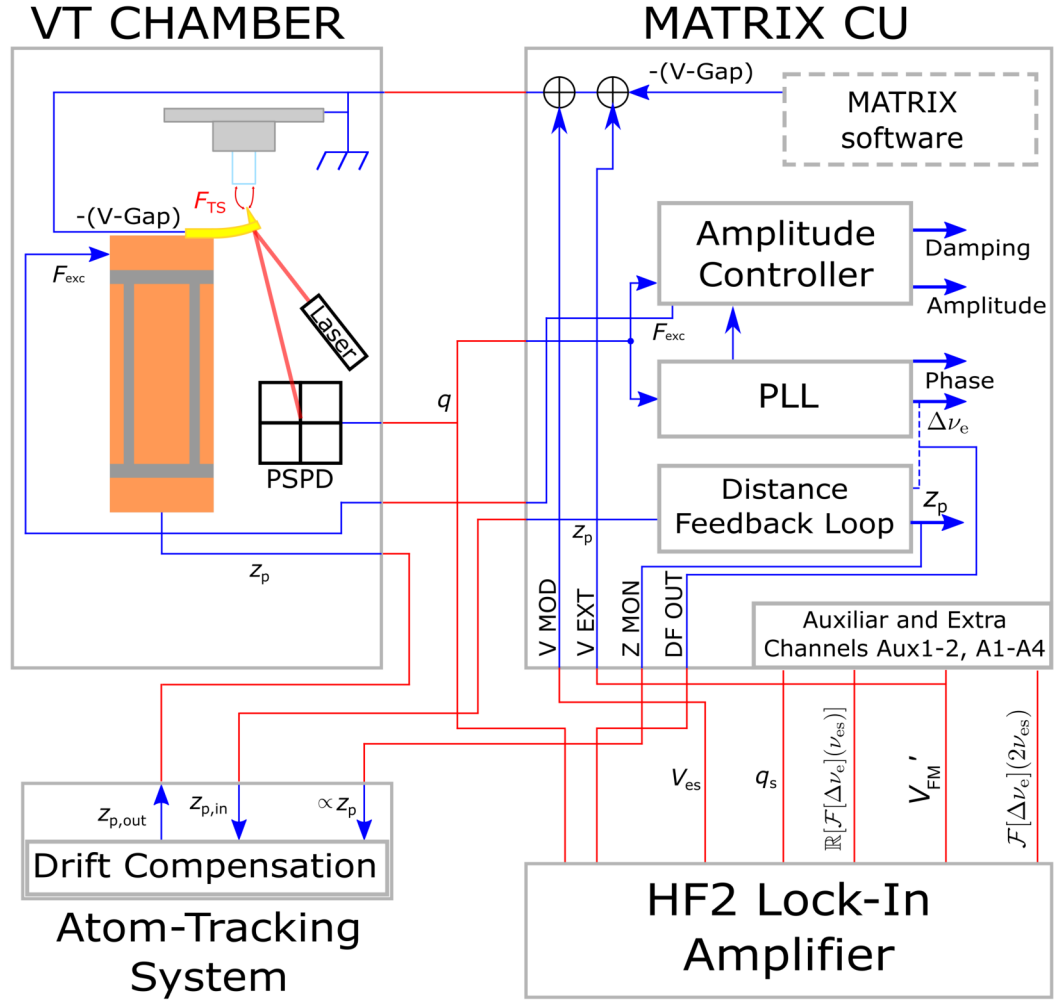


Figure 3.6.: Block diagram of the equipment connections for FM-KPFM measurements. Unlike figure 3.4, the corresponding connections for the STM imaging are not included since simultaneous STM and KPFM measurements are not possible.

The atom-tracking system is connected between the output of the MATRIX CU to the piezo-tube scanner and the connection to the piezo-tube scanner in the VT chamber: the z_p connection.

The HF2 is used to generate and analyze the KPFM signals and to extract the static deflection q_s . The two inputs of the HF2 are feed with the signals from the PSPD

and the DF OUT output from the MATRIX CU. Regarding the outputs of the HF2, the Signal Output 1 (it is not relevant whether it is 1 or 2, just to refer to some of them) is connected to the V MOD external input of the MATRIX CU. The four auxiliary DC outputs Aux 1 to Aux 4 are connected to the four auxiliary inputs in MATRIX CU. One of them, in turn, must be connected to the V EXT external input of the MATRIX CU.

Regarding the signal processing in the HF2, first I will refer to the static deflection q_s . The HF2 tracks the DC component of the signal from the PSPD, which corresponds to the static deflection q_s . This signal is output through one of the auxiliary outputs which are connected to the MATRIX CU.

The Signal Output 1 of the HF2 produces an oscillating voltage with amplitude V_{es} and frequency ν_{es} . The oscillating signal is added internally in the MATRIX CU to the voltages V-Gap and V-Ext and applied to the AFM tip inside the chamber: this voltage corresponds to the expression 2.29. As the output of the DF OUT connection in the MATRIX CU can output the frequency shift $\Delta\nu_e^2$, this signal can be processed by the HF2. I track the spectral components at frequencies ν_{es} and $2\nu_{es}$. The first spectral component is feed to one of the *PID tabs* in order to minimize it. The minimized spectral component is output by one of the auxiliary DC outputs, and so is the second spectral component. The signal which results from the *PID tab* is the voltage V_{FM}' , which is also by one of the auxiliary DC outputs. This output, in particular, must be the same one also connected to V EXT. Thus, this voltage is added to the V-Gap. Then, the real voltage applied between tip and sample during an FM-KPFM experiment in this setup is:

$$V_{FM} = -V_{Gap} + V_{FM}' \quad (3.3)$$

²Actually, it is not the frequency shift $\Delta\nu_e$, but the difference between this one and the $\Delta\nu_e$ -Setpoint, as explained in section 3.2. However, as I use it for tracking spectral components at frequency different from DC, it is still valid. This makes easier to follow the discussion.

Substrates

Contents

4.1 Au(111)	29
4.2 Calcite (10.4)	31

The goal of this work is performing a systematic study of KPFM experiments carried out on molecules deposited on insulators. The bulk insulator chosen as a substrate is calcite, which is one modification of the calcium carbonate (CaCO_3). The Au(111) surface has been chosen as a bare metallic substrate for tip characterization purposes.

4.1 Au(111)

The bulk structure of gold is face-centered cubic (fcc). Its lattice constant is 4.08 Å [91], from which is computed the interatomic bulk distance with a value of 2.88 Å. The (111) surface is the energetically most favourable surface. The interatomic surface distance is 2.81 Å (average distance measured [92]). This surface presents a reconstruction due to the rearrangement of the atoms along the $[\bar{1}\bar{1}0]$ direction: 23 atoms fill the space originally intended for 22 atoms. This constraint results in rearrangement and relaxation in the normal direction to the surface. Harten *et al.* [93] proposed a model to explain the resulting arrangement, described in figure 4.1. The profile shows modulations in the vertical coordinate and looks as two ridges. The resulting unit cell is described as $(22 \times \sqrt{3})$. The dimensions of the unit cell are 4.7 x 63 Å in the $[11\bar{2}]$ and $[\bar{1}\bar{1}0]$ directions [94], respectively.

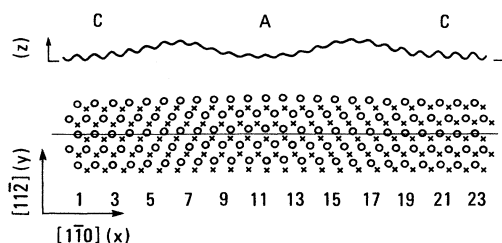


Figure 4.1.: Model for the reconstruction of Au(111) surface. Atoms of the second layer are presented by crosses, while the open circles denote the positions of the atoms of the reconstructed first layer. A and C mark the hcp and fcc regions, respectively. Adapted from [95].

Figure 4.1 depicts a model for the reconstruction of Au(111) surface. The modulations in the vertical direction are not equidistant: they exhibit an alternating distance between two consecutive ridges, reason why they look organized in pairs. The regions between two ridges in the same pair are hexagonal closed-packed (hcp) stacking areas (indicated by A) and the regions between two pairs of ridges (indicated as B) are fcc stacking domains. Figure 4.2 shows an STM image of the reconstructed Au(111) surface. In this image, the modulation from appears as parallel lines. The fcc-ridge-hcp-ridge-fcc periodicity is given by the width of the unit cell (63 Å) [94, 96].

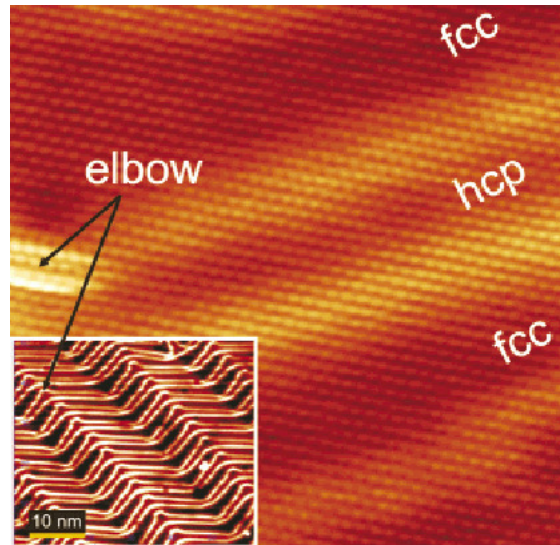


Figure 4.2.: STM image of the Au(111) surface showing atomic resolution. The bright areas in the image correspond to ridges due to the reconstruction. The fcc and hcp regions between the ridges and the elbows are indicated in the image. The spots in which the ridges change their orientation are referred as elbows. Adapted from [92].

The orientation of the lines changes in 120° every ~ 250 Å [94]. In a large scale, the appearance of the lines results in a zigzag structure (inset in figure 4.2). This is the reason for receiving the name of *herringbone reconstruction*. The corrugation amplitude is height different between the fcc regions and the ridges is estimated in 0.2 ± 0.05 Å, while the difference in height between the ridges and the depression (hcp region) is 0.12 ± 0.05 Å [94]. The apparent height (from STM measurements) a monoatomic step edge is ~ 2.35 - 2.4 Å [94, 96]. This is in good agreement with the height of a monoatomic step in bulk between two consecutive (111) surfaces (computed using the lattice constant value), which is 2.35 Å.

4.2 Calcite (10.4)

Calcium carbonate is formed by Ca^{2+} ions and CO_3^{-2} groups. Calcite is the most thermodynamically stable modification and crystallizes in a rhombohedral structure. Its symmetry is described by the space group $R\bar{3}c$ [97].

Calcite is an insulator. Baer *et al.* quantified the electronic bandgap by reflection electron energy-loss spectra (REELS) experiments in $E_g = 6.0$ eV [98]. Different density functional theory (DFT) simulations report similar values: 5.07 eV [99] and 5.06 eV [100]. Both authors attribute the difference with respect to the experimental value to typical DFT underestimation.

The most stable surface of calcite is the (10.4) cleavage plane, with a surface energy $\gamma_s = 510$ mJ/m² [100]. This surface belongs to the pg symmetry group and presents a rectangular unit cell. The dimensions of the unit cell are 4.99×8.1 Å (figure 4.3). These dimensions have been calculated [86] from the crystallographic bulk dimensions reported by Effenberger *et al.* [101]. The reported values are in good agreement with grazing incidence X-ray diffraction (GIXRD) [102], low energy electron diffraction (LEED) [103] and AFM [104] experiments. The lattice vectors are oriented in the $[010]$ and $[\bar{4}21]$ directions.

The unit cell contains two Ca ions and two carbonate groups CO_3^{-2} . The carbonate groups are rotated with respect to each other in the unit cell. Furthermore, they are also rotated 44.63° with respect to the surface plane [105], reason why one of the oxygen atoms protrudes the plane defined by the calcium atoms. As a consequence, the $[\bar{4}21]$ and $[42\bar{1}]$ are not equivalent. The protruding oxygen atoms of the carbonate groups do not align with the $[\bar{4}21]$ direction, but they alternately point to right and left, forming a zigzag pattern (black line in figure 4.3). The height of a monoatomic step edge is ~ 3 Å [86].

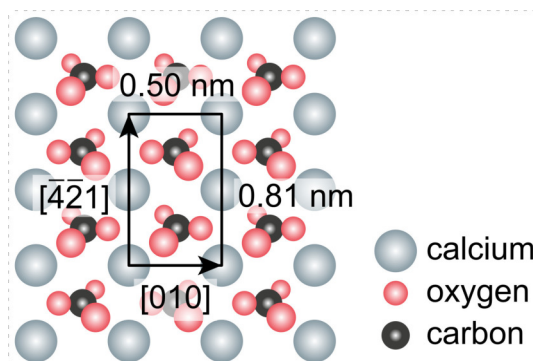


Figure 4.3.: Model of calcite (10.4) surface. The unit cell is composed of two calcium ions and two carbonate groups, which are rotated with respect to each other. The black line represents the zigzag of the topmost oxygen atoms of the carbonate groups along the $[\bar{4}21]$. Adapted from [86].

Calcite is a birefringent mineral. When light passes through the (10.4) surface, the light beam splits in two along the $[42\bar{1}]$ direction. This property is used to identify the absolute orientation of the crystal (10.4) surface, following a routine developed in our research group [86, 88].

KPFM Measurements: from Theory to Experiments

Contents

5.1	Introduction	33
5.2	Transfer Functions	35
5.2.1	Transfer Function of the PLL	35
5.2.2	Transfer Function of the Experimental System	38
5.3	Distance-Dependent Measurements	43
5.3.1	Amplitude Calibration	44
5.3.2	Static Deflection	45
5.3.3	Preparation of Metal-Coated AFM Tips	45
5.4	Use of Atom-Tracking System	46
5.5	Summary	46

The theory of Kelvin probe force microscopy (KPFM) was already introduced in section 2.4. However, it is not straightforward to perform a KPFM experiment to get quantitative information about the charge distribution on the sample surface. Deeper understanding of the equations is needed. In this chapter, the reasons why some parameters and signals require special treatment are explained, as well as the necessary procedures to follow before and during the experiment for appropriate data processing.

5.1 Introduction

As previously stated, only static and closed-Loop FM-KPFM experiments are presented in this thesis. According to the model proposed by Kantorovich *et al.* [36], both KPFM methods provide the same information about the charge distribution on the sample surface.

The frequency shift $\Delta\nu_e$ has a parabolic dependence on the bias voltage V_{bias} . Static FM-KPFM consists of recording $\Delta\nu_e$ (V_{bias}) curves. The position of the maximum of the parabola corresponds to the Kelvin V_{FM} signal:

$$V_{\text{FM}} = -V_{\text{CPD}} + \sum_{i=1}^N q_i W_{\text{FM}}(\mathbf{r}_i) \quad \text{with} \quad W_{\text{FM}}(\mathbf{r}) = \frac{\left\langle \frac{\partial^2 \hat{\Phi}_{\text{void}}}{\partial z_{\text{ts}}^2}(\mathbf{r}_i) \right\rangle_{\cap}}{\left\langle \frac{\partial^2 C_{\text{void}}}{\partial z_{\text{ts}}^2} \right\rangle_{\cap}} \quad (5.1)$$

This voltage minimizes the tip-sample electrostatic interaction.

The same result can be obtained by performing closed-loop FM-KPFM. This method relies on nullifying the first spectral component of the electrostatic force gradient $k_{\text{es,b}}$ (see equation (2.31)). Furthermore, the second spectral component $k_{\text{es,c}}$ (see equation (2.32)) is proportional to the second derivative of the capacitance of the empty tip-sample system C_{void} . Then, both spectral components must be recorded. However, it is not possible to measure these components directly, but through the spectral components at ν_{es} and $2\nu_{\text{es}}$ in the frequency shift $\Delta\nu_e$. From equation (2.9), it follows:

$$\mathcal{F}[\Delta\nu_e](\nu_{\text{es}}) = \frac{\nu_e}{2k} \cdot \langle k_{\text{es,b}} \rangle_{\cap} \quad (5.2)$$

$$\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}}) = \frac{\nu_e}{2k} \cdot \langle k_{\text{es,c}} \rangle_{\cap} \quad (5.3)$$

However, the frequency shift $\Delta\nu_e$ is measured using a PLL, which is an electronic device with an specific transfer function: the magnitude and phase of the output signal compared with the input signal is not constant for all frequencies. Then, I define the frequency shift output by the PLL as $\Delta\nu_{\text{e,PLL}}$. Its sign is defined by the phase shift $\phi_{\Delta\nu_{\text{e,PLL}}}$. The relation between the frequency shift $\Delta\nu_e$ and the frequency shift output by the PLL $\Delta\nu_{\text{e,PLL}}$ can be expressed as:

$$\mathcal{F}[\Delta\nu_{\text{e,PLL}}](\nu) = |G_{\text{PLL}}(\nu)| \cdot \mathcal{F}[\Delta\nu_e](\nu) \quad (5.4)$$

$$\phi_{\Delta\nu_{\text{e,PLL}}}(\nu) = \phi_{\text{PLL}}(\nu) + \phi_{\Delta\nu_e}(\nu) \quad (5.5)$$

where $|G_{\text{PLL}}(\nu)|$ and $\phi_{\text{PLL}}(\nu)$ are the gain of the PLL and the phase shift at the frequency ν and $\phi_{\Delta\nu_e}(\nu)$ is the phase shift of the spectral component of the frequency shift $\Delta\nu_e$ at the frequency ν .

From the previous summary, several remarks can be made:

- The magnitude and phase shift of the spectral components at the ν_{es} and $2\nu_{\text{es}}$ frequencies measured during an experiment depend on the electrostatic excitation frequency ν_{es} (see equations (5.4) and (5.5)).
- The Kelvin V_{FM} signal depends on the oscillation amplitude A of the cantilever: as explained in section 2.4.3, the V_{FM} signal is the sum over all point charges q_i localized between tip and sample. The charges are weighted by the FM-KPFM weight function $W_{\text{FM}}(\mathbf{r})$, which depends on the normalized electrostatic potential $\hat{\Phi}_{\text{void}}$ and the capacitance of the void tip-sample system C_{void} . As shown in equation (5.1), the FM-KPFM weight function is the ratio of the weighted averages over the tip oscillation of the quantities $\hat{\Phi}_{\text{void}}$ and C_{void} . Then, the oscillation amplitude A influences the value of the FM-KPFM weight function and, hence, of the V_{FM} signal.
- The Kelvin V_{FM} signal varies with the tip-sample distance z_{ts} : since the normalized electrostatic potential $\hat{\Phi}_{\text{void}}$ and the capacitance of the void tip-sample system C_{void} vary with the tip-sample distance, so does the FM-KPFM weight function (see equation (5.1)).

In order to perform quantitative FM-KPFM experiments which can be compared among each other, several procedures must be followed before and during the experiment. These procedures will be explained in the following sections.

5.2 Transfer Functions

5.2.1 Transfer Function of the PLL

During a KPFM experiment, it is necessary to record both spectral components $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ and $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. As described in section 2.4.3, both spectral components contain valuable information about the tip-sample system. However, before choosing an electrostatic excitation frequency ν_{es} , it is necessary to know the PLL bandwidth: if the frequency ν_{es} is larger than the PLL bandwidth, the spectral components will be attenuated. For this purpose, the transfer function¹ of the PLL must be known.

Usually, the PLL gain $|G_{\text{PLL}}|$ presents a plateau for frequencies close to DC (0 Hz) and a decreasing slope which damps the signals with frequency larger the bandwidth

¹The transfer function of a system describes the output signal with respect to the input.

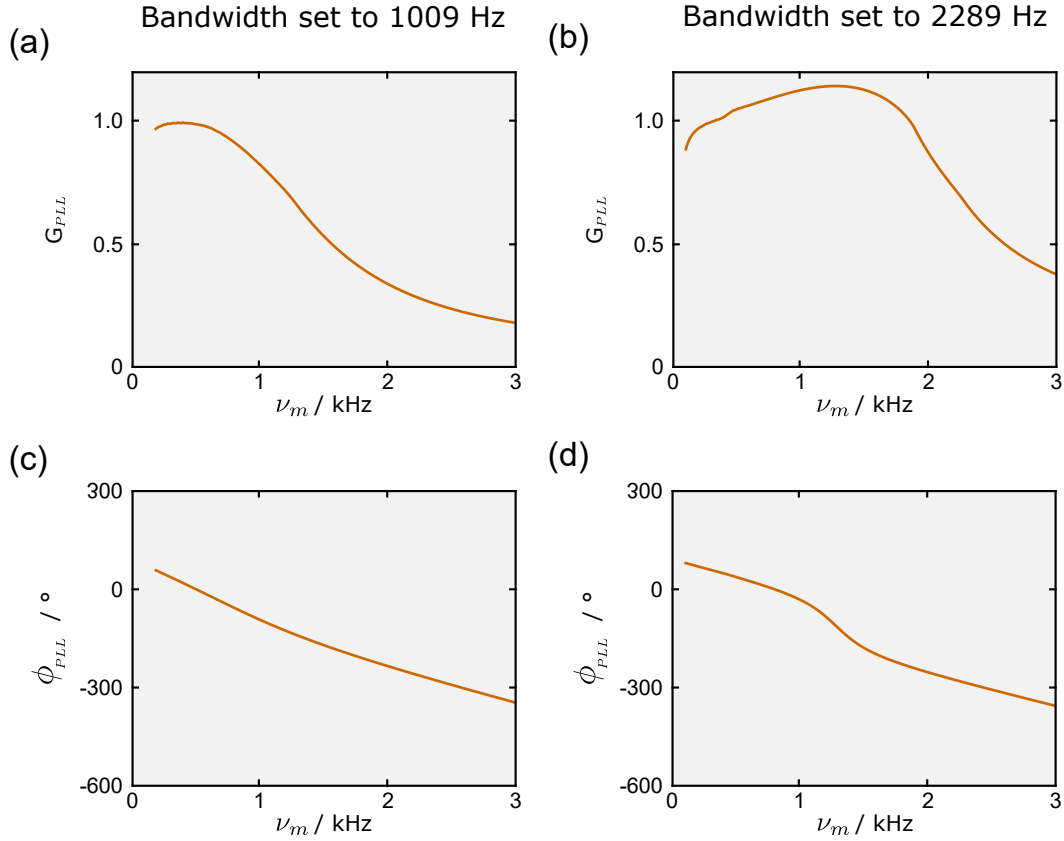


Figure 5.1.: Transfer functions of the MATRIX PLL for the bandwidth set to 1009 Hz ((a) and (c)) and 2289 Hz ((b) and (d)). Both transfer functions were recorded by applying a modulation magnitude $\nu_p = 100$ Hz and sweeping the modulation frequency ν_m from 100 Hz to 3 kHz.

[85, 106]. The magnitude of the signal is attenuated in a factor indicated by the PLL gain $|G_{PLL}|$ at that frequency. To measure the transfer function of a PLL, it is necessary to modulate the frequency at which the PLL is locked and sweep the modulation frequency to monitor the output signal. The steps of the process are explained in detail as follows:

- Connect to the input of the PLL an oscillating signal with a carrier frequency ν_C . During usual FM-AFM operation, the PSD signal is connected to the PLL input.
- Lock the PLL at the frequency ν_C as in any FM-AFM experiment.
- Modulate the frequency ν_C with an oscillating signal of peak frequency ν_p (the magnitude of the modulating signal) and modulation frequency ν_m ². The resulting frequency of the signal can be expressed as [85]:

²This signal simulates the output from the PSD during a KPFM experiment: ν_C as the excitation frequency ν_{exc} , ν_p as the magnitude of the first spectral component $k_{es,b}$ and ν_m as frequency of the electrostatic excitation ν_{es} .

$$\nu(t) = \nu_C + \nu_p \cos(2\pi\nu_m t) \quad (5.6)$$

- Sweep the frequency ν_m while recording the amplitude and phase of the output signal.
- Divide the amplitude of the output signal by the modulation magnitude ν_p .

Figure 5.1 shows the transfer function of the PLL included in the MATRIX CU for two bandwidths: 1009 Hz and 2289 Hz. The PLL gains $|G_{PLL}|$ are shown in (a) and (b) and phase shifts ϕ_{PLL} are presented in (c) and (d). The magnitude of the modulation applied ν_p was 100 Hz and the modulating frequency ν_m was swept from 100 Hz to 3 kHz.

For the PLL bandwidth set to 1009 Hz, the PLL gain $|G_{PLL}|$ (figure 5.1 (a)) exhibits a plateau of constants values (which are the maximum values) between 200 Hz and 600 Hz. According to the definition³, the PLL bandwidth is determined in 1253 Hz. This is in disagreement with the bandwidth set in the MATRIX software. This is the reason why in this thesis I distinguish between *bandwidth set to*, *bandwidth is* and *bandwidth =:* the first expression corresponds to the software setting, while the second and third expressions refer to the experimentally determined bandwidth. The phase shift ϕ_{PLL} (figure 5.1 (c)) shows an monotonic decrease. However, for the bandwidth set to 2289 Hz, the PLL gain $|G_{PLL}|$ (figure 5.1 (b)) shows no plateau. For frequencies smaller than 400 Hz, the gain shows similar values than for (a). For large frequencies, it presents a large overshoot. Considering the same maximum value as in (a) (on the plateau), the bandwidth experimentally determined is 2260 Hz. The phase shift ϕ_{PLL} (figure 5.1 (d)) shows a change in slope in the range of frequencies of the large overshoot.

Now, with the knowledge of the transfer function of the PLL for both bandwidth set to 1009 and 2289 Hz, I know the range of modulation frequencies that I can read out in the output of the PLL: the frequency shift output by the PLL $\Delta\nu_{e,PLL}$. However, before choosing the electrostatic excitation frequency ν_{es} , it is appropriate to study the first and second spectral components $\mathcal{F}[\Delta\nu_e](\nu_{es})$ and $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ in the experimental system depending on the frequency ν_{es} .

³As explained in section 3.2, the bandwidth of an electronic device is given by the difference between two cutoff frequencies. At these frequencies, the gain of the device is $1/\sqrt{2}$. Between the cutoff frequencies, there is a frequency range for which the gain is 1. In the case of a low-pass filter or a PLL, the bandwidth is given by the range of frequencies between DC and the cutoff frequency.

5.2.2 Transfer Function of the Experimental System

As explained in the previous section, it is convenient to check the first and second spectral components $\mathcal{F}[\Delta\nu_e](\nu_{es})$ and $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ as a function of the excitation electrostatic frequency ν_{es} . The most straightforward course is recording the transfer function of the experimental system. The steps to follow are:

- Bring the AFM tip to close proximity to the sample surface.
- Record a $\Delta\nu_e(V_{bias})$ curve and adjust the bias voltage to the position of the maximum of this parabola. The tip-sample electrostatic interaction is now minimized.
- Apply an oscillating voltage to the cantilever with an amplitude V_{es} and frequency ν_{es} .
- Disable the distance feedback loop. This is needed because the magnitude of the spectral components are expected to vary with the frequency ν_{es} , so do their contributions to the frequency shift $\Delta\nu_e$. If the distance feedback loop is enabled, it will change the z-piezo position z_p in order to keep the frequency shift $\Delta\nu_e$ constant and, as a consequence, the tip-sample distance z_{ts} . This would cause a distortion of the transfer function.
- Sweep the frequency ν_{es} while recording the amplitude and phase of the both spectral components at ν_{es} and $2\nu_{es}$.

Figure 5.2 shows the transfer function of the experimental system for PLL bandwidths set to 1009 Hz and 2289 Hz⁴. Plots (a) and (b) show the magnitude of the spectral components measured for the PLL bandwidth set to 1009 and 2289 Hz, respectively. Plots (c) and (d) present the phase shift ϕ of the spectral components measured for the PLL bandwidth set to 1009 and 2289 Hz, respectively. Once the tip was in close proximity to the sample surface, I recorded a $\Delta\nu_e(V_{bias})$ curve and set the bias voltage V_{bias} to 1.6 V, the position of the maxima. The electrostatic interaction between tip and sample was minimized, so its contribution to the frequency shift $\Delta\nu_e(V_{bias})$ decreased and the distance feedback loop approached the tip to the sample surface until the $\Delta\nu_e$ setpoint was reached again. Plot (a) shows the magnitude of both spectral components for PLL bandwidth set to 1009 Hz. The second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ (in blue) presents its maximum at the half of the frequency of the first spectral component $\mathcal{F}[\Delta\nu_e](\nu_{es})$ (in orange). This indicates the impossibility of having the maximum magnitude for both spectral

⁴All images and curves presented in this thesis were recorded using any of those two bandwidths.

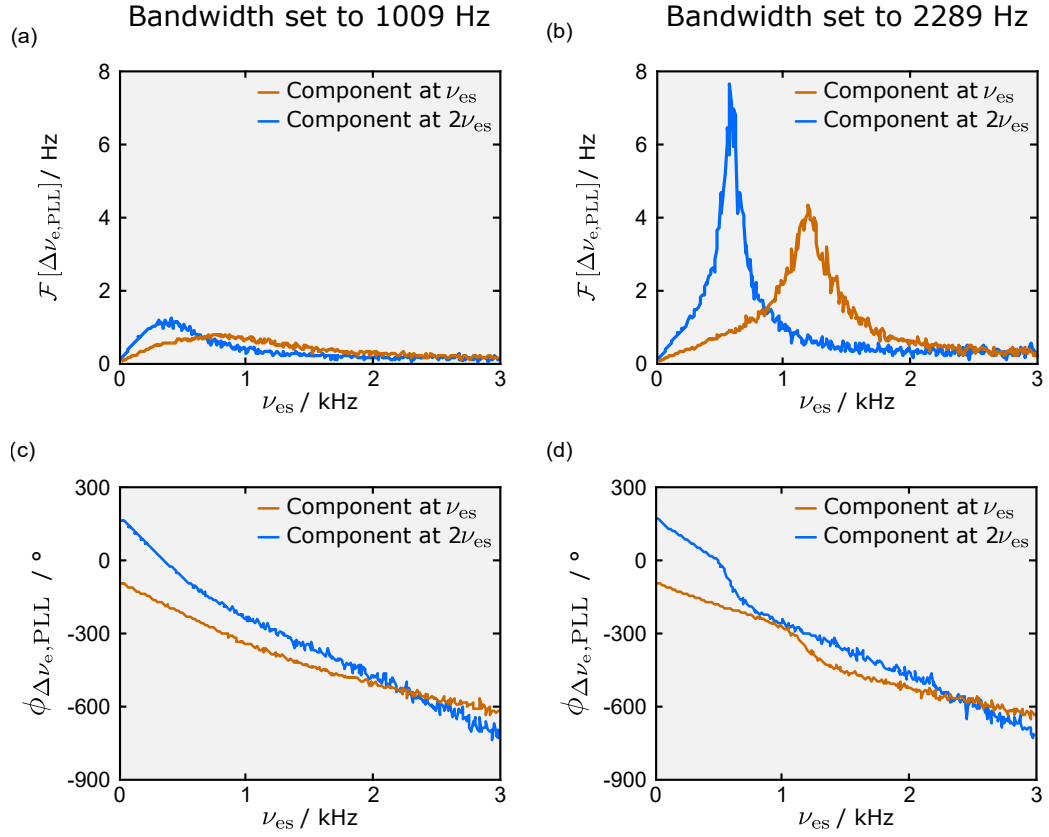


Figure 5.2.: Transfer functions of the experimental system for PLL bandwidth set to 1009 Hz ((a) and (c)) and 2289 Hz ((b) and (d)). The bias voltage V_{bias} was set to 1.6 V after recording the parabola $\Delta\nu_e(V_{\text{bias}})$.

components. Furthermore, the maximum of the second spectral component is larger than the maximum of the first spectral component. In plot (c), the phase shift ϕ of the two spectral components are different, but show a monotonic decrease.

For the PLL bandwidth set to 2289 Hz, plot (b) shows the magnitude of both spectral components. The magnitude of each spectral component is larger for this bandwidth, so the frequency ν_{es} of the maxima. However, the behaviour with respect to each other is the same as for bandwidth set to 1009 Hz (frequency of the maxima and magnitude with respect to each other). The phase shifts ϕ of both spectral components (d) show a change in their slopes for the range of frequencies where their magnitude is maxima.

Before choosing the electrostatic excitation frequency ν_{es} , the relation between frequency and period of an oscillation must be taken into account⁵. The smaller the frequency ν_{es} selected, the larger the time per point (in an image or a curve) or the slower the scanning speed. Thus, the selection of the frequency ν_{es} is a trade off between the magnitude of the spectral components and scanning speed

⁵The period of an oscillation is the inverse of the frequency of the oscillation. To record an specific number of cycles of an oscillation, the time for recording the cycles scales inverse with the frequency.

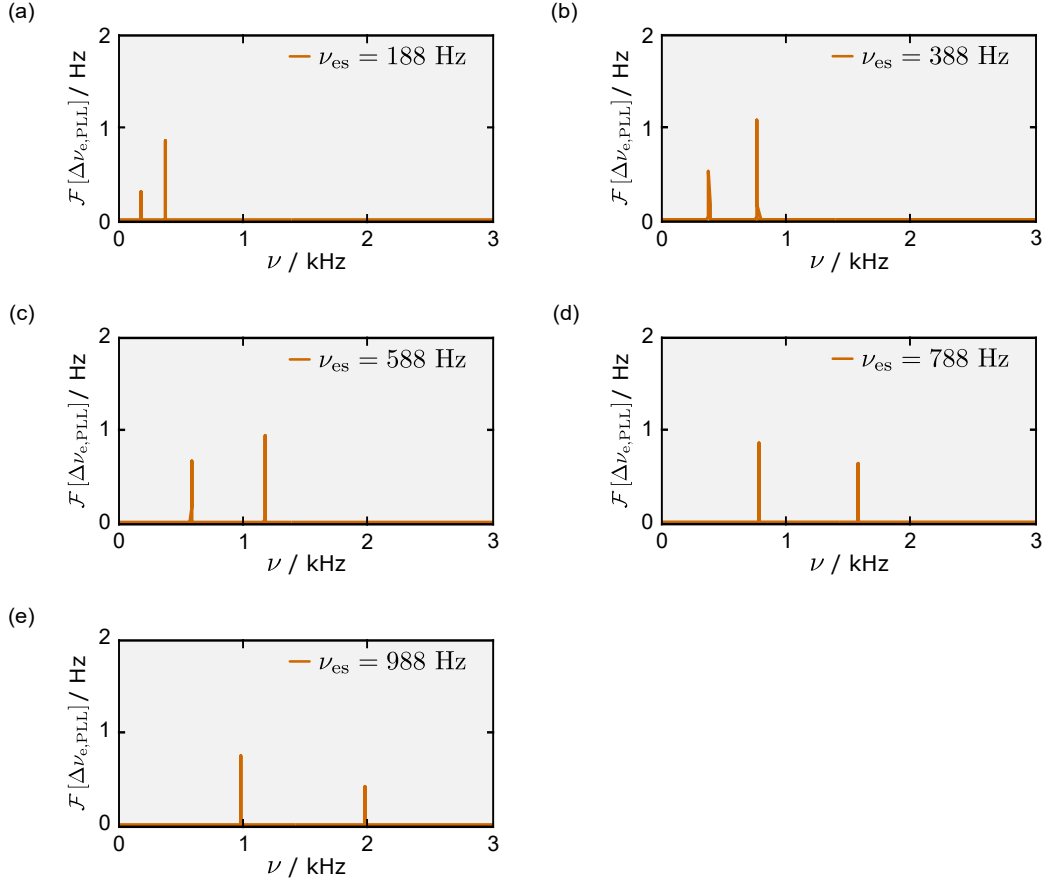


Figure 5.3.: Fast Fourier transform (FFT) of the frequency shift output by the PLL as $\Delta\nu_{e,PLL}$ using five different ν_{es} frequencies. The PLL bandwidth was set to 1009 Hz.

or duration of the experiment⁶. Figure 5.3 shows the fast Fourier transform (FFT) of the frequency shift $\Delta\nu_e$ with the PLL bandwidth set to 1009 Hz for different electrostatic excitation frequency ν_{es} . Figure 5.4 shows the same information, but the PLL bandwidth was set to 2289 Hz. Both figures show that, as the frequency ν_{es} increases, the distance between the peaks of the spectral components $\mathcal{F}[\Delta\nu_e](\nu_{es})$ and $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ increases, and their magnitude vary according to the plots (a) and (b) in figure 5.2. For example, it is possible to observe that the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ for the PLL bandwidth set to 2289 Hz and frequency $\nu_{es} = 588$ Hz (figure 5.4 (c)) corresponds to the maximum of the same spectral component in figure 5.2 (b). For this combination of PLL bandwidth and electrostatic excitation ν_{es} , the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ is significantly larger than for any other frequency ν_{es} .

For the FM-KPFM experiments presented in this work, I chose the frequency $\nu_{es} = 988$ Hz for a PLL bandwidth = 2289 Hz (figure 5.4 (e)). The time per pixel used is 3 ms (2 cycles of the oscillating signal plus extra time for the feedback loop

⁶The scanning speed or duration of the experiment are important issues to take into account, as in situations with large drift or in diffusion experiments.

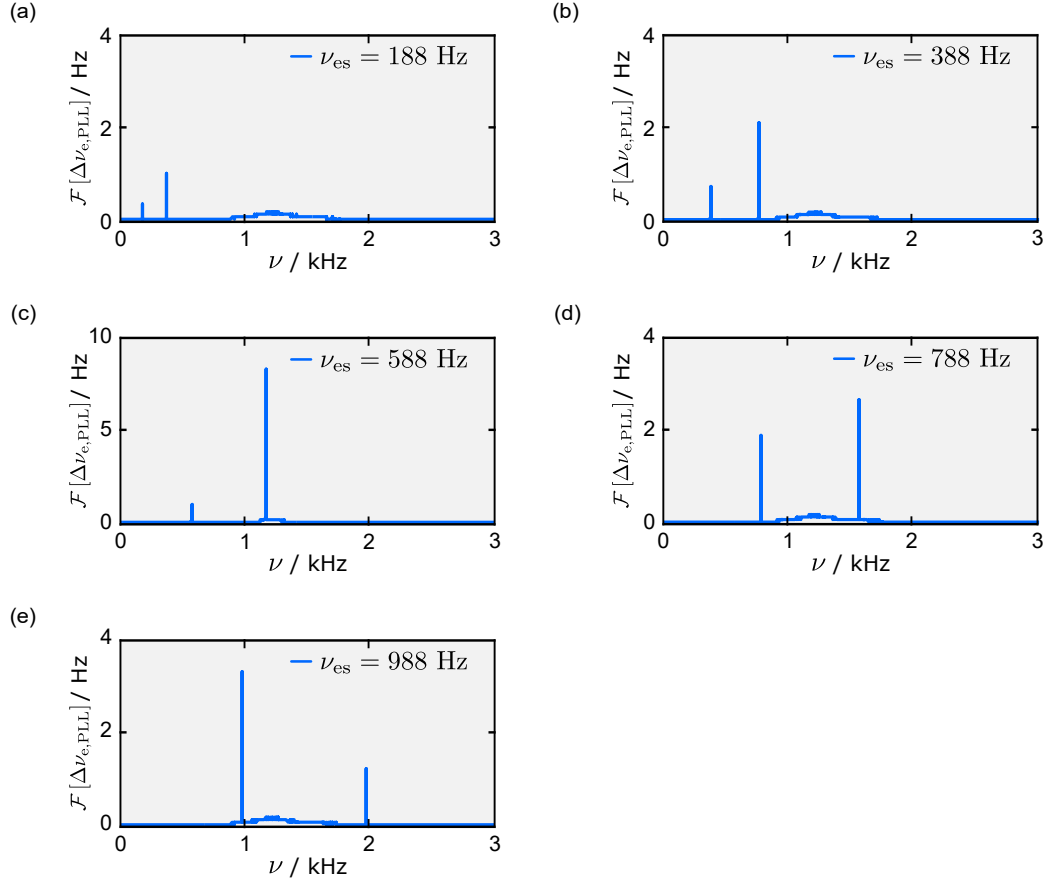


Figure 5.4.: Fast Fourier transform (FFT) of the frequency shift output by the PLL as $\Delta\nu_{e,PLL}$ using five different ν_{es} frequencies. The PLL bandwidth was set to 2289 Hz. The scale in the y-axis of the plot (c) is different from the rest, since $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ for ν_{es} is significantly larger than for the other frequencies.

to act). The magnitude of the first spectral component is significantly larger than the second spectral component. Since the first spectral component contains the information about the localized point charges in the tip-sample system, recording the first spectral component with larger magnitude is a priority.

According to the model proposed by Kantorovich *et al.* [36] and described in section 2.4.2, the first spectral component of the force gradient $k_{es,b}$ depends on the bias voltage V_{bias} , but the second spectral component $k_{es,c}$ is independent. In order to check this, I reduced the bias voltage V_{bias} to 0 V, kept the feedback loop disabled and recorded the transfer function of the experimental system. Figure 5.5 show the comparison of the transfer function of the experimental system for the PLL bandwidth set to 1009 Hz for bias voltage V_{bias} 1.6 V (orange colour) and 0 V (blue colour). Note that the higher value of the voltage implies smaller electrostatic interaction, as already mentioned. Plots (b) and (d) show the magnitude $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ and phase shift ϕ of the second spectral component. For the second spectral component, the data recorded in the two situations overlap, what proves that this component does not depend on the bias voltage V_{bias} . However, the magnitude $\mathcal{F}[\Delta\nu_e](\nu_{es})$ and

phase shift ϕ of the first spectral component (plots (a) and (c)) show very different values for the different bias voltage V_{bias} . This is a validation of the dependence of the first spectral component on the applied bias voltage V_{bias} , as stated in section 2.4.2.

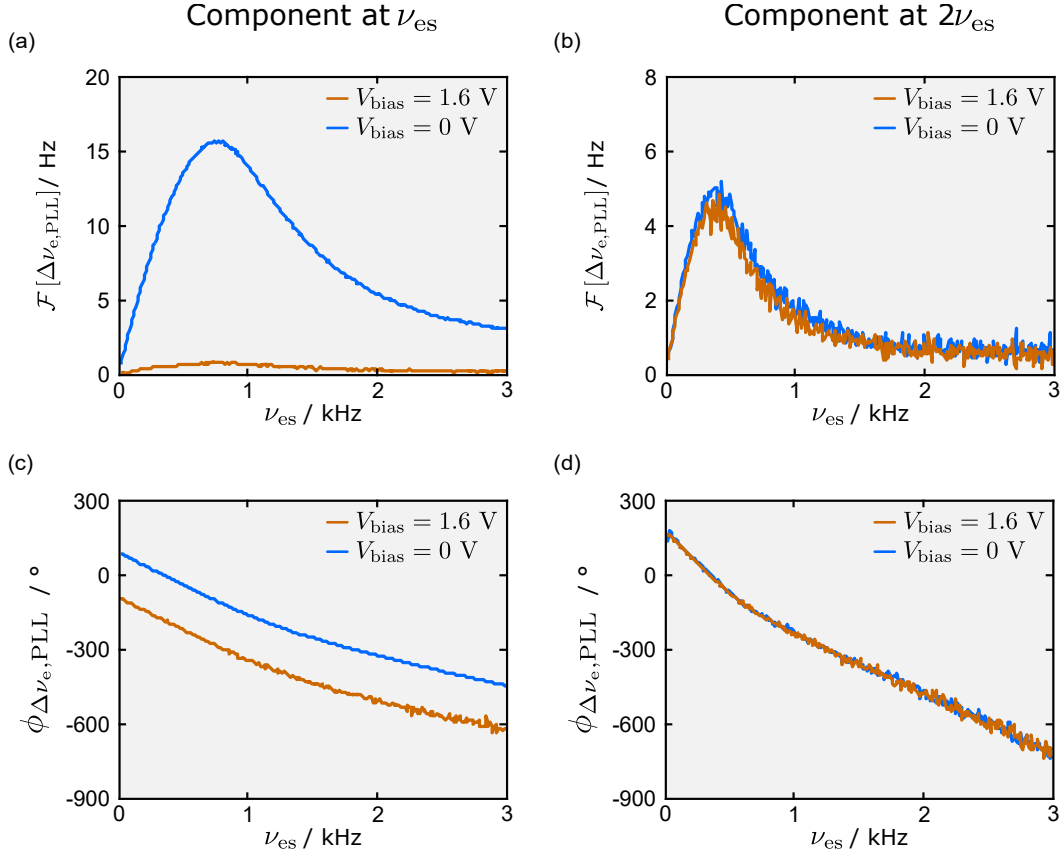


Figure 5.5.: Transfer functions of the experimental system for the PLL Bandwidth set to 1009 Hz and $V_{\text{bias}} = 1.6$ V and 0 V.

Once I studied the magnitude of the spectral components in the experimental system, I chose the electrostatic excitation frequency ν_{es} . Recording both spectral components was required, which implied choosing the excitation electrostatic frequency ν_{es} , at least, as the half of the PLL bandwidth. Furthermore, I needed to consider the scan speed: I intended to record two complete cycles of the oscillating frequency plus give extra time for the KPFM feedback loop to operate (this will be explain in the next chapter). Since the period of a signal (time-duration of a cycle) is inverse with the frequency, choosing an excessively small frequency implies a very large measurement time. This would make the measurement extremely slow. I chose the PLL bandwidth set to 2289 Hz: the experimentally determined bandwidth is 2260 Hz, so ν_{es} should be smaller than 1130 Hz. The electrostatic excitation frequency ν_{es} chosen is 988 Hz. All KPFM images and distance-dependent curves presented in this work were recorded using this frequency. As a last remark, in order to process the images and

curves of the first and second spectral components $\mathcal{F}[\Delta\nu_e](\nu_{es})$ and $\mathcal{F}[\Delta\nu_e](2\nu_{es})$, the PLL gains at frequencies ν_{es} and $2\nu_{es}$ must be used (see equation (5.4)).

5.3 Distance-Dependent Measurements

Equation (5.1) shows the dependence of the Kelvin V_{FM} signal on the tip-sample distance z_{ts} . This dependence has been shown in previous works [37, 39, 40]. Due to this distance dependence, two different V_{FM} images (slices parallel to the sample surface plane) are not comparable if they have been recorded at different tip-sample z_{ts} distances.

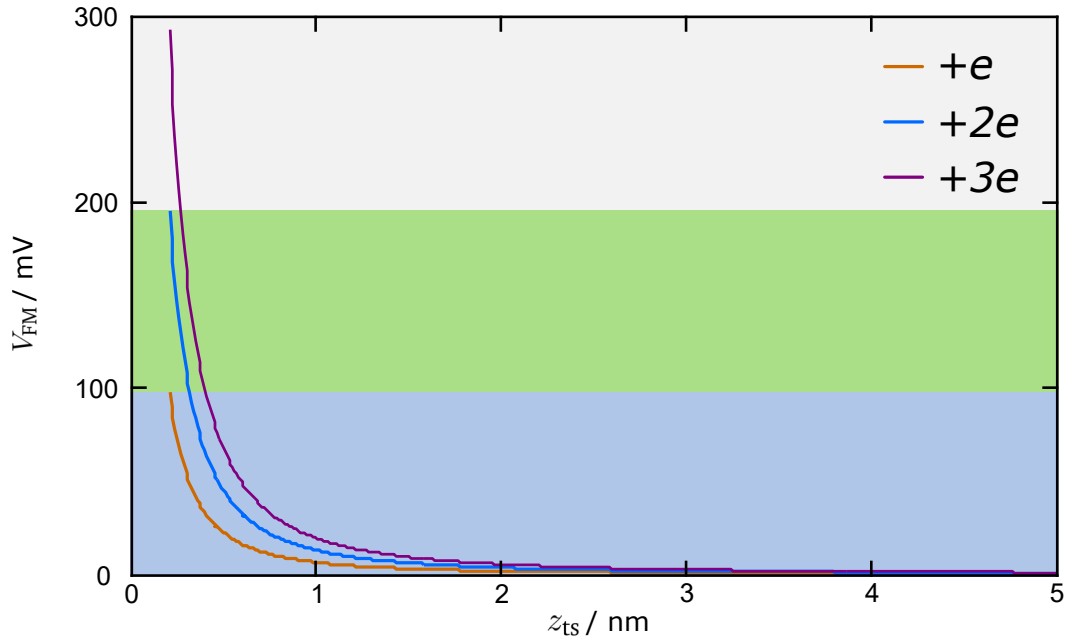


Figure 5.6.: Simulation of the Kelvin $V_{FM}(z_{ts})$ signal for 1, 2 and 3 positive elementary charges ($+e$) placed at $x = y = 0$ nm and $z = 0.2$ nm over the sample surface. The simulation is based in the spherical tip in front of a infinite metallic plate [82, 83], using a modification of the Python script used by Söngen *et al.* [38]. The colour areas in the background indicate the range of V_{FM} values which are common for some of the curves at some point of the simulated tip-sample distance z_{ts} : the blue area indicate the range of V_{FM} values common to the three curves; the green area indicate the range of V_{FM} values common to the curves corresponding to 2 and 3 elementary charges.

Figure 5.6 shows the simulation of the V_{FM} signal as a function of the tip-sample distance z_{ts} . The model used in the simulation assumes the tip-sample system as a metallic sphere in front of a metallic infinite plate [82, 83]. The simulation was performed using a modification of the Python script used by Söngen *et al.* [38]. For the simulation, the sphere (tip) is considered to be located at coordinates $x = y = 0$ nm. The sample surface is at $z = 0$ nm. One point charge is placed in $x = y = 0$ nm and $z = 0.2$ nm. Three different situations have been considered: the magnitude of the point charge is one elementary charge ($+e$), two ($+2e$) and three ($+3e$). The

oscillation amplitude A is considered to be 0 nm. The simulated distance-dependent V_{FM} curves are not constant when varying the tip-sample distance z_{ts} . Furthermore, it is possible to observe that, for some z_{ts} value, all curves exhibit present $V_{\text{FM}} \lesssim 100$ mV (V_{FM} range indicated by the blue area in the background in figure 5.6). The same fact can be observe for the curves corresponding to 2 and 3 elementary charges, but with $V_{\text{FM}} \lesssim 200$ mV (V_{FM} range indicated by the green area). This means that for different tip-sample distance z_{ts} , V_{FM} images recorded at different tip-sample distances may exhibit the same values. Thus, in order to perform quantitative KPFM experiments, distance-dependent measurements must be performed.

5.3.1 Amplitude Calibration

Both quantities $\Delta\nu_e$ and V_{FM} depend of the oscillation amplitude A (see equations (2.7) and (5.1)). Two values of any of these quantities recorded at the same tip-sample distance z_{ts} but different oscillation amplitude A are different.

Figure 5.6 presents the distance dependence of the Kelvin V_{FM} signal for an oscillation amplitude $A \sim 0$ nm. However, in a real FM-KPFM experiment, an oscillation amplitude A different from 0 nm is necessary. In order to compare different KPFM experiments, the oscillation amplitude A must be the same or, at least, as similar as possible. To measure the oscillation amplitude A , first I need to convert the signal from the PSPD, which is in V, to nm. The response S (in nm/V) relates the oscillation amplitude A of the cantilever (in nm) to the signal from the PSPD and, hence, the amplitude setpoint introduced in the software (in V).

The procedure of the amplitude calibration was introduced by Simon *et al.* [107] and is based on the formula of the *normalized frequency shift* γ introduced by Giessibl *et al.* [108]:

$$\gamma(z_{\text{ts}}, A) = \frac{kA^{3/2}}{\nu_e} \Delta\nu_e(z_{\text{ts}}, \nu_e, k, A) \quad (5.7)$$

The validity of the method lies on the fact that, for different oscillation amplitudes, the tip-sample distance at the lower turning point of the oscillation is the same. Then, the product of the normalized frequency shift $\gamma(z_{\text{ts}}, A)$, the spring constant k and eigenfrequency ν_e is independent of the oscillation amplitude A and the frequency shift $\Delta\nu_e$.

The method consists of varying the oscillation amplitude A and the frequency shift $\Delta\nu_e$ so the normalized frequency shift γ does not vary. The distance feedback loop changes the z-piezo displacement z_p so the frequency shift $\Delta\nu_e$ remains constant. The values of the z-piezo displacement values z_p *versus* the oscillation amplitude A

must be plotted and fitted to a line. The slope of the fitted line is the response of the cantilever S .

5.3.2 Static Deflection

During closed-loop FM-KPFM experiments, the electrostatic interaction between tip and sample is minimized by nullifying the first spectral component $\mathcal{F}[\Delta\nu_e](\nu_{es})$. Nevertheless, in addition to the non-electrostatic forces, there are still forces (*i.e.*, last term in equation (2.25)) that can shift the static deflection q_s of the cantilever.

The interest in performing distance-dependent measurements is monitoring the distance dependence of the Kelvin V_{FM} signal with the tip-sample distance z_{ts} . However, the different AFM and FM-KPFM channels are recorded with respect to the z-piezo displacement z_p . Then, the z-piezo displacement values must be corrected by adding the corresponding static deflection q_s values. This quantity that can be obtained by recording the static component of the PSPD signal⁷ (see equation (2.3)).

5.3.3 Preparation of Metal-Coated AFM Tips

Equation (5.1) shows that all point charges between tip and sample contribute to the Kelvin V_{FM} signal. The contribution of each point charge depends on its magnitude and the value of the weight function for charges $W_{FM}(r)$. Then, localized point charges on the tip apex (adsorbates, contamination, trapped charges in an oxide layer...) might contribute to the Kelvin V_{FM} signal. However, I am interested only in the charge distribution on the sample surface, and it is only the contribution of these charges I would like to record with the Kelvin V_{FM} signal. A procedure to clean and check the AFM tips must be developed.

Equation (5.1) indicates that, in the absence of localized point charges between tip and sample, the only contribution to the V_{FM} signal is the contact potential difference V_{CPD} . Then, upon varying the tip-sample distance, the V_{FM} signal must remain constant. Hence, $V_{FM}(z_{ts})$ experiments on a metallic substrate should unravel whether the tips are free of localized charges.

Gold coated Au-tips (type PPP-NCHAu) from NanoWorld (Neuchatel, Switzerland) were prepared by sputtering with Ar^+ ions. After the preparation, $V_{FM}(z_{ts})$ curves have been measured on a Au(111) single crystal⁸, expecting two possible results:

⁷The static deflection of the PSPD signal was recorded using the HF2 lock-in amplifier, by tracking the component at 0 Hz frequency (see figure 3.6)

⁸Au(111) was chosen as a metallic substrate due to its clearly recognizable surface reconstruction and, as the most energetically favourable Au surface, being the easiest metallic substrate to prepare.

- The Kelvin V_{FM} signal remains constant upon varying the tip-sample distance z_{ts} , so the tip can be used for KPFM experiments.
- The Kelvin V_{FM} signal is not constant upon varying the tip-sample distance z_{ts} and the tip must be prepared again.

5.4 Use of Atom-Tracking System

Several of the procedures described in the previous sections can be sensitive to thermal drift in Z-direction:

- For recording the transfer function of the experimental system, the distance feedback loop must be disabled to avoid variations of the tip-sample distance z_{ts} . However, if the thermal drift is significant, the transfer function can be distorted.
- The amplitude calibration procedure relies on trustworthy z_{p} data. The larger the thermal drift, the more imprecise is the calibration of the response S of the cantilever.
- The reason for performing distance-dependent measurements is to study the variation of the V_{FM} signal with the tip-sample distance z_{ts} . However, if the z_{p} data (from which the z_{ts} can be estimated) is affected by thermal drift, the result can be distorted.

In order to minimize the thermal drift in Z-direction and hence, its influence in the all the procedures previously described, it is recommended to use the atom-tracking system to minimize the thermal drift. The working principles and implementation of the atom-tracking system are explained in section 3.4.

5.5 Summary

In this chapter, I have explained the parameters and settings necessary to check before and during a quantitative KPFM experiment. One of the crucial parts is preparing metal-coated cantilevers free of localized point charges. For this procedure, the following steps must be followed:

- The transfer function of the PLL should be known before any FM-KPFM experiment.

- Prepare the metallic substrate. The preparation can be checked by STM measurements.
- Approach the metal-coated AFM tip to the sample and start recording images. The atom-tracking system can be used to correct the thermal drift in Z-direction from the very beginning of the experiment.
- Find a flat area on the surface to perform the amplitude calibration. After that, adjust the amplitude setpoint (in the MATRIX software, *A-vib*) to set the desired oscillation amplitude A .
- Record the transfer function of the whole experimental system and select the KPFM parameters and measurements settings (electrostatic excitation frequency ν_{es} , time per pixel,...).
- Perform the distance-dependent measurements $V_{\text{FM}}(z_{\text{ts}})$. During these measurements, record the static deflection q_s .
- If the V_{FM} signal is constant when varying the tip-sample distance, the tip is ready to be used in a quantitative KPFM experiment. However, if the V_{FM} signal is not constant, sputter the tip again and repeat the test on the metallic substrate.
- Perform the KPFM experiment on the sample intended to be measured.
- After the KPFM experiment, repeat the test on the metallic substrate. By this repetition of the test, it is possible to check if the tip gets contaminated during the previous experiment. If the V_{FM} signal remains constant when varying the tip-sample distance, the KPFM data is reliable.

KPFM Experiments: Preparation of Metal-Coated Silicon AFM Tips

Contents

6.1	Introduction	49
6.2	Preparation of the Metallic Substrate Au(111)	50
6.3	KPFM Feedback: Error Channel and Noise	56
6.4	Preparation of Metal-Coated Silicon AFM Tips	69
6.5	Stability of Au-Coated Silicon AFM Tips	102
6.6	Summary	109

6.1 Introduction

As explained in the previous chapter, performing quantitative KPFM experiments requires very specific steps for preparation. In this chapter, the preparation of the metallic substrate to test the metal coated tips is explained, including all problems encountered and details to consider and take into account. After that, the KPFM operation is discussed, *i.e.*, the information that is shown in the KPFM error signal (real part of the first spectral component of the frequency shift $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{es})]$) and the V_{FM} signal. Finally, the preparation of two Au-coated silicon tips is explained.

Distance-dependent measurements are a crucial part of the experimental results explained in this chapter. However, the MATRIX software does not record the phase shift ϕ channel for distance or voltage-dependent curves. Because of this, the phase shift ϕ distance-dependent curves are not presented. The phase shift ϕ images recorded before the distance-dependent curves are presented and commented: I worked under the assumption that if the PLL kept the phase shift ϕ constant at $-\pi/2$ in the images, it also kept it constant during the distance-dependent curves.

All physical quantities recorded during the distance-dependent curves require some unit conversion and/or offset corrections. Furthermore, due to technical problems, the quantities static deflection q_s and the second spectral component $\mathcal{F} [\Delta\nu_e] (2\nu_{es})$ could not be recorded in all experiments. A detailed description of the unit conver-

sion and offset corrections can be found in appendix B, as well as the implications of not recording the aforementioned quantities.

The preparation of the metal-coated tips by ion sputtering was only done for two tips. These tips are referred to as *first* and *second* tips. Two other tips could be used for KPFM experiments without being prepared by sputtering: these tips are referred to as *third* and *fourth* tips.

Hagen *et al.* [67] defined the *absolute* tip-sample distance as:

$$z_{ts} = z_0 + z_p + q \quad (6.1)$$

where z_0 the tip-sample distance when the cantilever and z-piezo position are at rest and at 0 nm, respectively. This quantity is unknown. Because of this, the distance-dependent curves in this thesis are plotted as a function of the z-piezo position z_p . For those experiments for which the static deflection q_s was recorded, the distance-dependent curves are plotted as a function of the center position z_c , neglecting the distance z_0 .

6.2 Preparation of the Metallic Substrate Au(111)

As explained in section 5.3.3, a metallic substrate is needed to check the preparation procedure of the metal-coated AFM tips. Having a metallic substrate totally free of localized point charges is difficult, since even in the UHV chamber, some species can adsorb on the sample surface. However, important levels of contamination (which can be charged), can be avoided. The best option is preparing a metal with a well-known surface reconstruction and check the surface by STM imaging. If the amount of contamination is too large, it could prevent the surface reconstruction to happen as expected. If not, it can just be identified in the images. Furthermore, it is convenient to ensure the reproducibility of the preparation.

The preparation of metallic single crystals consists of consecutive sputtering and annealing cycles. The sputtering procedure consists of bombarding the sample surface with Ar^+ ions. The impacting ions are intended to remove the adsorbate species and other contaminations from the single crystal surface. However, the ions do not only remove the contamination on the sample surface, but Au atoms too, resulting in a rough surface with holes and small terraces. The purpose of the annealing procedure is getting flat terraces: the heat transferred to the sample increases the mobility of the atoms on the surface so they rearrange, filling the craters on the surface and forming flat terraces.

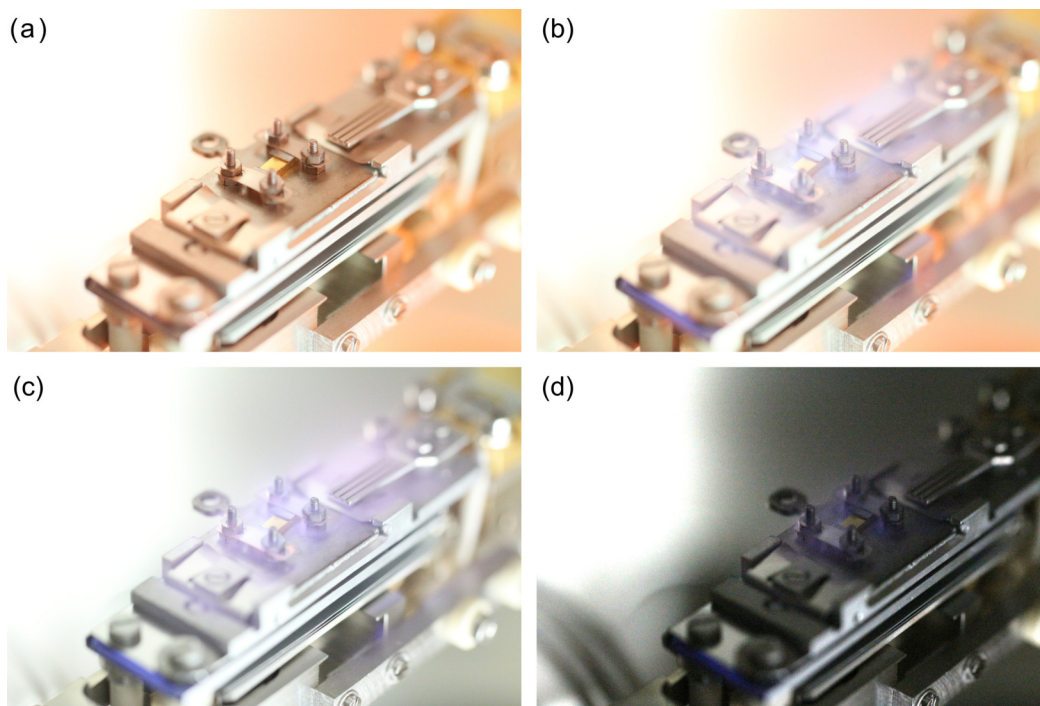


Figure 6.1.: Long-time exposure photographs of the Au(111) single crystal during the sputtering procedure. In the four images, the Au(111) sample stripe appears mounted in the sample holder and placed in the heating stage of the manipulator, in the preparation chamber. The exposure time of the photographs is 30 seconds. Image (a) shows the sample before the sputtering procedure started. The orange-like light is produced by the ion gauge used to measure the partial pressure inside the chamber. In image (b), violet sparks can be seen around the sample holder. These sparks are due to the impact of the ions on the heating stage. The ion gauge was switched off before taking image (c). The orange-like light has disappeared and it is easier to recognize the area where the sparks concentrate, so the region of the heating stage which the ions hit. Image (d) was taken after adjusting the size of the ion beam, so the Ar^+ ions mainly impact on the Au(111) sample.

An Au(111) single crystal (MaTeck GmbH, Jülich, Germany) was chosen as metallic substrate. For the sputtering procedure, the sputter gun ISE 5 from Scienta Omicron (Taunusstein, Germany) was used. The size of the ion beam can be adjusted by varying the parameter *focus* in the sputter gun ISE 5 controller. The sputtering procedure was carried out with an Ar partial pressure of $3 \cdot 10^{-6}$ mbar and 1.0 keV energy for a time period from 10 to 30 minutes¹. I decided to take long-time exposure photographs (30 seconds duration) of the sample Au(111) while sputtering. This procedure might give us information about the area where the Ar^+ ions impact for the *focus* and energy chosen. Figure 6.1 shows the procedure followed. Image (a) shows the Au(111) in the heating stage of the manipulator. This photograph was taken before starting the sputtering procedure. The orange-like background light is due to the ion gauge used to measure the partial pressure inside the chamber. In image (b), the sputtering procedure had already started. The area of the Au(111) sample appears covered by violet sparks, caused by the impacts of the Ar^+ ions. I did not know if sputtering an area larger than the sample surface could lead to

¹In order to have as large terraces as possible, the duration of the last sputtering cycle can be shorter than the previous ones.

contamination of the sample itself with clusters of the surrounding materials. For this reason, I decided to regulate the size of the ion beam just to sputter the sample surface. Before taking image (c), the ion gauge was switched off, so it is easier to recognize the area where the violet sparks extend. For taking image (d), the size of the ion beam was adjusted to sputter mainly the area of the Au(111) sample. In order to check the reproducibility of the sputtering process, I measured the drain current, which results from the impact of the Ar^+ ions in the heating stage of the manipulator. Every time I sputtered the Au(111) sample using the same parameters, I expected the drain current to be in the same range: in this case, the drain current was always between 2.8 and 3.2 μA .

For the annealing procedure, the sample was heated up to 860 K for a time period from 30 to 60 minutes². The temperature mentioned is approximate: the Omicron VT XA does not allow to measure the temperature directly at the sample, but in the heating stage. The manufacturer provided us with a calibration curve relating the temperature measured in the heating stage to the temperature measured on the sample. This calibration curve is included in appendix A. Then, by measuring the temperature at the heating stage, it is possible to estimate the temperature at the sample.

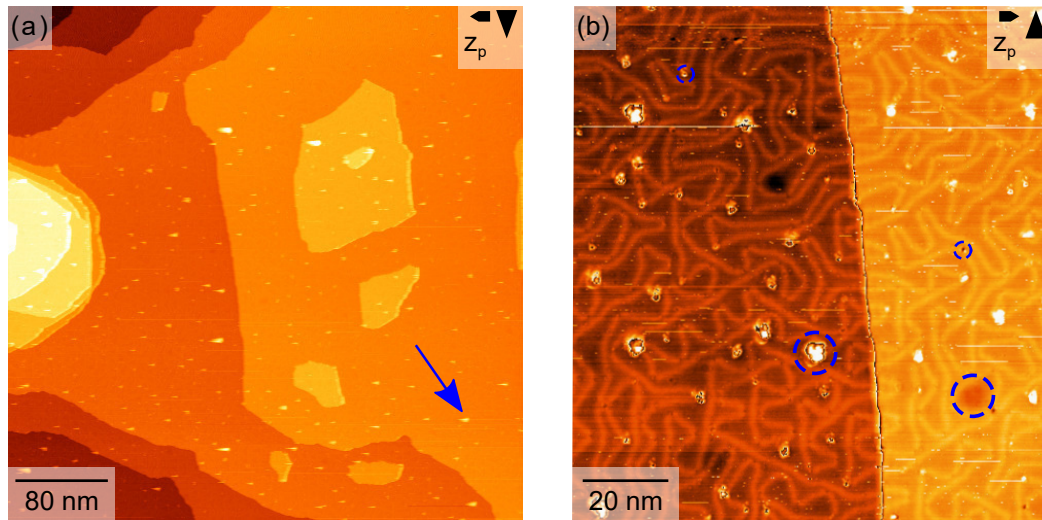


Figure 6.2.: STM images on a Au(111) sample ($V_{\text{bias}} = -100$ mV, $I_T = 100$ pA). The sample was prepared by several cycles of Ar^+ sputtering at 1.0 keV and annealing at 860 K. Image (a) is a large-scale image (440 nm x 440 nm). The blue arrow indicates the contamination present on the surface. Image (b) is a small-scale drift-corrected image (120 nm x 120 nm). A double colour scale is used to display both terraces with no information loss.

In order to check the preparation of the Au(111) sample, STM measurements were performed. The STM tips were mechanically etched from a platinum/iridium wire (ChemPUR, Karlsruhe, Germany). The voltage V_{bias} is applied to the tip. Figure 6.2

²In order to have as large terraces as possible and reduce the preparation time, the duration of the last annealing cycle can be larger than the previous ones.

shows STM images after preparing the Au(111) single crystal. Image (a) is a large-scale topography which shows large terraces. However, the surface is not clean, and contaminants can be observed (blue arrow). Image (b) is a small-scale topography. On both terraces, many clusters of contamination can be observed. Adsorbates of different size are present on both terraces and appear as protrusions (lower terrace, left part of the image) or depressions (upper terrace, right part of the image) as indicated with dashed blue circles. The herringbone reconstruction is not formed as expected: it seems to be pinned in the contaminants, no zig-zag pattern is formed and the ridges do not form pairs which separates the fcc and hcp regions (see description of the herringbone reconstruction reported in previous works in section 4.1). At this point it is important to repeat that STM topographies do not show the relative height of the features in the sample surface, but a convolution of height and local density of states. Thus, the apparent height of these unknown adsorbates it does not necessarily correlate with their size, but can be due to their electronic properties: the contaminants which appear as depressions can be less conductive than the surrounding Au atoms, so the distance feedback loop brings the STM tip closer to the sample, and these contaminants appear as depressions. Repeated sputtering and annealing cycles did not result in a cleaner sample surface.

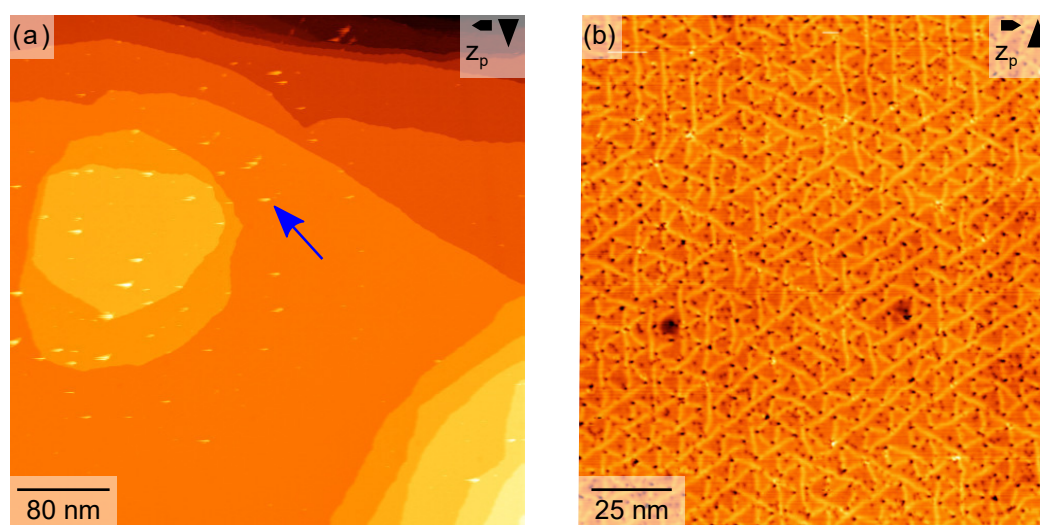


Figure 6.3.: STM images on a Au(111) sample after the new preparation procedure ($V_{\text{bias}} = -100$ mV, $I_T = 100$ pA). The sample was re-prepared by one cycle of Ar^+ by sputtering at 1.0 keV and annealing at 990 K. Image (a) is a large-scale image (440 nm x 440 nm). The blue arrow indicates the contamination present in the surface. Image (b) is a small-scale drift-corrected image (160 nm x 160 nm).

At this point, I assumed a contamination source is present close to the sample or even the sample itself might be contaminated. The results of the preparation suggest the presence of contaminants during the annealing procedure prevents the Au atoms to form flat terraces and the herringbone reconstruction as expected. I worked under the hypothesis that, even if the sputtering cycle is successful and the contamination

is removed, a possible contamination of the single crystal during fabrication was the origin of the problem: when annealing the sample, internal contaminations might be brought to the surface. In order to test this possibility, I repeated the preparation procedure, but increasing the heating temperature to 990 K (130 K higher than in previous annealing cycles). Figure 6.3 shows STM images of the Au(111) single crystal after the new preparation procedure. Image (a) is a large-scale topography. The sample surface still exhibits large terraces and the presence of contaminants (indicated by the blue arrow). Image (b) is a small-scale drift-corrected topography. The sample surface presents a larger amount of contaminations than after the previous preparation procedures. The herringbone reconstruction is even less evident than before, forming a triangular-like pattern in whose vertices the contaminants are found. It is possible to conclude that the contamination is related with heating up the sample, and this procedure is not suitable to clean this single crystal.

A new Au(111) single crystal was purchased from Surface Preparation Lab (Zandaam, The Netherlands). In order to prevent all possible contamination sources, I tested the quality of the Ar gas. Using the mass spectrometer, I measured the partial pressures of argon (Ar), oxygen (O₂), water (H₂O), nitrogen (N₂) and carbon monoxide (CO). I expect that the gas line connected to the sputter gun only contains Ar (the gas line was filled with an Ar bottle with a purity of 99.999%). Opening the valve to the chamber should imply a sudden increase in the partial pressure of Ar detected by the mass spectrometer. Sudden increases of O₂, H₂O and N₂ implies a leak in the gas line. Sudden increases of CO implies a contamination of the Ar bottle. Before starting the procedure, the base pressured measured by the ion gauge of the preparation chamber was $3 \cdot 10^{-12}$ mbar. The valve that connects the gas line to the preparation chamber was opened four times: until the partial pressure measured by the ion gauge was $1 \cdot 10^{-11}$ mbar, $5 \cdot 10^{-11}$ mbar, $1 \cdot 10^{-10}$ mbar and $2 \cdot 10^{-10}$ mbar. Only sudden increases of the Ar pressure were detected by the mass spectrometer. The H₂O pressure increased slowly. I assumed this increase of H₂O partial pressure measured was due to release of the adsorbed H₂O in the internal walls of the preparation chamber by scattering with the Ar atoms. I concluded that the Ar gas was clean and there was not possibility of it being a source of contamination.

I checked the area of impact of the Ar⁺ ions for the new sample too. Long-time exposure photographs (1 minute duration) were taken while sputtering the new sample. Figure 6.4 (a) shows the new Au(111) single crystal mounted on a sample. This photograph was taken during the sputtering procedure and the ion gauge was switched on, so the orange-like background like is present and hinders to distinguish the area where the violet sparks are. The photograph shown in (b) was taken after switching off the ion gauge, confirming that the violet sparks are mainly around the

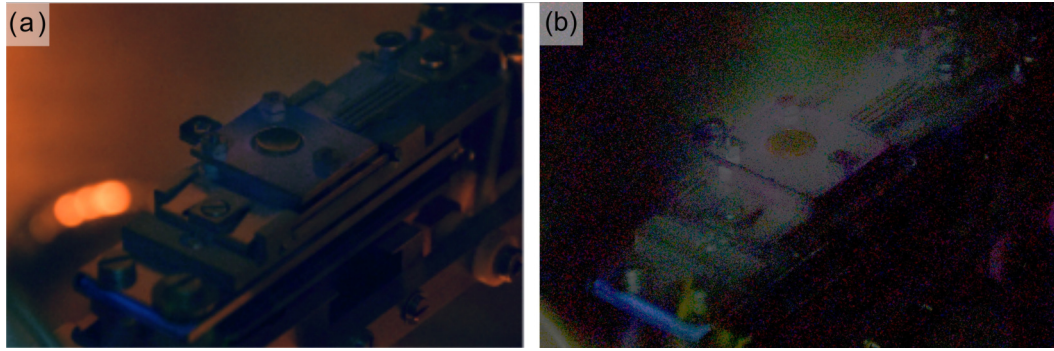


Figure 6.4.: Long-time exposure photographs of the new Au(111) single crystal. The exposure time of the photographs is 1 minute. Image (a) show the violet sparks after adjusting the size of the ion beam, so the Ar^+ ions mainly impact on the Au(111) sample surface. The orange-like light is originating from the ion gauge used to measure the partial pressure in the chamber. In image (b), the ion gauge was switched off, so the region the ions impact can be seen with higher accuracy.

Au(111) surface. The drain current measured for these parameters was within the range 0.9 to 1.3 μA .

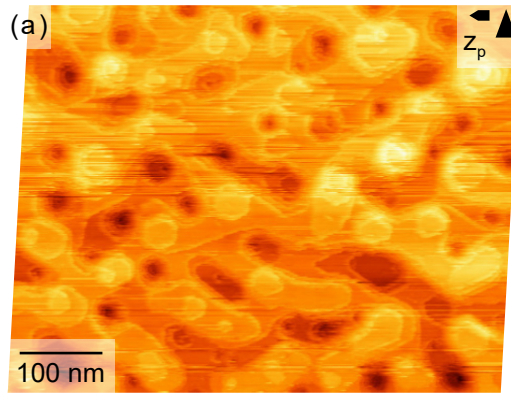


Figure 6.5.: STM images on Au(111) immediately after sputtering the sample surface with Ar^+ ions at 1.0 keV ($V_{\text{bias}} = -100$ mV, $I_T = 100$ pA).

In order to check that the ions hit the Au(111) sample surface, STM images were recorded right after sputtering, without annealing the sample. Figure 6.5 show a small-scale drift-corrected topography. The surface exhibits many protrusions, alike to craters, which I assume to be the result of the ion impacts. No contamination is visible. Thus, I concluded the sputtering process was successful.

Finally, the sample was prepared by repeated cycles of Ar^+ sputtering and annealing. The sputtering procedures were carried out with an Ar partial pressure of $3 \cdot 10^{-6}$ mbar and an energy of 1.0 keV for a time period from 10 to 30 minutes. During the annealing procedures, the temperature of the sample was risen to 730 K during 30 to 60 minutes. In order to check the success of the preparation, STM images of the Au(111) surface were recorded, which are shown in figure 6.6. The large-scale topography give in (a) shows large terraces and no obvious contamination.

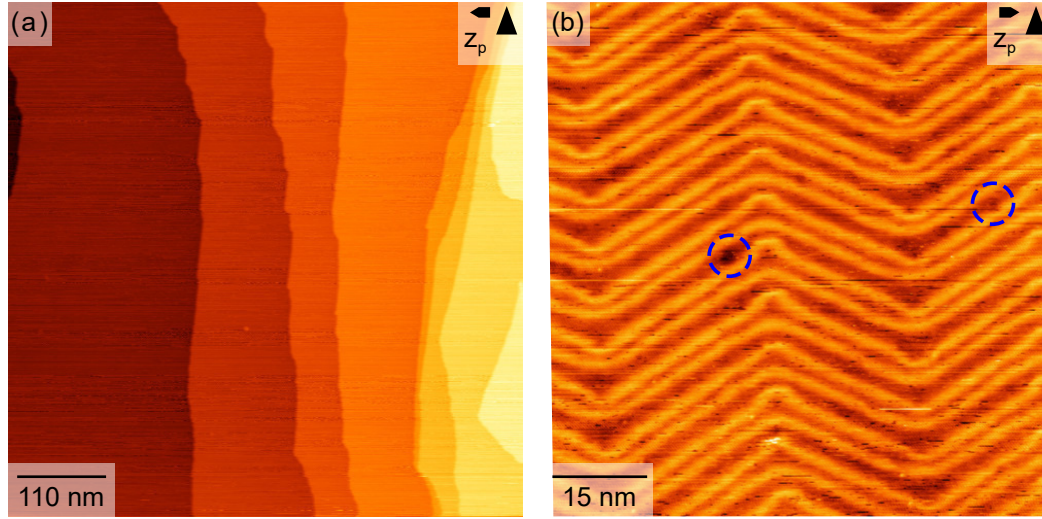


Figure 6.6.: STM images taken on a new Au(111) single crystal ($V_{\text{bias}} = -100$ mV, $I_T = 100$ pA). The sample was prepared by several cycles of Ar^+ sputtering at 1.0 keV and annealing at 730 K. Image (a) shows a large-scale image (650 nm x 650 nm). Image (b) is a small-scale drift-corrected image (80 nm x 80 nm).

The small-scale drift-corrected topography displayed in (b) shows the herringbone reconstruction has been formed as expected, with the correct zig-zag pattern and the ridges organized in pairs. The blue dashed circles show some adsorbates which do not pin or disturb the surface reconstruction. I concluded that the preparation procedure was successful and the new Au(111) single crystal can be used as a metallic substrate to check the contamination state of the metal-coated tips.

6.3 KPFM Feedback: Error Channel and Noise

As explained in section 2.4.3, closed-loop FM-KPFM relies on the nullification of the first spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ by applying the proper bias voltage V_{bias} , which corresponds to the V_{FM} value. In order to do this, first it is necessary to use a lock-in amplifier is used to detect this spectral component and later a feedback loop to nullify it. However, these two procedures add noise to the signal. As a result, the images/distance-dependent curves obtained in an experiment are not nullified (*i.e.*, they do not show a constant value 0 Hz), but present noise and sometimes periodical vibrations. In this section, I will discuss to which extent it is valid to consider nullified this signal. Furthermore, I will discuss whether the V_{bias} can be considered as the V_{FM} signal.

As already mentioned, for closed-loop FM-KPFM consists in nullifying the first spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$. However, due to the detection procedure, it is not possible to feed the KPFM feedback loop directly with this signal. As already explained in section 3.5, the HF2 lock-in amplifier is connected to the

MATRIX CU in order to apply an AC voltage, with magnitude V_{es} and frequency ν_{es} ³. In order to detect the two spectral components of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ and $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$, the frequency shift $\Delta\nu_e$ signal from the MATRIX CU is connected to the HF2 lock-in amplifier. There, I use two demodulators of the lock-in amplifier to detect the spectral components at the frequencies ν_{es} and $2\nu_{\text{es}}$. As already explained in section 3.3, these demodulators provide the magnitude A and phase shift ϕ of the signal with respect to an internal reference. The magnitude is the absolute value of the $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ signal and the phase shift defines the sign of the signal⁴. The magnitude can only be positive or zero. However, due to the noise level, the minimum magnitude detected by the lock-in amplifier will never be zero. For this reason, I have to feed the KPFM feedback loop with the real part of this signal, given by:

$$X = A \cdot \cos(\phi) \quad (6.2)$$

This signal can be positive, zero or negative. I feed the KPFM feedback loop with this signal. For this reason, I use this signal as error channel and not the magnitude. From now on, when I discuss the KPFM feedback and present V_{FM} data, I will present the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ as the error channel and not the magnitude $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$.

PPP-NCHAu cantilevers from NanoWorld (Neuchatel, Switzerland) were used in all experiments. Figure 6.7 shows the FM-AFM and FM-KPFM measurements on the new Au(111) sample: (a) presents the topography z_p ; (b) corresponds to the Kelvin V_{FM} ; (c) shows the frequency shift $\Delta\nu_e$; (d) presents the real part of the first spectral component of the frequency shift $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$, (e) corresponds the phase shift ϕ and (f) shows the magnitude of the second spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. All the values of the phase image (e) are around -90° (setpoint used for the PLL in all FM-AFM experiments shown in this thesis), which is a proof of the good performance of the PLL. Furthermore, the frequency shift $\Delta\nu_e$ image (c) shows all values within a small range around -18.4 Hz, the setpoint for the *distance feedback loop*. The topography z_p (image (a)) shows three different terraces and the two steps edges between them. The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ (image (d)) shows corrugation in the areas of the step edges similar to their shape in the topography (a), but it is flat in the terraces. Image (b) corresponds to the bias voltage applied to the tip, V_{bias} . As the error signal (image (b)) seems nullified in the terraces, but not on the step edges, the V_{bias} image is reliable on the terraces, but not in the step edges. The values of this V_{bias} signal in the areas corresponding to the terraces are very homogeneous. However, these values differ with the ones of the areas that correspond to the step edges. Furthermore, periodic oscillation with

³In all the measurements presented in this work, the electrostatic excitation frequency ν_{es} used is always 988 Hz.

⁴As labelled in [85], I refer to the real part of a signal as X and to the imaginary part as Y . The magnitude A and the phase shift ϕ of the signal is given by $A = \sqrt{X^2 + Y^2}$ and $\phi = \arctan(Y/X)$.

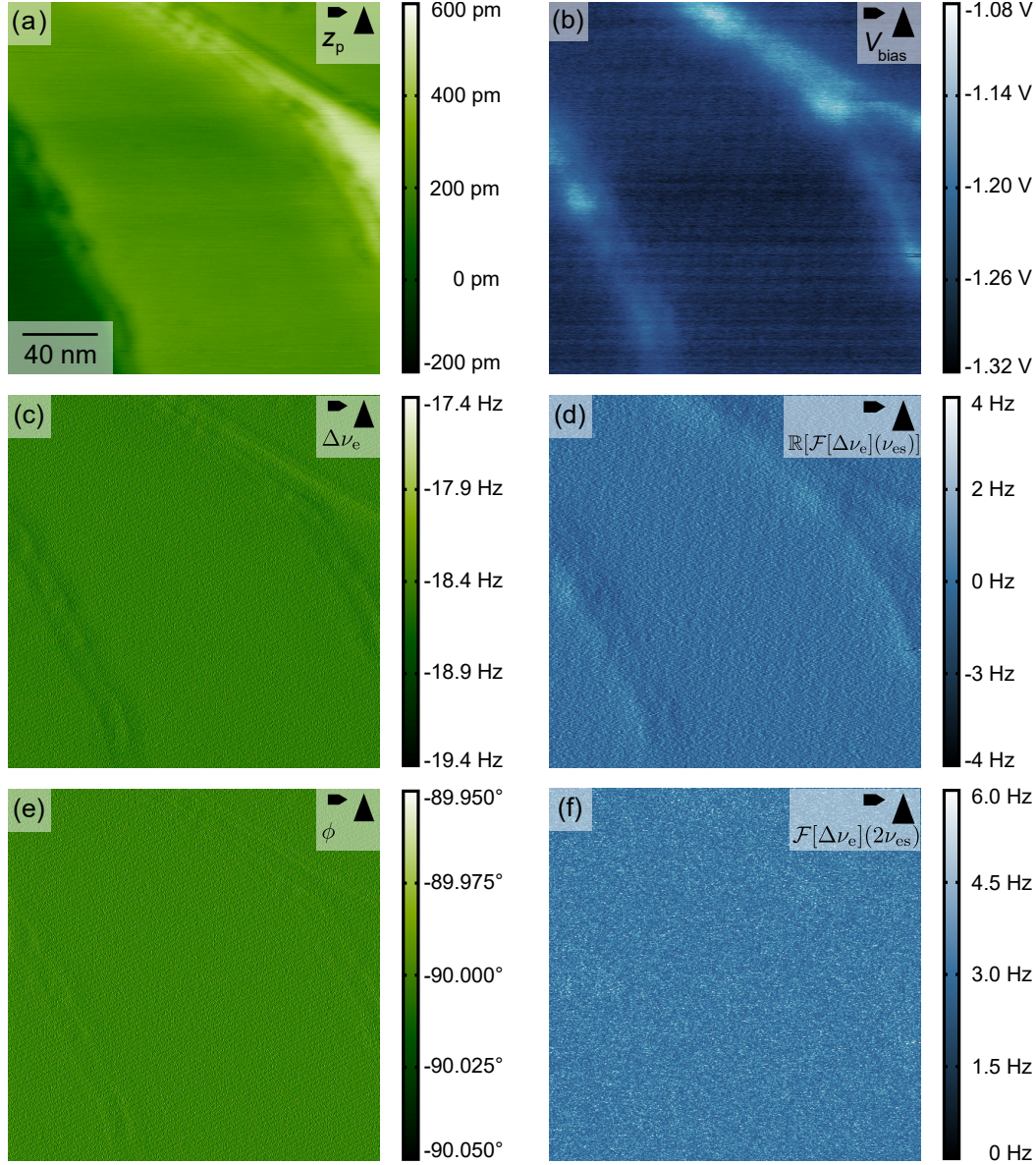


Figure 6.7.: FM-AFM and FM-KPFM images on Au(111). Images (a), (c) and (e) are the FM-AFM channels topography z_p , frequency shift $\Delta\nu_e$ and phase shift ϕ , respectively. Images (b), (d) and (f) are the FM-KPFM channels V_{bias} , the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ and the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$, respectively.

the same orientation and periodicity can be observed in both images (b) and (d). Additionally, an oscillation in the same direction as in the V_{bias} image (b) is seen. The magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$ (image (f)) shows no corrugation.

I consider that the oscillations shown in figure 6.7 (b) and (d) are due to the chosen gains for the KPFM feedback loop. Ideally, it should be possible to choose the KPFM feedback loop gains so the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ signal is nullified and, at the same time, no periodic oscillations are introduced in this signal or in the V_{FM} signal (the output of the KPFM feedback loop). However, in

our experience, sometimes it is extremely difficult to find the correct loop gains⁵. Finally, I had to accept that in some experiments it is just not possible to find the totally correct loop gains for the KPFM feedback. This procedure is a trade off between keeping the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ as close to 0 Hz as possible and not introducing periodic oscillations.

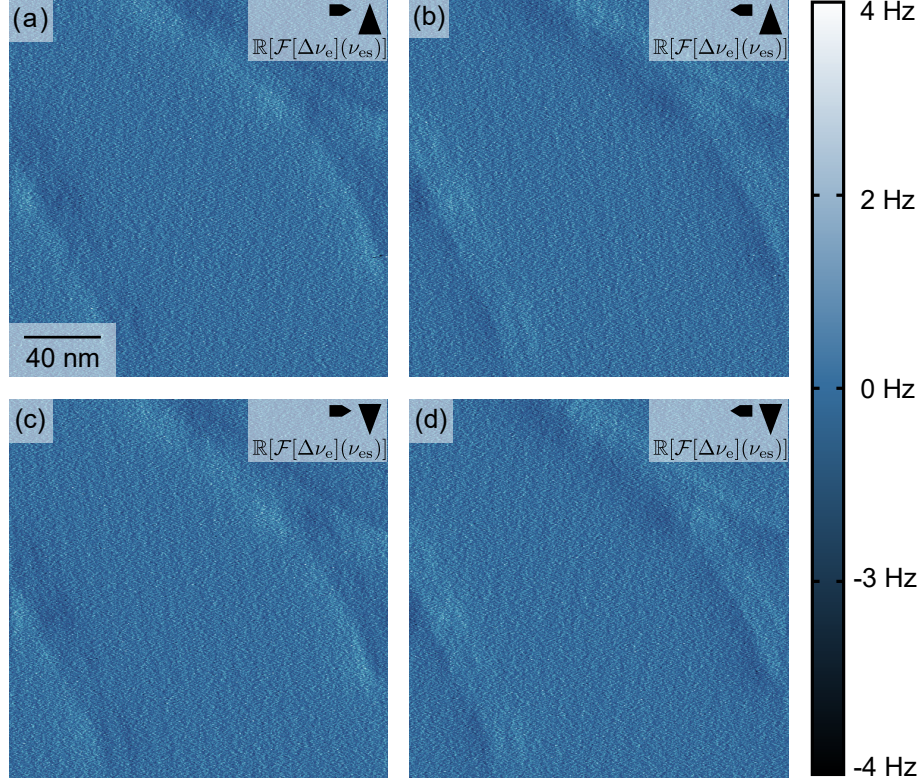


Figure 6.8.: Comparison of all four (Up and Down, Trace and Retrace) real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ images corresponding to the measurement shown in figure 6.7.

Is it possible to filter out this oscillation with no loss of information? First of all, the oscillation must be identified as a non-desired effect of the feedback loop. If the oscillation is due to the experimental system and/or measurement parameters (mechanical vibrations induced by the vacuum pumps, oscillation caused by the gains of the feedback loops,...), the orientation of the oscillation in the image should vary depending on the scanning directions of the image. If it does not vary, the oscillation will be due to the tip-sample interaction. This would be an indication of periodical molecular structures which exhibit a periodical signal. Figure 6.8 shows four images of the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$. The orientation of the oscillation is different depending on the image: for "Up" images ((a) and (b)), the orientation of the oscillation is opposite with respect to each other; "Down" images ((c) and (d)) are also opposite with respect to each other. The same

⁵In some cases, I have tried to find these correct loop gains (so the KPFM feedback loop nullifies the $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ signal but it does not introduce periodic oscillations in any of the $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ or V_{FM} signals) by trial and error for almost one hour and it was not possible.

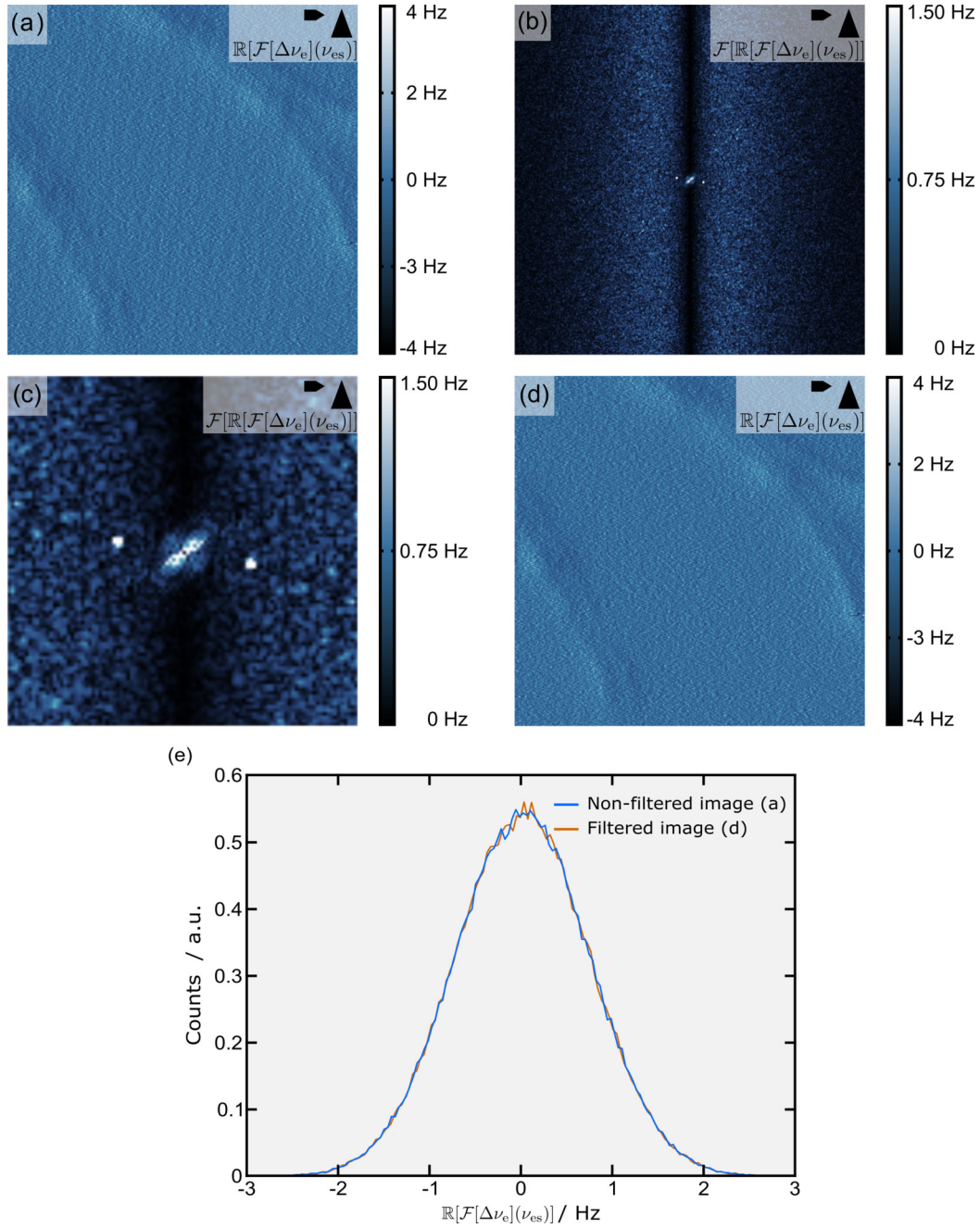


Figure 6.9.: Comparison of the non-filtered and filtered real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ images. Image (a) shows the non-filtered $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image. Image (b) is the FFT of image (a). Image (c) is a zoom around the center of image (b). Image (d) shows the filtered image. Plot (e) shows the histograms of the images (a) and (d).

observation applies for the "Trace" ((a) and (c)) and "Retrace" images ((b) and (d)). Furthermore, changing the scan speed during the experiment would change the orientation of the oscillation in both "Trace" and "Retrace" images, but the relative orientation between "Up", "Down", "Trace" and "Retrace" images would continue to be opposite. Since I have confirmed that the periodic oscillations are not due to any feature of the sample surface, I can proceed to filter it. For this purpose, I used the tool of Gwyddion [109] named as *2D FFT Filtering*. This tool performs and

displays an FFT of the image selected. The different contributions to the image can be included or discarded in the new filtered image. During the process, two new images are displayed: the first image is composed by the selected contributions and the second image with the excluded contributions. By a trial and error procedure, it is possible to filter out these undesired periodic oscillations.

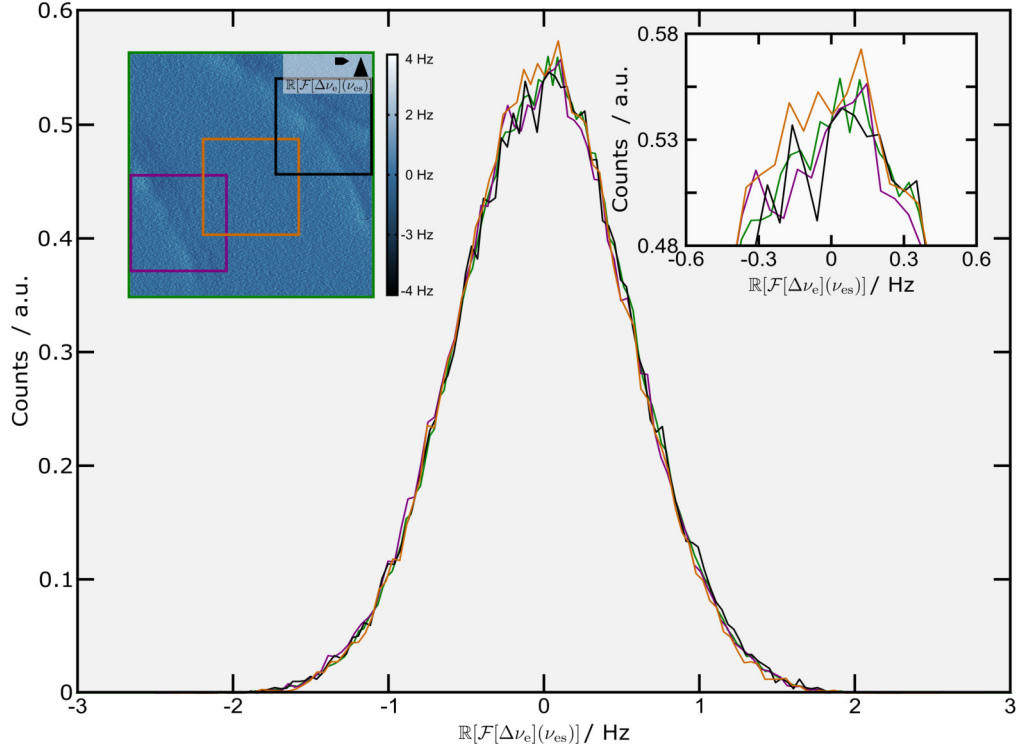


Figure 6.10.: Histograms of the filtered real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ images. Four histograms are compared: one of the whole image, two corresponding to two areas around the step edges and one in the terrace of the middle. The image is shown by an inset placed on the left of the plot. Each square indicates the area corresponding one histogram. The colour of the squares relate each area with its corresponding histogram. The inset on the right is a zoom around the peaks of the histograms.

Figure 6.9 presents the comparison of the non-filtered and filtered images of the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$. Image (a) is the same non-filtered image as the one shown in figures 6.7 (d) and 6.8 (a). Image (b) is the FFT of image (a). The zoom around the central region of image (b) is shown in (c). Image (d) corresponds to the filtered image of the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$. Plot (e) shows the histograms of the whole images shown in (a) and (d), in order to compare the non-filtered and filtered images. In the center of the FFT image shown in (b), three important features appear: a central one with clover shape exactly in the center of the image and two points, which are symmetric with respect to the center. A closer look to this features (image (c)) confirms this. In the filtered $|\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]|$ image (d), the oscillation is no longer present, but corrugation in the regions corresponding to the step edges is still visible. The histograms of both images presented in (e) show that they overlap for most

values: they only differ slightly around 0 Hz. This fact confirms that this channel can be filtered with no loss of information: the features due to the tip-sample interaction are still present, but there are not the periodic oscillations.

There are still some open questions about the features which appear in the filtered image. According to the theory exposed in section 2.4.3, in order to get the correct V_{FM} signal, the KPFM feedback loop must nullify the first spectral component $[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$. Thus, any image corresponding to this channel should show no corrugation: the value of all points in the image should be 0 Hz. However, as already mentioned, it is possible to observe corrugation in the areas corresponding to the step edges and noise in the whole image. In order to study the relevance of the corrugation around the step edges, I have made histograms of the whole image and of specific areas within the same image. These histograms are shown in figure 6.10. Furthermore, the figure includes two insets: the inset on the left corresponds to the filtered image. Squares indicate the areas of which the histograms were made of; the inset on the right is a zoom around the peak of the histograms. The histogram in green colour corresponds to the whole image. The histograms in purple and black colour corresponds to the areas around the step edges on the lower left and upper right areas, respectively. The histogram in orange colour correspond to the terrace in the middle of the image. It is possible to observe that the four histograms are quite similar: they overlap for most of their range, specifically for $|\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]| \lesssim 0.5$ Hz. The main difference among the histograms is around 0 Hz: all histograms are different. However, the histograms of the areas around the step edges and of the whole image are more similar between each other than with respect to the other histogram: the one in the terrace of the center of the image (these similarities and differences can be observed clearly in the onset on the right). Since these three histograms contain the areas around the step edges (the two histograms around each step edge and the one of the whole image which contains both step edges), it makes perfect sense that they are more similar between each other. In this image, the histogram of the area in the terrace in the middle is the more reliable and should be considered as the reference: no corrugation can be found within the area marked by the orange square, only the noise which is present in the whole image. Thus, the other three histograms differ from the expected nullified signal. This fact indicates that the signal result of the KPFM feedback loop, the V_{FM} image, is not fully trustworthy in the step edges and cannot be used for quantitative purposes. However, since the differences between the histograms are distributed very close to 0 Hz, the V_{FM} value in these areas, although inexact, does not differ so much in relative terms from the right value.

Once the corrugation around the step edges has been discussed, I need to focus in the noise present in the whole image. As discussed before, in agreement with the theory on which closed-loop FM-KPFM is based, I expected the real part of the first spectral

component $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{es})]$ image to be totally nullified. However, it is possible to observe noise in the whole image. According to our experience, it is impossible to nullify totally the real part of the first spectral component $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{es})]$, since the minimum of the signal it is possible to detect is limited by the level of noise. Thus, it is necessary to assume that the best performance only means minimizing the $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{es})]$ signal.

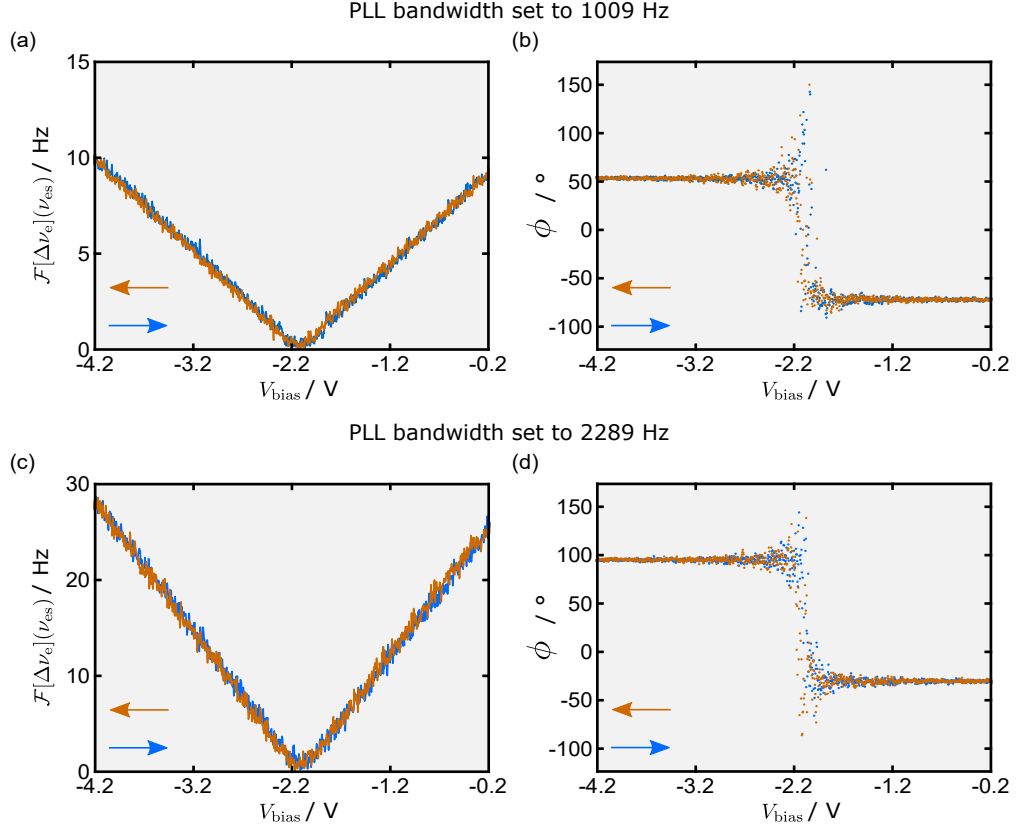


Figure 6.11.: First spectral component $\mathcal{F} [\Delta\nu_e] (\nu_{es})$ versus bias voltage V_{bias} . Plots (a) and (b) show the first spectral component $\mathcal{F} [\Delta\nu_e] (\nu_{es})$ for the PLL bandwidth set to 1009 Hz, while plots (c) and (d) correspond to the same signal for the PLL bandwidth set to 2289 Hz. Plots on the left ((a) and (c)) show the magnitude of the signal, while plots on the right ((b) and (d)) correspond to the phase shift. For recording these curves, the electrostatic excitation amplitude V_{es} and frequency ν_{es} were set to 500 mV and 988 Hz, respectively. The blue and orange arrows relate the sweep voltage direction with each curve.

The source of the noise present in the $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{es})]$ signal is the basic system used in FM-AFM experiments (thermal noise of the cantilever, PSPD, PLL). This noise is included in the $\Delta\nu_e$ signal. The final level of noise transferred in the $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{es})]$ depends on the lock-in detection. The noise distribution along the frequency spectrum depends on the individual components of the basic system and the measurement parameters of these components⁶. Then, the contribution of this noise to the $\mathcal{F} [\Delta\nu_e] (\nu_{es})$ depends on the measurement parameters of the individual

⁶One of this components is, for example, the PLL. Figures 5.3 and 5.4 show the FFT of the $\Delta\nu_e$ signal for different electrostatic excitation frequencies ν_{es} and the two different bandwidths used for the PLL: 1009 and 2289 Hz. In figure 5.4 (for the PLL bandwidth set to 2289 Hz), the noise around 1.2

components (PLL bandwidth, time per pixel,...) and on the electrostatic excitation frequency ν_{es} chosen. Due to the nature of the lock-in detection itself: a lock-in amplifier does not detect a signal **at** a specific frequency, but **around** a specific frequency: this range is determined by the bandwidth of this lock-in detector (in the case of the HF2 lock-in amplifier, the bandwidth of the demodulator). The bandwidth of the demodulator and the effective time TC to detect a signal with a lock-in amplifier are inversely proportional: if it could be possible to measure a signal for an infinite time, the bandwidth would be zero and the measured signal would correspond only to the selected frequency. But the time of the experiment cannot be infinite. It is mandatory to choose a finite time for the detection and take into account experimental issues, as explained before in section 5.2.2. This fact implies having some noise in the measurements which can mask the possible not totally nullified first spectral component $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$. It is possible to study this signal and the noise present in it by recording $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ versus bias voltage V_{bias} curves. However, before I discuss these curves, it is important to remember that, as explained in section 2.4.3, the first spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ is the weighted averaged of the first spectral component of the force gradient $k_{\text{es,b}}$. According to the model I use to describe the tip-sample electrostatic interaction, the quantity is given by equation (2.31). This quantity has a linear dependence with the bias voltage V_{bias} and, for a specific value, the V_{FM} value, it becomes zero. Then, as it presents a linear dependence on voltage, for $V_{\text{bias}} < V_{\text{FM}}$, $k_{\text{es,b}}$ has opposite sign than for $V_{\text{bias}} > V_{\text{FM}}$. Hence, this change in sign also happens in the $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ signal. In the case of our experimental system, the first spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ is detected by a lock-in amplifier. For $V_{\text{bias}} = V_{\text{FM}}$, the lock-in amplifier should provide a magnitude equal to zero. Therefore, as the magnitude is zero, there is not oscillation and the lock-in amplifier cannot determine a correct phase shift. The already described change in sign for $V_{\text{bias}} < V_{\text{FM}}$ and $V_{\text{bias}} > V_{\text{FM}}$ would be reflected in the phase shift, showing two different constant values for each one of these segments. But all this previous description corresponds to an ideal situation without noise. That is not the situation I face in a real experiment, as the curves presented in figure 6.11 show.

Figure 6.11 show the magnitude and phase shift of the first spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ versus the bias voltage V_{bias} . The two curves presented in the figure were recorded using two different Omicron PLL bandwidths: 1009 Hz and 2289 Hz. For both curves, the electrostatic excitation amplitude V_{es} and frequency ν_{es} used were 500 mV and 988 Hz, respectively. Plots (a) and (b) show the magnitude and phase shift of the first spectral component $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ for the PLL bandwidth set to 1009 Hz, while plots (c) and (d) show the magnitude and phase shift of the $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ for the PLL bandwidth set to 2289 Hz. In the magnitude

kHz is larger than for the rest of frequencies, and also different for the same frequency in figure 5.3 (for the PLL bandwidth set to 1009 Hz).

plots ((a) and (c)), I can observe that for the same V_{bias} value, the magnitude of the signal for the PLL bandwidth set to 2289 Hz is larger than for 1009 Hz. This has already been shown in section 5.2.2 (figures 5.3 (e) and 5.4 (e)). In both plots 6.11 (a) and (c) I can observe that the magnitude depends on the bias voltage almost as predicted: it decrease linearly with increasing bias voltage V_{bias} until it reaches a minimum ($V_{\text{bias}} \simeq -2.1$ V), and then increases again. It is mirrored with respect to the minimum: in the following, I will refer as these two parts of the curve as left and right branches. I can clearly observed that both curves present some noise, in both linear branches and the minimum. Due to this noise, both minima are below the level of noise. Thus, the magnitude of the signal is smaller than the noise for a specific bias voltage range. This voltage range is the error of the V_{FM} signal which can be determined. In both plots (a) and (c), the two curves corresponding to the two sweep voltage directions seem to overlap. This observation matches the theoretical model, which exhibits no dependence on the sweep direction of the bias voltage V_{bias} . Respect to the phase shift, in both plots (b) and (d) I can see that, for both PLL bandwidths and both voltage sweep directions, for $V_{\text{bias}} = -4.2$ V, all both curves are constant. As the V_{bias} approaches ~ -2.1 V, the phase shift becomes more unstable. Plot (a) shows that for this region, as the V_{bias} increases, the phase shift jumps around 50° . The larger is V_{bias} , the larger are the jumps, until it starts jumping around a different value, $\sim -75^\circ$. As V_{bias} increases, the phase signal becomes more stable. For $V_{\text{bias}} = -0.2$ V, the phase shift is constant again. Then, from the observation of both quantities I can conclude that I cannot extract information of these two quantities in the minimum. Our interpretation is the following. While $|V_{\text{bias}} - V_{\text{FM}}|$ is large (this is, while the bias voltage V_{bias} is clearly different from the V_{FM} value), the lock-in amplifier operates properly and both magnitude and phase shift can be detected. However, when $|V_{\text{bias}} - V_{\text{FM}}|$ is small enough, the magnitude of the signal is smaller than the noise level. The lock-in amplifier cannot detect the signal, only noise. Hence, it cannot compute the phase shift of the signal. This leads to unstability of the phase shift around -2.1 V (the position of the minimum in figure 6.11 (a) and (c)). Thus, the level of noise around a specific frequency determines the error of the V_{FM} signal in a closed-loop FM-KPFM experiment: there is a range of bias voltage V_{bias} for which the magnitude detected by the lock-in amplifier is smaller or equal to the noise. Within this range, the phase shift jumps between two different values which provide two different signs for the real part X of the signal. Thus, this is the V_{bias} for which the KPFM feedback loop considers the error signal is nullified and assigns it as the V_{FM} value.

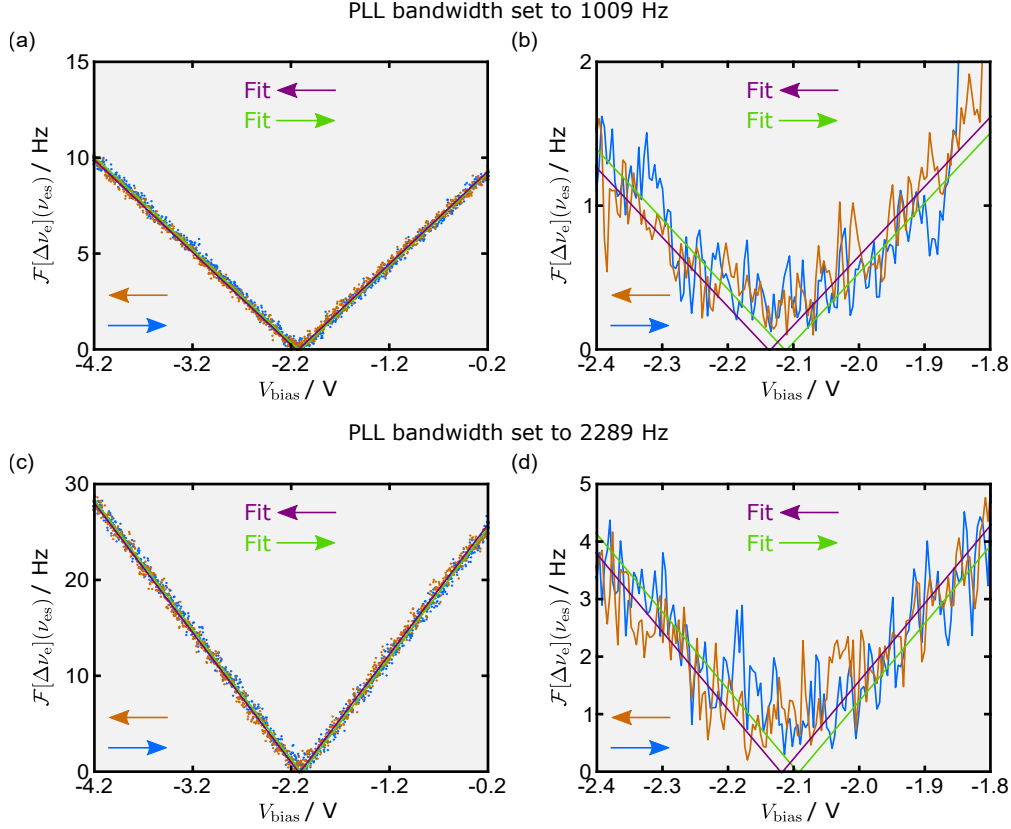


Figure 6.12.: Fitted magnitudes of the first spectral component $\mathcal{F}[\Delta\nu_e](\nu_{es})$ versus bias voltage V_{bias} . All plots show the magnitude signals and their corresponding fitted functions (absolute value of a linear function). The data fitted are the same curves presented in figure 6.11 (a) and (c). The upper two plots ((a) and (b)) correspond to the curve recorded for the PLL bandwidth set to 1009 Hz, while the lower two plots ((c) and (d)) correspond to the curve recorded for the PLL bandwidth set to 2289 Hz. The plots on the left ((a) and (c)) show the complete curves and their corresponding fits, while the plots on the right ((b) and (d)) correspond to the zoom around the minimum of each curve. The sweep voltage direction of each curve is indicated by the blue and orange arrows. The purple and green arrows relate the curve for each sweep voltage direction with the each linear fit. The values at which the fits cut the horizontal axis (the V_{FM} values) are summarized in table 6.1.

In order to get more insights, I decided to fit the four magnitude signals. The curves were fitted to the absolute value of a linear function:

$$\mathcal{F}[\Delta\nu_e](\nu_{es})(V_{\text{bias}}) = |a \cdot V_{\text{bias}} + b| \quad (6.3)$$

The magnitudes of this signal and their corresponding fits are presented in figure 6.12. Plots (a) and (b) correspond to the curves recorded with the PLL bandwidth set to 1009 Hz and their fitted functions, while plots (c) and (d) show the curves recorded with the PLL bandwidth set to 2289 Hz. Plots (b) and (d) are zoom around the minima of plots (a) and (c), respectively. The KPFM feedback loop does not make a voltage sweep in order to fit the data: it applies an specific bias voltage V_{bias} in order to minimize the KPFM error channel, which is the real part of the first spectral component of the $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$. Fitting the magnitudes and discussing the fit parameters is an illustrative method which provides important insight: it is useful

to see the noise distribution in the part of the branches of the curve and around the minimum and it shows the linear dependence of the bias voltage V_{bias} of each branch. Furthermore, I can determine a V_{FM} value for these specific cases. In plot (a) I can observe that the two fits (for positive and negative voltage sweep direction) present a good match with the experimental data, specially for the branches far away from the minima. In the zoom (plot (b)), it is possible to observe that the match is not good around both minima: as explained before, due to the noise the experimental data does not reach 0 Hz, while the fitted lines do. This observation supports what I have already stated before: the KPFM feedback cannot find with total accuracy the V_{bias} value which nullifies the real part of the first spectral component of the $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$. The KPFM feedback only minimizes it within a voltage range which, as already explained, is the error of the KPFM measurement. This error is of a few tens of millivolts. Respect to plots (c) and (d), I can observe that the noise is larger than in plots (a) and (b). This is clearly visible around the minimum in plot (d). For recording the curves, I used the electrostatic excitation frequency $\nu_{\text{es}} = 988$ Hz. Around this frequency, the noise is larger for the PLL bandwidth set to 1009 Hz than for 2289 Hz, as can be seen in figures 5.3 and 5.4. Larger noise might imply a larger error, but as it is possible to observe in figures 6.12 (b) and (d), the bandwidth does not play a crucial role.

Sweep voltage direction	V_{FM}	
	PLL BW set to 1009 Hz	PLL BW set to 2289 Hz
Negative	-2.136 ± 0.007	-2.118 ± 0.008
Positive	-2.111 ± 0.007	-2.093 ± 0.007

Table 6.1.: V_{FM} values obtained from fitting the magnitudes of the magnitude of the first spectral component $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ versus bias voltage V_{bias} , as shown in figure 6.12. BW stands for bandwidth.

The V_{FM} values resulting from the fit are summarized in table 6.1. The four values are very similar, all within a range of ~ 40 mV. However, none of the V_{FM} values are within the error range of the other values. Then, even when the experimental data seem to overlap, the results of fitting these data present important differences. Although I cannot discard a change in the tip apex, I attribute this difference to the noise. Thus, by direct observation of these data and from the fit, I know that the V_{FM} values obtained from KPFM feedback loop operation has some error due to the level noise. However, the error is sufficient small enough that in good approximation, I assume the applied voltage as the appropriate FM Kelvin signal: $V_{\text{bias}} = V_{\text{FM}}$.

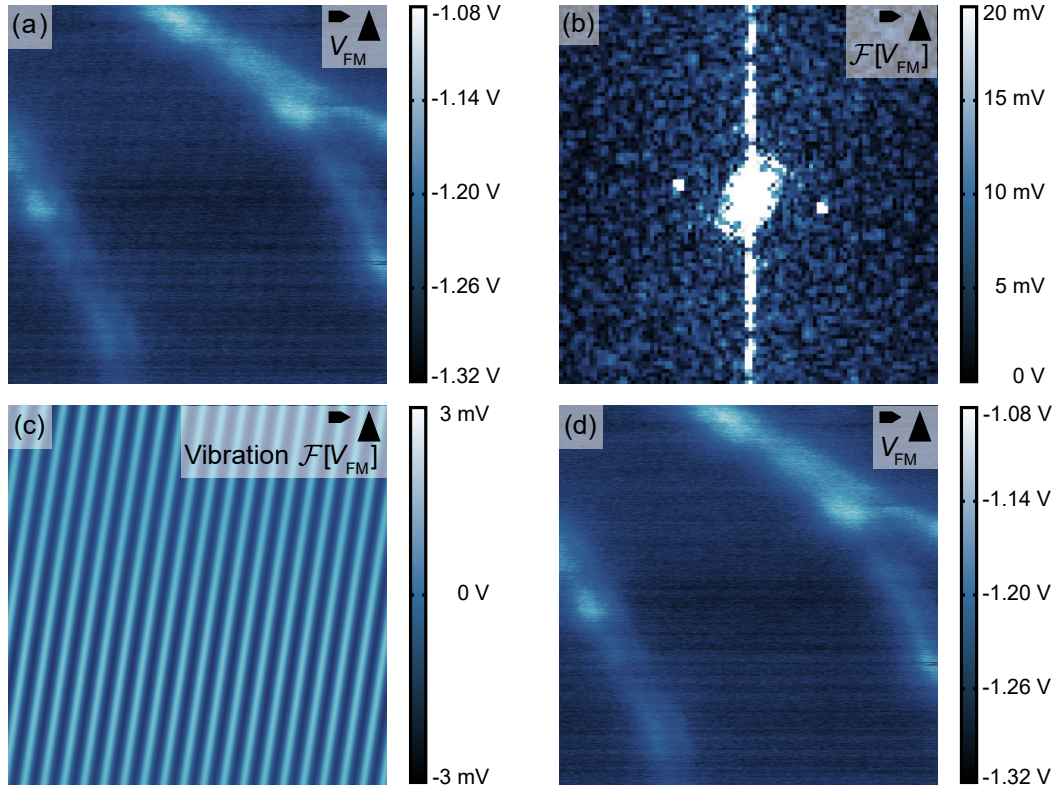


Figure 6.13.: Comparison of the non-filtered and filtered V_{FM} images. Image (a) shows the non-filtered V_{FM} image; the same V_{FM} image shown in figure 6.7 (a). Image (b) is the zoom focused on the center of the FFT of image (a). Image (c) is the filtered out contribution of the vibration to the V_{FM} image (b). Image (d) shows the filtered V_{FM} image.

Now, another discussions are the periodic oscillations in the V_{FM} images. The vibration of the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image presented in figure 6.13 (d) has been already discussed in this section. The corresponding V_{FM} image, shown in figure 6.13 (b), presents periodic oscillations with the same orientation and, from a visual observation, the same periodicity. A similar analysis as the one done with the $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image is presented in figure 6.13. Image (a) shows the already mentioned V_{FM} image. In order to analyze this periodic oscillation, an FFT image was computed. The zoom around the central part of the image is presented in (b). The most relevant features in the image are the two points which are symmetric with respect to the center of the image. The positions of this two points are the same as the ones in the FFT computed of the error channel (check figure 6.13 (c)). So, I consider the origin of this vibration is the same, the KPFM feedback loop operation. Using the same tool of Gwyddion as before, the *2D FFT Filtering*, I filtered out this contribution. Image (c) shows this contribution. I can see that all values are within a range of 6 mV. This is extremely important: when filtering out this contribution, its magnitude must be taken into account. Only if the magnitude of this contribution is small compared with the valid V_{FM} data from the image, the disturbance of the original data will be minimum and it is acceptable to do it. However, if their magnitude are comparable, I must not filter it out. In

this case, the oscillation has an amplitude of 3 mV in a KPFM image whose voltage range is between -1.32 and -1.08 V: it is much smaller and can be filtered out. In addition, it is necessary to discard the tip-sample interaction as possible origin of the periodical vibration. KPFM experiments on molecular self-assembled structures show a modulation in the Kelvin signal that corresponds to a modulation in the interaction of the tip-sample distance [19, 39]: periodical molecular structures might show a periodical V_{FM} signal. This periodical V_{FM} would not depend on scan speed or image direction. To discard this possibility, it is necessary to compare the images in the different scan directions, as indicated in figure 6.8, or changing the size of the scanned area and/or the relative orientation. As both conditions were fulfilled, it is appropriate to filter out this contribution. Image (d) presents the already filtered out V_{FM} image.

6.4 Preparation of Metal-Coated Silicon AFM Tips

In this section, I will discuss the preparation of the metal-coated AFM tips. Finding the right preparation parameters consists of preparing a metal-coated tip, measuring on the Au(111) sample and repeating the procedure until the tip is free of localized point charges. As explained before, the tip is free of localized point charges if the KPFM signal is constant upon varying the tip-sample distance. Thus, I need to compare different experiments. Because of this, I need to use the same measurement parameters in these experiments.

The oscillation amplitude A must be chosen so it is the same or, at least, as similar as possible in the experiments intended to be compared. Another parameter to take into account is the time between preparing the sample and the distance-dependent measurements. Although the experiments are performed in UHV, the vacuum is not free of possible charge contaminants, which can eventually adsorb on the sample surface and disturb the measurements. In order to check the possible variation of the $V_{\text{FM}}(z_c)$ curves upon keeping the sample in the chamber for some days, the Au(111) single crystal was prepared when the base pressure in the preparation chamber was lower than $1 \cdot 10^{-10}$ mbar. Right after the preparation, the sample was moved to the AFM chamber and kept there until these measurements were finished.

Figure 6.14 shows distance-dependent curves of two different experiments: two and six days after preparing the Au(111) single crystal. Plot (a) shows the averages of the frequency shift $\Delta\nu_e$ curves, plot (b) presents the averages of the Kelvin V_{FM} signal and plot (c) corresponds to the averages of the oscillation amplitude A versus the center position z_c . The oscillation amplitude A of both experiments is shown in plot (c). The difference between the oscillation amplitudes is around 20 pm, so I

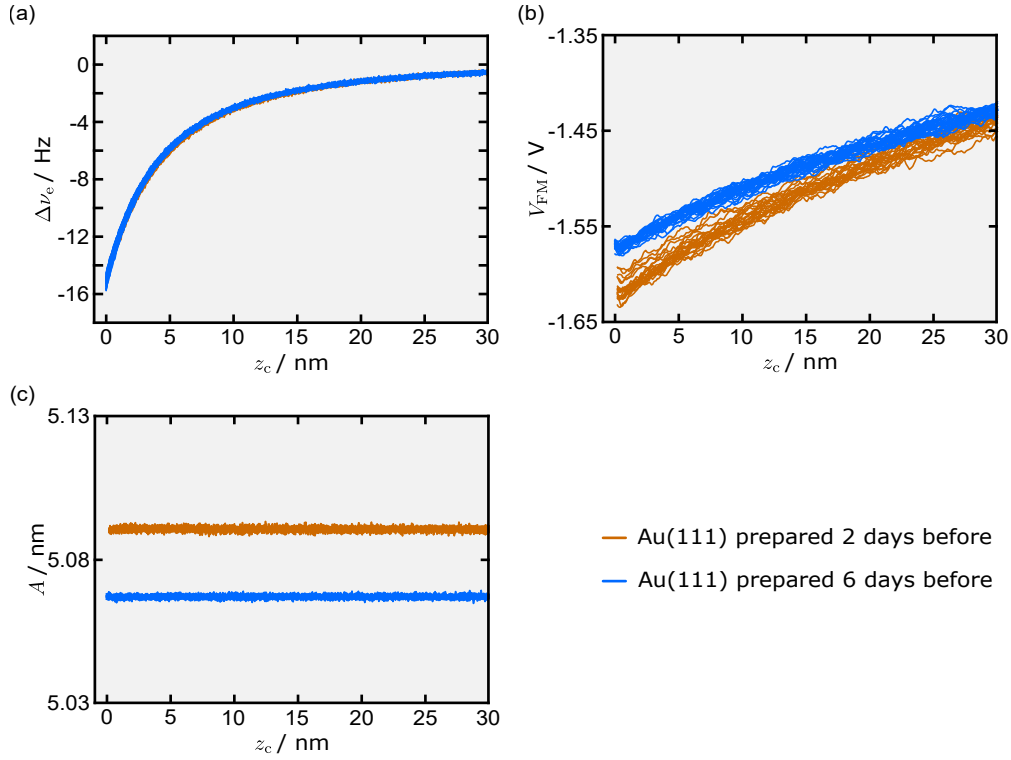


Figure 6.14.: Comparison of distance-dependent curves two and five days after preparing the Au(111) sample. The curves from the same experiment are presented in the same colour. Plot (a) presents the comparison of the frequency shift $\Delta\nu_e$, (b) shows the comparison of the Kelvin V_{FM} signal and (c) corresponds to the comparison of the oscillation amplitude A curves. All curves are plotted *versus* the tip center position z_c .

can assume that a direct comparison of the rest of the channels is justified. Before comparing $\Delta\nu_e(z_c)$ (shown in plot (a)) from different experiments, the offsets for large-tip sample distances must be corrected, as well as their relative position in the tip center position z_c coordinate (see appendix B). The curves from both days overlap almost completely. Considering that closed-loop FM-KPFM measurements were performed simultaneously, I can assume that the frequency shift $\Delta\nu_e$ is mostly dominated by Van der Waals interaction. Van der Waals forces acting between tip and sample have been modelled as the interaction between a flat surface and a sphere [110], a cone [110], a (truncated) pyramid [111] and combinations of spheres with cones and pyramids [110–112]. All these models for the tip-sample interaction show a dependence on the geometry of the tip apex. Tips with different geometries result in different distance dependencies of the forces F_{ts} and force gradients k_{ts} upon varying tip center position z_c . As the tip was not treated between the experiments and no tip crashes occurred, I could assume that the tip-sample interaction contributing to the frequency shift $\Delta\nu_e$ is similar in both experiments. Plot (b) shows the $V_{FM}(z_c)$ curves of both experiments. The $V_{FM}(z_c)$ values of the curves taken two days after preparation are distributed between -1.59 and -1.63 V, while six days later, the values are distributed around -1.57 V. For large tip center positions z_c , the curves of both days tend to converge. This indicates a different

charge distribution on the sample surface, which is an indication of the increasing contamination of the sample surface. Due to this visible change, the experiments for testing the metal-coated silicon AFM tips have been always done no longer than two days after preparing the Au(111) single crystal.

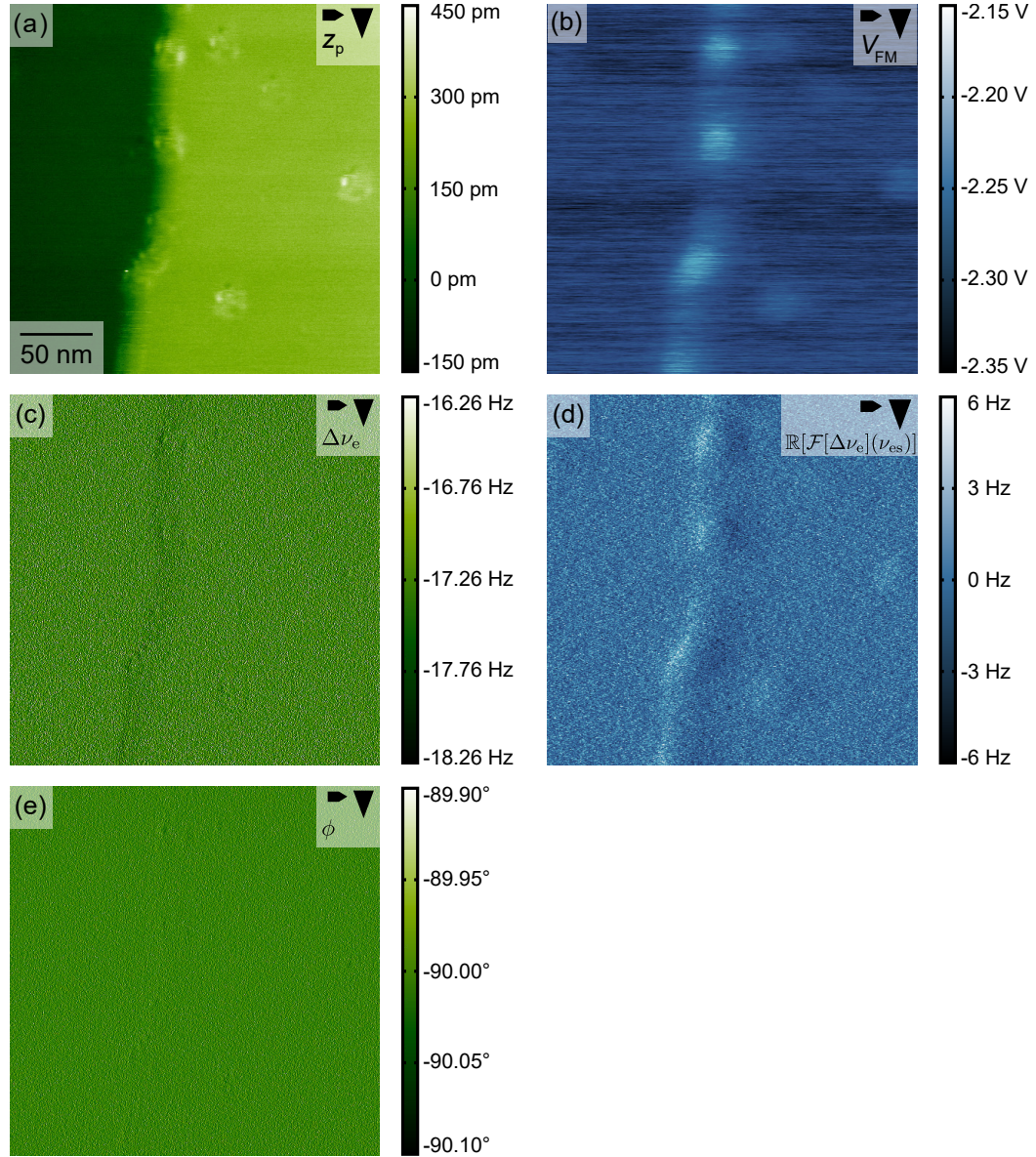


Figure 6.15.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *first* Au-coated silicon AFM tip before sputter it. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

Figure 6.15 shows FM-AFM and FM-KPFM images on the freshly prepared Au(111) sample. These images were recorded using a new and non-prepared Au-coated silicon AFM tip: (a) presents the topography z_p ; (b) corresponds to the Kelvin V_{FM} ; (c) shows the frequency shift $\Delta\nu_e$; (d) presents the real part of the first spectral component of the frequency shift $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ and (e) corresponds to the phase

shift ϕ . The phase shift ϕ and frequency shift $\Delta\nu_e$ images ((e) and (c)) show almost no corrugation and all values are distributed around the corresponding setpoints ($-\pi/2$ for the phase ϕ and -20 Hz for the frequency shift $\Delta\nu_e$). The topography (image (a)) shows two terraces and the step edge in between. Several features with a similar shape can be observed on the terrace to the right and the step edge. As these features have the same shape, I ascribe to a convolution of adsorbates with the tip.

The real part of the first spectral component of the frequency shift $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ (image (d)) shows a rather homogeneous signal on the terraces, but still some corrugation on the step edge and the features. The V_{FM} image (b) shows a uniform signal for the most of the image, although it exhibits higher values at the step edge and the features mentioned before. Some areas (top and center part of the image) show a increase or decrease in the signal in all the areas (no matter if it is on the terraces, the adsorbates or the step edge), parallel to the fast scan direction (horizontal): this could be due to a change in the apex of the tip [113]. If this explanation is true, the change is large enough to make a change in the V_{FM} image, but does not change the resolution of the topography z_p . The homogeneous signal of the terraces would mean a constant density of localized point charges or the absence of localized points charges. As the Au(111) single crystal was freshly prepared and no molecules were sublimated, I can conclude this signal means no point charges in these areas. Then, performing $V_{FM}(z_c)$ curves in these areas should show a variation in the V_{FM} signal if the tip apex has some non-neutral charged adsorbates (which can be considered as localized point charges). However, if the tip apex is free of localized point charges, the distance-dependent V_{FM} curves should be flat. To check this assumption, several distance-dependent curves were recorded.

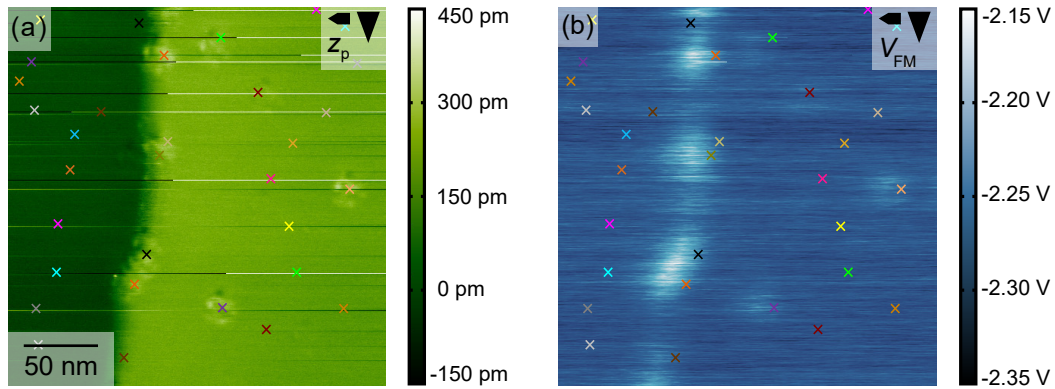


Figure 6.16.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *first* Au-coated silicon AFM tip before sputtering it. The crosses indicate the spots, where the distance-dependent curves shown in figure 6.17 were performed.

The distance-dependent curves were performed in the same area, two images after. Figure 6.16 shows the topography z_p and Kelvin V_{FM} image during which the

distance-dependent curves were performed. The crosses mark the specific spots, where the curves were performed. Figure 6.17 shows the four different channels recorded during performing the distance-dependent curves. The colours of the crosses in the topography and V_{FM} image and the curves in the plots relate each curve with the position, where it was performed.

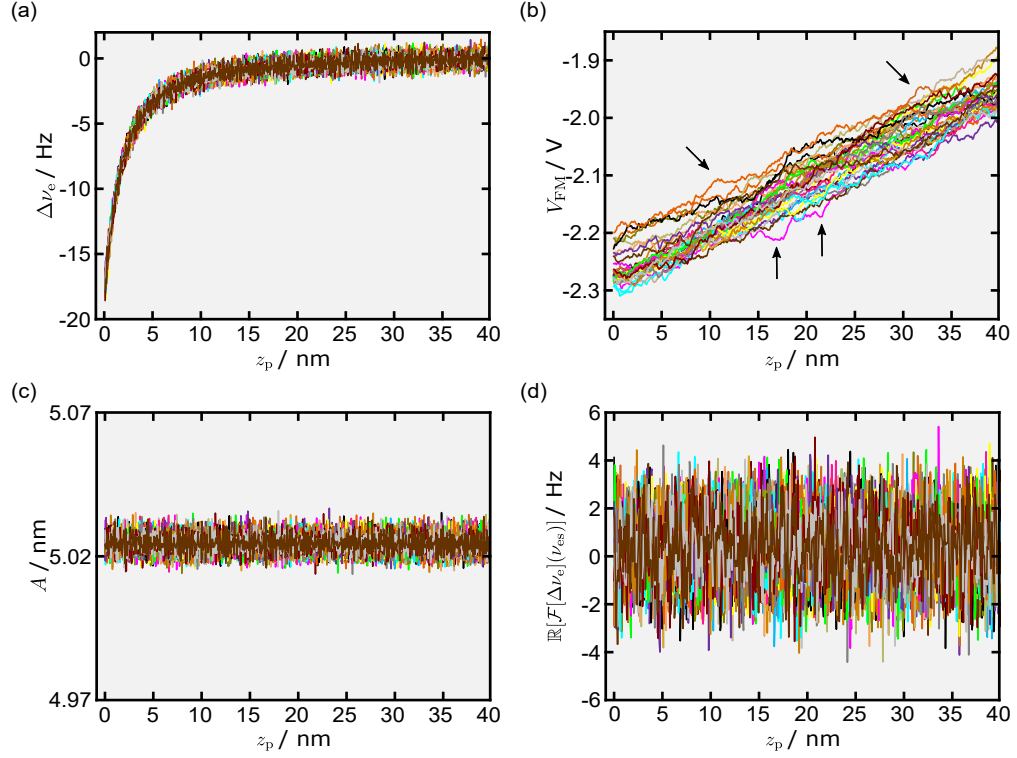


Figure 6.17.: Distance-dependent curves performed on the Au(111) single crystal with the *first* Au-coated silicon AFM tip before preparation. The colour of each curve correlates with the colour of the crosses in the images in figure 6.16. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ versus the z-piezo displacement z_p .

Figure 6.17 shows the distance-dependent curves performed with the *first* Au-coated silicon AFM tip. Plot (a) shows the frequency shift $\Delta\nu_e$, plot (b) presents the Kelvin V_{FM} signal, plot (c) corresponds to the oscillation amplitude A and plot (d) shows the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$. All channels are plotted *versus* the center position z_c . All oscillation amplitude A curves are constant for all z-piezo displacement z_p values. In this case, it is justified to compare the curves. All $\Delta\nu_e$ curves overlap: the largest variation in interaction corresponds to $z_p = 0$ to 5 nm and the curves are almost flat from there on. Plot (d) shows that all curves of the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ show no corrugation and noisy variations around zero, so I can consider the signal as properly nullified and the V_{FM} signal is trustworthy. Plot (b) show that all the V_{FM} curves present a variation with increasing the z-piezo displacement z_p , which implies the presence of localized point charges between tip and sample. Most of the curves, for $z_p = 0$, distribute between

-2.25 and -2.30 V, which corresponds to the areas in the V_{FM} images which exhibit an homogeneous signal. This distance-dependent variation implies localized point charges on the tip apex. Furthermore, there are few curves (two in orange colour, one in black, one in purple, one in olive and one in khaki) that present more positive value than the rest for all z_p values. These curves were performed in the proximity of the step edge or the contaminations/adsorbates, which exhibit more positive values in the V_{FM} image (figure 6.16 (b)). All curves exhibit large non-monotonic variations (indicated by black arrows in plot (b)) through the whole z_p path, which I have assigned to the feedback operation. However, for $z_p > 10$ -15 nm, some curves exhibit large and non-monotonic variations, as the orange with more positive values for $z_p = 10$ to 14 nm or the pink one with more negative numbers for $z_p = 15$ to 19 nm. The conclusion of this experiment is that is necessary to treat the Au-coated silicon AFM tips in order to removed the localized point charges present in the tip apex.

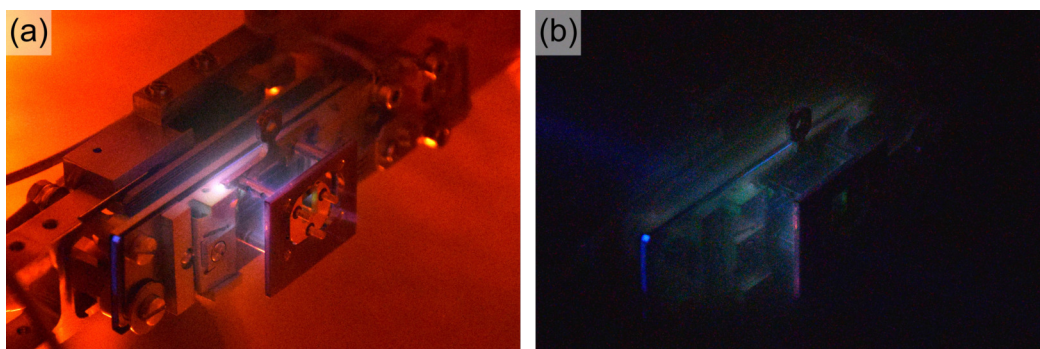


Figure 6.18.: Long-time exposure photographs of the sputtering procedure of Au-coated AFM tips. The exposure time of the photographs is 30 seconds. Image (a) shows the blue sparks after adjusting the ion beam size, so the Ar^+ ions mainly impact between the two plates of the tip transfer plate, where the AFM tip is localized. The orange-like light is originating from the ion gauge used to measure the partial pressure in the chamber. The ion gauge was switched off before taking image (b), so the region the ions impact can be seen with more accuracy.

In previous works in my group, silicon AFM tips have been prepared by sputtering with Ar^+ ions. The goal of this procedure is to remove the oxide layer formed due to the exposure to air. The procedure is carried out with an Ar partial pressure of $3 \cdot 10^{-6}$ mbar and 2.0 keV for 5 minutes. In order to check the reproducibility of the procedure, I measured the drain current produced in the heating stage by the impacting Ar^+ ions. The treatment of the Au-coated silicon AFM tips is similar, but as I did not intend to remove the Au-coating, I had to find new sputtering parameters. For this reason, I used a lower partial pressure and a lower energy: $2 \cdot 10^{-6}$ mbar and 1.7 keV were the parameters, which provide reproducible drain current values. Furthermore, I took long-time exposure photographs while exploring the right sputtering parameters. Figure 6.18 (a) shows the AFM tip holder inside the tip transfer plate, which is located in the heating stage. The sputtering procedure started before taking the image, and the orange-like light in the background generated in

the ion gauges is present (as in figure 6.1 (a), (b) and (c) and 6.4 (a)). The violet sparks are mainly visible between the two plates of the tip transfer plate. I can not see the AFM tip, but since I know it is between this two plates, I assume Ar^+ ions hit it. Before taking image (b), the ion gauges were switched off, so it is easier to see that the ions mainly hit between the two plates of the tip transfer plate. At this point, it is important to mention that the AFM tip is isolated from the tip transfer plate (it is only connected to one of the three legs of the tip holder), so the ions, which might impact on the tip cannot contribute to the drain current measured. For the first attempt, the sputtering procedure was done for 90 s.

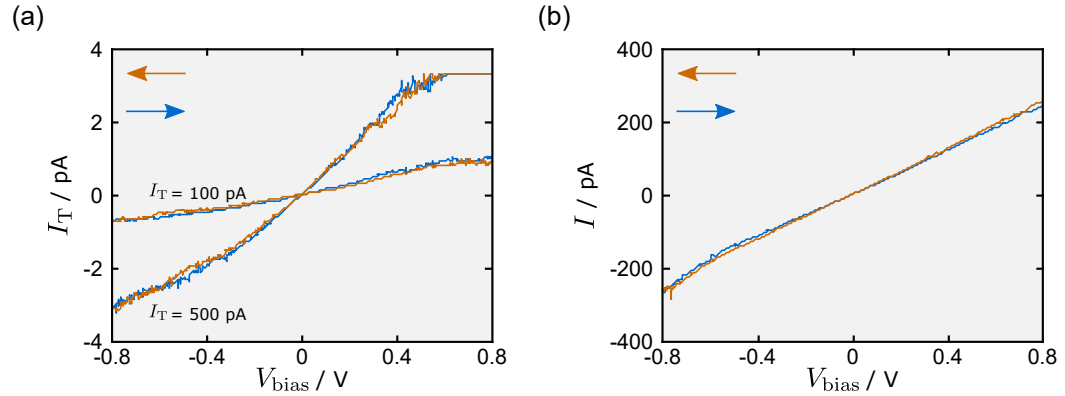


Figure 6.19.: Voltage-dependent $I_T(V_{\text{bias}})$ and $I(V_{\text{bias}})$ curves recorded with the *first* Au-coated silicon AFM tip on the Au(111) sample. For the curves shown in (a), the tip was in tunnelling range. Right before recording the curves, the bias voltage V_{bias} was set to -100 mV. The value I_T in the plots shows the tunnelling current setpoint at which each curve was recorded. For the curves shown in (b), the tip apex was in contact with the Au(111) surface. The bias voltage applied for all curves was $V_{\text{bias}} = -100$ mV. The blue and orange arrows relate the sweep voltage direction with each curve.

Once the tip was sputtered, I checked if the Au-coating was still present or was removed. $I_T(V_{\text{bias}})$ curves could be done to check the state of the AFM tip. I measured FM-AFM in order to place the tip at a clean spot. After I found it, I zoomed in as much as the system allows (0.1 nm x 0.1 nm) and stopped the measurement. After this, I introduced an offset large enough in the ΔZ option and, right after, disabled the distance feedback loop. As a result, the piezo-tube scanner contracted and the tip was retracted to a save position. At this point, I changed from FM-AFM to STM measurements, so I unlocked the PLL, stopped the mechanical excitation to the cantilever, changed to STM feedback and enabled the distance feedback loop. Then, the piezo-tube scanner elongated until a tunnelling current was detected: the tip was conductive and the z-piezo position z_p was kept constant in tunnelling range. At this point, I recorded several $I_T(V_{\text{bias}})$ curves, which are shown in figure 6.19. Plot (a) shows two curves recorded in tunnelling range. Right before recording this two curves, the bias voltage V_{bias} was set to -100 mV. The first and second curves were recorded at a tunnelling current setpoint of $I_T = 100$ and 500 pA respectively. For values around 0 V, the tunnelling current I_T of both curves shows

a linear dependence with the bias voltage V_{bias} , as expected from the tunnelling current formula (see equation (2.2)), while for larger values the current does not vary linearly, but exhibits some spikes and non-monotonic changes. The Ohmic behaviour of both curves around 0 V indicates a constant density of states $\rho_s(E_F)$, as expected for a metal. From this result, I could conclude that the Au-coating of the silicon AFM tip is still present on it. The larger slope (and values) in the second curve is defined by the tunnelling current formula (see equation (2.2)): as the tunnelling current setpoint was increased, the distance feedback loop brought the tip closer to the sample, so the tip center position z_c was reduced, which implies a larger current for the same applied V_{bias} . Furthermore, at this point, I disabled the distance feedback loop and changed the z-piezo position z_p in 2 nm towards the sample surface. I recorded another curve in this situation (in this case, as tip and sample are in contact, there is no tunnelling current I_T , just current I). This curve shows Ohmic behaviour too, which indicates that the Au-coating is still present in the tip. At this point, these curves are recommended only for identifying proper sputtering parameters and not before every experiment after finding the right parameters: making contact or crashing with the tip in the sample surface deforms the apex of the tip, which can distort the resolution of the FM-AFM and FM-KPFM images.

Figure 6.20 shows FM-AFM and FM-KPFM images on the Au(111) recorded using the sputtered Au-coated tip: (a) presents the topography z_p ; (b) corresponds to the Kelvin V_{FM} ; (c) shows the frequency shift $\Delta\nu_e$; (d) presents the real part of the first spectral component of the frequency shift $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$, (e) corresponds to the phase shift ϕ and (f) shows the magnitude of the second spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. The images are rather similar to the ones of the experiment carried out before treating the Au-coated tip. The phase shift ϕ and frequency shift $\Delta\nu_e$ images ((c) and (e)) show almost no corrugation while the topography z_p (a) shows two different terraces and the step edge in between. The resolution is clearly influenced by the deformation of the tip apex, clearly visible by the tip convolution manifested during the imaging of the contamination on the upper terrace (right part of the image). Furthermore, the step edge is not sharply imaged, but exhibit several fringes. Regarding the KPFM images, the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ looks rather homogeneous: all values are distributed around 0 Hz, but it shows some contrast in the step edge area. The Kelvin V_{FM} image shows quite homogeneous signal on the terraces, while higher values were imaged in the areas corresponding to the step edge and the contamination. The uniform variations of the Kelvin V_{FM} signal parallel to the fast scan direction reported in the previous experiment appear in this image too, but there is not a significant change of the resolution in the topography z_p . Finally, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$ shows no corrugation. After identifying the areas where the V_{FM} signal looks homogeneous, distance-dependent curves were performed in the same area. Figure 6.21 shows the topography z_p and Kelvin V_{FM}

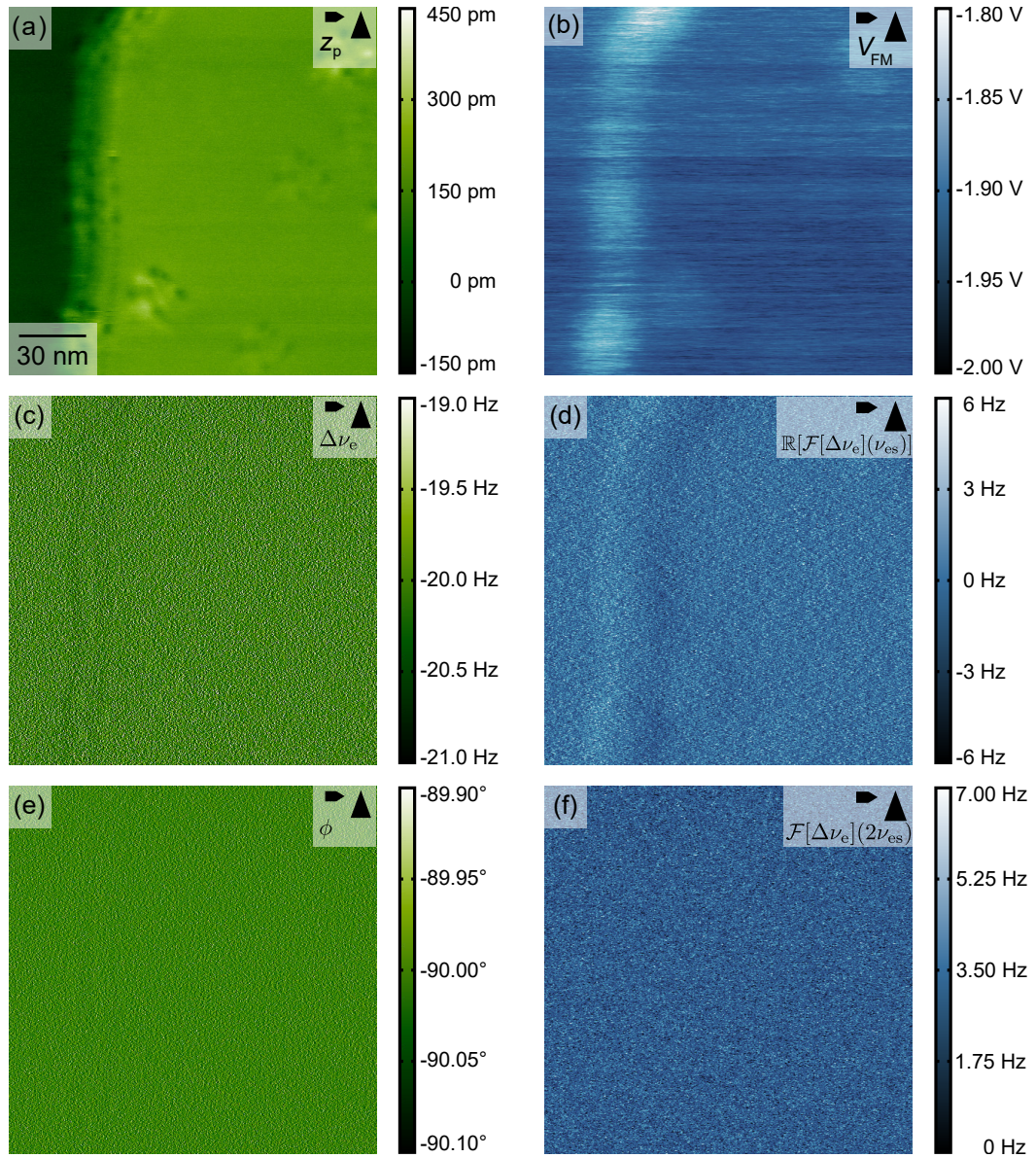


Figure 6.20.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *first* Au-coated silicon AFM tip after sputter it for 90 s. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b), (d) and (f) show the Kelvin V_{FM} signal, the real part of the *first* spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ and the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$, respectively.

image, at which the distance-dependent curves were performed, and figure 6.22 shows the six different channels recorded during the the distance-dependent curves. As in the data of the previous experiment, the colours of the crosses in the images and the curves in the plots relate each curve with the position, where it was performed.

Figure 6.22 shows the distance-dependent curves performed with the *first* Au-coated silicon AFM tip after sputter it for 90 s. Plot (a) shows the frequency shift $\Delta\nu_e$, plot (b) presents the Kelvin V_{FM} signal, plot (c) corresponds to the oscillation amplitude

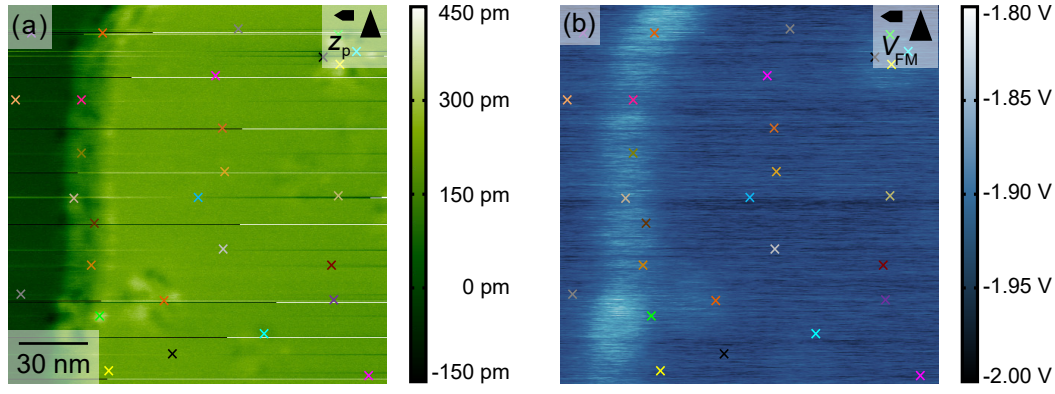


Figure 6.21.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *first* Au-coated silicon AFM tip after sputtering it for 90 s. The crosses indicate the spots, where the distance-dependent curves shown in figure 6.22 were performed.

A, plot (d) shows the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, plot (e) presents the static deflection q_s and plot (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. The static deflection q_s is plotted *versus* the z-piezo displacement z_p . All the remaining channels are plotted *versus* the center position z_c . The same remarks as in the previous experiment about the oscillation amplitude A are valid here: it remains constant for all curves at all tip center position z_c . Then, all the curves of the other channels are comparable between each other. All $\Delta\nu_e$ curves overlap: the largest variation in interaction corresponds to $z_c = 0$ to 5 nm and are almost flat for $z_c > 15$ nm. Plot (d) shows that all curves of the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ are, within the noise, 0 Hz, so I can assume that this channel is nullified for all curves and the V_{FM} curves are reliable. Plot (b) shows that all V_{FM} curves concentrate between -1.85 and -1.95 V for $z_c = 0$. Unlike the previous experiment, the tendency of all curves from $z_c = 0$ to 5-10 nm is closer to be constant. From there on, the slope of the curves tend to increase. However, the curves also present the large non-monotonic changes. Example of these changes can be observed (indicated in plot (b) by arrows in the corresponding colour) in the orange, green and cyan curves, or the brown, grey, yellow and black curves. The magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ curves show a non-linear decreasing signal with increasing the tip center position z_c . The curves seem to overlap, which implies no influence of the charge distribution, and all become zero for $z_c = 15$ to 20 nm. Nevertheless, all curves are rather noisy, which is a reason why it is difficult to make any strong statement. Finally, the static deflection curves show different tendencies, implying different static forces depending on the spot of the surface. In summary, in the two experiments performed until now, the V_{FM} signal seems to present two different distance-dependent regimes. In the first regime, which corresponds to the part of the z-piezo displacement z_p measured which is closer to the sample (from z_c 0 to ~ 10 nm), most of the curves present a similar tendency and similar values. In the second regime (from $z_c \sim 10$ nm on), the curves separate from each other and show non-monotonic variations independently

of the tip center position z_c . In the first region of the second experiment, the $V_{FM}(z_c)$ curves present a smaller slope. For this reason, the sputtering and testing procedure was repeated several times, up to a total sputtering time of 160 s.

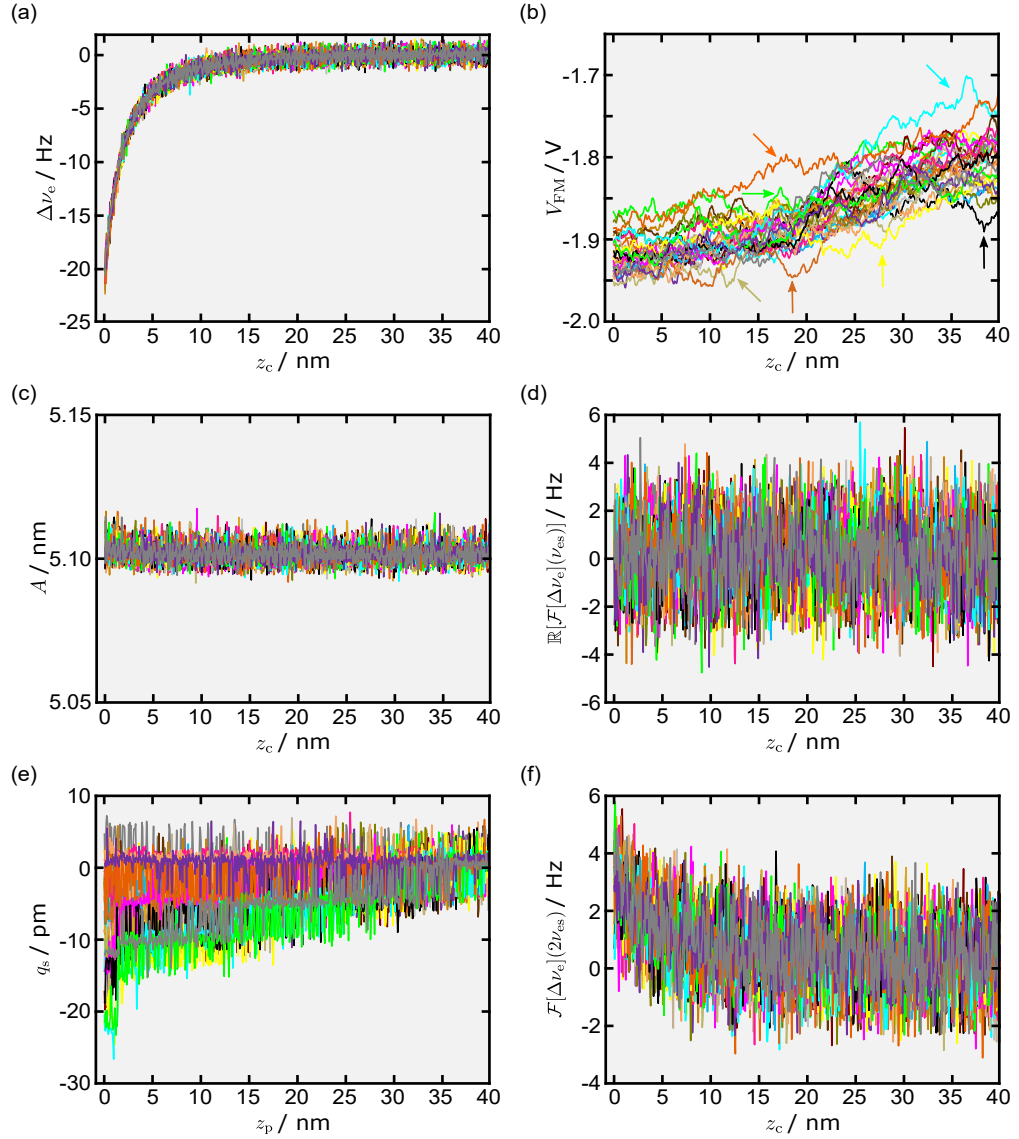


Figure 6.22.: Distance-dependent curves performed on the Au(111) single crystal with the *first* Au-coated silicon AFM tip after sputtering it for 90 s. The colour of each curve correlates with the colour of the crosses in the images in figure 6.21. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A , (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, (e) shows the static deflection q_s and (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. All channels are plotted *versus* the tip center position z_c except for the static deflection q_s , which is plotted *versus* the z-piezo displacement z_p .

Figure 6.23 shows FM-AFM and FM-KPFM images on the Au(111) recorded using the Au-coated tip after sputter it for a total time of 160 s. Image (a) presents the topography z_p , image (b) corresponds to the Kelvin V_{FM} , image (c) shows the frequency shift $\Delta\nu_e$, image (d) presents the real part of the first spectral component

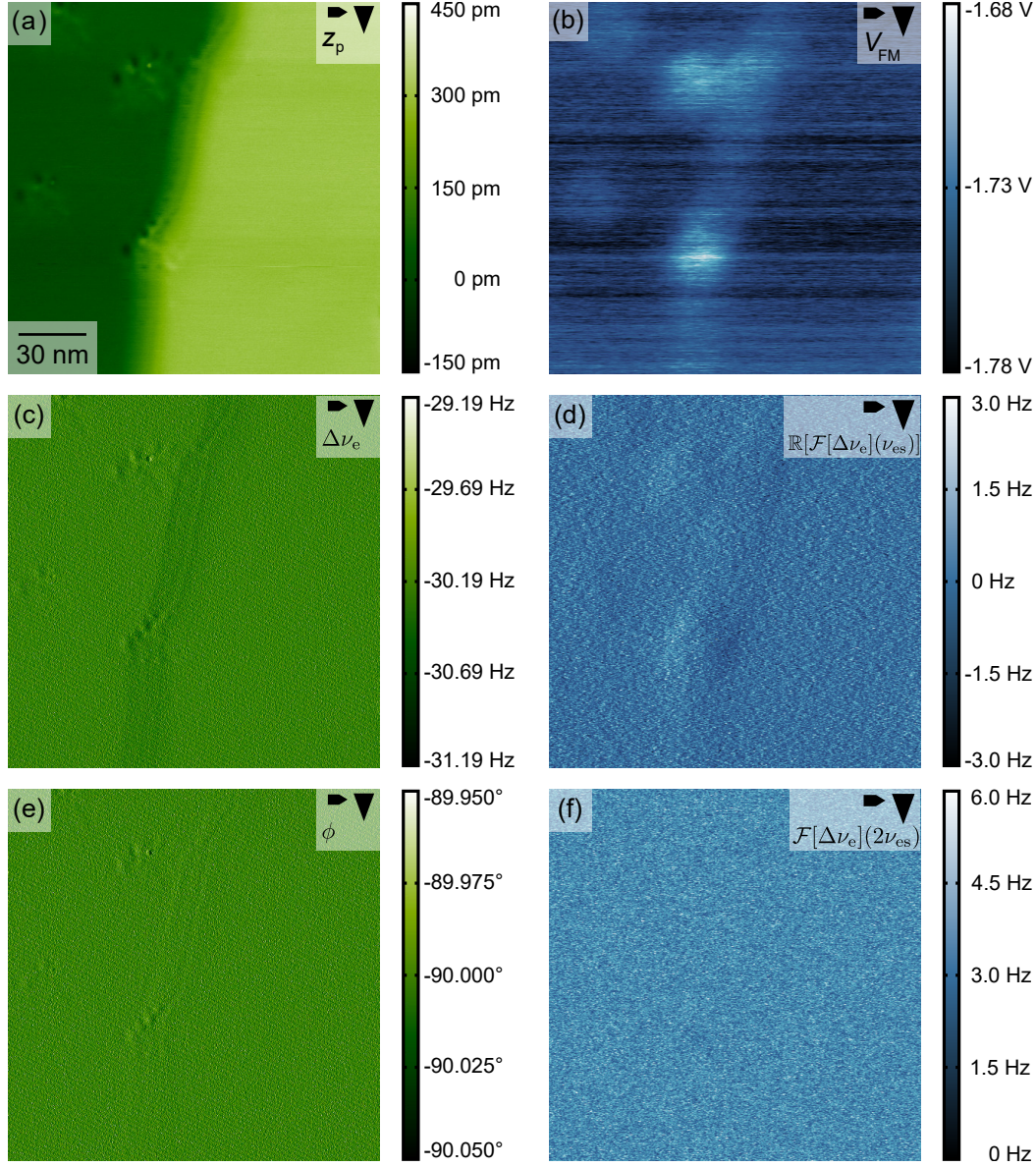


Figure 6.23.: FM-AFM and FM-KPFM images measured on Au(111) using the *first* Au-coated silicon AFM tip after sputter it for 160 s. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b), (d) and (f) show the Kelvin V_{FM} signal, the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ and the magnitude of the second spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})]$, respectively.

of the frequency shift $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$, image (e) corresponds to the phase shift ϕ and image (f) shows the magnitude of the second spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. As in the previous experiments presented, the phase shift ϕ and frequency shift $\Delta\nu_e$ images ((c) and (e)) show almost no corrugation. The topography z_p (a) shows two different terraces and the step edge in between. This time, contaminations appear much larger and is much worse resolved, indicating a considerable deformation of the tip apex. The real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ is almost completely nullified, but exhibits some contrast in the step edge area. The V_{FM} image shows rather homogeneous values on the terraces and

higher values around the step edge and the adsorbates. The variations of the V_{FM} signal both on terraces and the step edges are also present in this experiment. As before, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$ shows no corrugation.

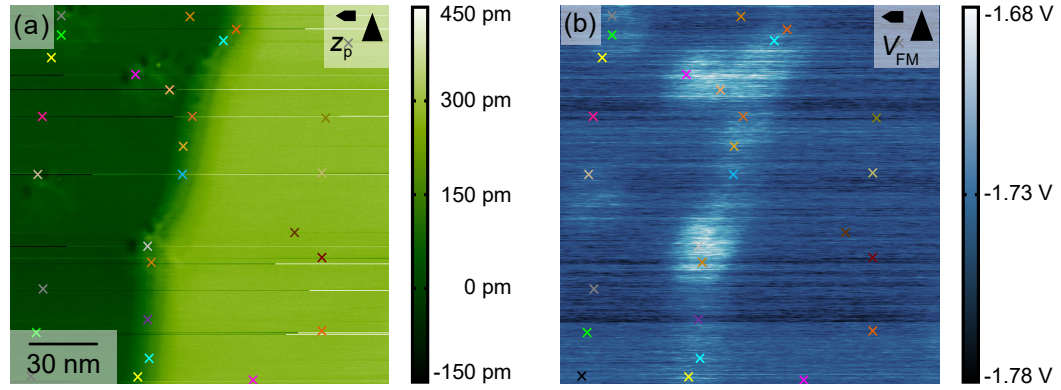


Figure 6.24.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *first* Au-coated silicon AFM tip after sputtering it for 160 s. The crosses indicate the spots, where the distance-dependent curves shown in figure 6.25 were performed.

The distance-dependent curves were performed in the same area. Figure 6.24 shows the topography z_p and Kelvin V_{FM} image, during which the distance-dependent curves were performed, and figure 6.25 shows the six different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curves in the plots relate each curve with the position, where it was performed.

Figure 6.25 shows the distance-dependent curves performed with the *first* Au-coated silicon AFM tip after sputter it for 160 s. Plot (a) shows the frequency shift $\Delta\nu_e$, plot (b) presents the Kelvin V_{FM} signal, plot (c) corresponds to the oscillation amplitude A , plot (d) shows the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$, plot (e) presents the static deflection q_s and plot (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. The static deflection q_s is plotted *versus* the z-piezo displacement z_p . All the remaining channels are plotted *versus* the center position z_c . The same remarks as in the previous experiments about the oscillation amplitude A are valid here: it remains constant for all curves at all the tip center position z_c . Then, the curves of the rest of the channels are comparable between each other. All the $\Delta\nu_e$ curves overlap: the largest variation in interaction correspond to $z_c = 0$ to 5 nm and tend to 0 Hz from there on. Plot (d) show that all the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ curves are, excluding the noise, nullified, so the V_{FM} curves are reliable. Plot (b) show that all the V_{FM} curves concentrate between -1.71 and -1.76 V for $z_c = 0$. In this case, again, the V_{FM} (z_c) curves exhibit two regions: one region closer to the sample, exhibiting a common behaviour of negative slope in most of the curves for $z_c = 0$ to 5-6 nm, and a second

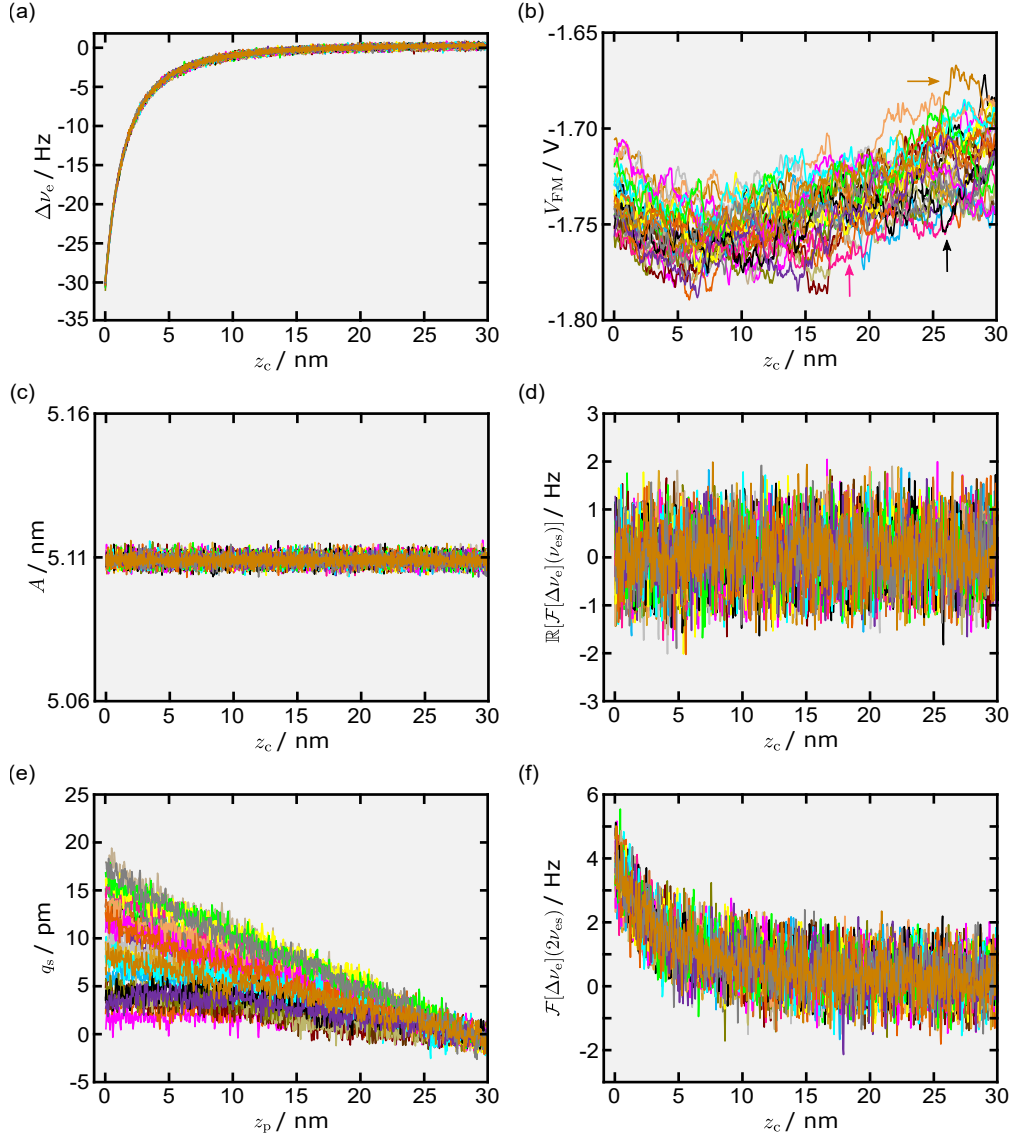


Figure 6.25.: Distance-dependent curves performed on the Au(111) single crystal with the *first* Au-coated silicon AFM tip after sputtering it for 160 s. The colour of each curve correlates with the colour of the crosses in the images in figure 6.24. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A , (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, (e) shows the static deflection q_s and (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. All channels are plotted *versus* the tip center position z_c but the static deflection q_s , which is plotted *versus* the z-piezo displacement z_p .

region, with positive slope and, again, large non-monotonic variations for $z_c = 5$ -6 to 30 nm. The black, pink and brown curves, indicated in plot (b) with arrows in the same colour, are good example of these large variations. In this case, the curves also tend to separate from each other in this second region. The magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ curves show a similar behaviour as in the previous experiment: non-linear decreasing signal with increasing the tip center position z_c . The curves seem to overlap, which implies no influence of the charge distribution, and all become zero for $z_c = 15$ to 20 nm, but due to the large noise,

it is difficult to state this for sure. Finally, as in the previous experiment, the static deflection curves show different tendencies.

As a conclusion, the curves do not follow a constant common trend. However, not all curves exhibit a monotonic slope, as the most positive pink curve for $z_c = 0$ nm, which for the range $z_c = 0$ to 5 nm decreases and increases again to the same values. I do not understand why the curves show two different tendencies. From all the z_c values measured in the curves, I do not understand why the curves seem constant or almost constant for small tip-sample distances and large slope for large tip-sample distances. In order to counter-check the results obtained with the closed-loop FM-KPFM mode, I recorded several $V_{FM}(z_c)$ curves until I found one as flat as possible: the curves exhibited variations around the same value for a considerable z_c range. Then, in the same spot, I recorded several $\Delta\nu_e(V_{bias})$ curves starting closer to the sample and increasing the frequency shift $\Delta\nu_e$ setpoint, so the tip center position z_c , at which the curves were recorded, varied. Figures 6.26 (a) and (b) show the $\Delta\nu_e(V_{bias})$ curves, while (c) and (d) show the oscillation amplitude $A(V_{bias})$ curves. These last mentioned plots show that the oscillation amplitude A of all curves both in negative and positive sweep voltage direction are constant for all V_{bias} value and overlap, so the $\Delta\nu_e(V_{bias})$ curves shown in plots (a) and (b) are trustworthy and comparable between them.

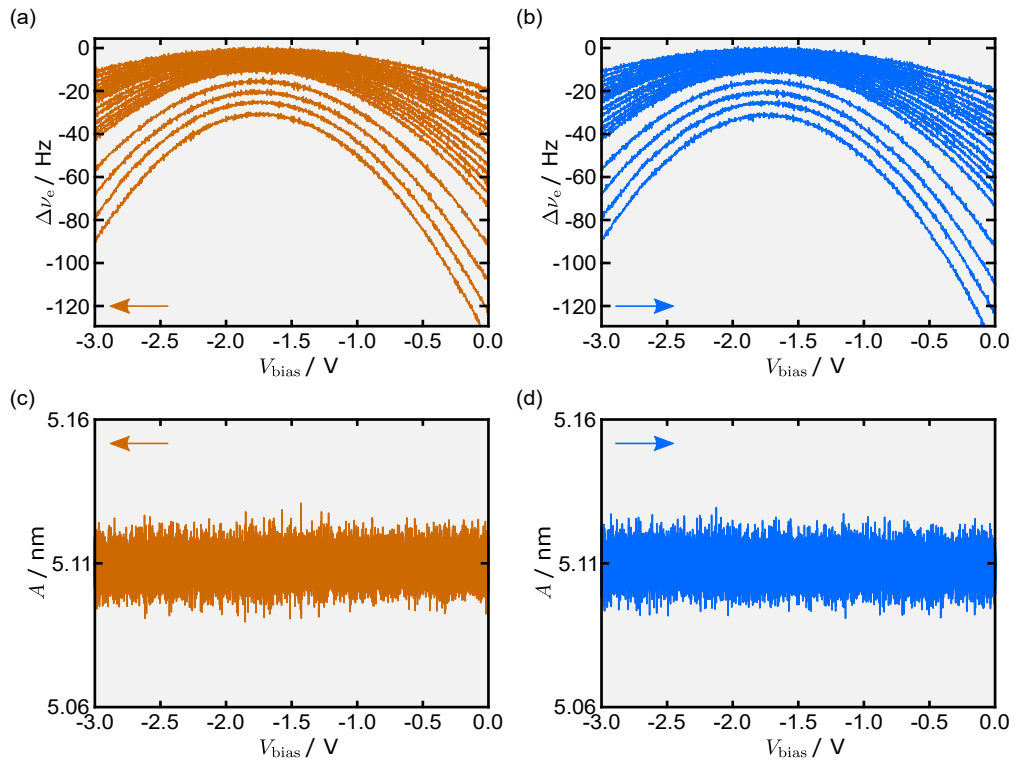


Figure 6.26.: Voltage-dependent curves recorded with the *first* Au-coated silicon AFM tip after sputtering it for 160 s. Plots (a) and (b) show the frequency shift $\Delta\nu_e(V_{bias})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

All $\Delta\nu_e(V_{\text{bias}})$ curves were fitted to a parabolic function of the type:

$$\Delta\nu_e(V_{\text{bias}}) = a \cdot (V_{\text{bias}} - b)^2 + c \quad (6.4)$$

According to the KPFM theory explained in section 2.4.3, the parameter b corresponds to the V_{FM} value, which is the bias voltage V_{bias} value that minimizes the tip-sample electrostatic interaction. The parameter c corresponds to the contributions to the frequency shift $\Delta\nu_e$ which are independent from the bias voltage V_{bias} applied between tip and sample. The intention of this part of the experiment is to compare the V_{FM} values got from the fit and compare it with the $V_{\text{FM}}(z_c)$ curve, but I did not have the z-piezo displacement z_p data corresponding to each one of the curves. The alternative method consisted of fitting the $\Delta\nu_e(z_c)$ curve to a 9th-degree polynomial function. From the result of this fit and the parameter c of each $\Delta\nu_e(V_{\text{bias}})$ curve fitted, the approximate value of the tip center position z_c at which each V_{bias} curve was performed can be computed.

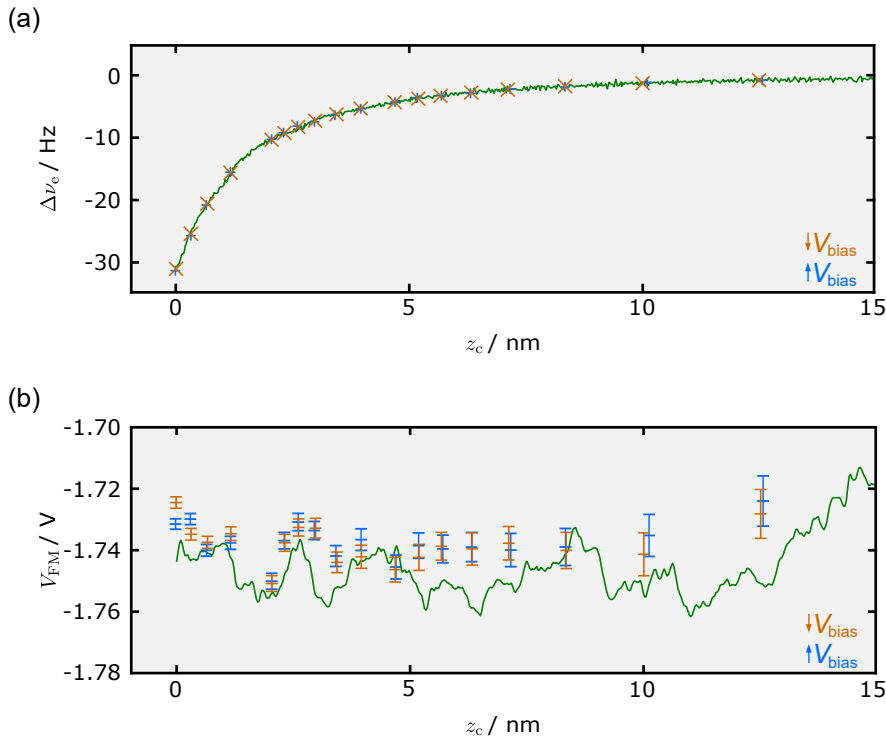


Figure 6.27.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{\text{bias}})$ curves of figure 6.26 (a) and (b), which were performed after sputtering the *first* Au-coated silicon AFM tip for 160 s. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

The comparison of the V_{FM} data obtained by both procedures is shown in figure 6.27. Plot (a) shows the comparison of the $\Delta\nu_e(z_c)$ curve with the fit parameter c of all $\Delta\nu_e(V_{\text{bias}})$. As explained before, the values of the fit parameter c were used to find the z_c value at which each curve was recorded. The plot (b) presents the comparison

between $V_{\text{FM}}(z_c)$ curve and the fit parameter b of all $\Delta\nu_e(V_{\text{bias}})$ curves. First of all, the $V_{\text{FM}}(z_c)$ curve is not strictly flat. It presents fluctuations within a range of 30 mV (from -1.76 to -1.73 V) for $z_c = 0$ to 10 nm. The question is "how flat" I can expect this curve to be. Comparing it with the profile shown in figure 6.13 (e), I realize that these values also fluctuate within a range of 30 mV around -1.28 V. This profile was taken in an area of the image considered to exhibit an homogeneous Kelvin V_{FM} signal. If the signal in this area can be considered to be homogeneous, the $V_{\text{FM}}(z_c)$ curve in figure 6.27 (b), which varies within a small voltage range for tip-sample distances spanning a range of more than 10 nm can also be considered flat. Furthermore, I know, as explained in section 6.3, that the closed-loop V_{FM} signal has an error of some tens of millivolts. On the other hand, the V_{FM} data extracted is plotted including the errors bars. For $z_c = 0$ to 2 nm, the data presents some variations, but from there on, the V_{FM} values exhibit no dependence on the tip center position z_c . The largest error, which corresponds to the V_{bias} curve recorded for the largest tip center position z_c , is 8 mV. With respect to the V_{FM} data extracted from fitting the $\Delta\nu_e(V_{\text{bias}})$ curves, which affects these points are plotted in pairs, each one corresponding to an opposite sweep direction of the bias voltage V_{bias} . No one of the pairs of points present the same V_{FM} value but, at least, they slightly differ. In the case of perfect parabolas, no matter the sweep direction, the fits should provide the same parameters. However, the $\Delta\nu_e(V_{\text{bias}})$ curves include noise, whose distribution can be different and affect the fit parameters. Another possible cause of these small variations are structural changes in the apex of the tip, as mentioned before as a possible cause of the uniform changes in the previously presented V_{FM} images [114]. A more detailed discussion about the data extracted in $\Delta\nu_e(V_{\text{bias}})$ curves will be given in section 6.5.

The results of the experiments performed using the *first* Au-coated silicon AFM tip are summarized in figure 6.28 by showing the averages of the recorded curves. Plot (a) shows the averages of the frequency shift $\Delta\nu_e$ curves, plot (b) presents the averages of the Kelvin V_{FM} signal, plot (c) corresponds to the averages of the oscillation amplitude A and plot (d) show the averages of the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. In the first experiment (in blue), the static deflection q_s and the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$ were not recorded. Due to the lack of static deflection q_s data, the averages of the curves corresponding to the first experiment are plotted *versus* the z-piezo position z_p . The data corresponding to the second and third experiment (in orange and purple) are plotted *versus* the center position z_c . Furthermore, not recording the $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$ signal in the first experiment explains why in plot (d) are only presented two averages. Regarding the oscillation amplitude A (plot (c)), the three averages are constant for all z_c/z_p values, since all the individual oscillation amplitude A curves are also constant. Their values are not exactly the same, but all are within a range smaller than 100 pm, which is enough to compare the rest of the quantities. The

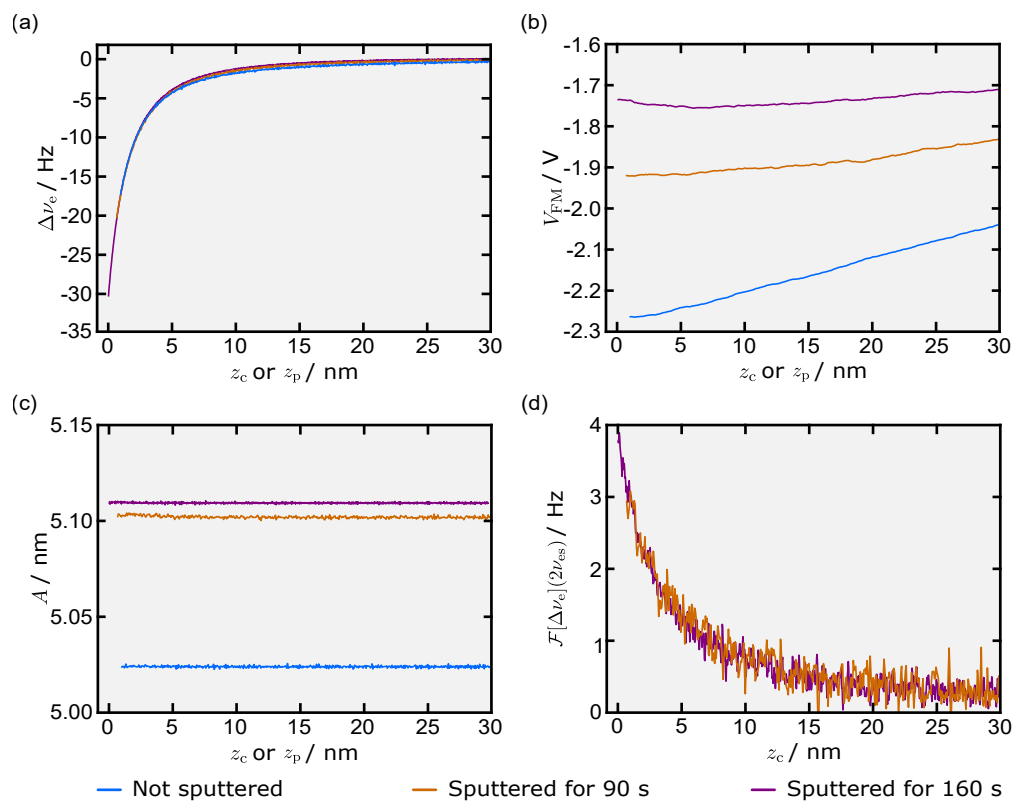


Figure 6.28.: Comparison of the averaged distance-dependent curves of the experiments with the *first* Au-coated silicon AFM tip. Plot (a) shows the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) presents the oscillation amplitude A and (d) shows the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. The curves corresponding to the experiment using the Au-coated silicon AFM tip before sputtering it are plotted *versus* the z -piezo displacement z_p , while the two experiments carried out after sputtering the tip are plotted *versus* the tip center position z_c . Furthermore, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ was not recorded for the experiment using the Au-coated AFM silicon tip before sputtering it, which is the reason why it is not included in plot (d).

three $\Delta\nu_e$ curves are rather similar, specially for the largest interaction region ($z_c/z_p = 0$ to 5 nm), but they do not overlap completely. This fact would indicate a change of the tip apex after the sputtering procedure, as previously discussed in Refs. [110–112]. For large distances, all of them tend to 0 Hz (meaning no interaction). In plot (b), it is noticeable that the V_{FM} values vary as the tip is sputtered and the curves become flatter. Furthermore, the three averaged V_{FM} curves show two different regions: one for $z_c/z_p = 0$ to 5–6 nm, where the averages show a flat or slightly negative slope, and another region from $z_c/z_p = 5$ –6 nm on, where the averages show a positive slope. Finally, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ (plot (d)) is rather similar for the two experiments performed after sputtering the tip. At this point, I can conclude that the tip is properly prepared: free of localized point charges and ready to use for KPFM measurements on molecules. Now, it is necessary to reproduce the result by applying the same procedure to a second tip.

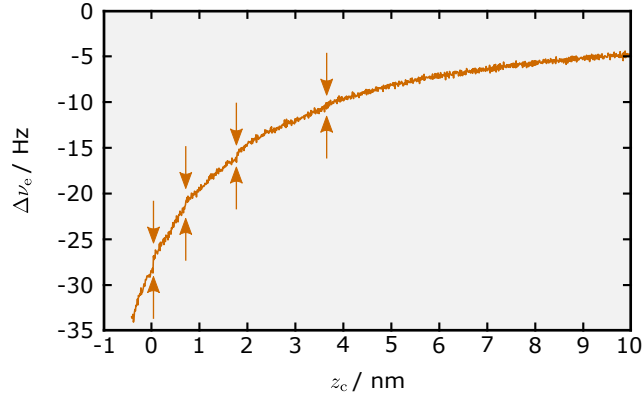


Figure 6.29.: $\Delta\nu_e(z_c)$ curve recorded on the Au(111) sample with the *second* Au-coated silicon AFM tip. $z_c = 0$ nm indicates the position of the tip right before the curve was performed. From that position, the tip was approached to the sample surface until $z_c = -0.4$ nm and then retracted up to $z_c = 10$ nm. The arrows indicate sudden variations or "jumps" in the frequency shift $\Delta\nu_e$.

A second non-sputter Au-coated silicon AFM tip was used to measure the Au(111) single crystal surface under similar conditions as done with the *first* tip. During the measurements, distance-dependent curves were performed in order to check the stability of the $\Delta\nu_e(z_c)$ curves before bringing the tip closer to the sample surface. Figure 6.29 shows an example. The tip was approached 0.4 nm towards the sample surface and then retracted until $z_c = 10$ nm. While retracting the tip, the $\Delta\nu_e$ signal presents sudden variations or "jumps" indicated by the arrows at $z_c \sim 0.05, 0.75, 1.8$ and 3.6 nm. These large variations of the interaction for a small variation of z_c (or even for a constant value in the case of the jump at $z_c \sim 0.05$ nm) indicate the presence of some unstable cluster of atoms or contamination of the tip apex. The larger the tip center position z_c , the smaller are the forces acting on this cluster/contamination. When the tip is close to the sample surface, the forces acting on this cluster/contamination are large: while the cluster is still attached to the tip apex, it can be elongated or extended towards the surface. Then, the tip-sample distance would be, actually, the distance between the sample surface and the lower extreme of the contamination. As the tip is retracted away from the sample surface, the forces acting on the contamination/cluster decreases, triggering a relaxation or contraction of the cluster (which it is still attached to the tip apex). This would lead to an effective increase of the tip center position z_c , which would change the frequency shift $\Delta\nu_e$ and end up in these variations. After recording this curve, I increased the frequency shift $\Delta\nu_e$ setpoint (approaching the tip to the sample). I expected an unstable scanning due to the possible movement of this cluster/contamination due to the tip-sample forces and the tip center position z_c variation done by the distance feedback loop.

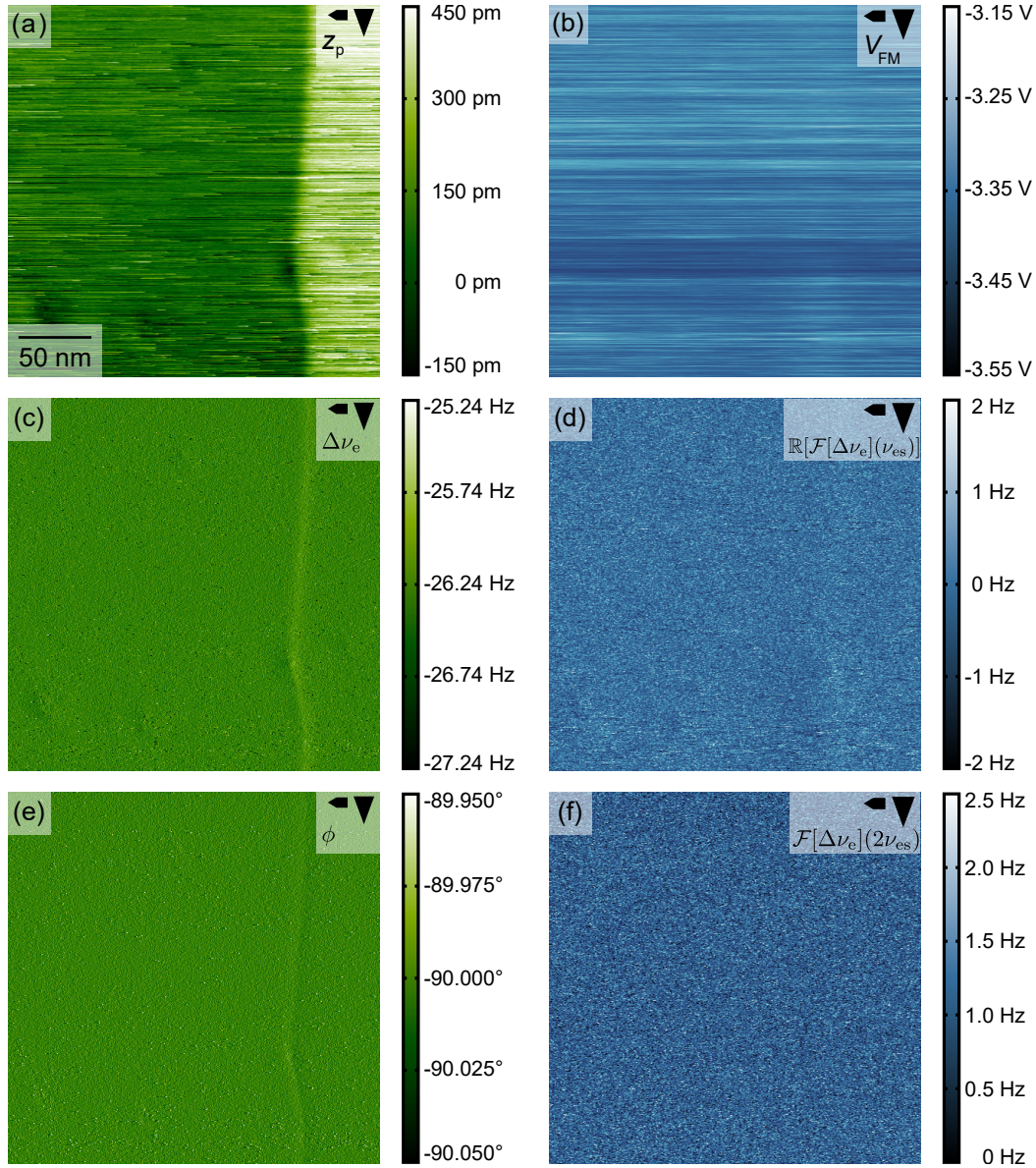


Figure 6.30.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *second* Au-coated silicon AFM tip before sputtering it. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b), (d) and (f) show the Kelvin V_{FM} signal, the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ and the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$, respectively.

Figure 6.30 shows FM-AFM and FM-KPFM images on the Au(111) recorded using the *second* Au-coated tip before sputtering it. Image (a) presents the topography z_p , image (b) corresponds to the Kelvin V_{FM} , image (c) shows the frequency shift $\Delta\nu_e$, image (d) presents the real part of the first spectral component of the frequency shift $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, image (e) corresponds to the phase shift ϕ and image (f) shows the magnitude of the second spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. As in the previous experiments presented, the phase shift ϕ and frequency shift $\Delta\nu_e$ images ((c) and (e)) show almost no corrugation. The topography z_p (a) shows two

terraces and the step edge in between. Some contamination can be guessed at the step edge and on the lower terrace (left part of the image). Unlike in the previous experiments, the topography z_p is extremely unstable, visible in the features parallel to the fast scan direction in the whole image (both terraces and step edge). The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ (image (d)) is nearly zero: only a small corrugation is can be seen in the area corresponding to the step edge. The V_{FM} image (b) shows the already mentioned variations in previous experiments: it increases and decreases parallel to the fast scan direction regardless of the specific surface area (terrace or step edge). However, this time these variations occur much more often and the magnitude of them are much larger, up to a point that, in order to include all points of the image in the colour scale, which corresponds to a range of more than 200 mV, no clear V_{FM} distribution values can be identified. Thus, it is not possible to see some correlation between the topography z_p and the V_{FM} images, as it was in previous experiments. The values displayed in the V_{FM} image correspond to a range of more than 200 mV. In this case, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ shows no corrugation. Continuing with the previous hypothesis, the presence of an unstable cluster of atoms on the apex of the tip would explain the instabilities shown in the topography z_p . Furthermore, if this cluster of atoms or contamination presents a non-neutral charged distribution, this implies having localized point charges moving between tip and sample during the scanning, which could explain the large variations and instabilities in the V_{FM} image.

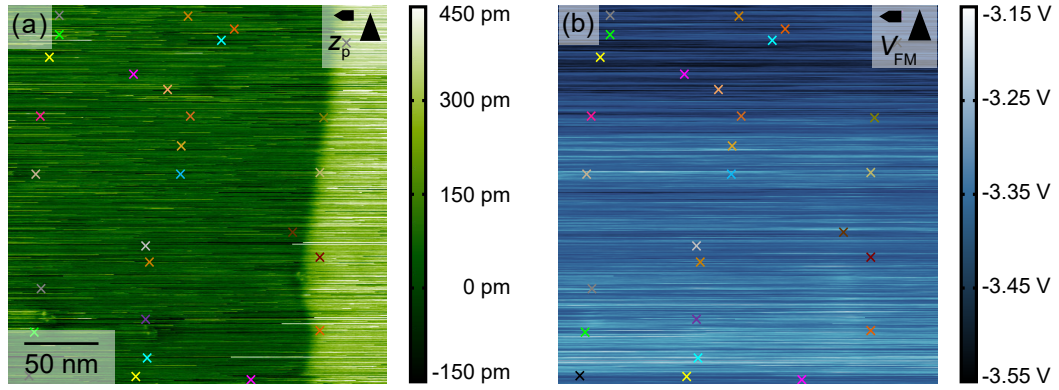


Figure 6.31.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *second* Au-coated silicon AFM tip before sputtering it. The crosses indicate the spots, where the distance-dependent curves shown in figure 6.32 were performed.

Recording the distance-dependent curves was the next part of the experiment. Figure 6.31 shows the topography z_p and Kelvin V_{FM} image, during which the distance-dependent curves were performed, and figure 6.32 show, the six different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curves in the plots relate each curve with the position, where it was performed.

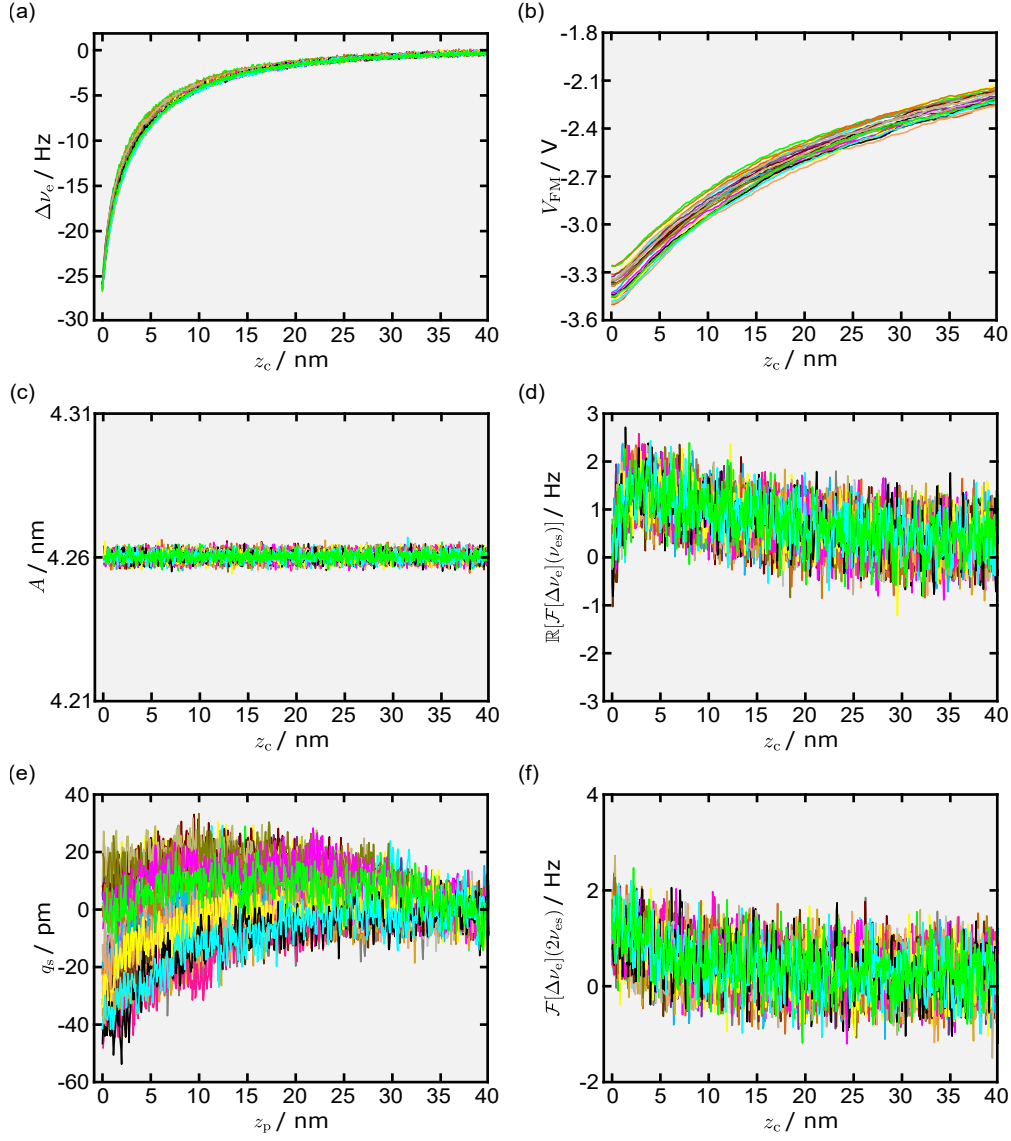


Figure 6.32.: Distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip before sputtering it. The colour of each curve correlates with the colour of the crosses in the images in figure 6.31. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A , (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, (e) shows the static deflection q_s and (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. All channels are plotted *versus* the tip center position z_c but the static deflection q_s , which is plotted *versus* the z-piezo displacement z_p .

Figure 6.32 shows the distance-dependent curves performed with the *second* Au-coated silicon AFM tip. Plot (a) shows the frequency shift $\Delta\nu_e$, plot (b) presents the Kelvin V_{FM} signal, plot (c) corresponds to the oscillation amplitude A , plot (d) shows the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, plot (e) presents the static deflection q_s and plot (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. The static deflection q_s is plotted *versus* the z-piezo displacement z_p . All the remaining channels are plotted *versus* the center position z_c . As in the previous experiments, all oscillation amplitude A curves remain constant for all tip center position z_c , so all the curves of the other quantities are

comparable to each other. All frequency shift $\Delta\nu_e$ curves overlap for large tip-sample distances, tending to 0 Hz, but most of them differ for $z_c < 20$ nm. This fact would fit with the hypothesis that the structure of the tip apex changes from curve to curve. Plot (d) shows that all the curves of the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ mostly overlap but, in this case, their values are not around 0 Hz for all tip-sample distances z_c : it was not possible to adjust the gains of the KPFM feedback loop in a way that this component was completely nullified. The curves distribute around 0 Hz for $z_c = 0$ nm; they show an increase with a large positive slope up to $z_c \sim 2$ nm and a slow decrease for the rest of the tip retraction. Then, the V_{FM} curves shown in plot (b) are not reliable for making any quantitative statement. Most of these curves do not overlap and for $z_c = 0$ nm, their values distribute within a range of ~ 300 mV, which fits with the voltage range displayed in the V_{FM} image in figure 6.31 (b). The magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ curves shows a similar behaviour as in the previous experiments: a non-linear decreasing signal with increasing the tip center position z_c . They seem to overlap and all become zero for $z_c = 10$ to 15 nm but, as before, this channel is so noisy that it is difficult to make a clear statement about it.

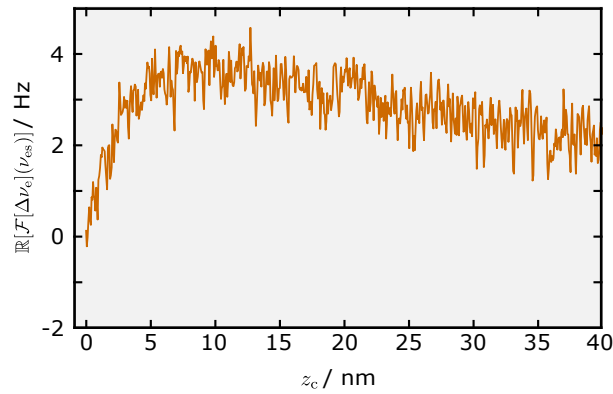


Figure 6.33.: Distance-dependent $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})](z_c)$ curve recorded on Au(111) with the *second* Au-coated silicon AFM tip. The curve was recorded while the KPFM feedback loop was disabled and a constant bias voltage $V_{bias} = -3.4$ V was applied between tip and sample.

The result of these measurements shows that the tip is contaminated and must be treated by sputtering with Ar^+ ions. However, there is still an open question: how relevant is the fact that the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ is not nullified? Figure 6.32 shows this channel in the case of a distance-dependent curve for which the KPFM feedback loop was disabled and a constant $V_{bias} = -3.4$ V was applied. The value of the $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curve for $z_c = 0$ nm is ~ 0 Hz, then the curve exhibits an increase up to $z_c \sim 5$ nm and a slow decrease for the rest of the tip retraction. This implies that the correct V_{FM} value for $z_c = 0$ nm is around -3.4 V, which fit with the curves measured in figure 6.32 (b). From there, up to $z_c = 5$ -6 nm the difference between the applied bias voltage V_{bias} value and the correct V_{FM} value increases and from there on this difference becomes smaller. The values

of the curves shown in figure 6.32 (d) are always closer to 0 Hz than the values of the curve of figure 6.33. This fact points that the values of the V_{FM} curves shown in figure 6.32 (b) are good enough to indicate approximate values and the tendency of the distance-dependent V_{FM} curves: the curves are not constant upon tip-sample variation. Since the part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ curve is not nullified, specially between $z_c = 0$ to 15 nm, it is not possible to identify or guess two different distance-dependent regimes in the V_{FM} curves, as has been done in the experiments performed with the *first* Au-coated silicon AFM tip after sputter it.

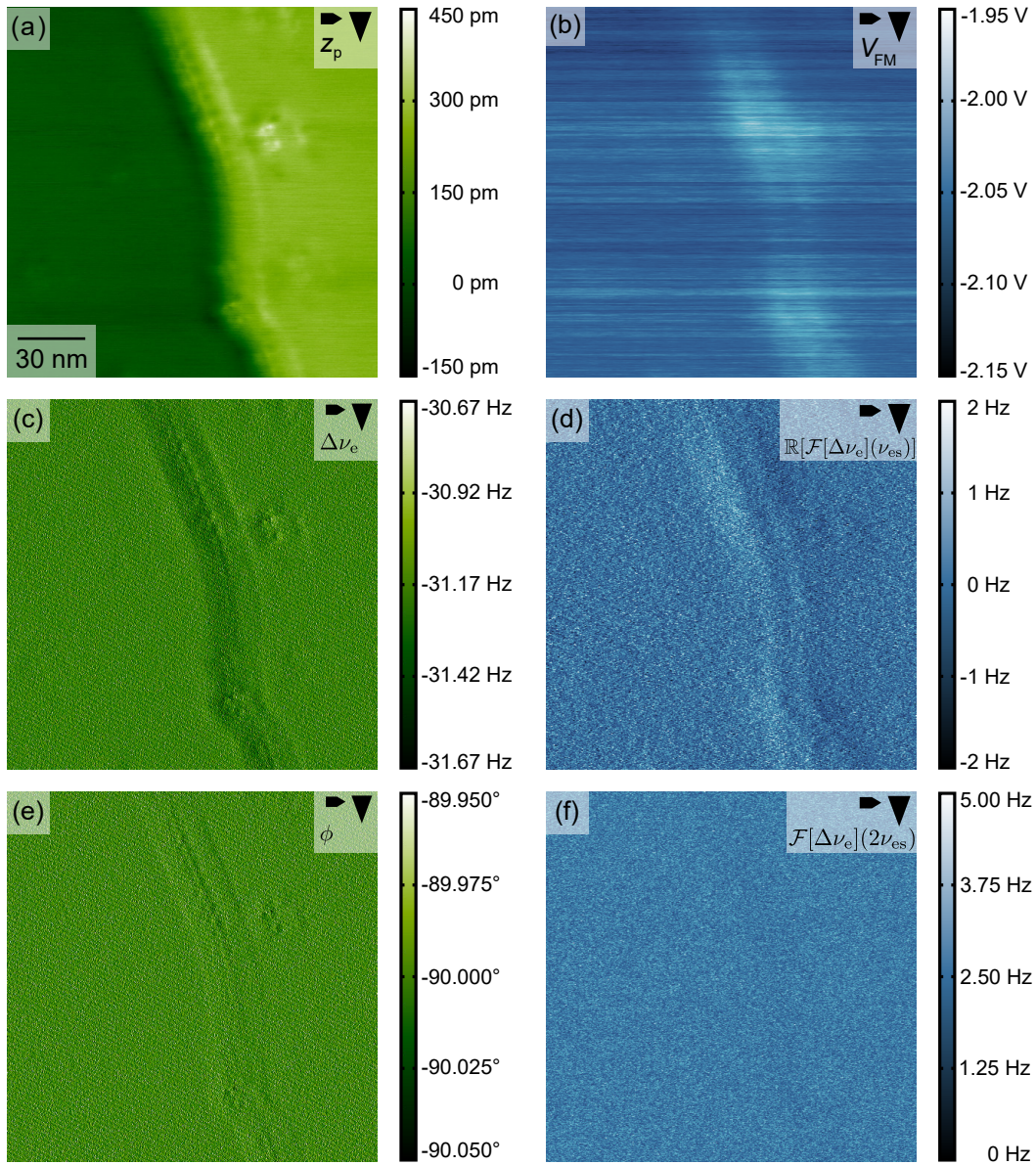


Figure 6.34.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *second* Au-coated silicon AFM tip after sputtering it for 90 s. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b), (d) and (f) show the Kelvin V_{FM} signal, the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ and the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$, respectively.

The *second* Au-coated silicon AFM tip was then sputtered with Ar^+ ions with an energy of 1.7 keV for 90 s. Right after, FM-AFM and FM-KPFM measurements were performed on the Au(111) sample. The images are shown in figure 6.34. Image (a) presents the topography z_p , image (b) corresponds to the Kelvin V_{FM} , image (c) shows the frequency shift $\Delta\nu_e$, image (d) presents the real part of the first spectral component of the frequency shift $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$, image (e) corresponds to the phase shift ϕ and image (f) shows the magnitude of the second spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. The frequency shift $\Delta\nu_e$ and phase shift ϕ images ((c) and (e)) exhibit basically no corrugation except for the area where the topography z_p shows the step edge that separates the two terraces. There is some contamination on both terraces, but the largest one is close to the step edge in the upper terrace. For this experiment, the topography z_p is really stable, unlike in the previous experiment, before sputtering the AFM tip. The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ (image (d)) exhibits some contrast in the step edge area and the aforementioned contaminations, but looks properly nullified in the rest of the image. The V_{FM} image (b) shows variations parallel to the fast scan direction, but much smaller than in the previous experiment, and it is possible to find a correlation between the topography z_p and the V_{FM} image: as in the experiments carried out with the *first* Au-coated silicon AFM tip, the terraces exhibit an uniform signal, while the areas corresponding to the step edge and the contamination present more positive V_{FM} values. Unlike in the previous experiment, the topography z_p looks very stable. Finally, as in previous experiments, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$ shows no corrugation.

After recording the images, the distance-dependent curves were performed in the same area. Figure 6.35 show the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 6.36 show the six different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curves in the plots relate each curve with the position, where it was performed.

Figure 6.36 shows the distance-dependent curves performed with the *second* Au-coated silicon AFM tip after sputter it for 90 s. Plot (a) shows the frequency shift $\Delta\nu_e$, plot (b) presents the Kelvin V_{FM} signal, plot (c) corresponds to the oscillation amplitude A , plot (d) shows the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$, plot (e) presents the static deflection q_s and plot (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. The static deflection q_s is plotted *versus* the z-piezo displacement z_p . All the remaining channels are plotted *versus* the center position z_c . All oscillation amplitude A curves are constant for all tip-sample distances z_c values, so the curves of the rest of the channels can be compared between each other. Unlike in the previous experiment, in which the frequency shift $\Delta\nu_e$ curves exhibited a clear difference depending on the spot at which they were

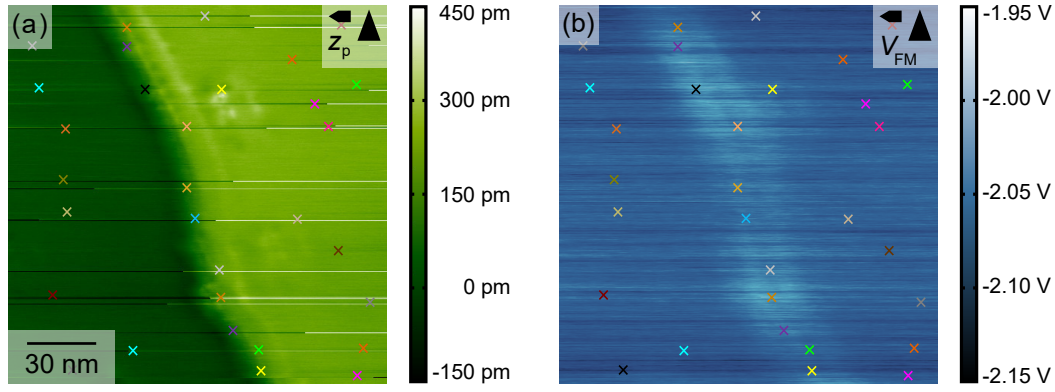


Figure 6.35.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *first* Au-coated silicon AFM tip after sputtering for 90 s. The crosses indicate the spots, where the distance-dependent curves shown in figure 6.36 were performed.

performed, in this experiment all of them overlap. Plot (d) shows that all curves of the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ are basically nullified, with their values distributed around 0 Hz. Then, the $V_{FM}(z_c)$ curves shown in plot (b) are reliable. For $z_c = 0$ nm, the values of the V_{FM} curves distribute within a 90 mV range around -2.04 V. Most of the curves show the same tendency: negative slope from $z_c = 0$ to 5-6 nm, almost constant up to 10-15 nm and positive slope from there on. This could be an indication of the tip apex to be free of localized point charges, but the curves were measure on point charges: closer to the sample the curves are not constant, but they are for larger tip-sample ditances. However, as shown in figure 6.35 (b), many of these curves were performed on the terraces, in areas where the V_{FM} signal looks homogeneous. As no molecules were sublimated on the Au(111) surface, this homogeneous V_{FM} signal cannot be due to constant point charge density. Then, the decreasing slope for the range $z_c = 0$ to 5-6 nm must still be assigned to the point charges on the tip. I cannot find a suitable explanation for the flat behaviour in the range $z_c = 5-6$ to 10-15 nm, specially considering the positive slope for $z_c > 10-15$ nm. The magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ curves, as in previous experiment, show a non-linear decreasing signal with increasing the tip center position z_c . For $z_c \sim 10$ nm, most of the curves reach 0 Hz, although as in previous experiments, this channel is very noisy and it is difficult to make a clear statement about it.

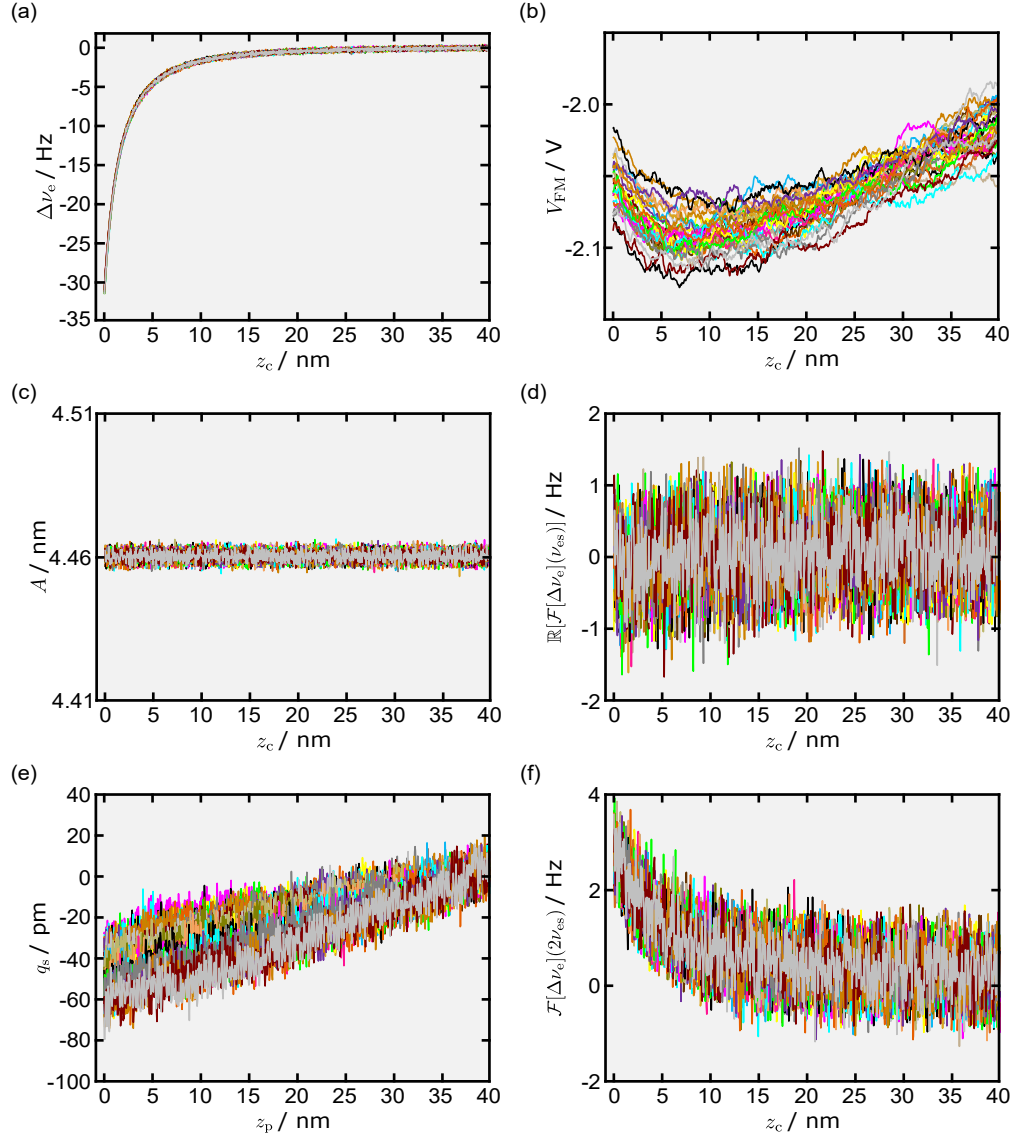


Figure 6.36.: Distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip after sputtering it for 90 s. The colour of each curve correlates with the colour of the crosses in the images in figure 6.35. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A , (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, (e) shows the static deflection q_s and (f) corresponds to the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. All channels are plotted *versus* the tip center position z_c but the static deflection q_s , which is plotted *versus* the z-piezo displacement z_p .

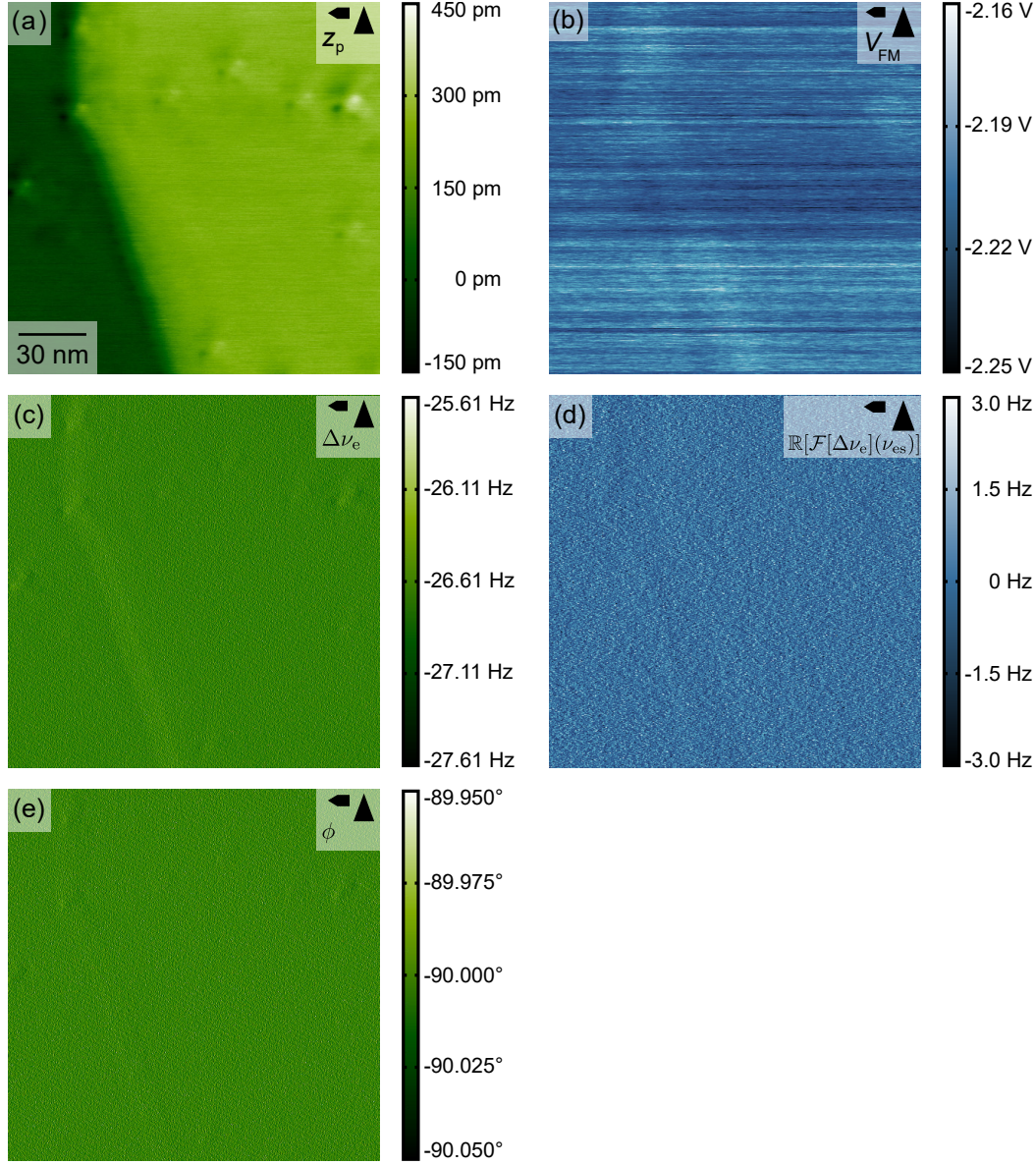


Figure 6.37.: FM-AFM and FM-KPFM images measured on Au(111) using the *second* Au-coated silicon AFM tip after sputtering it for 160 s. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

The *second* Au-coated silicon AFM tip was sputtered with Ar^+ ions with an energy of 1.7 keV for 70 s more, making a total sputtering time of 160 s. Figure 6.37 shows FM-AFM and FM-KPFM images on the Au(111) recorded using this newly sputtered Au-coated tip for 90 s. Image (a) presents the topography z_p , image (b) corresponds to the Kelvin V_{FM} , image (c) shows the frequency shift $\Delta\nu_e$, image (d) presents the real part of the first spectral component of the frequency shift $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ and image (e) corresponds to the phase shift ϕ . The frequency shift $\Delta\nu_e$ and phase shift ϕ images ((c) and (e)) show very small corrugation. The topography z_p (a) show two terraces with some adsorbates and the step edge in between. The shape of the contaminations is similar for all of them, indicating that actually it is shape of the

tip apex what appears in the images. The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ (image (d)) presents a very small corrugation in the area of the step edge, but the values distribute around 0 Hz in the rest of the image. The V_{FM} image shows many of the uniform variations parallel to the fast scan direction already mentioned in previous experiments. There are many of these variations, and their magnitude is similar to the difference between the step edge and the terraces. Nevertheless, in comparison with all previous experiments shown, the magnitude of the uniform variations is the smallest from all cases, as well as always within a small range. This is an indication of the stability of the tip apex. Furthermore, the difference in V_{FM} signal between the step edge and the terraces is the smallest from all experiments presented.

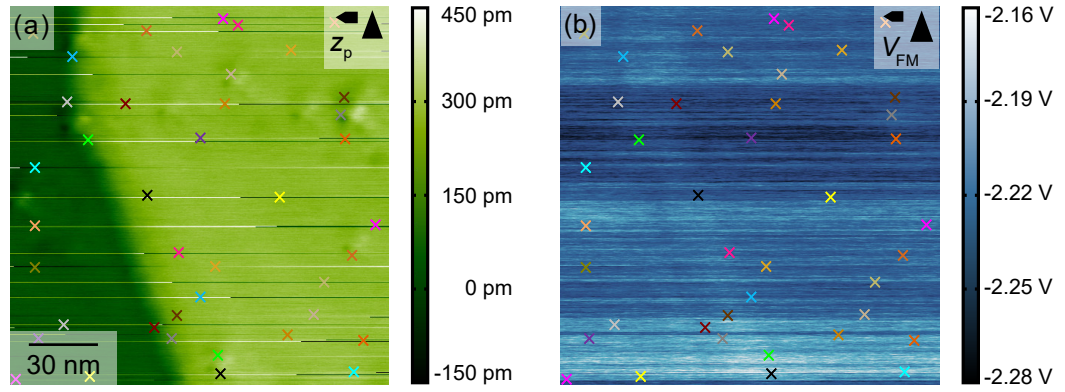


Figure 6.38.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *second* Au-coated silicon AFM tip after sputtering it for 160 s. The crosses indicate the spots where the distance-dependent curves shown in figure 6.39 were performed.

The distance-dependent curves were performed in the same area. Figure 6.38 shows the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 6.39 shows the four different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curve in the plots relate each curve with the position where it was performed.

Figure 6.39 shows the distance-dependent curves performed with the *second* Au-coated silicon AFM tip after sputter it for 90 s. Plot (a) shows the frequency shift $\Delta\nu_e$, plot (b) presents the Kelvin V_{FM} signal, plot (c) corresponds to the oscillation amplitude A and plot (d) shows the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$. All channels are plotted *versus* the center position z_c . All oscillation amplitude A curves are constant for all z -piezo displacement z_p values, so the curves of the rest of the channels can be compared between each other. This time, the frequency shift $\Delta\nu_e$ curves overlap too, showing no dependence of the place, in which they were recorded. Plot (d) shows that all the curves of the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, excluding the inherent noise, are nullified, so the $V_{FM}(z_c)$ curves shown in plot (b) are trustworthy. For $z_c = 0$ nm, the values

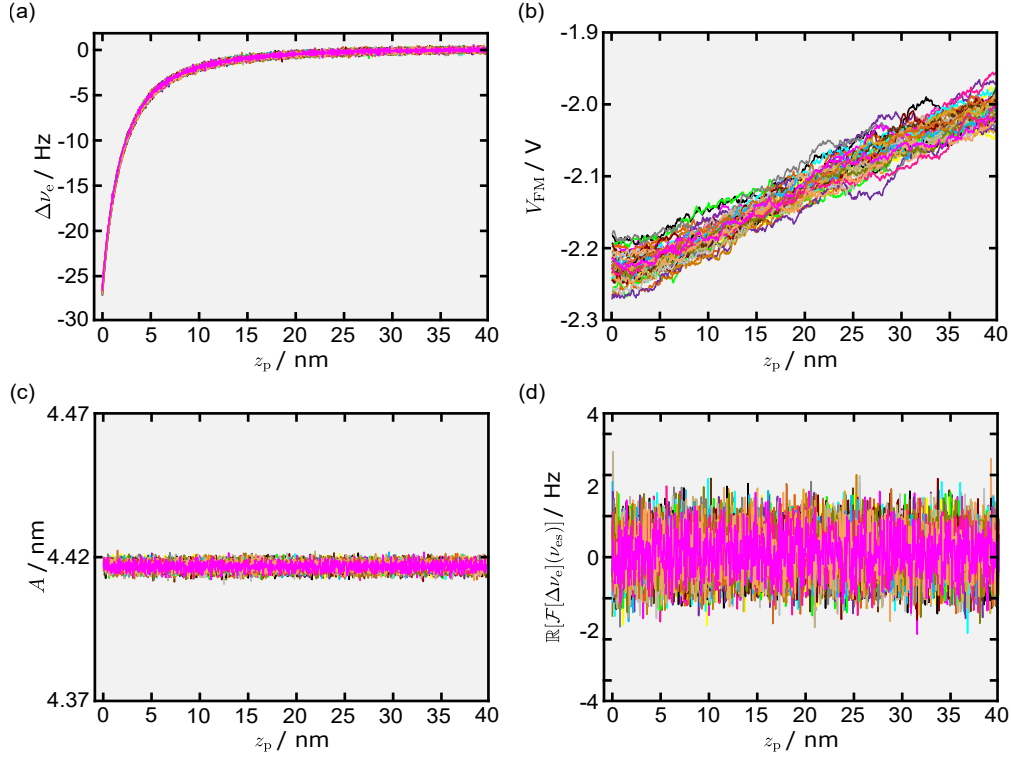


Figure 6.39.: Distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip after sputtering it for 160 s. The colour of each curve correlates with the colour of the crosses in the images in figure 6.38. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z -piezo displacement z_p .

of the V_{FM} curves distribute within a 90 mV range around -2.23 V. In this experiment, I observed two different distance-dependent regimes with respect to the tip center position z_c (from 0 to ~ 5 and from ~ 5 to 40 nm), as observed in the measurements performed with the *first* Au-coated silicon AFM tip after sputtering for 90 s and 160 s. The first one, from $z_c = 0$ to 4-5 nm, shows a flat behaviour (some curves look flat, while other ones show very small slope) and for $z_c > 4-5$ nm, the values increase with a positive slope and some curves show large and non-monotonic variations (see most negative purple curve for $z_c = 18$ to 20 nm or 25 to 30 nm or the most positive black curve for $z_c = 30$ to 35 nm). At this point, I considered the tip was already properly prepared but, in order to counter-check as I did with the *first* tip, I recorded distance-dependent curves until one of them showed this flat behaviour and then, in the same spot, recorded voltage-dependent curves to compare the V_{FM} values obtained by both techniques.

Figures 6.40 (a) and (b) show the $\Delta\nu_e$ (V_{bias}) curves, while (c) and (d) show the oscillation amplitude A (V_{bias}) curves. The plots (c) and (d) show that the oscillation amplitude A of all curves both in negative and positive sweep voltage direction are constant for all V_{bias} values, and it is the same in all curves. Then, the $\Delta\nu_e$ (V_{bias}) curves shown (plots (a) and (b)) are reliable and comparable between them.

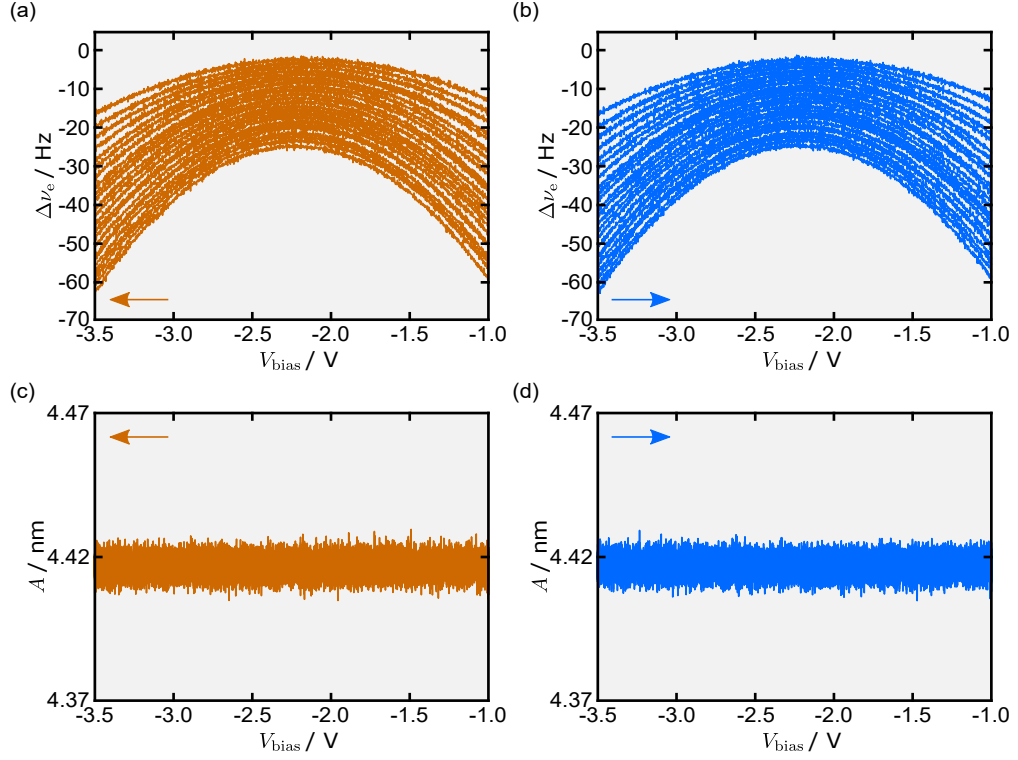


Figure 6.40.: Voltage-dependent curves recorded with the *second* Au-coated silicon AFM tip after sputtering it for 160 s. Plots (a) and (b) show the frequency shift $\Delta\nu_e(V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

Figure 6.41 (a) shows the comparison of the $\Delta\nu_e(z_p)$ curve with the contribution to the frequency shift $\Delta\nu_e(V_{\text{bias}})$ curve of the forces independent of the applied bias voltage (V_{bias}) (also referred to as fit parameter c ; see equation (6.4)). The plot (b) presents the comparison between $V_{\text{FM}}(z_p)$ curve and the V_{FM} value obtained from the $\Delta\nu_e(V_{\text{bias}})$ curves (previously mentioned as fit parameter b). The $V_{\text{FM}}(z_p)$ curve is not strictly flat, although it presents several plateaus ($z_c = 0$ to 2.5 nm, 2.5 to 4,...), in which the signal is basically constant (in the plateaus, the V_{FM} values fluctuates a few millivolts). The V_{FM} values obtained by fitting the $\Delta\nu_e(V_{\text{bias}})$ are rather similar to the $V_{\text{FM}}(z_p)$ curve for the first 5 Å, from which the values of negative and positive sweep voltage curves significantly differ and the values "jump", reproducing the plateaus but with higher values than in the $V_{\text{FM}}(z_p)$ curve. Nevertheless, I can conclude that the tip is properly prepared and can be used for carrying out KPFM experiments on molecules deposited on insulators.

The results of the experiments performed using the *second* Au-coated silicon AFM tip are summarized in figure 6.42 by showing the averages of the recorded curves. Plot (a) shows the averages of the frequency shift $\Delta\nu_e$ curves, plot (b) presents the averages of the Kelvin V_{FM} signal, plot (c) corresponds to the averages of the oscillation amplitude A and plot (d) show the averages of the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})$. The channels of the first and second

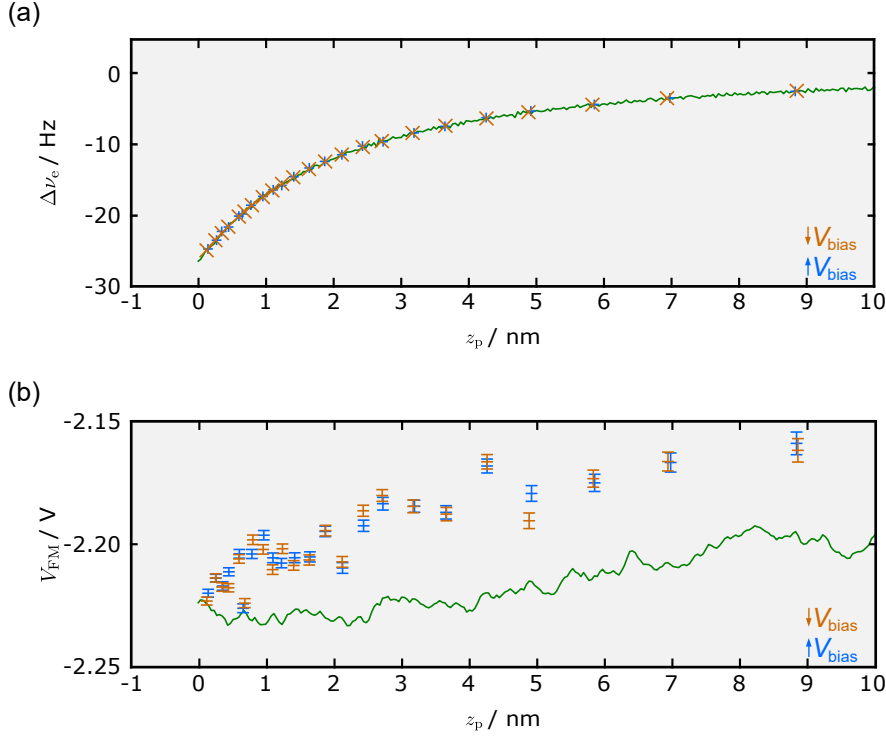


Figure 6.41.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{FM}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{bias})$ curves of figure 6.40 (a) and (b), which were performed after sputtering the *second* Au-coated silicon AFM tip for 160 s. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

experiment (in blue and orange) are plotted *versus* the center position z_c . In the last experiment (after sputtering the *second* Au-coated silicon AFM tip for 160 s), the static deflection q_s and the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ were not recorded. Then, the quantities of the last experiment are plotted *versus* the z-piezo displacement z_p and there are not averages of curves of this experiment of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ in plot (d). The averages of the oscillation amplitude A (plot (c)) of the three experiments are constant for all z_c/z_p values, since all the individual curves of each experiment are also constant. The values of the three experiments are not exactly the same: the oscillation amplitude A of the first experiment differs from the other two more than 150 pm which, in turn, present a difference of 50 pm. Thus, the first experiment can only be used for a qualitative comparison with the other two. This time, the average curves of the frequency shift $\Delta\nu_e$ (plot (a)) do not overlap, specifically the average of the curves of the experiment before sputtering the tip (in blue). A possible explanation is that the different oscillation amplitude A of the three experiments provide different $\Delta\nu_e$ (see equations (2.7) and (2.8)), since the $\Delta\nu_e$ curves, which almost overlap, correspond to the ones with oscillation amplitude A with a difference of only 50 pm. However, the clear instabilities during the measurements of the first experiment (figures 6.30 (a) and 6.31 (a)) and which were not present after sputtering the tip suggest a possible effect of the sputtering on the tip apex structure. This would lead

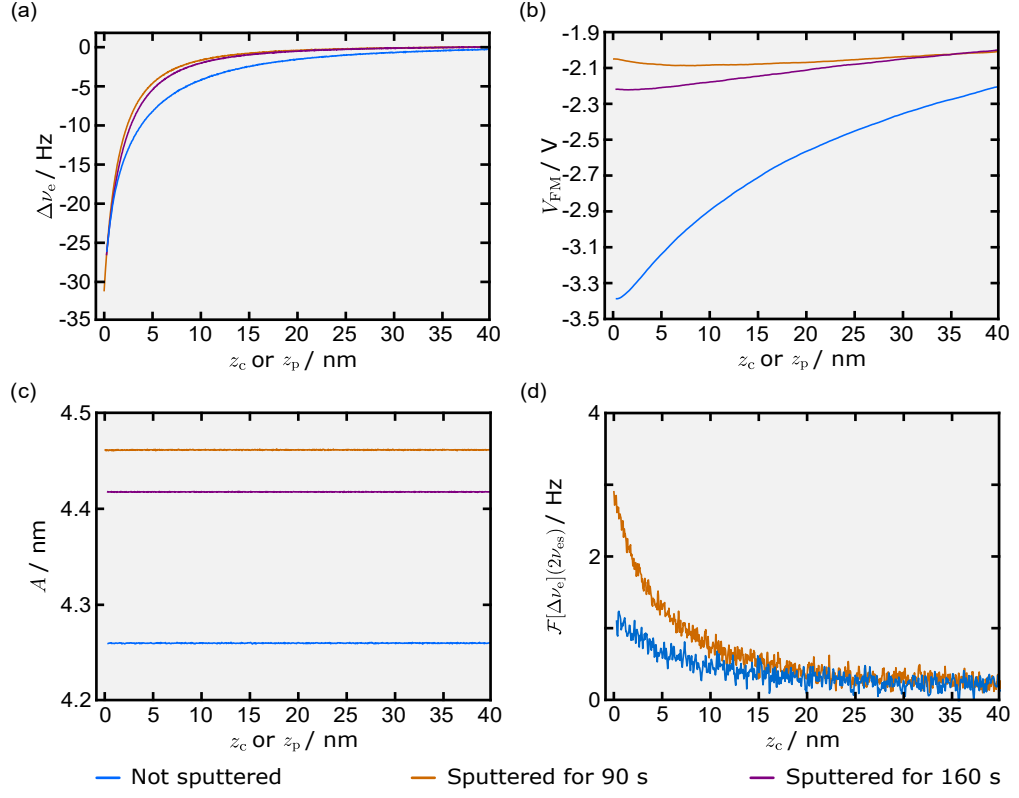


Figure 6.42.: Comparison of the averaged distance-dependent curves of the experiments with the second Au-coated silicon AFM tip. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$. The curves corresponding to the experiment using the Au-coated silicon AFM tip before sputtering it are plotted *versus* the z-piezo displacement z_p , while the two experiments carried out after sputtering the tip are plotted *versus* the tip center position z_c . Furthermore, the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ was not recorded for the experiment using the Au-coated AFM silicon tip after sputtering it for 160 s, which is the reason why it is not included in plot (d).

to a different interaction for the same tip-sample distance which implies different $\Delta\nu_e$. Regarding the averages of the V_{FM} curves, there is a large variation of the $V_{FM}(z_c/z_p = 0 \text{ nm})$ value for the curves before and after sputtering the tip for 90 s. The measurement performed after sputtering the tip for a total time of 160 s exhibits a more negative value than in the previous measurement, and a higher slope. This time, only two out of the three averaged V_{FM} curves (after sputtering 90 and 160 s) show the two previously noted different regions: one for $z_c/z_p = 0$ to 5-6 nm, where the averages show a flat or slightly negative slope, and another region from $z_c/z_p = 5-6 \text{ nm}$ on, where the averages show a positive slope. Finally, the averages of the magnitude of the second spectral component $\mathcal{F}[\Delta\nu_e](2\nu_{es})$ (plot (d)) exhibit a clear different behaviour. A plausible explanation is the effect of the sputtering on the apex of the tip, since this channel is related to the capacitance gradient (see section 2.4.3) and the capacitance between two conductors depends on their geometry.

The results of the experiments using both Au-coated silicon AFM tip point towards the fact that after preparing them up to a point in which the distance dependent V_{FM} curves show a constant signal. However, from the range of z_c or z_p values measured, the V_{FM} signal is only constant for the part of this range closer to the sample surface. For large tip center positions z_c (or z-piezo displacement z_p), the values of all recorded curves show a positive tendency upon increasing z_p . Although I have not found a clear explanation for this behaviour, the current hypothesis is that the $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$ signal is larger than the noise level only for few nanometres close to the sample surface. I continued the work this assumption and consider the procedure appropriate for preparing the Au-coated silicon AFM tips for performing KPFM experiments on molecules. Using the sputter gun ISE 5, the parameters are an Ar partial pressure of $3 \cdot 10^{-6}$ mbar with an energy of 1.7 keV for 160 s.

Later on, no tips could be properly prepared with the sputter gun ISE 5: the drain current measured during the sputtering procedure to check the reproducibility varied from attempt to attempt and even during the same one. The purity of the Ar line was checked as described in section 6.2, but it was clean. No evident cause of these fluctuations was found. However, another two Au-coated tips were found optimal for KPFM measurements on molecules: during scanning on the Au(111) sample, some contamination or adsorbates dropped off from the tip to the surface. After this, distance-dependent curves were recorded. As in the experiments performed using the *first* and *second* tips, from the range of z_c or z_p values measured, the V_{FM} signal is only constant for the part of this range closer to the sample surface (this is, from 0 to 5 to 10 nm). This data can be found in appendix C. Finally, I unmounted the sputter gun ISE 5 and mounted the sputter gun ISE 10. I could not assume that the parameters for preparing the Au-coated tips found for the ISE 5 were valid for the ISE 10. It was proved to be possible to prepare Au-coated silicon tips with the sputter gun ISE 10, but it was done on an previously prepared tip, which was contaminated after measurements on calcite. This data will be presented in the next chapter.

6.5 Stability of Au-Coated Silicon AFM Tips

In the previous paragraph I have presented the V_{FM} data extracted from voltage-dependent $\Delta\nu_e(V_{\text{bias}})$ curves as a counter-check of the closed-loop FM-KPFM data. However, using these curves for obtaining quantitative information is not always straightforward or even possible.

I can consider the situation of an AFM tip placed at a distance z_c from a sample surface. Between them, there are N point charges fixed at positions $\mathbf{r}_i$. Sweeping the bias voltage V_{bias} applied between tip and sample should result in a parabolic

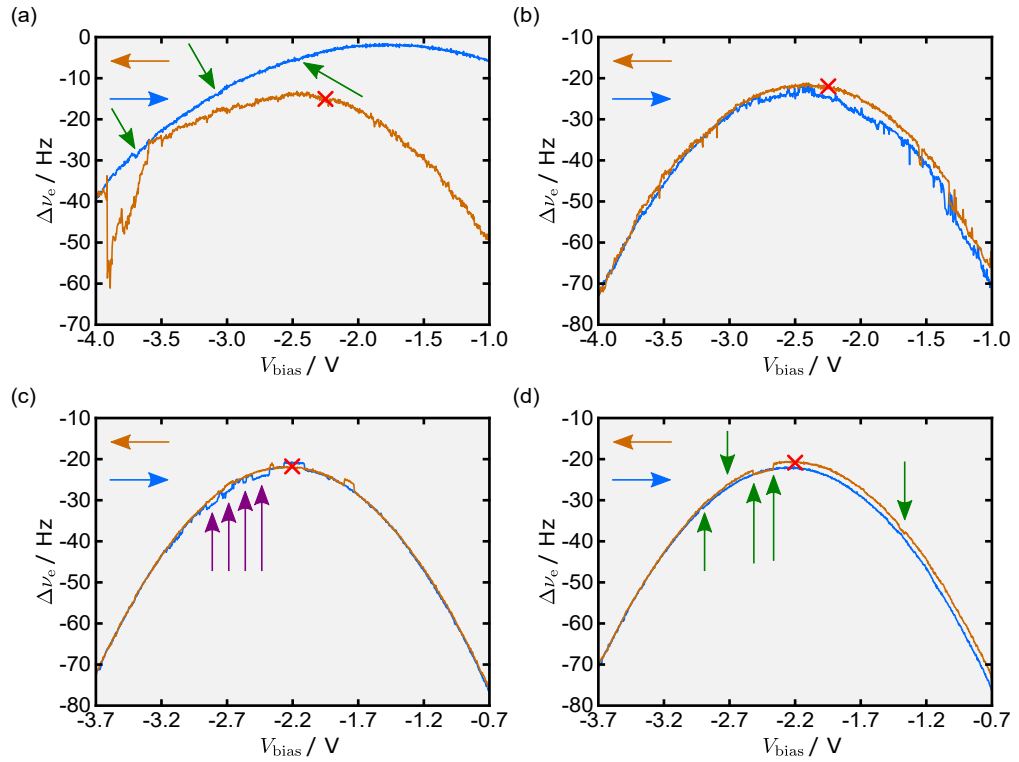


Figure 6.43.: Voltage-dependent $\Delta\nu_e$ (V_{bias}) curves, which exhibit instabilities. The negative sweep voltage curves are plotted in orange colour, while the positive sweep voltage curves are plotted in blue colour. The red crosses correspond to the V_{bias} value and $\Delta\nu_e$ setpoint, indicating the tip-sample interaction right before the curves were performed. The purple arrows in plot (b) indicate some curve segments between jumps. The green arrows in plot (a) and (d) indicate jumps in the curves.

frequency shift $\Delta\nu_e$ curve, as described in section 2.4.3. The position of the vertex of the parabola in the horizontal coordinate defines the V_{FM} value, which minimizes the tip-sample electrostatic interaction. For this V_{bias} value, the frequency shift $\Delta\nu_e$ (V_{FM}) value corresponds to the position of the vertex in the vertical coordinate. This frequency shift is caused by the non-electrostatic forces and by the non-voltage dependent term, which correspond to the contribution due to the image charges (see equation (2.26)). The theory does not show any influence of the resulting variation of the interaction on the sweep direction (from negative to positive values or vice versa). Applying this to an experiment implies that two $\Delta\nu_e$ (V_{bias}) curves performed for the same conditions (same point of the surface, V_{bias} value and $\Delta\nu_e$ setpoint) and within the same voltage range but in opposite sweep directions should result in two parabolas that overlap. However, during the experiments described in this chapter (which were performed with Au-coated silicon AFM tips on a Au(111) single crystal, *i.e.*, the most simple situation, namely a metallic tip and a metallic sample) this was not always been the case.

Figure 6.43 shows four different examples of $\Delta\nu_e$ (V_{bias}) parabolas. The plot (a) shows an extreme case of instabilities in the tip-sample system. The curves do not overlap. The negative sweep voltage curve, in orange (from positive to negative

values), exhibits a parabolic shape from -1.0 to ~ -3.5 V and passes through the red cross, which defines the V_{bias} value and $\Delta\nu_e$ setpoint of the tip-sample system before performing the curve. From -3.5 V to -4.0 V, it presents several jumps. The positive sweep voltage curve, in blue (from negative to positive values), exhibits parabolic behaviour, although it presents jumps around -3.6 V, -3.0 V and -2.5 V (indicated with green arrows). However, the positive sweep voltage curve does not pass through the red cross this time, indicating an important change in the tip-sample system. The negative and positive sweep voltage curves shown in plot (b) correspond to a much more stable situation, both curves present parabolic shapes. The curves recorded in both directions exhibit a large jump around -1.35 V and small jumps and spikes in the whole voltage range. These instabilities prevent to get reliable information by fitting the curves. The curves shown in plots (c) and (d) represent more stable situations, showing many small jumps, but almost no spikes. From this point on, I will refer to the parts of the curve parabolas delimited between two jumps as curve segments or just segments. Most of the segments of the four curves present a parabolic behaviour, with the exception of few spikes.

In some previous works, the voltage-dependent $\Delta\nu_e(V_{\text{bias}})$ curves have been used to characterized the charge state of single atoms or molecules. Gross *et al.* [23] performed STM and FM-AFM measurements on single Au atoms deposited on bilayer NaCl films grown on Cu(111). They changed the charge state of the Au atoms by applying bias voltage pulses, and studied different tip-sample interactions by recording $\Delta\nu_e(V_{\text{bias}})$ curves before switching the charge state of the atom. The result were two different $\Delta\nu_e$ parabolas, one for the neutral atom and one for the negatively charge atom: the difference in the horizontal coordinate (different V_{FM} value) indicates a different distribution of the charges on the system, while the difference in the vertical position (different $\Delta\nu_e(V_{\text{FM}})$ value) a different image charges contribution. In a later work, Steurer *et al.* [24] performed similar experiments on single Au atoms, too. This time, they showed the jumps in the $\Delta\nu_e(V_{\text{bias}})$ curves for specific V_{bias} values, attributing those changes to single-electron tunnelling from the Au atom to the metallic tip and vice versa. Later, Steurer *et al.* [26] reported a similar experiment in a more complicated system: pentacene molecules deposited on 13 and more than 20 ML-thick NaCl films growth on Cu(111). Sweeps in bias voltage V_{bias} resulted in detectable jumps in the frequency shift $\Delta\nu_e(V_{\text{bias}})$ which were abscribed to single electron transfer from the tip to the sample, vice versa or to the HOMO and LUMO levels of the molecule. Furthermore, the tunnelling of electrons between molecules nearby each other could also be detected. Leoni *et al.* [115] used the same procedure to characterized the charge state of a molecular switch: the $\Delta\nu_e(V_{\text{bias}})$ curves provided different values for V_{FM} and $\Delta\nu_e(V_{\text{FM}})$ depending on the charge state of the molecule. All these experiments in different species indicate that the change in the charge distribution within the tip-sample system can cause sudden variations or jumps in the frequency shift $\Delta\nu_e$ signal. The

problem with the experiments described in this chapter is that they were performed using a metal-coated tip on a metallic substrate, which should provide, as explained before, a perfect parabola with no jumps. The jumps and spikes in the frequency shift signal indicate the presence of unknown species in the tip-sample system. If the unknown species or contaminations are on the sample, performing a $\Delta\nu_e(V_{\text{bias}})$ curve at a different spot of the surface should result in the expected parabolic curve. However, if this is not the situation, it is fair to assume that the instabilities originate from the tip: this would be a hint of the presence of contaminations in the tip apex or an unstable cluster of metal coating, and the need of preparing the tip before moving to KPFM experiments on molecules.

Both negative and positive sweep voltage curves in figure 6.43 (c) and (d) present small jumps. It is possible to fit each one of the segments to a parabolic curve, although the accuracy of the extracted information depends of the length of the segment and the noise in it. The larger the segment, the more accurate will be the fit parameters extracted (more points to fit). The noisier the curve, the less accurate the fit parameters are (the total signal measured will deviate more from the electrostatic interaction). In order to get more reliable fit parameters, different segments, which are not consecutive and correspond to the same tip-sample system configuration (same tip-sample distance z_c , same number of charges N and same charge positions r_i) can be fitted as one segment. However, the difficulty is to identify whether they really correspond to the same tip-sample system configuration. In plot (c), the purple arrows indicate four segments of the positive sweep voltage curve which seem, at first sight, to correspond to the same configuration. Nevertheless, after taking a closer look, I would suggest that segments 1 and 4 correspond to same configuration, but 2 and 3 correspond to another one. In other words, the complication of getting reliable information from fitting small different segments together is the uncertainty of identifying whether the segments correspond to the same configuration.

Figure 6.44 shows a $\Delta\nu_e(V_{\text{bias}})$ curve, which present small jumps. The negative sweep voltage curve is displayed in (a), while the positive sweep voltage curve is shown in (b). The jumps presented in the negative sweep voltage curve (plot (a)) are difficult to identify, since their magnitudes are not large, but are comparable to the level of noise. The results of the fits are presented in table 6.2. The three values for V_{FM} are within a range of 330 mV (including errors), while the ones for the $\Delta\nu_e(V_{\text{FM}})$ vary in a range of 1.21 Hz (also including errors). Although the difference of the fit parameters is not extreme, a variation of 330 mV in the V_{FM} value is too large. Furthermore, the error⁷ of the $\Delta\nu_e(V_{\text{FM}})$ value corresponding to the third configuration is very large, specially when compared with the error of the V_{FM} for the other two configurations. This is a clear hint that the fit corresponding

⁷The error, as explained in the previous paragraph, is defined by the length and noise of the segment fitted.

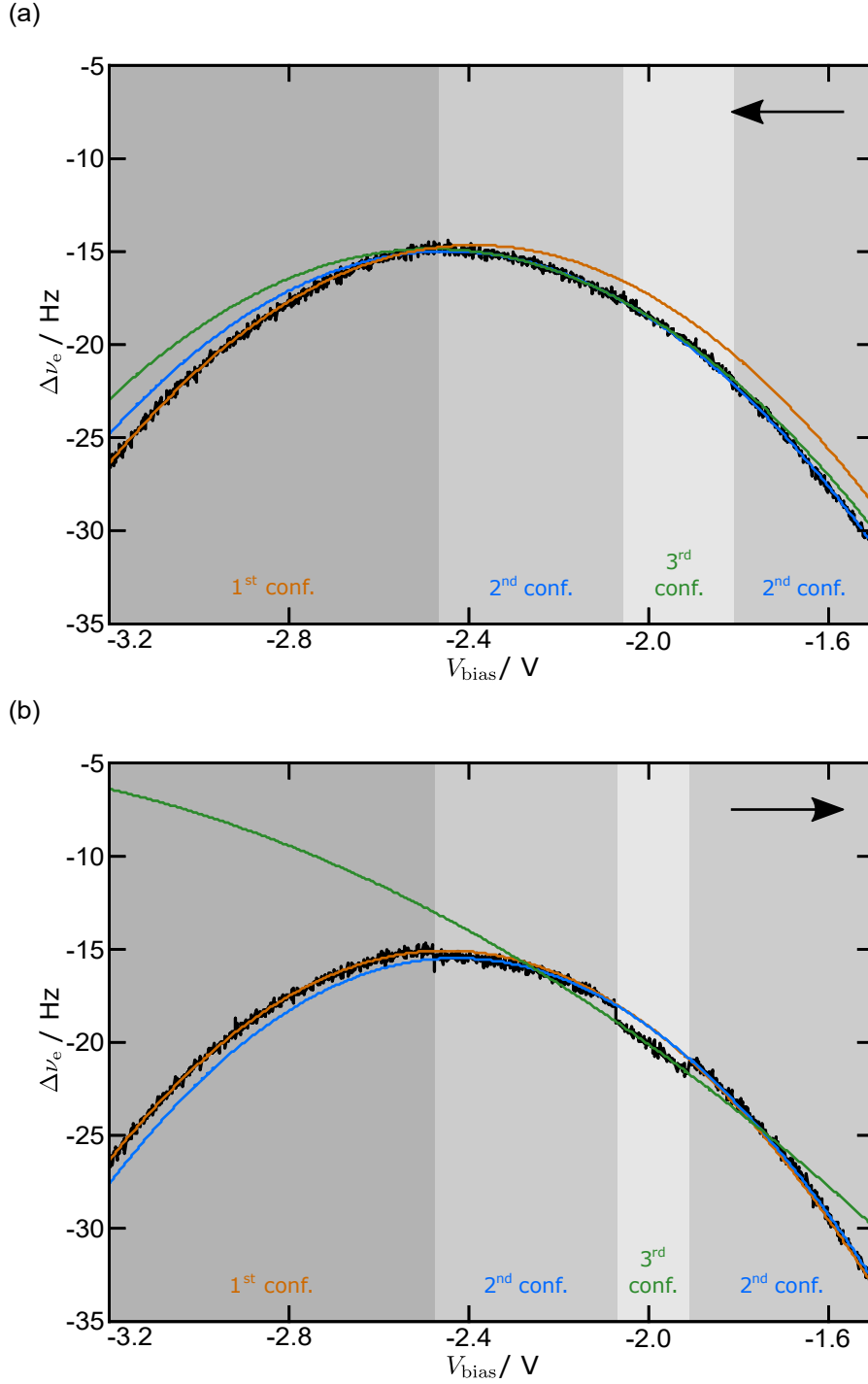


Figure 6.44.: Voltage-dependent $\Delta\nu_e$ (V_{bias}) curves which present some jumps. The negative sweep voltage curves is presented in (a), while (b) corresponds to the positive sweep voltage curve. The experimental curves are presented by the black line. The arrow in the upper right corner of each plot indicates the direction of the V_{bias} sweep. Different segments are considered in both curves due to the jumps. Segments which are considered to be part of the same tip-sample system configuration have the same grey level in the background. The parabolic fits are presented in colours, which correspond to the colour of the configuration (conf. states for configuration) indicated in the lower part of the plots.

to the third configuration is not good, and the information provided by it is not reliable. The positive sweep voltage curve (b) shows several jumps, but in this

case, they are clearly larger than the noise and, therefore, easier to identify. The results of the fits are presented in table 6.3. The parabolic fits of the first and second configuration provide V_{FM} values within a range of 32 mV (including errors) and $\Delta\nu_e$ (V_{FM}) values within 0.37 Hz difference (including errors), both values with rather small errors. However, the striking case is the third configuration. Its corresponding segment presents a reasonable curvature. Nevertheless, it is not very long and the noise level is quite large. This is clear disadvantage for the fit, which provides a parabola very different from the other two: both V_{FM} and $\Delta\nu_e$ (V_{FM}) values are considerably different than for the first and second configurations, and the errors of the fit parameters are larger than their value itself. This is a clear example of the low reliability of obtaining quantitative information by fitting short segments of data points with large noise.

Configuration	V_{FM}	$\Delta\nu_e$ (V_{FM})
First configuration	-2.38 ± 0.01	-14.72 ± 0.07
Second configuration	-2.446 ± 0.009	-15.04 ± 0.05
Third configuration	-2.5 ± 0.2	-14 ± 2

Table 6.2.: Fit results of the negative sweep voltage curve presented in figure 6.44 (a).

Configuration	V_{FM}	$\Delta\nu_e$ (V_{FM})
First configuration	-2.45 ± 0.01	-15.13 ± 0.07
Second configuration	-2.422 ± 0.006	-15.53 ± 0.04
Third configuration	-3 ± 8	-4 ± 70

Table 6.3.: Fit results of the positive sweep voltage curve presented in figure 6.44 (b).

The previous examples are useful to understand the reliability of the fit parameters. Nevertheless, for experiments as the ones presented in this chapter, with the aim of preparing metal-coated tips and test them in a metallic substrate, the take-home message is simpler: $\Delta\nu_e$ (V_{bias}) curves performed on a metallic substrate (in a clean area with no adsorbates) using a metal-coated tip must provide a perfect parabola with no jumps. If there are instabilities or large jumps, the tip apex is not clean or stable and must be treated. If there are small jumps and/or features difficult to distinguish from the noise, it is still possible to fit the whole parabola as a single segment and get a reliable quantitative information, providing fit parameters values, which would be in between the corresponding ones of the individual segments. This was the procedure followed in the static FM-KPFM measurements (recording voltage-dependent $\Delta\nu_e$ (V_{bias}) curves) for counter-checking the close-loop Kelvin V_{FM} (z_c/z_p) curves, presented in figure 6.27 and 6.41.

The last remark about using $\Delta\nu_e(V_{\text{bias}})$ curves with quantitative aim is related with drift in Z-direction. Figure 6.45 shows two consecutive $\Delta\nu_e(V_{\text{bias}})$ curves recorded in the same spot of the Au(111) surface: in (a), the negative sweep voltage curve was recorded before, while in (b), the first curve recorded was the positive sweep voltage curve. In plot (a), the negative sweep voltage curve almost passes through the red cross, which indicates the bias voltage V_{bias} value and frequency shift $\Delta\nu_e$ setpoint set right before performing the curve. For $V_{\text{bias}} = -4.0$ V (the value which delimits the lower voltage extreme), both negative and positive sweep voltage curves overlap. After that, the positive sweep voltage curve always presents more negative values than the negative sweep voltage curve. When a second curve was performed in the same sample surface spot, but inverting the order of the V_{bias} sweep direction (plot (b)), the same characteristics were observed, but in the opposite sense: the positive sweep voltage curve almost pass through the red cross, both negative and positive sweep voltage curve overlap for $V_{\text{bias}} = -1.0$ V (the value which delimits the upper voltage extreme) and the negative sweep voltage curve always presents more negative values than the positive sweep voltage curve. This means that the interaction for each V_{bias} value was larger (the frequency shift $\Delta\nu_e$ was smaller) for the second curve than for the first one, which indicates that the tip apex was approaching towards the sample surface. In order to get reliable information from this type of measurements, drift in Z-direction must be reduced as much as possible: by waiting long enough or using an atom-tracking system. Otherwise, the points of the curves will be recorded for different tip center positions z_c , and the data extracted from the fit will not be reliable.

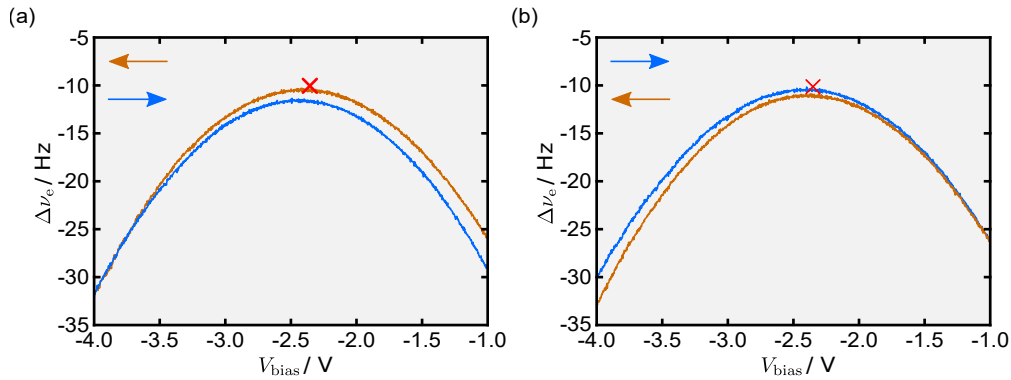


Figure 6.45.: Voltage-dependent $\Delta\nu_e(V_{\text{bias}})$ curves which exhibit drift in Z-direction. The negative sweep voltage curves are plotted in orange colour, while the negative sweep voltage curves are plotted in blue colour. The red crosses correspond to the V_{bias} value and $\Delta\nu_e$ setpoint, indicating the tip-sample interaction right before performing the curves.

6.6 Summary

A Au(111) single crystal was needed as a test sample for preparing metal-coated silicon AFM tips. Its preparation has been discussed. The size and position of the ion beam was checked by long-time exposure photographs and adjusted to only sputter the gold sample surface. The first single crystal was contaminated and not suitable for the required purposed. A second single crystal was purchased. This time, in order to avoid all possible contamination sources, the quality of the Ar gas was checked. This inspection concluded that the Ar line was clean and only this gas was present in the line. The ion beam size was adjusted in the same way as with the first single crystal. After sputtering the sample, STM images of the surface were recorded, with the conclusion that the Ar^+ ions were hitting the sample surface. After this, the Au(111) could be properly prepared, as proven by the herringbone reconstruction.

The noise and possible periodical oscillations present in the KPFM channels was discussed. I have discussed when it is appropriate to filter out the periodical oscillations which might present in these channels, which depends in identifying the source of the noise itself. The noise introduced by electrical noise, mechanical vibrations or feedback operations shows different orientation in different scan directions. Respect to the real part of the first spectral component of the frequency shift $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{\text{es}})]$, in closed-loop FM-KPFM, if the KPFM feedback loop operates properly, all values in these images must be distributed around 0 Hz. Because of this, filtering out the noise and/or the periodical vibrations does not have relevant implications. Furthermore, I have also discussed the meaning of the real part of the first spectral component $\Re [\mathcal{F} [\Delta\nu_e] (\nu_{\text{es}})]$. In correct KPFM feedback loop operation, there is a range of few tens of millivolts for which this channels is minimized. Within this voltage range, only one bias voltage V_{bias} value is the correct V_{FM} value, but I have no possibility of clarifying which one. I assume this range as the error of the Kelvin V_{FM} signal. Periodical oscillations that can also appear in the Kelvin V_{FM} signal. They can be due to the tip-sample interaction (for example, periodic molecular structures with a specific charge distribution that can appear as a vibration). Only if the tip-sample interaction is ruled out as the source the periodical oscillation can be filter out.

After that, it is enough to check that the contribution of the vibration to the image is not significant. The noise in the experimental system masks the small values of the magnitude of the first spectral component $\mathcal{F} [\Delta\nu_e] (\nu_{\text{es}})$, which makes it difficult to state whether this signal is nullified during KPFM feedback operation. This implies an unavoidable uncertainty about the question whether the applied bias voltage V_{bias} can be considered as the value which minimizes the electrostatic interaction between tip and sample, V_{FM} . In this work, it was considered as the appropriate value.

Experiments using Au-coated silicon AFM tips were performed on one Au(111) single crystal. The goal of those experiments was finding appropriate sputtering parameters to prepare these Au-coated tips before using them in KPFM experiments on molecules. The AFM tips would be ready when the V_{FM} signal upon varying tip-sample distance remains constant. I have recorded no distance-dependent V_{FM} curve which is constant for all the z_c or z_p range measured. On the contrary, I could obtain V_{FM} curves which are constant only for a part of the z-piezo displacement z_p range measured. This range of the z-piezo displacement z_p is actually the one closer to the sample. In electrostatics, all known models are inverse with the distance. Because of this, I have assumed that the partially constant V_{FM} curves are a reasonable indication of tip apex are free of localized point charges.

The stability of the Au-coated silicon AFM tips was discussed. Frequency shift *versus* bias voltage $\Delta\nu_e$ (V_{bias}) curves which present non-parabolic shape, large jumps or spikes indicate the instability of the tip used. This tip needs to be prepared. Small jumps are only detectable only if they are larger than the level of noise. It is possible to get quantitative information about the tip-sample electrostatic interaction by fitting this curves. Nevertheless, fitting curves with small jumps can be useful for qualitative discussions of the tip-sample electrostatic interaction.

KPFM Experiments: Calcite (10.4) and 2,5-DHBA on Calcite (10.4)

Contents

7.1	Introduction	111
7.2	Experiments on Calcite (10.4)	112
7.3	Experiments on 2,5-DHBA Deposited on Calcite (10.4)	133
7.4	Information About the Au-Coated Tips Used	154
7.5	Summary	156

7.1 Introduction

The goal of this work is preparing a suitable procedure to perform KPFM experiments on molecules deposited on bulk insulating substrates. In chapter 2, the model used for describing the tip-sample electrostatic interaction, referred to as the Kantorovich equation, has been explained. Using this as starting point, the main steps to follow for preparing and performing a quantitative FM-KPFM experiment were explained in chapter 5. One of the key elements of the experiment was described in chapter 6: finding out the preparation parameters of metal-coated AFM tips. Now, in this chapter, it is time to put all this together and use it for quantitative FM-KPFM experiments.

The first subjects to study is bare calcite. Our main interest when performing KPFM experiments on molecules deposited on thick insulators is studying the charge distribution within the molecular structures. However, it should not be discarded the influence of point charges on or within the calcite substrate to the total Kelvin V_{FM} signal. For this reason, it is interesting study separately the bare calcite by KPFM experiments.

The second target of the experiments is 2,5-DHBA deposited on calcite. KPFM experiments have already been performed in our group on this molecule by regular imaging [19] and by distance-dependent measurements [20, 37]. However, these

studies were not performed using metal-coated tips prepared and tested as described in chapter 6. In this chapter, I present two different experiments and use the same method to disentangle the contributions from calcite and molecules used by Neff *et al.* [37].

During all these experiments on calcite and on molecules, I had to check the state of the Au-coated tips before and after experiments. As previously discussed, when the tips are free of localized point charges, they are supposed to provide a constant V_{FM} signal upon z-piezo position z_{p} variation. At the end of the chapter, I include a small summary and discussion about the constant V_{FM} values provided by the different tips employed.

7.2 Experiments on Calcite (10.4)

The goal of this work is to study the V_{FM} signal of molecular structures deposited on thick insulators. This V_{FM} signal will have contributions from all point charges between the metallic tip and the metallic counter-electrode. Thus, although our main interest is studying the V_{FM} signal due to the molecular structures, I cannot ignore the contribution from the thick insulating substrate. In order to understand the V_{FM} signal provided by the bare substrate, I have performed three different experiments on calcite (10.4) without depositing molecules on top. The three already prepared Au-coated silicon AFM tips (described in section 6.4 and referred to as *second*, *third* and *fourth*) have been employed in these experiments.

The preparation of all calcite samples is described in the following. Right after transferring the calcite crystal to the UHV chamber, it was outgassed by annealing at ~ 580 K for 120 minutes. Then, the crystal was cleaved *in situ* and, in order to remove surface charges [52], annealed at ~ 520 K for 60 minutes. Before engaging the KPFM feedback, I usually perform standard FM-AFM measurements. This course of action allows to scan faster¹, so it is quicker to find a well suitable spot on the surface to measure on. At the beginning of the experiment, I perform $\Delta\nu_{\text{e}} (V_{\text{bias}})$ curves in order to determine an approximate V_{FM} value (the position of the maximum). This value is applied between tip and sample, so the electrostatic interaction is minimized. During most of the experiments on calcite performed in this group, as long as the tip-sample distance was not varied, the V_{FM} value remains unchanged and the contrast in the topography does not change. Lately, for a long period, when performing these $\Delta\nu_{\text{e}} (V_{\text{bias}})$ curves, we have observed drastic changes in the position of the maxima between two consecutive curves, independently of

¹Remember that, due to the electronics settings, the chosen electrostatic excitation frequency ν_{es} is 988 Hz. In order to measure two complete cycles, the time per point must be, at least, 2 ms plus extra time for the KPFM feedback to act.

the relative position where they were recorded. In the following, I explain this two different situations.

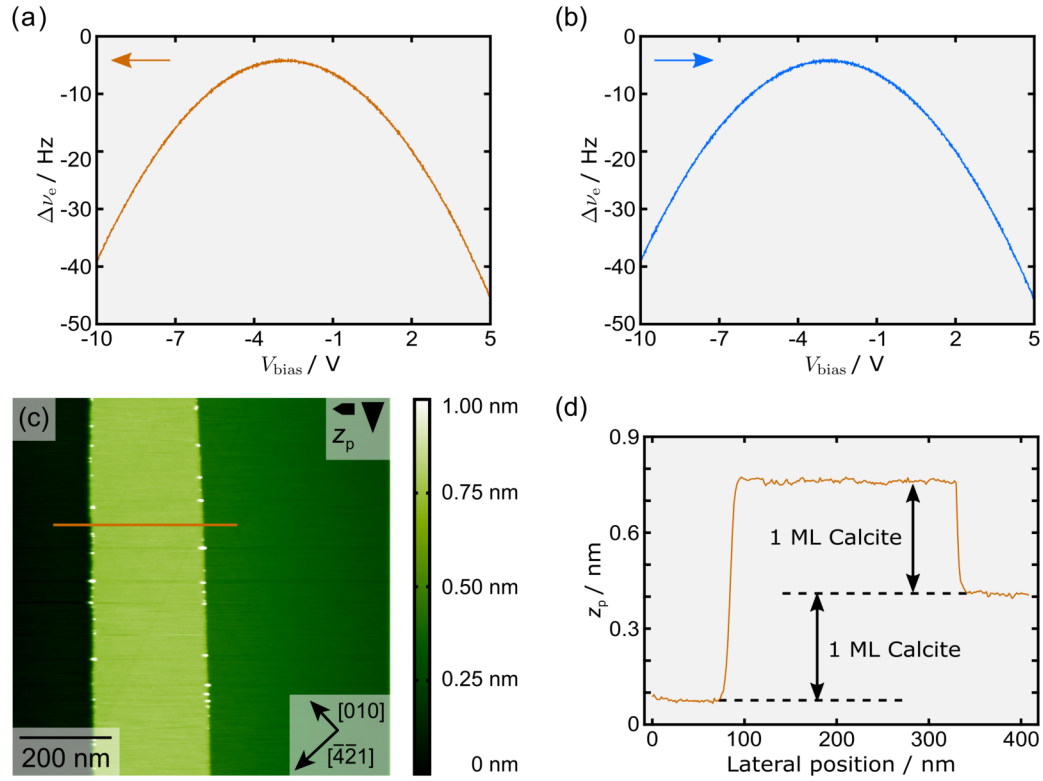


Figure 7.1: FM-AFM measurements performed on the calcite (10.4) surface. Plots (a) and (b) correspond to the negative and positive sweep voltage $\Delta\nu_e$ (V_{bias}) curve recorded at the beginning of the experiment. The blue and orange arrows in plots (a) and (b) indicate the sweep voltage direction of each curve. Right after recording the curve, the bias voltage V_{bias} was set to -3 V, value at which both curves present their respective maximum, approximately. Image (c) corresponds to the topography recorded several minutes after the curve. Two step edges are clearly resolved. The profile shown in plot (d) corresponds to the orange line depicted in the topography (c).

Figure 7.1 shows data recorded in a FM-AFM experiment performed on the calcite (10.4) surface. A *n*-doped silicon AFM tip (type PPP-NCH from NanoWorld, Neuchâtel, Switzerland) was employed. Plots (a) and (b) show the negative and positive sweep voltage $\Delta\nu_e$ (V_{bias}) curves, respectively, recorded right after starting the measurements. The topography z_p shown in (c) was taken minutes later. The profile (d) corresponds to the orange line depicted in (c). At the beginning of the experiment, a voltage-dependent curve was recorded in order to determine a V_{bias} value which minimizes, approximately, the tip-sample electrostatic interaction in all points of the area intended to measure. The frequency shift $\Delta\nu_e$ (V_{bias}) curve recorded at the beginning of this experiment is shown in (a) and (b) (negative and positive sweep voltage, respectively). Both curves present their maxima for, approximately, $V_{\text{bias}} = -3$ V. Right after recording this curve, the bias voltage V_{bias} was set to this value. The images were recorded at a speed of 1 second per line; furthermore, all scan directions were recorded (fast scan directions: forward and backward; slow

scan directions: up and down) [116]. Using these settings, recording one whole set of images takes more than 16.5 minutes. In this case, several sets of images were recorded before the topography shown in (c). These images were all recorded using the same frequency shift setpoint $\Delta\nu_e = -10$ Hz. The step edges of calcite were well resolved, as it can be observed in (c). The profile (d) shows with more detail two well resolved step edges. The difference in apparent height of the terraces fits with the previously reported values of a calcite monolayer [20, 86, 117]. Then, during a long scanning period with no change of the frequency shift $\Delta\nu_e$ setpoint (and therefore, not intended change of the tip-sample distance z_c), the electrostatic forces were minimized for the V_{bias} value set. In the experiments performed in this research group in UHV on calcite, this behaviour has been the usually observed in most samples. In some cases, the V_{bias} value corresponding to the maximum of the $\Delta\nu_e$ (V_{bias}) curve, *i.e.*, the V_{FM} value, changes between two consecutive parabolas in several volts, despite they were recorded in close spots on the surface or far away from each other. In this situation, discarding the sample and preparing a new one usually ended up in a measurement as depicted in figure 7.1.

If the applied V_{bias} value is not the corresponding V_{FM} value for specific spot in the surface and tip-sample distance z_c , the electrostatic interaction is not minimized. In this case, the frequency shift $\Delta\nu_e$ measured includes an important electrostatic contribution [15, 72, 74]. Thus, the topography obtained during the FM-AFM measurements does not necessarily correspond, even approximately, with the topology of the sample surface. Once I started the experiments on calcite, it was not possible to minimize the electrostatic interaction by applying a fixed V_{bias} value during FM-AFM measurements. This problem persisted on several samples (several crystals, each one outgassed, cleaved and annealed in UHV conditions several times). Figure 7.2 show FM-AFM data of one of this experiments. In this particular experiment a PPP-NCH *n*-doped silicon AFM tip was also used. Image (a) corresponds to the topography. Curves (b) and (c) correspond to $\Delta\nu_e$ (V_{bias}) curves recorded at the beginning of the image. Plot (d) corresponds to the profile indicated by an orange line in the topography (a). Plot (e) shows another $\Delta\nu_e$ (V_{bias}) curve. The scan lines in which the $\Delta\nu_e$ (V_{bias}) curves shown in (b), (c) and (e) were recorded are indicated on the left of the topography (a). Image (a) is a characteristic example of the previously described situation. The scanning speed was 1 second per line. At the beginning of this measurement, the bias voltage V_{bias} was set to 0 V. The image shows no well resolved step edges. The first $\Delta\nu_e$ (V_{bias}) curve recorded, displayed on (b), presents the maximum around -6.5 V. A second curve was recorded slightly after, which is shown in (c). It presents its maximum around -5 V. This is a variation of about 1.5 V. This situation can be unusual, but not necessarily implies a problem. The two curves were performed in different spots of the surface. One of the spots could have trapped charges around it, or maybe both could, but in a different amount. This difference in charge distribution would lead to a different V_{FM} value. After the

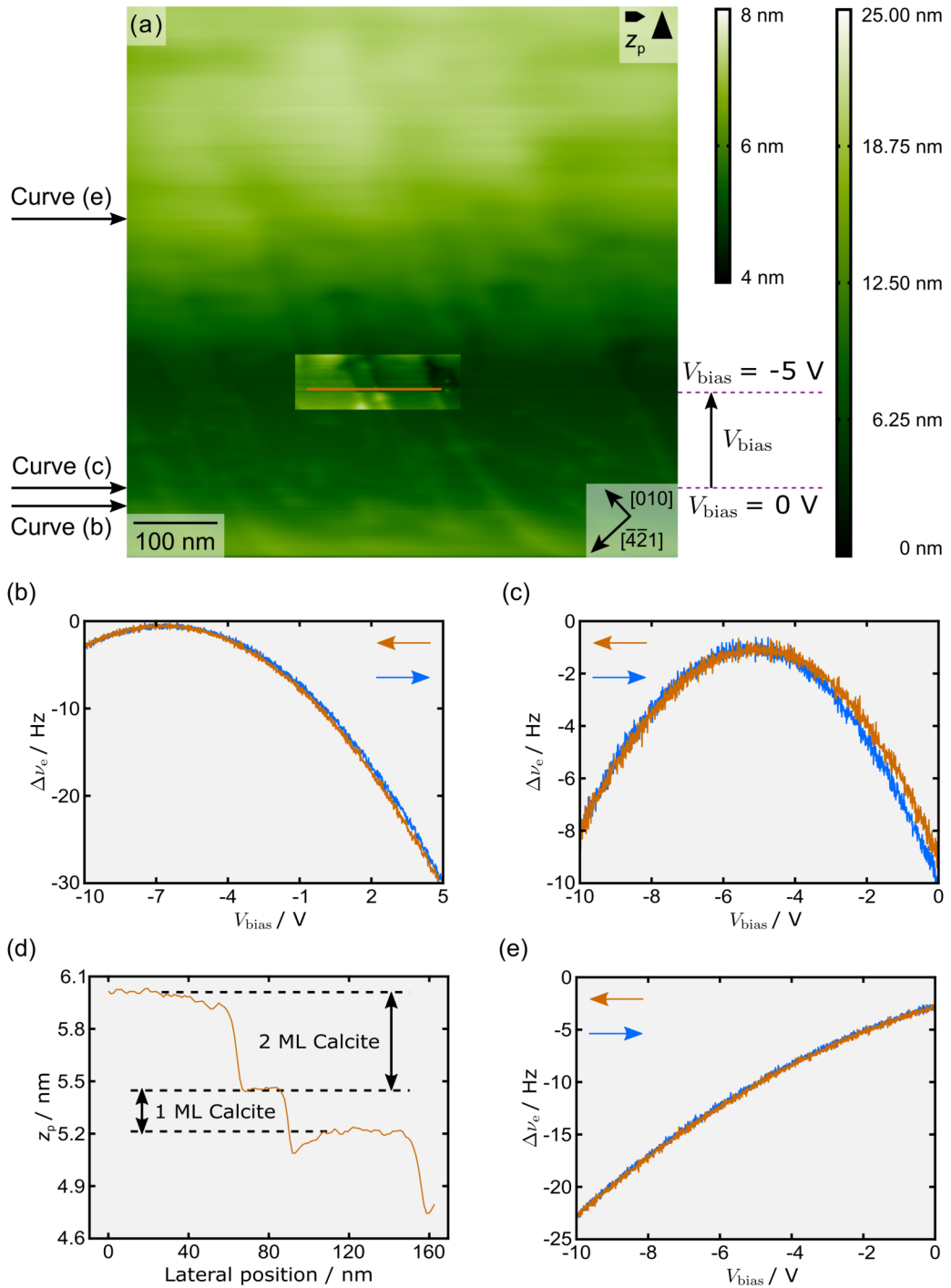


Figure 7.2.: FM-AFM measurements performed on the calcite (10.4) surface. Image (a) corresponds to the topography recorded on the calcite (10.4) surface. The bias voltage V_{bias} was set to 0 V at the beginning of the image. Two $\Delta\nu_e (V_{\text{bias}})$ curves were recorded in the lower part of the image, which are shown in plots (b) and (c), respectively. Right after, the bias voltage V_{bias} was set to -5 V, approximate value where the maxima of curve (c) is. The profile shown in (d) corresponds to this part of the image. Minutes later, the $\Delta\nu_e (V_{\text{bias}})$ curve shown in (e) was recorded. The blue and orange arrows in the plots (b), (c) and (e) indicate the sweep voltage direction of each curve. The large colourbar (from 0 to 25 nm) corresponds to the large image. The small colourbar (from 4 to 8 nm) corresponds to the zoom into the area where the profile was taken. The black arrows on the left of the topography indicate the line where the $\Delta\nu_e (V_{\text{bias}})$ curves were recorded. The purple lines on the right of the topography indicate the lines where the V_{bias} was changed.

second curve, the bias voltage V_{bias} was slowly reduced up to -5 V. During this slow variation of the V_{bias} value, the resolution of the topography changed. Different terraces can be identified, but the step edges in between are not well resolved. Plot (d) shows that the differences in apparent height of the terraces are in agreement with the values of a calcite monolayer and bilayer. However, the step edges are not well resolved (specially when comparing with them the ones in figure 7.1 (d)). After this line, the image slowly became blurred, up to the point of a contrast as bad as at the beginning of the image. This means that the V_{bias} value which minimizes the tip-sample electrostatic interaction has changed a few minutes after setting $V_{\text{bias}} = -5$ V. Another $\Delta\nu_e(V_{\text{bias}})$ curve was recorded slightly after, which is shown in (e). The maximum of this curve is for $V_{\text{bias}} > 0$ V, which implies a V_{FM} variation of more than 5 V. These fast and large variations of the V_{FM} value indicates a problem which I do not fully understand. However, the preparation procedure has been the same for years. As explained before, when a similar problem happened, the calcite crystal was discarded: working with a new one resulted in a satisfactory experiment. Different calcite crystals were cleaved and annealed several times, but the problem persisted. After all these attempts, I assume there is an unknown problem with the preparation. Finally, decided to perform all KPFM experiments on the same calcite sample: the crystal was cleaved and annealed only one time. Unlike on the experiments presented in chapter 6 on Au(111) and the KPFM experiments previously carried out in our research group, the KPFM feedback was engaged during the whole experiment. Proceeding on this way allowed us to measure a more reliable topography and, therefore, to find an appropriate spot on the calcite surface to measure on.

The first experiment on calcite was performed using, as referred to in the previous chapter, the *third* Au-coated silicon AFM tip. Figure 7.3 shows the images of this measurement on the calcite (10.4) surface: (a) presents the topography z_p ; (b) corresponds to the Kelvin V_{FM} ; (c) shows the frequency shift $\Delta\nu_e$; (d) presents the real part of the first spectral component of the frequency shift $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ and (e) corresponds the phase shift ϕ . The phase shift ϕ (e) and frequency shift $\Delta\nu_e$ (c) images show almost no corrugation. The topography (a) shows one step edge and two terraces. The step edge is not sharply resolved. This is probably due to convolution of the tip apex, which might be blunt and might have more than one protuberance. Features imaged several times can also be observed in the previous experiment performed on Au(111) using this tip (figures C.1 (a) and C.2 (a) shown in appendix C). The terraces do not look flat, but present corrugation similar to bumps. It can be due to some contamination or residual clusters of calcite after the cleaving. However, these bumps are very large to be contamination or residual molecules in the chamber² and their apparent height is just a fraction of the height of one calcite monolayer. Furthermore, the real part of the first spectral

²No molecules were sublimated in the UHV chamber for several months.

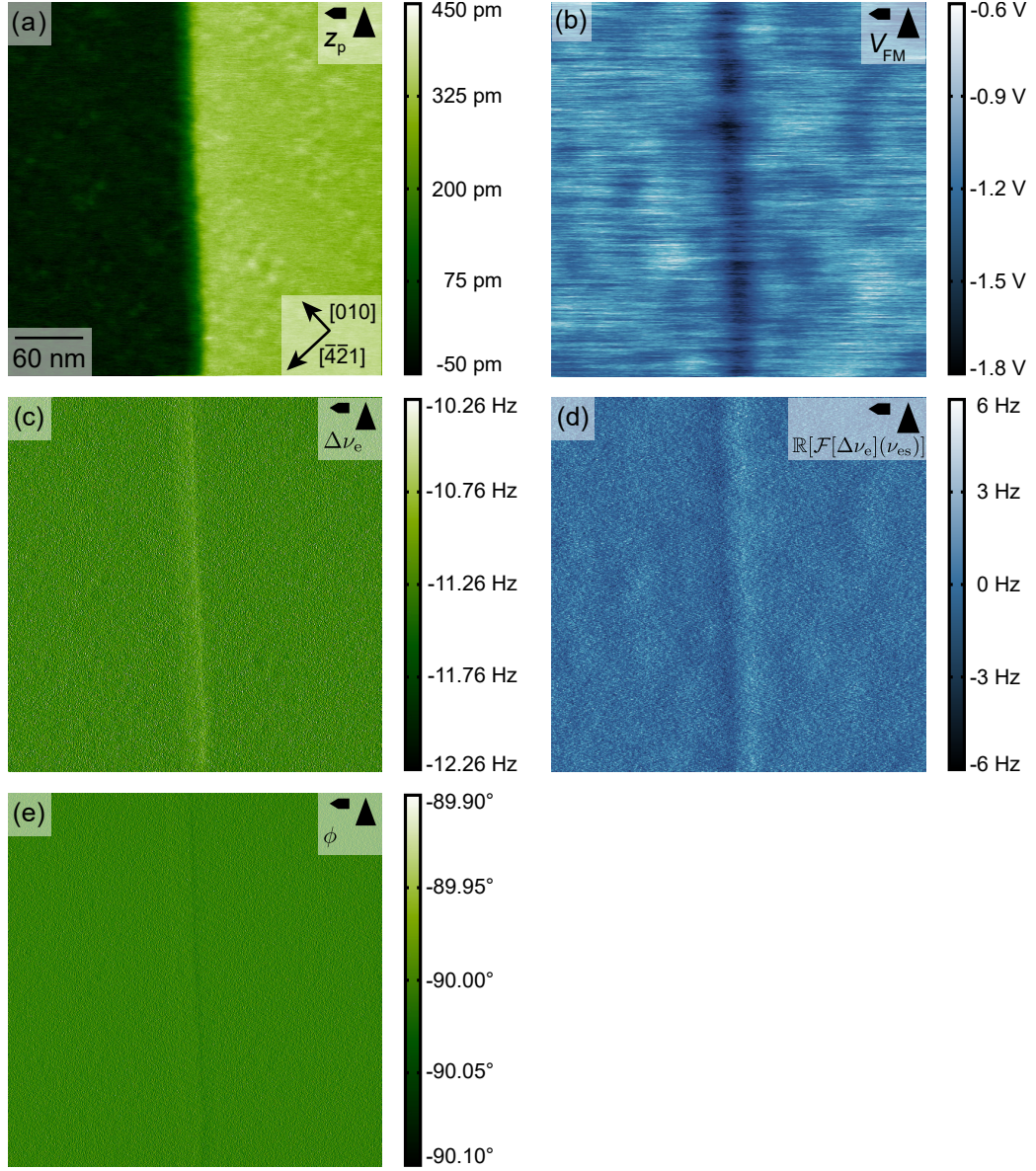


Figure 7.3.: FM-AFM and FM-KPFM images measured on the calcite (10.4) surface using the *third* Au-coated silicon AFM tip. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image (b) shows important corrugation not only on the step edge (as I have previously observed in the experiments performed on Au(111)) but on many other spots of the surface. The V_{FM} signal (d) is more negative around the step edge than on the terraces. Furthermore, there are some spots along the step edge in which the V_{FM} values are even more negative, but no remarkable feature can be observed in the topography on these same spots. This could be an indication of charge accumulation on the step edge. On the terraces, the values are not homogeneous, with around 1 V of difference between the more positive and more negative values. Some of the darker areas are located in the same spots as the bumps observed in the topography. Furthermore, this darker areas are located in

the same positions as the corrugation in the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$. Besides, considering the problem I experienced when measuring FM-AFM on calcite previously reported in this chapter and depicted in figure 7.2, I could consider that the "bumps" in the topography are actually due to the non-properly minimized electrostatic interaction. Reached this point, the next part of the experiment consisted of recording the distance-dependent curves. Figure 7.4 shows the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 7.5 shows the four different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curves in the plots relate each curve with the position where it was performed.

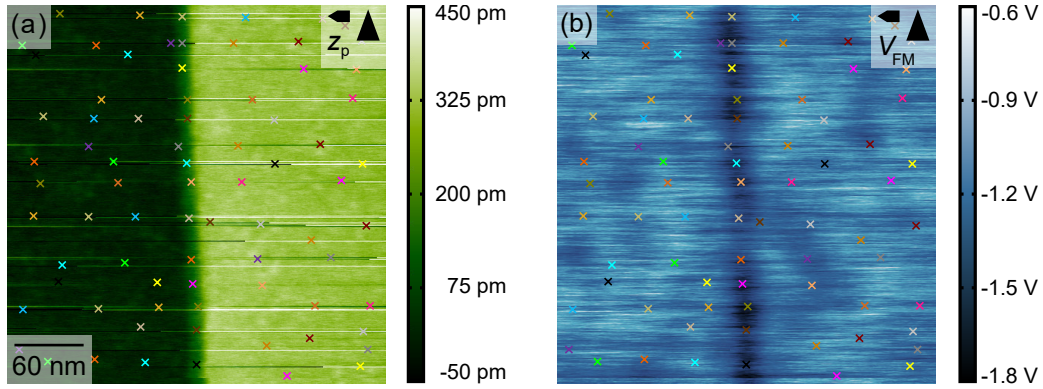


Figure 7.4.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *third* Au-coated silicon AFM tip. The crosses indicate the spots where the distance-dependent curves shown figure 7.5 were performed.

Figure 7.5 shows the distance-dependent curves performed in the previously measured calcite area. Plots (a) and (b) show the frequency shift $\Delta\nu_e$ and Kelvin V_{FM} curves, respectively, while (c) and (d) correspond to the oscillation amplitude A and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves, respectively. All oscillation amplitude A curves are constant for all z_p -piezo displacement z_p values. Thus, the information in the frequency shift $\Delta\nu_e$ and real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ is reliable. All frequency shift $\Delta\nu_e(z_p)$ curves overlap, which implies no dependence on the spot on which they were recorded. The curves corresponding to the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, shown in plot (d), are basically nullified, with their values distributed around 0 Hz. Thus, the V_{FM} curves are reliable. For $z_p = 0$ nm, the curves distribute between -0.8 and -1.8 V. It can be noted that most of them distribute between -0.8 and -1.3 V, which is the voltage range exhibited by the V_{FM} signal on the terraces: most of the curves were recorded on the terraces. The rest of the curves, for $z_p = 0$ nm, distribute between -1.3 and -1.8 V, which is the corresponding voltage range for the step edge area in the V_{FM} image. As the z_p -piezo displacement z_p increases, the values of the V_{FM} curves tend to increase, always showing non-monotonic large variations (two

examples are indicated in plot (b) with black arrow; some of them of hundreds of millivolts for $0 < z_p < 10$ nm, and even larger for $z_p > 10$ nm). The curves recorded on the step edge are always more negative than the ones on the terraces. A good example is the pink curve with $V_{\text{FM}}(z_p = 0 \text{ nm}) \simeq -1.8$ V. It was recorded on the step edge, specifically on one of the spots with more negative V_{FM} values. Despite the large variations previously referred to, I could conclude that all curves exhibit a positive slope. It would have been interesting to compare the distance-dependent closed-loop V_{FM} curves with the static V_{FM} data (extracted from $\Delta\nu_e(V_{\text{bias}})$ curves). However, as mentioned before, the position of the maxima of the $\Delta\nu_e(V_{\text{bias}})$ curves recorded on calcite vary significantly between two consecutive curves. Because of this, I considered that the possible information I could get from this measurements would not be reliable.

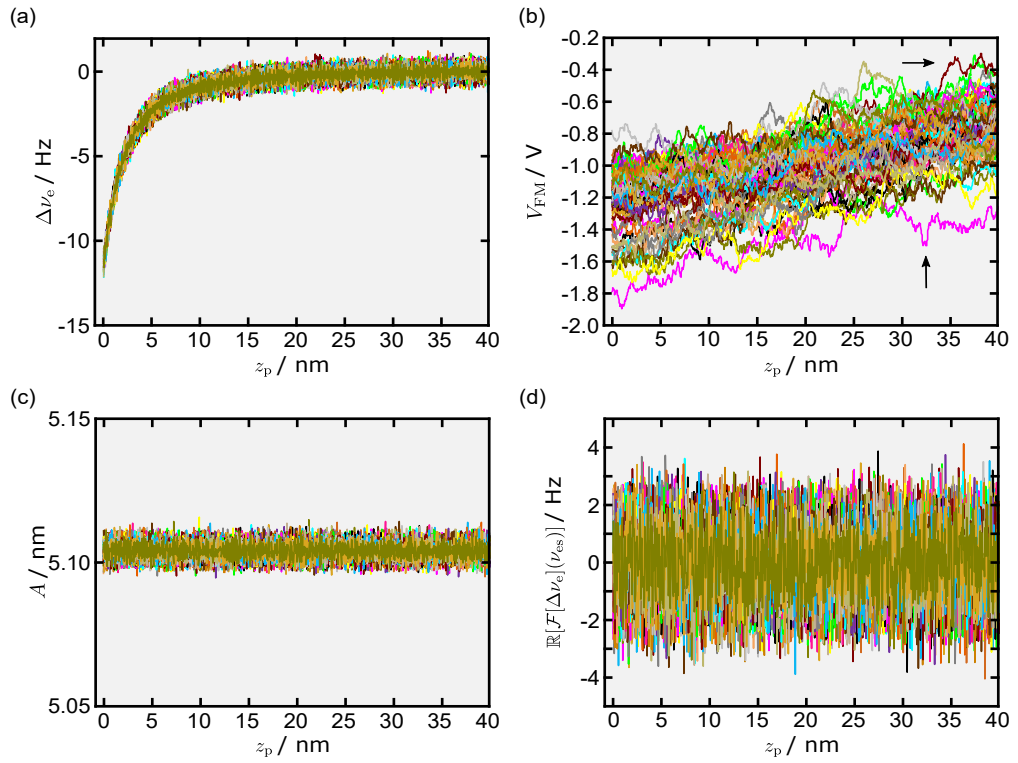


Figure 7.5.: Distance-dependent curves performed during the first experiment on the calcite (10.4). The *third* Au-coated silicon AFM tip was used. The colour of each curve correlates with the colour of the crosses in the images in figure 7.4. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ versus the z -piezo displacement z_p . The black arrows in (b) indicate the non-monotonic large variations.

After this experiment on calcite, the characterization of the state of the Au-coated silicon AFM tip was necessary. For this reason, the same kind of measurements on Au(111) as the ones presented in chapter 6 were done³. Most of the data from this experiment is collected in appendix D: full set of images (figure D.1), topography z_p

³The $I(V_{\text{bias}})$ curves were skipped. As I could not prepare more Au-coated tips, I decided to avoid situations which could/would deform more the tip apex.

and V_{FM} image with the crosses indicating the position where the distance-dependent curves were recorded (figure D.2) and the distance-dependent curves (figure D.3). The experiment for comparing closed-loop $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data was also performed. The data corresponding to the oscillation amplitude A (V_{bias}) and the frequency shift $\Delta\nu_e$ (V_{bias}) curves is collected in appendix D (figure D.4).

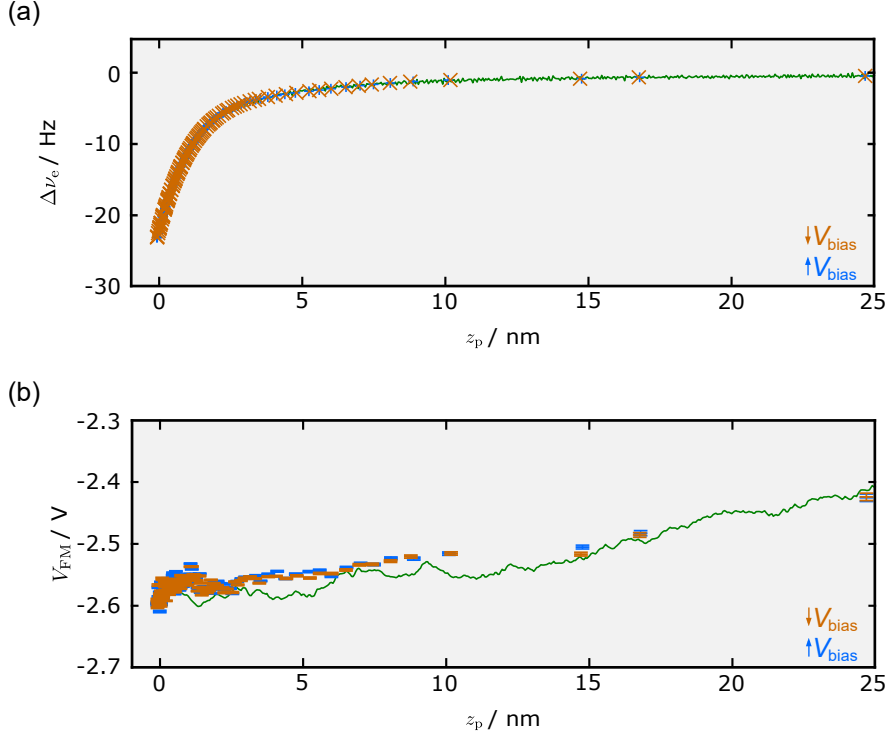


Figure 7.6.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{\text{bias}})$ curves of figure D.4 (a) and (b), which were performed after the first experiment on calcite using the *third* Au-coated silicon AFM tip. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

The comparison of the V_{FM} data obtained by both procedures is shown in figure 7.6. Plot (a) shows the comparison of the frequency shift $\Delta\nu_e(z_p)$ curve with the parameter c of all $\Delta\nu_e(V_{\text{bias}})$. From now on, I will refer to this parameter c as fitted $\Delta\nu_e(V_{\text{FM}})$ value (see equation (6.4)). Plot (b) presents the comparison of the closed-loop $V_{\text{FM}}(z_p)$ curve with the fitted V_{FM} data from the static FM-KPFM measurement. The $V_{\text{FM}}(z_p)$ curves look rather flat for $0 < z_p < 6$ nm. Around $z_p = 6$ nm, there is a jump and after that, for $6 < z_p < 12$ -13 nm, the curve still seems flat. From there on, the curve exhibits a positive slope. However, the fitted V_{FM} data from the static FM-KPFM measurement shows a different behaviour. For the $0 < z_p < 1$ nm, it shows an increase of nearly 50 mV. Then, for $1 < z_p < 5$ nm, it presents several jumps, although showing flat behaviour. For $z_p > 5$ nm, the points exhibit an increasing tendency, although there are just a few points and it is not conclusive: the points for $z_p \simeq 10$ and $z_p \simeq 15$ nm correspond to very similar V_{FM} values. Then, both closed-loop and static V_{FM} results show different behaviour for $0 < z_p < 1$ nm

and $10 \text{ nm} < z_p$, and similar for $1 < z_p < 5 \text{ nm}$. It is possible that, when performing these curves, the tip slightly moved to a different spot on the surface with point charges on/around it. This would explain the non-constant V_{FM} values for $0 < z_p < 1\text{-}2 \text{ nm}$. Nevertheless, I conclude that the Au-coated tip was free of localized charges right when the closed-loop $V_{\text{FM}}(z_p)$ curve was recorded. This fact points to consider the calcite distance-dependent curves recorded using this tip (figure 7.5 (b)) as trustworthy data (recorded with a tip free of localized point charges). As the V_{FM} curves clearly shows a distance-dependence signal, I can conclude that the calcite surface presents localized point charges. This charge distribution is not homogeneous; otherwise, the V_{FM} signal in figure 7.3 (b) and figure 7.4 (b) would be homogeneous (at least, on the terraces) and it is not. This is a clear indication of a non-homogeneous charge distribution. It is unclear if it is only due to the topmost layer of calcite or could be due to inner layers⁴.

The second measurement on calcite was performed using, as referred to in the previous chapter, the *second* Au-coated silicon AFM tip. Figure 7.7 collects the images of this second experiment on the calcite (10.4) surface: (a) shows the topography z_p ; (b) corresponds to the Kelvin V_{FM} ; (c) presents the frequency shift $\Delta\nu_e$; (d) shows the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ and (e) corresponds the phase shift ϕ . As in the previous experiment, the phase shift ϕ (e) and frequency shift $\Delta\nu_e$ (c) images show almost no corrugation. The topography z_p (a) shows one step edge and two terraces. The step edge is not well resolved, showing several edges. This is probably due to the presence of several protuberances in the tip apex (this kind of possible multi-imaging of features can be observed in the last experiment performed on Au(111) also using this tip: figures 6.37 (a) and 6.38 (a) shown in appendix C). Again, the terraces exhibit large corrugation. These features are oriented along the same (or at least, quite similar) direction. This is probably due to the possible multi-tip (or a tip apex with several protuberances). This time, instead of protuberances or bumps, the corrugation looks as depressions, which differs from the previous experiment. This difference could be due to a different interaction of the contamination with a different tip apex, or that the measurements were done at a different tip-sample distance z_c . In this case, compared with the previous experiment, a contrast inversion could take place. All this, without ruling out the possibility that trapped charges on or below the calcite surface are responsible for this effect. The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ image (b) exhibits remarkable corrugation on the area corresponding to the step edge and the depressions. The V_{FM} image (d) shows, as in the previous experiment, more negative values on the step edge compared to the terraces. Furthermore, it is possible to distinguish some darker spots (meaning more negative V_{FM} signals) on the step

⁴The non-homogeneous V_{FM} signal could be due to adsorbates or contamination but, as discussed before, the features in the topography are too large and, at the same time, its apparent height too small to be contaminants.

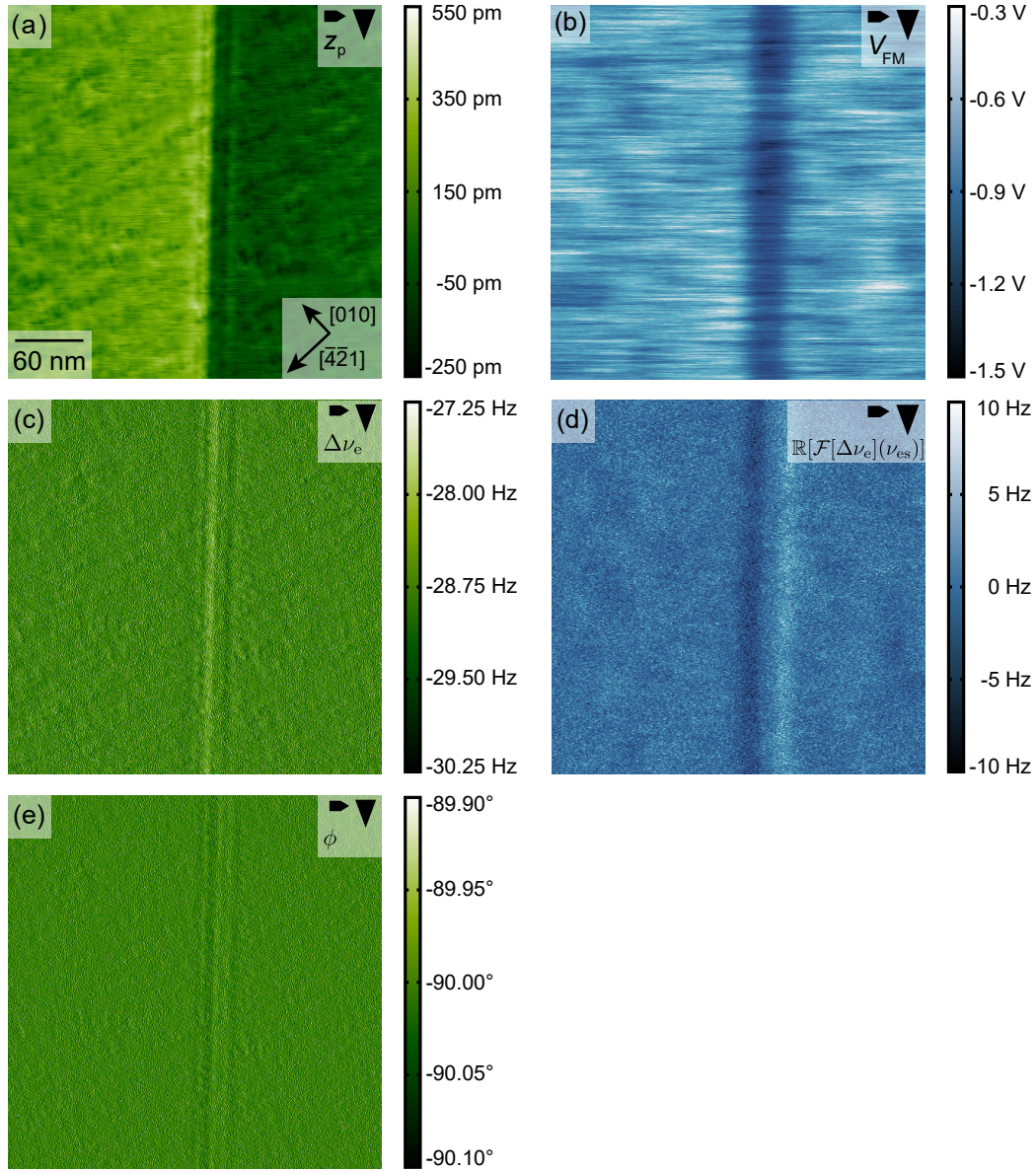


Figure 7.7.: FM-AFM and FM-KPFM images measured on the calcite (10.4) surface using the *second* Au-coated silicon AFM tip. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

edge. However, these darker spots correspond to some of the depressions on the step edge in the topography z_p . Also as in the previous experiment, the V_{FM} signal is not homogeneous on the terraces, with around 1 V of difference (again) between the more positive and more negative values. Nevertheless, in this measurement, respect to the terraces, it is not possible to correlate the more negative areas in the V_{FM} image and the features in the topography. The correspondence of the non-properly minimized electrostatic interaction in the $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image with the features in the topography, which are always imaged as depressions, supports the theory also presented in the previous experiment: the sample surface and/or the topmost calcite layers might have trapped charges. It is possible that the electrostatic interaction

is not totally minimized and this affects the topography [15, 72]. The depressions present in the topography could be due to contamination, although as in the previous experiment, they are too large. The next part of the experiment was recording the distance-dependent curves. Figure 7.8 shows the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 7.9 shows the four different channels recorded during the distance-dependent curves.

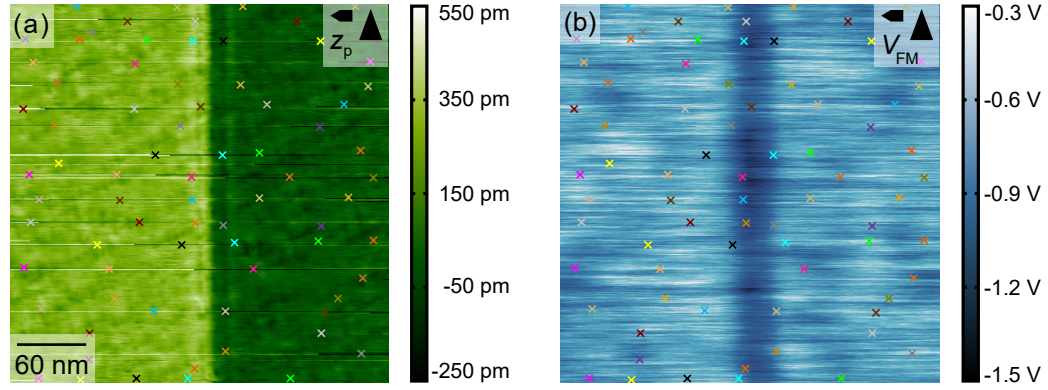


Figure 7.8.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *second* Au-coated silicon AFM tip. The crosses indicate the spots where the distance-dependent curves shown figure 7.9 were performed.

Figure 7.9 presents the distance-dependent curves performed on the calcite area indicated in figure 7.8 . Plots (a) and (b) present the frequency shift $\Delta\nu_e$ and Kelvin V_{FM} curves, respectively, while (c) and (d) show the oscillation amplitude A and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves, respectively. The usual remarks about the previous experiment can be done: all oscillation amplitude A curves are constant for all z_p values, so the information in the frequency shift $\Delta\nu_e$ channel and in the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ is trustworthy. All frequency shift $\Delta\nu_e(z_p)$ curves overlap, indicating no dependence on the spot on the surface on which they were performed. The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves (plot (d)), distribute around 0 Hz, so this signal can be considered nullified for all curves. From this, it follows that the V_{FM} curves (plot (b)) are reliable. For $z_p = 0$ nm, the V_{FM} curves distribute between -0.4 and -1.2 V. Actually, as in the previous experiment, there is a clear distinction: most of the curves were performed on the terraces, and the values $V_{FM}(z_p = 0$ nm) of these curves concentrate between -0.4 and -0.8 V. This voltage range agrees with the one displayed in figure 7.8 (b). The curves recorded on the step edge concentrate, for $z_p = 0$ nm, between -0.8 and -1.2 V, which agrees, again, with the V_{FM} image. A notorious example is the turquoise curve with $V_{FM}(z_p = 0$ nm) $\simeq$ -1.2 V. This curve is significantly more negative than the other curves: it was recorded on a darker spot on the step edge (top central part of figure 7.8 (b)). Unless in the previous experiment, the V_{FM} curves show a different distance-dependence:

for $0 < z_p < 10$ nm (approximately), as the z-piezo position z_p increases, the values of the V_{FM} curves decrease. Nevertheless, it is possible to observe the previously mentioned non-monotonic large variations (indicated by black arrows in plot (b)). For $z_p > 10$ nm, the V_{FM} curves increase, but with a lower rate. As a general observation, and despite the large non-monotonic variations, the curves show a negative slope for $0 < z_p < 10$ nm and positive slope for $z_p > 10$ nm.

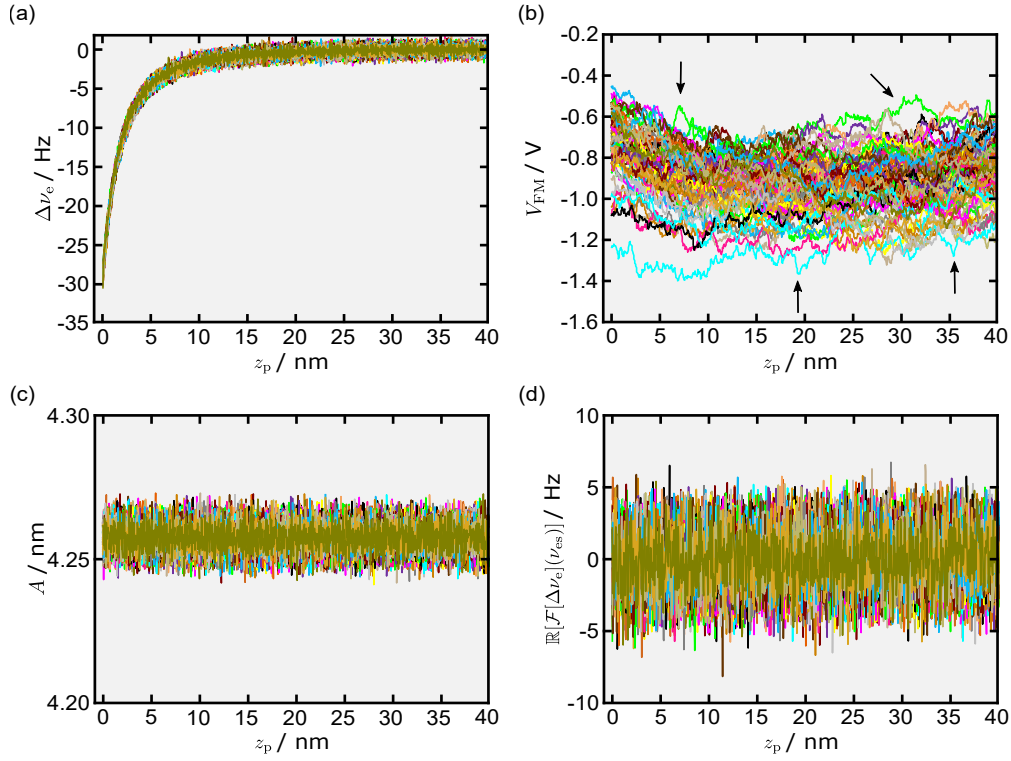


Figure 7.9.: Distance-dependent curves performed during the second experiment on the calcite (10.4). The second Au-coated silicon AFM tip was used. The colour of each curve correlates with the colour of the crosses in the images in figure 7.8. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z-piezo displacement z_p .

In order to check the state of the Au-coated silicon AFM tip (if it is still free of localized point charges or not), I performed the same kind of experiment on Au(111) as the ones presented in chapter 6. As before, most of the data of this experiment is also collected in appendix D (figures D.5, D.6 and D.7). As in the previous experiments, the comparison between the closed-loop $V_{FM}(z_p)$ curve and fitted V_{FM} data was done. The data corresponding to the oscillation amplitude A (V_{bias}) and the frequency shift $\Delta\nu_e$ (V_{bias}) curves is collected in appendix D (figure D.8).

The comparison of both procedures is presented in figure 7.10. Plot (a) shows the comparison of the frequency shift $\Delta\nu_e(z_p)$ curve with the fitted $\Delta\nu_e(V_{FM})$ data from the static FM-KPFM measurement. Plot (b) presents the comparison of the closed-loop $V_{FM}(z_p)$ curve with the fitted V_{FM} data from the static FM-KPFM measurement.

The closed-loop $V_{\text{FM}}(z_p)$ curve shows a negative tendency for $0 < z_p < 8$ nm, presenting a small increase for $z_p \simeq 9$ nm and a decreasing tendency then until $z_p \simeq 12$ -13 nm. From there on, it looks flat. The fitted V_{FM} data from the static FM-KPFM measurement shows a sudden decrease for $0 < z_p < 1$ nm. From there on, the V_{FM} signal continues decreasing, but with a lower rate. For $z_p > 15$ nm, it seems to show flat behaviour but with the last point, whose value increases. Thus, both procedures show similar tendencies. I assume that the tip apex was contaminated with point charges during the experiment on calcite: this contamination could happen before recording any distance-dependent curve or between recording two curves. There is no procedure to check this possibility. The only fact I can conclude is that the V_{FM} distance-dependent curves recorded on calcite using this tip (figure 7.9) are not trustworthy data.

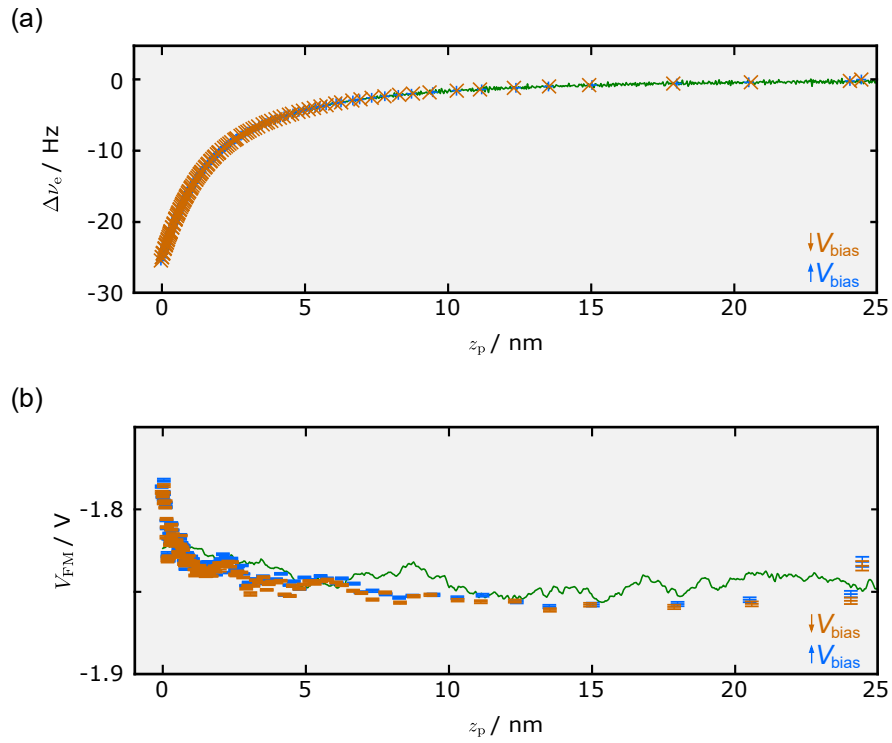


Figure 7.10.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{\text{bias}})$ curves of figure D.8 (a) and (b), which were performed after the second experiment on calcite using the *second* Au-coated silicon AFM tip. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

The third measurement on calcite was performed using, as referred to in the previous chapter, the *fourth* Au-coated silicon AFM tip. Figure 7.11 displays the images of the third experiment on the calcite (10.4) surface: (a) presents the topography z_p ; (b) shows the Kelvin V_{FM} ; (c) corresponds the frequency shift $\Delta\nu_e$; (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ and (e) corresponds the phase shift ϕ . Also in these measurements, the phase shift ϕ (e) and frequency shift

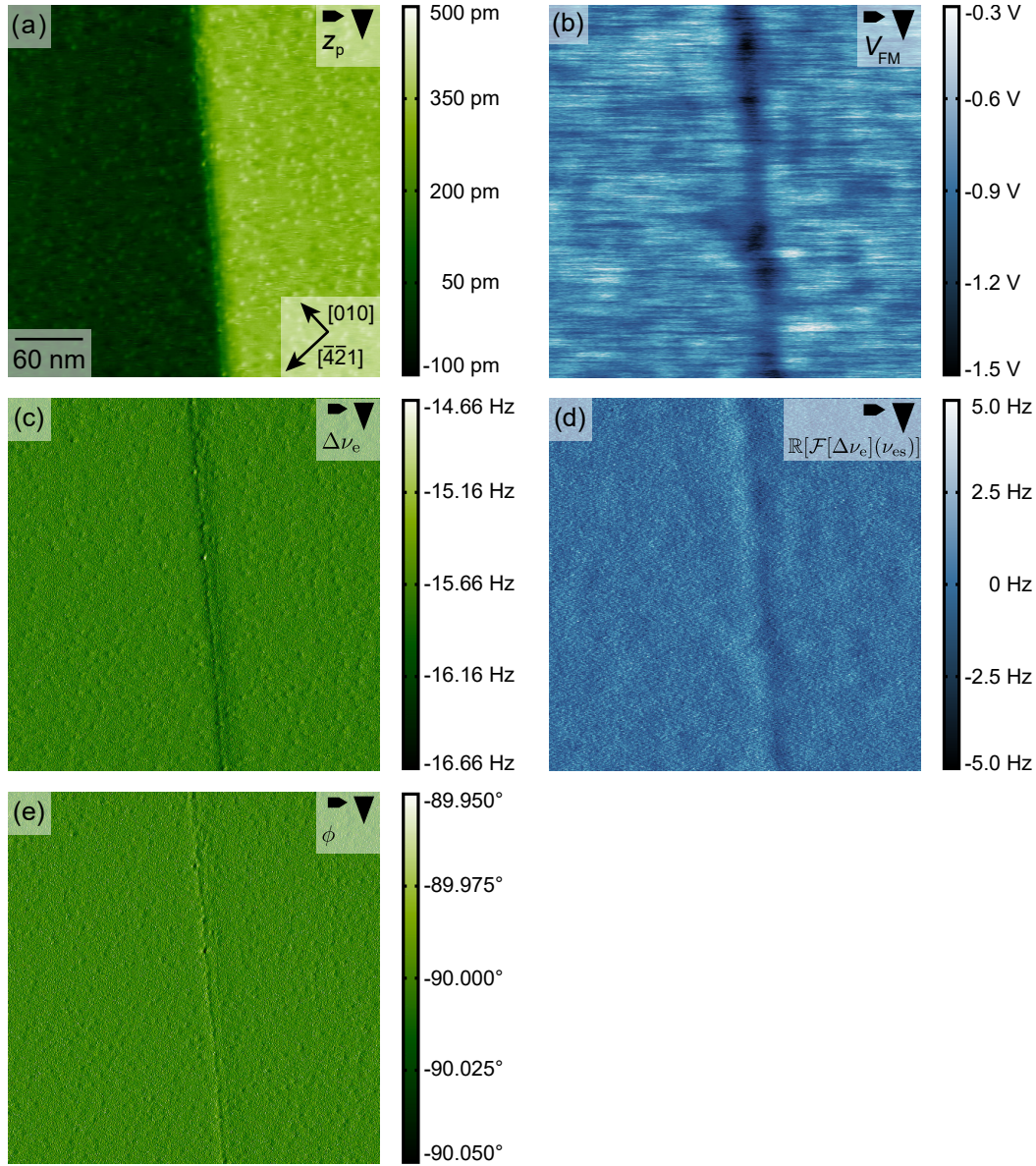


Figure 7.11.: FM-AFM and FM-KPFM images measured on the calcite (10.4) surface using the *fourth* Au-coated silicon AFM tip. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

$\Delta\nu_e$ (c) images show almost no corrugation. The topography shows one step edge and two terraces. The step edge is not well resolved (as previous experiments), showing a shadow and several edges (also seen in the measurement on Au(111) using this very same tip: figures C.6 (a) and C.7 (a) shown in appendix C). This fact indicates that the tip has a blunt apex or a multi-apex (tip apex with several protuberances). The terraces do not look flat, but exhibit large corrugation. In this experiment, the corrugation shows both protrusions and depressions. Besides, these protrusions and depressions are oriented along the same direction, which also points to the tip apex with several protuberances. As in the previous experiments, all this bumps and depressions could be different species or contamination, but they are too

large and no molecules were sublimated in the chamber for long time. They could also be due to the non-proper nullified the electrostatic interaction. Indeed, the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image (b) is not flat on the area corresponding to the step edge and on many spots of the terraces, indicating that the electrostatic interaction was not completely minimized. This fact supports the possible crosstalk origin of the corrugation imaged on the terraces. The V_{FM} image (d) shows, as in the two previous experiments, more negative values on the step edge than on the terraces. Moreover, some very localized spots on the step edge exhibit even more negative values. These spots are localized in the same position as some of the unidentified features in the topography localized on the step edge. On the terraces, the V_{FM} signal exhibits a wider range of values: some areas show as negative V_{FM} values as on the step edge, while other ones even 1 V more positive. In this case, due to the large amount of features imaged in the topography, it is difficult to establish a correspondence between them and the distribution of values in the V_{FM} image. The next part of the experiment was recording the distance-dependent curves. Figure 7.12 shows the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 7.13 shows the four different channels recorded during the distance-dependent curves.

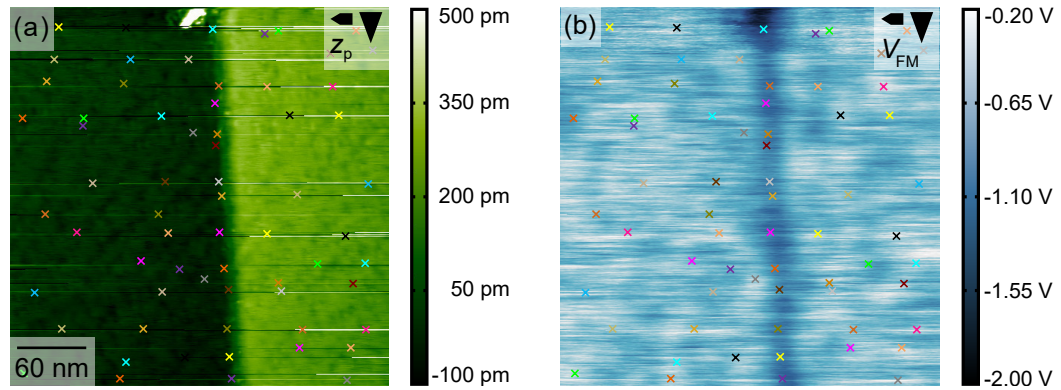


Figure 7.12.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *fourth* Au-coated silicon AFM tip. The crosses indicate the spots where the distance-dependent curves shown figure 7.13 were performed.

Figure 7.13 shows the distance-dependent curves recorded in the calcite area indicated in figure 7.12. Plots (a) and (b) show the frequency shift $\Delta\nu_e$ and Kelvin V_{FM} curves, respectively, while (c) and (d) present the oscillation amplitude A and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves, respectively. As in previous experiments, all oscillation amplitude A curves are constant for all z_p values. Then, both frequency shift $\Delta\nu_e$ and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves are reliable. All frequency shift $\Delta\nu_e$ curves overlap. This fact implies no difference of interaction depending on the spot of the surface on which each one was performed. All real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves (d) are minimized (the noise is distributed

around 0 Hz). Therefore, the V_{FM} curves are reliable. As in the previous experiments, it is possible to distinguish which curves have been performed on the terraces and which ones on the step edge (these last ones are more negative for $z_p = 0$ nm). A notorious example is the turquoise curve with $V_{\text{FM}}(z_p = 0 \text{ nm}) \simeq -1.6$ V. Figure 7.12 (a) shows a large feature on the upper part of the image, on the lower terrace, close to the step edge. The corresponding V_{FM} image (in (b)) shows that this spot exhibits much negative values than on the surrounding areas. The turquoise curve was recorded there. In general, I can conclude that the curves exhibit a negative slope for $0 < z_p < 10$ nm. For $z_p > 10$ nm, excluding the aforementioned large variations (indicated by black arrows), the curves show a positive slope, although the absolute rate is smaller than for $0 < z_p < 10$ nm.

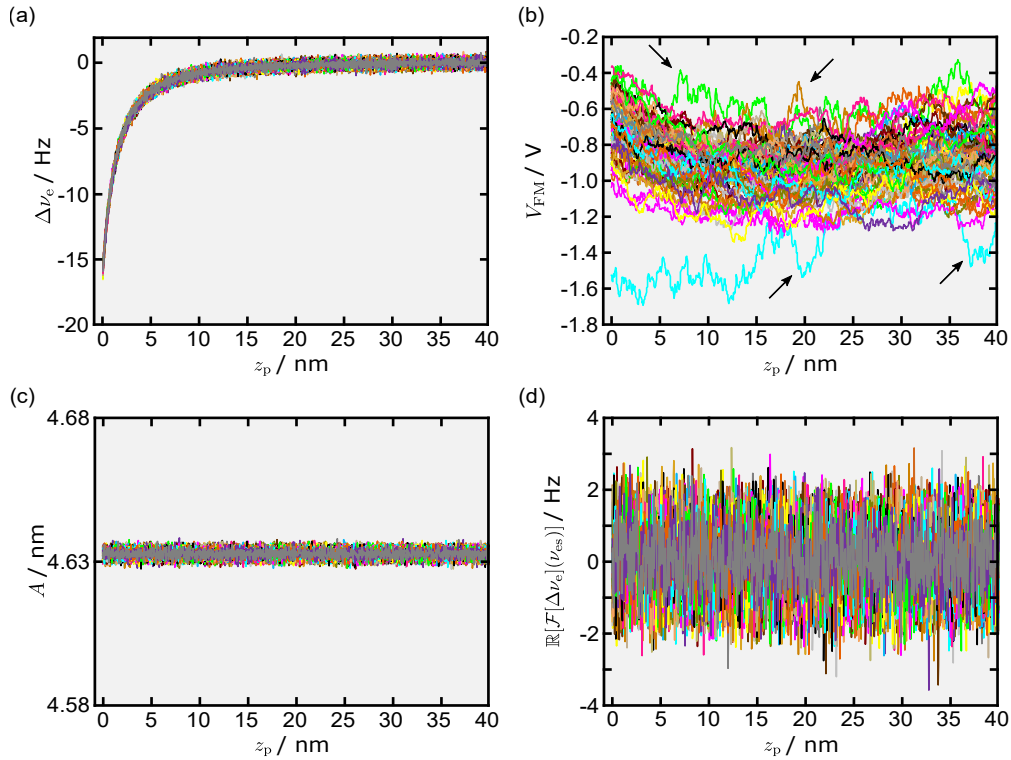


Figure 7.13.: Distance-dependent curves performed during the third experiment on the calcite (10.4). The *fourth* Au-coated silicon AFM tip was used. The colour of each curve correlates with the colour of the crosses in the images in figure 7.12. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ versus the z -piezo displacement z_p .

As usual, after the experiment on calcite, I performed the experiment on Au(111) to check the state of the Au-coated silicon AFM tip. The main data is also collected in appendix D (figures D.9, D.10 and D.11). The measurements for comparing closed-loop $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data were also performed. The data corresponding to the oscillation amplitude A (V_{bias}) and the frequency shift $\Delta\nu_e$ (V_{bias}) curves can be found in appendix D (figure D.12).

The comparison of both procedures is presented in figure 7.14. Plot (a) shows the comparison of the frequency shift $\Delta\nu_e(z_p)$ curve with the fitted $\Delta\nu_e(V_{FM})$ data from the static FM-KPFM measurement. Plot (b) presents the comparison of the closed-loop $V_{FM}(z_p)$ curve with the fitted V_{FM} data from the static FM-KPFM measurement. The closed-loop $V_{FM}(z_p)$ curve shows a positive slope for all z_p values, with no flat regions. The V_{FM} data extracted from the $\Delta\nu_e(V_{bias})$ curves show a sudden increase for $0 < z_p < 0.5$ nm. From there on, the V_{FM} signal continues increasing, although at a lower rate. From this, I can conclude that both procedures show a similar result, and the tip presents localized point charges in the tip apex. As in the previous experiment, I cannot determine if this contamination happened before recording the curves on calcite or during it, so the conclusion is the same: the distance-dependent curves recorded on calcite using this tip (figure 7.13 (b)) are not trustworthy data.

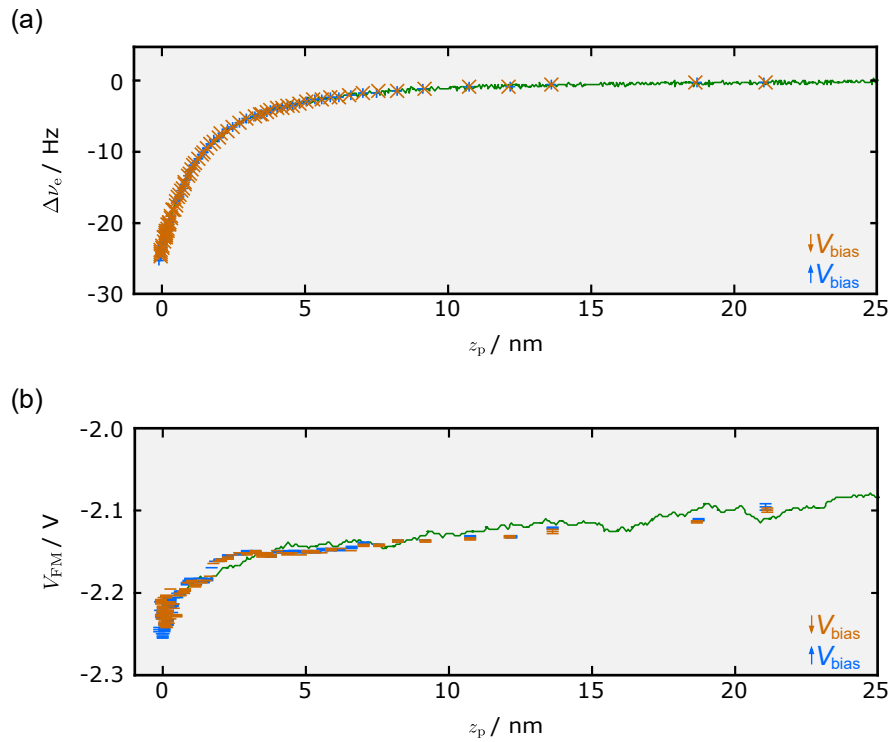


Figure 7.14.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{FM}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{bias})$ curves of figure D.12 (a) and (b), which were performed after the third experiment on calcite using the *fourth* Au-coated silicon AFM tip. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

In order to compare the three experiments on calcite, the averages of the main channels are plotted together in figure 7.15. As in the previous chapter, the V_{FM} plot only provides an approximate idea of the common trend of all curves, but it is not suitable for a quantitative analysis. This is due to the fact that the V_{FM} curves of each experiment do not overlap, unlike the frequency shift $\Delta\nu_e$ and oscillation amplitude A curves. Furthermore, two out of the three experiments summarized in

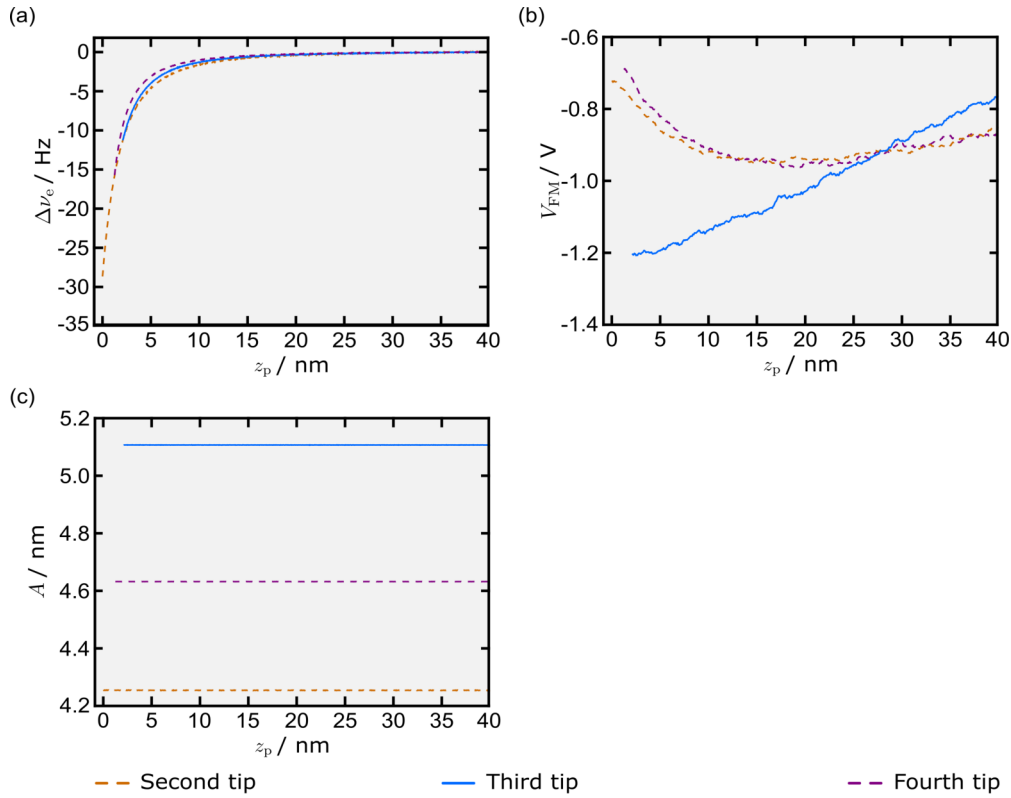


Figure 7.15.: Comparison of the averaged distance-dependent curves of three experiments performed on calcite (10.4). Plot (a) shows the frequency shift $\Delta\nu_e$, (b) presents the Kelvin V_{FM} signal and (c) shows the oscillation amplitude A versus the z-piezo displacement z_p . The curves in dashed lines correspond to the experiments after which the Au-coated tips used were found contaminated with localized point charges: *second* and *fourth* tips.

this figure were performed using a contaminated tip with localized point charges: the corresponding experiments are indicated with dashed lines. Plot (a) presents the averages of the frequency shift $\Delta\nu_e$ curves, plot (b) shows the averages of the V_{FM} curves and plot (c) the averages of the oscillation amplitude A curves. In plot (c), I can appreciate that the oscillation amplitude A of the three experiments is quite different. This difference could have an important influence in the frequency shift $\Delta\nu_e$ and V_{FM} curves. However, this difference is about 10% in respect to the average of oscillation amplitude A curves of each experiment. Under this consideration, I assume it is suitable for a qualitative discussion about the averages of the other channels. The averages of the frequency shift $\Delta\nu_e$ curves (plot (a)) do not overlap. Besides the already discussed difference in oscillation amplitude A , the different averages of the $\Delta\nu_e$ curves could be due to their different tip apex (respect to each other). Another possible explanation is that the experiments were done in different spots of the calcite surface⁵. The averages of the V_{FM} curves corresponding to the experiments performed using the *second* and the *fourth* tips (contaminated tips) exhibit negative slope for $0 < z_p < 16$ -17 nm and from there on, positive

⁵The experiments were performed in the approximate same area of the calcite sample surface. However, I cannot discard an important deviation between the exact spots when the tip was brought close to the sample surface.

(but smaller in absolute value) from there on; however, the average of the curves performed using the third tip shows a positive slope for all z_p values. These two different tendencies could be due to the different oscillation amplitude A . However, the average curve corresponding to the experiment recorded with the *fourth* tip indicates the opposite. The difference in oscillation amplitude A between this average curve (using the *fourth* tip) and the other two is quite similar ($\simeq 0.37$ nm respect to the experiment using the second tip and $\simeq 0.47$ nm respect to the experiment using the third tip). However, despite this fact, the averages of the V_{FM} curves of the experiments performed using the second and the fourth tip are very similar between them and, at the same time, very different from the average corresponding to the experiment using the third tip. Thus, I should not assume the reason for the aforementioned similar distance-dependence is due to the different oscillation amplitude A . A possible explanation is the other fact this two experiments have in common: after they were finished, the test experiment on Au(111) determined both tips were contaminated. This leaves, as already mentioned, only one valid experiment (out of three).

At this point, I would like to make a remark about the collected data in the three experiments on calcite. In all of them, all distance-dependent $\Delta\nu_e$ curves of each experiment (figures 7.5 (a), 7.9 (a) and 7.13 (a)) overlap. This fact that the total tip-sample force F_{ts} (or, as I am discussing FM-AFM measurements, total tip-sample force gradient k_{ts}) is the same for all curves at all z-piezo positions z_p , with no difference of being recorded on different spots on the surface. As already explained in section 2.4.2, one of the contributions to the total tip-sample force F_{ts} is the electrostatic force F_{es} (or total force gradient k_{ts} is the electrostatic force gradient k_{es}). When performing closed-loop FM-KPFM, the total force gradient k_{ts} presents three spectral components. Each of these spectral components contribute to the total frequency shift $\Delta\nu_e$ measured during a FM-KPFM experiment. The first spectral component of the frequency shift $\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})$, whose real part is mostly nullified in the three experiments on calcite presented in this section (figures 7.5 (d), 7.9 (d) and 7.13 (d)). For this to happen, the tip-sample voltage V_{bias} applied must be the V_{FM} value for each tip-sample distance. All the distance-dependent V_{FM} curves of the three experiments (figures 7.5 (b), 7.9 (b) and 7.13 (b)) show a wide range for all z-piezo positions z_p . Because of this, it would be interesting to know how much do these V_{FM} values contribute. For studying this, distance-dependent curves at fixed V_{bias} values (no feedback for KPFM engaged) should be recorded. The frequency shift $\Delta\nu_e$, as the first spectral component of the frequency shift $[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ (and if possible, the second $[\mathcal{F}[\Delta\nu_e](2\nu_{\text{es}})]$) would be the quantities of interest. The results of this experiment should be compared with the results of a closed-loop FM-KPFM experiment, in order to correlate the V_{FM} values with their contribution to the frequency shift $\Delta\nu_e$. Of course, this should be done when the problem with the calcite preparation is solved. As I have already shown, after some time of measuring

with a fixed V_{bias} value, the interaction tip-sample interaction changes for unknown reasons.

As it has already been discussed before, in the experiment (the first experiment on calcite described in this chapter, performed using the *second* Au-coated tip) the V_{FM} signal is not constant upon varying the z-piezo position z_{p} for all curves. This is an indication of the presence of point charges on the calcite surface. Nevertheless, only one valid KPFM experiment on calcite is not enough to make further conclusions. As shown by Söngen *et al.* [38], the weight function $W_{\text{FM}}(\mathbf{r}_i)$ (shape, magnitude and sign in each point $\mathbf{r}_i$) depends on the tip apex. They computed the weight functions $W_{\text{FM}}(\mathbf{r}_i)$ modelling the tip apex as a sphere, for which a radius was assumed. I cannot assume that all tips will have the same tip apex radius and that is considering that the tip apex has spherical shape), so the V_{FM} data collected with each one of these tips cannot be considered univocal. Thus, more experiments on different samples and using different Au-coated tips are necessary. However, at that time, I had two handicaps. The first problem is the preparation of the calcite samples (which has continued until recent days). It makes no sense to keep doing experiments on calcite samples which do not behave as the samples on which the experiments on molecules (self-assembly, diffusion, on-surface synthesis,...) have been performed. The second handicap was the impossibility of preparing more Au-coated cantilevers using the sputter gun ISE 5⁶, I decided to use the *third* Au-coated tip (the one which provided a flat V_{FM} signal upon varying z_{p} in closed-loop KPFM mode; see figure 7.6) on experiments on molecules deposited on calcite. These experiments are described in the following section.

⁶At that moment, the sputter gun ISE 5 was still installed in the UHV chamber. As explained at the end of section 6.4, at some point we uninstalled this sputter gun and installed a newer model, the ISE 10. It will be clearly specified in the next section which tips were prepared with that new sputter gun and on which experiments it was used.

7.3 Experiments on 2,5-DHBA Deposited on Calcite (10.4)

The 2,5-DHBA molecule is one of the six isomers of the dihydroxybenzoic acid. The molecule is depicted in figure 7.16.

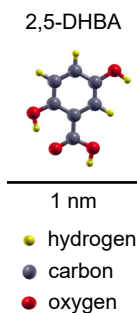


Figure 7.16.: 2,5-DHBA molecule. Adapted from [118].

The molecular structures formed by this molecule upon deposition on calcite (10.4) have been previously studied in this research group. Kittelmann *et al.* [19] identified two molecular structures at room temperature, named striped and dense. Figure 7.17 (a) is a well representative topography of the FM-AFM experiments described above. The islands similar to parallel lines correspond to the striped structure, as indicated. The dense structure corresponds to the islands with a homogeneous apparent height in respect to the bare calcite, which is indicated by orange arrows. The striped structure is shown as the alternating stripes with different apparent height along the $[0\bar{1}0]$ direction. The dense structure, however, is a uniform and close-packed structure formed by bright spots. The most energetically favourable structures that matches with these experimental observations were computed using density functional theory (DFT). For the striped structure, Paris *et al.* [6] considered that the most stable structure contains six molecule per cell. These six molecules are grouped in three dimers, with one of them lying onto the surface and the other two almost in vertical position. The alternating orientation of the dimers in respect to the calcite surface (lying-vertical) fits with the striped structure observed in FM-AFM measurements. The vertical dimers interact with each other by π -stacking. The interaction between vertical and flat dimers takes place by hydrogen bonding. The interaction between the vertical dimers and the substrate is electrostatic, while the interaction between the flat dimers and the substrate is due to hydrogen bonds and Van der Waals. For the dense structure, the result of the DFT calculations suggests one molecule per calcite unit cell as the most stable configuration. All molecules forming these islands are upright standing. They are anchored to the surface via hydrogen bonds of the carboxylic group to the carbonate group of the surface. The DFT calculations concluded that, within the hydrogen bond, the proton

of the carboxylic group is closer to the protruding oxygen of the carbonate group than to the molecule. This was considered by Kittelmann *et al.* [19] as a deprotonation. The molecules are not totally vertical, but tilted due to the π - π interaction between neighbouring molecules along the $[0\bar{1}0]$ direction.

Different time-dependent and temperature-dependent experiments have been performed [6, 118, 119]. It was found that, at room temperature, after a few hours of deposition, the striped structure disappears and only the dense structure remains [6].

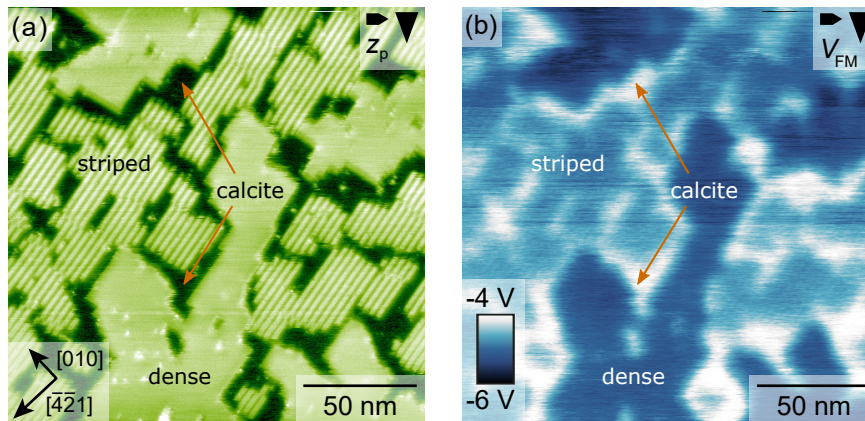


Figure 7.17.: Topography z_p (a) and Kelvin V_{FM} signal of 2,5-DHBA deposited on calcite. The areas corresponding to the two molecular structures, striped and dense, are indicated. Furthermore, the regions corresponding to bare calcite are pointed with orange arrows. Adapted from [37].

In order to study the charge distribution within these molecular structures, KPFM measurements were also performed [19, 37]. Figure 7.17 (b) shows the corresponding V_{FM} image of the topography depicted in (a). The dense structure shows a more negative V_{FM} signal than the striped structure. Moreover, both kind of islands exhibit more negative values than the calcite. The difference in V_{FM} signal between the two structures is attributed to the different interaction of the molecules in each structure with the calcite surface. As in the dense structure the proton of the carboxylic group is closer to the calcite surface, this molecular structure provides a more negative V_{FM} signal. It is interesting to note that the V_{FM} signal on the calcite looks very homogeneous, with values distributed within 200 or 300 mV around -4 V. This fact is in opposition with the V_{FM} images and distance-dependent curves shown in section 7.2, which display a range of ~ 1 V. Neff *et al.* [37] also presented distance-dependent V_{FM} measurements. The V_{FM} curves are distributed in three well distinguished groups: curves recorded on the striped structure, on the dense structure and on calcite. Although some differences can be observed between curves of the same group, these differences are negligible compared to any curves from any other group. All these KPFM experiments were performed using *n*-doped silicon AFM cantilevers (type PPP-NCH from NanoWorld, Neuchatel, Switzerland).

They were prepared following the standard procedure within this research group: sputtered with Ar^+ ions at 2 keV for 5 min in order to remove the oxide layer and possible contaminants. During these KPFM experiments, J. L. Neff discarded any tip which provided frequency shift $\Delta\nu_e(V_{\text{bias}})$ curves presenting non-parabolic shape and/or presenting hysteresis [120]. However, distance-dependent experiments on Au(111) as the ones described in section 6.4 were not performed. For this reason, although the tips were stable enough to provide $\Delta\nu_e(V_{\text{bias}})$ curves according to the Kantorovich equation described in section 2.4.2, their apex might have been contaminated with localized point charges, which could have contribute to the total V_{FM} signal. For this reason, it is interesting to perform distance-dependent V_{FM} measurements with prepared metal-coated silicon AFM tips.

In the following, two different KPFM experiments on 2,5-DHBA deposited on calcite are described. The calcite sample is the same one of the experiments described in section 7.2. The molecules were purchased from Sigma-Aldrich (Munich, Germany) with a purity of $> 99\%$. Prior to sublimation, the molecules were first outgassed. Right after, the Knudsen cell was heated up to 337 K in order to deposit the molecules on the calcite sample. During the sublimation, the calcite sample was kept at room temperature, as well as during both experiments.

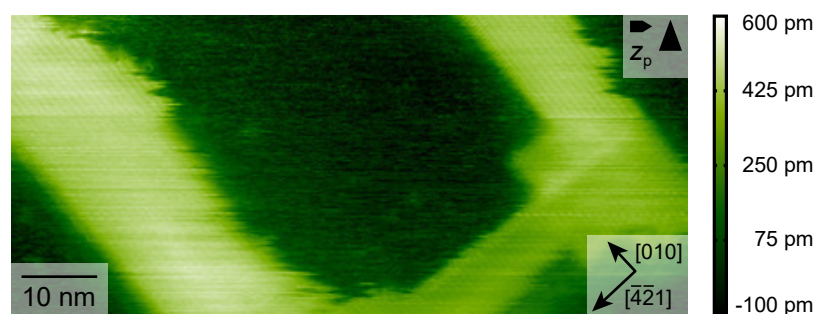


Figure 7.18.: Drift corrected FM-AFM topography of a 2,5-DHBA island of the dense structure on calcite (10.4).

Figure 7.18 shows the topography of a 2,5-DHBA island on calcite. The image was recorded several hours after the molecule deposition. According to the shape of the island, I could conclude it corresponds to the dense structure [118]. No striped islands were found.

For the first experiment on 2,5-DHBA molecules, the tip used was (as referred to before) *third* Au-coated silicon AFM tip. As a reminder, after experiment on calcite using this tip, the closed-loop KPFM experiments on Au(111) provided a flat curve upon varying z_p , while the static KPFM measurements did not provide a flat curve upon varying z_p , but a small variation for $0 < z_p < 1$ nm and seemed flat regions with jumps for the rest of the z_p measured.

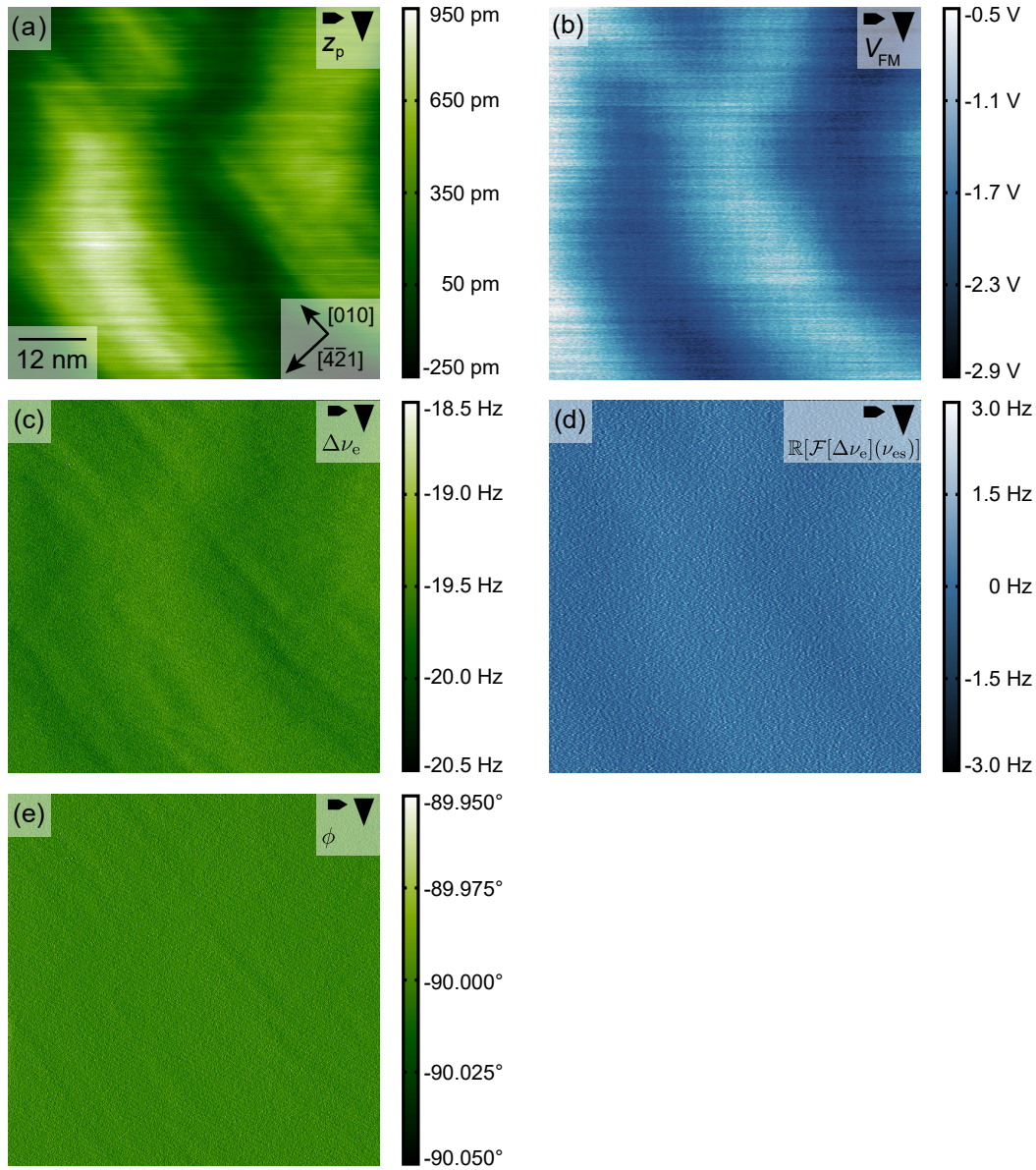


Figure 7.19.: FM-AFM and FM-KPFM images measured on 2,5-DHBA deposited on calcite using the *third* Au-coated silicon AFM tip. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

Figure 7.19 shows the images of this measurement: (a) shows the topography; (b) presents the Kelvin V_{FM} ; (c) corresponds to the frequency shift $\Delta\nu_e$; (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ and (e) corresponds to the phase shift ϕ . The phase shift ϕ (e) and frequency shift $\Delta\nu_e$ (c) images show some corrugation, but not relevant. The resolution of the topography (a) is not as good as in topography shown in figure 7.18, but is still possible to distinguish three different molecular islands. The edges of the islands are not well resolved, probably due to a blunt tip apex. According to their shape, the islands also correspond to the dense structure [118]. I can observe that the apparent height of the island on the left is larger than the other two. Nevertheless, from many previous experimental

observations and theoretical calculations, if the amount of molecules is less than one monolayer (which is the case in this experiment), the dense structure does not present a second layer. For this reason, I attribute this different apparent height to a deformed tip apex. The real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image (b) shows almost no corrugation, only some around the edges of the islands. The V_{FM} signal (d) shows more negative values on the islands than on the calcite, which fits with the observations of Neff *et al.* [37] (see figure 7.18). In this image I can observe that the areas between calcite and molecular islands are not so well defined as in the example shown in figure 7.17 (b), but a blurred "transition" between the areas of the calcite and the islands. As in the topography, I attribute these not well defined edges to the deformed tip apex. Nevertheless, the image corresponds to a specific tip-sample distance and only provide qualitative information, not enough for extracting a general conclusion (see figure 5.6). Recording distance-dependent curves was necessary. Figure 7.20 shows the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 7.21 shows the four different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curves in the plots relate each curve with the position where it was performed.

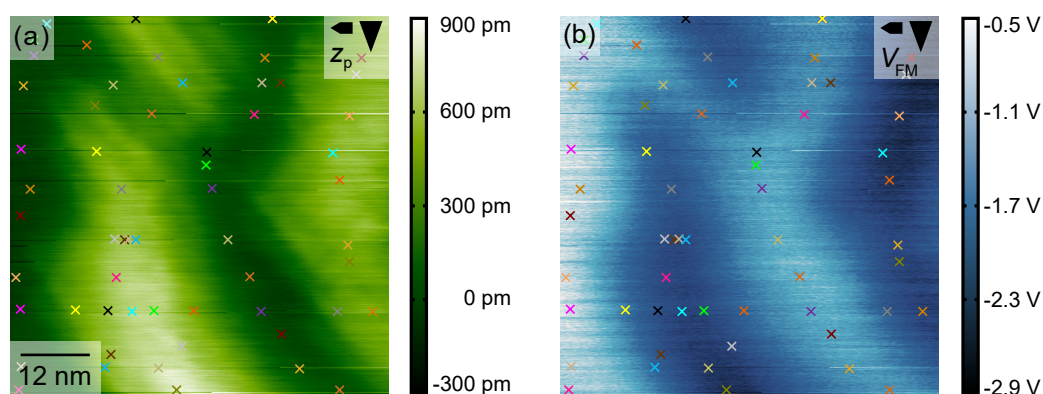


Figure 7.20.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *third* Au-coated silicon AFM tip. The crosses indicate the spots where the distance-dependent curves shown figure 7.21 were performed.

Figure 7.21 shows the distance-dependent curves recorded on the area indicated in figure 7.20. Plots (a) and (b) present the frequency shift $\Delta\nu_e$ and Kelvin V_{FM} curves, respectively, while (c) and (d) show the oscillation amplitude A and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves, respectively. All oscillation amplitude A curves are constant for all z_p values. Then, both frequency shift $\Delta\nu_e$ and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves provide reliable information. This time, all frequency shift $\Delta\nu_e$ curves only overlap for $z_p > 30$ nm, which clearly indicates a difference in interaction depending on the spot of the surface where they were recorded. All real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ curves (d) are mostly nullified (0 Hz plus noise), so the

V_{FM} curves are trustworthy. For $z_p = 0$ nm, the curves distribute between -2.8 and -0.7 V approximately. For $z_p > 0$ nm, all curves increase, showing an asymptotic tendency to a value. This value seems to be different to many or most of the curves: for $z_p = 40$ nm, the values of the curves vary between -0.75 and 0 V approximately. This observation is in disagreement with the data presented by Neff *et al.* and what I expected: curves recorded on two different species should provide two groups of curves with two different tendencies and two different values (or range of values) for specific z-piezo position z_p values. And in this experiment, this did not happen.

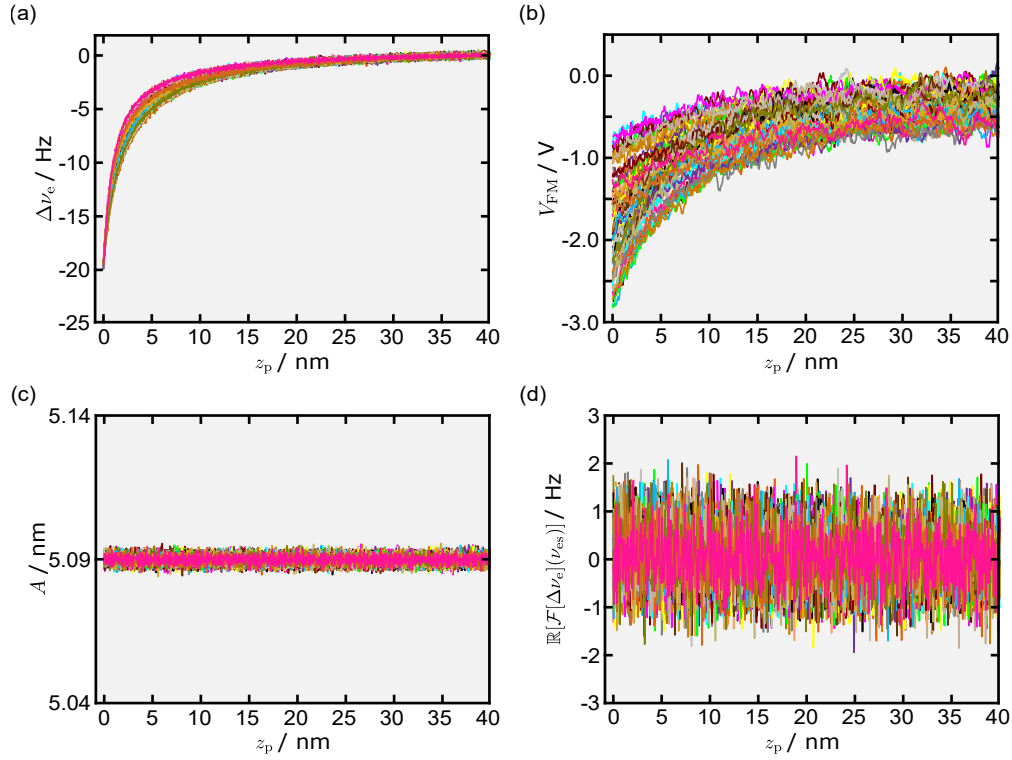


Figure 7.21.: Distance-dependent curves performed during the first experiment on 2,5-DHBA deposited on calcite. The *third* Au-coated silicon AFM tip. The colour of each curve correlates with the colour of the crosses in the images in figure 7.12. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ versus the z-piezo displacement z_p .

After the experiment on molecules, I repeated the usual measurements on Au(111). Most of the data from this experiment is collected in appendix D (figures D.13, D.14 and D.15). The measurements for comparing closed-loop $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data were performed too. The data corresponding to the oscillation amplitude $A(V_{\text{bias}})$ and the frequency shift $\Delta\nu_e(V_{\text{bias}})$ curves can be found in appendix D (figure D.16).

The comparison of both procedures is presented in figure 7.22. Plot (a) shows the comparison of the frequency shift $\Delta\nu_e(z_p)$ curve with the fitted $\Delta\nu_e(V_{\text{FM}})$ data from the static FM-KPFM measurement. Plot (b) presents the comparison of the closed-loop $V_{\text{FM}}(z_p)$ curve with the fitted V_{FM} data from the static FM-KPFM measurement. The closed-loop V_{FM} curve shows a large increase upon z-piezo displacement z_p : more than 200 mV from 0 to 20 nm. This change upon varying z_p also appears in the static V_{FM} data. Despite the values of the static V_{FM} data are slightly smaller, the V_{FM} change upon varying distance is clear. Therefore, the tip apex was contaminated with localized point charges.

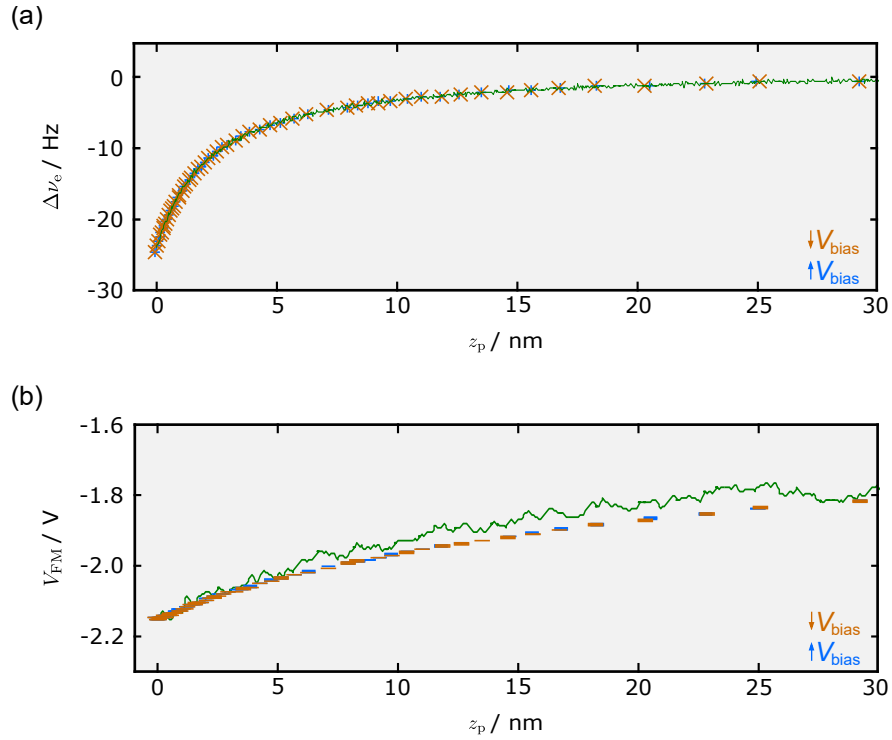


Figure 7.22.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{\text{bias}})$ curves of figure D.16 (a) and (b), which were performed after the first experiment on 2,5-DHBA deposited on calcite using the *third* Au-coated silicon AFM tip. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

It is not possible to find out if this contamination happened before recording all distance-dependent curves or during this process. Furthermore, the V_{FM} curves shown in figure 7.21 (b) although they look similar, they present different distance-dependencies. Taking this into account, it is even possible that the tip apex changed many times while recording the curves (picking up and dropping point charges). Another possible cause is the calcite sample, which is the same sample of the experiments described in the previous section⁷. The contribution of this sample to the total V_{FM} signal might cause this wide variety of curves. One more possible reason for it is the tip apex. As the topographies in figures 7.20 (a) and 7.19 (a) show, the edges of the molecular islands are not well defined: some of them are very broad, other ones appear twice or even three times. This fact indicates a broad tip apex with multiple protuberances. A broad apex implies more point charges contributing to the V_{FM} [38]. To illustrate this assumption, as an example, I can consider a distance-dependent curve recorded on calcite, but very close to the molecular island edge. In this case, point charges within the molecular island located very close to its edge can contribute to the V_{FM} signal of this curve recorded on calcite. There, the larger is the tip apex radius (again, assuming an spherical tip apex), the more point charges of the island can contribute to the total V_{FM} signal. One of these theories could explain the not well defined edges of the different regions in the V_{FM} signal. Or maybe all of them. Or a combination of only of them. The only thing I can do is showing the data analysis that it is followed from the KPFM model I use.

As stated previously mentioned, the V_{FM} signal for an specific tip-sample distance z_c on an specific spot on the surface is the weighted averaged of all point charges between tip and metallic counter-electrode. Then, a V_{FM} curve recorded on bare calcite will have contributions of the point charges on and inside the calcite. However, a V_{FM} curve recorded on the molecular island will have contributions from the point charges within the molecular island and the calcite substrate below them, as appointed in equation (7.1):

$$\begin{aligned} V_{\text{FM}} &= -V_{\text{CPD}} + \sum_{i=1}^N q_i W_{\text{FM}}(\mathbf{r}_i) \\ &= -V_{\text{CPD}} + \sum_{i=1}^{N_c} q_{i,c} W_{\text{FM}}(\mathbf{r}_{i,c}) + \sum_{i=1}^{N_m} q_{i,m} W_{\text{FM}}(\mathbf{r}_{i,m}) \end{aligned} \quad (7.1)$$

The first part of this equation refers to the general situation: V_{CPD} is the contact potential difference, $\mathbf{r}_i$ is the position of each individual point charge q_i , N is the total number of point charges and $W_{\text{FM}}(\mathbf{r}_i)$ is the *FM weight function* at the position

⁷As described in section 7.2, several calcite samples were prepared and it was not possible to measure FM-AFM and get well defined terraces and step edges. It was only possible during FM-KPFM measurements, and the result showed very different V_{FM} values in the measured areas.

of each individual point charge r_i . The second part of the equation has the same physical meaning, differentiating between the point charges on calcite and on the molecules with the subscripts c and m , respectively. Then, if the curves recorded on calcite were all similar (overlapping each other, same approximate values for the same z -piezo displacement z_p values,...), I could assume that the charge distribution on the calcite surface, the inner layers and so on is the same in all points on which distance-dependent curves were recorded. From there, I could also assume that it is homogeneous in all the sample surface. These assumptions would allow us to subtract the average⁸ of all V_{FM} curves recorded on calcite to the curves recorded on the molecular island. However, before subtracting the curves, I should first take into account a limitation of our system already described in chapter 3: all distance-dependent curves are recorded considering the first point of the z -piezo displacement z_p as "0 nm". The implications of this disadvantage and the way to correct its effects is explained in the following using figure 7.23.

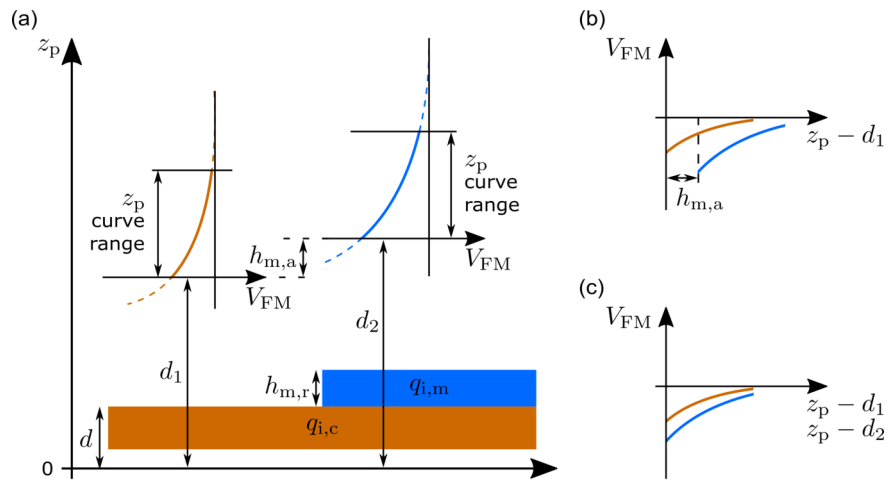


Figure 7.23.: Scheme of the distance-dependent curve recording process. This process is explained using as example two V_{FM} distance-dependent curves. Figure (a) depicts two V_{FM} curves recorded on two different species: calcite and molecules. The real and apparent height of the molecular islands are indicated by $h_{m,r}$ and $h_{m,a}$. Figure (b) show both examples of V_{FM} curves plotted together, with no change in their relative position. Figure (c) show the same plot, but the curves are shifted: this is how the Omicron VT AFM/STM XA stores the curves.

Figure 7.23 depicts the process of recording distance-dependent curves using the Omicron VT AFM/STM XA. Figure (a) shows an scheme of two distance-dependent curves recorded on two different species: calcite and a molecular island, each one of them with localized point charges denoted by $q_{i,c}$ and $q_{i,m}$. The vertical axis corresponds to the z -piezo position z_p . The point at which the system considers as "0 nm" (which in the Omicron VT AFM/STM XA is at the middle of the z -piezo range) is

⁸As I have observed in the experiments on Au(111), even when the distance-dependent V_{FM} curves are very similar, there is always a small difference between each other. The curves recorded on calcite and 2,5-DHBA by Neff *et al.* showed the same situation. As in the experiment I have described this is not even the case, the most appropriate way of proceeding is guessing that I could subtract the average of all V_{FM} curves and not any specific curve.

indicated. The sample surface (in this case, calcite) is at a vertical distance d from the 0 of the z-piezo range. This distance d can change from experiment to experiment. The height of the molecular island is noted by $h_{m,r}$, where m stands for molecules and r for real. During an FM-AFM experiment, a frequency shift $\Delta\nu_e$ setpoint is chosen. The *distance feedback loop* keeps the frequency shift $\Delta\nu_e$ equal to that fixed setpoint by adjusting the z-piezo position z_p . That is how I get the topography channel. However, the height of the molecular islands in the recorded topography does not necessarily correspond to the real height $h_{m,r}$, since the interaction of the molecules and the calcite with the tip is different. This is the apparent height of the molecular island $h_{m,a}$ (a stands for apparent).

As it has been shown before, during the acquisition of the topography of a sample surface, it is possible to record distance-dependent curves. The correct way of comparing two distance-dependent curves of any SPM channel is as figure 7.23 (b) depicts: respecting the relative position of each curve respect to the absolute 0 of the z-piezo position z_p . However, in the system I work with this is not the case. As explained in chapter 3, the first point of the z-piezo displacement z_p is always recorded as 0 nm. A direct comparison of the curves would lead to a situation as depicted in (c). Until now, this was not a real problem, since I only worked with one species in our sample (gold in sections 6.3 and 6.4, calcite in section 7.2). But in this case (and in any future distance-dependent KPFM experiment of molecules on insulating substrates), specially if I want to use equation (7.1) to subtract the calcite contribution to the molecular island curves, I have to make this correction. In order to do this, I use the position where each individual curve was recorded (see figure 7.20 (a)) to find out the real value of the z-piezo position z_p (d_1 or d_2 in figure 7.23) at that point. Each value was added to all z_p values of each curve⁹. Figure 7.24 show the V_{FM} curves differentiating between the ones recorded on calcite and the ones recorded on 2,5-DHBA islands and the comparison between their averages.

Figure 7.24 (a) shows all curves recorded on calcite, while (b) shows the curves recorded on molecules. Both group of curves present a common tendency, although the curves do not overlap on top of each other. In general terms, the curves recorded on molecules are more negative than the curves recorded on calcite. The correction of the z-piezo position z_p is specially useful to distinguish that the curves which do not look similar before the correction are equivalent after the correction, just measured in a different z-piezo range. Since the curves on calcite do not overlap (showing a common behaviour), it is not appropriate to subtract any of the V_{FM}

⁹To be entirely precise, the z_p value found in the topography does not correspond to the values d_1 or d_2 . As explained in appendix B, the offset in all topography are adjusted so the calcite surface correspond (approximately) to 0 nm. Nevertheless, the relative z_p value between two points where two different curves were performed is kept

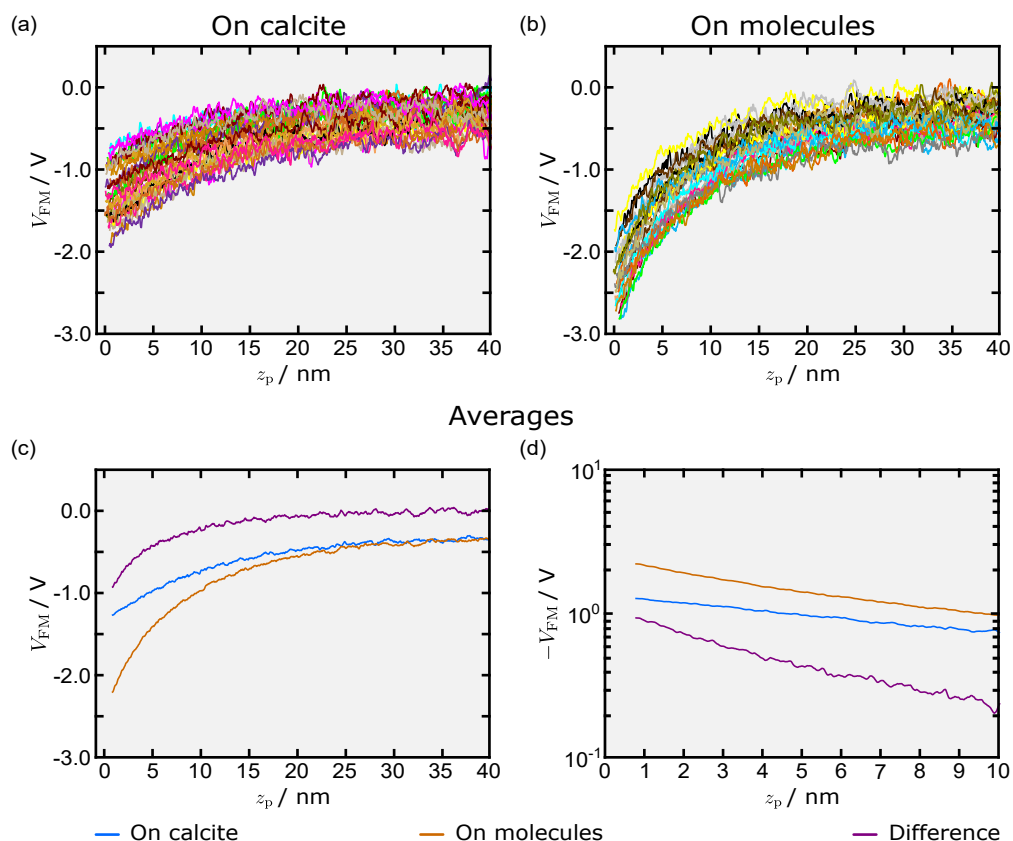


Figure 7.24.: Distinction (recorded on calcite or on molecules) of the V_{FM} curves corresponding to the measurement shown in figure 7.21 and comparison of their averages. The curves recorded on calcite are shown in plot (a), while the ones recorded on molecules are shown in plot (b). The plots (c) and (d) correspond to the linear and logarithmic comparison of the averages of the curves shown in (a) and (b) and the difference between them, respectively. Note that, as the logarithm of a negative number does not exist and most of the values of the V_{FM} averages are negative, plot (d) shows the logarithmic plot of these averages but with opposite sign. Furthermore, the logarithmic plot is shown only for $0 < z_p < 10$ nm for practical reasons: as both averages have very similar values for large z_p , the values of the difference are, besides very noisy, much smaller and prevents to display with detail the averages and the difference for small z_p values. The complete logarithmic plot can be found in appendix F, specifically figure F.1.

curves recorded on calcite or the average of all of them to the curves recorded on the molecules. However, in order to show how the data treatment should be done in an experiment in which the contribution from the calcite can be considered the same in all spots of the surface, I have proceeded with the averages of both groups of curves. In order to compute the averages, as the curves were shifted in z -piezo position z_p , it was necessary to interpolate the data before average. The data interpolation was computed with MATLAB, using a linear interpolation (function `interp1`, method '`linear`'). Plot (c) show the comparison of the averages of the curves recorded on calcite and on molecules. For large tip-sample distances, they tend to a similar value, but as the this distance is reduced, the differences are clear. The difference¹⁰ clearly shows a tendency to 0 V for large tip-sample distances,

¹⁰With difference, I mean the result of subtracting the average of the curves recorded on calcite to the average of the curves recorded on molecules.

and a clear decay to more negative values when this distance is reduced. In order to study the distance dependences of the averages and its difference, plot (d) is the corresponding logarithmic plot from 0 to 10 nm¹¹. The logarithmic plot of the average corresponding to calcite curves looks linear. This indicates an exponential tendency of the curve in the linear representation. However, the logarithmic plot of the average corresponding to molecules presents a non-linear tendency. Then, the linear representation of this curve is not exponential. Once more, I have to remark that this is only a way to analyse and interpret the data. The averages indicate a general tendency, but as figures 7.24 (a) and (b) show, the curves present a wide variety of distance-dependencies, which are more evident for small z-piezo displacements z_p .

At this point, I ended up with all Au-coated silicon AFM tips contaminated with point charges (previously referred to as *second*, *third* and *fourth*). At this point (as briefly commented at the end of section 6.4), I decided to vent the UHV chamber to dismount the sputter gun ISE 5 and mount a newer model, the sputter gun ISE 10. I could not assume that the same parameters for sputtering Au-coated tips (energy, time,...) would work, so I had to repeat part of the process described in section 6.4. I used a new tip, named as *fifth* tip for repeating this process. I used the same Ar partial pressure and energy as with the old sputter gun: $2 \cdot 10^{-6}$ mbar and 1.7 keV. This new sputter gun had a different controller in which two more parameters must be set: *extractor* and *focus*. In order to choose these parameters, I repeated the procedure of taking long-time exposure photographs (check figure 6.18 in section 6.4) to ensure the area around the tip was hit by the Ar⁺ ions and check the drain current. Finally, the values for the parameters *focus* and *extractor* were chosen in $\simeq 1610$ -1620 for both, providing a drain current of 1.2-1.3 μ A. I sputter for 30 s, repeated the measurements on Au(111), sputter for 10 s more and again, measure on Au(111). The results are compared in figure 7.25.

Figure 7.25 shows only the three V_{FM} curves. All channels of these three curves are shown in figure E.1, which can be found in appendix E. The blue curve corresponds to the tip before sputtering it. It shows a large change of more than 100 mV in the from 0 to 10 nm. This variation for the same z-piezo displacement z_p range is much smaller after sputtering the tip for 30 s (orange curve). Finally, the tip was sputter for 10 s more and the curve looks basically flat for this z_p range. Thus, I can conclude that the aforementioned parameters for preparing Au-coated tips with the new sputter gun ISE 10 were found.

I decided to take one of the old tips to prepare it again and carry out a second experiment of 2,5-DHBA on calcite. I chose the *second* tip and, using the new

¹¹Displaying the whole z_p range hinders to observe the averages and the difference with detail for small z-piezo position z_p values. The plot of the whole range is shown in figure F.1 (appendix F).

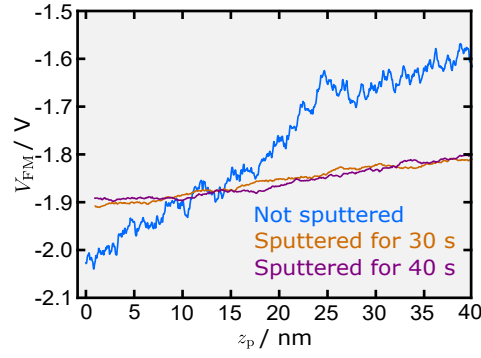


Figure 7.25.: V_{FM} distance-dependent curves performed on the Au(111) single crystal with the *fifth* Au-coated silicon AFM tip: procedure to find the new preparation parameters using the new sputter gun: ISE 10. The figure including all channels can be found in appendix E, specifically, the figure E.1.

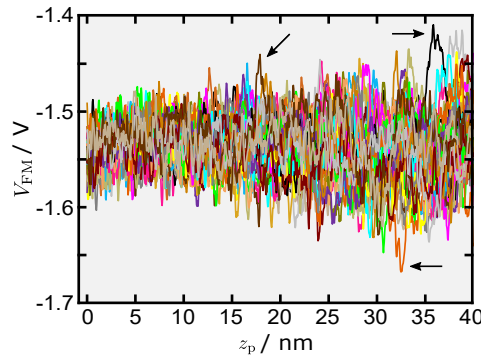


Figure 7.26.: V_{FM} distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10. The figure including all channels can be found in appendix E, specifically, the figure E.4

preparation parameters, sputter it only for 15 s more. As this tip was already sputter (as mentioned in section 6.4) for 160 s, I decided to sputter it for a shorter time to prevent removing completely the Au-coating. Right after, I measured on Au(111) to check the state of the tip apex. The full set of images (figure D.1) and the topography z_p and V_{FM} image with the crosses indicating the position where the distance-dependent curves were recorded (figure D.2) and the distance-dependent curves (figure D.3) are collected in appendix E. Figure 7.26 shows only the V_{FM} curves. All channels of these three curves are shown in figure E.4, which can be found in appendix E. In figure 7.26, I can observe that, even when the curves do not look constant, all curves fluctuate between -1.5 and -1.6 V (approximately) for $0 < z_p < 10$ nm. Beyond 10 nm, the curves still fluctuate around a constant value, but the large variations (indicated with black arrows in the plot) already described in previous experiments, are still present. Furthermore, the measurements for comparing closed-loop $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data were performed too. The data corresponding to the oscillation amplitude $A(V_{\text{bias}})$ and the parabolas $\Delta\nu_e(V_{\text{bias}})$ can be found in appendix D (figure D.16).

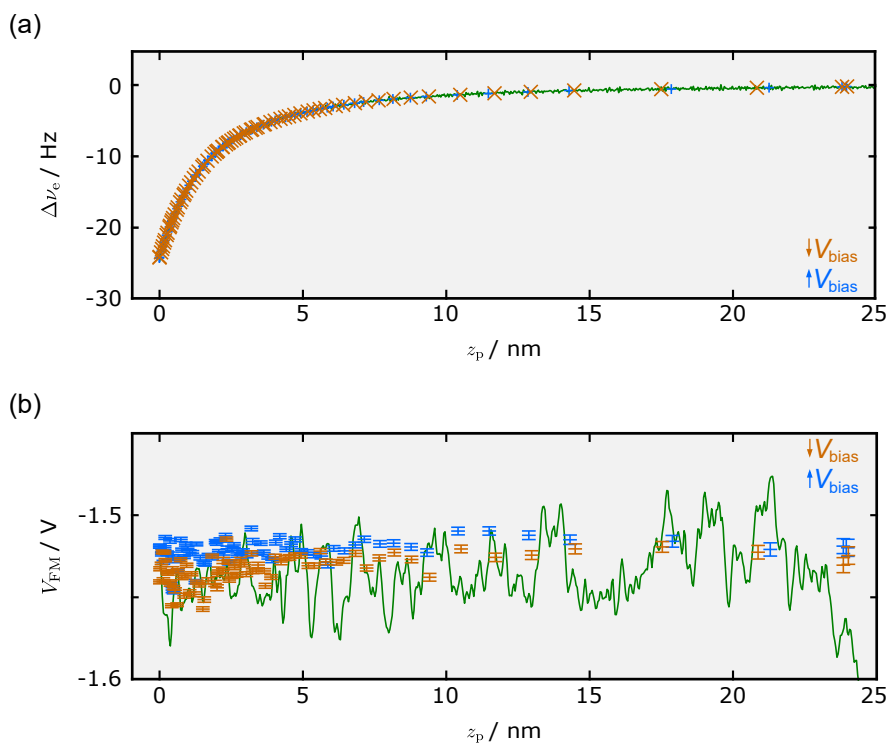


Figure 7.27.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{\text{bias}})$ curves of figure E.5 (a) and (b), which were performed after sputtering the *second* Au-coated silicon AFM tip for 15 s more. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

The comparison of both procedures is presented in figure 7.27. Plot (a) shows the comparison of the frequency shift $\Delta\nu_e(z_p)$ curve with the fitted $\Delta\nu_e(V_{\text{FM}})$ data from the static FM-KPFM measurement. Plot (b) presents the comparison of the closed-loop $V_{\text{FM}}(z_p)$ curve with the fitted V_{FM} data from the static FM-KPFM measurement. Upon z-piezo displacement z_p , the closed-loop V_{FM} curve shows variations around -1.55 V. Moreover, the static V_{FM} data shows some jumps for small z_p values, but as the z-piezo displacement z_p increase, the V_{FM} values basically do not vary. Then, the *second* tip can be considered free of localized point charges and used on an KPFM experiment to measure 2,5-DHBA.

As a last remark about this topic, the sputtering parameters found using the new ISE 10 sputter gun might need for attempts for a fine tune. It has been tested in two tips, but sputtering for different times. It is possible that the time used for sputtering the *fifth* tip could be insufficient on a tip with more contamination. For this reason, until this procedure is reproduce with more Au-coated tips, the sputtering time should not be assumed as definitive.

Since we opened the UHV chamber, I had to prepare the sample again. The calcite crystal was outgassed, cleaved and annealed one more time. The molecules were outgassed before sublimation.

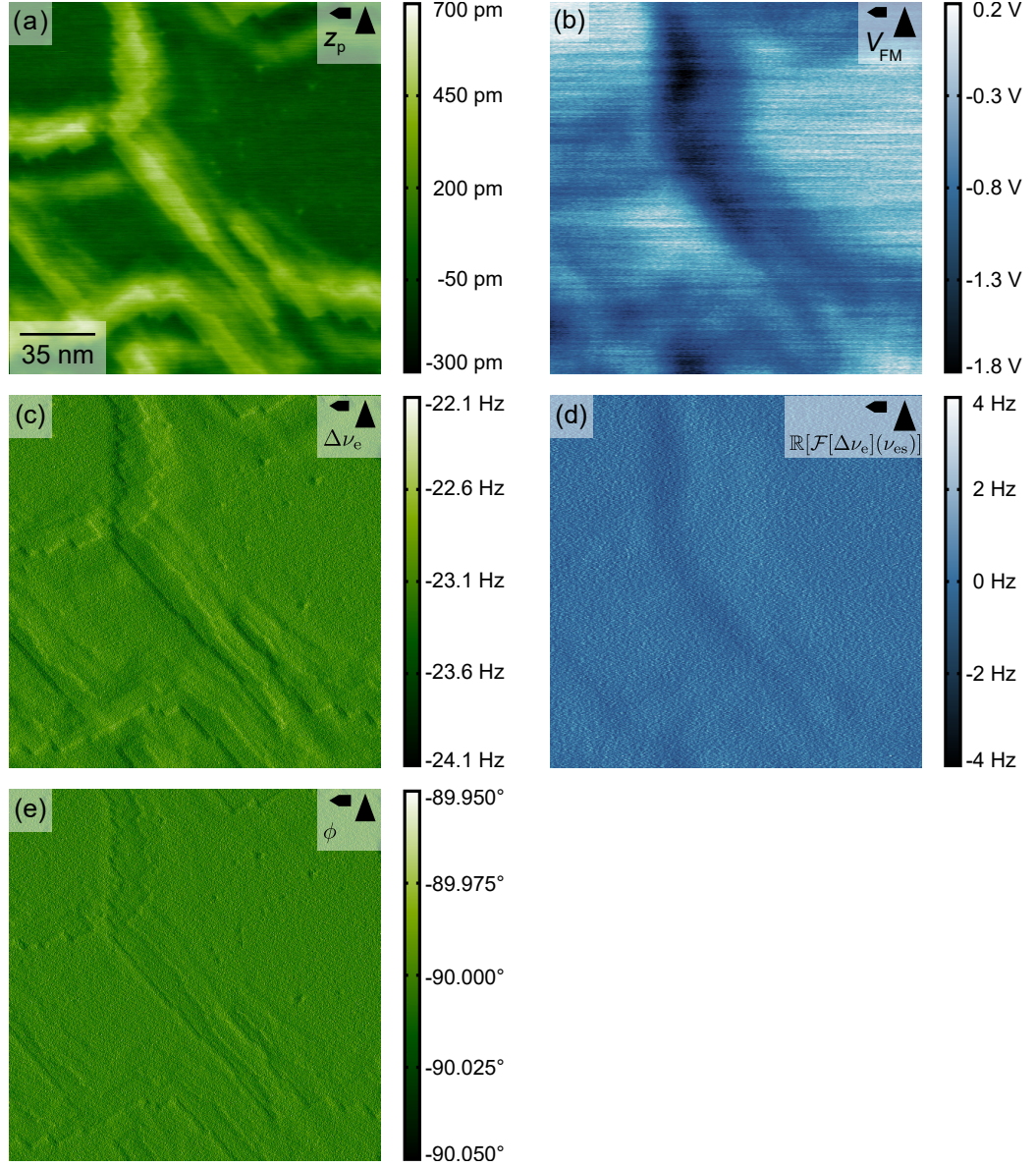


Figure 7.28.: FM-AFM and FM-KPFM images measured on the calcite (10.4) surface using the *second* Au-coated silicon AFM tip. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

Figure 7.28 shows the images of this measurement: (a) presents the topography; (b) shows the Kelvin V_{FM} ; (c) presents the frequency shift $\Delta\nu_e$; (d) corresponds to the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ and (e) presents the phase shift ϕ . The phase shift ϕ (e) and frequency shift $\Delta\nu_e$ (c) images show some corrugation, but not important. The topography (a) shows several molecular islands. Their long shape and rectangular corners point to be the dense structure [118]. Their edges, which are imaged several times and not sharp evidence that the apex of the *second* tip presents more than one protuberance, as shown in previous experiments (see figure D.5 in appendix D). The real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ image (d) shows almost no corrugation, mostly around

the area where the long island (which goes from the bottom to the top of the image) is. The V_{FM} signal (d) shows more negative values on the island than on the calcite. Actually, the V_{FM} values are significantly more negative on the upper part of the aforementioned island placed on the top middle of the image. Besides, the edges between calcite and molecular island are not well defined: this is much more pronounced than in the previous experiment. I ascribe this effect to the deformed tip apex. As stated in the previous experiments, this image is only useful to get qualitative information: the V_{FM} signal is different on the molecular island than on the calcite, which I could already guessed, since they are different species. The experiment for recording distance-dependent curves was necessary. Figure 7.29 shows the topography z_p and Kelvin V_{FM} image during which the distance-dependent curves were performed, and figure 7.30 shows the four different channels recorded during the distance-dependent curves. The colours of the crosses in the images and the curves in the plots relate each curve with the position where it was performed.

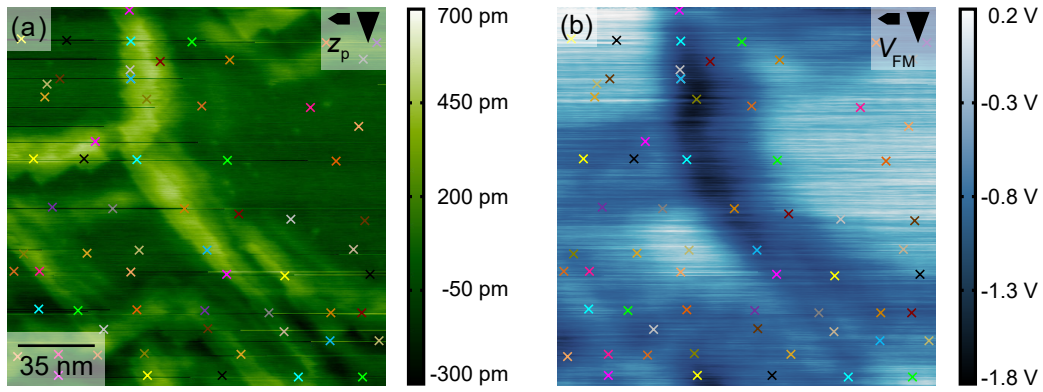


Figure 7.29.: Topography z_p (a) and Kelvin V_{FM} (b) images. These measurements were performed using the *second* Au-coated silicon AFM tip. The crosses indicate the spots where the distance-dependent curves shown figure 7.30 were performed.

Figure 7.30 shows the distance-dependent curves recorded on the area indicated in figure 7.29. Plots (a) and (b) correspond to the frequency shift $\Delta\nu_e$ and Kelvin V_{FM} curves, respectively, while (c) and (d) present the oscillation amplitude A and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ curves, respectively. All oscillation amplitude A curves are constant for all z_p values. Then, the frequency shift $\Delta\nu_e$ and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ curves provide reliable information. This time, the frequency shift $\Delta\nu_e$ curves only overlap for $z_p > 20$ nm. Then, there was a clear dependence of spot of the surface where the curves were recorded. All curves of the channel first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ (d) are nullified (noise around 0 Hz), so the V_{FM} curves are trustworthy. For $z_p = 0$ nm, the curves distribute between -1.6 and -0.3 V approximately. Unlike the previous experiment on 2,5-DHBA, this time the V_{FM} curves do not show a similar or common distance-dependence, but a wide variety

of them. There are curves which fluctuate around the same value for all z_p values, curve which tend to increase or decrease upon increasing z_p , curves with a change of tendency... There is not any indication of a common behaviour of the V_{FM} curves depending on the spot where they were recorded.

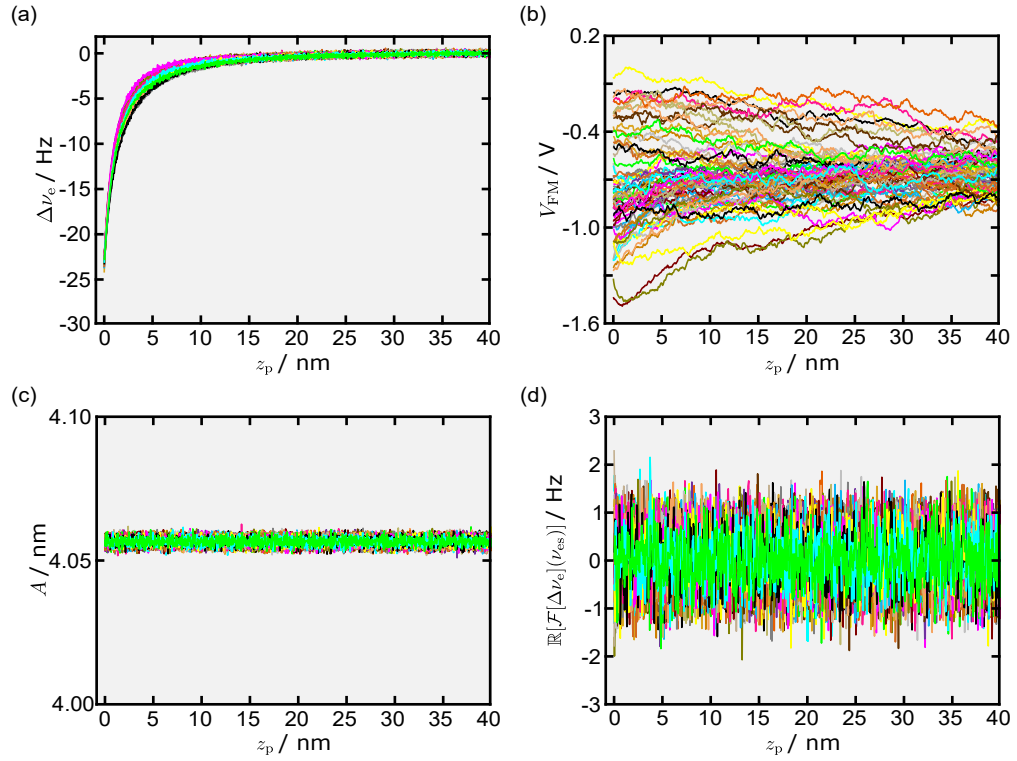


Figure 7.30.: Distance-dependent curves performed during the second experiment on 2,5-DHBA deposited on calcite. The *second* Au-coated silicon AFM tip. The colour of each curve correlates with the colour of the crosses in the images in figure 7.29. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z-piezo displacement z_p .

After the experiment on molecules, I repeated the usual measurements on Au(111). Unfortunately, during the measurement, the tip accidentally crashed on the surface. After that, I proceeded recording distance-dependent curves. Figure 7.31 shows one of the V_{FM} curves (all channels corresponding to this curve can be found in appendix E, in figure 7.31). The curve shows a clear non-flat distance-dependence, which indicates the presence of localized point charges on the tip apex. Then, I have a second experiment on molecules which I cannot fully trust.

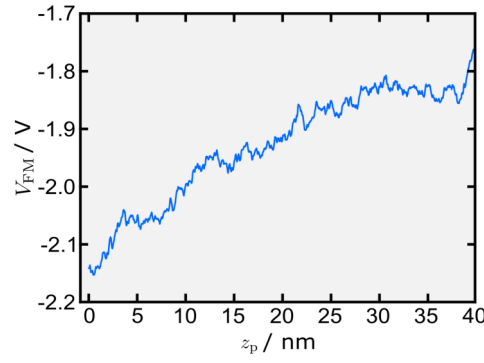


Figure 7.31.: V_{FM} distance-dependent curves performed on the Au(111) single crystal with the second Au-coated silicon AFM tip after the second experiment on 2,5-DHBA deposited on calcite. The figure including all channels can be found in appendix E, specifically, the figure E.7

Nevertheless, there was still the possibility of checking the state of the tip apex before the crash. Usually, I compare one distance-dependent closed-loop V_{FM} curve and fitted V_{FM} data from a large collection of $\Delta\nu_e (V_{\text{bias}})$ curves. Hence, I decided to use the distance-dependent $\Delta\nu_e (z_p)$ and voltage-dependent $\Delta\nu_e (V_{\text{bias}})$ curves performed during the FM-AFM measurements¹² as substitution to this process. Unfortunately, I only had three $\Delta\nu_e (V_{\text{bias}})$ curves recorded at different frequency shift $\Delta\nu_e$ setpoints (and, hence, three different tip-sample distances). The data corresponding to the oscillation amplitude $A (V_{\text{bias}})$ and the frequency shift $\Delta\nu_e (V_{\text{bias}})$ curves can be found in appendix E (figure E.6). The V_{FM} data extracted from this curves is shown in figure 7.32. Plot (a) shows the comparison of the frequency shift $\Delta\nu_e (z_p)$ curve with the fitted $\Delta\nu_e (V_{\text{FM}})$ data from the static FM-KPFM measurement. Plot (b) presents the comparison of the closed-loop $V_{\text{FM}} (z_p)$ curve with the fitted V_{FM} data from the static FM-KPFM measurement. The approximate z_p values and exact V_{FM} value of these points are collected in table 7.1. The z-piezo z_p range in which these curves were recorded is only 2 nm. The variation from the points corresponding to the first $\Delta\nu_e (V_{\text{bias}})$ curve to the second (counting from smaller to larger z_p values) is almost 50 mV. From the second to the third the change is only of a few 12 mV. The three points hint a negative tendency of $V_{\text{FM}} (z_p)$, which could tend to a constant value after a few nanometres or continue decreasing. With only these three $\Delta\nu_e (V_{\text{bias}})$ curves it is not enough to determine the state of the tip apex. In the absence of more data, I should assume that the tip was contaminated. Nevertheless, I will proceed with a more accurate analysis of the distance-dependent experiment on 2,5-DHBA on calcite, as it was done in the previous experiment.

¹²During FM-AFM measurements, I usually record different distance-dependent $\Delta\nu_e (z_p)$ to check the tip-sample interaction. Usually, after varying the frequency shift $\Delta\nu_e$ setpoint (and hence, the tip-sample distance), I record voltage-dependent $\Delta\nu_e (V_{\text{bias}})$ curves in order to adjust the V_{bias} value to the maximum of each parabola.

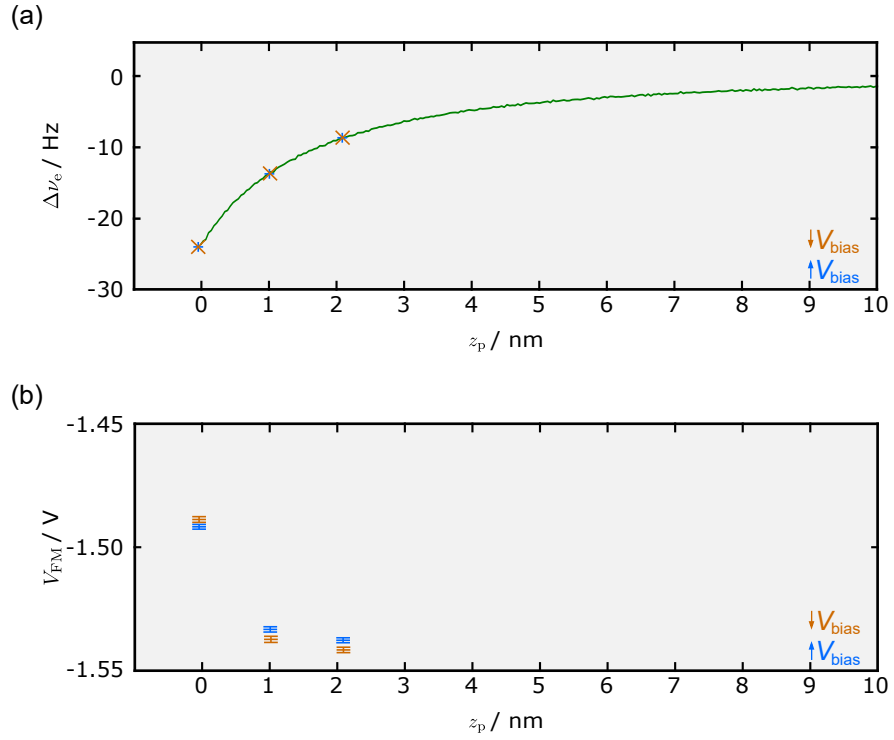


Figure 7.32.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{FM}(z_p)$ curve and fitted V_{FM} data of the $\Delta\nu_e(V_{bias})$ curves of figure E.6 (a) and (b), which were performed after the second experiment on 2,5-DHBA deposited on calcite using the *second* Au-coated silicon AFM tip. The distance-dependent curves are plotted in green. The data extracted from the negative sweep voltage V_{bias} is plotted in orange, while the data extracted from the positive sweep voltage V_{bias} is plotted in blue.

$\Delta\nu_e(V_{bias})$ curve	z_p value	V_{bias} sweep direction	V_{FM} value
First	~ 0 nm	$\downarrow$	-1.492 V
		$\uparrow$	-1.489 V
Second	~ 1 nm	$\downarrow$	-1.537 V
		$\uparrow$	-1.533 V
Third	~ 2 nm	$\downarrow$	-1.531 V
		$\uparrow$	-1.525 V

Table 7.1.: V_{FM} values of the points of figure 7.32. The curves are counted from smaller to larger z_p values. The z_p value indicated the approximate position at which the curves were recorded. In the field V_{bias} sweep direction, the down (up) arrows indicates that the curve was recorded with a negative (positive) sweep voltage. The V_{FM} value indicates the position of the maxima of the frequency shift $\Delta\nu_e(V_{bias})$ curves.

Figure 7.33 (a) shows all curves recorded on calcite, while (b) shows the curves recorded on molecules. As in the previous experiment, the correction of the z-piezo position z_p was done. However, it did not show that any of the curves overlap (which would have meant that the overlapping of the curves were the result of measuring the same contribution, but along a different z-piezo z_p range). I observe that, in general terms, the curves recorded on molecules are more negative than the curves recorded on calcite. Some of the curves recorded on calcite fluctuate around constant values (without stating that they look constant), while other curves show a small increase or decrease upon increasing the z-piezo displacement z_p . In the case of the curves recorded on molecules, some of them also fluctuate around a constant value, but many of them show an pronounced increase for $0 < z_p < 5$ to 10 nm. Just a few show a different behaviour: a decrease or a much more pronounced increase for all the z_p values in both cases. But the most relevant observation for our next purpose is that, again, the curves recorded do not overlap. This fact means that I cannot assume that the contribution of the calcite to the V_{FM} signal is homogeneous in the whole calcite surface. For this reason, it is not strictly correct to subtract any of the V_{FM} curves recorded on calcite or the average of all of them to the curves recorded on the molecules. Anyhow, as in the previous experiment, I will discuss the averages of both groups of curves, which are shown in figure 7.33 (c). The method for interpolating the data before averaging was the same as in the previous experiment. For small z_p values (0 to $\simeq 2$ nm), it is possible to observe that the average of the curves recorded on calcite show a small curvature. From $z_p = 10$ nm on, it looks linear, with a small negative slope. On the other hand, the average of the curves recorded on the molecules clearly exhibits a non-linear tendency for the $0 < z_p < 5$ nm, and from there on is basically linear. The difference¹³ shows a very similar distance-dependence to the average corresponding to molecules, since the one of calcite is almost constant. In order to study the distance dependences of the averages and its difference, plot (d) is the corresponding logarithmic plot from 0 to 10 nm¹⁴. The logarithmic plot of the average corresponding to calcite curves looks linear. It is possible to observe several jumps two jumps at ~ 5 and ~ 9 nm. The average of the curves recorded on molecules, in this logarithmic representation, looks linear for $0 < z_p \lesssim 5$ nm. For larger z_p values, it shows a small convex curvature. Finally, the logarithmic representation of the difference looks linear for $0 < z_p \lesssim 2$ nm. From there on, there are small variations (up and down) along what looks as linear. The linear behaviours of both averages and of the difference (even in only an specific z_p range) on this plot indicates the exponential distance-dependent on z_p .

¹³As in the previous experiment, with difference I mean the result of subtracting the average of the curves recorded on calcite to the average of the curves recorded on molecules.

¹⁴As for the previous experiment, the logarithmic plot is shown for a smaller z-piezo z_p range for the aforementioned practical reasons. The plot of the whole range is shown in figure F.2 (appendix F).

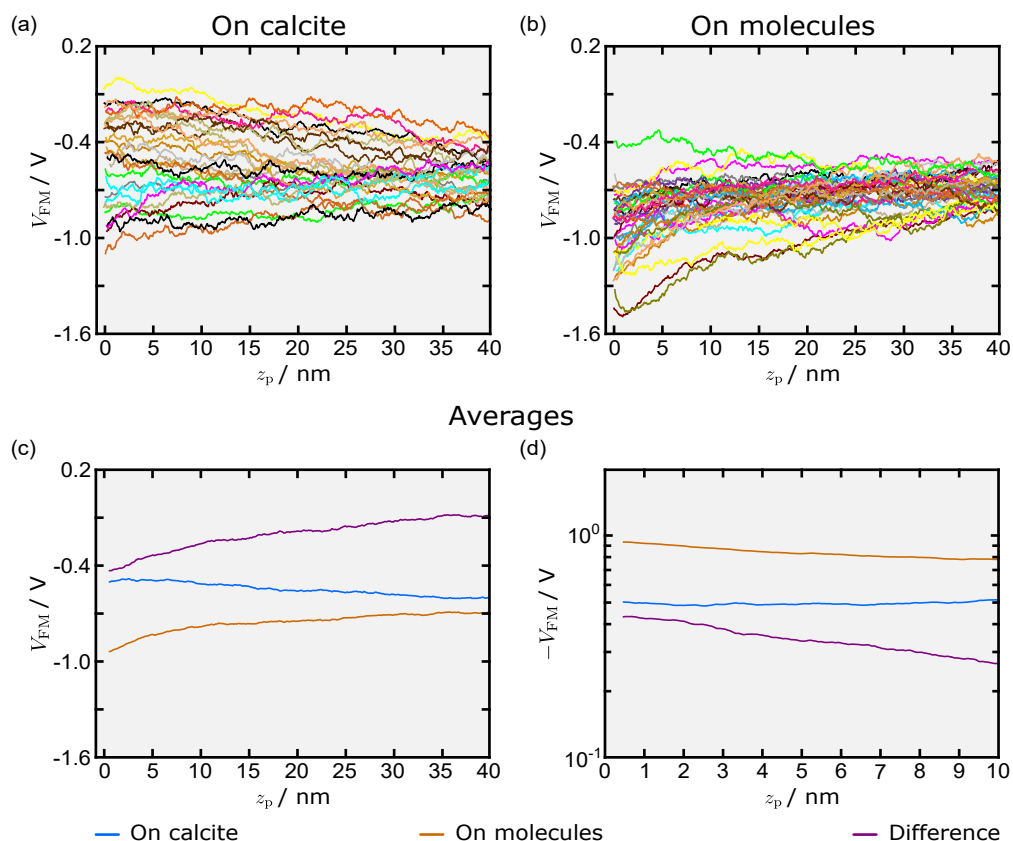


Figure 7.33.: Distinction (recorded on calcite or on molecules) of the V_{FM} curves corresponding to the measurement shown in figure 7.30 and comparison of their averages. The curves recorded on calcite are shown in plot (a), while the ones recorded on molecules are shown in plot (b). The plots (c) and (d) correspond to the linear and logarithmic comparison of the averages of the curves shown in (a) and (b) and the difference between them, respectively. Note that, as the logarithm of a negative number does not exist and most of the values of the V_{FM} averages are negative, plot (d) shows the logarithmic plot of these averages but with opposite sign. Furthermore, the logarithmic plot is shown only for $0 < z_p < 10$ nm for practical reasons: as the values of both averages come closer for large z -piezo position z_p , the values of the difference are smaller and prevents to display with detail the averages and the difference for small z_p values. The complete logarithmic plot can be found in appendix F, specifically figure F.2.

I cannot extract a general conclusion about the charge distribution of 2,5-DHBA deposited on calcite from this two experiments. There is clear evidence of the contamination of the Au-coated tip used in the first experiment. Besides, it is unknown if the tip used on the second experiment was contaminated. Thus, the data collected during both experiments on 2,5-DHBA is not fully trustworthy. I can only conclude with certainty that most of the curves recorded on molecules are more negative than the ones recorded on calcite. Although I could discriminate between the contribution of the calcite and of the molecular islands to the V_{FM} signal, this method is only valid if the contribution of the calcite is homogeneous in all the calcite surface, which it is not. More experiments with properly prepared metal-coated tips are required in order to get more insight in this system.

7.4 Information About the Au-Coated Tips Used

An essential part of this has been finding out the preparation parameters of Au-coated silicon AFM tips. As already described before, the V_{FM} signal measured in a FM-KPFM experiment has two differentiated contributions: the contact potential difference V_{CPD} between the metallic tip and the metallic sample or counter-electrode (the sample holder in the case of an insulating thick substrate) and the localized point charges between tip and sample. This relation is expressed in equation (2.28), which now I reproduce again in order to make the discussion easier to follow:

$$V_{\text{FM}} = -V_{\text{CPD}} + \sum_{i=1}^N q_i W_{\text{FM}}(\mathbf{r}_i) \quad (7.2)$$

From this equation, it follows that if there are not localized point charges between tip and metallic sample/counter electrode, upon varying the tip-sample distance, the V_{FM} signal should be flat. This value should correspond to the contact potential difference V_{CPD} . As stated before, this quantity is the difference between the work functions of the two metals normalized to the elementary charge e . I decided to use Au-coated tips and an Au(111) single crystal. Table 7.2 collect some theoretical and experimental work function values of Au single crystals with facets (100), (110) and (111) and polycrystalline. According to table 7.2, Au(111) work function is 5.31 eV.

Au surface	Theoretical Φ Values / eV	Experimental Φ Values / eV
(100)	6.16	5.47 [121, 122]
(110)	5.40	5.40 [121], 5.37 [122]
(111)	6.01	5.31 [121, 122]
Polycrystalline		5.22 [123]

Table 7.2.: Work functions of crystalline and polycrystalline Au.

The coating of the PPP-NCHAu tips can be considered as polycrystalline (information provided by NanoWorld [124]). This is the result of coating procedure, in which regular PPP-NCH cantilevers are coated with Au clusters. The exact size of each cluster is unknown, so it is the surface of the Au clusters exposed to the outside of the final Au-coated tip. I could assume that the tip coating work function is 5.22 eV, as table 7.2 indicates for polycrystalline Au. Thus, the contact potential difference V_{CPD} between the Au(111) single crystal and the Au-coated tip should be 90 meV.

About the experiments on Au(111), table 7.3 summarize information of the five Au-coated tips used in this work and some relevant information: how they were prepared, the KPFM mode used to determine the V_{FM} value, the approximate V_{FM} value¹⁵ and the figure which shows the distance-dependent $V_{\text{FM}}(z_p)$ curves and/or the fitted V_{FM} data from the static FM-KPFM measurements.

Au-coated AFM tip	Prepared by	KPFM mode	V_{FM} value / V	Figure
First	Sputtered with ISE 5	CL V_{FM}	-1.70 to -1.76	6.25
		static vs. CL V_{FM}	-1.71 to -1.76	6.27
Second	Sputtered with ISE 5	CL V_{FM}	-2.17 to -2.27	6.39
		static vs. CL V_{FM}	-2.15 to -2.25	6.41
Second	Sputtered with ISE 10	CL V_{FM}	-1.50 to -1.60	7.26
		static vs. CL V_{FM}	-1.45 to -1.60	7.27
Third	Not sputtered	CL V_{FM}	-2.25 to -2.35	C.3
		static vs. CL V_{FM}	-2.28 to -2.32	C.5
Fourth	Not sputtered	CL V_{FM}	-2.19 to -2.25	C.8
		static vs. CL V_{FM}	-2.18 to -2.25	C.10
Fifth	Sputtered with ISE 10	CL V_{FM}	~ -1.89	E.1

Table 7.3.: Summary of experiments done on Au(111) using Au-coated silicon AFM tips and the V_{FM} (range of) values.

After checking the V_{FM} (range of) values, I could make some observations:

- No one of the V_{FM} values is close to the 90 mV computed by assuming the work functions of Au(111) and polycrystalline Au as the ones in table 7.2. Not only that, the V_{FM} range which less deviates from the computed V_{CPD} is -1.45 to -1.60 V, what is more than 1 V of difference. Any other pair combination of the listed work functions does not provide a fair match. Thus, I do not understand the mismatch of the experimental V_{FM} values with the computed V_{CPD} value.
- All tips exhibit different (ranges of) V_{FM} values: only the ones of the *second* and *fourth* tip could be considered as equivalent. Nevertheless, as indicated in the table, the *second* tip was originally prepared using the ISE 5 sputter gun (the *old* one). The second time it was prepared, the *new* ISE 5 sputter gun was employed. In this case, the range of the V_{FM} values considerably decreased.

¹⁵As already described in chapter 6, not all V_{FM} curves in an experiment presented a z_p range for which they were strictly constant (for example, some of them presented jumps). Furthermore, it is possible that several curves in an experiment had a flat region, but not with the same value. For this reason, I refer to it as approximate V_{FM} value and, in most cases, is given in a range.

- Even when most tips exhibit different V_{FM} (range of) values, all of them are concentrated between -1.45 and -2.35 V, which is a range of 900 mV.

According to these observations, before coming to any conclusion, a larger sample of KPFM experiments on Au(111) using Au-coated tips (after preparing them) is needed. Since the Au(111) sample has always been prepared in the same way and, assuming that is a perfect single crystal, the different (range of) V_{FM} values must be ascribed to the Au-coated silicon AFM tips. As only five tips employed, it is not possible to find a correlation between the V_{FM} (range of) value(s). The only conclusion I could state is as follows. If measuring on Au(111) shifts the V_{CPD} depending on the tip used, this value would shift in KPFM experiments on molecules deposited on insulators¹⁶. For this reason, the absolute value of the V_{FM} signal on KPFM experiments on molecules should never be used for quantitative analysis.

7.5 Summary

First of all, due to a combination of different technical problems, I could not have freshly prepared Au-coated tips for all the experiments described in this chapter. Because of this, I had to use tips whose deformed apex results in the distorted imaging of the sample surfaces features, as the step edges of calcite or molecular islands, which are not well defined or appear several times in the images. In some images, even the apparent height of the molecular islands is different depending on the area. In a standard situation, the experiments on calcite and on 2,5-DHBA on calcite would have been performed with freshly prepared tips with good lateral resolution. The main cause of the deformed apex of these tips were the $I(V_{\text{bias}})$ curves performed in contact with the Au(111) surface (see section 6.4). These curves were performed in order to check if the current I was linear (or not) around 0 V, which indicates that the silicon AFM tips still had the Au coating (or not). For this reason, these curves should only be done when looking for the right preparation parameters. Once these parameters have been found, these procedure must be skipped for tips intended to use in proper KPFM experiments.

Respect to the results of the experiments described in this chapter, it is difficult to state a conclusion about the measurements on bare calcite. The tips of two out of three experiments resulted contaminated with localized point charges. This means that the data recorded during these two experiments on calcite is not trustworthy. From the other experiment, due to the non-flat behaviour upon varying z_p , I know there were point charges on the calcite. However, as explained at the beginning of

¹⁶In a KPFM experiment on a thick insulator, the sample (calcite in our experiments) would be mounted in a metallic sample holder (in our case, stainless steel, with $\Phi = 4.3$ eV [125]), which would be, together with the Au-coated tip, what contributes with the V_{CPD} to the V_{FM} signal

section 7.2, it was not possible to prepare calcite samples for which the scanning during standard FM-AFM measurements was stable. As the calcite samples I measured on were not stable, I cannot assume the presence of point charges on the calcite surface on this sample as something common for all calcite samples. Moreover, as two out of three experiments on calcite ended up in contaminated tips, this indicates the ease of tips being contaminated. Finally, as explained before, the weight function $W_{\text{FM}}(\mathbf{r}_i)$ depends on the shape of the tip. Hence, so does the V_{FM} signal. For this reason, the result of the KPFM experiments done using only one tip are not univocal. Thus, a larger sample of experiments is needed just to have some on which I can rely on. For these reasons, a remarkable bigger amount of experiments on different calcite samples and with different metal-coated tips are necessary. But only after finding out the problem with the calcite preparation and having available stable samples.

The experiments on 2,5-DHBA deposited on calcite were inconclusive. Both experiments showed non-constant V_{FM} curves upon z_p variation, which implies the presence of point charges in the system. However, the tip used in the first experiment was contaminated and I have relevant hints that suggest the tip used in the second experiment was also contaminated. For this reason, I cannot consider these data as trustworthy. Furthermore, the Kelvin V_{FM} signal on the calcite was not equivalent in all spots on which it was measured. Because of this, the method used to separate the contribution of the molecular island and of calcite to the Kelvin V_{FM} signal is not strictly correct in these two experiments. However, in a situation in which the charge contribution on the calcite surface can be considered homogeneous, this analysis procedure is valid. As with the experiments performed on bare calcite, in order to get a conclusion about this system, more experiments on different calcite substrates and with different metal-coated tips are necessary.

As a last remark, the absolute value of the V_{FM} signal cannot be used for a quantitative analysis. This fact has been pointed by the different ranges of V_{FM} values of the experiments on Au(111) done using metal-coated different tips.

Summary

This thesis describes a systematic study of KPFM experiments in UHV. Different experiments on Au(111), calcite (10.4) and molecules deposited on calcite (10.4) are presented. In particular, this work provides evidence of the contribution of localized point charges on the AFM tip to the KPFM signal. Therefore, I put the focus on the preparation and test of metal-coated AFM tips before and after KPFM experiments on molecules.

I present a systematic study on Au(111) using metal-coated tips. Distance-dependent closed-loop FM-KPFM measurements were recorded on areas free of localized point charges. These measurements provided a KPFM signal which varies upon changing the tip-sample distance. This fact directly points to the presence of point charges on the tip apex. In order to obtain tips free of localized point charges, I developed a preparation procedure based on sputtering the tips with Ar ions. The success of the preparation was confirmed by repeating the distance-dependent KPFM measurements on Au(111): if the KPFM signal is constant, the tips can be considered free of localized point charges. This test procedure has been applied to five different metal-coated tips. The value at which the KPFM signal remains constant upon changing the tip-sample distance is different for most of them. This is an indication that the absolute value of the KPFM signal depends on the tip used.

The experiments on calcite (10.4) were not conclusive. All distance-dependent KPFM curves recorded during the three experiments presented a distance-dependent signal, what is an indication of the presence of point charges between tip and sample. Nevertheless, the curves of each experiment presented different tendencies and absolute values. The theory predicted that measurements on the same species should result in similar distance-dependent KPFM curves, which did not happen. This could be due to the impossibility of getting charge-free surface calcite samples. Furthermore, out of three experiments, only in one them the metal-coated tips were not contaminated after the experiment. This situation means that only one of the experiments provided reliable data. However, it is not enough to obtain a general conclusion of the KPFM data on calcite (10.4).

From the two measurements on 2,5-DHBA deposited on calcite (10.4) we got a similar result. The distance-dependent KPFM curves exhibited a non-constant signal

upon tip-sample distance variation, indicating the presence static point charges between tip and sample. However, the curves recorded were not similar for the same species and not clearly different for different species, as we expected from the theory. The later tests on Au(111) also showed a non-constant KPFM signal, which implies both tips were contaminated and both data sets obtained were not reliable. Nevertheless, the data of both experiments were analyzed following a method previously used in our group. First, we have to assume that the charge distribution on the calcite sample is homogeneous across the whole sample surface. Then, we can consider the calcite contribution to the distance-dependent KPFM curves to be the same regardless the spot of the surface where the curve was recorded. This way, the contribution of the molecules to the KPFM signal can be separated from the calcite. The results of the experiments on calcite and on molecules deposited on calcite show that for most experiments, the tips get contaminated with point charges in their apex, providing no reliable KPFM data. Thus, it is necessary to perform numerous experiments in order to increase the possibility of obtaining trustworthy KPFM data.

In summary, this thesis provides an overview on how to perform KPFM experiments on insulating substrates in UHV. The experiments on Au(111) confirm the prediction of the theory: localized point charges on the tip also contribute to the KPFM signal. I present a procedure to prepare and test the metal-coated tips. The measurements on Au(111) provide evidence that the KPFM signal is not univocal for all tips: the absolute value depends on the tip used. The experiments on calcite and on molecules deposited on calcite evidence high probability of the metal-coated tip to be contaminated. Thus, it is necessary to perform large amount of experiments in order to obtain reliable KPFM data.

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Temperature Calibration Curve of Heating Stage

The Omicron VT AFM/STM XA is not designed to directly measure the temperature of a sample placed in the heating stage. The temperature can only be estimated using a thermocouple in contact with the heating stage. For this, the manufacturer provided us with calibration curves shown in Figure A.1. In this plot, the temperature measured with the thermocouple and at a sample plate placed in the heating stage are given as a function of the power of heating.

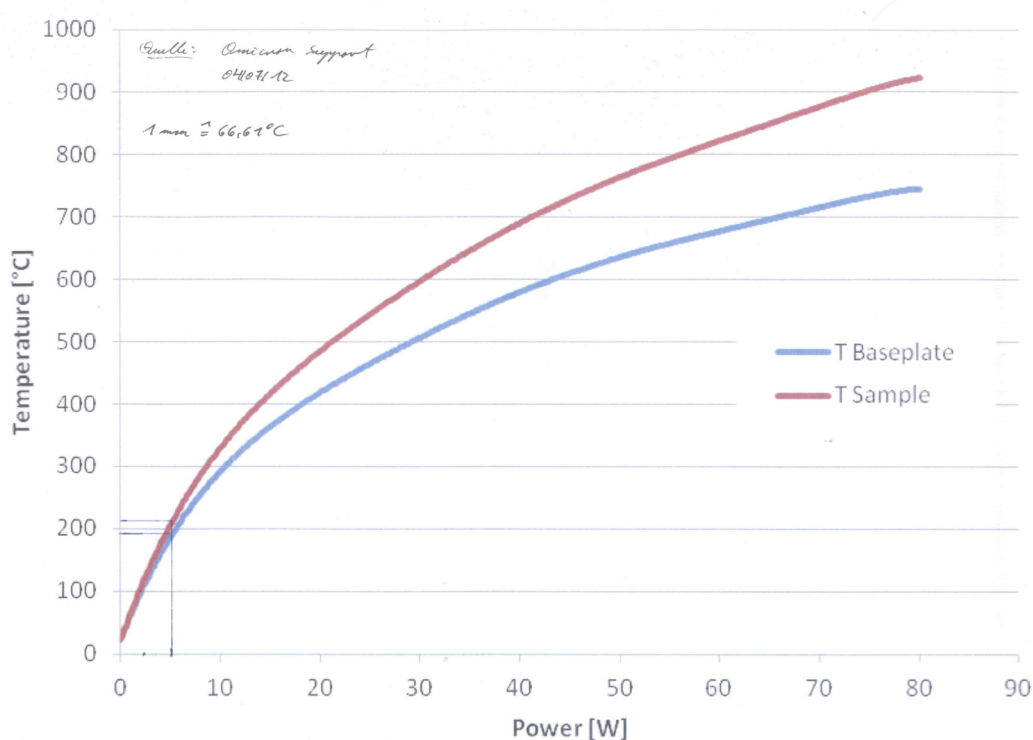


Figure A.1.: Calibration curve for estimating the temperature of a sample placed in the heating stage of the manipulator.

Data Analysis

In this appendix, the treatment and the presentation of the data is described.

The images presented in this thesis were treated with Gwyddion [109]. For drift correction [116], the program *EasyDrift* was used [119]. The following procedure was applied to treat the images:

- The topography z_p images were processed with Gwyddion by aligning rows (lines). A manual plan subtraction has been applied too. Furthermore, the offset was corrected so the height of the lower terrace of the substrate is around "0 nm".
- Although the phase shift ϕ is $-90^\circ(-\pi/2)$, the MATRIX software resets it to 0° . In order to present the images in agreement with the experimental details, an offset of -90° has been added to the image.
- The Kelvin V_{FM} images must be corrected by subtracting the V-Gap value set in the software (see equation (3.3)).
- The images of the spectral components of the frequency shift $\Delta\nu_e$ are recorded in V. In order to convert them to Hz, they were multiplied by a factor, which includes the output gain of the DF OUT of the MATRIX CU (in Hz/V), the output gain of the HF2 (in V/V_{rms}) and a factor $\sqrt{2}$ (conversion from V_{rms} to V). Furthermore, I presented the spectral components of the frequency shift $\Delta\nu_e$ and not the ones of the frequency shift output by the PLL $\Delta\nu_{e,PLL}$ (see section 5.1). In order to overcome the convolution with the transfer function of the PLL, I also divided each image by the PLL gains $|G_{PLL}(\nu)|$ at their corresponding frequencies ν_{es} and $2\nu_{es}$.

The distance-dependent curves were exported with Vernissage [126] to ASCII format in delimiter separated files and treated using MATLAB. The following procedure was applied to the channels:

- For large tip-sample distances z_{ts} , the interaction between tip and sample must be zero. For this reason, when retracting the tip during distance-dependent

curves, the frequency shift curves $\Delta\nu_e$ should tend to 0 Hz. However, experience has shown that during an experiment, the eigenfrequency ν_e of the cantilever might vary. This fact implies that for large tip-sample distances z_{ts} , the frequency shift $\Delta\nu_e$ does not always tend to 0 Hz. In order to compare different experiments, the offset of the curves for large distances z_{ts} is forced to pass through 0 Hz.

- The data of the oscillation amplitude channel A are recorded in V. In order to convert the data to nm, the distance-dependent curves must be multiplied by the response S of the cantilever (in nm/V) (see Section 5.3.1). Furthermore, the values recorded do not correspond to the oscillation amplitude, but to the peak-to-peak amplitude. For this reason, the curve data must be multiplied by a factor 0.5.
- As for the images, the Kelvin V_{FM} curves must be corrected by subtracting the V-Gap value set in the software (see equation (3.3)).
- The distance-dependent curves of the spectral components of the frequency shift $\Delta\nu_e$, as the images, are recorded in V. The same conversion factor as for the images was applied to the curves.
- The static deflection q_s is obtained from filtering the DC component of the deflection q of the cantilever. As explained in section 3.1, the cantilever is mounted on a piezo-tube scanner. It was observed that moving macroscopically the AFM head in vertical direction leads to vertical movement of the laser spot on the PSPD. This is due not to the movement of the cantilever, but to the change in relative positions of the AFM head and the PSPD. It might be possible that, while the distance-dependent curves, this very same effect occurs. In this situation, any variation of the static component of the deflection q of the cantilever, *i.e.*, the static deflection q_s is entangled with the previously mentioned effect. This can be corrected by forcing the curves to pass through 0 nm for large tip-sample distances, under the assumption that the rest position of the cantilever is not shifted for large tip-sample distances z_{ts} . Furthermore, the static deflection q_s must be converted to nm by multiplying by the response S of the cantilever.

Together with the data of the different channels, the values of the z-piezo position z_p are recorded. The interest of these measurements is to study the variation of these quantities with the tip-sample distance z_{ts} . The recorded piezo position z_p data cannot be totally corrected to consider it as the tip-sample distance z_{ts} , but some corrections can be done, as explained below:

- Possible relaxation of atoms in the apex of the tip can shift the real tip-sample distance z_{ts} . However, we cannot quantify these relaxations, so this effect cannot be corrected.
- There is an uncertainty of the relative position of the sample surface: the distance z_0 (see section 6.1). This effect can not be corrected, since the only way checking its position is crashing the tip into the sample surface.
- The MATRIX software does not store the real z-piezo displacement z_p values. The system always considers as "0 nm" the value of the piezo position z_p at which the feedback places the tip to keep the actual frequency shift $\Delta\nu_e$ equal to the setpoint. Just to illustrate the situation, for a given $\Delta\nu_e$ setpoint (in the MATRIX software is referred to Δf -Setpoint) a z_p curve can be done by retracting the tip, for example, 10 nm. The z_p value of the first point of the curve will be stored as 0 nm and the last as 10 nm. Right after that, the tip can be approach or retracting by varying the $\Delta\nu_e$ setpoint and record another curve by retracting the tip in the same amount. Again, the z_p values of the first and last point will be stored as 0 and 10 nm. This issue prevents us from correcting the possible drift in Z direction, for which the pristine and non-modified z-piezo displacement z_p values are necessary.
- It is possible that the plane of the sample surface and the XY scanning plane of the piezo-tube scanner are not parallel. A correction cannot be made for the same reason explained in the previous section, which is: the way the z_p values are stored. We can assume that, for a set of distance-dependent curves recorded using the same parameters (oscillation amplitude A , frequency shift $\Delta\nu_e$ setpoint), storing the first point of the curves as "0 nm" is a good enough correction of the possible misalignment of the planes.
- The static deflection q_s can be added to the z_p values.

Nevertheless, the distance-dependent curves from experiments, in which the static deflection q_s was recorded, are plotted against the tip center position z_c , but the q_s is plotted against the z-piezo displacement z_p .

The voltage-dependent curves were also exported with Vernissage [126] to ASCII format in delimiter separated files and treated using MATLAB:

- The frequency shift $\Delta\nu_e$ curves presented as part of static FM-KPFM measurements were treated following the same procedure as the distance-dependent curves: offset correction. The offset subtracted was the same than for the corresponding distance-dependent $\Delta\nu_e$ curve with which it is compared. The

remaining voltage-dependent frequency shift $\Delta\nu_e$ presented in section 6.5 and section 7.2 were not corrected.

- The data of the oscillation amplitude channel *A* were converted to nm by the same procedure follow with the distance-dependent curves.

The transfer functions and FFT's shown in chapter 5 were treated with MATLAB.

KPFM Experiments on Au(111): Part 1

Figures C.1, C.2, C.3, C.4 and C.5: measurements performed on Au(111) using the *third* Au-coated silicon AFM tip after dropping something off on the surface while scanning.

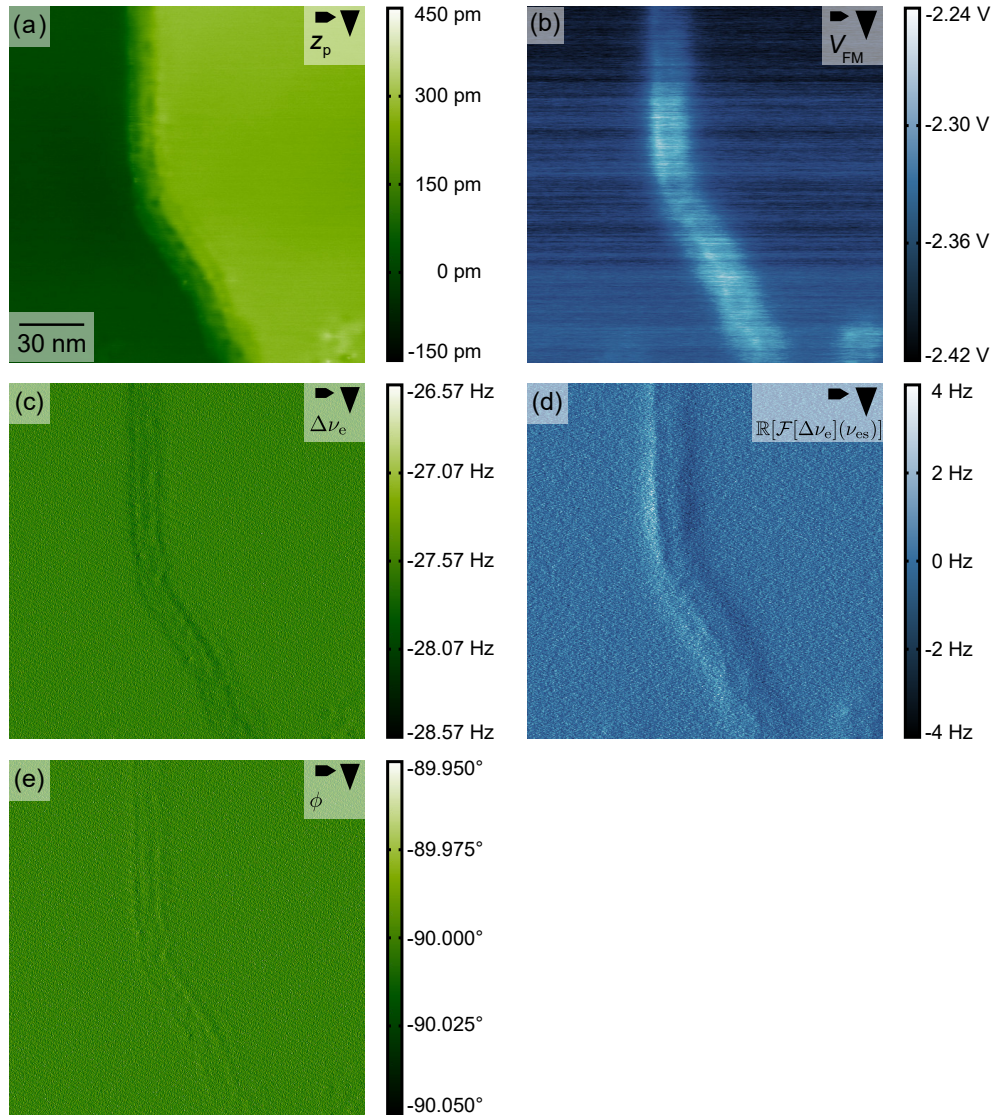


Figure C.1: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *third* Au-coated silicon AFM tip after dropping something off on the surface while scanning. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

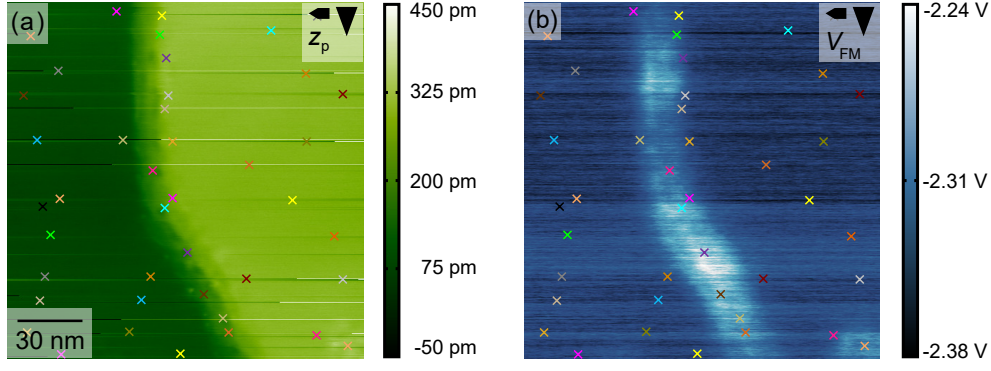


Figure C.2.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *third* Au-coated silicon AFM tip after dropping something off on the surface while scanning. The crosses indicate the spots where the distance-dependent curves shown in figure C.3 were performed.

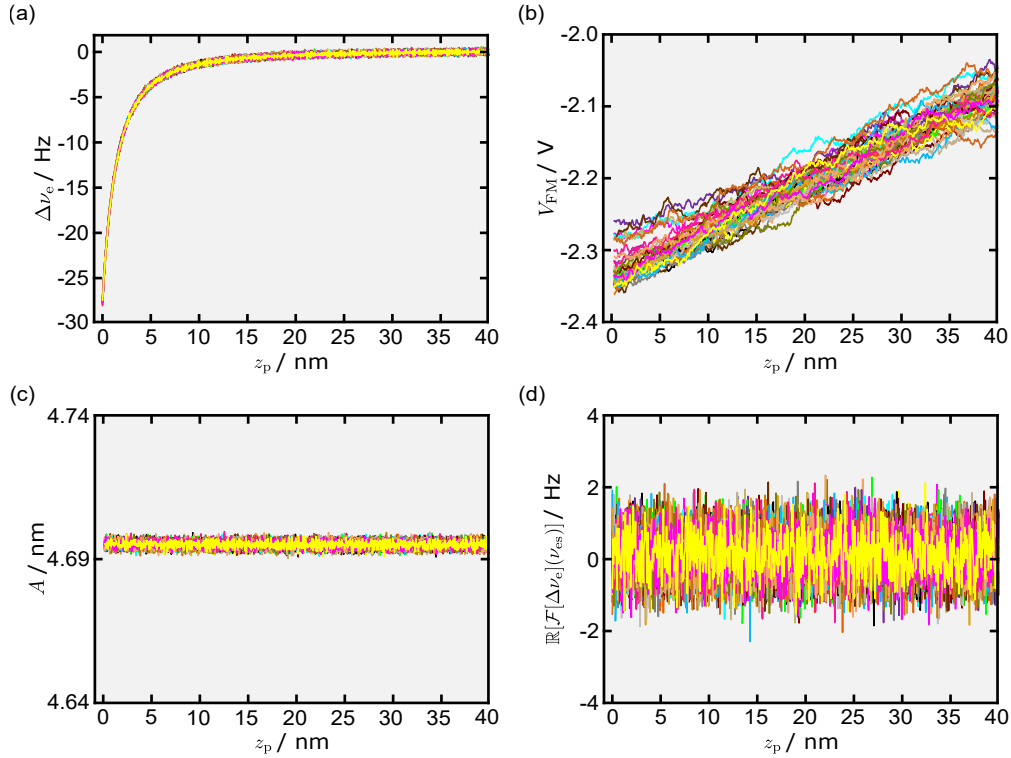
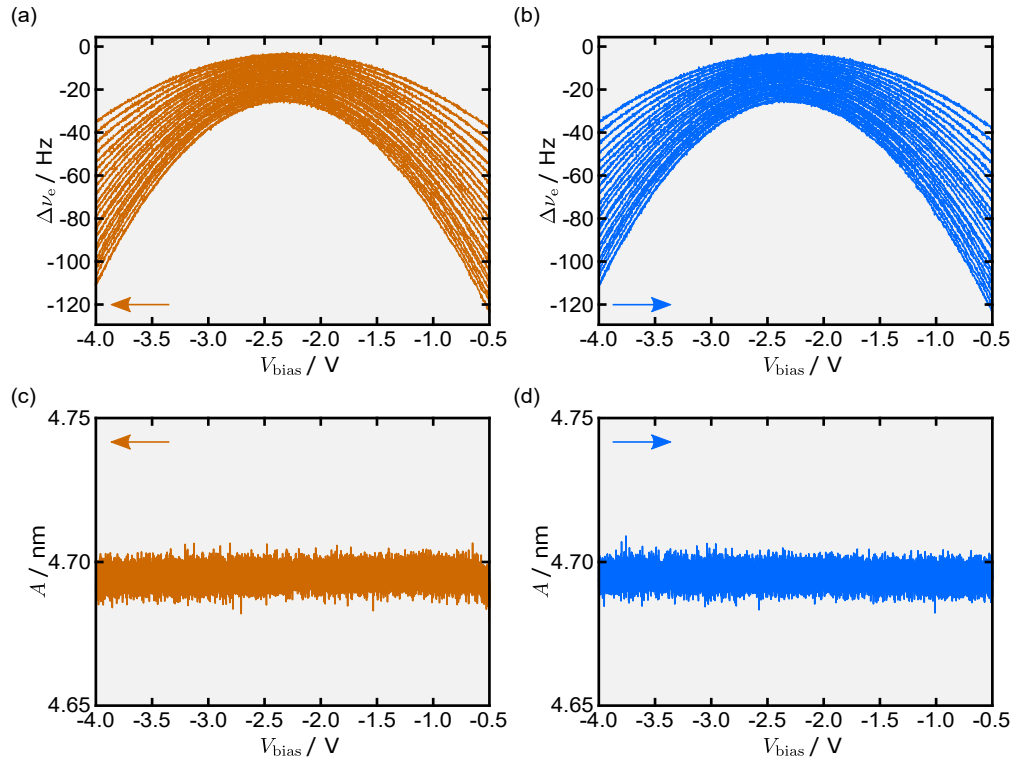


Figure C.3.: Distance-dependent curves performed on the Au(111) single crystal with the *third* Au-coated silicon AFM tip after dropping something off on the surface while scanning. Plot (a) shows the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) the oscillation amplitude A and (d) the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z-piezo displacement z_p .



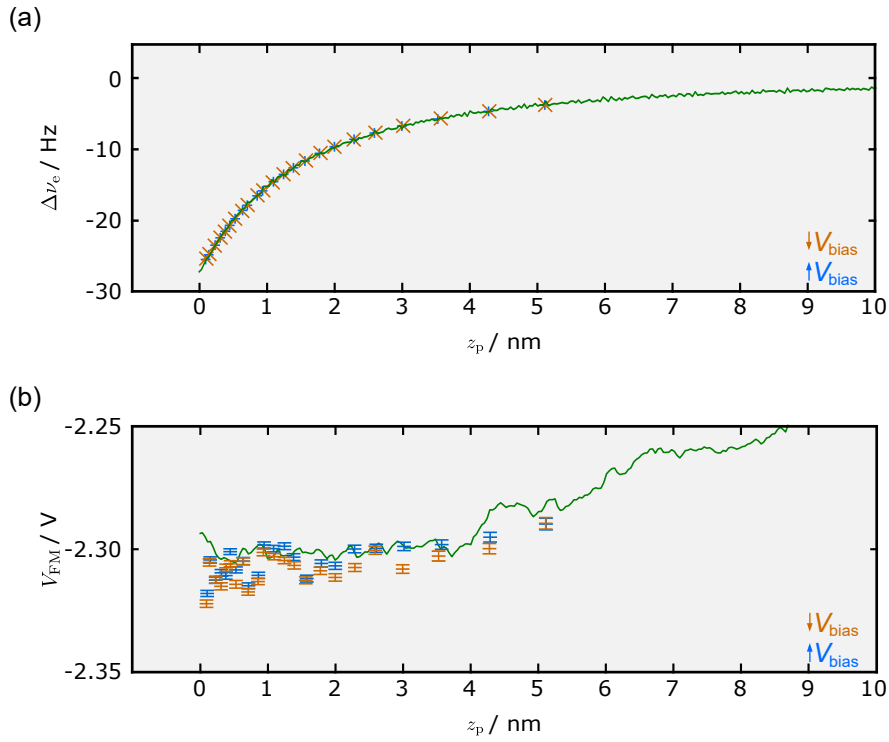


Figure C.5.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of $\Delta\nu_e(V_{\text{bias}})$ curves of figure C.4 (a) and (b), which were performed after the *third* Au-coated silicon AFM tip dropped something off on the surface while scanning. The distance-dependent curves data are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves are plotted in orange, while the data extracted from the positive sweep voltage V_{bias} are plotted in blue.

Figures C.6, C.7, C.8, C.9 and C.10: measurements performed on Au(111) using the *fourth* Au-coated silicon AFM tip after dropping something off on the surface while scanning.

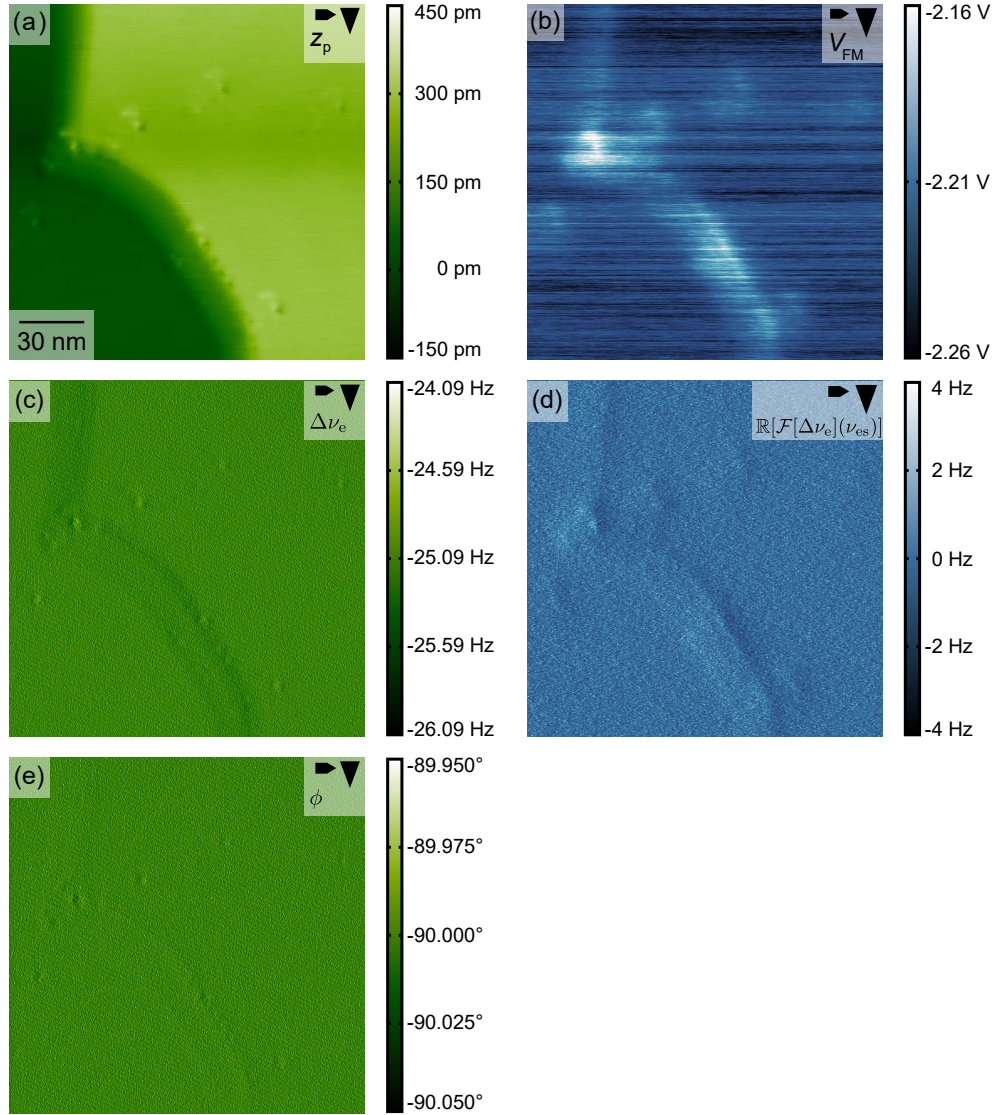


Figure C.6.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *fourth* Au-coated silicon AFM tip after dropping something off on the surface while scanning. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

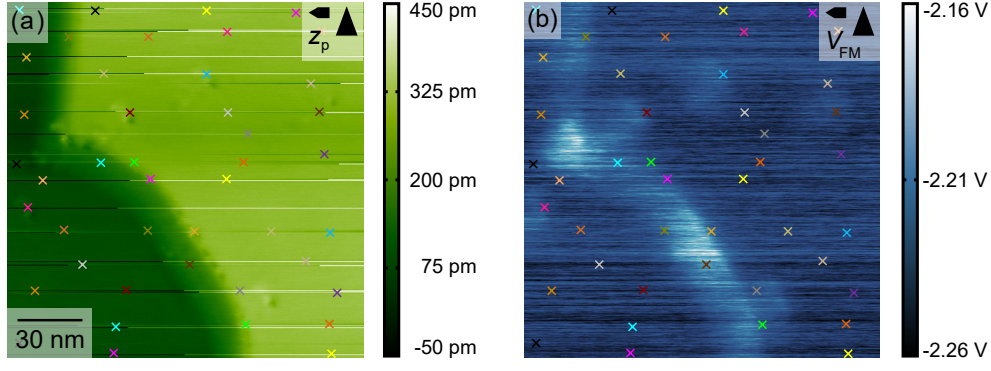


Figure C.7.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *fourth* Au-coated silicon AFM tip after dropping something off on the surface while scanning. The crosses indicate the spots where the distance-dependent curves shown in figure C.8 were performed.

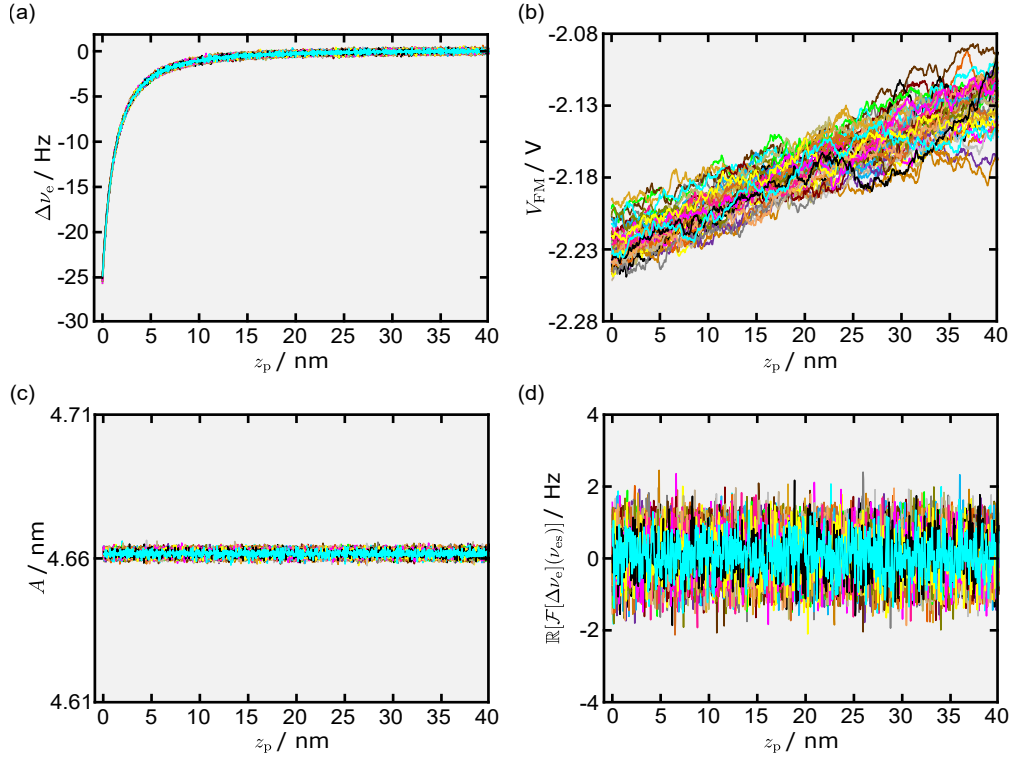


Figure C.8.: Distance-dependent curves performed on the Au(111) single crystal with the *fourth* Au-coated silicon AFM tip after dropping something off on the surface while scanning. Plot (a) shows the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) the oscillation amplitude A and (d) the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z -piezo displacement z_p .

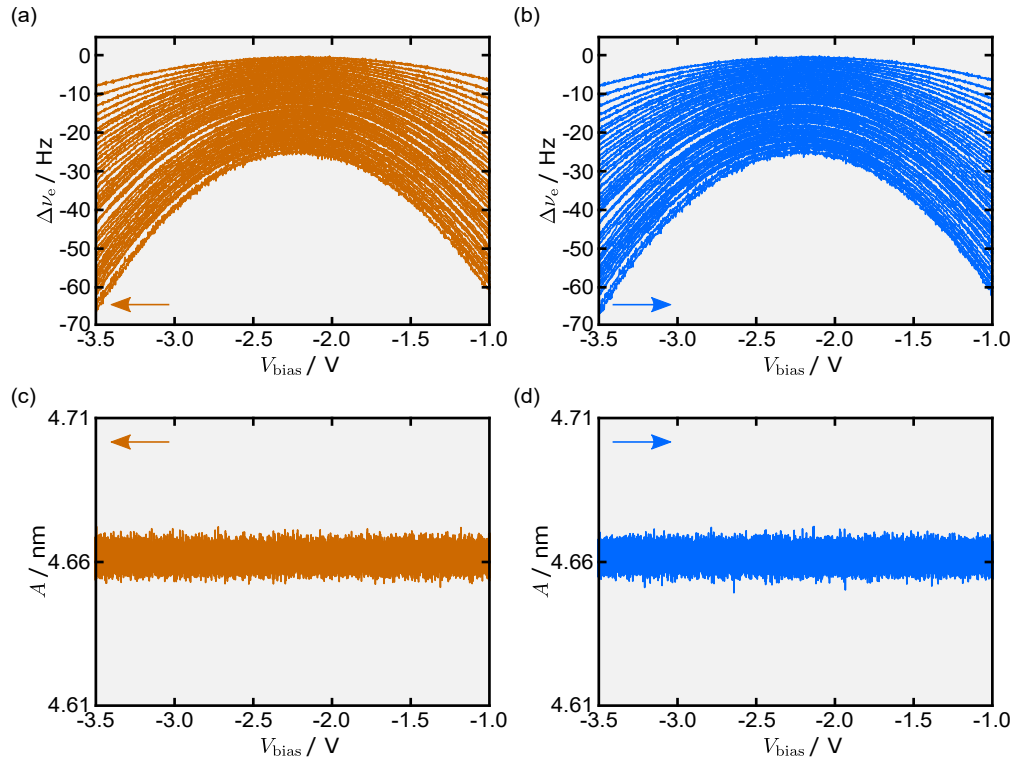


Figure C.9.: Voltage-dependent curves recorded with the *fourth* Au-coated silicon AFM tip after dropping something off on the surface while scanning. Plots (a) and (b) show the frequency shift $\Delta\nu_e (V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

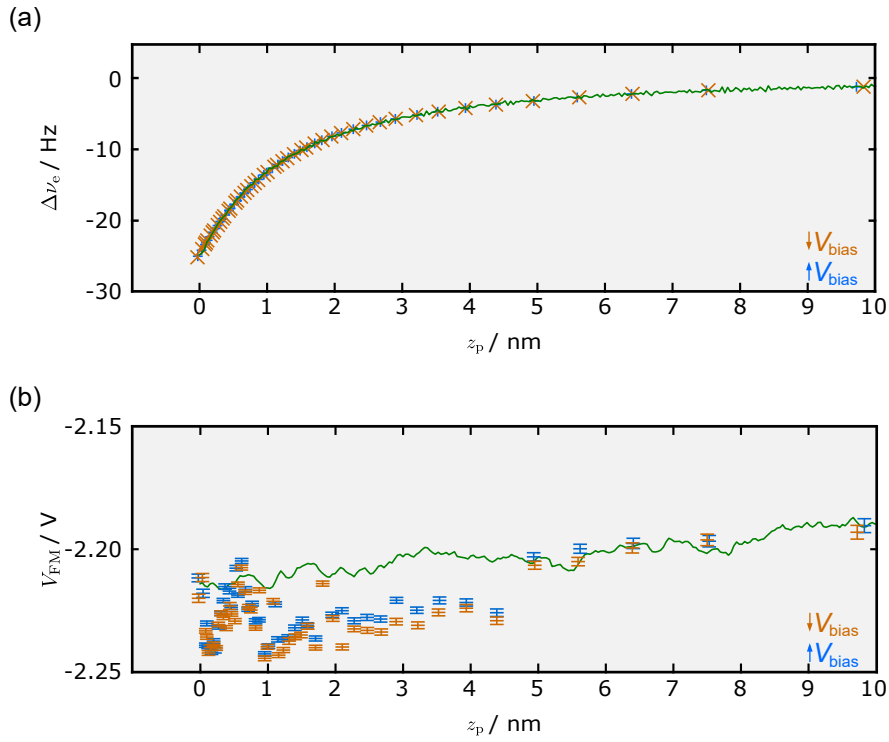


Figure C.10.: Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of $\Delta\nu_e(V_{\text{bias}})$ curves of figure C.9 (a) and (b), which were performed after the *fourth* Au-coated silicon AFM tip dropped something off on the surface while scanning. The distance-dependent curves data are plotted in green. The data extracted from the negative sweep voltage V_{bias} curves are plotted in orange, while the data extracted from the positive sweep voltage V_{bias} are plotted in blue.

KPFM Experiments on Au(111): Part 2

Figures D.1, D.2, D.3 and D.4: measurements performed on Au(111) after the first experiment on calcite (10.4) using the *third* Au-coated silicon AFM tip.

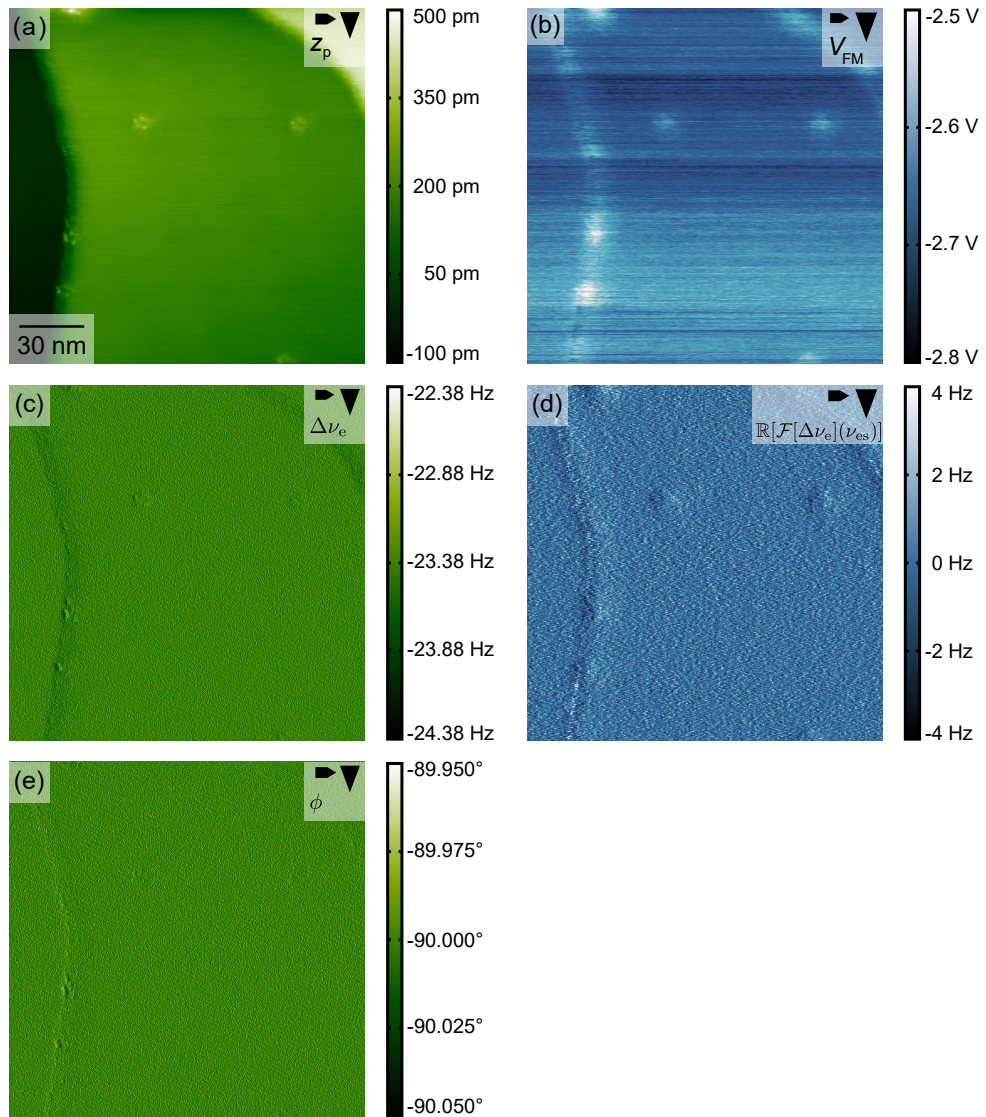


Figure D.1.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *third* Au-coated silicon AFM tip. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

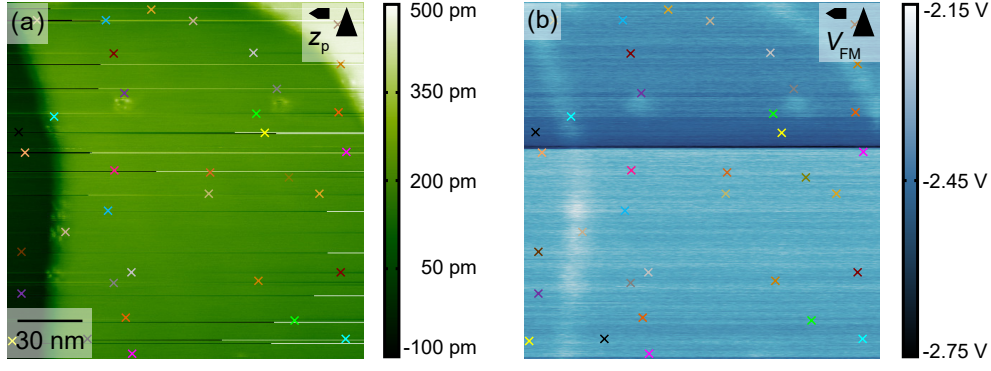


Figure D.2.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *third* Au-coated silicon AFM tip. The crosses indicate the spots where the distance-dependent curves shown in figure D.3 were performed.

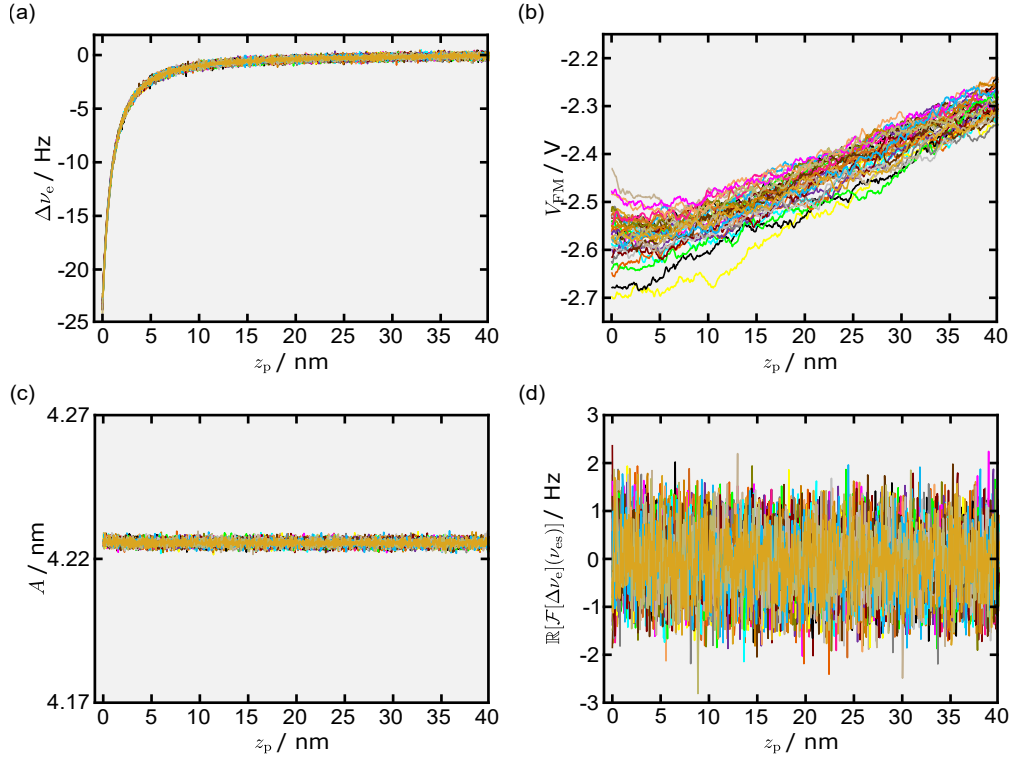


Figure D.3.: Distance-dependent curves performed on the Au(111) single crystal with the *third* Au-coated silicon AFM tip after measuring on calcite. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z-piezo displacement z_p .

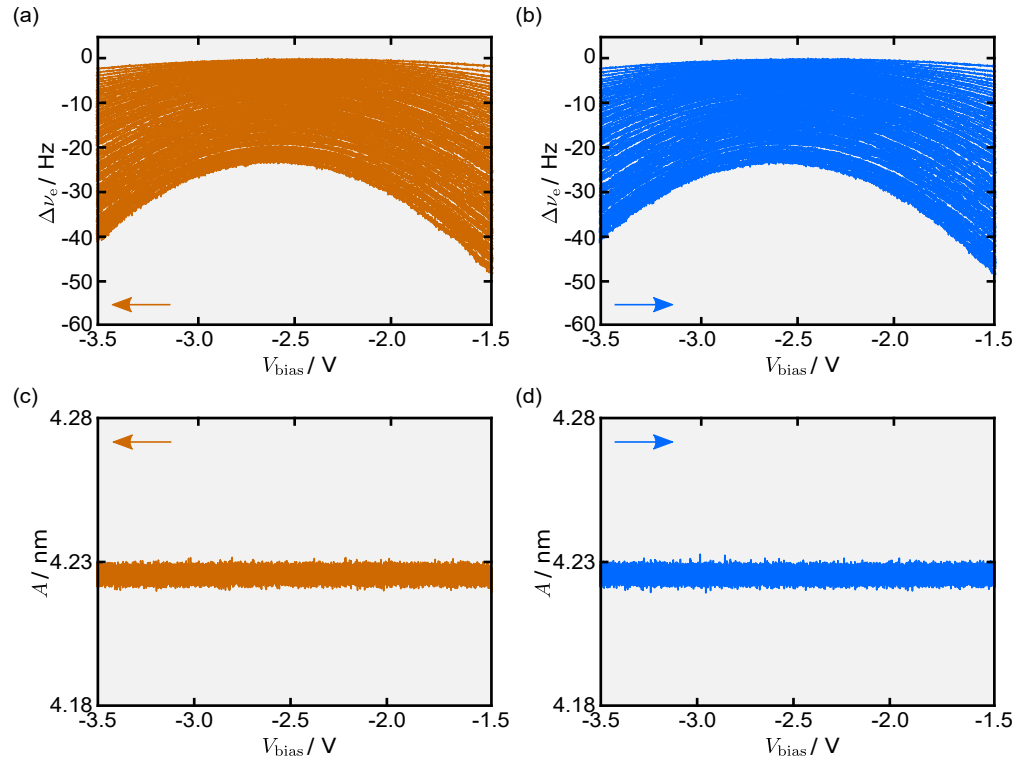


Figure D.4.: Voltage-dependent curves recorded with the *third* Au-coated silicon AFM tip after measuring on calcite. Plots (a) and (b) show the frequency shift $\Delta\nu_e (V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

Figures D.5, D.6, D.7 and D.8: measurements performed on Au(111) after the second experiment on calcite (10.4) using the *second* Au-coated silicon AFM tip.

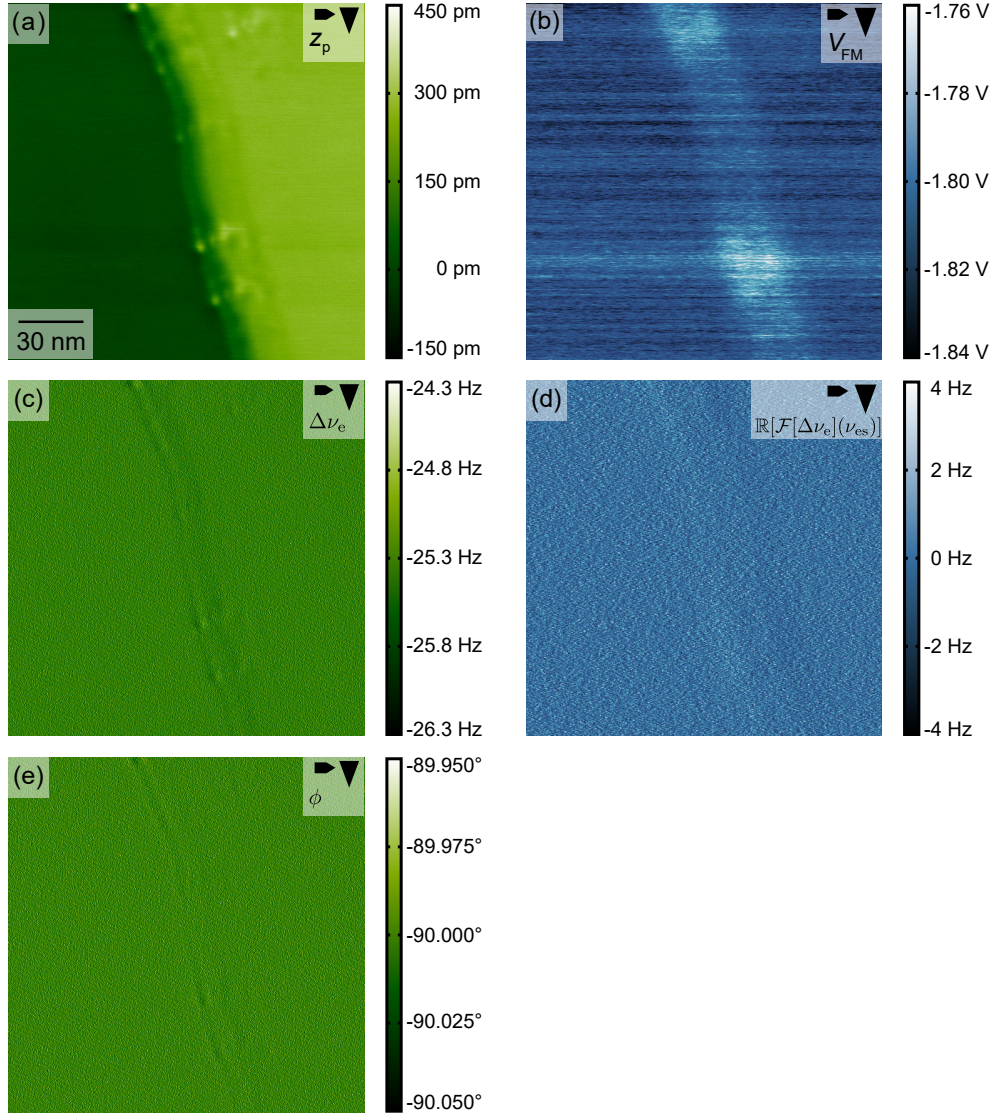


Figure D.5.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *second* Au-coated silicon AFM tip after measuring on calcite. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

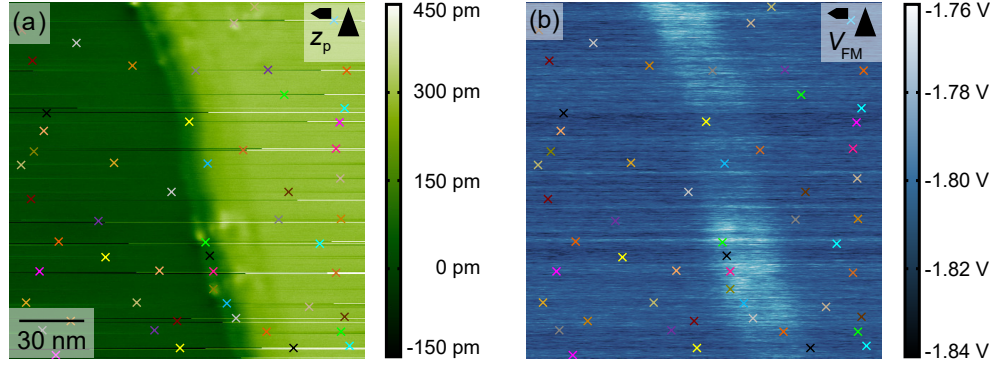


Figure D.6.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *second* Au-coated silicon AFM tip after measuring on calcite. The crosses indicate the spots where the distance-dependent curves shown in figure D.7 were performed.

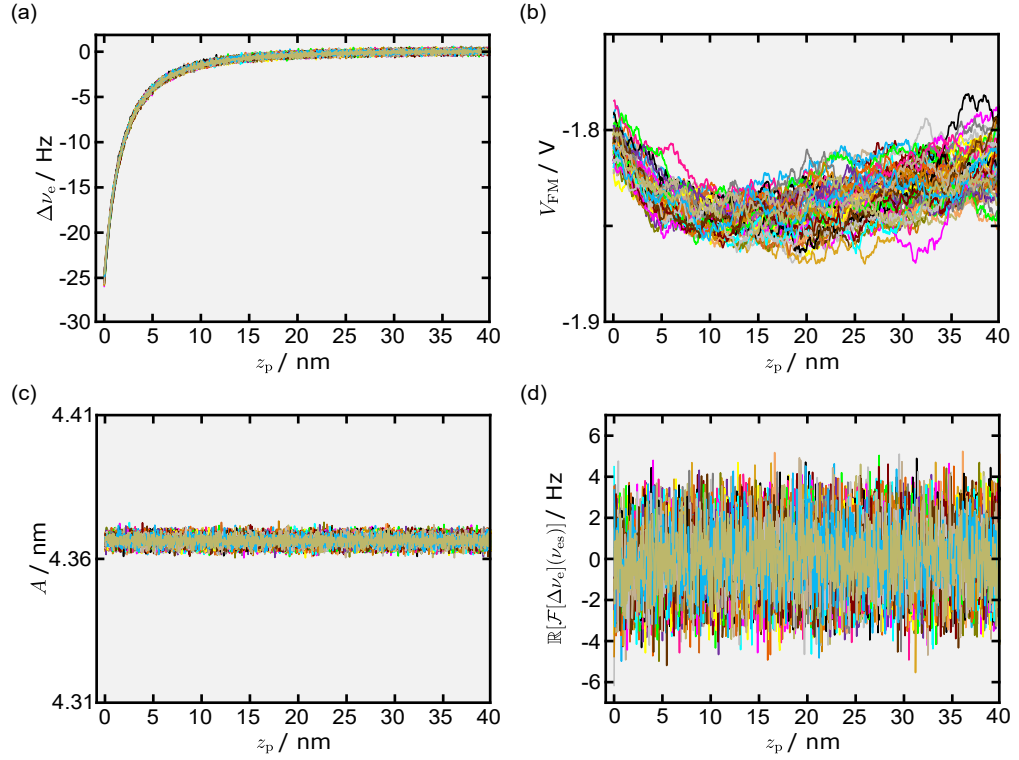


Figure D.7.: Distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip after measuring on calcite. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z-piezo displacement z_p .

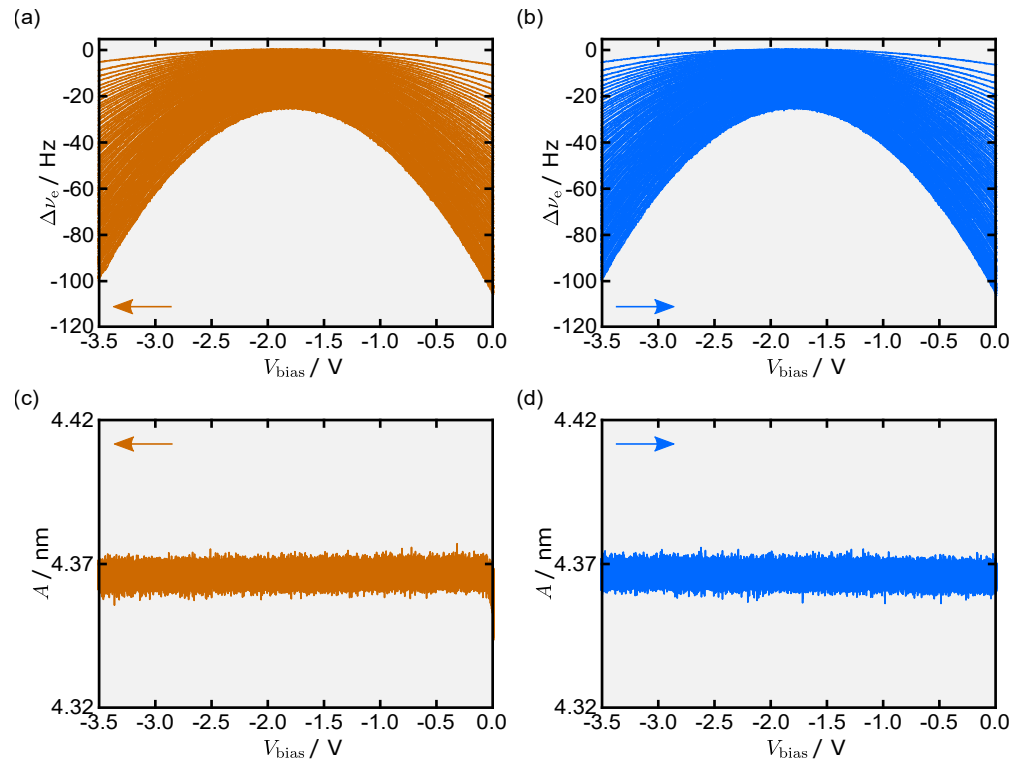


Figure D.8.: Voltage-dependent curves recorded with the *second* Au-coated silicon AFM tip after measuring on calcite. Plots (a) and (b) show the frequency shift $\Delta\nu_e$ (V_{bias}) curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

Figures D.9, D.10, D.11 and D.12: measurements performed on Au(111) after the third experiment on calcite (10.4) using the *fourth* Au-coated silicon AFM tip.

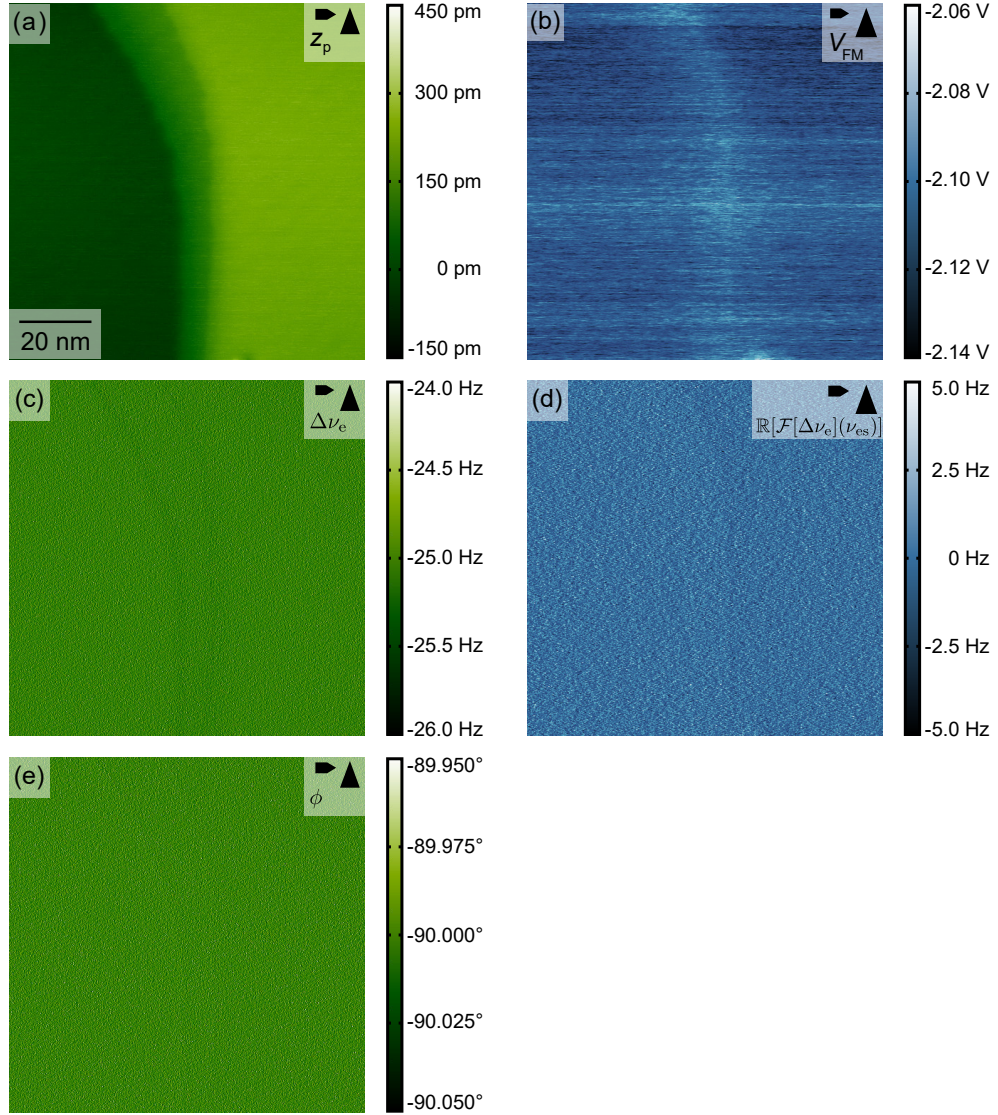


Figure D.9.: FM-AFM and FM-KPFM images measured on the Au(111) sample using the *fourth* Au-coated silicon AFM tip after measuring on calcite. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

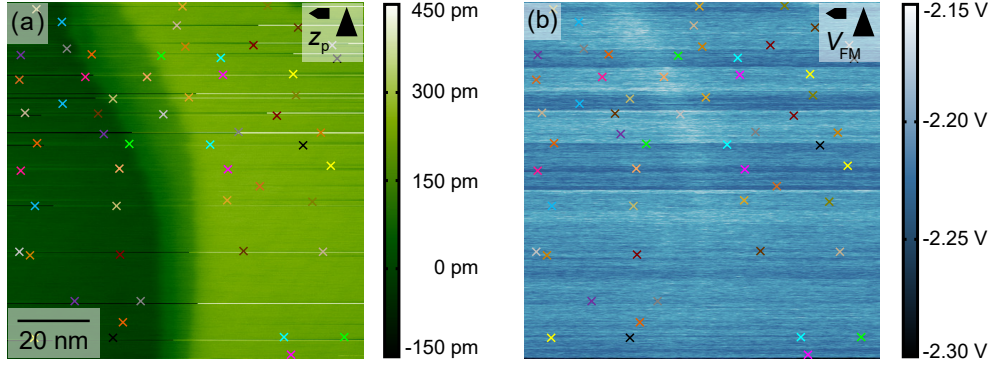


Figure D.10.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *fourth* Au-coated silicon AFM tip after measuring on calcite. The crosses indicate the spots where the distance-dependent curves shown in figure D.11 were performed.

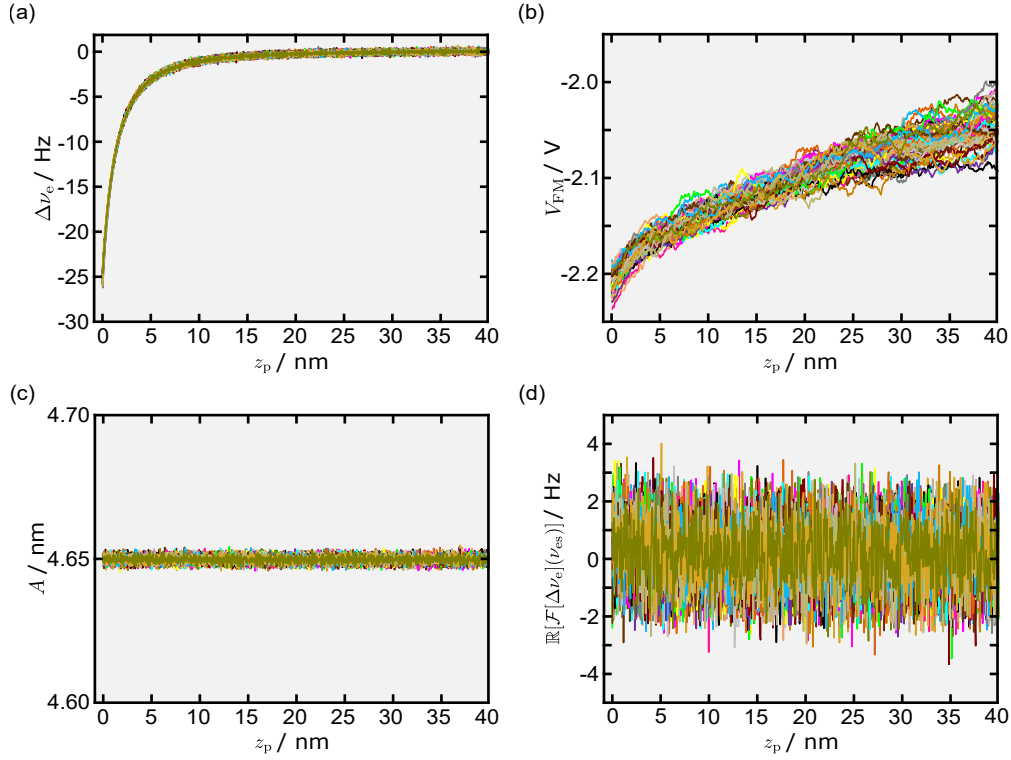


Figure D.11.: Distance-dependent curves performed on the Au(111) single crystal with the *fourth* Au-coated silicon AFM tip after measuring on calcite. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z -piezo displacement z_p .

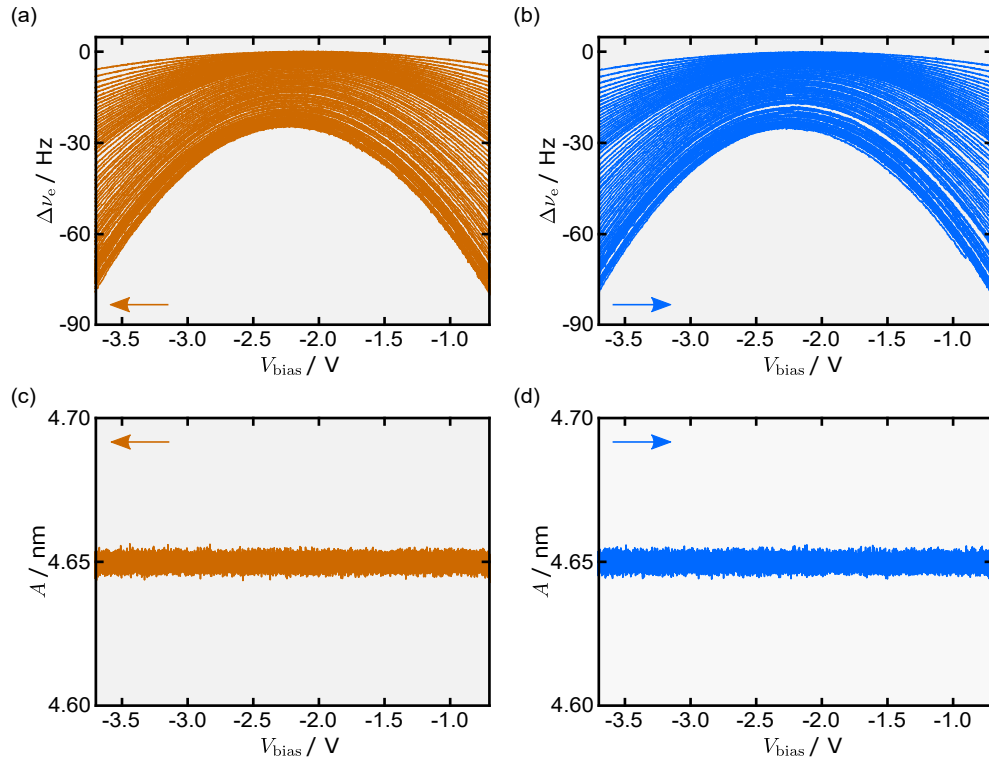


Figure D.12.: Voltage-dependent curves recorded with the *fourth* Au-coated silicon AFM tip after measuring on calcite. Plots (a) and (b) show the frequency shift $\Delta\nu_e (V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

Figures D.13, D.14, D.15 and D.16: experiments performed on Au(111) after the first experiment on 2,5-DHBA deposited on calcite (10.4) using the *third* Au-coated silicon AFM tip.

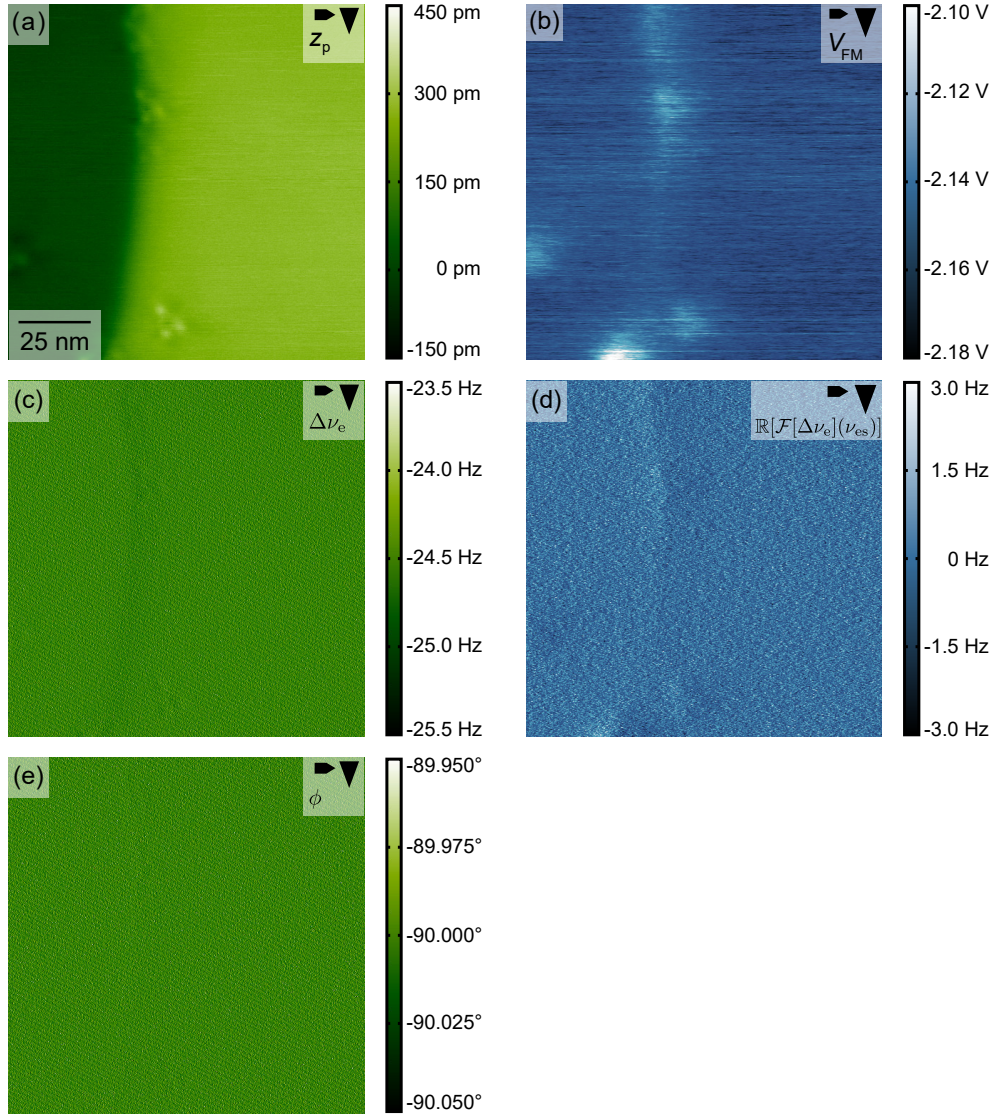


Figure D.13.: FM-AFM and FM-KPFM images measured on Au(111) using the *third* Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

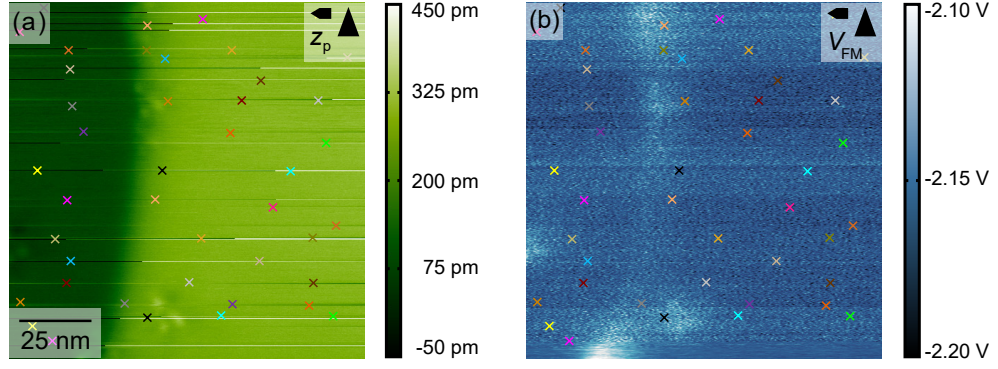


Figure D.14.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *third* Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite. The crosses indicate the spots where the distance-dependent curves shown figure D.15 were performed.

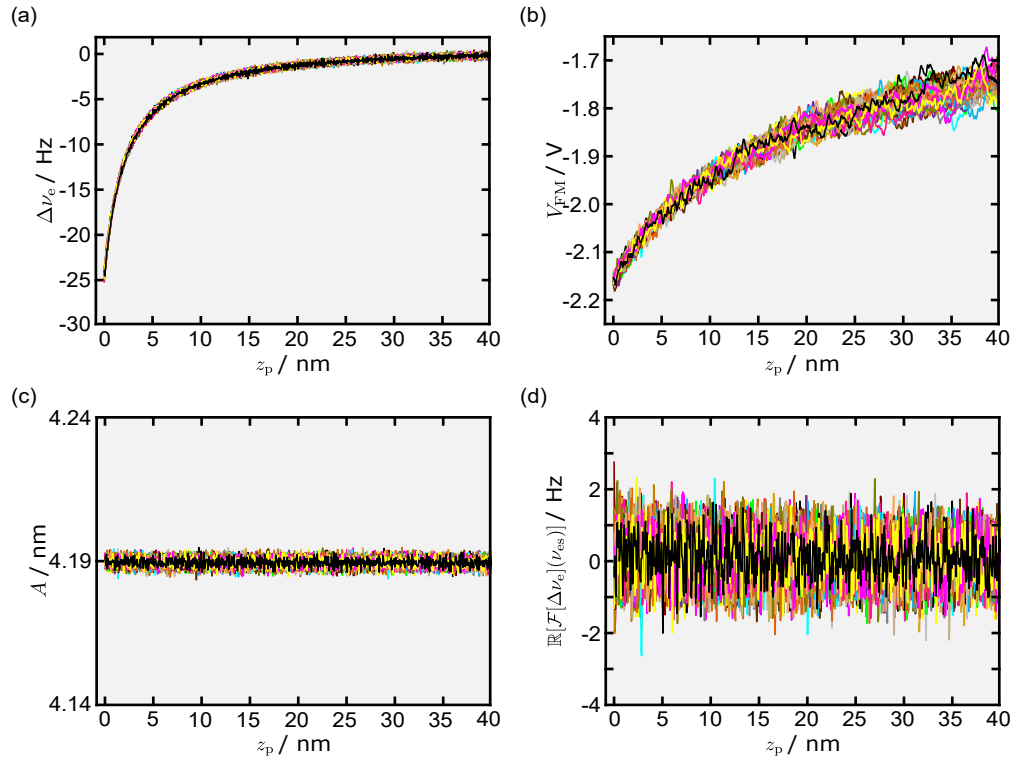


Figure D.15.: Distance-dependent curves performed on the Au(111) single crystal with the *third* Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$ versus the z-piezo displacement z_p .

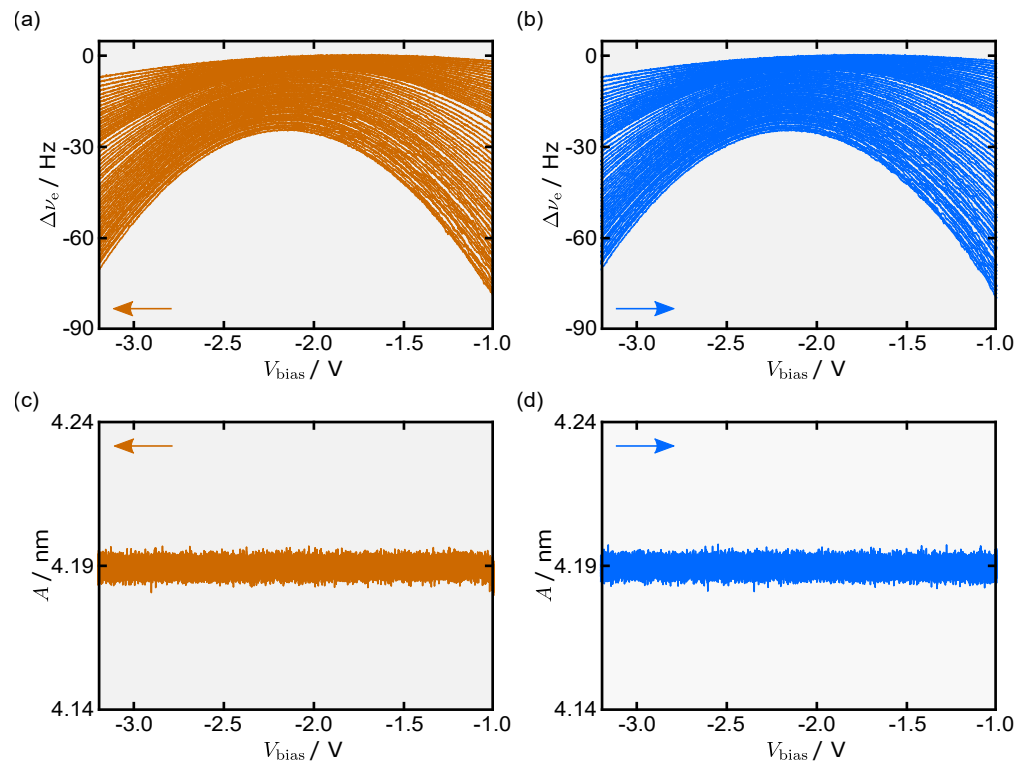


Figure D.16.: Voltage-dependent curves recorded with the *third* Au-coated silicon AFM tip after measuring 2,5-DHBA deposited on calcite. Plots (a) and (b) show the frequency shift $\Delta\nu_e(V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

KPFM Experiments on Au(111): Part 3

Figure E.1: distance-dependent curves performed on the Au(111) during the process of finding out the sputtering parameters for the new sputter gun ISE 10. Measurements done using the *fifth* Au-coated silicon AFM tip.

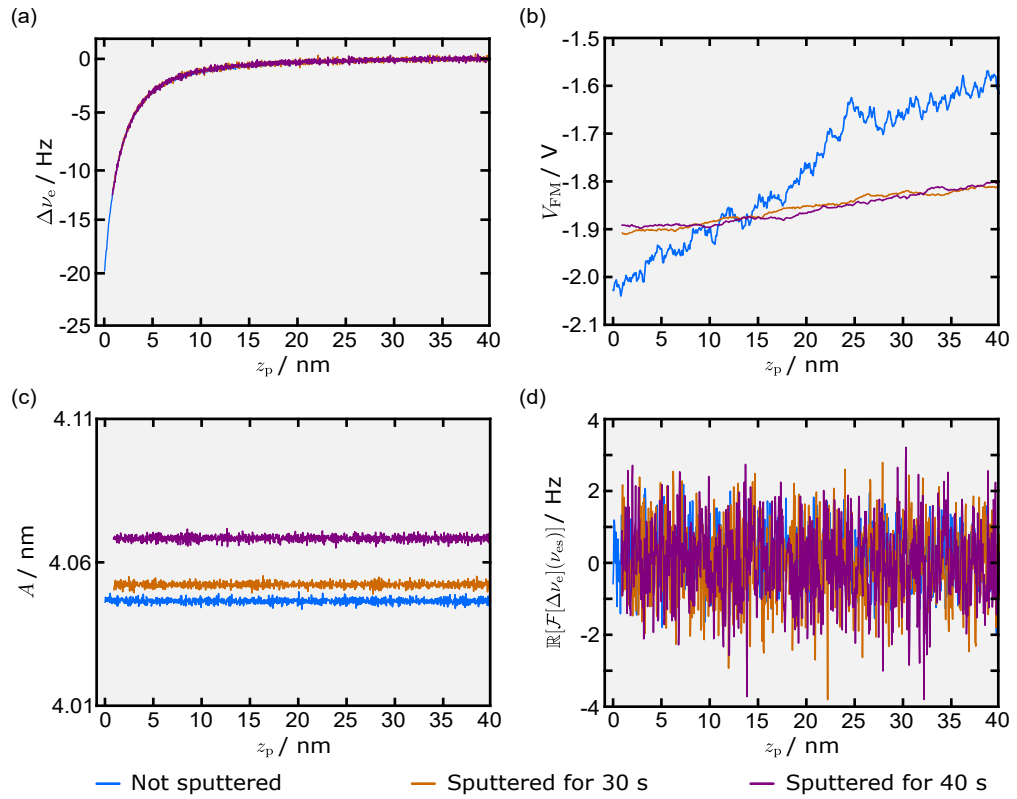


Figure E.1.: Distance-dependent curves performed on the Au(111) single crystal with the *fifth* Au-coated silicon AFM tip: procedure to find the new preparation parameters using the new sputter gun: ISE 10. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows to the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ versus the z-piezo displacement z_p .

Figures E.2, E.3, E.4 and E.5: measurements performed on Au(111) after the preparing the *second* Au-coated silicon AFM tip using the new sputter gun ISE 10.

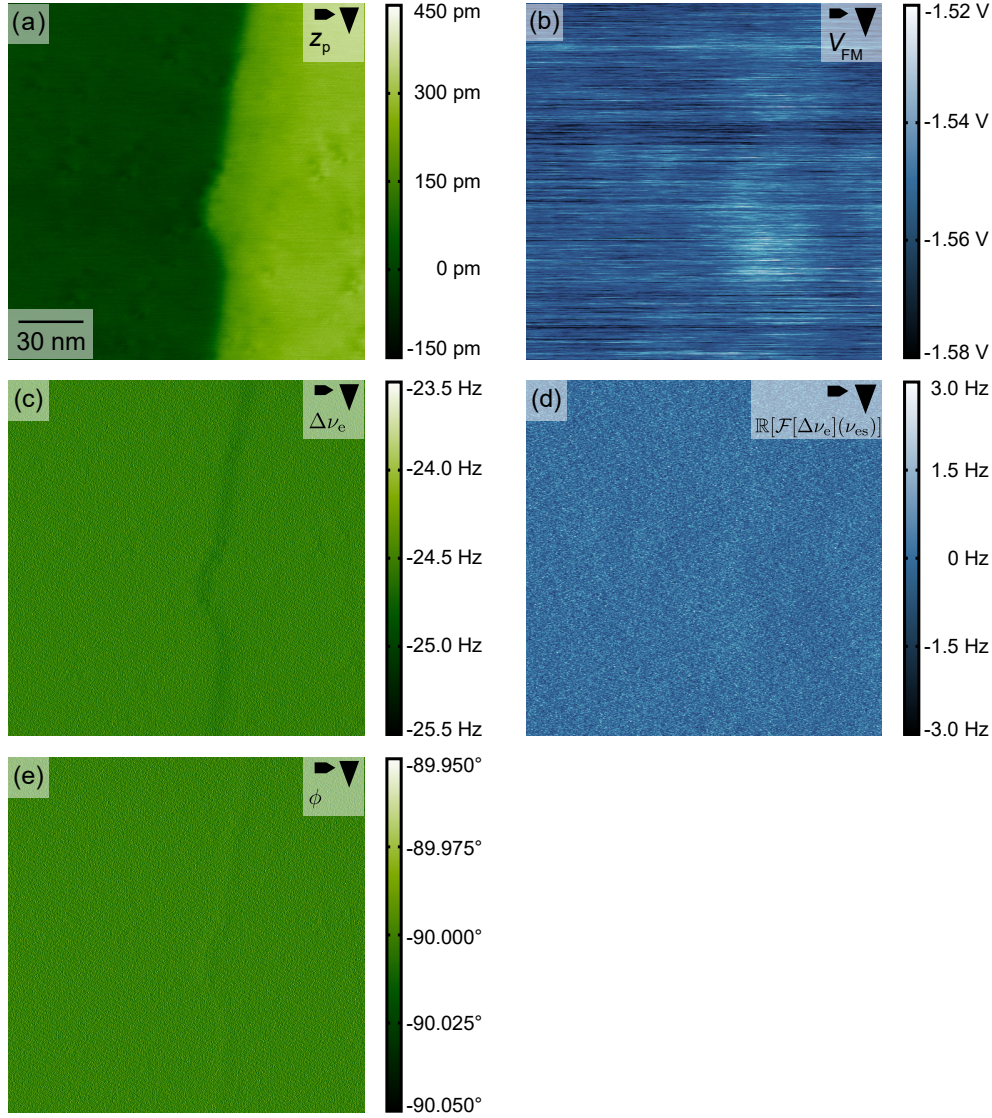


Figure E.2.: FM-AFM and FM-KPFM images measured on Au(111) using the *second* Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10. Images (a), (c) and (e) correspond to the topography z_p , the frequency shift $\Delta\nu_e$ and the phase shift ϕ , respectively. Images (b) and (d) show the Kelvin V_{FM} signal and the real part of the first spectral component $\mathbb{R}[\mathcal{F}[\Delta\nu_e](\nu_{es})]$, respectively.

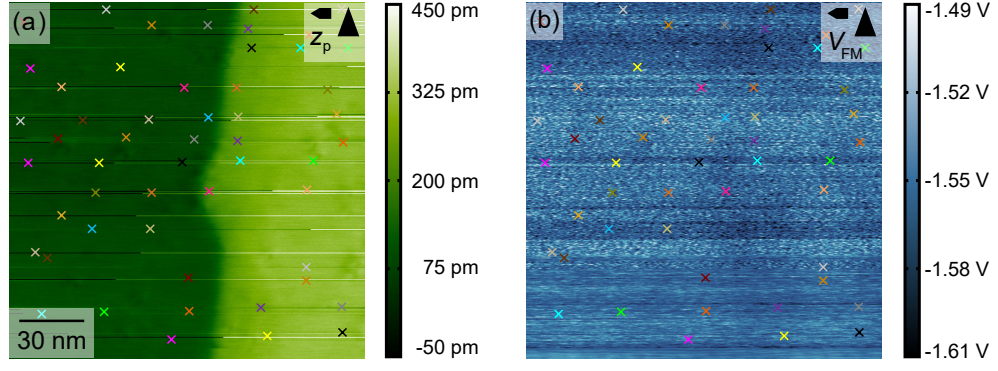


Figure E.3.: Topography z_p (a) and Kelvin V_{FM} signal (b) images. These measurements were performed using the *second* Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10. The crosses indicate the spots where the distance-dependent curves shown figure D.15 were performed.

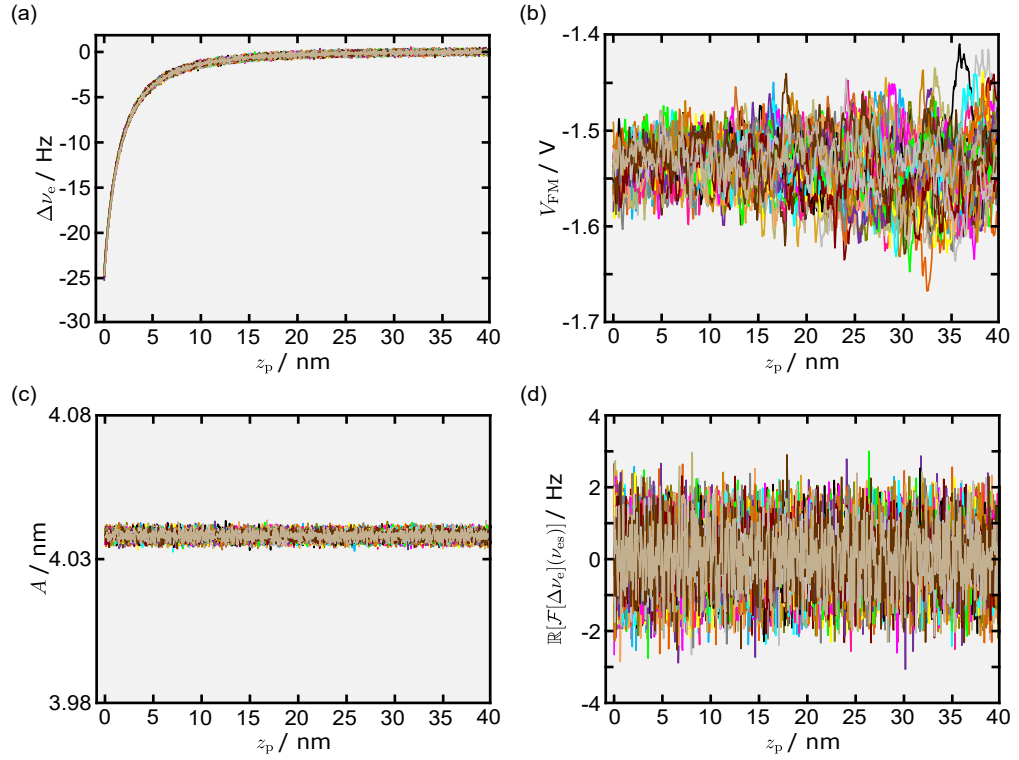


Figure E.4.: Distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{es})]$.

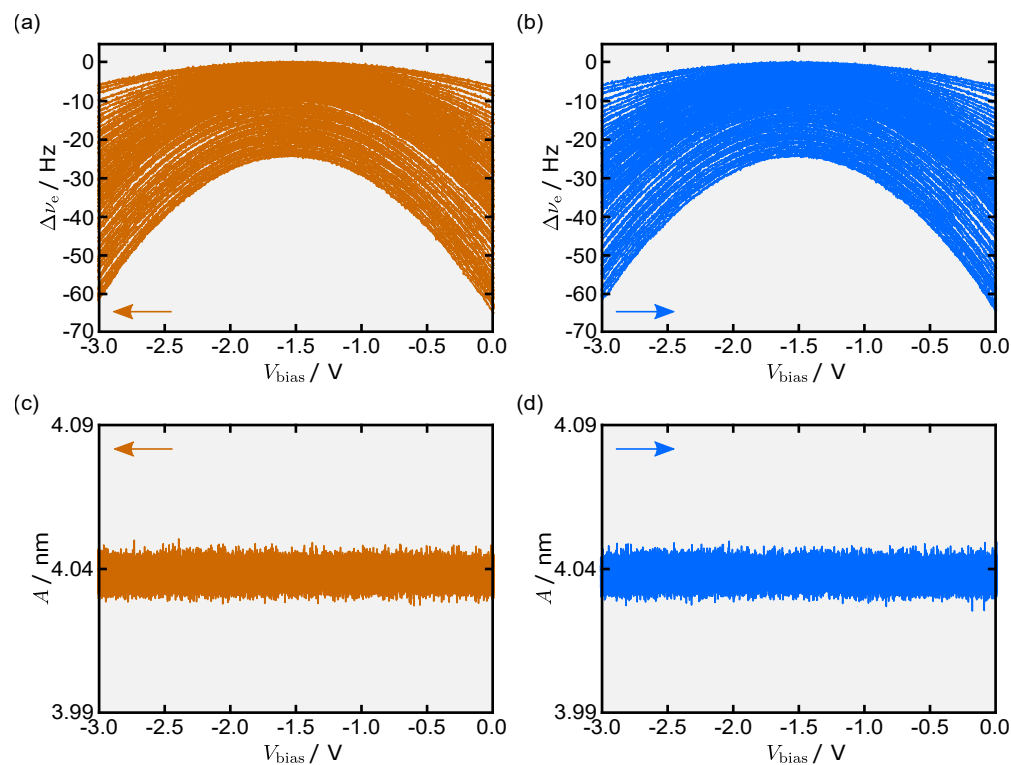


Figure E.5.: Voltage-dependent curves recorded with the *second* Au-coated silicon AFM tip after measuring 2,5-DHBA deposited on the calcite (10.4) surface. Plots (a) and (b) show the frequency shift $\Delta\nu_e(V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

Figures E.6 and E.7: measurements performed on Au(111) after the second experiment on 2,5-DHBA deposited on calcite (10.4) using the *second* Au-coated silicon AFM tip.

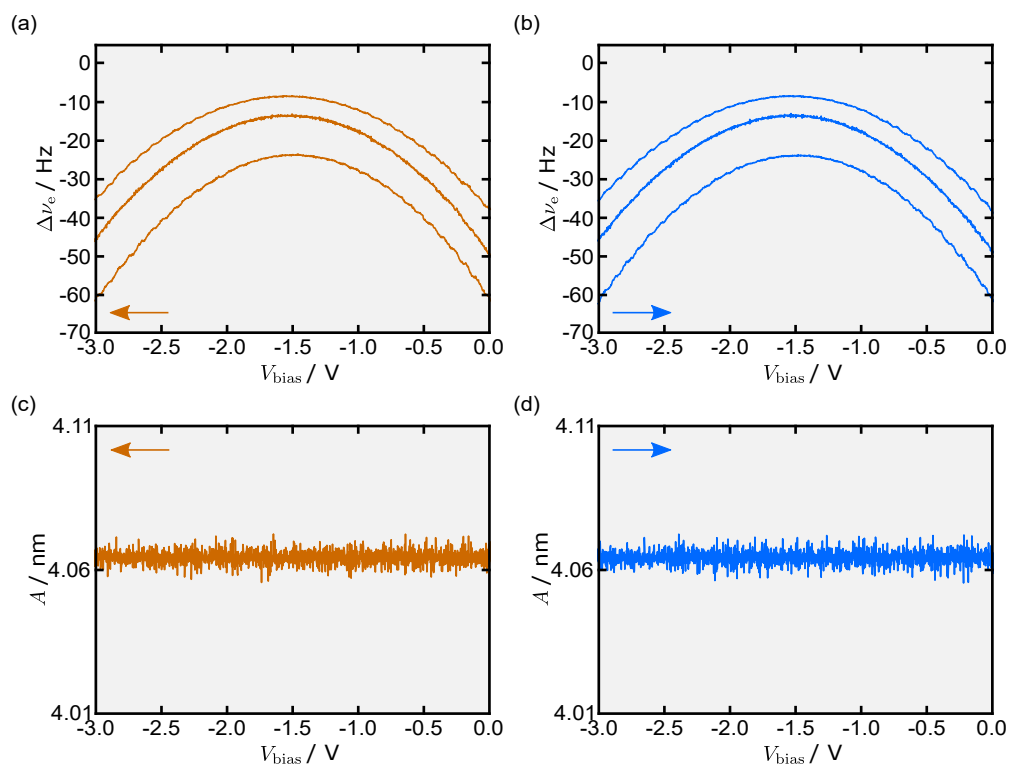


Figure E.6.: Voltage-dependent curves recorded with the *second* Au-coated silicon AFM tip after measuring 2,5-DHBA deposited on the calcite (10.4) surface. Plots (a) and (b) show the frequency shift $\Delta\nu_e(V_{\text{bias}})$ curves. Plots (c) and (d) present the oscillation amplitude A . The blue and orange arrows indicate the sweep voltage direction.

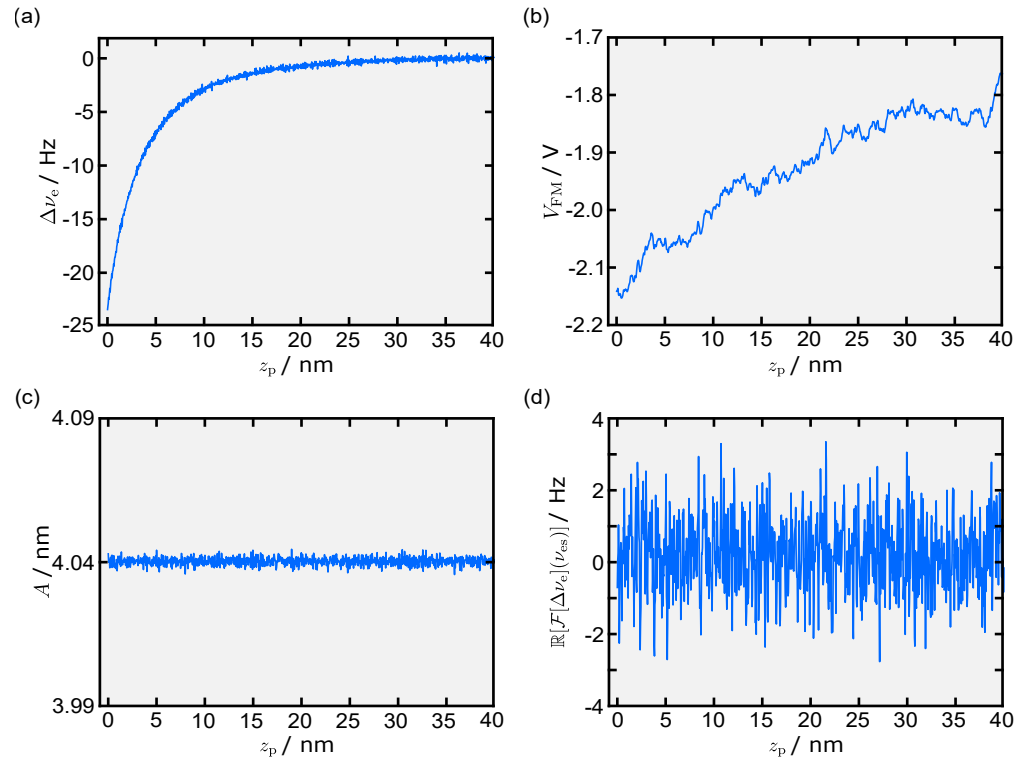


Figure E.7.: Distance-dependent curves performed on the Au(111) single crystal with the *second* Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite. Plot (a) presents the frequency shift $\Delta\nu_e$, (b) shows the Kelvin V_{FM} signal, (c) corresponds to the oscillation amplitude A and (d) presents the real part of the first spectral component $\Re[\mathcal{F}[\Delta\nu_e](\nu_{\text{es}})]$ versus the z-piezo displacement z_p .

KPFM Distance-Dependent Measurements on Calcite (10.4)

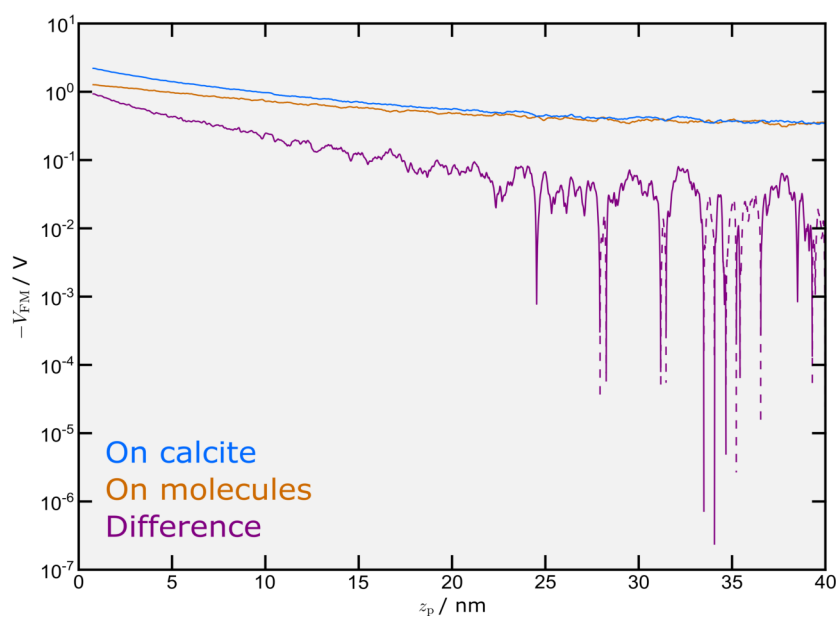


Figure F.1.: Logarithmic comparison of the averages of the distance-dependent V_{FM} curves recorded on calcite and on molecules. This plot shows the z -piezo range corresponding to the linear plot of figure 7.24 (c) shown from section 7.3.

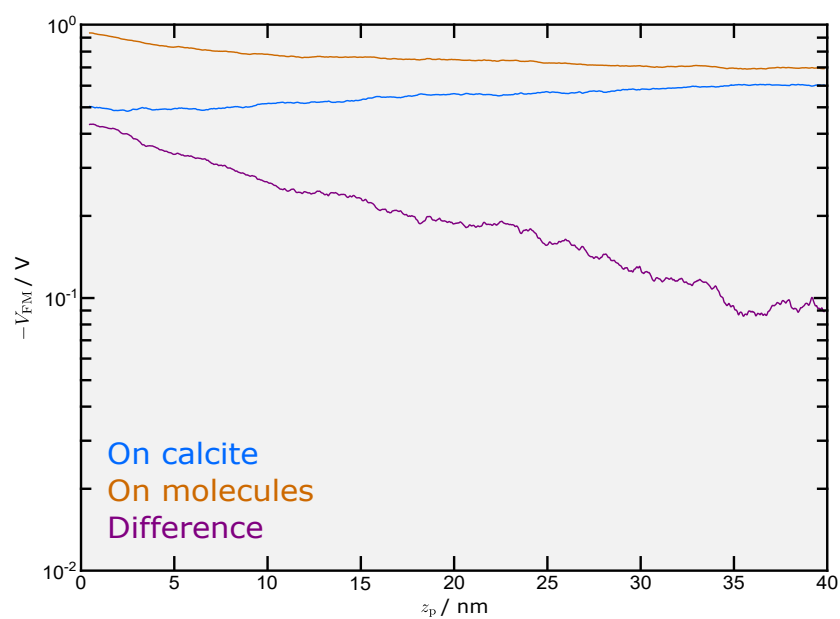


Figure F.2.: Logarithmic comparison of the averages of the distance-dependent V_{FM} curves recorded on calcite and on molecules. This plot shows the z-piezo range corresponding to the linear plot of figure 7.33 (c) shown from section 7.3.

List of Figures

2.1	Scheme of atomic force microscopy (AFM) in frequency modulation (FM) operation	8
2.2	Scheme of tip and sample with point charges in between	13
3.1	Photographs of the UHV chamber	19
3.2	Photograph of a Knudsen cell mounted on a molecule sublimator . . .	20
3.3	Photograph of the VT SPM XA scanhead and sample stage	21
3.4	Block diagram of the equipment connections for standard STM or FM-AFM imaging	23
3.5	Transfer function of the external voltage inputs V_{EXT} and V_{MOD} . . .	24
3.6	Block diagram of the equipment connections for FM-KPFM measurements	27
4.1	Model for the reconstruction of Au(111) surface.	29
4.2	STM image of the Au(111) surface showing atomic resolution	30
4.3	Model of calcite (10.4) surface.	31
5.1	Transfer functions of MATRIX PLL. Bandwidth set to 1009 Hz and 2289 Hz.	36
5.2	Transfer functions of the experimental system for PLL bandwidth set to 1009 Hz and 2289 Hz.	39
5.3	FFT of the frequency shift output by the PLL as $\Delta\nu_{e,PLL}$ using different ν_{es} frequencies. PLL bandwidth set to 1009 Hz.	40
5.4	FFT of the frequency shift output by the PLL as $\Delta\nu_{e,PLL}$ using different ν_{es} frequencies. PLL bandwidth set to 2289 Hz.	41
5.5	Transfer function of the experimental system. PLL bandwidth set to 1009 Hz and $V_{bias} = 1.6$ V and 0 V.	42
5.6	$V_{FM}(z_{ts})$ simulation: point charges on the sample surface.	43
6.1	Long-time exposure photographs of the Au(111) single crystal during the sputtering procedure.	51
6.2	STM images on a Au(111) sample.	52
6.3	STM images on a Au(111) sample after new preparation procedure. . .	53
6.4	Long-time exposure photographs of the new Au(111) single crystal . .	55
6.5	STM images on Au(111) sample immediately after sputtering the sample surface.	55
6.6	STM images taken on a new Au(111) single crystal.	56

6.7	FM-AFM and FM-KPFM images on Au(111)	58
6.8	Comparison of all four real part of the KPFM 1 st spectral component images.	59
6.9	Comparison of the non-filtered and filtered real part of the 1 st spectral component images.	60
6.10	Histograms of the filtered real part of the 1 st spectral component images.	61
6.11	KPFM 1 st spectral component <i>versus</i> bias voltage V_{bias}	63
6.12	Fitted magnitudes of the 1 st spectral component <i>versus</i> bias voltage V_{bias}	66
6.13	Comparison of the non-filtered and filtered V_{FM} images.	68
6.14	Comparison of distance-dependent curves two and five days after preparing the Au(111) sample.	70
6.15	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>first</i> Au-coated silicon AFM tip before sputter it.	71
6.16	Distance-dependent curve marks in images. Measurements done using the <i>first</i> Au-coated silicon AFM tip before sputtering it.	72
6.17	Distance-dependent curves on Au(111). Measurements done using the <i>first</i> Au-coated silicon AFM tip before preparation.	73
6.18	Long-time exposure photographs of the sputtering procedure of Au-coated AFM tips	74
6.19	Voltage-dependent I_T (V_{bias}) and I (V_{bias}) curves recorded with the <i>first</i> Au-coated silicon AFM tip on the Au(111) sample.	75
6.20	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>first</i> Au-coated silicon AFM tip after sputter it for 90 s.	77
6.21	Distance-dependent curve marks in images. Measurements done using the <i>first</i> Au-coated silicon AFM tip after sputtering it for 90 s.	78
6.22	Distance-dependent curves on Au(111). Measurements done using the <i>first</i> Au-coated silicon AFM tip after sputtering it for 90 s.	79
6.23	FM-AFM and FM-KPFM images measured on Au(111) using the <i>first</i> Au-coated silicon AFM tip after sputter it for 160 s.	80
6.24	Distance-dependent curve marks in images. Measurements done using the <i>first</i> Au-coated silicon AFM tip after sputtering it for 160 s.	81
6.25	Distance-dependent curves on Au(111). Measurements done using the <i>first</i> Au-coated silicon AFM tip after sputtering it for 160 s.	82
6.26	Voltage-dependent curves recorded with the <i>first</i> Au-coated silicon AFM tip after sputtering it for 160 s.	83
6.27	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent V_{FM} (z_p) of figure 6.26 (a) and (b), which were performed after sputtering the <i>first</i> Au-coated silicon AFM tip for 160 s.	84
6.28	Comparison of the averaged distance-dependent curves of the experiments with the <i>first</i> Au-coated silicon AFM tip.	86
6.29	$\Delta\nu_e$ (z_c) curve recorded on the Au(111) sample with the <i>second</i> Au-coated silicon AFM tip. The curve exhibit jumps.	87

6.30	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>second</i> Au-coated silicon AFM tip before sputtering it.	88
6.31	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip before sputtering it.	89
6.32	Distance-dependent curves on Au(111). Measurements done using the <i>second</i> Au-coated silicon AFM tip before sputtering it.	90
6.33	Distance-dependent KPFM 1 st spectral component curve recorded on Au(111) with the <i>second</i> Au-coated silicon AFM tip. Curve recorded with KPFM feedback disabled.	91
6.34	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>second</i> Au-coated silicon AFM tip after sputtering it for 90 s.	92
6.35	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip after sputtering for 90 s.	94
6.36	Distance-dependent curves on Au(111). Measurements done using the <i>second</i> Au-coated silicon AFM tip after sputtering it for 90 s.	95
6.37	FM-AFM and FM-KPFM images measured on Au(111) using the <i>second</i> Au-coated silicon AFM tip after sputtering it for 160 s.	96
6.38	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip after sputtering it for 160 s.	97
6.39	Distance-dependent curves on Au(111). Measurements done using the <i>second</i> Au-coated silicon AFM tip after sputtering it for 160 s.	98
6.40	Voltage-dependent curves recorded with the <i>second</i> Au-coated silicon AFM tip after sputtering it for 160 s.	99
6.41	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent $V_{\text{FM}}(z_{\text{p}})$ of figure 6.40 (a) and (b), which were performed after sputtering the <i>second</i> Au-coated silicon AFM tip for 160 s.	100
6.42	Comparison of the averaged distance-dependent curves of the experiments with the <i>second</i> Au-coated silicon AFM tip.	101
6.43	Voltage-dependent $\Delta\nu_{\text{e}}(V_{\text{bias}})$ curves which exhibit instabilities.	103
6.44	Voltage-dependent $\Delta\nu_{\text{e}}(V_{\text{bias}})$ curves which present some jumps and corresponding parabolic fits.	106
6.45	Voltage-dependent $\Delta\nu_{\text{e}}(V_{\text{bias}})$ curves which exhibit drift in Z-direction.	108
7.1	Frequency shift vs. bias voltage $\Delta\nu_{\text{e}}(V_{\text{bias}})$ curves, topography and profile recorded on the calcite (10.4) surface.	113
7.2	Topography, frequency shift vs. bias voltage $\Delta\nu_{\text{e}}(V_{\text{bias}})$ curves and profile recorded on the calcite (10.4) surface.	115
7.3	FM-AFM and FM-KPFM images measured on the calcite (10.4) surface using the <i>third</i> Au-coated silicon AFM tip.	117
7.4	Distance-dependent curve marks in images. Measurements done using the <i>third</i> Au-coated silicon AFM tip.	118

7.5	Distance-dependent curves performed during the first experiment on the calcite (10.4). The <i>third</i> Au-coated silicon AFM tip was used. . . .	119
7.6	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent $V_{\text{FM}}(z_p)$ of figure D.4 (a) and (b), which were performed after the first experiment on calcite using the <i>third</i> Au-coated silicon AFM tip.	120
7.7	FM-AFM and FM-KPFM images measured on the calcite (10.4) surface using the <i>second</i> Au-coated silicon AFM tip.	122
7.8	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip.	123
7.9	Distance-dependent curves performed during the second experiment on the calcite (10.4). The <i>second</i> Au-coated silicon AFM tip was used. .	124
7.10	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent $V_{\text{FM}}(z_p)$ of figure D.8 (a) and (b), which were performed after the second experiment on calcite using the <i>second</i> Au-coated silicon AFM tip.	125
7.11	FM-AFM and FM-KPFM images measured the calcite (10.4) surface using the <i>fourth</i> Au-coated silicon AFM tip.	126
7.12	Distance-dependent curve marks in images. Measurements done using the <i>fourth</i> Au-coated silicon AFM tip.	127
7.13	Distance-dependent curves performed during the third experiment on the calcite (10.4). The <i>fourth</i> Au-coated silicon AFM tip was used. . . .	128
7.14	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent $V_{\text{FM}}(z_p)$ of figure D.12 (a) and (b), which were performed after the third experiment on calcite using the <i>fourth</i> Au-coated silicon AFM tip.	129
7.15	Comparison of the averaged distance-dependent curves of three experiments performed on calcite (10.4).	130
7.16	2,5-DHBA molecule.	133
7.17	Topography z_p (a) and Kelvin V_{FM} signal of 2,5-DHBA deposited on calcite. Adapted from [37].	134
7.18	Drift corrected FM-AFM topography of a 2,5-DHBA island of the dense structure on calcite (10.4).	135
7.19	FM-AFM and FM-KPFM images measured on 2,5-DHBA deposited on calcite using the <i>third</i> Au-coated silicon AFM tip.	136
7.20	Distance-dependent curve marks in images. Measurements done using the <i>third</i> Au-coated silicon AFM tip.	137
7.21	Distance-dependent curves performed during the first experiment on 2,5-DHBA deposited on calcite. The <i>third</i> Au-coated silicon AFM tip. .	138

7.22	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent V_{FM} (z_p) of figure D.16 (a) and (b), which were performed after the first experiment on 2,5-DHBA deposited on calcite using the <i>third</i> Au-coated silicon AFM tip.	139
7.23	Scheme of the distance-dependent curve recording process.	141
7.24	Distinction (recorded on calcite or on molecules) of the V_{FM} curves corresponding to the measurement shown in figure 7.21 and comparison of their averages.	143
7.25	V_{FM} distance-dependent curves performed on the Au(111) single crystal with the <i>fifth</i> Au-coated silicon AFM tip: procedure to find the new preparation parameters using the new sputter gun: ISE 10.	145
7.26	V_{FM} distance-dependent curves performed on the Au(111) single crystal with the <i>second</i> Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10.	145
7.27	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent V_{FM} (z_p) of figure E.5 (a) and (b), which were performed after sputtering the <i>second</i> Au-coated silicon AFM tip for 15 s more. . .	146
7.28	FM-AFM and FM-KPFM images measured the calcite (10.4) surface using the <i>second</i> Au-coated silicon AFM tip.	147
7.29	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip.	148
7.30	Distance-dependent curves performed during the second experiment on 2,5-DHBA deposited on calcite. The <i>second</i> Au-coated silicon AFM tip.149	
7.31	V_{FM} distance-dependent curves performed on the Au(111) single crystal with the <i>second</i> Au-coated silicon AFM tip after the second experiment on 2,5-DHBA deposited on calcite.	150
7.32	Comparison of the Kelvin V_{FM} signal: closed-loop and static distance-dependent V_{FM} (z_p) of figure E.6 (a) and (b), which were performed after the second experiment on 2,5-DHBA deposited on calcite using the <i>second</i> Au-coated silicon AFM tip.	151
7.33	Distinction (recorded on calcite or on molecules) of the V_{FM} curves corresponding to the measurement shown in figure 7.30 and comparison of their averages.	153
A.1	Calibration curve for estimating the temperature of a sample placed in the heating stage of the manipulator.	171
C.1	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>third</i> Au-coated silicon AFM tip after dropping something off on the surface while scanning.	177

C.2	Distance-dependent curve marks in images. Measurements done using the <i>third</i> Au-coated silicon AFM tip after dropping something off on the surface while scanning.	178
C.3	Distance-dependent curves performed on the Au(111) single crystal with the <i>third</i> Au-coated silicon AFM tip after dropping something on the surface while scanning.	178
C.4	Voltage-dependent curves recorded with the <i>third</i> Au-coated silicon AFM tip after dropping something off on the surface while scanning.	179
C.5	Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of $\Delta\nu_e(V_{\text{bias}})$ curves of figure C.4 (a) and (b), which were performed after the <i>third</i> Au-coated silicon AFM tip dropped something off on the surface while scanning.	180
C.6	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>fourth</i> Au-coated silicon AFM tip after dropping something off on the surface while scanning.	181
C.7	Distance-dependent curve marks in images. Measurements done using the <i>fourth</i> Au-coated silicon AFM tip after dropping something off on the surface while scanning.	182
C.8	Distance-dependent curves performed on the Au(111) single crystal with the <i>fourth</i> Au-coated silicon AFM tip after dropping something on the surface while scanning.	182
C.9	Voltage-dependent curves recorded with the <i>fourth</i> Au-coated silicon AFM tip after dropping something off on the surface while scanning.	183
C.10	Comparison of the Kelvin V_{FM} signal: closed-loop distance-dependent $V_{\text{FM}}(z_p)$ curve and fitted V_{FM} data of $\Delta\nu_e(V_{\text{bias}})$ curves of figure C.9 (a) and (b), which were performed after the <i>fourth</i> Au-coated silicon AFM tip dropped something off on the surface while scanning.	184
D.1	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>third</i> Au-coated silicon AFM tip.	185
D.2	Distance-dependent curve marks in images. Measurements done using the <i>third</i> Au-coated silicon AFM tip.	186
D.3	Distance-dependent curves on Au(111). Measurements done using the <i>third</i> Au-coated silicon AFM tip after measuring on calcite.	186
D.4	Voltage-dependent curves recorded with the <i>third</i> Au-coated silicon AFM tip after measuring on calcite.	187
D.5	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>second</i> Au-coated silicon AFM tip after measuring on calcite.	188
D.6	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip after measuring on calcite.	189
D.7	Distance-dependent curves on Au(111). Measurements done using the <i>second</i> Au-coated silicon AFM tip after measuring on calcite.	189

D.8	Voltage-dependent curves recorded with the <i>second</i> Au-coated silicon AFM tip after measuring on calcite.	190
D.9	FM-AFM and FM-KPFM images measured on the Au(111) sample using the <i>fourth</i> Au-coated silicon AFM tip after measuring on calcite.	191
D.10	Distance-dependent curve marks in images. Measurements done using the <i>fourth</i> Au-coated silicon AFM tip after measuring on calcite.	192
D.11	Distance-dependent curves on Au(111). Measurements done using the <i>fourth</i> Au-coated silicon AFM tip after measuring on calcite.	192
D.12	Voltage-dependent curves recorded with the <i>fourth</i> Au-coated silicon AFM tip after measuring on calcite.	193
D.13	FM-AFM and FM-KPFM images measured on Au(111) using the <i>third</i> Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite.	194
D.14	Distance-dependent curve marks in images. Measurements done using the <i>third</i> Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite.	195
D.15	Distance-dependent curves on Au(111). Measurements done using the <i>third</i> Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite.	195
D.16	Voltage-dependent curves recorded with the <i>third</i> Au-coated silicon AFM tip after measuring 2,5-DHBA deposited on calcite.	196
E.1	Distance-dependent curves on Au(111). Measurements done using the <i>fifth</i> Au-coated silicon AFM tip: procedure to find the new preparation parameters using the new sputter gun: ISE 10.	197
E.2	FM-AFM and FM-KPFM images measured on Au(111) using the <i>second</i> Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10.	198
E.3	Distance-dependent curve marks in images. Measurements done using the <i>second</i> Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10.	199
E.4	Distance-dependent curves on Au(111). Measurements done using the <i>second</i> Au-coated silicon AFM tip after preparing it with the new sputter gun: ISE 10.	199
E.5	Voltage-dependent curves recorded with the <i>second</i> Au-coated silicon AFM tip after measuring 2,5-DHBA deposited on the calcite (10.4) surface.	200
E.6	Voltage-dependent curves recorded with the <i>second</i> Au-coated silicon AFM tip after measuring 2,5-DHBA deposited on the calcite (10.4) surface.	201
E.7	Distance-dependent curves on Au(111). Measurements done using the <i>second</i> Au-coated silicon AFM tip after measuring on 2,5-DHBA deposited on calcite.	202

F.1	Logarithmic comparison of the averages of the distance-dependent V_{FM} curves recorded on calcite and on molecules. This plot shown the z-piezo range corresponding to the linear plot of figure 7.24 shown from section 7.3.	203
F.2	Logarithmic comparison of the averages of the distance-dependent V_{FM} curves recorded on calcite and on molecules. This plot shown the z-piezo range corresponding to the linear plot of figure 7.33 shown from section 7.3.	204

List of Tables

3.1	Relation of the different voltages names.	23
3.2	Bandwidth of the external voltage inputs.	24
6.1	V_{FM} values obtained from fitting the magnitude of the 1 st spectral component <i>versus</i> bias voltage V_{bias} from figure 6.12.	67
6.2	Fit results of the negative sweep voltage curve presented in 6.44 (a). .	107
6.3	Fit results of the positive sweep voltage curve presented in 6.44 (b). .	107
7.1	V_{FM} values of the points of figure 7.32	151
7.2	Work functions of crystalline and polycrystalline Au.	154
7.3	Summary of experiments done on Au(111) using Au-coated silicon AFM tips and the V_{FM} (range of) values.	155

List of Abbreviations

SPM scanning probe microscopy (or microscope)

AFM atomic force microscopy (or microscope)

STM scanning tunnelling microscopy (or microscope)

KPFM Kelvin probe force microscopy

UHV ultra-high vacuum

DHBA dihydroxybenzoic acid

LDOS local density of states

PSPD position sensitive photo-diode

FM frequency modulation

PLL phase-locked loop

CPD contact potential difference

HOPG highly oriented pyrolytic graphite

AM amplitude modulation

FEM finite elements method

VT variable temperature

CS cooling stage

HS heating stage

CU control unit

FFT fast Fourier transform

fcc face-centered cubic

hcp hexagonal closed-packed

REELS reflection electron energy-loss spectra

DFT density functional theory

GIXRD grazing incidence X-ray diffraction

LEED low-energy electron diffraction

Talks & Poster Presentations

Talks

(presenting author underlined)

- **Towards understanding the role of charge transfer in the stabilisation of molecular assemblies**

F. Romero Lairado, M. Nimmrich, M. Kittelmann, R. Bechstein, A. Kühnle
(ACRITAS End of Year 1 Meeting, February 2014, Dublin, Ireland)

- **Towards understanding the role of charge transfer in the stabilisation of molecular assemblies**

F. Romero Lairado, M. Nimmrich, M. Kittelmann, R. Bechstein, A. Kühnle
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Poster Presentations

(presenting author underlined)

- **FM-KPFM in UHV: testing and preparing metal-coated tips**

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Colophon

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Declaration

Hiermit versichere ich, dass ich die vorliegende Arbeit selbst angefertigt und nur die genannten Quellen benutzt habe.

Mainz, den 05. June 2018

Francisco Romero Lairado

