Investigations of the role of physisorbed hydrogen in STM experiments

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vorgelegt von
Matthias Stocker
aus Illerrieden
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Amtierender Dekan:
Prof. Dr. Peter Dürre

1. Gutachter:
apl. Prof. Dr. Berndt Koslowski

2. Gutachter:
Prof. Dr. Joachim Ankerhold

Betreuer:
apl. Prof. Dr. Berndt Koslowski

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Chapter 1

Introduction

During the last 30 years, technology has developed in an unprecedented way. It is similar to the Cambrian explosion at about 530 Million years ago [1], where in a short period of time an incredible amount of new species emerged on planet earth. Comparing the first personal computers from the 1980s with state of the art smartwatches one can see that technology made progress in orders of magnitudes in every possible aspect [2, 3]. This explosive development in technology is directly connected to the ability to access smaller length scales in research and manufacturing because it allows to reduce the size and increase the density of electronic junctions in new products.

As we approach these small length scales the surface itself shifts more and more into focus. Therefore, a detailed understanding of the properties of surfaces is very important. Such properties are the topography, electronic or magnetic behavior, chemical reactivity, adhesive forces, wetting properties, and many more. Experimentally, there are different approaches to collect this information. It is possible to investigate large areas to get an average of certain properties, or the properties are investigated locally on small length scales. The latter allows for a detailed understanding of the fundamental phenomena in nature paving the way for new concepts for future technologies.

To access characteristics on the nanometer scale, different microscopy and spectroscopy techniques are nowadays available. Examples of these techniques include TEM (Transmission Electron Microscopy) [4], SEM (Scanning Electron Microscopy), SHIM (Scanning Helium Ion Microscopy) [5], STED (Stimulated Emission Depletion) [6], AFM (Atomic Force Microscopy) [7, 8] and STM (Scanning Tunneling Microscopy/Microscope) [9, 10, 11]. Throughout this dissertation STM is used to access these small length scales.
With the invention of the scanning tunneling microscope [12] the question of what information can be gathered with this new instrument arose. Soon after imaging topography became a standard procedure, STS (*Scanning Tunneling Spectroscopy*) emerged [13] which opened the ability to measure properties such as the local density of states [14], the local barrier height [15], or even vibrational modes by means of IETS (*Inelastic Electron Tunneling Spectroscopy*) on an atomic scale [16].

It is well known in literature that spectroscopic data has to be processed carefully in order to get quantitative results. Examples of such measurements are the *I-V* spectroscopy, which contains information on the density of states of tip and sample [17, 18, 19] or IETS, where the faint signatures in the spectra have to be carved out of background noise [20, 21, 22].

In order to investigate energetically sharp signatures experiments are performed at low temperatures to eliminate thermal broadening [10, 23]. Due to different thermal coupling the temperature of tip and sample may differ causing possible thermoelectric contributions to the tunneling current. Although the temperature difference was anticipated in literature indicated by measurements on superconducting samples which exposed unusual tunneling curves [24], the effect was never investigated in detail. But for the evaluation of data it is crucial to know the temperatures of tip and sample as precisely as possible.

The tip of an STM is not only a relevant factor in spectroscopy but also in topography. As will be shown in this dissertation, atomic resolution which was presented as a great breakthrough is not necessarily a benefit on all surfaces [25]. It can also indicate a contamination of the system. In recent years several groups tried to control the influence of the tip by functionalizing it. One way this can be done is by picking up certain atoms or molecules, such as Xe [26] or CO [27] and using them as sensor. Hydrogen was also introduced in the tunneling junction resulting in a tremendous increase in intramolecular resolution [28].

Over the years, several groups reported on another interesting phenomena occurring if hydrogen is present in the tunneling junction. A two-level system was observed in *I-V* spectroscopy [29, 30, 31]. By increasing the tunneling bias over a certain threshold depending on the tip-sample separation a switching behavior could be observed. Although the transition between the two levels was attributed to the vibrational energies of hydrogen in the physisorption well, a physical explanation of the measured phenomena was still lacking.
The present dissertation contains three major objectives. The first is an improvement of the evaluation process of IETS data using Wavelet analysis. This requires a detailed understanding of all parameters especially the temperatures of tip and sample. Therefore, the second one is the calibration of these temperatures using a superconductive sample. Further influences of the tip on topography and spectroscopy are studied in the third objective, where the influence of hydrogen in the tunneling junction is investigated with different tips.

Starting from basic considerations on tunneling in chapter two, different spectroscopy methods will be introduced. The experimental setup, needed for the investigations, is also described. In chapter three the required properties of hydrogen will be summarized briefly and the adsorption mechanism of molecular hydrogen on noble metal surfaces will be presented. Additionally, the physisorption potential of a molecule in between two electrodes in close separation will be derived.

The fourth chapter addresses the evaluation of IETS spectra. After a discussion of the fundamentals of IETS, a method for the processing of data will be shown. This is in close analogy to the dissertation of Maurer [32] and Koslowski et al. [20]. A new method of data evaluation will be introduced using Wavelet analysis. It improves the evaluation process because it allows to automatize and systematize the procedure.

Tunneling curves of a superconductor-isolator-normal conductor junction are investigated in chapter five. After the theoretical background is derived and the preparation of Nb(110) films is shown, a method will be introduced which explains how to determine the temperatures of a superconducting sample and a normal conducting tip independently [33].

The effect of hydrogen in the tunnel junction is investigated in the sixth chapter. It will be shown that the material of the tip plays a significant role. Where the hydrogen dissociates at a tungsten tip leading to a modified imaging mechanism, it is trapped in the junction when using silver tips. The latter is also responsible for characteristic features in spectroscopy. It will be shown that these features can be deduced from specific vibrational modes of a single molecule in the junction. Due to a separation dependent potential, forces are generated causing a deflection of the tip apex. It will be seen that the apex of silver tips are surprisingly soft. Several measurements and evaluations will consolidate the presented model.

Finally, experiments will be presented, where lines of adatoms are pulled out of the surface by applying a bias pulse when hydrogen is present. It will be shown that this leads to a degradation of the herringbone reconstruction on Au(111).
Chapter 2

Fundamentals

2.1 Scanning tunneling microscopy

With the invention of the Scanning Tunneling Microscope by Binning and Rohrer [12] in the early 1980s, a new era begun in the field of surface science. The basic principle of this instrument is a sharp needle, called the 'tip', which is brought in close proximity to a sample surface. While a bias voltage is applied to the tip a current can be measured because of the tunneling effect. Moving the tip in lateral directions, information on the topography of the sample can be extracted from the current. Soon after this invention a number of additional techniques were developed, such as Atomic Force Microscopy [7], Kelvin Probe Microscopy [34], Potentiometry [35] and many more [10, 36, 37].

As the stability of scanning tunneling microscopes improved, it became possible to perform spectroscopic measurements known as Scanning Tunneling Spectroscopy (STS) [38, 13]. Here, the tip stays at one location and properties such as the density of states of the sample are probed locally. In modern scanning probe microscopy this is an every day tool to analyze surfaces on the atomic scale.

In this section the fundamental theoretical relations for describing STM will be introduced employing the WKB approximation which are sufficient to understand the imaging mechanism in STM and the basic spectroscopy modes.

2.1.1 Basics on tunneling in STM

Since the tunneling effect plays a fundamental role in physics and is therefore extensively addressed in basic physics courses, it will not be discussed here from scratch. However, the explanation of a one dimensional tunneling contact and
thereby the STM begins with the basic equation of the so called one dimensional WKB approximation, first derived by Simmons [39, 40] as

\[ I(V,z) \propto \int_{-\infty}^{\infty} \rho_b(E) \cdot \rho_t(E - eV) \cdot T(E,eV,z) \cdot [f_D(\tau_t,E - eV) \cdot (1 - f_D(\tau_s,E))] dE. \]  

(2.1)

WKB is the acronym of Wenzel, Kramers and Brillouin, who calculated the tunneling current, \( I \), between two electrodes using a semi-classical approximation [41, 42, 43]. The parameters \( z \) and \( V \) are the most important parameters in STM, namely the distance between tip and sample, \( z \), and the bias, \( V \). The bias is treated in units of energy, which means \( e \) is hereby set to unity for reasons of simplicity. \( \rho \) corresponds to the density of states (DOS) at a given energy \( E \), \( f_D \) represents the Fermi-Dirac statistic at temperature \( \tau \), and the indices ‘t’ and ‘s’ correspond to tip and sample respectively. \( T \) is the transmission coefficient which is, according to the one dimensional WKB approach [44], given by

\[ T(E,V,z) = \exp \left[ - \int_{z_0}^{z} k(z') dz' \right] = \exp \left[ - \int_{z_0}^{z} \sqrt{\alpha (\Phi(z') - E)} dz' \right], \]  

(2.2)

where \( k(z) \) corresponds to the wavenumber in the phase integral, \( \alpha = \frac{8m}{h^2} \), and \( \Phi \) equals the barrier height. Assuming that the work functions of tip and sample are equal, \( \Phi_t \approx \Phi_s = \Phi \), and that the trapezoidal approximation is valid, it is possible to use the relation \( \Phi(z) = \Phi + \frac{V}{2} \), corresponding to a rectangular barrier. Thereby, the transmission coefficient can be written as

\[ T(E,V,z) = \exp \left[ - \int_{z_0}^{z} \sqrt{\alpha (\Phi + \frac{V}{2} - E)} dz' \right]. \]  

(2.3)

The energy diagram corresponding to a transmission coefficient with a rectangular barrier is depicted in figure 2.1.

With this basic equations one can understand most properties of the tunneling junction in STM.

### 2.1.2 Topography

An essential characterization method in surface science is imaging of the topography. STM provides the possibility to analyze a sample down to the atomic scale. The section above shows that the tunneling current is highly sensitive to small
changes of the tip-sample separation, since the tunneling current depends exponentially on $z$. The decay length for typical tunneling barriers is about 30 pm. This is the key to high resolution imaging with a STM. The measured topography always corresponds to a convolution of the real topography with the DOS of both, tip and sample. This may lead to different images at different bias voltages.

In principle there are two different imaging techniques, namely the constant-height mode and the constant-current mode. A schematic drawing is shown in figure 2.2.

In the constant-height mode the tip is scanned in a plane parallel to the average surface. Since the current is very sensitive to changes of the tip-sample separation, the current signal can be used to draw conclusions on the texture of the surface. This mode allows for a high scanning speed, since no $z$ control is needed and therefore the feedback loop is not active. Additionally, this mode needs a special crash-protection to prevent the destruction of the tip and/or the sample.

The constant-current mode uses a feedback loop to keep the current between tip and sample constant. This means the tip follows the profile of the surface and the voltage applied at the $z$-piezo is directly proportional to the height of the topography.
This mode is the standard topography mode in STM. It has been used for all images shown in this dissertation.

Images have been recorded by scanning rows forward and backward, resulting in two topography images. With this additional information, artifacts such as structures depending on the scanning direction can be detected. Additionally, the current signal was recorded in a separate image to ensure that the speed of the feedback loop is fast enough. This speed has to be controlled manually by a potentiometer.

2.1.3 Spectroscopy

Apart from taking images of surfaces the second class of measurements in STM is the scanning tunneling spectroscopy (STS). It allows probing different properties of the surface locally. In principle, spectroscopy means to measure one quantity in dependence of another quantity. In the setup used here, the parameter field consists of three parameters, the current, $I$, the bias, $V$, and the tip-sample separation, $z$. Measuring one parameter, varying another and having the third one fixed, it is possible to obtain three measurement procedures:

- **$I$-$V$ spectroscopy**: $z$ is kept constant, $V$ is varied, and $I$ is measured.
- **$I$-$z$ spectroscopy**: $V$ is kept constant, $z$ is varied, and $I$ is measured.
- **$z$-$V$ spectroscopy**: $I$ is kept constant, $V$ is varied, and $z$ is measured.

These modes are discussed in more detail in the following.

2.1.3.1 $I$-$V$ spectroscopy

The most common spectroscopy mode is the $I$-$V$ spectroscopy. The tip-sample separation is set by the reference parameters $I_0$ and $V_0$. The feedback loop is switched off and $I(V)$ is measured while the tunneling bias, $V$, is varied.

In order to analyze features in this characteristic curve more precisely the first derivative is also recorded using lock-in technique. Therefore, a modulation amplitude which has to be adjusted depending on the expected width of the signatures is added to the bias and the derivative, $\frac{\partial}{\partial V} I(V)$, is measured (see also section 2.1.3.4). $\frac{dy}{dx}$ is used for convenience. Using equation (2.1) and a Taylor expansion at $V = 0$ one obtains for this measurement
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\[ \frac{\partial V}{\partial I}(V) \propto \rho_s(V) \cdot \rho_t(0) \cdot T(E,V,z) + \int_0^V \rho_s(E) \cdot T(E,V,z) \left[ \frac{\partial V}{\partial I}(E-V) - \sqrt{\frac{\alpha \cdot z \cdot \rho_t(E-V)}{4 \sqrt{\Phi + \frac{V}{2} - E}}} \right] dE. \tag{2.4} \]

Since the microscope is working under low temperature conditions, the Fermi-Dirac function is assumed to be a step function, thus changing the integration limits to \( 0 < E < V \). However, this approximation is not true for signatures measured close to the Fermi level \( (V \approx k_B T) \) and will be treated separately in chapter 5.

Assuming also a constant DOS of the tip near the Fermi level \( (\rho_t = \text{constant}) \) and a tunneling barrier which is substantially higher than the applied tunneling bias \( (V \ll \Phi) \), this expression can be solved with respect to the sample DOS to

\[ \rho_s(V) \propto \frac{1}{T(E-V)} \left( \frac{\partial V}{\partial I}(V) + \frac{\sqrt{\alpha \cdot z}}{4 \sqrt{\Phi}} \cdot I(V) \right). \tag{2.5} \]

This means, that the DOS of the sample can be extracted by measuring the conductivity, \( \frac{\partial V}{\partial I}(V) \), and the current, \( I(V) \).

It is also possible to measure the second harmonic with a lock-in amplifier, which corresponds to the second derivative with respect to the bias. This method is known as IETS \( (\text{Inelastic Electron Tunneling Spectroscopy}) \) and will be explained in detail in section 4.

Some additional remarks shall be given here concerning the limits of I-V spectroscopy. In reality, the DOS of the tip is not constant. Further information on influences of this effect on the measurement and how this can be used to obtain information on both the tip and the sample can be found in the dissertation of Holger Pfeifer and additional references [45, 17, 18].

The frequency of the modulation amplitude which is added to the bias is in the range of several hundred Hz. This is important when adjusting the scanning parameters concerning steps of the varied bias and number of data points. A suitable integration time for one point measuring the first derivative is about ten periods of the modulation and about 50 periods for the second derivative. This leads to long time spans during which the distance between tip and sample should stay constant without drift effects. Additionally, the modulation amplitude itself has an impact on the shape of certain features. This will be addressed in section 2.1.3.4.
Since the separation between tip and sample is kept constant, this mode corresponds to other applications such as macroscopic metal-insulator-metal (MIM) junctions. This method allowed to probe the $I-V$ curve of superconducting layers in the 1960s [46, 47]. Molecular layers could be also investigated in large scale tunneling junctions [48].

### 2.1.3.2 I-z spectroscopy

In this spectroscopy mode the tip-sample separation, $z$, is varied and $I(z)$ is measured, while the feedback loop is switched off. Additionally, a small modulation can be added to the $z$ signal and $\partial_z I$ can be measured. Another form of measuring $I-z$ spectra is to vary the set current at closed feedback loop. The advantage of this method is the better control of the measured range, since otherwise the current can exceed the possible resolution of the $IV$ converter.

This leads to the definition of the so-called "apparent barrier height" [49, 50]

$$\Phi_{app}(V) = \frac{1}{\alpha} \left( \frac{\partial_z I(V,z)}{I(V,z)} \right)^2.$$ (2.6)

For $V \to 0$ the apparent barrier height corresponds to the local barrier height, $\Phi$.

In order to get more information on the dynamic of the barrier in the tunneling junction, the differential barrier height was introduced by Koslowski et al. [45] as

$$\Phi_{diff}(V) = \frac{1}{\alpha} \left( \frac{\partial_z \partial_V I(V,z)}{\partial_V I(V,z)} \right)^2.$$ (2.7)

Since the bias is kept constant while measuring $I(z)$ every measurement corresponds to one data point in the $\Phi(V)$ plot.

For small bias voltages where $\rho_s = \rho_t \approx \text{constant}$ we recall the equations (2.1) and (2.2). This leads to

$$I(z) = C \cdot \int_0^V e^{-\int_0^z k(z')dz'} dE = C' \cdot e^{-\int_0^z k(z')dz'} V.$$ (2.8)

A differentiation with respect to $z$ gives

$$\frac{dI(z)}{dz} = C' \cdot e^{-\int_0^z k(z')dz'} k(z) \cdot V$$ (2.9)

and hence
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\[ k(z) = -\frac{dI(z)}{dz} \cdot \frac{1}{I(z)}. \]  

(2.10)

Thereby, the inverse decay length or wavenumber, \( k(z) \), can be extracted from measured data.

2.1.3.3 z-V spectroscopy

The last spectroscopy mode to be mentioned is the z-V spectroscopy. In this mode the feedback loop is switched on. The bias, \( V \), is ramped; the displacement of the tip, \( z(V) \), and the conductivity, \( \partial_V I(V) \), are recorded. Since the set current is not changed, the feedback loop controls the tip-sample separation in a way that the tunneling current stays at a constant level. Therefore, this mode is useful for the investigation of structures which are unstable at a changing or a higher tunneling current, such as organic molecules or other softly bound adsorbents on surfaces [51, 52].

While measuring in this mode, the parameters have to be controlled precisely to avoid the assignment of too low bias voltages. In this case the current increases leading to a 'pole' in \( \partial_V I(V) \) and the tip could crash into the sample and damage the tip apex or the sample. In order to analyze the local DOS a method was proposed similar to equation (2.5) which leads to the relation

\[ \rho_s(V) \propto \left( \frac{1}{\rho_t(0) \cdot T(E = V,z)} \left( \partial_V I(V,z) + \frac{\sqrt{\alpha \cdot z}}{4\sqrt{\Phi}} \cdot I_0 \right) \right) \]  

(2.11)

for \( V \ll \Phi \) and \( \rho_t = \text{const} \) [53]. A simple procedure shown in reference [32] based on the assumption that \( \rho_s = \rho_t = \text{constant} \) for \( V \to 0 \) allows for a fast correction of the pole at zero bias

\[ \rho_s(V) \propto \partial_V I(V,z) \cdot V. \]  

(2.12)

Again, the influence of the DOS of the tip can not be neglected. A deconvolution process can be found in the literature [18, 19, 54].

2.1.3.4 Signal broadening

Measured data is often influenced by external parameters that generate a broadening of features. In STS, mainly two effects contribute to this broadening. In this
section, first the modulation broadening due to the usage of lock-in technique and second the thermal broadening due to non-zero temperature is analyzed.

**Modulation broadening**

Physical properties are often directly linked to a derivative of a measurable quantity. Examples are the velocity, \( v = \frac{dx}{dt} \), heat capacity \( c = \left( \frac{\partial U}{\partial T} \right)_V \), or more related to STM the conductivity \( \sigma = \frac{dI}{dV} \). Since numerical differentiation often results in significant noise, Lock-In technique is used to determine a derivative by electronic means. To measure the derivative with respect to the bias, \( V \), a modulation voltage with a small amplitude, \( V_{\text{mod}} \), and frequency, \( \omega \), is added to the tunneling voltage. The measured tunneling current then corresponds to \( I = f(V + V_{\text{mod}} \cos(\omega t)) \). The frequency \( \omega \) has to be high enough that the feedback loop is not responding to the modulation and other distortions in the frequency spectrum such as multiples of the power line. In this section the implications of the modulation amplitude on measured features in the derivative shall be investigated in accordance with the references [55, 56, 33].

The mathematical expression for the detection of the first derivative of a function \( f(x) \) can be written as

\[
F_\omega(x) = \frac{2}{\tau} \int_0^\tau f(x + x_{\text{mod}} \cos(\omega t)) \cdot \cos(\omega t) dt. \tag{2.13}
\]

\( F_\omega(x) \) corresponds to the signal measured with the lock in amplifier, \( f(x) \) is the actual quantity that is measured and \( x_{\text{mod}} \) is the modulation amplitude. A substitution with \( X = x_{\text{mod}} \cdot \cos(\omega t) \) and using \( \tau = \frac{\pi}{\omega} \) yields

\[
F_\omega(x) = \frac{2}{\pi} \int_{-x_{\text{mod}}}^{x_{\text{mod}}} f(x + X) \cdot \frac{X}{x_{\text{mod}} \cdot \sqrt{x_{\text{mod}}^2 - X^2}} dX \tag{2.14}
\]

and a subsequent partial integration leads to

\[
F_\omega(x) = \frac{2}{\pi} \int_{-x_{\text{mod}}}^{x_{\text{mod}}} f'(x + X) \cdot \sqrt{x_{\text{mod}}^2 - X^2} dX. \tag{2.15}
\]

This means the measured signal can be written as a convolution \( F_\omega(x) = (f' \circ \Phi_\omega)(x) \) of the exact derivative \( f' \) and a window function

\[
\Phi_\omega(X) = \begin{cases} 
\frac{2}{\pi} \sqrt{\frac{x_{\text{mod}}^2 - X^2}{x_{\text{mod}}^2}} & \text{for } |X| < x_{\text{mod}} \\
0 & \text{for } |X| \geq x_{\text{mod}} \end{cases} \tag{2.16}
\]
This window function is shown in figure 2.3a. Assuming a peak-like feature with a natural line width of $W \rightarrow 0$ the FWHM (full width at half maximum) is stretched by a factor of $\sqrt{3} \cdot x_{\text{mod}} = 1.72 \cdot x_{\text{mod}}$ and the shape of the feature is slightly transformed. Normally, in STS the effective amplitude is given that is $x_{\text{rms}} = x_{\text{mod}} / \sqrt{2}$, which results in an effective broadening of the line width of $\sqrt{6} \cdot x_{\text{rms}} = 2.45 \cdot x_{\text{rms}}$.

The same formalism is now used for the second derivative [56]. In this case the second harmonic $2\omega$ is measured leading to the ansatz

$$F_{2\omega}(x) = \frac{2}{\tau} \int_{0}^{T} f(x + x_{\text{mod}} \cos(\omega t)) \cdot \cos(2\omega t) dt.$$ (2.17)

Using the same substitution $X = x_{\text{mod}} \cos(\omega t)$ as before, one gets

$$\frac{2}{\tau} \cos(2\omega t) dt = \frac{2}{\pi x_{\text{mod}}^2} \cdot \frac{(x_{\text{mod}}^2 - 2X^2)}{\sqrt{x_{\text{mod}}^2 - X^2}} dX$$ (2.18)

and hence the integral yields

$$\frac{\pi x_{\text{mod}}^2}{2} \cdot F_{2\omega}(x) = \int_{-x_{\text{mod}}}^{x_{\text{mod}}} f(x + X) \frac{(x_{\text{mod}}^2 - 2X^2)}{\sqrt{x_{\text{mod}}^2 - X^2}} dX.$$ (2.19)

This time, two partial integrations are performed resulting in

$$\frac{\pi x_{\text{mod}}^2}{2} \cdot F_{2\omega}(x) = \int_{-x_{\text{mod}}}^{x_{\text{mod}}} f''(x + X) \frac{(x_{\text{mod}}^2 - X^2)^{3/2}}{3} dX.$$ (2.20)
Again a convolution of the exact second derivative with a window function is obtained \( F(x)_{2\omega} = (f'' \circ \Phi_2)(x) \). The window function is given by

\[
\Phi_{2\omega}(X) = \begin{cases} 
\frac{2}{3\pi} \left( \frac{x^2}{x_{\text{mod}}} \right)^{3/2} & \text{for } |X| < x_{\text{mod}} \\
0 & \text{for } |X| \geq x_{\text{mod}}.
\end{cases}
\] (2.21)

The FWHM of this instrumental function is given by \( 1.22 x_{\text{mod}} \), which results in an effective broadening of about \( 1.73 x_{\text{rms}} \). Figure 2.3b shows the progression of this function. Compared to the window function of the first derivative which resembles a compressed semicircle this window function is sharper. The shape of a peak function will not be influenced greatly, as it is close to a Gaussian peak.

Applying this broadening to \( I-V \) measurements, \( x \) and \( x_{\text{mod}} \) correspond to \( V \) and \( V_{\text{mod}} \). The measured quantity, \( f(x) \), is then given by the current, \( I(V) \).

**Temperature broadening**

The second effect mentioned here is the temperature broadening. When dealing with small signatures, such as the superconducting gap (see chapter 5) or vibrational modes in IETS (see chapter 4), the impact of non-vanishing temperature smearing has to be taken into account. In order to evaluate this effect a simple model is used. One starts with equation (2.1) and assumes a constant DOS of the tip and the sample, a constant transmission coefficient, and an additional tunneling channel which opens at \( E = h\nu \). For the sake of simplicity the efficiency is set to unity \( \eta = 1 \) and no natural line width is used, so we set \( \mathcal{W} = 0 \). Therefore, only the Fermi distribution is left in the equation of the tunneling current (see also [56, 32]):

\[
I(V,T) \propto C \cdot \int_{-\infty}^{\infty} \left[ f_D(\tau_t, E - V) \cdot (1 - f_D(\tau_s, E - h\nu)) \right] dE = C \frac{(V - h\nu \cdot e^x)}{e^x - 1}. \] (2.22)

Here, both electrodes have the same temperature \( \tau_s = \tau_t = T \) and \( x = (V - h\nu)/k_B T \) is substituted. In the first derivative a step function occurs at \( h\nu \) which is thermally broadened

\[
\frac{dI}{dV}(V,T) = C \cdot e^x \frac{e^x - 1 - x}{(e^x - 1)^2}. \] (2.23)

The second derivative exposes a peak-like signature
The described broadenings can be seen in figure 2.4. For the first derivative (blue) a step-like feature is shown which is smeared by a factor of about \(4 \cdot k_B\) (20% to 80%). The second derivative of the model function without the broadening corresponds to a \(\delta\)-peak. Thermal broadening increases the FWHM of the resulting peak to \(5.4 \cdot k_B\).

**Effective broadening**

In order to estimate the expected peak width for the measurement, assuming a natural line width of \(W\), one has to add the different contributions geometrically

\[
\text{FWHM}_\omega = \sqrt{W^2 + (4 \cdot k_B)^2 + (2.4 \cdot V_{\text{rms}})^2}.
\]  

\[
\text{FWHM}_{2\omega} = \sqrt{W^2 + (5.4 \cdot k_B)^2 + (1.7 \cdot V_{\text{rms}})^2}.
\]
2.2 Experimental setup

2.2.1 The UHV-Cluster

Most of the experimental work in this dissertation was done under ultra-high vacuum (UHV) conditions at the UHV cluster of the Institute of Solid State Physics at the University of Ulm. The cluster, or parts of it, are already described in earlier thesis [57, 32, 18, 58, 59].

The laboratory is situated in the basement in order to exhibit almost no disturbing vibrations from the building as the ground underneath consists of solid rock. The UHV cluster is a compound of eight chambers which are all pumped individually and are connected by UHV valves. This offers the opportunity of doing the preparation of samples and performing different analysis techniques in-situ. A schematic drawing and a photograph for better visualization are shown in figure 2.5 on the facing page.

The individual chambers of the system are aligned in three perpendicular axes with individual magnetically driven transfer units for each axis. The longest axis is aligned horizontally and contains the preparation chamber (3) with a small effusion cell (8) attached to it; the chamber of the RT-STM (2) (Room Temperature Scanning Tunneling Microscope); a transfer chamber (6), which is also the crossing point of all axes; and the chamber for surface analysis (4). The next axis, which is also arranged horizontally, contains the small plasma chamber (5), where oxygen or hydrogen plasma can be applied. Behind that comes the aforementioned crossing point and, at the end of this transfer line, the LT-STM (1) (Low Temperature Scanning Tunneling Microscope) is situated. The third axis is mounted vertically and connects the load lock (7) with the transfer chamber.

The load lock is used to bring samples or STM-tips into the vacuum system. The chamber is pumped by a rotary vane pump and a turbomolecular pump. Up to two samples can be attached to the vertical transfer axis with tweezers when the flange is opened. After pumping the load lock for about 30 minutes the samples can be moved to the transfer chamber. Up to eight samples can be stored in a carousel here. The base pressure of the transfer chamber is at $8 \cdot 10^{-9}$ mbar. This chamber can be pumped independently but, due to mechanical noise which is disturbing the measurements in the STM, it is most frequently pumped via the plasma chamber.
2.2. EXPERIMENTAL SETUP

The following sections describe the properties and configurations of the single chambers in more detail. Also, a particular description of the LT-STM itself is given. This will show the unique character of the setup which is used in this dissertation.

2.2.2 LT-STM

The heart of the UHV cluster is the homebuilt STM. Figure 2.6 depicts a schematic drawing of the cryostat and figure 2.7 shows a picture of the base plate. The microscope itself is located in the middle of the LT-STM chamber (A) beneath the cryostat. It is surrounded by the radiation shields held at the temperature of liquid nitrogen (B,b) and liquid helium (C,c). The liquids are stored above. The tank of liquid nitrogen (D) with a volume of 21 l is a hollow cylinder which contains the tank of the liquid helium (D) with a volume of 8 l. Vacuum insulation is between the outer shell of the cryostat and each of the tanks. Beneath the microscope chamber a titanium sublimation pump and an ion getter pump are located, which give rise to a base pressure of below $10^{-10}$ mbar measured at the latter pump. Since the pressure gauge is working at room temperature and the microscope is held at 5 K, the pressure at the location of the microscope is at least one order of magnitude lower according to Amonton’s law ($\frac{p_1}{p_2} \propto \frac{T_1}{T_2}$ at constant volume).
A crucial factor to the outstanding performance of this LT-STM is the reduction of mechanical and electronic noise as well as the simple but effective radiation shielding. Mechanical stability is achieved through several mechanisms. As already mentioned the entire setup is situated in a very low-noise laboratory. Additionally, the LT-STM chamber is mounted on a pneumatic support lifting the LT-STM chamber by about 2 mm at a pressure of 2.5 bar. The helium tank (E) is constructed like a bell with a very soft anchor at the top leading to a decoupling from the outer nitrogen tank (D). In a final step, the microscope is build upon a base plate which is attached to the bottom of the helium tank with springs at an eigenfrequency of below 1 Hz. The base plate is equipped with an eddy current damping consisting of strong magnets at the bottom of the plate and a copper plate at the bottom of the helium radiation shield.

The thermal isolation from radiation is implemented via highly reflective coated shields which surround the microscope chamber (A) at liquid nitrogen (B,b) and liquid helium (C,c) temperature, as mentioned above. The temperature can be
2.2. EXPERIMENTAL SETUP

measured at the base plate with a calibrated Cernox resistor. The procedure to measure the temperature of the scanner is given in chapter 5. During the last four years several radiation leaks have been successfully closed reducing the temperature at the base plate from 5.9 K to 4.9 K and the temperature at the scanner from above 10 K to below 8.4 K.

Figure 2.7 shows a photograph of the microscope chamber. As already mentioned, the base plate (a) is suspended by three springs (d). Additionally, there are three rods that can push the base plate down to the bottom of the helium shield to lock the base plate while samples are transferred or the tip is changed. A mirror (e) enables viewing the apex of the tip from the window flange in such a way that a rough tip-approach can be done manually. On the right side, a sample holder (g) is located which is used to either store a sample at low temperature, or the tip holder, when the tip is exchanged.

The actual scanner (f) is situated in the center of the base plate. The scanner consists of a segmented piezoelectric tube glued into a holder that can slide on the scanner base using an inertial drive with three point bearings. Tungsten-carbide
spheres are glued to the holder and slide in notches of HSS steel connected to the base of the microscope. The notches are driven by shear piezos. The sample is placed in front of the scanner in a sample holder, both of which are made of titanium. They are connected by screws which are isolated with ring washers made of ceramics. Since titanium and ceramics have almost the same thermal expansion coefficient, thermal drift is minimized.

A great deal has to be paid to all wires that are connected to the microscope to ensure that they do not pick up any mechanical noise. The wire for the tunneling current is taped at the sample holder and guided carefully along the shortest path through the radiation shields. In order to suppress the Maxwell current between the tunneling bias and the sample, a loose wire is brought to the back of the sample holder. The bias amplitude applied at this wire can be set manually at the electronic unit.

One of the most crucial components in STM is the tunneling tip. In this setup, the tip can be exchanged in-situ. In principle two different kinds of materials, namely tungsten and silver, are used. The tips are etched from wires with a diameter of 0.25 mm. Tungsten tips are etched using NaOH, whereas silver tips are etched in a two step process using CH\textsubscript{4}O and H\textsubscript{2}O\textsubscript{2}. Afterwards the tips are cleaned with demineralized water in order to remove etching residues. Then they are transferred into the UHV cluster. An annealing step at temperatures up to $>1200^\circ$C (W) and $500^\circ$C (Ag) for about 30 minutes ensures that no adsorbates or oxide layers contaminate the tips. Recently, an additional sputtering step was implemented and tested. So far, the sputtered tips have not shown signs of whiskers at the tip apex and could be used for measurements without further treatment as, for example, field emission. Details on the preparation and the performance of the tips can be found in the bachelor thesis of Hannes Hille [60].

All electronics and software have are homebuilt and designed by Berndt Koslowski. A principle explanation of the electronic modules is given in reference [61].

2.2.3 RT-STM

A second STM operating at room temperature was inserted into the UHV cluster in 2011. A detailed description can be found in [58]. The STM is designed similar to the LT-STM and therefore provides a faster alternative, compared to low temperature investigations. For future applications it is planned to exchange the STM by an AFM equipped with a tuning fork [62].
2.2. EXPERIMENTAL SETUP

2.2.4 Preparation chamber

Most of the sample preparation was done in this chamber. The chamber is pumped by a rotary vane pump and a turbo-molecular high vacuum pump. Finally, a titanium sublimation pump is installed which can be cooled down to the temperature of liquid nitrogen. The base pressure is then around $5 \cdot 10^{-11}$ mbar.

In order to manipulate the samples the chamber is equipped with a precision manipulator which has five degrees of freedom. Namely, it can be shifted in all three spatial directions and can be rotated vertically around the polar angle $\theta \approx 120^\circ$ as well as horizontally by $\varphi \approx 270^\circ$. The sample holder is equipped with a resistive heater made of boron nitride which can reach temperatures up to $900^\circ$C. The temperature can be monitored by an external pyrometer.

The preparation chamber offers various techniques for the deposition of different films. A DC magnetron sputter unit ($SPECS^{TM}$) with a niobium target is installed as well as a triple beam evaporator ($Omicron^{TM} EFM 3$), where three different materials can be mounted simultaneously. With the latter unit very low deposition rates are achieved (0.2-10 monolayer/minute). Further, an evaporation boat is available inside the chamber, which can be equipped with a variety of materials. A micro balance is available to monitor the growth of the film thickness. Another preparation tool is an ion-gun ($SPECS^{TM} IQC 12/38$). The energy of the ions can be set up to 3 kV corresponding to an ion-current of about 10 $\mu$A [63]. It can be used to clean the surface of a substrate by sputtering. Up to four different gases can be let into the chamber via the gas inlet of the ion gun controlled by a gas flow unit ($Bronkhorst^{TM}S-6111A-2RH$). For example, oxygen can be dosed into the chamber for a controlled oxidation of the sample surface.

An effusion cell is attached to the preparation chamber for the evaporation of organic molecules. The extension of the preparation chamber is individually pumped via an external pumping unit reaching a base pressure of about $1 \cdot 10^{-7}$ mbar. The effusion cell can be heated by a tungsten filament and temperature can be measured with a $Al/Cr$-thermocouple. The temperature can be tuned up to $550^\circ$C.

2.2.5 Analysis chamber

The analysis chamber provides a number of surface analysis tools. The chamber is pumped by an ion getter pump, which leads to a base pressure of below $8 \cdot 10^{-10}$ mbar. Samples can be annealed by an electron impact heater up to $2000^\circ$C.
This is in particular useful for the preparation of tungsten tips because of the high
temperatures that are needed to remove the oxide layer.

In order to analyze the chemical composition of the surface layers of a sample, X-
Ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy
(UPS) are available. The X-rays are generated by electrons which are acceler-
ated in a high electric field and directed on an aluminum/magnesium anode. The
ultraviolet light is produced with a helium lamp. The respective energies of the
created photons are 1.4 keV (X-ray) and up to 40 eV (UV light). Electrons are
then emitted from the sample due to the photoelectric effect and the binding en-
ergy can be determined. The electron energy analysis is done by a hemispherical
analyzer (SPECSTM, Phoibos). Further tools are a low energy electron diffrac-
tometer (LEED) to determine the surface crystal structure. A mass spectrometer
in combination with the sample heater enables the possibility of thermal desorption
spectroscopy (TDS).

2.2.6 Plasma chamber

The plasma chamber is used to generate either hydrogen or oxygen plasma. The
chamber is pumped by a rotary vane pump in combination with a turbomolecular
pump. The base pressure is below 2·10^{-10} mbar.

Hydrogen, oxygen or deuterium can be attached in pressure cans (Linde Min-
canTM). The gas flow for the RF-plasma generation is controlled manually with a
leak valve. The plasma is then ignited and controlled by a radio frequency controller
(advanced energyTM - RFX600).

The plasma chamber is also used to expose the samples in the LT-STM chamber
to a gas at a specific pressure. This is done by opening the valves between STM
and plasma chamber and monitoring carefully the pressure in the LT-STM chamber
by controlling the valve at the pressure cans.
Chapter 3

Properties of hydrogen

Hydrogen plays a major role in different fields. Starting as the main ingredient of the biggest fusion plant in our solar system, the Sun, or even triggering biological reactions by hydrogen tunneling [64, 65]. The smallest atom is not only one of the possible candidates for future automotive solutions by fuel cells, it is also the driving force of life itself. Since hydrogen is an important part in the investigations of this thesis, some of the properties relevant in this framework are addressed here.

3.1 Physical properties of hydrogen

Under normal conditions hydrogen is present in molecular form. This already suggests a number of parameters such as the energy needed to dissociate the hydrogen molecule into two single atoms. This dissociation energy is about 4.478 eV [66]. Another property is the vibrational energy of the hydrogen molecule where the two atoms vibrate contrary to each other along their connecting axis. The first transition energy is given by $\nu(0\rightarrow1) = 516$ meV [66].

Another quantity is the rotational energy. In a simple model it can be approximated by a rigid rotor. The corresponding formula for those rotational states using the moment of inertia, $I$, and the quantum number of the rotational state, $J$, is given by

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2I}. \quad (3.1)$$

This leads to the following values for the energy levels and transition energies:
J=0 0 meV  
J=1 15.0 meV  
J=2 45.1 meV  para:  J(0→2) = 45.1 meV  
J=3 90.2 meV  ortho:  J(1→3) = 75.2 meV  

Kolos et al. [67] used a more sophisticated approach to calculate the energies and obtained:

J=0 0 meV  
J=1 14.69 meV  
J=2 43.94 meV  para:  J(0→2) = 43.94 meV  
J=3 87.48 meV  ortho:  J(1→3) = 72.79 meV  

The nucleus of the hydrogen atom consists of only one proton. Therefore, the spin of the nucleus is either \(\frac{1}{2}\) or \(-\frac{1}{2}\). Since the hydrogen molecule consists of two atoms, the spins of the nuclei can either be anti-parallel (\(J = \text{even}, \text{para-hydrogen}, p-H_2\)) or parallel (\(J = \text{odd}, \text{ortho-hydrogen}, o-H_2\)). At room temperature those two species are mixed by a factor of \(\frac{p-H_2}{o-H_2} = \frac{1}{3}\). At low temperatures the ratio shifts in and more \(p-H_2\) is present [68, 69, 70].

3.2 Adsorption of hydrogen on surfaces

Atoms or molecules can adsorb on surfaces depending on chemical and physical properties of both. In principle, there are two different types of adsorption that are briefly explained in the following subsections.

3.2.1 Chemisorption

One adsorption mechanism is the so called chemisorption. As the name implies this is a chemical adsorption, meaning that surface and adsorbate share a chemical bond. In most cases, this manifests in a hybridization of partly-filled shells of the adsorbate and states at the surface. The result is a low-lying bonding and an unfilled high-lying antibonding state. Thereby, always a charge transfer occurs.

For gas molecules this is often accompanied by dissociative chemisorption on reactive surfaces [71].
3.2. ADSORPTION OF HYDROGEN ON SURFACES

3.2.2 Physisorption

Another form of adsorption is the physisorption, where an adsorbent is trapped in an energetically favorable physisorption well located near the surface. This well is composed of a repulsive and an attractive interaction. A short introduction will be given here. For further discussions the reader is referred to the references [72, 73, 74].

If two atoms are brought together in close proximity a strong repulsive force is exerted on the atoms. This is the so called Pauli repulsion and originates from the Pauli exclusion principle which states that two electrons cannot occupy the same quantum state at the same time. With the characteristic strength, $U$, and characteristic inverse range, $\alpha$, this leads to a repulsive potential of

$$U_{\text{rep}}(z) = U \cdot e^{-\alpha z}. \quad (3.2)$$

On the other hand, there is an attractive force which originates from the van der Waals interaction between a small particle and a flat surface:

$$U_{\text{att}}(z) = -\frac{C}{(z - Z_w)^3} \cdot f(k(z - Z_w)). \quad (3.3)$$

using the van der Waals constant $C$, a characteristic distance $Z_w$, and $f(x) = (1 - 2x(x+1) + 1)e^{-2x}$.

In the current dissertation homonuclear diatomic molecules are used, therefore the orientation of the molecule with respect to the surface has to be taken into account. In analogy to [73] the second order Legendre polynomial $P_2(cos(\theta))$ scaled by the parameter $\lambda$ which depends on the material of the plane, is added to the repulsive potential. Correspondingly, $0.05 \cdot P_2(cos(\theta))$ is added to the attractive potential, where $\theta$ is the angle between surface normal and the main axis of the molecule. This leads to the repulsive potential

$$U'_{\text{rep}}(z) = U \cdot e^{-\alpha z}[1 + \lambda \cdot P_2(cos(\theta))] \quad (3.4)$$

and the attractive potential

$$U'_{\text{att}}(z) = -\frac{C}{(z - Z_w)^3} \cdot f(k(z - Z_w))[1 + 0.05 \cdot P_2(cos(\theta))]. \quad (3.5)$$
Table 3.1 – Parameters used to calculate the physisorption potential for different surfaces, $a_0 = 0.53$ nm (taken from [73]).

<table>
<thead>
<tr>
<th>Surface</th>
<th>$U$ (eV)</th>
<th>$\alpha \left( \frac{1}{a_0} \right)$</th>
<th>$\lambda \left( \frac{1}{a_0} \right)$</th>
<th>$C$ (eV)</th>
<th>$Z_w (a_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(111)</td>
<td>5.84</td>
<td>1.283</td>
<td>0.20</td>
<td>5.28</td>
<td>0.31</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>4.92</td>
<td>1.214</td>
<td>0.19</td>
<td>4.81</td>
<td>0.38</td>
</tr>
<tr>
<td>Cu(110)</td>
<td>5.74</td>
<td>1.209</td>
<td>0.19</td>
<td>4.54</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Figure 3.1 – (a) Superposition (black) of repulsive (red) and attractive (blue) potential on a flat surface. (b) Physisorption potential of a diatomic molecule for different angles $\theta$ with respect to the surface normal. Here, $\theta = 0^\circ$ corresponds to a molecule parallel to the surface normal.

Constants for different materials are listed in table 3.1. Figure 3.1a displays the corresponding curves for an Au(111) surface. The superposition $U_{\text{phys}} = U_{\text{rep}}' + U_{\text{att}}'$ (black) of the repulsive potential (red) and the attractive potential (blue) creates a well in front of the surface. The depth of the well is circa 40 meV and the minimum is located at about 0.2 nm in front of the surface.

In figure 3.1b the dependence of the physisorption potential on the angle $\theta$ is shown. The case $\theta = 0^\circ$ corresponds to a molecule which is oriented parallel to the surface normal. As the molecule is rotated at steps of 30°, the depth of the potential well decreases. Consequentially, the molecule is preferably adsorbed in an upstanding orientation with respect to the surface.
Modeling the tip potential

The actual experiments are not performed between two flat surfaces, but between a STM tip and a flat surface. Therefore, the influence of the tip shape on the resulting potential has to be examined. Schmidt et al. [75] calculated a correction factor $\mu$ for the van der Waals interaction of neutral atoms with small nanospheres leading to $U_{\text{cor}} = \mu \cdot U_{\text{att}}'$. The factor is given by

$$\mu(R,Z'_w) = \frac{\left(1 + 6 \left(1 + \frac{Z'_w}{R}\right)^4 - 3 \left(1 + \frac{Z'_w}{R}\right)^2\right)}{4 \left(1 + \frac{Z'_w}{R}\right)^3 \cdot \left(1 + \frac{Z'_w}{R}\right)^4}. \quad (3.6)$$

$R$ represents the radius of the nanosphere and $Z'_w$ is the average distance of the atom from the surface and, hence, corresponds to the characteristic distance, $Z_w$, mentioned above. $\mu(R)$ is plotted in figure 3.2 using the characteristic distance of silver. The value lies within the interval [0,1] and the deviation decreases with increasing radius, as expected.

Applying this correction factor to the physisorption potential, a small deviation of the potential depth can be seen. If the electrode of the tip consisted of only one atom with a radius of about 0.34 nm the depth of the potential well would be reduced by 7 meV. For a sphere with a radius of about 2 nm the deviation, compared to a plane, is already less than 0.8 meV. This corresponds to a change of the energy levels of $< 1 \%$. Because of this small variation, the effect of the tip shape is neglected in the following, especially, since the radius of a STM tip is significantly larger than 2 nm [76].
3.2.3 Physisorption between two electrodes

Now, a model can be built which describes the setup accurately. The inset in figure 3.3 shows a sketch of the expected situation of the measurement: A flat gold surface at the bottom and a silver tip at a given separation, \( d \), shown at the top of the sketch. As will be shown in this section, a hydrogen molecule in between those electrodes will be trapped.

Since the tip shape can be neglected, the adsorption potentials of two flat surfaces can be superposed to describe the potential between tip and sample in a one dimensional model. The dashed lines in figure 3.3 represent the physisorption potentials of the undisturbed surfaces of Au (left) and Ag (right). The solid curves correspond to the superposition of both potentials at different tip-sample separations. The gold surface is always situated at \( z = 0 \), whereas the tip is situated at \( z = d \).

The system of both electrodes is now defined as Au:Ag.

For separations \( z > 0.6 \) nm the potential forms an asymmetric double well. The well on the side of the gold electrode is deeper because of the higher van der Waals constant of gold which implicates an enhanced attractive force. As the separation gets smaller only a single well remains. At a separation of about 0.45 nm the depth of
the well reaches a maximum. By decreasing the separation even further the depth of the well decreases until its binding character vanishes because of the increasing influence of the repulsive interaction which can be seen in the exponential behavior in equation (3.4).

This separation dependent potential is valid for all homo-nuclear diatomic molecules. To calculate the actual energy levels of an individual molecular species, the Schrödinger equations for the potential curves for all separations have to be solved. Since the analytic expression of the potential is rather complex, the problem is solved numerically. For this purpose an algorithm called Numerov [77, 78] was used to determine the energy levels with respect to the separation. This algorithm is a common tool to solve ordinary differential equations of second order numerically. It was executed in Maple™ using reference [79] and double checked with a routine implemented in Matlab™ with the help of Jennifer Gosner from the Institute of Complex Quantum-systems of the Universität Ulm. The step width of the potential was chosen to be $1 \times 10^{-13}$ nm. The tolerance of the energy levels was set to $dE = 10^{-15}$ eV. Those energy levels correspond to a translational vibration of the molecule perpendicular to the surface.

Figure 3.4a shows the energy levels for a hydrogen molecule in dependence of the separation. It also displays the ground state energies of the undisturbed surfaces of Au(111) (magenta) and Ag(111) (green). The ground state of the Au:Ag system (blue) has a minimum energy at a separation of about $d = 0.44$ nm and converges asymptotically towards the ground state of Au(111) for large tip-sample separations. The first (red) and second (black) excited states have minima at $d = 0.49$ nm and $d = 0.55$ nm, respectively. For small separations $d < 0.3$ nm all three curves rise to positive values which do no longer correspond to binding states.

The transition energies of the $(\text{Au:Ag})_{0 \rightarrow 1}$ excitation (red) and the $(\text{Au:Ag})_{0 \rightarrow 2}$ excitation (black) are shown in figure 3.4b. The transition $(\text{Au:Ag})_{0} \rightarrow \text{Au}_{0}$ (magenta) corresponds to the depth of the lateral physisorption well. Therefore, it appears that a hydrogen molecule is trapped in a local well only for separations greater than 0.34 nm. This also suggests, that a hydrogen molecule which is excited to an energy higher than the lateral depth will most probably be kicked out of the physisorption well between tip and sample. A $(\text{Au:Ag})_{0 \rightarrow 1}$ excitation, where the molecule remains in the junction, can only occur for a tip-sample separation between 0.39 nm and 0.75 nm. For the same reason a $(\text{Au:Ag})_{0 \rightarrow 2}$ excitation occurs only between 0.46 nm and 0.68 nm.
Figure 3.4 – (a) Separation dependent energy levels in the tip-sample physisorption well are displayed [ground state (blue), first (red), and second (black) excited state]. The levels of the ground states on undisturbed Au(111) and Ag(111) surfaces are shown in magenta and green, respectively. (b) The transition energies $(\text{Au:Ag})_0 \rightarrow 1$ (red), $(\text{Au:Ag})_0 \rightarrow 2$ (black) and $(\text{Au:Ag})_0 \rightarrow \text{Au}_0$ (magenta) which corresponds to the depth of the lateral well, also depend on separation.

Note that the energy levels and transition energies are calculated assuming planar surfaces instead of a tip. In reality, there is still room for deviations which can lead to shifts in energy or additional energy levels.
Chapter 4

Evaluation of IETS spectra

Inelastic electron tunneling is an important tool used to analyze single molecules [21, 80, 16] even on the atomic scale [81, 82]. In recent studies the spectra were mostly interpreted in a rather qualitative way and only excitations with an efficiency in the range of several percent were analyzed [22, 83].

In order to get a detailed information on the vibrational structure, measurements need to be performed at the ultimate limit of noise. Also, a great effort has to be taken to extract the real information out of the collected data. Therefore, a sophisticated approach has been developed to get optimal results. In this chapter two approaches, which have been developed in our group are shown. After some basic considerations regarding IETS the analysis of rich inelastic electron tunneling spectra [20] is briefly resumed. This approach is also discussed in Norbert Maurer’s dissertation [32], where the statistical relevance of the data is analyzed in detail. Afterwards, a new approach using Wavelet analysis is shown and discussed. This procedure leads to a significant improvement of processing speed and quality of the data by establishing more automation and systematization.

4.1 Fundamentals of IETS

Tunneling electrons may excite inelastic components such as the vibrations of molecules, adsorbates, or bulk atoms (phonon excitation). This opens the possibility to investigate vibrational modes with STM. The principle mechanism of an inelastic transition is shown in figure 4.1. When the bias exceeds the excitation energy of a vibration $E = \hbar \omega$, a new tunneling channel opens which leads to an increase of the slope of the current and a positive step in conductivity.
CHAPTER 4. EVALUATION OF IETS SPECTRA

Figure 4.1 – Schematic explanation of inelastic features in the tunneling current. In (a) an \( I-V \) curve without any inelastic features is shown in black. The current resulting from an inelastic excitation at an energy of \( E = \hbar \omega \) is depicted in red. The sum reveals an increase of the slope above the threshold energy. In (b) the corresponding conductivity is displayed showing a step at the energy of the inelastic excitation. This results in a peak on the positive side of the second derivative of the current \( \frac{\partial^2 I}{\partial V^2} \) and a negative peak on the negative side, correspondingly, which is shown in the last plot (c).
Since the change in the slope of the current and the steps in conductivity are usually very hard to detect due to the small efficiency ($\Delta \sigma / \sigma_0 \approx 0.1..10\%$), the second derivative is measured using Lock-In technique. As can be seen in the figure, the inelastic feature appears symmetric in energy in the first derivative and antisymmetric in the second derivative of the current. As mentioned in section 2.1.3.4, the expected linewidth for a positive or negative peak, neglecting the natural line width, is given by

$$\text{FWHM} = \sqrt{(5.4 \cdot k_B T)^2 + (1.7 \cdot V_{\text{mod}})^2}. \tag{4.1}$$

This leads to a restriction in the experimental conditions. In order to get an appropriate resolution and to prevent an overlap of neighboring modes, the modulation broadening should be in the range of the thermal broadening, this means $5.4 \cdot k_B T \approx 1.7 \cdot V_{\text{mod}}$ which corresponds to $V_{\text{mod}} \approx 1-2\text{meV}$ at $T = 5\text{K}$.

The next restriction is given by the minimal integration time $t_{\text{int}}$ needed for each point to measure an inelastic signal of efficiency, $\eta$. Assuming Johnson noise in the current, the lock-in amplifier captures a noise floor in the current signal of $i_r^2 = 4k_B T_{\text{IV}} B / R_{\text{IV}}$, where $T_{\text{IV}}$ corresponds to the temperature of the $I$-$V$ converter, which has a feedback resistance, $R_{\text{IV}}$. The bandwidth of the lock-in amplifier is given by $B = 3/(32 t_{\text{int}}) \ [84]$. The inelastic current at a modulation amplitude, $V_{\text{rms}}$, and a tunneling conductance, $\sigma_0$, is given by $i_{\text{iets}} = \kappa \eta \sigma_0 V_{\text{mod}}$, with an instrumental factor of the lock-in measurement, $\kappa$, which is set to unity. With $B < i_{\text{iets}}^2 R_{\text{IV}} / (4k_B T_{\text{IV}})$, this leads to equation (2) in reference [20] which is

$$t_{\text{int}} > \frac{12}{32} \frac{k_B T_{\text{IV}}}{i_{\text{iets}}^2 R_{\text{IV}}} \frac{3}{8 \left( \kappa \eta \sigma_0 V_{\text{rms}} \right)^2 R_{\text{IV}}}. \tag{4.2}$$

The time for measuring a single data point can now be estimated using the parameters: $T_{\text{IV}} = 300\text{ K}$, $\eta = 1\%$, $\sigma_0 = 10 \text{pA}/0.1\text{ V}$, $V_{\text{mod}} = 1\text{ meV}$, and $R_{\text{IV}} = 10^9\Omega$, yielding $i_{\text{iets}} = 2\text{ fA}$ and hence $t_{\text{int}} = 0.4\text{ s}$. The energy steps between the data points should be in the range of $k_B T$, since peak detection is only working properly if a peak consists of about five data points. Inelastic signals are in an energy range of 100 to 400 meV requiring about 400 to 1600 data points. With these relations in mind, the duration of a whole spectrum can easily be calculated: It would take about 160 to 640 s. More than $t_{\text{spec}} = 120\text{ s}$ is not possible with the LT-STM because of drift effects. Therefore, the measurement of the spectrum is repeated several times. Calculating an average over $N$ independent spectra reduces the noise by a factor of $\sqrt{N}$.
4.2 Data evaluation

In figure 4.2a a $\partial^2 I/\partial V^2$ curve representing an average of 60 independent measurements is shown. The spectra were recorded on a bare Au(111) single crystal surface in an fcc (face-centered cubic) site. It is nearly impossible to recognize single features corresponding to an inelastic signal because the signals are small and electronic background is superimposing the spectrum. The first step is the application of a weak Savitzky-Golay filter (7 points, 2nd order). This filter reduces the scattering but will not change the shape or position of a peak if the required number of five data points per peak is recorded. In the second step, the data is split in even and odd components. Figure 4.2b shows both components in red (odd) and green (even). For further evaluation only the odd component is used, since inelastic features are expected to be antisymmetric in energy, as explained above.

The spectrum still contains a background due to small changes in the local electronic density of the tip or the sample. The background can be subtracted since electronic contributions are smooth on a scale of the width of inelastic features. This was done by creating a spline fit of the baseline with support points at a separation of about 20 meV using the software *fityk (Version 0.9.8)*. This step is shown in figure 4.2c. Multiple Gaussian peaks (blue curve in figure 4.2d) are fit to the resulting curve (red) until the residue approximately resembles the scatter (grey) of the measured data.

The positions of the Gaussian peaks which have an amplitude higher than the scatter are the inelastic transition energies. The positions of the peaks are transferred to a barcode stripe on the upper panel of figure 4.2d. The barcode is generated for comparison with other measurements or theory.

Although the described method provides good results with respect to mode positions, it suffers from some drawbacks. A major uncertainty is the determination of the support points for the spline fit of the baseline. This has to be done manually by choosing the desired position. Therefore, this step is not systematic or standardized and has to be repeated several times to check if the evaluation process has an influence on the result.

A second drawback is the time consuming fitting of the Gaussian peaks using the software, *fityk (Version 0.9.8)*. Starting with the peaks of highest amplitude the residue is reduced stepwise by adding new peaks to the fit curve. However, the software is not able to find all maxima precisely and often needs manual guidance for the parameters in order to gain reasonable fitting results.
Figure 4.2 – Procedure to determine inelastic features from measured data recorded on a blank Au(111) single crystal: a) Measured data (black) and scatter (grey); b) data split in symmetric (green) and antisymmetric (red) part; c) antisymmetric part with baseline (dashed blue); d) data (red); scatter (grey); and fit with Gaussian peaks (blue). The determined barcode of the peak positions is shown at the top of the diagram.
4.3 Wavelet analysis

Therefore, a new approach in analyzing IETS spectra using Wavelet Analysis is shown in this section. It can be easily integrated in the already used routine and resolves the listed drawbacks.

Wavelet analysis is a widely distributed tool in geophysics and meteorology [85, 86] helping to unravel correlations in datasets over extended periods of time. A popular example is the investigation of the weather phenomenon El Niño [87]. Wavelet analysis was also transformed and used in completely different applications such as for example XPS [88, 89] or EELS [90].

Explained in just a few words, Wavelet analysis compares a distinct signal with a linear dataset producing a 2D pattern, which reveals correlations according to the primary signal at altering scale. In a more mathematical way the Wavelet transform describes a convolution of a sequence $x$ with a so called mother function, $\Psi$, which is scaled by a factor $\sigma$ and translated by $t$, where $x$ represents the dataset and $\Psi$ is the distinct signal. This means

$$ W_n(\sigma, t) = \frac{1}{\alpha} \int_{-\infty}^{\infty} \Psi\left(\frac{(t' - t)}{\sigma}\right) x(t') \, dt'. $$ (4.3)

Since this convolution takes place in Fourier space the mother functions must be $L^2$ integrable. Therefore, not every arbitrary function can be used. In literature, different mother functions $\Psi_n$ are prevalent. In this case, a Mexican-hat Wavelet is applied corresponding to equation

$$ \Psi(t) = \frac{2}{\sqrt{3\sigma \pi^2}} \left(1 - \frac{t^2}{\sigma^2}\right) e^{-\frac{t^2}{2\sigma^2}}. $$ (4.4)

This mother function is the second derivative of the Gaussian peak function consisting of a dominant positive peak and two negative peaks as shown in figure 4.3. The modes in IETS are expected to be Gaussian peaks, which also explains the choice of this Wavelet. Other Wavelets such as Daubechies or Morlet show an oscillating behavior which is not reasonable for the detection of peaks.

The dataset displayed in figure 4.2a was transformed by a Mexican hat Wavelet. The corresponding 2D plot is shown in figure 4.4. This plot is created by convolving the mother function with the dataset leading to a measure of conformity. Each point in the plot corresponds to the convolution of the dataset with the mother function centered at that particular position. The width of the mother function is varied in
4.3. WAVELET ANALYSIS

Figure 4.3 – Mexican-hat mother function with $\sigma = 1$ is shown.

Figure 4.4 – Wavelet transform of the dataset displayed in figure 4.2. The dashed red line corresponds to the width, $\sigma$, which is expected for the modes in IETS measurements.

Each row of the plot, starting from $\sigma = 2|E_{\text{max}}|$ and decreasing logarithmically by 16 rows per octave from the top to the bottom. This means the y-axis presents the logarithmic width $\sigma$ of the mother function.

With this, a measured dataset can easily be transformed into a Wavelet plot. By using the amplitude broadening and thermal broadening as explained above (see section 2.1.3.4), the expected line width of the modes can be calculated. The row in the Wavelet plot corresponding to this line width then provides the information on the positions of the measured modes. This row is indicated by the dashed red line in figure 4.4. The cross section along this line is displayed in figure 4.5. Here, the positive side of energy is shown in red and the negative side is shown
Figure 4.5 – Generation of a barcode using the Wavelet method. Positive side (red), negative side (magenta) and antisymmetric part (black) of the dataset are compared to verify the mode positions. The barcode determined with the fitting method is shown on top (blue).

in magenta. Since the nature of inelastic modes is antisymmetric with respect to energy, the values of the negative energy side are inverted. For the black curve, the measured data was first split into a symmetric and an antisymmetric part, as already explained in the section above, and then the odd part was transformed by the Wavelet method.

The positive peaks in this cross section correspond to the position of the peaks in the IETS signal. Using these positions a barcode can be created as shown at the top of the figure. These results can be compared easily with the former evaluation method (blue barcode). The blue and black colored barcodes represent an average of positive and negative bias. When splitting the data in odd and even parts, features can be generated accidentally which are attributed to inelastic transitions during the evaluation procedure. Since the red and magenta colored barcodes are not an average and represent positive and negative side, the validity of a peak can be verified if it is contained in both barcodes.

Comparing the different barcodes, it can be seen that the third, fourth and fifth mode in the blue barcode are better resolved using the Wavelet method since they split into more peaks. The seventh mode at about 67 meV is not valid considering
the red and magenta barcode, which means this peak was created by splitting data into odd and even parts. The other peaks are in good agreement.

For an analysis of the efficiencies, this method does not provide good results since the shape of the mother function is not exactly Gaussian. Therefore, the fit routine has to be performed as described in the upper part. But the positions can be used directly from the barcode of the Wavelet analysis, which reduces time and effort when applying the fit routine.

The major advantage of this method is speed, because data does not have to be processed by different pieces of software but is evaluated in one step. Another advantage is the fact that the background does not have to be subtracted manually, which eliminates the subjective interaction of the operator in the evaluation process. Therefore, Wavelet analysis establishes a more standardized and reproducible method for the evaluation of IETS data.
Chapter 5

Calibrating the temperature of the tip

5.1 Motivation

In order to perform measurements at the edge of feasibility, all parameters involved in the setup have to be known. One crucial parameter in tunneling experiments is the temperature (see section 2.1.3.4), especially, if the investigated signatures are sensitive to changes in temperature, such as the Kondo effect [91], or if energetically small signatures have to be resolved, like in spin-polarized tunneling [92], or inelastic electron tunneling [93].

Because of the way most STMs are constructed, it is possible that the two electrodes, tip and sample, exhibit different temperatures. As described in section 2.2.2 a calibrated Cernox resistor is mounted on the base plate in order to measure the temperature precisely. The scanner of the STM which contains the tip is in loose thermal contact with the base plate, since it is only connected via three ball bearings and seven long copper wires with a diameter of 0.1 mm. In order to calibrate both temperatures, a simple procedure was developed using a superconducting sample and a normal conducting tip [33].

In the following, the theoretical background is derived and the preparation of the superconducting sample, namely the Nb(110) film, is shown. After the experiment is described, the calibration procedure is presented.
5.2 Theoretical background

In the framework of my diploma thesis [58] the tunneling current and its dependen-
cies on the various parameters in a superconductor - normal conductor junction in
STM have been introduced. For the sake of completeness, it is repeated here and
some additional remarks are given.

I. Giaever showed [46] that the tunneling current through a superconductor - isolator
- normal conductor junction can be written as was already stated in the fundamental
equation of STM (2.1):

\[
I(V) \propto \int n_n(E - V) \cdot n_s(E) \cdot (f_0(E - V, T_n) - f_0(E, T_s))dE. \quad (5.1)
\]

Here, \(E\) is the energy, \(V\) is the bias that is applied to the tip, \(n_s (n_n)\) and \(T_s (T_n)\)
are the densities of states with the temperature of the superconductor ‘s’ and the
normal conductor ‘n’, respectively, and \(f_0\) is the Fermi-Dirac distribution. The den-
sity of states of a superconductor with a weak coupling strength was derived in the
BCS theory (Bardeen-Cooper-Schrieffer [94]) and refined by K. Maki for low tem-
peratures \(T \rightarrow 0\) K [95]. Since these experiments were carried out at temperatures
of 5 to 10 K, Maki’s refinement is not necessary here.

Hence, the DOS of the superconducting electrode is given by

\[
n_s(E) = n_0 \cdot \frac{|E|}{\sqrt{E^2 - \Delta(T_s)^2}}, \quad (5.2)
\]

where \(\Delta(T_s)\) is the half width of the superconducting gap. The temperature depen-
dence of \(\Delta\) is shown later on. With \(n_0\) and \(n_n\) being set constant, which is a valid
assumption in this energy regime, and normalized to unity, the tunneling current
reads

\[
I(V) \propto \int \frac{|E|}{\sqrt{E^2 - \Delta(T_s)^2}} \cdot \left( \frac{1}{1 + \exp \left( \frac{E - V}{k_B T_n} \right)} - \frac{1}{1 + \exp \left( \frac{E}{k_B T_s} \right)} \right) dE. \quad (5.3)
\]

This integral has to be evaluated numerically and thus, the tunneling current has
to be differentiated numerically, as well. In the experiment \(I-V\) spectroscopy (see
section 2.1.3.1) is used to determine the derivative of the tunneling current. Since
these measurements are performed in a very low energy regime one has to keep
in mind the modulation broadening due to the lock-in technique (section 2.1.3.4).

The calculation of the influence of different amplitudes showed that amplitudes of
(1.0, 0.4, 0.2) mV correspond to a relative change of (9.6, 2.6, 0.7) %. By setting the modulation amplitude to 0.2 mV this effect can be neglected.

Furthermore, the dependency of the superconducting gap on the temperature, $\Delta(T_s)$, is required. Therefore, equation (3.27) in [94] must be evaluated, that is:

$$\frac{1}{N(0)V} = \int_0^\infty \frac{d\Delta}{\sqrt{\Delta^2 + \Delta_0^2}} \tanh\left(\frac{1}{2} k_B T \sqrt{\Delta^2 + \Delta_0^2}\right)$$

(5.4)

Bardeen et al. motivate the approximations $\Delta_0 \approx 1.76 \cdot k_B T_c$ and $\frac{\hbar \omega_D}{\Delta_0} \approx \sinh\left(\frac{1}{N(0)V}\right)$. Inserting these in equation (5.4) and using the relations $\eta = \frac{1}{N(0)V}$, $\delta = \frac{\Delta(T)}{\Delta_0}$, and $\tau = \frac{T}{T_c}$, yields

$$\eta \approx \int_0^{\sinh(\eta)} \frac{dz}{\sqrt{1 + z^2}} \tanh\left(\frac{1.76 \delta}{2 \tau} \sqrt{1 + z^2}\right).$$

(5.5)

With $N(0)V = 0.32$ for Niobium, which was experimentally determined by Wolf et al. [96], this equation can be solved numerically for a given $\delta$. The curve achieved with this method can be approximated by a rather simple formula describing the behaviour of $\Delta(T)$ with an accuracy of about 1 %:

$$\Delta(\tau) = \left(1 + \frac{1}{2} \tau + 0.24 \tau^2\right) \cdot \Delta_0 \cdot \sqrt{1 - \tau}.$$

(5.6)

At temperatures close to $T_c$ this leads to the well known limit of $\Delta(\tau) = 1.74 \Delta_0 \cdot \sqrt{1 - \tau}$.

### 5.3 Preparation of superconducting Nb(110) films

In order to perform measurements on superconducting samples, Nb(110) films were deposited onto sapphire(0001) substrates. Those substrates were annealed to about 1000°C for one hour under ambient conditions before being transfered to the UHV system. The films were prepared by DC magnetron sputtering using a target of purity 99.95 % (*Lesker*TM). They were deposited at a rate of 10 nm/min for about 10 minutes at a substrates temperature of 900°C. After sputtering, the samples were held at high temperature for another minute. This treatment reduces the surface roughness significantly and leads to larger terraces. Since Niobium has a highly reactive surface the sample is transferred to the LT-STM chamber immediately after preparation.
The surface exposes a Nb(110)-\((\sqrt{3} \times \sqrt{6})\) surface reconstruction [97, 98]. Figure 5.1a shows an overview of a freshly prepared surface. Extended terraces with a step height of one atomic layer can be seen. On a large scale the sample exhibits a threefold symmetry reminiscent of the sapphire substrate. Figure 5.1b shows a close-up taken inside a terrace showing atomic corrugation. Two domains of the reconstructed surface oriented at an angle of \((110 \pm 2)^\circ\) are visible. The domain wall is highlighted by a red line. Further characterization of the Niobium films can be found in [58, 18, 99]. However, it should be mentioned that the surface reconstruction given in these references is wrong, since at that time the calibration of the lateral sensitivity of the piezo was not accurate enough.

I-V spectroscopy in a wide energy range reveals features related to critical points of the Nb band structure, which was also shown by Dietrich and Pfeifer [100]. I-V curves in the small bias regime taken at low temperatures show the expected characteristics of a superconductor. The electronic background due to variations in the DOS is very smooth compared to the superconducting features.

5.4 Experimental preconditions

Sample were prepared according to the procedure described above. The surface was then examined by STM checking that the topography is flat and the spectroscopy shows typical features.
In order to validate the method described in this chapter, a temperature dependent measurement is preferable. Therefore, the base plate was heated by the 1 kΩ resistor integrated specifically for this purpose, using a Statron 3231.1 power supply. The temperature was monitored by the calibrated Cernox resistor. At each step it is necessary to wait a sufficiently long time until the temperature reaches an equilibrium and no further drift effects can influence the data acquisition.

For the determination of the required parameters $I-V$ spectroscopy was performed in a bias range of $-20 < V < 20 \text{ meV}$.

5.5 Results of the tip calibration

A representative example of a $\partial V / I$ curve measured on Nb(110) is shown in figure 5.2a (blue dots). Typical measurements yield an accuracy of about 1 %. By averaging over 15 consecutive scans this could be improved to 0.05 %. The $I-V$ spectroscopy was performed at a temperature of $T_m = T_s = (5.02 \pm 0.01) \text{ K}$ measured at the base plate which is in direct thermal contact with the sample. Inspecting the curve closely, a dip around zero bias can be seen sinking to about 40 % compared to the conductivity at higher bias, as well as two maxima on both sides of the dip.

For further data procession, the measured $\partial V / I$ curve is normalized to the normal conducting state and split into symmetric and antisymmetric component, where only the former is used furthermore. This action is valid since the antisymmetric component has its origin in a small variety of the electronic DOS and the contributions due to superconductivity should always be symmetric under the given premises. The symmetric component is shown as the black solid curve. Comparing this to the measured curve shows that the data points determining essentially the superconducting features in this $\partial V / I$ curve, i.e. the points within the gap region, are not affected significantly by the splitting.

In 5.2b the symmetric component is shown in black dots. One theoretically calculated $\partial V / I(V)$ curve is shown in solid green, where the temperatures of both, tip and sample, are set to the measured value of $T_n = T_s = 5.0 \text{ K}$. The superconducting gap parameter is set to $\Delta(T = 5.02 \text{ K}) = 1.53 \text{ meV}$, which fits the width of the gap of the measured curve but leads to a deviation of about 15 % at the minimum conductivity at zero bias and of about 30 % at the maximum conductivity outside the gap.

For a better agreement of theory and experiment, a Levenberg-Marquart algorithm is used to fit the involved parameters. Therefore, $T_n$ and $\Delta$ act as free parameters, whereas $T_s$ is set to the measured temperature, since the result barely depends
on this parameter. In fact, the fit routine tends to be interrupted due to an almost singular Hessian/covariance matrix [58]. As a result of the fit the value for the temperature of the tip increases by more than 3 K to (8.45 ± 0.03) K, and the superconducting gap parameter is determined to be Δ = (1.53 ± 0.01) meV. The corresponding $\partial_{V}I$-$V$ curve (red) shows an excellent agreement when compared to the symmetric component of the measured curve (black dots) reducing $\chi^2$ by two orders of magnitude.

By heating the base plate, this procedure can be applied to a whole series of $\partial_{V}I$-$V$ curves at different temperatures. This is presented in the inset of figure 5.3a. It also shows the dependency of the depth of the gap on the measured temperature.
\( \sigma_0/\sigma_n(T_m) \). As the temperature rises the gap closes and at approximately 9.2 K the superconducting feature can no longer be seen. This result fits perfectly to the expected value for the critical temperature of Niobium [101, 102]. The plot also reveals the additional thermal smearing of the slightly warmer tip, since the slope of this plot would be higher for a junction where both electrodes have the same temperature.

\[ \sigma_0/\sigma_n(T_m) \]

\[ \text{bias (meV)} \]

\[ T_m (K) \]

\[ \sigma/\sigma_n \]

\[ 0.4 \]

\[ 0.6 \]

\[ 0.8 \]

\[ 1.0 \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

\[ 9 \]

\[ 10 \]

\[ 1.2 \]

\[ 1.0 \]

\[ 0.8 \]

\[ 0.6 \]

\[ 0.4 \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

\[ 9 \]

\[ 10 \]

\[ 12 \]

\[ 11 \]

\[ 10 \]

\[ 9 \]

\[ 8 \]

\[ 0.0 \]

\[ 0.5 \]

\[ 1.0 \]

\[ 1.5 \]

\[ \Delta \text{(meV)} \]

\[ T_n (K) \]

\[ T_m (K) \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

\[ 9 \]

\[ 10 \]

\[ 0.0 \]

\[ 0.5 \]

\[ 1.0 \]

\[ 1.5 \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

\[ 9 \]

\[ 10 \]

\[ 4 \]

\[ 5 \]

\[ 6 \]

\[ 7 \]

\[ 8 \]

\[ 9 \]

\[ 10 \]

\[ 0.0 \]

\[ 0.5 \]

\[ 1.0 \]

\[ 1.5 \]

\[ \]
In figure 5.3b it can be seen that the evaluated temperature of the tip $T_n(T_m)$ increases linearly with the measured temperature (blue squares). A linear fit was applied to the data. It starts with an offset of 3.3 K compared to the sample temperature of 5 K and rises at a rate of $(0.70 \pm 0.04) \frac{K}{K}$. This corresponds to a rise of the temperature of the tip caused by radiation of about 15.6 K. The superconducting gap parameter is shown in red. A normalized, theoretically calculated $\Delta(T)$ curve (see above for details) is then scaled so that the variance is minimal. The resulting curve fits nicely to the measured data and displays the characteristic parameters of the superconductor. The transition temperature is then given by $T_c = (9.25 \pm 0.02) K$ matching again very well with literature values [101]. The superconducting gap parameter can be determined as $\Delta_0 = \Delta(T=0 \text{ K}) = (1.62 \pm 0.04) \text{ meV}$. This leads to the relation $2\Delta_0 = 4.06 \cdot k_B T_c$ which is also in a good agreement with literature ($2\Delta_0 = 3.84 \cdot k_B T_c$ [103], $2\Delta_0 = 4.20 \cdot k_B T_c$ [104]).

### 5.6 Summary

With the procedure presented in this chapter it was shown that the temperature of the tip and the sample may be different. Since the temperature of the superconducting sample was known, the temperature of the normal conducting tip and the superconducting gap acted as free parameters. Applying a fit to $\partial V/\partial I$ curves using a Levenberg-Marquart algorithm and the WKB approximation, those parameters could be determined.

At a base temperature of about 5.0 K the tip temperature was estimated to be 8.45 K. With increasing temperature the properties of the superconductor, such as the critical temperature, $T_c$, and the behavior of the superconducting gap parameter, $\Delta(T)$, were reproduced. The temperature of the tip increased with $T_n = (4.69 \pm 0.33) K + (0.70 \pm 0.04) \cdot T_s$. It was shown that the heating of the tip corresponds to a temperature radiation of about 15.6 K.
Chapter 6

Hydrogen adsorbed on noble metals

6.1 Introduction and motivation

Over the last 30 years many groups investigated atomic or molecular hydrogen on metal surfaces. Since hydrogen is the simplest atom it serves as a good model for fundamental research. Starting in the 1980s, Avouris et al. [105] and later Svensson and Andersson conducted several experiments with EELS (Electron Energy Loss Spectroscopy) investigating molecular adsorption processes of hydrogen on different noble metal surfaces. They identified the rotational and vibrational transitions of the hydrogen molecule adsorbed on undisturbed surfaces [106, 107, 108, 109, 110, 111, 68].

Although hydrogen is not directly visible in STM, the influence of physisorbed molecular hydrogen in the tunnel junction was investigated in a number of different studies. The group of D. Eigler investigated hydrogen on copper surfaces and first reported about a two-level system and negative differential conductance occurring with hydrogen physisorbed on a noble metal surface [29]. Several groups tried to model the $I-V$ curves [112, 30]. Later, this system was investigated by a combination of STM/AFM, where a stochastic resonance was documented [31]. It was also possible to detect the rotational modes of molecular hydrogen, as was shown first by Natterer and by Li on different substrates [113, 114, 115]. In the group of W. Ho hydrogen molecules were also used to probe the orbitals and binding potentials of adsorbed molecules [116, 117].
Another discovery was made in the group of S. Tautz where hydrogen has been used to enhance the resolution of STM on organic molecules [118, 119, 120]. The so called STHM (Scanning Tunneling Hydrogen Microscopy) was then extended by using other atoms and molecules such as noble gases or CO molecules as a functionalized tip with increased resolution [121, 27]. Hapala et al. provided a theoretical explanation on the imaging mechanism where the front atom or molecule is moving due to forces acting between tip and sample [122, 123].

In this chapter different adsorption effects of hydrogen will be investigated. It was observed, that a tremendous difference in the measured signals arise from using different materials for the tip. In section 6.3, the results of a tungsten tip on Au(111) are presented (Au(111):H₂:W). In section 6.4, the tip is made of silver (Me(111):H₂:W). Here, the effects on gold and copper are more or less the same since hydrogen gets physisorbed between the electrodes in a potential well.

### 6.2 Preparation of single crystals

Within the framework of this work the preparation of single crystals was added to the repertoire of sample materials available for experiments in our UHV cluster. Apart from the fact that there are no grain boundaries, single crystals offer a large variety of advantages as substrate material. High purity and a low defect density give optimal conditions for a nearly perfect surface, which is crucial in STM. The crystals can also be reused after a simple cleaning procedure.

The single crystals [here: Au(111), Ag(111), and Cu(111)] were purchased from MaTecK™. The purity is declared to be 5N (99.999%). The dimensions of the crystals are 5 mm x 10 mm x 2 mm and the accuracy of the orientation of the surface is polished to < 0.1°. This corresponds to an expected lateral width of the terraces of at least 150 nm.

The crystals are cleaned in the preparation chamber of the UHV cluster. The individual steps of the preparation and a standard characterization by means of XPS and STM are described in this section.

When crystals are mounted for the first time and transferred into the vacuum system one expects that the surface is covered with a thick layer of different adsorbents. UPS shows no sign of a surface state whatsoever. This indicates that the surface is highly contaminated or terraces are too small to develop a surface state. Further analysis of this layer with XPS shows a strong peak at about 286 eV which can be attributed to the binding energy of carbon 1 s. This confirms the assumption
6.2. PREPARATION OF SINGLE CRYSTALS

Table 6.1 – Typical cleaning procedure for single crystals: Altering cycles of sputtering (S) and annealing (A) are performed to remove contaminations.

<table>
<thead>
<tr>
<th>Technique</th>
<th>setting</th>
<th>$I_{em} , (\mu A)$</th>
<th>duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1300 V</td>
<td>20 - 30</td>
<td>15</td>
</tr>
<tr>
<td>A</td>
<td>350 - 400°C</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>800 V</td>
<td>15 - 20</td>
<td>10</td>
</tr>
<tr>
<td>A</td>
<td>350 - 400°C</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>800 V</td>
<td>10 - 15</td>
<td>5</td>
</tr>
<tr>
<td>A</td>
<td>350 - 400°C</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>800 V</td>
<td>10 - 15</td>
<td>2</td>
</tr>
<tr>
<td>A</td>
<td>350 - 400°C</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>250 - 300°C</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

of a contaminating layer on the crystal. Therefore, the surface has to be cleaned carefully to remove the carbon.

The cleaning procedure of the sample surfaces is almost the same for all materials used at this setup [124]. In principle, there are two preparation techniques that are combined to clean and prepare the surface. Sputtering (S) erodes the top layers but also roughens the surface of the crystal while annealing (A) recovers a flat surface due to thermal activation of the surface atoms.

As a first step after inserting a crystal into the UHV cluster the crystal is annealed to approximately 75 % of the melting point of the corresponding element for at least two hours. This annealing step reduces the contaminating layer on the surface but also leads to a segregation resulting in a diffusion of impurities from the bulk to the surface. In the next steps, repeated cycles of sputtering and annealing are applied to clean the surface as shown in table (6.1). The values were figured out experimentally and yielded good results.

Sputtering was done with a commercial ion gun ($SpecsLab^{TM}$ IQ 12/38) at energies of 800 - 1300 V using ionized Argon atoms. Two different geometries for the incident angle of the Argon beam with respect to the samples were used. At an angle of 0° the sample is hit perpendicular to the surface and at an angle of 45° the sample is hit under grazing incidence, which leads to a higher sputter yield and therefore to a stronger erosion of the surface [125]. The ion current was controlled by adjusting
the Argon partial pressure in the preparation chamber. Typically, this pressure was in the range of \((1 - 5) \cdot 10^{-7}\) mbar. In the present setup, it is not possible to measure the ion current reaching the sample. Therefore, it was estimated according to the specification sheet [63] to be in the range of \(1 - 2\ \mu\text{A}\). This corresponds to an erosion rate of approximately \(2.5 - 5\) atomic layers per minute (given a sputter yield of \(4.0\) [126]).

The steps of a typical cleaning procedure are listed in table (6.1). \(I_{em}\) is the emission current displayed at the control unit of the ion gun. One has to ensure that the extractor current is in the same order of magnitude as \(I_{em}\); otherwise the unit is not working correctly. The first sputtering step with higher energy is only necessary if the substrate is highly contaminated. After that, the sputtering time and the emission current, \(I_{em}\), decrease with each step. In between two sputtering steps the sample is annealed for 15 minutes at around \(350\)°C for Ag and around \(400\)°C for Au and Cu. After each annealing step, the sample is allowed to cool down for approximately three minutes before the next sputtering step starts. The last annealing step is done for 30 minutes, where the temperature is reduced by about 50 degrees for the last 10 minutes. This treatment promises a low defect density and large terraces. For new substrates, these steps have to be repeated several times until the desired purity of the surface is achieved.

In order to monitor and quantify the cleaning process, XPS sprectra were taken after each cycle of sputtering and annealing while preparing a single crystal for the first time. Figure 6.1 shows two exemplary XPS spectra of a contaminated Cu(111) surface before treatment (black) and a clean surface after several cycles of sputtering and annealing (red). The prominent features at about \(930\) eV and \(950\) eV belong to the Cu 2p binding energies. As already mentioned, the most significant change in the spectra is the reduction of the carbon feature at circa \(286\) eV and the disappearance of the signature of oxygen at about \(531\) eV compared to the spectrum of the contaminated surface (see also [127]).

The inset in figure 6.1a shows the evolution of the carbon layer (black) versus the number of cycles. The thickness of the layer was calculated from the XPS spectra using a simple model of homogeneous carbon coating. In order to get more accurate results the C 1s, O 1s and Cu 2p peaks were recorded with a higher resolution and the peak areas were fit by means of Gaussian profiles. Oxygen (blue) was only visible in the first three measurements. As the number of cycles increases, the fraction of copper atoms (red) in the surface layers increases. It can be seen that the crystal is clean after nine cycles, because the carbon peak completely vanished.
Figure 6.1 – (a) XPS measurement of a Cu(111) crystal before (black) and after (red) the cleaning procedure. The inset shows the composition of the surface layers after each cleaning step. Copper (red), Carbon (black), and Oxygen (blue) are plotted versus the number of cycles. The surface appears clean after nine cycles. (b) UPS measurement taken after first (black), fourth (green) and ninth (red) cycle. 3d states of Cu are visible after five cycles and the red curve also features the surface state.
UPS spectra were recorded after the first (black), fourth (green), and ninth (red) cycle that are shown in figure 6.1b. After the first cycle no features can be seen. After the fourth and ninth cycle the 3d states of Cu can be detected between $E \approx 2 - 4$ eV. After nine cycles the onset of the surface state at $E \approx 0.4$ eV was detected in the spectrum, as expected from a clean Cu(111) surface.

**Topography**

After preparation, the crystals are investigated by means of STM. Therefore, three major criteria have been established to characterize the quality of the surface preparation.

1. Terraces visible in the topography should be sufficiently large. In this case, sufficiently means a lateral expansion of more than 50 nm in each direction. If the size of the terrace is considerably smaller the time of the last annealing step has to be increased.

2. The steps between the terraces should follow straight lines along the crystalline axes. Experience shows that cooling the crystal too fast results in a high kink density. The step height should also be checked to verify that there are no lattice dislocations which can lead to steps in the top layers of the surface, too. These dislocations can be detected because their height is not equal to a monoatomic step height in the STM image [128].

3. A defect density below $5 \cdot 10^2 \text{nm}^{-2}$ should be achieved in order to perform local spectroscopic measurements. If the density exceeds this value the sputtering time has to be increased to remove more material from the surface and/or the time for the last annealing step has to be decreased since impurities can segregate to the surface.

An overview scan of Cu(111) and Au(111) is shown in figure 6.2 and figure 6.3a, respectively. They both show large terraces in the order of $>100$ nm, which demonstrates that the time of annealing was long enough. The terrace steps are running in straight lines with a low kink density. The step height was determined to $h_{\text{Cu}(111)} = (0.205 \pm 0.005)$ nm and $h_{\text{Au}(111)} = (0.239 \pm 0.004)$ nm which is in agreement with the expected values of $h_{\text{Cu}(111)} = 0.209$ nm and $h_{\text{Au}(111)} = 0.235$ nm.

The third criteria mentioned is the defect density. At the Au(111) surface these defects mostly appear as small protrusions at the elbow site because of its high
6.2. PREPARATION OF SINGLE CRYSTALS

Figure 6.2 – STM image of a freshly prepared Cu(111) surface. The inset shows the tunneling current of a close-up scan measured with slow feedback loop, exposing defects and a step.

Figure 6.3 – (a) Overview and (b) close-up of a Au(111) surface exposing the herringbone reconstruction. The reconstruction is highlighted by the blue line in (b) and the different areas are labeled in (b). (c) shows the cross section along the red arrow.
reactivity or depressions with a small depth of \( \approx 40 \text{ pm} \). In this case, the defect density is about \( 5 \cdot 10^{-3} \text{nm}^{-2} \). On Cu(111) the defects occur randomly on the surface. The inset in figure 6.2a shows a close-up of the Cu(111) surface. Here, the image displays the tunneling current measured with a slow feedback loop because it reveals a better contrast. The dark line corresponds to a step edge. Standing wave patterns can be seen parallel to it. These are Friedel oscillations [129, 130, 131, 132], which originate from self-interference of electrons in the surface state being scattered at the step edge. The image also shows four point defects indicated by the circular wave pattern. In the topography image they appear as small dips of up to 20 pm depending on the applied bias. Since the defects are so small it is likely that only one atom of the surface layer is either an impurity atom or an atom which is modified to a weak binding. The defect density has been determined to be about \( 2.5 \cdot 10^{-2} \text{nm}^{-2} \).

The Au(111) surface exposes the \((22 \times \sqrt{3})\) herringbone reconstruction where 23 atoms of the surface layer share the space of 22 atoms of the bulk [128, 133, 25, 134]. This stacking fault leads to fcc \((\text{face-centered cubic})\) and hcp \((\text{hexagonally closed-packed})\) regions on the surface separated by soliton walls. These walls are aligned in a zigzag pattern which is indicated by the blue line in figure 6.3a. Figure 6.3b shows a close-up of a Au(111) surface with the different regions labeled. The cross section along the red arrow, averaged over the width of the hatched rectangle, is shown in figure 6.3c. The solitone walls of the herringbone reconstruction are about 15 pm high and no atomic corrugation is visible. Noise in this image was determined to be less than 0.5 pm by analyzing cross sections along flat lines.

**Spectroscopy**

The quality of a freshly prepared surface is investigated by means of STS. Figure 6.4a shows \(I-V\) curves of a clean Au(111) (black) and a Cu(111) surface (red). Both curves show similar characteristics. The most prominent feature is the onset of the surface state which is clearly visible as a positive step in the conductivity with an exponential decay. The onset is at about -500 meV for the gold surface and at about -450 meV for the copper surface. This is in good agreement with literature [135]. If this feature is resolved clearly without other significant peaks in the displayed energy range, tip and sample are assumed to be "spectroscopically clean". Additional peaks in \(I-V\) curves often indicate a contaminated tip. In this case, the tip has to be conditioned by either pulsing the tip bias to \(\pm 10 \text{ V}\) or touching the surface
Figure 6.4 – (a) $I-V$ spectroscopy of freshly prepared Au(111) (black) and Cu(111) (red) surfaces. The curves show the onset of the surface state at $E \approx -500$ meV. (b) Differential barrier height evaluated from $I-z$ spectroscopy measurement at the same surfaces. Cu(111) has a lower differential barrier height because the work function of the surface is lower than the one of Au(111).

carefully with the tip. If this treatment does not improve the result field emission can be applied.

Using $I-z$ spectroscopy, it is possible to extract the height of the tunneling barrier. Figure 2.1 shows a schematic sketch of the dependency of the tunneling barrier height on the work functions of tip and sample. Work functions for different materials are shown in table 6.2. Since Au(111) has a work function which is about 0.3 eV higher than the one of Cu(111) a higher differential barrier height for the gold sample is expected, provided that the same tip material is used.

Table 6.2 – Work functions for different materials and surfaces taken from literature [136]

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\Phi$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(111)</td>
<td>5.31</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>4.98</td>
</tr>
<tr>
<td>Ag polycrystalline</td>
<td>4.26</td>
</tr>
<tr>
<td>W polycrystalline</td>
<td>4.55</td>
</tr>
</tbody>
</table>
In figure 6.4b the differential barrier height measured on Au(111) (black) and Cu(111) (red) and evaluated according to equation (2.7) is plotted versus the applied bias. Both measurements were performed using a Ag tip. The large error bars of the measurement on Au(111) are due to a lower number of recorded spectra per point. The measurement on the gold surface shows a differential barrier height of about $\Phi_{\text{Au}} = (3.3 - 3.7) \text{ eV}$. For $E \approx 0 \text{ V}$ the differential barrier height has a value of about 3.7 eV. For high absolute bias voltages the differential barrier height is reduced. The curve also features the onset of the surface state at -0.5 eV. However, the expected slope for a two dimensional state of 0.5 eV/eV [32, 45] was not detected in this example.

The differential barrier height measured on the copper surface at $E \approx 0 \text{ V}$ is about 2.9 eV. This is lower by about 0.8 eV compared to Au(111) and confirms the conclusion made above. The curve is in the range of $\Phi_{\text{Cu}} = (2.7 - 3.1) \text{ eV}$ and increases constantly in the measured range by about 0.1 eV/eV. In this measurement the onset of the surface state is not visible.
After preparing a clean Au(111) surface according to the description given in section 6.2 the crystal was transferred into the LT-STM chamber. It was ensured by STS that the characteristic features of a clean surface, as described in the section above, were present. The following experiments were performed with a tip etched from a tungsten wire.

While 10×10 nm² images were recorded, the sample was exposed to hydrogen at a partial pressure of about 1·10⁻⁶ mbar. The hydrogen was dosed by use of a leak valve mounted at the Plasma chamber. When opening the valves between the chambers the hydrogen reached the LT-STM. The pressure was monitored using the pressure gauge of the ion getter pump. It is worth mentioning, that the radiation shields around the microscope were either closed or opened leaving a gap of about 5 mm. Since molecular hydrogen gets physisorbed at cold surfaces below 22 K [137] it takes some time until a sufficient amount of hydrogen reached the sample surface underneath the tip.

Figure 6.5 shows some example images taken at different times after the hydrogen flow was started. The images are scanned from top to bottom in 256 lines. Recording one image took about 4 minutes. At the beginning (0 min) the surface looks clean; four point defects are visible and marked by the red arrows. The defect at the top appears as a protrusion. The other defects manifest themselves indirectly as radial wave patterns at the surface. After 32 minutes of exposure a first change becomes discernible. The appearance of the three hidden defects switches to depressions of depth ≈ 40 pm. The image after 36 minutes exhibits several distorted lines with noise in the range of 10 pm. Concurrently, the noise in the current image increases to about 30 % of the set current, \( I_{\text{set}} = 1 \text{ nA} \) (not shown). This indicates that the tip apex is in an unstable state. The fourth image after 40 minutes shows a step in the topography of height 40 pm from line 37 to line 38 from the top of the image (blue arrow). After that, the topography shows a faint regular structure. All images taken afterwards also exhibit this feature.

This regular feature remained the same even if the scanning parameters, such as, scanning speed, tunneling voltage, and tunneling current were changed. This excludes any artifacts due to the scanning itself. A closer look (see figure 6.6) shows that the regular structure is due to the atoms in the surface of the sample. The four bright vertical lines in the image correspond to the soliton walls of the surface reconstruction. In between, the three uppermost layers exhibit either a
Figure 6.5 – STM images taken at different times during 60 min- 
utes exposure to hydrogen at a partial pressure of $1 \cdot 10^{-6}$ mbar 
$(10 \times 10 \text{nm}^2$, 1 V, 1 nA). Defects (red arrows) change their 
appearance after 32 minutes. Instabilities in the junction cause dis-
torted lines after 36 minutes. After 40 minutes exposure atomic 
corrugation is discernible (blue arrow).
6.3. AU(111):H₂:W

Figure 6.6 – STM image with atomic resolution of an Au(111) surface with a hydrogen contaminated W-tip (11.3 × 5.6 nm², 50 mV, 1 nA). The red box highlights the 22 × √3 unit mesh of the herringbone reconstruction. The rows of the atoms (red line) are not ordered in straight lines (blue line).

fcc stacking for the wider area or a hcp stacking for the narrower area. Atomic resolution on Au(111) was never reached before with this particular STM with a tip that was not contaminated by an organic molecule.

The red box in figure 6.6 highlights the 22 × √3 unit mesh of the herringbone reconstruction. In other words, 23 atoms of the surface layer share the space of 22 atoms in the bulk [138]. The red line in the figure follows the rows of atoms in the surface in <110> direction. A slight deviation from a straight line (shown in blue) can be seen. This was predicted using DFT (Density Functional Theory) calculations by Wang et al. [134, 139].

Another interesting phenomenon is shown in figure 6.7. Two images were recorded successively using the same scanning options with one spectroscopy measurement between the two scans. The spectroscopy showed no specific sign of a changing tip such as a jump in current or separation. Nevertheless, where the first image shows the atomic corrugation as protrusions of about 2.2 pm height, the second image shows them as dips of about 1.5 pm depth in the topography. This contrast inversion was also reported by Barth et al. [128].

6.3.1 Calibration of the lateral piezo settings

Measuring sizes and distances on the nanometer and picometer scale is one of the greatest advantages when using scanning probe microscopy. In order to calibrate
the piezo it is crucial to have a reference sample for which all structural parameters are known.

The scale in STM can easily be calibrated by measuring cross sections over terraces in images of well characterized single crystals. The height of a step on Au(111), for example, is $\sqrt{3}/3 \cdot a$ where $a = 0.408$ nm is the lattice constant of Au [140]. However, calibrating the lateral displacement of the tip is not that easy since measuring the size of extended objects such as molecules always includes information of the tip radius. Therefore, a regular structure of well known features such as atomic corrugation would be perfect for calibration. Measurements with hydrogen on Au(111) always showed an increase in noise in the signal of the tunneling current whenever the tip moved from one atom to the next one as can be seen in figure 6.8a. Fourier transforming the image of the tunneling current (see figure 6.8b) allows for a precise calibration of the lateral piezo displacement. The displacement of the atoms parallel and perpendicular to the soliton walls on reconstructed Au(111) is given by the lattice constant $a$ and $22/23 \cdot a$, respectively. For this tip-sample system the piezo calibration was set to $(72.2 \pm 0.5) \text{ nm V}^{-1}$.

Note that this calibration is only valid for tips with the same length. Since the lateral movement of the tip is caused by a bending of the piezo, a change of the length by 1 mm results in a change of about 4 % of the lateral sensitivity due to the intercept theorem.
6.3. AU(111):H₂:W

6.3.2 Spectroscopy with adsorbed hydrogen

Changing the bias to values above 200 mV causes a tremendous increase in the noise of the tunneling current. Therefore, $I-V$ measurements in a wider bias range could not be performed. Instead, $IETS$ measurements in a low bias regime were carried out and compared to measurements without hydrogen.

Figure 6.9 displays the results after evaluation of two $IETS$ measurements measured with the same macroscopic tip. The red line shows the root-mean-square of the scatter of the measurement, which means only peaks above the red line are valid peaks. The peak positions were determined using the Wavelet method. Afterwards Gaussian peaks were fit to the odd part of the spectrum at fixed positions in order to get the amplitude and width with the method shown in section 4.

The hydrogen-free Au(111) surface shows a mode at 4 meV, which can be compared to the two modes of the hydrogen-contaminated surface at 3 meV and 6 meV. The other modes of the hydrogen-free surface at 18 meV, 24 meV, and 46 meV are also detected on the hydrogen-contaminated surface. But here they are close to the limit of noise. The peak at 36 meV on the hydrogen free surface shifts to 38 meV and is also strongly damped. Additionally, at 30 meV a strong peak is found when hydrogen is present. The measurements were performed at different positions on the surface. No significant deviations were detected.
In summary, inelastic features above 10 meV are damped in the measured range from -55 meV to 55 meV and an additional mode at about 30 meV is detected on Au(111) in the presence of hydrogen using a tungsten tip.

### 6.3.3 Interpretation

Several studies showed that hydrogen tends to dissociate at tungsten surfaces [137, 141, 142] and forms a chemisorbed layer of atomic hydrogen at the surface. For example, Barnes et al. [143] showed with EELS that hydrogen forms a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction on W(100). They also measured various vibrational modes in the region between 55 - 250 meV. Those correspond to the vibrations of the hydrogen atom which is bound to one or more tungsten atoms. Here, the vibration of the chemisorbed hydrogen atom can be attributed to the mode which was detected at 30 meV. Since the surface of the tip is not regularly ordered, this mode can change because of different binding geometries of the hydrogen atoms at the tip apex.
With the available methods it is not possible to resolve the true configuration of the hydrogen at the tip. Therefore, figure 6.10 shows only a sketch of a tip covered with hydrogen atoms.

An explanation of the drastic enhancement of resolution can be adapted from the imaging mechanism proposed by Weiss et al. and Hapala et al. [122, 123, 28], where functionalized tips were used to get high-resolution images of organic molecules. In that case the front atom is pushed laterally by Pauli repulsion. It was shown that this interaction is sensitive to small changes in the electron density even in the sub-molecular regime. In the present work the front atom may be a single hydrogen atom and the Pauli repulsion is due to the corrugation of the core electrons of the gold surface. This also explains the noise which was obtained in the image of the tunneling current shown in figure 6.8. Here, the front atom may flip as the tip is scanned over the surface creating noise in the current.

The remaining question is why the atomic resolution on a noble metal surface is lost in STM without a molecule at the tip apex. A simple answer could be that the surface state is situated in a plane in front of the surface. The electrons contributing to the tunneling current will always be dominated by those surface state electrons and therefore the surface of noble metals appears flat in most STM topography measurements.
6.4 Me(111):H$_2$:Ag

The basic results of this section are going to be published in a journal article [144]. Within the framework of this dissertation several properties are addressed in more detail as compared to the publication. Furthermore, additional measurements on a Cu(111) surface are shown.

The same experiment as described in section 6.3 was performed with a silver tip instead of a tungsten tip. Again, the sample was exposed to hydrogen at a partial pressure of about $1 \cdot 10^{-6}$ mbar. Too much hydrogen leads to a deterioration of the vacuum pressure. Therefore, the radiation shields could be opened by about 5 - 10 mm in order to minimize the time of exposure. Opening the shields leads to an increase of the temperature of the STM by about 1 - 2 K. Simultaneously to the exposure, $\partial V/I$-curves were recorded. After approximately 10 minutes, a significant change in the conductivity could be observed. The hydrogen flow was then stopped and the radiation shields were closed.

Figure 6.11 shows the evolution of the $\partial V/I$-curves with time. The start and stop of the hydrogen exposure is marked with vertical red lines. Right of the second line the change in the conductivity can be seen very clearly. A constant increase of the conductivity appears symmetrically around zero bias with a width of about 20 meV. Beyond that increase, a sharp dip which could even become negative can be seen by the dark feature at $|V| \approx 15$ meV. At $|V| \approx 20$ meV a positive step is observed. Such $\partial V/I$-curves will be analyzed in more detail later in this section. When the signature shows up first, the width seemed to increase slightly and noise decreases with every additional spectrum taken. However, after about one hour the system was in a steady state and further recording of $\partial V/I$-curves over several hours showed no changes anymore. Intentional modifications of the system can be induced by a short pulse of the tunneling bias or the $z$-piezo voltage leading to a modification of the tip apex in most cases.

By heating the sample to a temperature above 22 K, the characteristic feature in $\partial V/I$-V vanished. Since hydrogen gets physisorbed on noble metal surfaces below this temperature [137] this indicates that the signature is connected somehow to physisorbed hydrogen on the surface.
6.4.1  \( I\)-\( z \) measurements

Before the \( \partial V \)-\( I \)-\( V \) curves are analyzed, a model has to be developed in order to describe the curves accurately and extract the relevant parameters from measurements. After ensuring that the signature in \( \partial V \)-\( I \)-\( V \) shows only a single excitation, \( I\)-\( z \) measurements were performed. As shown in section 2.1.3.2, the inverse decay length \( k_V(z) \) at constant bias can be extracted from this spectroscopic measurement. Instead of varying the tip-sample separation and recording \( I(z) \), better results could be achieved by varying the set-current at closed feedback loop. This way, \( z\)-\( I \) was measured and then converted to \( I(z) \). The derivative with respect to the separation \( \frac{dI(z)}{dz} \) was then calculated numerically. A direct measurement of \( \partial_z I\)-\( z \) with lock-in technique did not improve the result.

\( I\)-\( z \) spectroscopy measurements were performed at different biases. A representative selection of measured inverse decay lengths on Au(111) is shown in figure 6.12 (red curves). \( \Delta z \) corresponds to the change in the tip-sample separation which is given by the piezo voltage. The left side of the diagram corresponds to a smaller tip-sample separation. With decreasing bias a peak is formed which shifts away from the sample as the bias is decreased. The amplitude of the peak is in the range of the background, \( k_0 \), which is approximately 20 nm\(^{-1}\) to 23 nm\(^{-1}\) and corresponds to the expected barrier height between Au and Ag of 3.5 - 4.5 eV. The width of the peak is about 40 pm to 50 pm and independent of bias. For higher...
bias the amplitude decreases until the peak vanishes. At this point it is not clear whether the peak is just outside the measured range or it is completely gone. A second measurement with a different tip and extended range was taken at 40 meV (dashed black curve) which does not show a peak. This curve will be analyzed in more detail, later.

Fitting a Lorentzian peak with height $k_1$ and constant background $k_0$ to the inverse decay lengths (blue curves) shows great agreement. With this, a mathematical model can be developed which describes the different spectroscopic measurements.

### 6.4.2 Basic mathematical model

The basic idea of the analytical model is to introduce a Lorentzian in $k$, where the amplitude and the center depend on bias. The ansatz for the inverse decay length is then given by

$$k(z) = k_0 + \frac{k_1}{1 + 4 \left( \frac{z - z_c(V)}{w_2} \right)^2}.$$ 

(6.1)
where $k_0$ is a constant background, $k_1$ is the amplitude of the peak, $z_c(V)$ is the center of the peak, and $w_z$ the width of the Lorentzian. Assuming the validity of the WKB approximation, the ansatz (6.1) can be introduced into the transmission coefficient, $T = \exp(-P)$. The phase integral, $P$, then reads

$$P = \int_{z_1}^{z} k(z') dz' = k_0 z + \frac{k_1}{2} \left( \arctan \left( \frac{2z - z_c(V)}{w_z} \right) + \arctan \left( \frac{z_c(V)}{w_z} \right) \right)$$  \hspace{1cm} (6.2)

with the classical turning points $z_1 = 0$ and $z$.

Figure 6.13 sketches the energy diagram representing equation (6.1). The model comprising a peak in $k(z)$ is now used to calculate the characteristic features of $I$-$V$ and $\frac{\partial V}{I}$-$V$ curves. Starting with the current, equation (2.1) is used for the calculation. Since the density of states $\rho_s$ and $\rho_t$ are constant in this energy regime and the temperature is low, a simplified version can be used. The current then is

$$I \propto \int_{V_0}^{V} e^{-P} dE$$  \hspace{1cm} (6.3)

with the phase integral $P$ given in equation (6.2). Calculating the derivative with respect to bias leads to the conductivity

$$\partial_V l = \left( 1 + V \cdot k_1 \partial_V z_c \left( \frac{1}{(z - z_c(V))^2} - \frac{1}{(z_c(V))^2} \right) \right) \cdot \exp(-P).$$  \hspace{1cm} (6.4)

The conductivity contains two Lorentzian peaks of width $w_z$, centered at $z_c(V)$ and $z - z_c(V)$ which are transformed to a center and width in bias, $V_{c1}(z)$, $V_{c2}$ and $w_V \approx |w_z/\partial_V z_c|$, respectively. $V_{c1}(z)$ shifts with changing tip-sample separation and $V_{c2}$ is constant. The model function can be seen in figure 6.14. Since the Lorentzian peak in $k(z)$ shifts towards the sample with increasing bias, $\partial_V z_c$ is negative leading
to a negative peak in $\partial V I - V$ at $V_{c1}(z)$ and a positive peak at $V_{c2}$. The arc tangent in the exponential of the phase integral leads to smeared steps in $\partial V I - V$ at the same positions and with the same sign as the peaks.

Normalizing the latter formula with respect to $I$ then yields

$$\frac{\partial V}{I} = \frac{1}{V} - k_1 \partial V z_c \left( \frac{1}{(z - z_c(V)) \omega_v^2} - \frac{1}{(z_c(V)) \omega_v^2} \right),$$

leaving only the peak functions and a constant offset, $\frac{1}{V}$.

However, for physical reasons some approximations have to be made:

- The step caused by the arc tangent in $e^{-P}$ can be replaced by a simple step function since the width, $\omega_v$, is small.

- The modulation amplitude leads to an inhomogeneous broadening of peak and step. Therefore, a Gaussian or Voigt profile might lead to better fitting results for the peak and for the step an error function ($\text{erf}$) is used.

- The lower integration boundary creating the second peak and step at $V_{c2}$ can be neglected. They would be far outside the measured range and, as will be shown later, they are of no physical relevance.

Therefore, only one negative peak and a step at $V_{c1}(z) = V_c$ are left to describe the measured data. Thus, a model function for $\partial V I - V$ curves can be written as
\[ \partial_{V} I(V) = \text{Peak}(V, \sigma_{0}, V_{c}, \omega_{V}, A) + B \cdot \left( 0.5 \cdot \text{erf} \left( \frac{(V - V_{c})}{\omega_{V}} \cdot \sqrt{2} \right) + 0.5 \right). \]  

(6.6)

The parameters \( V_{c} \) and \( \omega_{V} \) depicting the position and width of peak and step, respectively, have already been introduced above. \( \sigma_{0} \) corresponds to the conductivity at zero bias. The remaining fit parameters are \( A \) and \( B \), where \( A \) corresponds to the area of the peak and \( B \) represents the step height. \( \text{Peak} \) is a placeholder for a 'Lorentzian', 'Gaussian', or 'Voigt' profile.

### 6.4.3 I-V measurements

In a next step \( I-V \) spectroscopy was performed. By changing the set-current at consecutive measurements, the tip-sample separation was varied. An example set of \( I-V \) and \( \partial_{V} I-V \) curves measured at different tip-sample separations are shown in figure 6.15a and b, respectively.

The \( I-V \) spectroscopy shown here was performed at low biases (\( |E| < 30 \text{ meV} \)) and high tunneling current (\( |I_{\text{max}}| = (10 - 60) \text{ nA} \)) which corresponds to a small tip-sample separation. All curves exhibit similar features. Figure 6.15c shows an exemplary \( I-V \) curve at positive bias with the characteristic parameters. The conductivity at zero bias, \( \sigma_{0} \), a step at a critical bias, \( V_{c} \), where the elastic channel is stalled by a factor of \( \alpha_{\text{elastic}} \), and an inelastic channel is opened with an efficiency of \( \eta_{\text{inelastic}} \) with respect to \( \sigma_{0} \). The first derivatives, shown in figure 6.15d, illustrates the measurement in more detail. A constant conductivity at zero bias followed by a negative peak with area \( A \) which corresponds to the negative slope in \( I-V \). The change in the slope before and after \( V_{c} \) in the \( I-V \) curve corresponds to a step in the conductance of height, \( B \).

In figure 6.16 \( \partial_{V} I-V \) curves at different tip-sample separation are shown. The curves were normalized to the current, \( I \), as shown in equation (6.5) and the \( 1/V \) term was removed. One can see the peak center, \( V_{c} \), shifting to higher energies and the amplitude rising for increasing conductance, \( \sigma_{0} \). This indicates that the area of the peak is not only rising because of a higher conductance but also the ratio \( A/\sigma_{0} \) is increasing as the tip approaches the sample.

In order to extract the characteristic parameters from the measurement, two approaches were used: Either the \( I-V \) curve or the \( \partial_{V} I-V \) curve can be fit. For the latter, the model function was already introduced above with equation (6.6) and shown in figure 6.15d. The parameters defined in figure 6.15c can be derived by
Figure 6.15 – (a) $I$-$V$ and (b) $\partial_V I$-$V$ curves measured at different tip-sample separations. (c) A sketch of an $I$-$V$ curve with a set of characteristic parameters is shown. (d) Explanation of the fit parameters $\sigma_0$, $V_c$, $A$, and $B$. The model functions are used to fit an (e) $I$-$V$ curve and a (f) $\partial_V I$-$V$ curve (dashed lines). Inset in (f) shows different peak functions for the fit routine: Lorentzian (black); Gaussian (green); and Voigt profile (dark green).
Figure 6.16 – Conductance normalized to current, $\frac{\partial V}{I-V}$, with subtracted $\frac{1}{V}$ term is shown as was derived in equation (6.5). The peak position and amplitude increase with increasing $\sigma_0$.

The relations: $\alpha_{\text{elastic}} = \frac{A}{\sigma_0 V_c}$ and $\eta_{\text{inelastic}} = \frac{B}{\sigma_0} - \alpha_{\text{elastic}}$. Integration of (6.6) and consideration of the parameters provides a fit function for $I$-$V$ curves

$$I(V) = \sigma_0 \cdot \left[ 1 + \frac{\alpha_{\text{elastic}}}{2} \left( \text{erf} \left( \frac{2(V - V_c)}{w_V} \right) + \text{erf} \left( \frac{2(-V - V_c)}{w_V} \right) + 2 \right) \right] V$$

$$+ \eta_{\text{inelastic}} \left( \text{sign}(V - V_c) \cdot (V - V_c) + \text{sign}(-V - V_c) \cdot (V + V_c) \right) + I_0.$$  

(6.7)

Here, the parameters $\sigma_0$, $\alpha_{\text{elastic}}$, $\eta_{\text{inelastic}}$, $V_c$, and $w_V$ can be directly extracted from the fit function. The sign represents the inelastic current at zero temperature.

Exemplary data and the result of fitting an $I$-$V$ and a $\partial V/I$-$V$ curve are shown in figure 6.15e and f, respectively. The fit routine for the current converged quickly and yielded small errors. A small deviation at the step edges can be seen. This deviation will be treated later. The routine for the fit of the derivative showed larger errors and needed some manual assistance in order to converge if the curves were measured in the regime of low currents.

Figure 6.15f also shows the result of using different peak functions (dashed lines). The inset shows a close-up of the transition region marked by the rectangle. Using a Lorentzian profile (black) the base of the peak is a bit broader, whereas a Gaussian peak is a bit narrower. A convolution of both, called Voigt profile (dark green),
6.4.4 Investigation of the peak shape

In order to determine the best fit function for the peak, the influence of the modulation amplitude is studied and different peak shapes are compared. This reveals the actual shape of the peak and the line width can be determined.

As mentioned above, the fit functions are Lorentzian, Gaussian and Voigt. The corresponding formulas are

\[
\text{Lorentzian} = \frac{2A}{\pi} \cdot \frac{w_l}{4 \cdot (V - V_c)^2 + w_l^2}
\]

\[
\text{Gaussian} = \frac{A}{w_g \sqrt{\pi/2}} \cdot \exp \left[ -2 \left( \frac{V - V_c}{w_g} \right)^2 \right]
\]

\[
\text{Voigt} = \int_{-\infty}^{\infty} \text{Gaussian}(x, w_g) \cdot \text{Lorentzian}(V - x, w_l) \, dx \quad (6.8)
\]

where \(A\) corresponds to the area of the peak and \(w_l\) or \(w_g\) correspond to the width of the Lorentzian or Gaussian, respectively.
### Table 6.3 – Value of the fit parameter for the peak area, $A$. Different peak profiles were used to fit the modeled peaks in figure 6.17 at different modulation amplitude.

<table>
<thead>
<tr>
<th>$V_{\text{mod}}$ (meV)</th>
<th>$A$(Lorentzian)</th>
<th>$A$(Gaussian)</th>
<th>$A$(Voigt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.7182</td>
<td>1.0002</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0016</td>
<td>0.7186</td>
<td>1.0019</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0742</td>
<td>0.7575</td>
<td>1.0177</td>
</tr>
<tr>
<td>5.0</td>
<td>1.7084</td>
<td>0.9324</td>
<td>0.9331</td>
</tr>
</tbody>
</table>

A $\partial V/I$-V curve with a single Lorentzian peak is assumed to fully explain changes caused by applying different modulation broadenings. The model peak of width $w_l = 1$ and $A = 1$ is convoluted with the window function of equation (2.16). Figure 6.17 shows a Lorentzian in the first derivative in black. Applying a small modulation of $V_{\text{mod}} = 0.1$ meV does not change the peak considerably. However, with increasing modulation amplitude the peak shape is changing significantly. At a modulation amplitude of $V_{\text{mod}} = 1.0$ meV the height is already reduced and the shape is slightly changed. At $V_{\text{mod}} = 5.0$ meV the peak is completely degenerated.

All peaks in this figure were fit by the three candidate peak profiles to identify the best fit function. In table 6.3 the areas of these fits are displayed because $A$ is the most important parameter of the peak function for the evaluation. The value corresponds to the conformity of the fit to the peak without modulation.

Obviously, the Lorentzian fit function is best for $V_{\text{mod}} = 0$ meV and $V_{\text{mod}} = 0.1$ meV. For an amplitude of $V_{\text{mod}} = 1.0$ meV Voigt seems to be the best choice with a deviation of less than 2 %. At $V_{\text{mod}} = 5.0$ meV a Voigt is still slightly better than a Gaussian with a deviation of about 7 %. That means that Lorentz and Voigt are favorable for different modulation amplitudes.

Figure 6.18 shows measured $\partial V/I$-V curves with modulation amplitudes ranging from 0.1 meV to 5 meV. As expected, the peak shape is changing significantly with changing amplitude. Also shape and width of the step in $I(V)$, shown in the inset, is changing with amplitude.

Fitting the peak at smallest modulation amplitude a Lorentzian leads to a correlation of $R^2 = 99.7 \%$ (dashed orange line) and the width corresponds to $w_V = (0.825 \pm 0.004)$ meV. For modulation amplitudes of $V_{\text{mod}} \geq 0.2$ meV a Voigt peak is used. This is shown exemplary for $V_{\text{mod}} = 1$ meV (dashed red line). Fits to the data with $V_{\text{mod}} = 2$ meV and $V_{\text{mod}} = 5$ meV did not yield a very good correlation. This can be
explained by the fact, that Lock-in broadening is not Gaussian shaped but more of an ellipsoidal broadening, as was shown above. Another effect at higher modulation amplitudes is that the peak center $V_c$ shifts by about 0.42 meV towards higher energies at an amplitude of $V_{mod} = 1$ meV. The reason for the shift is because of the broadening of the step.

According to equation (2.25), the effect of modulation broadening can be subtracted from the measured line width by transforming the relation for the FWHM. Table 6.4 shows the width of the measured peak, $w_V$, compared to the reduced line width, $w_r$, which was calculated using

$$w_r = \sqrt{w_V^2 - (1.22 \cdot V_{mod})^2}. \quad (6.9)$$

Even though the width is corrected by the modulation amplitude the reduced line width cannot be reproduced accurately for all amplitudes. Furthermore, thermal broadening for a signal in conductivity, is around $w_t = 4 \cdot k_B T = 1.72$ meV at 5 K, which is two times higher than the measured line width at lowest modulation amplitude. This phenomena can be explained by a switching behavior where the electrons can excite a two-level system leading to a step in the DOS which is not thermally broadened. Now, the thermal broadening of only one electrode has to be
Table 6.4 – Peak width, $w_V$, at different modulation amplitudes and reduced line width, $w_r$, calculated according to equation (6.9).

<table>
<thead>
<tr>
<th>$V_{\text{mod}}$ (meV)</th>
<th>$w_V$ (meV)</th>
<th>$w_r$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.825</td>
<td>0.816</td>
</tr>
<tr>
<td>0.2</td>
<td>0.866</td>
<td>0.831</td>
</tr>
<tr>
<td>0.5</td>
<td>1.06</td>
<td>0.878</td>
</tr>
<tr>
<td>1</td>
<td>1.85</td>
<td>1.49</td>
</tr>
<tr>
<td>2</td>
<td>4.80</td>
<td>4.13</td>
</tr>
<tr>
<td>5</td>
<td>8.65</td>
<td>6.14</td>
</tr>
</tbody>
</table>

taken into account. This leads to a width of about $w_t = 2 \cdot k_B T = 0.86$ meV, which is in good agreement with the width found in the data.

In order to choose a suitable modulation amplitude for the measurements and data evaluation a compromise has to be found. On the one hand, precise measurements require a small modulation amplitude. On the other hand, stable measurements with reasonable integration times and low error bars require higher amplitudes. The best results are achieved by setting the modulation amplitude to $V_{\text{mod}} = 1$ meV.

6.4.5 Rotational modes

Several groups reported the detection of rotational transitions of hydrogen molecules adsorbed on noble metal surfaces. Svensson and Bellman performed EELS measurements [108, 111, 110] revealing the rotational transitions on copper. In 2013, Natterer and Li showed that this transition is detectable by STM on boron-nitride and Au(110) [113, 115, 145, 114]. Yu et al. reported a shift of the rotational transition energies in the presence of physisorbed magnesium porphyrin molecules [116].

Most of the measured curves in the current experiments on Cu(111) and Au(111) show a very weak signal for the rotational transitions. Nevertheless, in some rare cases a strong signature was detected at about 40-45 meV which is attributed to the rotational transition $J/(0 \rightarrow 2)$ of para-hydrogen. Measurements exposing strong rotational features also show multiple excitations in the region of the physisorption energy. Figure 6.19a displays exemplary $\partial I/V$ measurements on Cu(111) [inset of panel (a)]. A close-up of the region of interest reveals the positive peak in the con-
Figure 6.19 – (a) Close-up of $\partial V/I-V$ measurements on Cu(111) at different tip-sample separations with the rotational mode $J(0 \rightarrow 2)$ at about 45 meV is displayed. (b) A close-up of an IETS measurements on Au(111) reveals an s-shaped feature. Both insets show an overview of the corresponding $\partial V/I-V$ spectra. High conductivity corresponds to small tip-sample separation.
ductance at about 45 meV shifting slightly towards higher energies with increasing conductivity.

In contrast, panel (b) shows a close-up of the second derivative measured on Au(111) at different tip-sample separations. The inset displays again the conductivity over a wider range. Multiple excitations can be seen clearly in this plot as well as a negative peak at around 40 meV which is attributed to the rotational transition. Consequently, an s-shaped feature appears in the inelastic signal.

Since the rotational transition is an inelastic feature, one expects a positive step in the conductivity rather than a negative peak. Although, negative components in inelastic signals were predicted by calculations of Viljas et al. [146], surprisingly, the intensity of the transition measured on Au(111) is nearly constant although the tip-sample separation is varying. The transition energy is shifting slightly from 41.2 meV to 42.6 meV as the tip approaches the surface by about 0.1 nm. This is in contrast to the observation reported by Li et al. [115], where the rotational energy decreases with decreasing tip-sample separation.

A possible explanation of the peak in the conductance and the constant intensity over a range of tip-sample separations is given by a simple saturation model. If the excited rotational state of the molecule is saturated, the additional channel which was opened by the inelastic transition is closed for a time period corresponding to the lifetime of the rotation, $\tau_{\text{rot}}$. The resulting saturation current is then given by $I_s = \frac{e}{\tau_{\text{rot}}}$ where $e$ is the elementary charge. This constant current is switched on when the transition energy is reached and leads to a step in $I$-$V$ and consequently to a peak in $\partial V/\partial I$.

Assuming a Gaussian peak in the conductance, the data of the second derivative in panel (b) was fit with the first derivative of a Gaussian. The area which corresponds to the saturation current was estimated to $I_s = (0.65\pm0.07)$ pA corresponding to a lifetime of the excited state of $(0.25\pm0.03)$ $\mu$s. However, this is not a representative result because the rotational modes have not been detected in all measurements. Furthermore, some measurements on Au(111) show a strong positive feature, too. Further quantitative analysis of the rotational transitions of physisorbed hydrogen is not possible at this point.
6.4.6 Dependence of the characteristic parameters on the tip-sample separation

Data shown in figure 6.15 and figure 6.16 indicate a strong dependence of the characteristic parameters ($\alpha_{\text{elastic}}$, $\eta_{\text{inelastic}}$, and $V_c$) on the tip-sample separation. In figure 6.20 an exemplary set of parameters is shown. The different colors indicate two independent measurements performed with different tips and measured at different tip-sample separations. The phrase ‘different tip’ means in this case, that the whole tip and sample system was freshly prepared or at least one pulse event was between two measurements. The parameters are evaluated from $I$-$V$ curves using equation (6.7).

All figures are shown with respect to the externally controlled tip-sample separation, $\Delta z_{\text{ex}}$. While measuring $I$-$V$ curves, $z$ is recorded in a separate channel opening the possibility to extract $\Delta z_{\text{ex}}$ directly from the spectroscopy file. This method is not preferential because of drift effects that occur, especially if measuring over a long time period (several hours). A better method is to perform an $I$-$z$ spectroscopy applying the same bias which is used as set point for the $I$-$V$ spectroscopy. An exponential can be fit to the resulting $z(I)$-curve and $\Delta z_{\text{ex}}$ can be calculated using the set current of the associated $I$-$V$ curve.

Figure 6.20a shows the critical bias, $V_c$, corresponding to the bias at where the step in $I$-$V$ occurs. With increasing tip-sample separation, $V_c$ is decreasing constantly from about 24 meV to about 7 meV. In figure 6.20b $\alpha_{\text{elastic}}$ is shown. Starting with a value of -60 %, the damping has a maximum of -65 % at a relative distance of about 0.07 nm. As the tip is retracted further from the sample the damping decreases strongly to -40 %. For larger tip-sample separations even small positive values were found (shown later). The inelastic efficiency, $\eta_{\text{inelastic}}$, depicted in the third plot 6.20c, is very low at small tip-sample separations, whereas it increases up to about 10 % at larger tip-sample separations. For different tips and samples the absolute values of the parameters vary because of the individual properties of the tunneling junction.

Although negative values may appear for the efficiency of an inelastic channel [146], a positive contribution of the inelastic channel to the conductivity was assumed for the vibrating molecule. If an electron excites the molecule in the junction the additional channel is blocked for a certain time, $\tau$, until the excitation decays. If the tunneling rate multiplied by the inelastic efficiency exceeds the inverse lifetime, a saturation arises.
Figure 6.20 – Characteristic parameters of two exemplary I-V spectroscopy measurements are displayed in red and black. The x-axis shows the change in tip-sample separation, $\Delta z_{ex}$. The parameters are: (a) critical bias, $V_c$; (b) damping of the elastic channel, $\alpha_{elastic}$; and (c) efficiency of the inelastic channel, $\eta_{inelastic}$. Inset: lifetime $\tau$ was determined to be $(1.76 \pm 0.07)$ ns. All parameters are evaluated from I-V curves.
The lifetime of the transition calculated by $\tau = \frac{e^{\sigma_0 \eta_{\text{inelastic}} V_c}}{\eta_{\text{inelastic}} V_c}$ is shown in figure 6.20. The large error bars at small separations are due to the small values of the efficiencies. Within the limits of the resulting errors the lifetime is constant and was estimated to be $(1.76 \pm 0.07)$ ns. The constant value supports the idea of a saturated state in this separation regime. In earlier calculations and experiments published by Persson and Hellsing [147, 148] the lifetime of the vibrational states of laterally free hydrogen molecules was estimated to be lower but increasing rapidly for increasing separation from the surface. With the potential landscape formed by the tip and the sample, the center of mass of the molecule is pulled away from the surface for tip-sample separations larger than 0.4 nm resulting in a longer lifetime. For smaller tip-sample separations the center of mass of the molecule is pushed towards the surface and the lifetime is expected to decrease rapidly.

### 6.4.7 Interpretation

In this section, a physical model is developed to describe the mechanism behind the observed phenomena. In the previous sections data showed a two level system where the state switches from one level to the other at $V_c$. The main assumption for the following model is that the probability of an excited state is '1' for $|V| > V_c$ and '0' for $|V| < V_c$ disregarding the transition region. This saturation phenomenon was shown detailed in earlier experiments by Gupta et al. [29] and Lotze et al. [31]. In section 3.2.2 the physisorption potential, the corresponding vibrational energies, and the transition energies were derived. In the model developed there, a single hydrogen molecule is situated between tip and sample in a perpendicular position with respect to the surface. In this configuration, the vibrational energy levels of a hydrogen molecule are changing when the separation of the electrodes is varied, as is shown in figure 3.4. This separation dependent energies lead to forces in the presence of the molecule exerted on the walls of both sides of the junction. The value of the acting force, $F$, can be calculated by differentiating the energy levels with respect to the separation

$$F(z) = -\frac{dE}{dz}. \quad (6.10)$$

The result is shown in figure 6.21a for the ground state $E_0$ (blue) and first excited state $E_1$ (red). The change of the force created by the transition from ground state to first excited state $E_{0 \rightarrow 1}$ is shown in black. These forces are in the range of several ten piconewton and change the direction from negative to positive values.
Figure 6.21 – (a) Resulting forces of ground state $E_0$ (blue), first excited state $E_1$ (red), and transition $E_{0\to1}$ (black). (b) Sketch of the expected model system. Due to the physisorption potential, the vibrating H$_2$ molecule exerts a force on the mechanically soft tip apex leading to a deflection. (c) The peak in $k(z)$ (compare figure 6.13) originates from increase in tip-sample separation.
for increasing separation. Positive values correspond to a repulsive and negative values to an attractive interaction.

In figure 6.21b a sketch of the suggested model is shown. The force of the vibrating hydrogen molecule causes a deflection of the tip apex. A part of the tip apex, either a single atom or a cluster of atoms, is then pushed further away or pulled closer to the surface, depending on the sign of the force. This leads to a change of the effective tip-sample separation which can be monitored observing the tunneling current. Therefore, it has to be distinguished between the true tip-sample separation, \( z_{\text{in}} \), and the external tip-sample separation, \( z_{\text{ex}} \), which is controlled by the piezo element.

This means that the peak observed in \( k(z) \) (figure 6.12) is due to a change of the true tunneling separation, \( z_{\text{in}} \). A sketch of the mechanism is shown in figure 6.21c, where the peak is transformed to an increased tunneling distance.

Using this knowledge, spectroscopic data shown above can now be interpreted. Figure 6.22 explains the occurrence of the features in \( I-V \) spectroscopy. This kind of spectroscopy is performed with constant external tip-sample separation. Starting the measurement at high negative bias, the conductivity is constant (red data and arrow) until the bias reaches the transition energy valid for this particular tip-sample separation, \( E_{1\rightarrow0}(z_1) \). Once the transition occurs, i.e. the hydrogen turns to the ground state, the force acting on the tip decreases and, therefore, the true tip-sample separation \( z_{\text{in}} \) decreases as well. This is shown by the small black arrow pointing to the left with length, \( \delta s \). As the measurement continues the conductivity is again constant but at a higher value due to the smaller tip-sample separation. At positive values, when the bias reaches the transition energy again, \( E_{0\rightarrow1}(z_2) \), this time coming from lower values (dashed olive curve), the force increases and the tip-sample separation of the starting condition is restored (dashed orange curve). This leads to a hysteresis in energy, \( \Delta E_{0\rightarrow1} \), which is already visible in figure 6.15c and analyzed in more detail later.

The model of the displaced tip apex also explains why the peaks in the \( \partial I/V \) curves are sharper than expected from IETS. Once the molecule is exited by an electron that is slightly higher in energy due to the broadening effect, the tip is pushed further away. At a larger tip-sample separation smaller energies are required to excite the molecule. Therefore, the excited state \( \nu = 1 \) is stable. This corresponds to the transition from olive to orange in figure 6.22. The same mechanism can be seen for the opposite effect from blue to red. As soon as the molecule is not excited and the tip is pulled towards the sample, more energy is required to excite the molecule,
which leads again to a stable state \( \nu = 0 \). This switching behavior is the reason for the small width of the transition, \( w_V = 2k_B T \), discussed above.

At larger separations (\( z_{in} > 0.65 \text{ nm} \)) corresponding to lower conductance, the gradient of the transition energy gets positive. Therefore, the change of the force changes sign leading to a reversal of the effect. The excited level, \( \nu = 1 \), exerts a smaller force pulling the tip towards the sample. This leads to a change in the sign of \( \alpha_{\text{elastic}} \).

So far, the described model does not explain the origin of the inelastic efficiency measured in the data, especially since the excited state is saturated which does not explain a non-constant inelastic contribution. The mechanism proposed for the inelastic channel is similar to Raman scattering but with electrons instead of photons. It also resembles the stimulated emission of phonons in carbon nanotubes shown in reference [149]. A tunneling electron may absorb the vibrational energy of the excited hydrogen molecule leaving the molecule in the ground state (Anti-Stokes). The molecule is then immediately excited by a subsequent electron (Stokes) leading to two additional channels for the tunneling electrons. The \( \frac{1}{z} \)-behavior of \( \eta_{\text{inelastic}} \) in figure 6.24 indicates a nearly constant rate of this phenomenon. The calculated lifetime may now be attributed to the lifetime of the vibron.
6.4.8 Evaluation of the tip compliance

With the \( z \) dependence of the acting force and the model shown above at hand, it is now possible to evaluate the compliance of the tip. Since the system is, in the given context, very fragile and the values of the characteristic parameters shown in figure 6.20 can change upon small modifications of the tip, the compliance has to be evaluated for each measurement independently. For this type of evaluation, only measurements exhibiting a single excitations should be used. Otherwise the physisorption well is not defined unambiguously and the characteristic parameters cannot be extracted properly.

The flow chart shown in figure 6.23 is used to determine the compliance, \( C \). In the first step, one has to make a reasonable guess for the compliance. Experience shows that the compliance lies in the range of \( C = (1 - 5) \frac{m}{N} \). This is comparable to the lateral compliance of a single CO molecule at the tip of an AFM which was determined in the group of F. Giessibl to be about \( 4.0 \frac{m}{N} \) \[150\].

In the next step, a relationship between the externally controlled \( z_{ex} \) and the true tip-sample separation, \( z_{in} \), has to be developed. The true tip-sample separation consists of two components displayed on the right side of figure 6.24. One is the distance given by the piezo, \( z_{ex} \). The absolute value of this component cannot be measured directly. However, the change in the externally controlled separation, \( \Delta z_{ex} \), can be measured leading to \( z_{ex} = z_{offset} + \Delta z_{ex} \). The second component is the deflection caused by the force acting on the electrodes because of the vibrating molecule in the junction. This term can be positive or negative, depending on the sign of the force. The real tip-sample separation is then given by \( z_{in} = z_{offset} + \Delta z_{ex} + C \cdot \partial_z E_1 \).

For the calculation of \( z_{in}(z_{ex}) \) the force of the excited molecule, \(-\partial_z E_1\), is used because the set point of the measurement is set to \( V_{start} > V_c \) for all measurements.
Figure 6.24 – Calculation of \( z_{\text{in}}(z_{\text{ex}}) \) for different compliances, \( C = 2.0 \, \text{m/N} \) (red), \( C = 3.5 \, \text{m/N} \) (green), and \( C = 5.0 \, \text{m/N} \) (blue) are displayed. With increasing compliance the overall deflection increases. \( z_{\text{in}} = z_{\text{ex}} \) is shown for comparison. The sketch on the right shows the composition of the true tip-sample separation.

Therefore, the force can be derived numerically for \( z_{\text{in}} = 0.35 - 0.8 \, \text{nm} \). The relation of \( z_{\text{in}} \) and \( z_{\text{ex}} \) can be solved for different compliances, \( C \), using for example Maple\textsuperscript{TM}:

\[
fsolve(z_{\text{in}} = -dE1(z_{\text{in}}) \cdot C + z_{\text{ex}}, z_{\text{in}}).
\]  \hspace{1cm} (6.11)

In figure 6.24 the results for three different compliances, \( C = (2.0, 3.5, 5.0) \, \text{m/N} \) are shown in red, green, and blue. For better comparison \( z_{\text{in}} = z_{\text{ex}} \) is shown in black. At a separation of about 0.49 nm the values of \( z_{\text{ex}} \) and \( z_{\text{in}} \) are equal. This is expected since the curve of the force crosses zero at this point. At small separation the force acting on the tip pushes the tip apex away resulting in an increase of \( z_{\text{in}} \) compared to the separation set by the piezo, \( z_{\text{ex}} \). For larger separation the tip is pulled towards the surface resulting in a decrease of \( z_{\text{in}} \). By increasing the compliance, \( C \), the overall deflections increase.

The inverse function \( z_{\text{ex}}(z_{\text{in}}) \) is then used to scale the x-axis of the theoretical values to the parameters evaluated from data to enable a comparison of both curves. In the next step, \( V_c(z_{\text{ex}}) \) is plotted (see inset in figure 6.25a). The theoretical curve, \( E_{0\to1}(z_{\text{ex}}) \), has to be adjusted to the measured data by adding an offset, \( z_{\text{offset}} \). In
principle, with the estimation of this offset the absolute tip-sample separation can be calculated.

α_{\text{elastic}} is shown in figure 6.25a. With the ansatz given above, an elastic deformation of the tip causes a modification of the length of the tunneling junction by δs. Therefore, the change in the phase integral is given by ∆P = k₀δs. For the (ν = 0 → 1) transition, the change of the force is given by ∂_z E_{0→1}. Considering the compliance, the value of the deformation can be estimated by δs = −C · ∂_z E_{0→1} if ∂_z E_{0→1} ≈ ∂_z E_0(z + δs) − ∂_z E_1(z). With this relation, the theoretical curve for α_{\text{elastic}} can be calculated by

\[
1 + α_{\text{elastic}} = e^{-\Delta P} \\
α_{\text{elastic}} = e^{-C \cdot k_0 \cdot ∂_z E_{0→1}} - 1.
\] (6.12)

Depending on the agreement of the theoretical and empirical values, the compliance of the tip, C, has to be adjusted and the procedure has to be performed again. The theoretical curves, shown in orange and green, are calculated with a compliance of C = 2.0 mN and C = 4.0 mN, respectively. The offset in the tip-sample separation has been estimated to be z_{\text{offset}} = 0.49 nm. In figure 6.25b several measurements performed with different tips are shown in different colors. In this figure the theoretical curves for three different compliances C = (2.0, 3.0, 4.0) mN are displayed. The offsets were adjusted individually to ∆z_{\text{offset}} = (0.34, 0.36, 0.40) nm for best correspondence.

Although the conformity of data and theory is convincing, some deviations can be observed in the diagrams, especially α_{\text{elastic}} shows a different behavior for small tip-sample separation and the transition energy is not in perfect correspondence with the measurements. These deviations can be explained by the following arguments. First of all, for the calculation of the physisorption potential two flat surfaces were assumed. The potential landscape may change if the shape of the tip apex or local deviations of the physisorption parameters are taken into account. Also, a one dimensional model was used where a three dimensional model may provide different solutions for the potential in the tunneling junction. Especially, the influence of lateral modes is neglected in the one dimensional approximation. Those effects may lead to additional states and, hence, additional transition energies as well as shifts of the energy levels can be expected. Another important parameter is the inverse decay length, k₀, which is used to scale the exponential in the theoretical
Figure 6.25 – (a) Shows the damping of the elastic channel, $\alpha_{\text{elastic}}$ evaluated from data, (red and black dots) and theoretical curves, $e^{-C k_0 \partial_z E_{0\rightarrow 1}} - 1$, (orange and green line), with $C = (2.0, 4.0) \text{ mN}$. Inset: Transition energy, $V_c$, measured on Au(111) (red and black dots). Lines correspond to theoretical transition energies, $E_{0\rightarrow 1}$. Theory was mapped with $z_{\text{ex}}(z_{\text{in}})$ and adjusted with an offset of $z_{\text{offset}} = 0.49 \text{ nm}$. (b) The parameters $\alpha_{\text{elastic}}$ and $V_c$ (inset) measured on Au(111) with different tips are shown. Three different compliances $C = (2.0, 3.0, 4.0) \text{ mN}$ and offset $\Delta z_{\text{offset}} = (0.34, 0.36, 0.40) \text{ nm}$ (orange, magenta, green) are plotted for comparison.
\( \alpha_{\text{elastic}} \). \( I-Z \) measurements for different tips show that the value of this parameter may change by up to 20\% leading to values of \( k_0 = [19 \text{ - } 23] \text{ nm}^{-1} \).

The reduction of \( \alpha_{\text{elastic}} \) at small tip-sample separation can be explained by two additional effects. Firstly, the assumption \( \partial_z E_{0 \rightarrow 1} \approx \partial_z E_0(z + \delta s) - \partial_z E_1(z) \) made above is no longer valid at small tip-sample separation because the deflection \( \delta s \) then decreases with smaller separation (shown later in section 6.4.7). According to equation (6.12) this results in a reduction of \( \alpha_{\text{elastic}} \). Secondly, the compliance is not necessarily constant. This means, by changing the force, the change of the tip-sample separation does not necessarily follow a linear dependency.

The measurements presented up to now were all taken in the same high conductance regime. In order to validate the model presented in this section, it would be important to see the evolution of \( \alpha_{\text{elastic}}(z) \), especially in the regime where the force changes sign and \( \alpha_{\text{elastic}} \) is expected to change sign as well. This requires a measurement over a wider range of conductances which also requires an exchange of the \( IV \) converter. Figure 6.26 shows the parameters, \( \alpha_{\text{elastic}} \) (black) and \( \eta_{\text{inelastic}} \) (blue), of a measurement in a range of more than 0.3 nm, which corresponds to a
dynamic range of three orders of magnitude with respect to zero bias conductivity. Because of this large range the curves were measured in three runs (indicated by different symbols) to change the IV converter and to adjust the range of the lock-in amplifier to optimal values.

At high conductivity (filled circles) the parameters were evaluated using $I-V$ curves and equation (6.7). For the two measurements at low conductivity (squares and triangles) $\delta_V I-V$ curves were analyzed using equation (6.6). However, the equation had to be modified by adding an additional peak with opposite sign in the regime where $\alpha_{\text{elastic}}$ changes sign (squares). The two peaks occur at different energies with $\Delta E \approx 2 \text{ meV}$. The damping is evaluated for both peaks which then contribute to an effective damping, $\alpha_{\text{elastic,eff}} = \alpha_{\text{elastic,1}} + \alpha_{\text{elastic,2}}$.

Close to the sample, $\alpha_{\text{elastic}}$ starts at high values already indicating a high compliance. At $\Delta z_{\text{ex}} \approx 0.2 \text{ nm}$ the expected change of sign takes place. A maximum is reached at $\Delta z_{\text{ex}} \approx 0.26 \text{ nm}$ and afterwards $\alpha_{\text{elastic}}$ converges to zero for increasing tip-sample separation. $\eta_{\text{inelastic}}$ is rising from about 10 % to a maximum of about 40 % at $\Delta z_{\text{ex}} \approx 0.2 \text{ nm}$ and drops of to zero for higher separations. The maximum of $\eta_{\text{inelastic}}$ and the change of sign of $\alpha_{\text{elastic}}$ occur at the same tip-sample separation. The decrease of $\eta_{\text{inelastic}}$ can be explained by a reduction of the lateral confinement which may suppress the Raman-like excitation.

A theoretical curve for $\alpha_{\text{elastic}}$ calculated with a compliance of $C = 4.0 \frac{\text{mN}}{\text{N}}$ and an offset of $z = 0.47 \text{ nm}$ is depicted by the red line. The agreement of model and evaluated data is striking. All features expected such as the zero-crossing of $\alpha_{\text{elastic}}$ corresponding to a change of the direction of force from repulsive to attractive interaction, the maximum, and the convergence to zero for high tip-sample separations are present in the data. This excellent conformity proofs the direct relation of $\alpha_{\text{elastic}}$ and the physisorption potential of hydrogen between two noble metals.

### 6.4.9 Hysteresis in $I-V$ curves

As mentioned in section 6.4.7 a hysteresis is expected in $I-V$ spectroscopy because the transitions $E_{1 \rightarrow 0}$ and $E_{0 \rightarrow 1}$ take place at different tip-sample separations. According to the explanation illustrated in figure 6.22 and the sketch in figure 6.24, those separations are given by
Figure 6.27 — (a) Deflection of the tip, δs, and (b) width of the hysteresis, ΔE₀→₁, calculated theoretically assuming different compliances for the tip, \( C = (2.0, 3.5, 5.0) \, \text{m/N} \).

\[
\begin{align*}
  z_{\text{in},1} & = z_{\text{ex}} + C \cdot \partial_z E_1(z_{\text{in},1}) \quad (6.13) \\
  z_{\text{in},2} & = z_{\text{ex}} + C \cdot \partial_z E_0(z_{\text{in},2}) = z_{1,1} + \delta s \quad (6.14)
\end{align*}
\]

which is the externally controlled \( z_{\text{ex}} \) plus the deflection according to the force of the corresponding state, \( \nu = 0 \) or \( \nu = 1 \). The displacement of the tip, \( \delta s \), can now be written as

\[
\delta s = z_{\text{in},2} - z_{\text{in},1} = C \cdot \partial_z E_1(z_{\text{in},1}) - C \cdot \partial_z E_0(z_{\text{in},2})
= C \cdot (\partial_z E_0(z_{\text{in},1} + \delta s) - \partial_z E_1(z_{\text{in},1})). \quad (6.15)
\]

With that, the value of the hysteresis, \( \Delta E_{0\rightarrow 1} \), is calculated using

\[
\Delta E_{0\rightarrow 1}(z_{\text{in}}) = E_{0\rightarrow 1}(z_{\text{in},2}) - E_{0\rightarrow 1}(z_{1,1}) = E_{0\rightarrow 1}(z_{1,1} + \delta s) - E_{0\rightarrow 1}(z_{1,1}). \quad (6.17)
\]

In order to determine the expected values and solve equation (6.15) for \( \delta s(z_{\text{in}}) \), analytic expressions of the functions are favorable. Therefore, \( \partial_z E_0(z) \) and \( \partial_z E_1(z) \) were fit by a fifth order polynomial yielding correlations of better than 99.9%. Thus, \( \delta s \) and \( \Delta E_{0\rightarrow 1} \) can be evaluated by solving equation (6.15) for \( \delta s \). The result is shown in figure 6.27 assuming different compliances of \( C = (2.0, 3.5, 5.0) \, \text{m/N} \).
To measure this effect, several $I$-$V$ curves were recorded at the same position but different tip-sample separations. A modulation amplitude of $V_{\text{mod}} = 1$ meV was applied to the bias. All curves share one intersection at $V = 0$ meV and $I = 0$ nA which can be used to correct for offsets in bias or current. The curves are displayed in figure 6.28. For better comparison negative bias and currents were inverted. Data at positive bias is shown in red and data at negative bias is shown in black. For high bias the curves are not equal because of a variation in the DOS.

Measurements were recorded starting from negative bias as indicated by the arrows. The first transition $E_{1 \rightarrow 0}$ occurs at a lower energy than the second transition $E_{0 \rightarrow 1}$. This is consistent with the prediction made above.

With increasing tip-sample separation, indicated by the smaller current, the difference of the transition energies, $\Delta E_{0 \rightarrow 1}$, is decreasing. The measured hysteresis, $\Delta E$, depending on the tip-sample separation is shown in figure 6.29 (black dots). An offset of $2 \cdot \Delta E_{\text{mod}}$ has to be added to the data because modulation shifts the transition energy by about $\Delta E_{\text{mod}} = 0.42$ meV on both sides according to section 6.4.4. Two theoretical curves are displayed with a compliance of $C = 2.0 \ \text{mN}$ (red) and $C = 1.0 \ \text{mN}$ (blue).
Figure 6.29 – Hysteresis, $\Delta E_{0\rightarrow1}$, of I-V curve depending on the tip-sample separation is displayed (black dots). An offset of $2\Delta E_{mod} = 0.84$ meV had to be added because of the modulation amplitude of 1 meV. Theoretical $\Delta E_{0\rightarrow1}$ with a compliance of $C = 2.0 \ \text{m/N}$ (red solid curve) and $C = 1.0 \ \text{m/N}$ (blue solid curve) is shown.

Deviations between theory and experiment can be explained by two arguments. Firstly, even small changes in the physisorption potential may lead to significant changes in $\delta s$ and $\Delta E_{0\rightarrow1}$. Secondly, the modulation amplitude leads to a shift in energy in the measured curve because of the step in the I-V curve. At a large step the measured transition energy will shift away from the true transition energy more than at a small step. This means at small tip-sample separation, where the step is large, the shift should be large as well and for small tip-sample separation the shift should be small. Taking this into account improves the conformity of the plot. Nevertheless, the predicted hysteresis can be extracted from measured data and, in principle, the result fits to theory consolidating the interpretation of a soft tip.

6.4.10 Correcting the inverse decay length

In figure 6.12 the inverse decay length $k(\Delta z)$ is shown. The dashed black line was measured at 40 meV well above the transition energy $E_{0\rightarrow1}$ leading to an excited molecule ($\nu = 1$). The inverse decay length is measured and displayed with respect to the externally controlled tip-sample separation leading to $k(\Delta z_{ex})$. In figure 6.30 this curve is shown again (black). With the model developed, the behavior
of $k(\Delta z_{ex})$ can be easily explained. As the tip approaches the sample the force acting on the tip is getting larger and the deflection increases. For the evaluation of $k(z)$ equation (2.10) is used. By using the values from the measurement, the equation depends on the externally measured tip-sample separation, $z_{ex}$, leading to

$$ k(z_{ex}) = \frac{dI(z_{ex})}{dz_{ex}}. \quad (6.18) $$

In order to transform the inverse decay length to depend on the real tip-sample separation, $z_{in}$, a correction factor has to be introduced. To calculate this factor $z_{ex}(z_{in})|_{C}$ was determined for different compliances, $C$. The derivate is then used to scale the inverse decay length

$$ k(z_{in}) = k(z_{offset} + \Delta z_{ex}) \cdot \frac{d_{ex}(z_{in})|_{C}}{d_{in}}. \quad (6.19) $$

$I$-$z$ measurements performed at the same bias without hydrogen in the junction showed a constant inverse decay length for those tip-sample separations. Therefore, the offset and the compliance are adjusted until $k(z_{in})$ is constant. The red
line in figure 6.30 shows the best result for this measurement. The compliance was determined to be $C = 0.2 \ \text{mN}$ with an offset of $z_{\text{offset}} = 0.45 \ \text{nm}$. This low compliance indicates a hard tip apex. The associated $I-V$ measurements taken with the same tip showed only a small damping, $\alpha_{\text{elastic}}$, which confirms the low compliance.
6.5 Pulling Au atoms

Having molecular hydrogen in the tunneling junction, an interesting effect was observed by applying a high bias (>5.5 eV) to the junction. To do so, the tip was placed on the clean surface using typical tunneling parameters (-70 meV, 1 nA). A short pulse of about 10 ms and -7.2 eV was applied to the tip. Afterwards, the image shown in figure 6.31a was taken at a tunneling bias of -70 meV. The position of the tip at the instant of the pulse is marked by the red cross. In this image, four straight lines of different length protrude from the surface. The lines are oriented in three different directions with an angle of 120°. The bright halo surrounding the lines and the lower side of the step edge can be attributed to an artifact at the tip because it was gone after the next pulse had been applied to the tip.

This procedure could be repeated reproducibly at a minimum bias pulse of 5.5 eV. The polarity of the pulse did not matter. No correlation was found between the exact

![Image of STM measurements](image)

**Figure 6.31** – STM measurements after pulsing the tunneling bias to \(|V|>5.5\) eV are shown. (a) After the first pulse (red cross) four protruding lines appear on the surface (50x50x0.4 nm³, -70 meV, 0.5 nA). (b) Scanning the surface with high bias creates many lines on the surface (50x50x0.5 nm³, -7.2 eV, 0.5 nA). (c) Zoom to a single line and cross section in red (10x10x0.2 nm³, -75 meV, 1 nA) shows the good correspondence to the height of a single atom [59].
position, length, or direction of the lines and the position of the tip or the strength of the bias pulse. In some cases the lines were generated at a distance of more than 10 nm away from the pulse position. However, it seemed that the lines appeared only in the same terrace on which the pulse was applied. In figure 6.31b the image was scanned with a bias of -7.2 eV. This lead to a complex pattern of different lines on the surface. By repeating this scan several times, only a few more lines were created and afterwards the pattern seems to have reached saturation.

In figure 6.31c, one of the lines is shown in more detail. Also a cross section is shown in the right panel along the red line depicted in the image. The height of the lines were determined to be at around $(0.17 \pm 0.02)$ nm at $|V| < 100$ meV corresponding nicely to the height of a single Au adatom of about 0.15 nm in this bias regime [59, 151].

By taking a closer look on the gold surface beneath the lines, it can be seen that the herringbone reconstruction changed compared to the clean surface. In figure 6.31b the reconstruction has nearly vanished and, after the saturated state has been reached, the reconstruction disappeared completely.

This effect was not yet reported in the literature neither experimentally nor postulated by theory. Since the lines reach a saturation at some point and the herringbone reconstruction vanishes, a possible mechanism would be that the surface layer of the gold substrate is taking the same configuration as the bulk layers. That means one atom out of 23 atoms is pulled out of the surface layer forming chains of adatoms. Since the phenomenon only occurs in the presence of molecular hydrogen after applying a sufficiently high bias, one can assume that the hydrogen dissociates in the tunneling junction and diffuses across the surface. The dissociation energy of hydrogen is 4.478 eV [66]. The atomic hydrogen then triggers a reaction were a chain of atoms is pulled out of the surface and the reconstruction of the surface layer is removed. Similar result were reported from self-assembled monolayers of alkanethiolate on Au(111) where adatoms are created and the herringbone reconstruction is lifted [152, 153]. By comparing the length of the solitone walls $(295 \pm 15)$ nm, which corresponds approximately to the number of additional atoms in the surface layer, with the length of the chains of adatoms $(283 \pm 17)$ nm, the theory can be verified.

In figure 6.32 an $I-V$ measurement performed along a line perpendicular to the protrusion is displayed. The spectra were recorded at the positions marked with a cross in the inset of the figure. Away from the protrusion (red) the typical feature of $\partial^2 V / I-V$ curves with hydrogen present in the junction can be observed. The spectra show
a constant conductivity for $|V| > 15$ meV, a transition region for $|V| = |V_c| \approx 7$ meV, and an elevated conductivity for $|V| < |V_c|$. The spectrum taken on the protrusion (blue) shows a symmetric increase of the conductivity around zero bias without the characteristic behavior of H$_2$:Au(111). This may be due to a depletion of hydrogen molecules on top of the atomic chain because of a decrease of the depth of the physisorption potential.

6.6 Summary

Effects of hydrogen molecules physisorbed on noble metal surfaces were analyzed in this chapter. It was shown that using a silver or a tungsten tip has a great influence on the observed phenomena.

The general preparation techniques for single crystals of Au(111), Cu(111), and Ag(111) were presented at the beginning of the chapter. The crystals were cleaned in alternating steps of sputtering and annealing until a sufficiently clean surface was achieved. The result was then checked by XPS to verify the chemical purity of the surface, by STM to check the topography, and by STS to see whether tip and sample were spectroscopically clean.
In the first experiments a tungsten tip was used in combination with a Au(111) sample. After the system was exposed to $H_2$ the hydrogen dissociated at the tungsten surface and the topographical resolution on an Au(111) surface increased so that atomic resolution was achieved. This could be used to recalibrate the lateral displacement of the STM. Inelastic electron tunneling spectroscopy measurements revealed a damping of the phononic structure and an additional contribution at about 30 meV which was attributed to the vibration of a chemisorbed hydrogen atom. A possible explanation for the increased resolution was presented adapting the results of Hapala et al. [122] and Weiss et al. [119], where the hydrogen atom at the very front of the tip apex is moving due to Pauli repulsion and thus, improves the resolution.

For the second experiment the tip material was changed to silver. Au(111) and Cu(111) were used as samples. Exposing the system to molecular hydrogen led to distinct characteristic features in $I-V$ and $I-z$ spectroscopy. The latter was used to determine the inverse decay length, $k(z)$, which showed a peak shifting with varying bias. This peak was modeled mathematically to develop a model function for $I-V$ spectra by applying the WKB approximation. The characterization of such spectra showed a damping of the elastic channel by $\alpha_{\text{elastic}}$ as well as an opening of an inelastic channel of efficiency $\eta_{\text{inelastic}} > 0$ at a critical bias, $V_c$.

An analysis of the peak shape and line width of $\partial V/I-V$ curves at different modulation amplitudes revealed that a Lorentzian function yields best fitting results for low modulation broadening resulting in a line width of about $0.82 \text{ meV} \approx 2k_BT$. A Voigt Peak gave better results for higher amplitudes. Further measurements were conducted with a modulation amplitude of 1 meV. Hereafter, the rotational modes of a hydrogen molecule in the junction at about $E_{\text{rot}} = 42 \text{ meV}$ were investigated. The absolute intensity of the peak did not change at various tip-sample separations for the displayed measurement on Au(111). This phenomenon was attributed to a saturation effect.

In the next step the dependence of the characteristic parameters on the tip-sample separation was evaluated. While the critical bias and the elastic damping decreased with increasing separation, the inelastic efficiency increased.

Assuming a saturated state, the measured phenomenon was interpreted with a simple physical model of a soft tip apex with a compliance $C$. The tip is pushed towards or pulled away from the surface according to the force exerted from a hydrogen molecule in the separation-dependent physisorption potential. Because of the deflection of the tip apex, one has to distinguish between the real tip-sample sepa-
ration, $z_{\text{in}}$, and an external tip-sample separation, $z_{\text{ex}}$, given by the piezo. By exciting the molecule in the junction, the force increased leading to a sudden change of the deflection. This could be used to calculate the damping $\alpha_{\text{elastic}} = e^{-C \cdot k_0 \cdot \delta s \cdot E_{0\rightarrow1} - 1}$. $V_c$ was attributed to the transition energy $E_{0\rightarrow1}$.

Additional measurements with different microscopic tips were presented and compared to theory. Adjusting the theoretical curves to those measurements revealed a compliance of the tip of $(2.0-4.0) \frac{mN}{\mu m}$. These values seemed convincing since the compliance of a single CO molecule at the tip of an AFM was determined to about $4.0 \frac{mN}{\mu m}$ [150]. Deviations from the theoretical curves were explained by the simple model for the physisorption potential, the varying inverse decay length $k_0$ and the change of $\delta s$ for small tip-sample separation. Another series of measurements over a wider range of separations showed the expected change of sign of $\alpha_{\text{elastic}}$. It also showed a maximum in the inelastic channel, $\eta_{\text{inelastic}}$, which decays to zero for large separations. This measurement was considered a proof for the simple mechanical model.

The model of a soft tip apex also predicts a hysteresis in $I-V$ measurements. The deflection of the tip at the transition, $\delta s$, and the value of the hysteresis, $\Delta E_{0\rightarrow1}$, were evaluated theoretically. In order to compare it to experiment, an offset had to be added because the measurement was performed while applying a modulation amplitude causing a shift in the measured transition energy, $V_c$. The shift due to the modulations amplitude also caused some deviations from theory.

Finally, a method was presented correcting the inverse decay length $k(z_{\text{ex}})$ to $k(z_{\text{in}})$ at a bias above $V_c$. It was possible to determine the compliance ($C = 0.2 \frac{mN}{\mu m}$) and the offset ($z_{\text{offset}} = 0.50 \text{ nm}$) of an exemplary curve.

A new phenomenon on Au(111) was discussed in the final section of the chapter. Applying a bias of more than $5.5 \text{ eV}$, corresponding approximately to the dissociation energy of hydrogen, to the junction caused an irreversible change of the topography if hydrogen was present. Straight lines, forming an angle of $120^\circ$, with a height of about $0.17 \text{ nm}$ appeared randomly on the surface. The phenomenon was attributed to gold atoms which are pulled out of the surface layer resolving the herringbone reconstruction. $I-V$ spectroscopy revealed a smearing of the hydrogen signature which may be due to the locally changed physisorption potential.
Chapter 7

Summary and Conclusion

The present dissertation contains three major objectives. The first is an improvement of the evaluation process of IETS data using Wavelet analysis. This requires a detailed understanding of all parameters especially the temperatures of tip and sample. Therefore, the second one is the calibration of these temperatures using a superconductive sample. Further influences of the tip on topography and spectroscopy were studied in the third objective, where the influence of hydrogen in the tunneling junction was investigated with different tip materials.

In the framework of this work several improvements of the setup and the sample preparation were achieved. With the shielding of radiation leaks the temperature of the tip could be lowered by 1 K. The preparation of single crystals was added to the repertoire of sample materials and was explained in chapter six. Terraces > 50 nm with a defect density below $5 \cdot 10^{-2}$ nm$^{-2}$ could be prepared reproducibly.

Chapter four focused on the quantitative investigation of vibrational modes using IETS measurements. The analysis of this spectroscopy method, as shown in earlier publications, was briefly discussed. First, the measured data is filtered and split into even and odd components. The background of the odd component is then corrected manually and Gaussian peaks are fit to the spectrum to get the positions of the vibrational modes. This method is very time consuming and not standardized because of the manual subtraction of the background. Therefore, a complementary evaluation technique, namely the Wavelet analysis, was introduced to avoid individual treatment of each measured curve. Measured data was transformed with a Mexican-hat mother function of width $\sigma$ that is expected for peaks in IETS experiments. Local maxima then correspond to the position of inelastic features. These positions were transferred to a barcode plot which can be used for further analysis.
The presented method is an improvement and supplement of the former evaluation process. It showed good correspondence of results and allows for automation.

Chapter five focused on the calibration of tip and sample temperature. A superconducting Nb(110) film and a normal conducting tungsten tip which is in loose thermal contact were used for this procedure. \( I-V \) spectroscopy showed typical features of a superconductor - normal conductor junction in STM. Using the WKB approximation to calculate \( I(V) \) curves with different temperatures for tip and sample allowed to discriminate the different temperatures by applying a Levenberg-Marquart algorithm. The temperature of the superconducting sample, \( T_s \), was directly measured at the base plate since it is in good thermal contact. Accordingly, the free parameters were the temperature of the normal conducting tip, \( T_n \), and the superconducting gap parameter, \( \Delta \). At a sample temperature of 5.02 K the tip temperature was elevated to be more than 3 K above the sample temperature to \((8.45 \pm 0.03)\) K.

By heating the base plate the temperature dependence of the parameters was investigated. The transition temperature was determined to be \( T_c = (9.25 \pm 0.02)\) K, which is in good agreement with literature. The temperature dependence of the superconducting gap parameter, \( \Delta(T) \), also matched very well with the theoretically expected curve. The relation \( 2\Delta(0) = 4.06 \cdot k_B T_c \) lies well within the values found in former experiments. A first order approximation of the temperature of the normal conducting tip led to a linear dependence of: \( T_n = (4.69 \pm 0.33)\) K \(+ (0.70 \pm 0.04) \cdot T_s\) indicating a background temperature of heat radiation of about 15.6 K.

In chapter six of the present dissertation the influence of hydrogen in the tunneling junction was investigated. It was shown that the material of the tip has an important influence on the phenomena occurring after molecular hydrogen was brought into the STM chamber. Using a tungsten tip, the topographic resolution of the microscope on a plane gold surface increased so that atomic resolution was achieved. IETS revealed a damping of inelastic features above 10 meV if hydrogen was present and an additional mode at about 30 meV which was attributed to a vibrational mode of a hydrogen atom measured by Barnes et. al [143]. These effects were explained by a dissociative chemisorption of hydrogen at the tungsten tip [137]. The front atom may then be a hydrogen atom which moves due to Pauli repulsion leading to an enhanced resolution as proposed by Weiss et al. and Hapala et al. [28, 122].

A different phenomenon was observed using a silver tip. Characteristic features in \( I-V \) and \( I-z \) spectroscopy appeared after the sample was exposed to hydrogen in the LT-STM chamber. First, the inverse decay length, \( k(z) \), was evaluated revealing a
peak that shifts with varying bias on a constant background. This shifting peak was used as an ansatz for a mathematical model to describe $I$-$V$ data by using the WKB approach. The best fit function for the peak in $\partial_{V} I$-$V$ was determined depending on the modulation amplitude. For small modulation amplitudes $V_{\text{mod}} \leq 0.1$ meV a Lorentzian showed best correspondence, a Voigt peak was found to fit best for higher amplitudes. Measurements at very low modulation amplitude revealed a line width of about 0.82 meV which corresponds to thermal broadening of only $2 \cdot k_{B} T$. This was attributed to a non-linear switching behavior in the tunneling junction.

Some data also contained information on the rotational transition energies of hydrogen. The $J(0 \rightarrow 2)$ transition was observed on Cu(111) and on Au(111). A measurement performed on Au(111) was shown where the second derivative of the current exposed a constant signal with changing tip-sample separation. A saturation effect of the rotational channel could explain this result.

In a next step the characteristic parameters extracted from $I$-$V$ spectroscopy were studied depending on separation. While the characteristic bias, $V_{C}$, and the elastic damping, $\alpha_{\text{elastic}}$, decreased with increasing tip-sample separation, the inelastic efficiency, $\eta_{\text{inelastic}}$, increased up to 40%.

The phenomenon was interpreted such that the vibrating hydrogen molecule exerts a force due to the separation dependent physisorption well leading to a deflection of the mechanically soft tip apex. This interpretation explains the behavior seen in all measured curves. With the method for the evaluation of the tip compliance presented hereafter, the values for the compliance of different tips could be determined. Within the model, it was found that the apex of a silver tip would be surprisingly soft with values in the range of $C = (2.0 - 4.0) \cdot 10^{7}$ N/m. Since $\alpha_{\text{elastic}}$ is related to $\partial z E_{0 \rightarrow 1}$ a change of the sign was expected. This change was observed in a measurement which was performed over a wide range of tip-sample separations to proof the correctness of the physical model. Another verification was given by the evaluation of the hysteresis in $I$-$V$ spectroscopy. A correction factor for the inverse decay length measurement with a bias above the transition energy was derived. Due to the deflection of the tip $k(z_{\text{ex}})$ has to be transformed to $k(z_{\text{in}})$ leading to a constant value of the inverse decay length.

Recalling previous experiments of other groups, some of the measured phenomena can be explained with the physical model presented in this work. For example, the two-level system which was not specified earlier [29, 31, 30] is now directly attributed to a transition of the hydrogen in the physisorption potential. The shift of
this transition energy [115] is explained by the change of the physisorption potential and the deformation of the tip apex with separation.

Finally, a new phenomenon was observed where pulses of the tunneling voltage above 5.5 eV generated protrusions in straight lines when hydrogen was present. The lines were attributed to Au-adatoms pulled out of the surface by dissociated hydrogen because the herringbone reconstruction vanished. $I-V$ measurements revealed the corresponding change in the physisorption landscape on the protrusions.

For future experiments one can think of exploiting the soft tip apex as a sensor for small forces in the regime of piconewtons. For example, forces of single molecules adsorbed on the surface could be probed with a common STM setup instead of a combined and therefore complex AFM-STM setup [154]. Another idea is using the information of the separation dependent measurements and extract local properties of the physisorption potential such as the parameters of the van der Waals interaction on single molecules or at step edges of surfaces.
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• Matthias Stocker, Simon Röger, and Berndt Koslowski: "The hydrogen molecule in a vice"
  Physics Boat, Helsinki, 2015 (Talk)
Lebenslauf

Persönliche Daten

Name Matthias Michael Stocker
Geburtstag 05. Dezember 1985
Geburtsort Laupheim

Schulische Laufbahn

09/1992 - 07/1996 Grundschule Illerrieden
09/1996 - 07/2005 Illertal-Gymnasium Vöhringen
Abschluss: Abitur

Akademische Laufbahn

10/2005 - 05/2011 Studium der Physik an der Universität Ulm
Abschluss: Diplom
08/2008 - 02/2009 Auslandsaufenthalt an der Universität Uppsala
Schweden
08/2011 - 12/2015 Wissenschaftlicher Mitarbeiter am Institut für Festkörperfysik, Universität Ulm

Ulm, Dezember 2015
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Die Danksagung wurde aus Gründen des Datenschutzes entfernt.
Erklärung

Ich versichere außerdem, dass ich die beigefügte Dissertation nur in diesem und keinem anderen Promotionsverfahren eingereicht habe und dass diesem Promotionsverfahren keine endgültig gescheiterten Promotionsverfahren vorausgegangen sind.

Ulm, den .................................................................

Matthias Stocker