

Electron Transport Studies – An Electrochemical Scanning Tunneling Microscopy Approach

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Elektronentransportstudien – Ein Elektrochemischer Ansatz mittels *in situ* Rastertunnelmikroskopie

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Abstract in English

Since the introduction of the semiconductor-based technology 60 years ago, the development of electronic devices was mostly fostered by the trend towards the miniaturisation of logic elements. For nearly 40 years, a smaller size of a single circuit element automatically meant an increase of performance and a decrease of an energy consumption. However, now the “inorganic” technology already reached the nanodomain with feature sizes less than 100 nm. At this scale the quantum effects play a significant role. Thus, the macroscopic technology approaches its physical limits: it is still possible to produce smaller logic elements, but their characteristics may not be improved. The existing trend predicts a decrease of the size of logic elements down to size of a single atom in a short time. Therefore, quantum effect are expected to determine the properties of future logic elements.

A molecule-based electronics might have the potential to develop as an alternative to traditional inorganic devices. According to this concept, ultimately a single molecule is used as an element of electric circuit. The molecular approach provides several unique possibilities. Molecular design allows to use molecules with specifically adjusted properties to implement localized functions. The “bottom-up” fabrication via self-organization and recognition of molecular building blocks allows to produce structures with a high reproducibility and well-defined properties. Finally, the specific properties of molecular structures allow to construct functional devices.

Current studies on molecular electronics are focused on the following fundamental questions:

1. How to synthesize functional molecules?
2. How to prepare electrical circuits and to incorporate hybrid structures?
3. What are the electrical properties of such circuits?
4. What is the correlation between molecular structure and their functionality?
5. How to use molecular electronic devices in a real life applications?

To address these questions, joint efforts of physicists, chemists and electrical engineers; experimentalists and theoreticians, are required. Studies of electron transfer (ET) properties of single molecular junctions are of importance for fundamental science as well. They challenge both experimental and theoretical branches of modern science. At present time, the major part of our knowledge on the properties of single molecules is still based on the results of investigations carried out under ultra-high vacuum and/or at low temperatures. These conditions are not appropriate for production systems.

Experiments at electrified solid-liquid interface (*i.e.*, in electrochemical environment) represent an interesting alternative approach for addressing fundamental concepts

and principles of the ET processes. Aqueous electrolytes represent a natural environment for “living” functional macromolecules. And last, but not least: electrochemists have more than a century of experience in studying molecular systems at interfaces. Meeting and cooperation of electrochemists with mesoscopic and surface science physicists open new prospectives in the field of molecular electronics.

Our group works in the field of electrochemical surface science – a combination of approaches, characteristic for electrochemistry and physical surface science. The work presented here describes the application of scanning tunneling microscopy (STM) and electrochemical techniques to investigate the ET in various systems. With respect to molecular electronics, it covers topics 2 to 4 of the agenda presented above. A strong emphasis is put on methodological aspects of the experiments carried out. The experimental results are accomplished by the theoretical description of the studied processes, well known as well as derived in the frame of existing collaborations. Thus, I demonstrate how our approach contributes to the overall development of molecular electronics and to the understanding of ET at different levels.

An introduction, a description of principles and procedures of experiments are presented in chapters 1–3. Chapter 4 describes a basic electrochemical scanning tunneling microscopy (EC STM) experiment. Au(111)-(1 × 1) substrates were employed in all studies. The substrate was modified by ionic adlayers, formed by the coadsorption of Cu^{2+} with SO_4^{2-} or Cl^- . Steady state STM images were recorded and used to evaluate the structure of the respective adlayers. Transitions between different adlayers were followed in time resolved STM experiments. The obtained information on the kinetics and mechanisms of phase transitions is not accessible by macroscopic electrochemical methods based on current-potential or current-time measurements. Current-distance scanning tunneling spectroscopy (STS) was used to probe the tunneling response of bare Au(111)-(1 × 1), $\text{Cu}^{2+}\text{--SO}_4^{2-}$ and $\text{Cu}^{2+}\text{--Cl}^-$ adlayers. The $I - z$ curves exhibit characteristic responses of the bare and/or adsorbate-modified adlayer.

Chapters 5–7 describe measurements of the conductance of single atomic and molecular junctions employing the STM “stretching” techniques in three archetypal systems. The latter consists of bringing an STM tip in contact with a metal surface or adlayer and monitoring the current through the junctions upon retraction of the tip. Stable quantum point contacts (QPCs) or single molecular junctions (SMJs) result in constant current plateaus in the respective $I - z$ curves. They are then analyzed statistically to extract the conductance of single junctions.

Chapter 5 describes the stretching experiments with Au QPCs. I introduced various statistical approaches to determine the conductance of a single junctions. The obtained results are in good agreement with existing experimental and theoretical data. However, they also demonstrate new properties of Au QPCs, such as an electronic shell effect and a correlation between electrical and mechanical properties of Au QPCs.

Chapter 6 describes stretching experiments in an archetypal molecular system. SMJs are formed with alkanedithiols (SnS) chemically bound to two Au electrodes via thiol (SH) linkers. Detailed experiments are carried out with 1,8-octanedithiol (S8S). Electrochemical properties and the structure of the self-assembled monolayers (SAMs) formed by S8S are in agreement with other results. Two types of SAMs – a densely packed adlayer of vertically oriented molecules or a layer of flat lying molecules – may be formed upon variation of the assembly conditions. The S8S SAMs were used as substrates in the stretching experiments. They demonstrated, that the S8S conductance is unaffected by the variation of the environment (Ar atmosphere, aqueous electrolyte, in-

ulating organic solvent mesitylene), but the probability of SMJ formation is enhanced by the presence of molecules in solution. The latter condition was used to explore the chain length dependence of the SnS conductance. The careful investigation demonstrated three types of SMJ formed for each SnS molecule. Complementary *ab initio* simulation (F. Evers, A. Bagrets, Forschungszentrum Karlsruhe) demonstrated that the variability of the SMJ conductance is caused by the interplay of the Au-SH contact and to an intrinsic conformational degree of freedom of the SnS molecules.

Chapter 7 presents conductance studies with SMJs formed by Au and 4,4'-bipyridine (44BP) – a molecule with two pyridyl rings. The latter is an intrinsically conjugated, highly conductive anchoring group. It binds via the formation of a donor-acceptor bond between a lone electron pair of the N atom and an empty s -orbital of Au. Four different types of SMJs, each having a potential-independent conductance, were found. The overall range of conductance values covers more than 2 orders in magnitude. Complementary *ab initio* simulations of the conductance in Au-44BP-Au SMJs demonstrated a much stronger effect of contact geometry and molecular conformation (*i.e.*, tilt angle between two pyridyl rings), compared to the case of SnS . The latter is closely related to the nature of the donor-acceptor coupling between the pyridyl ring and the Au leads.

Finally, the results of experiments on the ET enhancement employing the redox-active molecules (N-hexyl-N'-(6-thiohexyl)-4,4'-bipyridinium) were analyzed (chapter 8). The current-voltage electrochemical scanning tunneling spectroscopy (EC STS) experiments carried out were reported elsewhere (Zhihai Li, Ph.D. thesis, RWTH Aachen, 2007). The theoretical model of A. Kuznetsov and J. Ulstrup adopted by me, was employed to describe the observed phenomena. A very good agreement between experimental data and predictions of the model was found. The applicability and limitation of the model and of the corresponding experiments were discussed.

Zusammenfassung auf Deutsch

Seit der Einführung der auf Halbleiter basierenden Technologien vor 60 Jahren wurde die Entwicklung elektronischer Bauteile vor allem durch den Trend zur Miniarisierung von Logikelementen vorangetrieben. Während der vergangenen 40 Jahre führte die Verkleinerung eines einzelnen IC-Bausteins zu höherer Leistung und einem kleineren Energieverbrauch. Heute hat die "Silizium-basierende" Technologie die Nanowelt in der Größenordnung von unter 100 nm erreicht. Dabei gewinnen Quanteneffekte wachsende Bedeutung. Die makroskopische Technologie erreicht zunehmend ihre physikalischen Grenzen. Es ist zwar möglich, noch kleinere Logikelemente herzustellen, aber deren Eigenschaften werden nur wenig verbessert bezogen auf den Kostenaufwand. Extrapolationen basierend auf Moore's Law sagen eine Verkleinerung der Logikelemente bis hin zur Größe einzelner Atome innerhalb der nächsten Jahre voraus. Es ist daher zu erwarten, dass zunehmend Quanteneffekte die Eigenschaften zukünftiger Logikelemente bestimmen werden.

Auf der Suche nach alternativen Ansätzen zur anorganischen, Silizium-basierenden Elektronik stellt die Vision einer Molekül-basierende Nanoelektronik eine attraktive Alternative dar. Der molekulare Ansatz eröffnet einzigartige Möglichkeiten: gezielt synthetisierte Moleküle ermöglichen die Implementierung lokalisierter Funktionen mit einstellbaren Eigenschaften. Mithilfe von "bottom-up" Strategien, basierend auf Selbstorganisation und Erkennung molekularer Komponenten, können molekulare Nanostrukturen mit wohldefinierten Eigenschaften reproduzierbar hergestellt werden. Die spezifischen Eigenschaften solcher molekularer Strukturen können zu neuartigen Bauelementen, z. B. mit Dioden-, Transistor oder einer Speicherfunktion, führen.

Gegenwärtig konzentrieren sich die Aktivitäten auf dem Gebiet einer Molekül-basierenden Elektronik auf die folgenden grundlegenden Fragestellungen:

1. Wie können funktionale Moleküle hergestellt werden?
2. Wie können elektrische Schaltkreise gebaut und Hybridstrukturen integriert werden?
3. Welche sind die elektrischen Eigenschaften solcher Schaltkreise?
4. Welche Korrelationen existieren zwischen Molekülstruktur und dessen Funktionalität?
5. Welche technologischen Anwendungsgebiete sind für nanoelektronische Bauelemente basierend auf molekularen Strukturen potentiell relevant?

Zur Adressierung dieser Fragestellungen sind enge Kooperationen zwischen Vertretern unterschiedliche Fachdisziplinen, wie z. B. Physik, Chemie, Elektrotechnik als auch zwischen Experimentatoren und Theoretikern essentiell. Untersuchungen zum

Elektronentransfer in (Einzel-)molekularen Brücken sind sowohl im Bereich der modernen Grundlagenforschung als auch für potentielle Applikationen in einer zukünftigen Nanoelektronik von großer Bedeutung. Gegenwärtig basieren unsere Kenntnisse zum Verhalten von Einzelmolekülen insbesondere auf Arbeiten im Ultrahochvakuum und (oft) bei tiefen Temperaturen. Die Übertragung dieser experimentellen Ansätze auf applikationsrelevante Fragestellungen ist komplex.

Experimente an potential-kontrollierten fest-flüssig Grenzflächen (z.B. in einer elektrochemischen Umgebung) stellen eine interessante Alternative dar, um grundlegenden Konzepte und Prinzipien von Elektronentransferprozessen unter definierten Bedingungen zu adressieren. Wässrige Elektrolyte repräsentieren die natürliche Umgebung für eine Vielzahl funktionaler biologischer (und nichtbiologischer) Makromoleküle. Darüber hinaus verfügen Elektrochemiker mehr als einhundert Jahre Erfahrungen aus methodischen, konzeptionellen und experimentellen Untersuchungen zu molekularen Systemen an Grenzflächen. Die Kombination elektrochemischer Ansätze mit Konzepten aus der mesoskopischen und Oberflächenphysik eröffnet spannende neue Perspektiven für das noch junge Gebiet einer Molekül-basierenden Elektronik.

Unsere Gruppe arbeitet auf dem Gebiet der elektrochemischen Oberflächenwissenschaften, und kombiniert klassische elektrochemische Ansätze mit modernen experimentellen Ansätzen und Konzepten aus der Oberflächenphysik. Die vorliegende Dissertation beschreibt Anwendungen von Rastertunnelmikroskopie (STM) in Kombination mit makroskopischen elektrochemischen Techniken zum Studien von Elektronentransferprozessen für ausgewählte Systeme. Bezogen auf die Fragestellungen zu einer Molekül-basierenden Elektronik werden speziell die Themen 2 bis 4 adressiert. Neue methodische Entwicklungen der experimentellen Ansätze werden mit der theoretischen Beschreibung der studierten Prozesse und Beobachtungen kombiniert. Letztere basierend auf gemeinsamen Arbeiten mit Kooperationspartnern (Bagrets, Evers) sowie ausgewählten, in der Literatur veröffentlichten Ansätzen (phänomenologische Theorie zum Elektronentransport von Kuznetsov und Ulstrup). Die vorgelegte Arbeit demonstriert an ausgewählten Beispielen den wichtigen Beitrag elektrochemischer Ansätze für die Entwicklung und potentielle Implementierung einer Molekül-basierenden Elektronik sowie zum Verständnis von Elektronentransferprozessen.

Die Arbeit ist wie folgt gegliedert: Der Einleitung folgt in den Kapiteln 1 bis 3 die Beschreibung der Grundlagen der verwendeten experimentellen Techniken und Ansätze. Kapitel 4 diskutiert die Unterpotentialabscheidung (UPD) von Kupfer auf Au(111)-(1 × 1) in H₂SO₄ in Ab- und Anwesenheit kleiner Mengen Chlorid. Neben den "steady state" Strukturen von Substrat und ausgewählten Schichten co-adsorbierter Cu²⁺, SO₄²⁻ oder Cl⁻ Ionen wurden Strukturübergänge zwischen diesen Adsorbatschichten mittels zeitaufgelöster *in situ* STM Experimente studiert. Basierend auf rastertunnelspektroskopischen Strom-Abstandsmessungen (*I* – *z* STS) wurden elektronische Spektren für die Adsorbat-freie Au(111)-(1 × 1) Oberfläche sowie die Cu²⁺–SO₄²⁻ und die Cu²⁺–Cl⁻ – UPD Adsorbatschichten gemessen. Der Verlauf der *I* – *z* Charakteristiken konnte mit der Struktur der elektrochemischen Doppelschicht in Ab- und Anwesenheit der Cu – UPD Schichten korreliert werden.

In den Kapiteln 5 bis 7 werden Messungen zum Ladungstransport in atomaren und molekularen (Einzel-) brücken vorgestellt. Die Methode basiert auf der kontrollierten Bildung metallischer Nanokontakte bzw. molekularer Brücken zwischen einer STM Spitze und einem reinen bzw. Adsorbat-bedeckten Metallsubstrat. Das Aufbrechen der gebildeten Kontakte bzw. Brücken wird während des "Zurückziehens" der STM

– Spitze in Form von $I - z$ Charakteristiken aufgezeichnet. Die Bildung von stabilen Quantenpunktkontakten (QPK) oder Einzelmolekül-Brücken (SMJ) repräsentiert sich in Plateaus der $I - z$ Kurven. Die experimentell gemessenen Einzelkurven wurden mittels verschiedener statistischer Ansätze ausgewertet, um die Leitfähigkeit von Einzelbrücken zu extrahieren.

Kapitel 5 beschreibt Transportexperimente mit Goldnanokontakten (Au-QPK). Um die Leitfähigkeit und andere Charakteristika von Einzelkontakten zu ermitteln, wurden verschiedene statistische Ansätze entwickelt. Die erhaltenen Ergebnisse sind in guter Übereinstimmung mit bekannten experimentellen und theoretischen Daten, und zeigen darüber hinaus auch neue Eigenschaften von Au-QPK, wie z.B. einen elektronischen “Shell Effekt” sowie eine direkte Korrelation zwischen den elektrischen und mechanischen Eigenschaften von Au-QPK.

Kapitel 6 beschreibt Einzelmolekül Transportexperimente mit molekularen Brücken bestehend aus Alkandithiolen (SnS) im Kontakt mit zwei Goldelektroden über Thiol-Endgruppen. Detaillierte Experimente wurden insbesondere mit 1,8-Octandithiol (S8S) durchgeführt. Zunächst wurden die elektrochemischen Eigenschaften und die Struktur der selbstorganisierten S8S Monoschichten auf Au(111)-(1 × 1) untersucht. Bei kleinen Bedeckungsgraden sind die S8S Moleküle planar orientiert, während sie bei hohen Bedeckungsgraden eine ungeordnete, dicht-gepackte Adsorbatschicht senkrecht orientierter Moleküle bilden. Beide Typen der Adsorbatschicht kamen in den Einzelmolekültransportexperimenten in unterschiedlicher Umgebung (Argon Atmosphäre, wässriger Elektrolyt, Mesitylen) zum Einsatz. Die Wahrscheinlichkeit der Bildung von Einzelmolekülbrücken ist am grössten, wenn in der Volumenphase (Lösung) S8S Moleküle angeboten werden. Unter diesen Bedingungen wurde auch die Abhängigkeit der Leitfähigkeit der Einzelmolekülbrücke SnS von der Kettenlänge studiert. Die sorgfältigen experimentellen Studien zeigten die Existenz von drei unterschiedlichen Gruppen von Einzelmolekülleitfähigkeiten. Komplementäre *ab initio* Simulationen von A. Bagrets und F. Evers (Forschungszentrum Karlsruhe) ergaben, dass die experimentell gefundenen 3 Typen von Einzelmolekülleitfähigkeiten auf Unterschiede in der Au-SH Kontaktgeometrie sowie der Konformation der SnS Moleküle zurückgeführt werden können.

In Kapitel 7 werden Ergebnisse einer Studie zur molekularen Leitfähigkeit von 4,4'-Bipyridin (44BP), ein Molekül bestehend aus 2 Pyridyl-Ringen, immobilisiert zwischen zwei Goldelektroden vorgestellt. 44BP ist intrinsisch konjugiert und besitzt zwei elektrisch gut leitende Ankergruppen, welche durch Herausbildung einer Donor-Akzeptor Bindung zwischen dem freien Elektronenpaar am Ringstickstoff mit dem unbesetzten s -Orbital eines benachbarten Goldatoms hybridisieren. Die Experimente ergaben vier unterschiedliche Einzelmolekülleitfähigkeiten, die nahezu unabhängig vom angelegten Elektrodenpotential sind. Der Bereich der gefundenen Werte erstreckt sich über zwei Größenordnungen. Komplementäre *ab initio* Simulationen ergaben einen dominierenden Effekt der Kontaktgeometrie und der molekularen Konformation (Rotationswinkel zwischen den beiden Pyridylgruppen) auf die Leitfähigkeit der SMJ. Der Einfluss beider Faktoren ist im Falle von 44BP deutlich stärker als für molekulare Brücken mit SnS . Ursache ist die dominante Donar-Akzeptor Bindung zwischen dem Pyridyl-Ring und den beiden Goldelektroden.

In Kapitel 8 werden Experimente zum Elektronentransfer mit dem redoxaktiven Molekül (N-hexyl-N'-(thiohexyl)-4,4'-bipyridin) vorgestellt. Die experimentellen Untersuchungen basieren auf gemeinsamen Studien mit Dr. Z. Li (Ph.D. thesis, RWTH

Aachen, 2007). Zur theoretischen Beschreibung der gefundenen Tunnelresonanzen wurde ein Modell von A. Kuznetsov und J. Ulstrup adaptiert und geeignet modifiziert. Zwischen den experimentellen Daten und dem angepassten theoretischen Modell konnte eine sehr gute Übereinstimmung gezeigt werden. Das Kapitel schließt mit einer kritischen Diskussion zu den Vorteilen und Grenzen des vorgeschlagenen theoretischen Modells sowie der gewählten experimentellen Ansätze.

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Chapter 1

Introduction

1.1 Modern electronics: achievements and challenges

Integrated circuits will lead to such wonders as home computers – or at least terminals connected to a central computer – automatic controls for automobiles, and personal portable communications equipment.

Gordon E. Moore, *Cramming more components onto integrated circuits*, (1965) [1].

In the course of the 20th century the social role of scientific community, before always considered in the popular opinion as keeping away from the topics of the every day, experienced a tremendous change. With the narrowing of the distance between fundamental science and applied technologies in the course of progress, the academic science starts to directly affect the life of the whole social hierarchy. The time gap between a discovery in the natural science and its practical application shortened in many cases down to 5-10 years. Many of today's every day comforts are results of the fundamental investigations done only few decades ago, and this process is still accelerating.

One of the most tremendous and visible developments during last few decades is that in the field of electronics resulting in devices overcoming all earlier expectations, in particular computers. The functionality of electronic devices is based on logic elements performing specific tasks of data storage and operations with them. Albeit of some pre- and early- 20th century efforts involving mechanical systems, data manipulation was and is still implemented via electromagnetic phenomena such as charge storage or magnetization, current rectification and gating. The earliest widely used general purpose programmable computers (first generation) exploited properties of vacuum tubes working as electrical logic elements. The vacuum tubes have been known since the beginning of the twentieth century and were employed in particular in radio receivers. The discovery of the rectification in metal-semiconductor contacts [2] and the invention of the transistor by John Bardeen, William Shockley and Walter Brattain in 1947 [3, 4], who were awarded the Nobel prize in Physics for this achievement, led to a fundamental change in the electronic technology. The silicon-based transistors were cheaper, smaller, consumed less energy, and produced less heat than a vacuum tube. They constituted a basis for the second generation computers (*ca.* 1955–1965). Originally the invention wasn't considered as a radically new technology (new paradigm) but rather seen as a larger step within the existing frame (see *e.g.* discussion of the process of paradigm shift [5] during the replacement of vacuum tubes by transistors in ref. [6]). A further development was needed to exploit its potential. A key breakthrough was coming with the principle of p-n junction isolation allowing to electrically separate manufactured elements on a chip rather than to prepare them individually. Afterwards

the integrated circuits (IC) invented in parallel by Jack Kilby and Robert Noyce around 1960 [7] replaced single transistors. For this work Jack Kilby was honoured by the Nobel Prize in Physics in 2000 together with Zhores Alferov and Herbert Kroemer.

The arrays of logic elements implemented as an IC provided the technological background for the third generation of computers (*ca.* 1960–1970). The further development of IC led to the conception of the microprocessor (Ted Hoff, 1969) as an ultimate IC containing all logic elements of a general purpose computing device on a single chip. A microprocessor designed as a central processing unit (CPU) is a key element of computers of the modern fourth generation, among those the appearance and development of the personal computers is the most fascinating achievement.

After the invention of IC the development in the field of electronics and computing was mostly fostered by the trends towards miniaturisation of electronic devices [7]. It was pointed out in 1965 by G. E. Moore [1] that the economical factors lead to the nearly a exponential development of the amount of electrical elements (*e.g.*, resistors, diodes, transistors) on a single chip. The modern assays of “Moore’s law” [7–11] show that transistors getting a factor of two smaller, faster, and cheaper every 12-24 months. Except of the increase of the doubling time, this trend so far was not attenuated.

Since the advent of semiconductor technology almost 60 years ago, the fundamental principles laying down its functionality were not altered. The introduction of new technological processes [7] didn’t affect Moore’s Law; actually, their appearance allowed to continue the predicted trend. For nearly 40 years, a smaller size of a transistor automatically meant a faster and less energy-consuming transistor. However, now the inorganic semiconductor-based transistor technology already reached the nanometer domain with feature sizes being less than 100 nm. At this scale the quantum effects play a significant role. Thus, the technology of the “macroscopic world” approaches its physical limits.

It is still possible to produce smaller transistors, but they not necessary will enjoy improved characteristics [11]. Nanoscaled physical effects plaguing transistors’ performance include [7, 8]:

- parasitic resistances and capacitances become comparable with the useful ones;
- leakage due to the tunneling through the insulating silicon oxide layer;
- dielectric breakdown of the latter due to the high local electric fields;
- increase of the contact resistance due to the dopant concentration reaching its equilibrium value;
- the time of the signal propagation in the interconnects becomes comparable with the switching time of the transistor;
- quantum mechanical confinement in the small device leads to the quantification of its energy spectrum with the energy levels being dependent on the device dimensions;

as well as others. Beside the nanoscale-specifics, the common scaling challenges must be overcome as well.

Although there are solutions possible within the existing paradigm, the accumulation of the challenges calls for the shift to new paradigms. At the moment there is no consensus about the heir of the silicon neither in the academic nor in engineering communities. Whatever the new technology would be, experts [7, 10, 11] leave 10-30

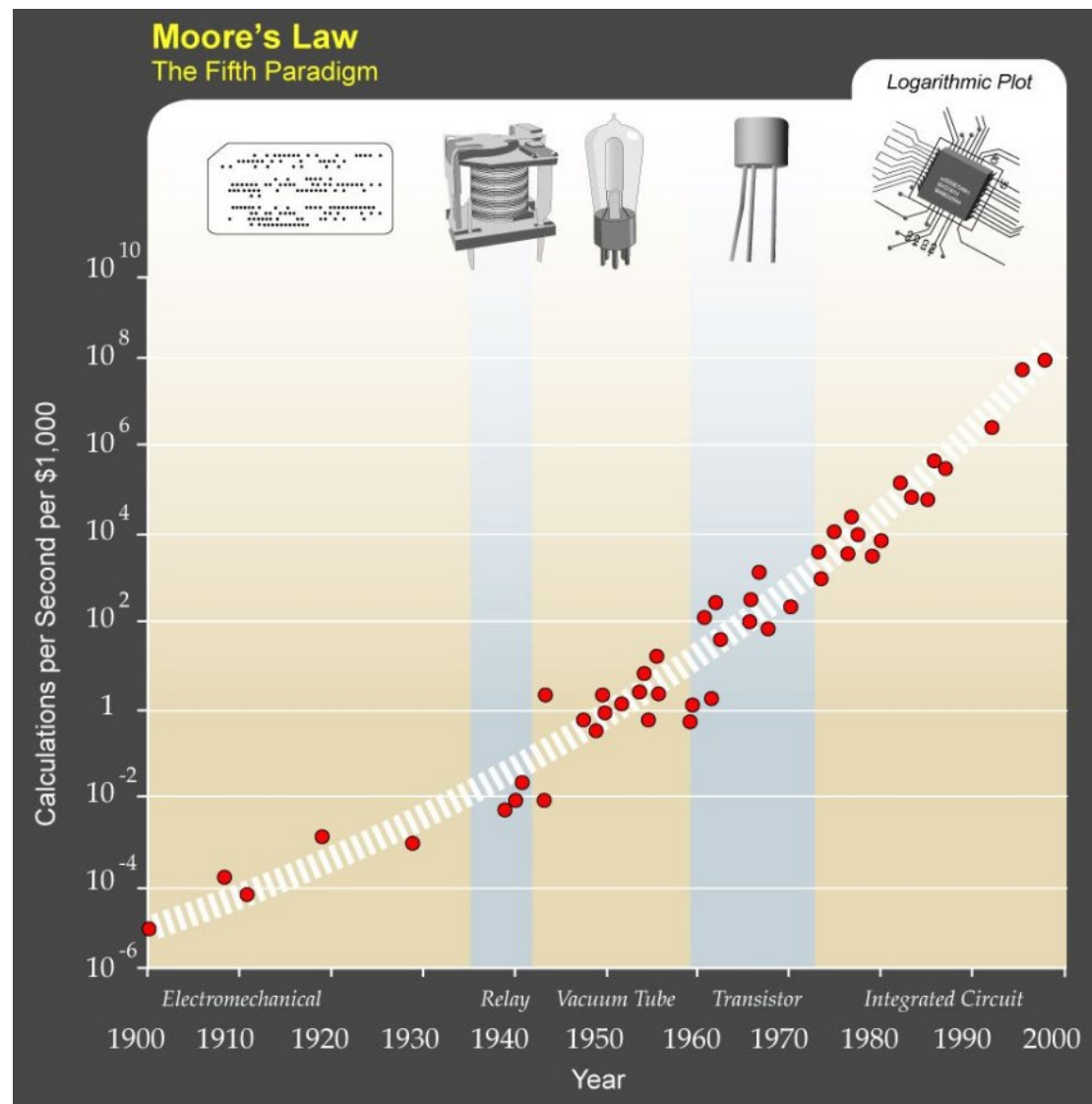


Fig. 1-1: Extended Moore's Law [12].

years for the silicon-based transistors incorporating novel elements only in the technological bottlenecks (hybrid technology). Then the exponential development of the IC as we know it now will decline. However, a successful future technology of logic elements should develop in the same direction towards further performance improvement, lower power consumption and heat generation. Thus, the trend predicted by Moore's law will be continued in some way. Such extended Moore's Law [12] was shown to put the development of the IC into the general perspective of progress of computational facilities' (Fig. 1-1), in a similar way as the development of the technological concepts contributed to the overall development of the IC paradigm. Consequently, it is expected due to economical reasons that the new paradigm will allow to continue the existing trends.

The key question now is the fundamentals of the new paradigms. There are many academic concepts aimed to address this issue. Major directions of these developments [7, 10] are:

- In spintronics the information is encoded into the electronic spin. A single transistor exhibits a ferromagnetic source and drain, and the spin-polarization of the injected electron is controlled by the gate voltage. This approach may be particularly interesting for data storage applications.
- In one-dimensional devices the transport through a nanometer thin wire (carbon nanotubes (CNTs), semiconductor nanowires, crossbar nanostructures, etc.) is controlled by a metal-oxide gate. Advantages of this configuration include an enhanced mobility of these devices over bulk systems and the possibility of phase coherent transport, while challenges include very small current-carrying capabilities of the wires and large contact resistances.
- The superconducting devices use flux quanta as the switching element. The expected performance would be very good (high speed, low dissipation, scalability), but the need for significant and expensive cooling as well as difficulties in manufacturing create major difficulties to its usage.
- In resonant tunneling devices the switching is performed by shifting the phase of an electron and having it constructively or destructively interfere with another one. The dimensional control required to manufacture these devices is far beyond current techniques.
- In quantum cellular automata the cells are switched by moving electrons from one cell to another. This results in a quantum computer. Its usage for general purpose will be challenging. However, it may have a superior performance for specific tasks.
- In optical approaches the optical elements change their properties to store or emit a photon. This is far above the current level of technology.
- In molecular electronics the single molecules are used as a circuit elements. It is a well thought out approach with major challenges including low current carrying capabilities, poor self-assembly techniques, low reproducibility, and low on/off ratios.

We believe that the molecular electronics is a very promising technology of the future. Our group is using a surface science approach combined with electrochemical methods to study electron transport in nanoscale systems. Current challenges and prospectives in this fast developing field will be discussed in the next chapters.

1.2 Introducing molecular electronics

Within biological systems, however, some tasks performed by solid-state devices in electronic applications are performed, instead, by organic molecules; such tasks include storage and transfer both of energy and of electrons. ... It seems to us reasonable to examine the potential use of molecules as components of electronic circuitry by looking, as a start, at the current-voltage characteristics of a single molecule acting as a rectifier.

Arieh Aviram, Mark A. Ratner, *Molecular rectifiers* [13].

The basic idea of the molecular electronics was suggested by Arieh Aviram and Mark A. Ratner in the middle of 1970s. Inspired by the numerous examples found in nature, they considered a usage of a “*simple organic molecule*” incorporated in a “metal | molecule | metal” assembly – molecular junction (MJ) – as a part of an electrical circuit [13]. Using the analogy to a *p-n* semiconductor junctions, a donor-bridge-acceptor (DBA) structure of the molecule was proposed, where D is a strong electron donor, *e.g.*, tetrathiafulvalene (TTF), A is a strong electron acceptor, *e.g.*, tetracyanoquinodimethan (TCNQ) and B is a saturated bridge electrically isolating donor and acceptor parts (Fig. 1–2). The proposed rectification is due to the electron

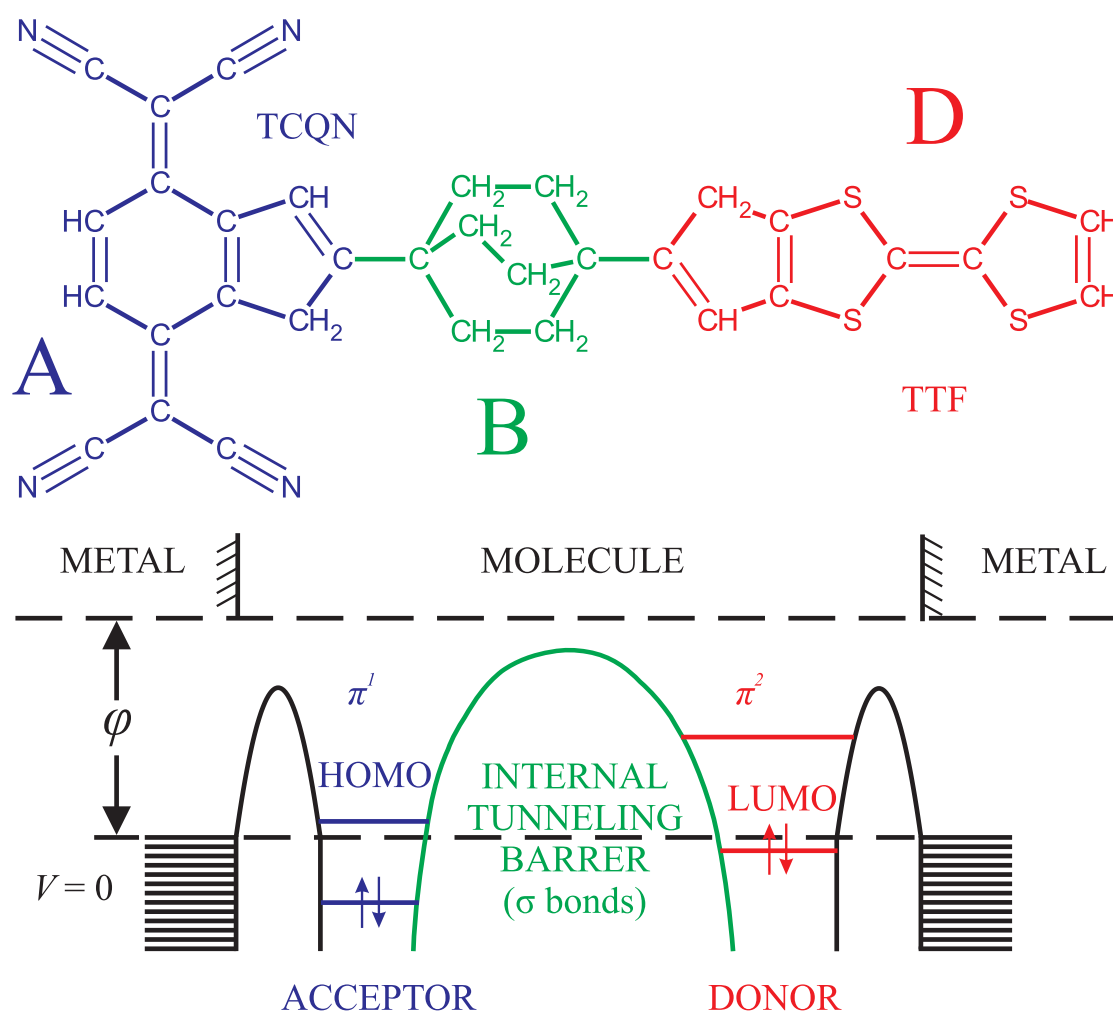


Fig. 1–2: Structure of the proposed molecule-rectifier and the energetic diagram of the junction [13].

transfer (ET) passing only in the direction cathode→acceptor→donor→anode.

For a proper rectification behavior, the lowest unoccupied molecular orbital (LUMO) (“*affinity level*”) of the acceptor should lie at or slightly above the Fermi level of the adjusted electrode and above the highest occupied molecular orbital (HOMO) (“*ionizing level*”) of the donor. When a sufficiently high bias V is applied to the junction, so that the Fermi level of the metal is aligned with the LUMO of the acceptor, latter is filled by the electron tunneling from metal. This process is mostly determined by the energy of the acceptor LUMO and the metal work function ϕ . At the donor end the electron is transferred to the metal when the HOMO is aligned with the Fermi level of the metal as well. Now the intermolecular motion of the electron from the donor to the acceptor will occur under the effect of an electric field. Repetitive cycles provide an enhanced ET via the molecule. The proposed three step transfer mechanism is not valid for the ET in the reverse direction when applying a bias of opposite sign. The reverse transport may occur only under higher bias of opposite sign with a HOMO of the acceptor and a LUMO of the donor being aligned with the Fermi levels of the metals or being above/below it. Thus, rectification is expected. Such expectations are confirmed by the results of calculations [13].

The mechanism proposed in [13] was not the primary one for the experimentally observed rectifications in MJ. Indeed, there are two additional factors leading to the rectification in assemblies [14]. The first factor is a Schottky barriers at the “metal|molecule” interfaces: the asymmetry of the surface dipoles formed at both interfaces leads to the asymmetry of a current-bias response. The second factor is an asymmetry in the placement of the part of the molecule whose molecular orbital must be accessed during conduction MJ, *e.g.*, because of the presence of a long alkyl “tail”. The true unimolecular rectification as it was described in [13] is still to achieve.

Modern simulations [15] suggested that the unimolecular rectifying behaviour may be observed only if the voltage is not dropped completely at interface and asymmetrically distributed across the MJ. Otherwise the deformation of the molecule under the applied bias results in effectively symmetric voltage profiles for forward and reverse bias voltages.

Despite of not being completely valid, the model of unimolecular rectification as proposed by Aviram and Ratner [13] triggered multiple theoretical and experimental investigations of the ET through the MJ. The new field characterized by combining the “molecular” and “semiconductor” paradigms was born and named “molecular electronics”.

At the moment molecular electronics is seen as a concept of single molecules being either the active elements in hybrid organic-inorganic electronics or executing elementary device functions [16]. The molecular approach provides several unique possibilities. Molecular design allows to use molecules with specifically adjusted properties to implement localized functions such as charge transfer or storage, or molecular rectification [14]. “Bottom-up” fabrication via self-organization and recognition of molecular building blocks allows to produce structures with a high reproducibility and well-defined properties. Finally, the specific properties of the molecular structures allow to construct functional devices.

Molecular electronics is a fast developing field. Many reviews and books [17–25] on this topic appeared in recent years.

A separate comment should be given concerning the electrochemical approach to molecular electronics. At present time, the major part of our knowledge on the subject

is still based on the results of investigations carried out under ultra-high vacuum (UHV) and/or at low temperatures. These are not always appropriate for real production systems. Studies on electrified solid-liquid interfaces (*i.e.*, in electrochemical environment) represent an interesting alternative approach for addressing fundamental concepts and principles. The electrical field at the interface reaches magnitudes of 10^9 V/m, which is comparable to that employed in field-effect transistors [26–28]. Aqueous electrolytes represent a natural environment for “living” macromolecules. And last, but not least: electrochemists have more than a century of experience in studying molecular systems at electrified solid-liquid interfaces. Meeting and cooperation of electrochemists with mesoscopic and surface science physicists open new perspectives in the field of molecular electronics.

Current studies on molecular electronics are focused on the following fundamental questions:

1. How to synthesize functional molecules?
2. How to prepare electrical circuits and to incorporate hybrid structures?
3. What are the electrical properties of such circuits?
4. What is the correlation between molecular structure and their functionality?
5. How to use molecular electronic devices in real life applications?

To address these questions, joint efforts of physicists, chemists and electrical engineers; experimentalists and theoreticians, are required. The topic of our electrochemical surface science group is related to topics 2 to 4 of this agenda. In this work I will present results showing how our approach contributes to the overall development of molecular electronics and the understanding of ET in various systems.

1.3 Thesis outline

The work included in this thesis was carried out in the Institute of Bio and Nanosystems 3 (previous name: Institute of Thin Films and Interfaces 3) of the Forschungszentrum Jülich (FZJ) in the time from October 2003 to September 2007 under the supervision of Priv. Doz. Dr. Thomas Wandlowski. The Ph.D. studies of the author were supported by the Deutsche Akademische Austausch Dienst (DAAD) and the FZJ.

The structure of the thesis is as follows. After this introduction, chapter 2 describes in details concepts and techniques used in this work. Chapter 3 presents details of experimental procedures. In order to master the technique of electrochemical scanning tunneling microscopy, the study of some known as well as new properties of the ionic adlayers formed by the coadsorption of Cu^{2+} cations with SO_4^{2-} or Cl^- anions was carried out. The results are presented in chapter 4. The experimental strategies to the studies of the conductance in nanoscale systems employing scanning tunneling microscopy were tested in experiments on the formation of gold quantum point contacts described in chapter 5. Chapter 6 and chapter 7 present the results of conductance measurements in two types of gold–molecule–gold single molecular junctions incorporating alkanedithiols and 4,4'-bipyridine. Chapter 8 demonstrates results of the analysis of tunneling mediated by molecules with a redox-active viologen core. Finally, the general conclusions are formulated in chapter 9.

Chapter 2

Principles and techniques

This chapter presents a short summary of basic concepts relevant to this work and introduces the corresponding nomenclature. The detailed introduction is included in every experimental subchapter.

2.1 Basics of charge transfer

The area of charge transfer phenomena in “chemical” systems is closely related to the “physical” subject of electrostatics and electrodynamics. In electrostatics the interactions between fixed charged particles are considered. Electrodynamics, or electricity and magnetism, is a theory dealing with electric charges which move in space and produce electromagnetic fields, which, in turn interact with charges. In this paragraph I will briefly describe the concepts of electrostatic and electrodynamics [29] relevant to this work.

2.1.1 Electric charge and field

The electric charge is a fundamental conserved property of matter, which determines electromagnetic interactions. The interaction force of two electrically charged objects is determined by the amount and sign of electric charge Q . In general, two objects having a charge of the same sign are repelling each other, the objects of opposite sign are attracting. If the distance between electrically interacting objects is much higher than their own sizes, they may be considered as point charges. The interaction force of two point charges is given by Coulomb’s law and depends on the distance l between them as well as on the medium:

$$|\vec{F}_{12}| = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 l} \quad (2.1)$$

Here $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$ is a fundamental constant of the electrostatic interaction called dielectric permittivity of the vacuum; $\epsilon > 1$ is a characteristic of the electrostatic interaction in the medium called dielectric constant (in vacuum $\epsilon = 1$ by definition).

The interaction of charged objects occurs via the electric field. The electric field is characterized by its strength $\vec{X}$ defined as the ratio of the acting force $\vec{F}$ to the charge of a probe particle Q (taking the sign into account):

$$\vec{X} = \vec{F}/Q \quad (2.2)$$

The energy of the electric field interaction with a charge is characterized by the electric potential φ of the field. The latter is a ratio between the interaction energy W and the charge:

$$\varphi = W/Q \quad (2.3)$$

As long as the energy and, consequently, the potential, is defined up to a constant factor, the zero of the potential scale may be selected arbitrary. Here and further I will use a convention that zero potential corresponds to the absence of an electric field, *i.e.*, the absence of electric interactions. The potential at a certain point may be defined as an energy required to transfer a unity charge from the vacuum to that point. The electric field strength is the potential gradient taken with an opposite sign:

$$\vec{X} = -\nabla\varphi \quad (2.4)$$

Thus, from the energetic point of view, charged particles tend to move in electric field in order to decrease the interaction energy.

2.1.2 Electric conduction at the macroscale

The electric conduction is understood as an organized movement of electrically charged particles under the effect of an electric field. Due to the nanoscale size of actual charge-carriers and a huge amount of them involved in the charge transfer at the macroscale, it is possible to consider a continuous charge density instead of individual particles:

$$\rho(\vec{r}) = \sum N_i(\vec{r}) \cdot Q_i(\vec{r}) \quad (2.5)$$

where N_i and Q_i are concentration (local number of particles per volume unit) and charge of individual types of charge-carriers at the point $\vec{r}$. The total charge contained in certain volume V is then equal to

$$Q = \int_V \rho dV \quad (2.6)$$

The rate of the charge movement is expressed as current – an amount of charge transferred per time unit through a certain surface S :

$$I_S = \Delta Q_S / t \quad (2.7)$$

or, for non-uniform transfer, as

$$I_S(t) = \partial Q_S / \partial t \quad (2.8)$$

The “local” rate of the charge transfer is known as a current density

$$\vec{j}(\vec{r}) = \sum n_i(\vec{r}) \cdot Q_i(\vec{r}) \vec{v}_i(\vec{r}) = \rho(\vec{r}) \vec{v} \quad (2.9)$$

where $\vec{v}_i$ and $\vec{v}$ are velocities of individual types of charge-carriers in the electric field and their average velocity. The current density has the dimension of current per surface area. $\vec{j}$ at every point of the surface S and an amount of current through this surface are related by the equation

$$I_S = \int_S \vec{j} d\vec{S} \quad (2.10)$$

The ratio between the strength of the applied electric field and the current density in a static medium is known as conductivity σ ¹

$$\vec{j} = \sigma \vec{X} \quad (2.11)$$

Higher σ means that the media is better conducting. The materials are classified according to the values of σ as “real” conductors having high conductivities², insulators having low conductivities and semiconductors having intermediate conductivities. The exact mechanism of conductance depends on the media. According to the nature of charge-carriers, electronic and ionic types of conductance are distinguished. The typical examples of such conductors are correspondingly metals³ and liquid or solid electrolytes.

2.1.3 Transport studies

Practically it is rather difficult to create defined electric fields in a specific medium. Instead a potential difference, also known as voltage, voltage bias or just bias $V = \Delta\phi$ is applied to the sample, *e.g.* two electrodes with defined potential difference are attached to the sample. According to the direction of the flow of charge-carriers, the electrodes are often referred to as source and drain. It should be noted that the conductance is a non-equilibrium process. Indeed, provided sufficient time is available, the movement of the charge-carrier would compensate the potential difference in one conducting phase. Thus, under equilibrium condition the potential inside the conducting phase is equal. The latter is actually an electrostatic definition of “conductor” [29, P. 33].

The dependence of the current (or current density) measured on electrodes upon an applied bias⁴ is known as a transport characteristics, which is in particular determined by the mechanism of charge transport. However, certain types of $I - V$ dependencies may be deduced (Fig. 2–1).

As a typical and simplest example of a $I - V$ transport characteristics I will consider a long and thin wire of a metal with length l and a cross-section area S . The metal phase is characterized by a constant strength of the electric field $\vec{X}$ in the whole volume, thus

$$|\vec{X}| = \frac{V}{l} \quad |\vec{j}| = \frac{\sigma V}{l} \quad I = |\vec{j}| \cdot S = V \frac{\sigma S}{l} = G \cdot V = \frac{V}{R} \quad (2.12)$$

The proportionality between current and bias (Fig. 2–1A, green line) is known as Ohm’s law and quantitatively expressed by the resistance R or the conductance G . The ohmic behavior at any bias value is characteristic for an ideal resistor, but normally observed as a low bias limit of transport characteristics for other conducting systems. The non-ohmic behavior is characterized by an average conductance or resistance

$$\overline{G}(V) = \frac{1}{\overline{R}(V)} = \frac{I(V)}{V} \quad (2.13)$$

¹ In anisotropic media σ is a tensor of the second rank.

² The term “conductor” is widely used in various fields of physics and chemistry and its implied definition may strongly vary.

³ For a solid media with an electronic type of conductance the classification according to electronic structure is introduced further. Thus, the difference between conductors and semiconductors are not only quantitative, but qualitative, as it may be seen by the temperature dependence of the conductance [30, P. 723] – the conductance decreases with temperature for a metal and increases for a semiconductor.

⁴ The electrodes which are used to measure the current are not necessary the same as those used to apply a bias. So, up to 4 electrodes may be used to characterize transport properties of a sample.

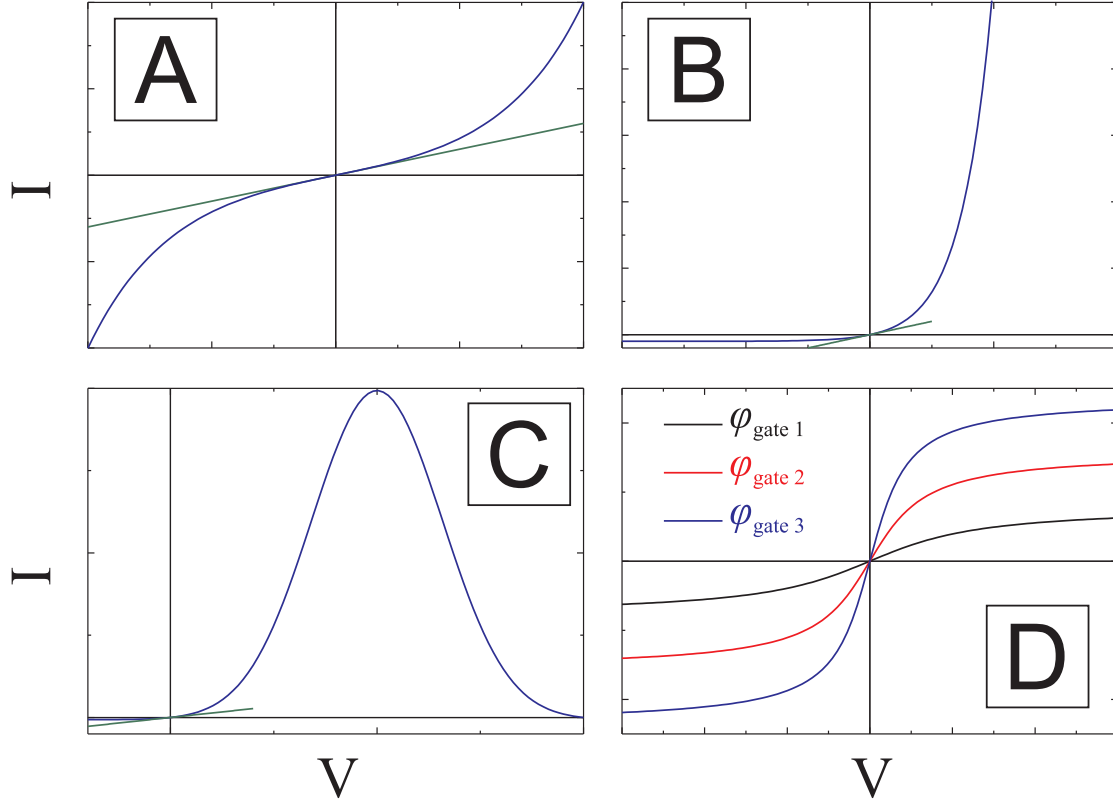


Fig. 2–1: Examples of transport characteristics: (A) symmetric response, (B) rectification, (C) NDR, (D) gating. The green lines show linear approximations (ohmic behavior) at low bias voltages.

or, more frequently, by differential characteristics

$$G(V) = \frac{1}{R(V)} = \frac{\partial I}{\partial V} \quad (2.14)$$

A real, non-ideal conducting system may exhibit deviations from the linear dependence, which are typically stronger with an increase of the bias (blue line in Fig. 2–1A). The symmetry of the characterized system with respect to the direction of current flow is reflected in a symmetrical $I - V$ curve (blue line in Fig. 2–1A). For many practical applications, in particular for implementations of electronic logic elements, more complicated $I - V$ characteristics are required. The desired effects include

- rectification (Fig. 2–1B) – a behavior of an electronic element (a diode), when current is allowed to pass in one direction and blocked in the opposite;
- negative differential resistance (NDR) (Fig. 2–1C), when $I - V$ dependence passes over a global or local maximum so that the differential resistance (Eqn. 2.14) is negative in certain range of bias value;
- gating (Fig. 2–1D), when the magnitude of the current passing between two measuring electrodes is controlled by the potential of a third, the gate electrode.

as well as others. Further I will refer to these features of $I - V$ characteristics.

The application of the bias to non-conductive sample leads to a charging current. It results in a charge accumulation on the adjacent electrodes until an equilibrium is

reached. The amount of charge transferred is related to the applied bias according to [29, Sec. 2.8]

$$Q = CV \quad (2.15)$$

where C is the capacitance. For the flat condenser (or capacitor) constructed from two parallel plates with an area S separated by the insulator of a thickness l with a dielectric constant ϵ it is equal to

$$C = \frac{S}{\epsilon \epsilon_0 l} \quad (2.16)$$

2.2 Electronic structure of solids

The solid media with electronic conductance play a key role. The main assumptions underlying models of the electronic structure of solids are the following [30]:

- The atomic nuclei are fixed on the crystal lattice at regular positions.
- The electrons in the inner shells of each atom are tightly bound to the atom core, *i.e.*, they belong to certain atomic nucleus.
- Electrons in the “outer shells” are not bound to atoms but move freely in the crystal lattice, effectively bound to the whole solid.
- All atoms together form a collective potential in which the outer electrons are moving. The electrons in turn provide bonds that keep all the atoms together.

In this paragraph I will introduce concepts related to the electronic structure of solid bodies.

2.2.1 Free electron gas model

In the classical model the electrons in a solid metal body were considered as an ideal gas. However, the quantum-mechanical effects are important for the understanding of the electronic structure of the solids'. The electrons are particles with quantum properties and may only occupy energetic levels (*i.e.*, to have energy) corresponding to certain discrete values of energy, although the energy difference between levels may be negligible.

Electrons are also fermions, *i.e.* they have half-integer spins, here $\frac{1}{2}$. They have a specific property that two fermions with the same quantum state cannot exist in one system⁵. One parameter determining the quantum state is a projection of electron spin on a certain axis, which could be $+\frac{1}{2}$ or $-\frac{1}{2}$, *i.e.* two electrons may occupy a single energy level, but only if they have different spin projections. In the processes related to the charge transfer we don't distinguish between such electrons (spin degeneracy) and just bearing in mind that two electrons may occupy one energy level.

These quantum effects were accounted in a model of the quantum free electron gas. In this model pairs of electrons with energies from its possible minimum value ϵ_0 to ϵ are filling energy states, which density per volume unit $g(\epsilon)$ is given by

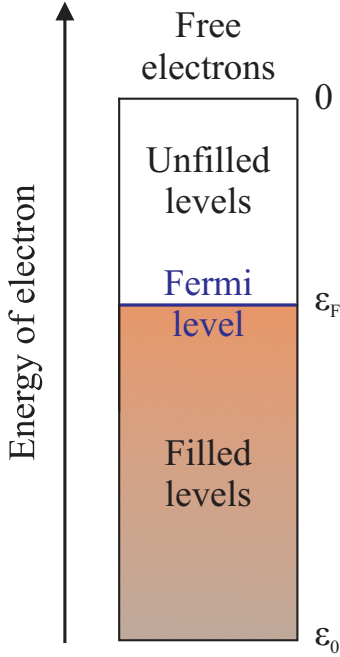
$$g(\epsilon) = \left(\frac{4\pi(2m_e)^{\frac{3}{2}}}{h^3} \right) (\epsilon - \epsilon_0)^{\frac{1}{2}} \quad (2.17)$$

⁵ For electrons it is also known as an empirical “Pauli exclusion principle”.

where $m_e = 9.11 \times 10^{-31}$ kg is the electron mass, $h = 6.626 \times 10^{-34}$ J·s is the Planck constant.

At low temperatures all electrons fill the lowest possible energy levels up to a certain energy. The energy that marks the boundary between the filled and the empty energy levels at very low temperatures (*i.e.*, 0 K) and the occupied level with a highest energy are called Fermi energy and Fermi level. The former is given by the following expression:

$$\varepsilon_F - \varepsilon_0 = \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \frac{h^2 N^{\frac{2}{3}}}{2m_e} \quad (2.18)$$



At finite temperature the thermal motion of electrons causes the broadening of the border between occupied and empty energy levels. This leads to the formation of small transitional area of partially filled levels around the Fermi level. The probability that electrons occupy energy states with the energy ε is given by Fermi-Dirac distribution function:

$$f_{FD}(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_F}{kT}\right)} \quad (2.19)$$

where T is the temperature and $k = 1.38 \times 10^{-23}$ J·K⁻¹ is the Boltzmann constant. The transitional area has a width of few kT . For a typical metal $\varepsilon_F - \varepsilon_0$ has a value of a few eV. Thus, at room temperature the broadening of the transition area is *ca.* 3 orders of magnitude smaller than the whole energy scale. The Fermi-Dirac distribution allows to give another definition of the Fermi level as an energy level with an occupation probability equal to 0.5.

Fig. 2-2: The energy diagram of metal.

The Fermi level is a very important concept of the electronic structure of metals. The Fermi level both accepts and donates electrons and thus, as it was introduced in Sec. 2.1.1, the potential of the metal phase is related to

the Fermi energy⁶:

$$\varphi_M = -\varepsilon_F / e \quad (2.20)$$

where $e = 1.62 \times 10^{-19}$ C is the elementary charge. The minus sign accounts for the negative charge of the electron.

2.2.2 Band model

In the energy band model the electrons are assumed to occupy molecular orbitals (MOs) delocalized over the whole solid body. Unlike the free electron gas model, the former describes well the properties of non-metal solids and in particular semiconductors [30].

The formation of bands may be described in the following way. The movement of the electron around an atomic nucleus may be approximated as a movement in a potential well created by the attraction of a positively charged atomic core. In this system the electron has a well defined quantum states with a corresponding energy and tends to occupy the level with a smallest energy – a ground state. When two atoms are brought together, new states (MOs) are formed with energies lower (bonding) and

⁶ The more correct description requires usage of electrochemical potential $\bar{\mu}$ including both “electrical” and “chemical” interaction of the electron with the phase (see Sec. 2.3.2 on page 34).

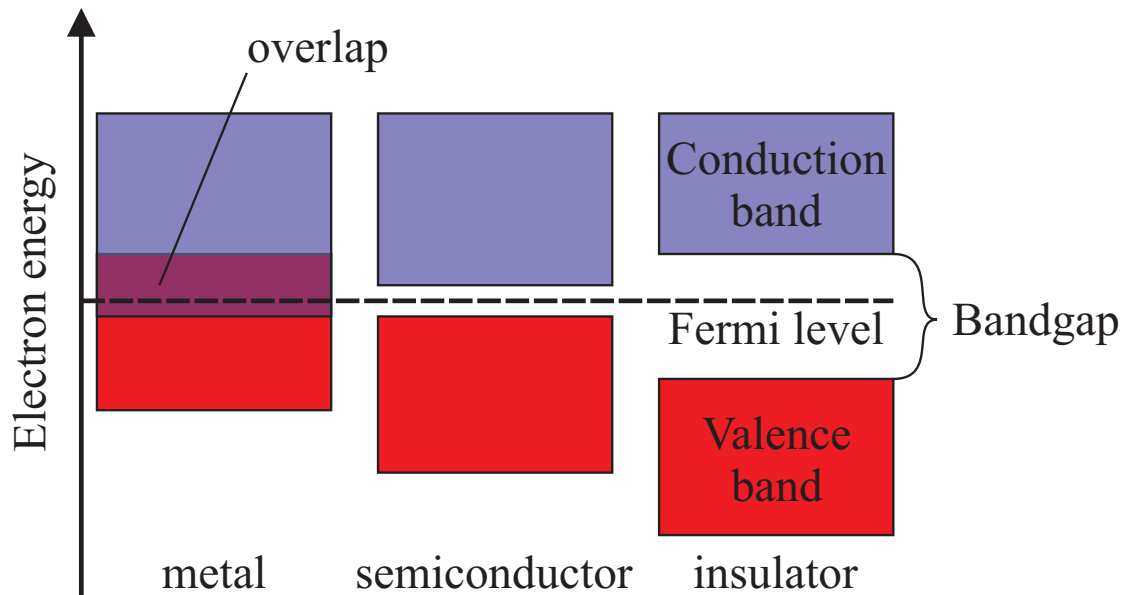


Fig. 2–3: Comparison of the electronic band structures of metals, semiconductors and insulators.

higher (antibonding) than an average of the two atomic orbitals. The electrons occupying low energy orbitals are bound to atoms and may leave the system only if they acquire additional energy to switch to the antibonding state.

Each additional atom adds another orbital and contributes to the formation of another MO. In the limit of an infinitely large number of atoms constituting one system an infinitely large number of MOs forms. Bonding and antibonding states fill finite energy ranges with a negligible difference between the energies of the neighbouring MOs – valence band (VB) and conductance band (CB). The names are due to the fact, that the electrons on the former are locally bound, while they can freely move within the whole solid body for the latter.

Within the band model the material is characterized as a conductor, semiconductor or insulator by the relative separation of the valence and the conduction bands (Fig. 2–3) – a band gap. If they overlap or the band gap is very small, the situation is equivalent to the free electron gas model – a thermal activation is enough to provide mobility of electrons and allow them to respond to an electric field.

The separation between the VB and the CB hinders the electronic conduction. At $T = 0$ K they are completely filled and empty, so that there are no charge-carriers available. With the increase of T the tail of the Fermi-Dirac distribution spans the gap and some electrons transfer from the lower band to higher. The electrons in the CB and the positively charged vacancies in VB (holes) are able to transport the electric current. Unlike in case of conductors, the conductivity of semiconductors increases with the temperature due to the increase of the charge-carrier concentration. If the band gap is too large, however, there is a negligible amount of electrons promoted from the VB to the CB at conventional temperatures, and the material acts as an insulator. The value of the band gap separating semiconductors and insulators is estimated as 1.5 eV.

Semiconducting materials exhibit many interesting electronic properties and constitute a material basis of modern electronics. The separation of electrons and holes as a result of thermal activation is characteristic for intrinsic semiconductors – pure materials such as silicon and germanium or compounds such as GaN or CdS are typical

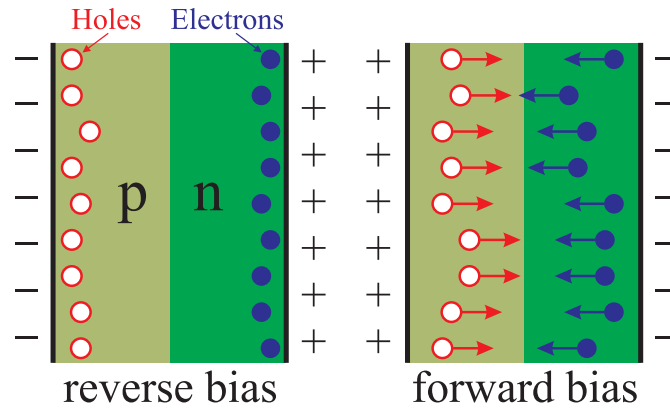


Fig. 2–4: A p - n junction under reverse and forward bias.

examples. As a result, an intrinsic semiconductor has an equal amount of positive and negative charge-carriers. In extrinsic semiconductors the non-native charge-carriers are introduced by a doping procedure, when some native atoms are replaced by the dopant atoms of another elements (in a ratio of about 1 to 10^9). If the dopant atoms can trap electrons, they withdraw electrons from the VB and form holes which allow other electrons to move. The current in the doped semiconductor is transferred due to positive holes, and it is called p -type semiconductor. If the dopant atoms provides an excess of electrons, they occupy the CB, which gives rise to a conduction by electrons, or a n -type semiconductor.

As an example of a typical application of a semiconductor to form a logic element I will consider a p - n junction – the interface of a p -type and n -type semiconductor. When a “reverse bias” is applied to the junction, *i.e.*, a negative electrode is attached to the p -type semiconductor and a positive one – to the n -type semiconductor (Fig. 2–4, left), the charge-carriers in each semiconductor are attracted by the nearby electrode. As a results, no charge flows across the junction. By attaching positive electrode to the p -type semiconductor and the negative electrode to the n -type semiconductor, a “forward bias” is applied (Fig. 2–4, right). Now electrons are moving towards the positive electrode and holes are moving in the opposite direction. As a result, the current is flowing, which magnitude depends on the applied bias and concentration of charge-carriers. Thus, the p - n junction, or diode, demonstrates a behaviour known as “rectification” (Fig. 2–1B on page 28). More complicated $I - V$ characteristics as introduced in Sec. 2.1.3 (Fig. 2–1 on page 28) could be realized using various semiconducting materials.

2.3 Electrochemistry

2.3.1 Brief introduction of electrochemistry

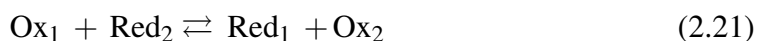
Electrochemistry is a branch of physical chemistry dealing with the interrelation of electrical and chemical effects. The field of electrochemistry covers a wide variety of concepts, effects, systems and methods. In this subchapter I describe only those notions of electrochemistry, which are relevant to this work and only in a necessary scope. For the detailed and wide description I refer to the textbooks and reviews available, for example a *de facto* standard work on electrochemistry by Allan J. Bard and Larry R. Faulkner [31].

The origin of electrochemistry [32] goes back to the experiments of Luigi Galvani and Alessandro Volta in the end of the 18th century. The field of electrochemistry enjoyed an extensive development of theoretical, practical, methodological and technological aspects in the 19th and 20th century. The established “classical” or “pure” electrochemical experiments are characterized by studies of relations between “electrochemical” parameters of the systems such as electrode potential, current flowing through the interface, accumulated charge, *etc.*, for various substrates and solutions in equilibrium or under dynamic conditions. At present the focus of the field is shifting towards more specific applications, to studies of the chemical behavior and to approaches combined with other experimental techniques [31, preface].

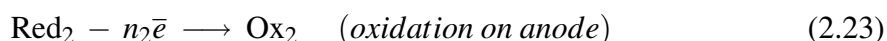
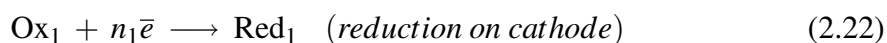
The whole field of electrochemical phenomena is often separated in two parts. The topic of ionics refer to solutions and electrolytes. The electrolytes are substances dissociating in a polar solvent to ions, which act as charge-carriers and provide an ionic type of conductance in solution. Typical electrolytes are salts, acids and bases. The driving force for the dissociation is an energy gain due to the solvation of the ions formed by the molecules of the solvent. The most frequently used polar solvent is water.

The topic of electrodics is an electric charge transfer processes through the interface between two phases. A considerable number of these process take place on a solid-liquid interface, the solid phase being typically a metal and the liquid being an electrolyte solution. In this section I will mostly focus on this subject, in particular the ET between metal electrodes and species in a liquid phase close to it.

Conceptionally electrode processes are closely related to oxidation-reduction reactions where electrons are transferred between the species of different type:



where Ox and Red are the oxidized and the reduced forms of the reactants forming a redox couple. In electrochemical systems the oxidation and the reduction processes are spatially separated and an actual exchange of electrons occurs via the electrodes. Thus, the whole reaction may be split onto half-reactions:



By definition, the electrodes at which oxidation or reduction take place are called cathode or anode correspondingly. Therefore, oxidation and reduction are often referred to as anodic and cathodic processes.

Conventionally, half-reactions are written in the direction of the reduction (Eqn. 2.22) independently on its actual preferential direction. Using these half-reactions, it is

possible to consider only one process on the electrode acting as a donor or an acceptor of electrons with a practically unlimited capacity. According to the relation known as the “Faraday’s law”, the ratio between the amount of electrical charge Q passed through the electrode and the amount of transformed substance ν are related by

$$\nu = \frac{Q}{n_i e N_A} = \frac{Q}{n_i F} \quad (2.24)$$

where $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$ is Avogadro’s number and $F = 96485 \text{ C} \cdot \text{mol}^{-1}$ is a Faraday constant.

2.3.2 Electrode potential

The electrode potential is a fundamental notion in electrochemistry. The potential difference in an electrochemical cell controls the direction and a rate of interfacial ET. Thus, the measurement and control of the electrode potential is also one of the most important aspects of experimental electrochemistry.

Electrochemical potential

The absolute electric potential ϕ of a phase may be defined as an energy required to transfer an imaginary charge from the vacuum into the phase (Sec. 2.1.1). “Imaginary” is used here to denote the object which, unlike a real particles such as electron, proton or other ions, isn’t interacting “chemically”, *i.e.*, via short-range forces, with its surrounding. The electron in a metal may be considered as a particle, not interacting with a crystal lattice (Sec. 2.2.1). Thus, the electric potential of the metal is equal to its work function – an energy required to release an electron from the Fermi level of the metal – which can be determined experimentally. In ionic conductors, such as electrolyte solutions the potential cannot be determined in this way due to the strong non-electrostatic interaction between the charge-carriers and medium⁷. In other words, there are both “chemical” and “electrostatic” components of the interaction energy involved [31, P. 60].

Although one cannot experimentally distinguish two components of energy, they could be theoretically separated by introducing the electrochemical potential $\bar{\mu}_i$ of the species i in a certain phase. The concept of the electrochemical potential was proposed by Butler [33] and Guggenheim [34, 35]. It may be formally defined in a similar way as the chemical potential μ_i of non-charged species. The latter is well-known from chemical thermodynamics and appears as the “chemical driving force” in the full differential of the Gibbs energy G :

$$dG = -SdT + Vdp + \sum_i \mu_i d\nu_i \quad (2.25)$$

$$\mu_i = \left(\frac{\partial G}{\partial \nu_i} \right)_{p, T, \nu_j \neq i} \quad (2.26)$$

where S , T , V and p are entropy, temperature, volume and pressure. If we now consider species with a charge number $Z_i = Q_i/e$, its energy is also affected by the electric field.

⁷ Moreover, in electrolyte solutions, unlike in case of solid ionic conductors, it is not even possible to separate stationary “medium” and movable “charge-carriers”.

This is accounted for in the electrochemical Gibbs energy $\bar{G}$, whose full differential is equal to:

$$d\bar{G} = -SdT + Vdp + \sum_i \mu_i dv_i + \sum_i Z_i \phi F dv_i = dG + \sum_i Z_i F \phi dv_i \quad (2.27)$$

$$\bar{\mu}_i = \left(\frac{\partial \bar{G}}{\partial v_i} \right)_{p, T, v_{j \neq i}} = \mu_i + Z_i F \phi \quad (2.28)$$

where ϕ in this case is an internal potential of the phase. In equilibrium implied by the usage of the thermodynamical approach, the latter is the same in all points inside the conducting phase (see Sec. 2.1.2).

The concept of the electrochemical potential is a generalization of either electrostatics or chemical thermodynamics. Under certain conditions it may be reduced to both the chemical potential and the electrostatic potential. Their combination in form of the electrochemical potential is vital for the correct thermodynamic description of chemical reactions involving charge transfer processes between two phases [31, see examples in Sec. 2.2.4].

Interfacial equilibrium

As it was discussed above, the absolute electric potential of any conducting phase cannot be determined in a thermodynamically strict process. However, these values are not of great importance. Much more useful is a difference in the absolute phase potentials between an electrode and an electrolyte, which is the driving force of electrochemical processes. It may be evaluated by considering the equilibrium at an interface, *i.e.*, an equilibrium of the half-reaction.

To illustrate this approach, I will consider an important example showing the interfacial charge transfer: a metal electrode Me immersed in a solution containing its cations Me^{n+} . The half-reaction may be written as



When the metal and the solution phases are in equilibrium, the electrochemical potential of all components is equal between phases, in particular $\bar{\mu}$ of the metal ions in the metal phase and in the solution:

$$\bar{\mu}_{\text{Me}^{n+}}^{\text{Me}} = \bar{\mu}_{\text{Me}^{n+}}^{\text{sol}} \quad \text{or} \quad \mu_{\text{Me}^{n+}}^{\text{Me}} + nF\phi^{\text{Me}} = \mu_{\text{Me}^{n+}}^{\text{sol}} + nF\phi^{\text{sol}} \quad (2.30)$$

$$\phi^{\text{Me}} - \phi^{\text{sol}} = \frac{1}{nF} \left(\mu_{\text{Me}^{n+}}^{\text{sol}} - \mu_{\text{Me}^{n+}}^{\text{Me}} \right) = \frac{1}{nF} \left(\mu_{\text{Me}^{n+}}^{\text{sol},0} - \mu_{\text{Me}^{n+}}^{\text{Me}} \right) + \frac{RT}{nF} \ln(a_{\text{Me}^{n+}}) \quad (2.31)$$

where $a_{\text{Me}^{n+}}$ is an activity of the ions Me^{n+} in solution and $R = kN_A$ is an universal gas constant.

An equation of this type was first obtained by Hermann Walther Nernst in 1888 [36, 37]. It is now known as a “Nernst equation”. A system following the Nernst equation is said to be thermodynamically or electrochemically equilibrated, or nernstian. It is possible to show in a similar way that the Nernst equation may be derived for any interfacial equilibrium (Eqn. 2.22 on page 33) involving components from the solution and the electrode phases. It states that the difference in the absolute potentials of electrode and solution phases being in equilibrium depends both on the nature of the redox-pair and on the activity of its components, or, *vice versa*, a potential difference across an interface determines the composition of the phases near the electrode at equilibrium.

Equilibrium in an electrochemical cell

Experimentally it is not possible to deal with an isolated interface. Instead, one must study properties of an electrochemical cell, which is composed of two electrodes separated by at least one electrolyte phase. The “electron-donating” and “electron-accepting” electrodes are called cathode and anode (see also Eqn. 2.22 and 2.23 on page 33). The difference of the absolute potentials of the phases with an electronic conductance (*i.e.*, electrodes) is called cell potential E_{cell} and could be measured *e.g.* by a high impedance voltmeter if two phases have the same nature. Practically, the latter condition is fulfilled by connecting electrodes to a voltmeter with the wires of the same metal.

According to the definition (Sec. 2.1.1), the potential difference measured on the electrodes is equal to the ratio of the energy required to transfer a non-interacting positive probe charge through the whole circuit. The path of the probe charge would be as follows:

Connecting wire 1 $\rightarrow$ Anode $\rightarrow$ Solution $\rightarrow$ Cathode $\rightarrow$ Connecting wire 2

Therefore, the cell potential is equal to

$$E_{cell} = (\varphi_s - \varphi_a) + (\varphi_c - \varphi_s) + \sum (\Delta\varphi_{ij}) \quad (2.32)$$

where φ_a , φ_c and φ_s are correspondingly the electric potentials of anode, cathode and solution and $\Delta\varphi_{ij}$ are the potential differences on various metal–metal interfaces. The latter equation may be rewritten as

$$E_{cell} = const + (\varphi_c - \varphi_s) - (\varphi_a - \varphi_s) \quad (2.33)$$

The electrochemical cell is in equilibrium if there is an equilibrium on each phase boundary (*i.e.*, each half-reaction is in equilibrium) and a cell potential is compensated by the external voltage source. A potential difference existing between two electrolyte phases contributes to the cell potential as well. Thus, for the thermodynamic investigation it is avoided or eliminated using special approaches. The electric potential difference on each metal–solution interface is related to the chemical potential by the relations such as Eqn. 2.31 and affects the common cell potential.

Reference electrodes and electrode potential

In most situations one is interested in the processes occurring at one electrode, which is called the working electrode (WE). The other half-reaction is standardized by using a reference electrode (RE) made up of phases with a known and constant composition. The primary RE defined by the International Union for Pure and Applied Chemistry (IUPAC) and accepted by the electrochemical community is a standard hydrogen electrode (SHE), which is a Pt electrode immersed into an aqueous solution of H_2SO_4 with the activity of the H^+ ions equal to 1 and in the presence of gaseous H_2 with a pressure of 1 atm. Thus, by definition, the electrode potential of the half-reaction



is zero at any temperature. The potential in the equilibrated cell consisting of a SHE (Eqn. 2.34) and the redox-pair under discussion



is defined as an electrode potential of the half-reaction (Eqn. 2.35).

A comment should be given about the sign of the electrode potential. It is determined by the direction of the spontaneous reaction (*i.e.*, in the absence of an external voltage) in the aforementioned cell: the reduction of H^+ and the oxidation of H_2 correspond to the negative and the positive potential of the second redox-pair. According to the Eqn. 2.33, in this way we consider the half-reaction in question as a cathodic process, *i.e.*, reduction, and the hydrogen half-reaction as an anodic process, *i.e.*, oxidation.

The equilibrium potential E_{eq} of the redox-couple (Eqn. 2.35) in dependence on the thermodynamic activity of the components is described by the Nernst equation:

$$E_{eq} = E_{Ox/Red}^0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} \quad (2.36)$$

The electrode potential $E_{Ox/Red}^0$ corresponds to the standard conditions of both components and is called the standard electrode potential of the half-reaction. For practical reasons one often replaces the thermodynamic activities by concentrations. Eqn. 2.36 transforms to

$$E_{eq} = E^{0'} + \frac{RT}{nF} \ln \frac{c_{Ox}}{c_{Red}} \quad (2.37)$$

where $E^{0'}$ is the experimentally determined formal potential, instead of the standard potential E^0 . The former, however, often represents a good estimation of the latter.

By using a limited number of standard electrode potentials it is possible to calculate the equilibrium cell potential for a large number of the cells formed by combination of half-reactions. According to the Eqn. 2.33, the cell potential is

$$E_{cell} = E_c - E_a \quad (2.38)$$

where E_c and E_a are the electrode potentials of the cathode and of the anode *vs.* a common RE. The half-reactions as summarized in tables are always written in the direction of the reduction independently on the actual direction of the interfacial process. The cell potential is related to the change of the Gibbs energy in the total oxidation-reduction reaction (Eqn. 2.21) as

$$\Delta G = -nFE_{cell} \quad (2.39)$$

where n is the total number of electrons involved in the oxidation-reduction reaction. The latter is determined by the stoichiometry of the two half-reactions.

Besides the SHE, which is often difficult to use in practice, other REs are employed. Notable examples include the saturated calomel electrode (SCE) (see Sec. 3.5.2), the silver–silver chloride electrode, as well as many others. The equilibrium potentials of the secondary RE *vs.* SHE are well known and, if necessary, the values of the electrode potential *vs.* a secondary REs may be easily recalculated between each other and into the primary scale of the SHE. The alternative scale of the electrode potential is not affecting the actual potential difference between the metal and the solution phase. As Eqn. 2.38 suggests, the experimentally accessible value of the cell potential is unaffected by the potential scale as well.

The measurement and the control of the electrode potential do not require an equilibrium cell. Indeed, the cell potential could be varied by applying an external voltage. The correctly chosen RE has a fixed potential, therefore the change of the cell potential is attributed to the variation of the E_{WE} ⁸. The driving of the WE out of equilibrium is

⁸ Further I will use E assuming E_{WE} .

often referred to as polarization. The potential of the WE is controlled with respect to the RE and it is equivalent to the control of the Fermi level of the WE. The latter is raised when E is shifted towards negative values and lowered when E is driven in the positive direction:

$$\Delta\epsilon_F = -e\Delta E \quad (2.40)$$

The electrode processes driven by the variation of electrode potential will be described in more details in Sec. 2.3.4.

In certain cases it is not possible to use a true RE employing a redox-couple being in equilibrium. In this case a quasireference electrode (QRE) could be used, which is usually a metal (Ag, Pt, ...) wire immersed into a solution. The expectation is that the potential of the wire, although unknown, remains constant in a series of experiments under similar conditions. The actual potential of the QRE must be calibrated *vs.* a true RE, for example by measuring the potential of a redox pair, whose potential is known in the scale of the RE.

The interesting question arising with respect to the electrochemical definition of an electrode potential is its relation to the absolute potential of the phase (*e.g.*, the Fermi level) as it was defined in Sec. 2.1.1. I note that the exact determination of the potential of the solid conducting phase, which is in interfacial equilibrium with the solution phase, is not possible. For most purposes in electrochemistry it is sufficient to reference the electrode potential *vs.* one standard RE, but it is sometimes of interest to have an estimate of the absolute electrode potential, *i.e.*, with respect to the free electron in vacuum. Based on certain assumptions (see *e.g.* [31, Sec. 2.2.5] and [38, 39]), the absolute potential of the SHE was estimated as 4.5 ± 0.1 V. Using this value, an absolute potential may be calculated for any electrode.

2.3.3 Structure of the charged solid-liquid interface

The application of the potential E (*vs.* RE) to the WE in an electrochemical system has several consequences. The shift of the absolute potential ϕ of the metal phase, *i.e.*, the shift of the metal Fermi level was already discussed in Sec. 2.3.2. The latter also implies the change of the number of electrons in the metal phase, *i.e.*, an accumulation of the charge. As it was already mentioned above, the excess charge cannot be stored inside the conductive phase and it is concentrated on the surface of the metal. The latter leads to the adsorption of ions from the solution side in a kind of compensating reaction. The separated charges at the interface form a structure known as an electrical double layer (EDL). Besides the electrode potential, the EDL is another fundamental concept in electrochemistry (see *e.g.* [31, Sec. 13]).

Except for some special cases, the dimensions of the metal surface are much bigger than the “thickness” of this “transitional” zone. Therefore, the former is typically treated as an infinite flat structure. An important aspect of the EDL is the potential distribution in the transitional zone, which affects electrochemical processes. Various structure models of the EDL were proposed allowing to evaluate in a one-dimensional (1D) problem the distribution of ions and the electrostatic potential as a function of the distance to the electrode z . The metal surface is usually considered as an impenetrable boundary with an imposed potential $\phi(z=0) = \phi_M$, while at a sufficient distance the potential is equal to that of the solution: $\phi(z \rightarrow \infty) = \phi_s$. For the sake of simplicity, further in this section I will use a potential scale with reference to the potential of the

solution:

$$\psi(z) = \varphi(z) - \varphi_s \quad (2.41)$$

The latter corresponds to the potential of the electrode bearing no charge: a potential of zero charge (PZC) $E_{q=0}$.

The first ideas about the structure of the solid-liquid interface were developing for more than 70 years. The very first attempts to describe the structure of the EDL were reported by Herman von Helmholtz as early as in 1853 [40–42]. He also coined the term EDL (“*die elektrische Doppelschicht*”). According to his suggestions, the counter-charge in solution also resides at the surface and fully compensates the charge of the metal, forming a structure completely equivalent to a flat capacitor. Therefore, there is a linear variation of potential $\psi(z)$ with the distance inside the EDL. The capacitance of the EDL predicted by this model is constant provided that the plate separation and dielectric constant of the medium ϵ between the plates is not changing (Eqn. 2.16 on page 2.16). However, it was soon found that C_{EDL} varies with E as well as with electrolyte concentration. A more sophisticated model of EDL was required.

The next advance towards the understanding of the structure of the EDL was independently introduced in a very similar manner by Georges Gouy in 1909 [43, 44] and David Leonard Chapman in 1913 [45]. Instead of charged ions confined on the surface, they considered a model of the “diffuse⁹ layer” of charged species. It forms at finite distance from the electrode as a result of the interplay between electrostatic interactions of the ions with the charged electrode and their thermal motion. They assumed that the ions in solution follow a Boltzmann distribution and the electrostatic potential is induced by the distributed point charges.

The statistical mechanical model allowed to obtain an analytical solution for the distribution of ions in solution; potential distribution; the charge of the surface and the capacitance of a charged layer; as a function of electrolyte concentration, electrode potential and distance from the metal surface. The comprehensive description of the model as well as its solution may be found in electrochemical textbooks, *e.g.*, [31, Sec. 13.3.2]. Without going into details, I list the results obtained within the Gouy-Chapman model for the symmetric $Z : Z$ electrolyte, *i.e.*, (Cation)^{Z+}(Anion)^{Z−}, whose bulk concentration is c .

The electrostatic potential of the boundary ψ_0 and its surface charge q are related by the equation

$$\psi_0 = \frac{2RT}{ZF} \ln \left(\sqrt{1 + \frac{q^2}{8\epsilon\epsilon_0 RT c}} + \frac{q^2}{2\sqrt{2\epsilon\epsilon_0 RT c}} \right) \quad (2.42)$$

The potential drop ψ decreases almost exponentially with the distance to the electrode

$$\psi(z) = \frac{4RT}{ZF} \operatorname{atanh} \left[\tanh \left(\frac{ZF\psi_0}{4RT} \right) \exp(-\kappa_d z) \right] \approx \psi_0 \exp(-\kappa_d z) \quad (2.43)$$

The latter approximation is valid if ψ_0 is sufficiently small and $(ZF\psi_0/4RT) < 0.5$, *i.e.*, $Z\psi_0 < 50$ mV at normal conditions. The value of κ_d is a spacial decay constant of the potential and is given by

$$\kappa_d = \sqrt{\frac{2c}{\epsilon\epsilon_0 RT}} ZF \quad (2.44)$$

⁹ Not to be confused with the diffusion layer: “the region in the vicinity of an electrode where the concentrations are different from their value in the bulk solution” [46, see corresponding definitions].

Its reciprocal is regarded as a characteristic thickness of the diffuse layer. The latter decreases with the charge and the concentration of ions, which is phenomenologically described as a more effective screening of the electrode by ions.

The concentrations of ions in the diffuse EDL follow Boltzmann's law:

$$c_i(z) = c \exp\left(-\frac{W_i}{kT}\right) = c \exp\left(-\frac{Q_i\psi}{kT}\right) = c \exp\left(-\frac{Z_i F \psi}{RT}\right) \quad (2.45)$$

The interfacial capacitance of the diffuse EDL is

$$C_d = \frac{ZF}{2RT} \sqrt{8\epsilon\epsilon_0 RT c + q^2} \quad (2.46)$$

The minimum value of the capacitance corresponds to the uncharged surface and is proportional to $Z\sqrt{c}$.

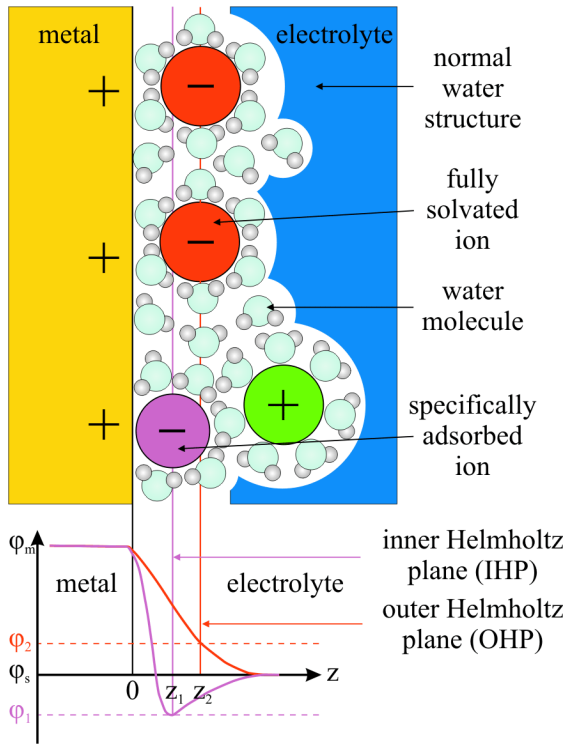


Fig. 2–5: Top: structure of the metal/electrolyte interface and potential distribution in EDL for specifically (violet) and non-specifically (red) adsorbed ions. Bottom: the potential drop across the interface in case of non-specific (red) and specific (violet) ion adsorption. Redrawn from [47].

electrolyte concentrations.

The resulting scheme of the EDL is sketched in Fig. 2–5 using positively charged metal surface as an example. The metal surface constitutes of one capacitor's "plate" or a "layer", the other "layer" consists of the ions adsorbed from the solution (either surface-confined or not). The attraction of ions by purely electrostatic forces is referred to as a "non-specific adsorption" (Fig. 2–5, red). It is also characterized by the retention

The weakness of the model of Gouy and Chapman, despite of its outstanding theoretical background, was an assumption of ions being point charges able to penetrate to the electrode. Among other artefacts, this caused an infinite increase of the simulated capacitance to be obtained at high polarizations.

The formulation of the classical model of the EDL was completed by the work of Otto Stern [48], who combined both approaches of Helmholtz and Gouy-Chapman. Taking a finite size of the ions into account, Stern demonstrated that the EDL could be considered as an equivalent of two capacitors connected in series. Their capacitances correspond to the "inner" or "compact" layer (C_c) similar to that described by Helmholtz and the "diffuse" layer of Gouy-Chapman (C_d). The total capacitance is

$$\frac{1}{C_{EDL}} = \frac{1}{C_c} + \frac{1}{C_d} \quad (2.47)$$

The former dominates at high potentials (with reference to $E_{q=0}$) and solution concentration, while the latter is more pronounced at low potentials and low

of the ions' solvation shell; the centers of these ions at closest approach define the so-called outer Helmholtz plane (OHP). This situation applies to most of the cations but only for a small number of anions. Many anions have only a weakly bound solvation shell, which can be partially stripped as anions contact the electrode surface (Fig. 2–5, violet). They may form “chemical-like” bond with the metal in a process known as “specific adsorption” and often accompanied by the partial discharge of the adsorbed ions. The centers of specifically adsorbed ions constitute the inner Helmholtz plane (IHP).

The thickness of a compact layer lying between the metal surface and one of the Helmholtz planes could be estimated to be roughly the radius of the solvated ions, *i.e.*, *ca.* 3 Å [47]. The capacitance of the EDL depends on the electrode material, the electrolyte and the applied voltage. In aqueous solutions of ionic electrolytes it varies between 20 and 100 $\mu\text{F}\cdot\text{cm}^{-2}$. Assuming only a compact layer contribution and using the aforementioned plate separation, a relative dielectric constant $\epsilon \approx 5 - 10$ is estimated, which is much lower than $\epsilon \approx 81$ for the bulk water. The low value is explained by the considerable cut of the rotational degrees of freedom for the water molecules trapped in the gap. Due to the high EDL capacitance and a minute gap an extremely high electric field strength $X \approx 10^9$ V/m may be easily generated at the electrode surface by applying moderate potentials.

Stern suggested that the potential difference in the compact layer drops from $\psi(0) = \varphi_M - \varphi_s$ not completely, but only to some residual value (Fig. 2–5, see plot below). It is typically referred to as φ_1 and φ_2 for specifically and non-specifically adsorbed ions respectively. In some cases the chemisorption of ions leads to the change of the sign of the surface charge due to overcharging. This effect leads to the adsorption of counterions in the close vicinity of the IHP, instead of being driven out of the EDL by the electric field.

The ions being further away from the electrode surface constitutes the Gouy-Chapman diffuse layer. The electric field strength in the diffuse layer is much smaller than in the compact one. The thermal motion of the ions and the solvent molecules is weakly restricted and the relative dielectric constant of the solvent is approximately equal to that in the bulk of the solution.

The equations of the Gouy-Chapman theory are applied with distinct corrections: the boundary is not an electrode surface, but the plane of the ion's of closest approach (*e.g.*, OHP or IHP). For non-specifically adsorbed ions $q_{\text{OHP}} = -q$, while for specifically adsorbed ions the situation may differ due to the aforementioned partial charge transfer to the electrode.

Further ideas about the structure of the solid-liquid interface were emerging with new experimental techniques and results available. Notable examples include electrochemical studies of the surfaces with specifically adsorbed organic substances and a corresponding model of EDL developed on demand for the description of experimental observations. Another more recent direction of the EDL studies includes simulation using atomistic and first-principle models such as Monte-Carlo (MC), molecular dynamics (MD) and density functional theory (DFT). For the details I refer to the existing reviews on this field [49–52].

2.3.4 Electrode processes

Electrode reactions

Historically the early electrochemical experiments were concentrated on potentiometric measurements of the potentials in the absence of interfacial reactions as a function of the substrate and solution composition. With certain exceptions, the potentiometric experiments are well described within a thermodynamic approach, *i.e.* the equilibrium exist or is expected to be established in a cell (Fig. 2–6). The cell potential method was proved to give useful information about the thermodynamic characteristics of chemical processes. However, a much wider variety of the processes are dynamic. They can be controlled via the electrode potential, which is a universal driving force of interfacial processes, unique for the electrochemical methods. As a consequence, the majority of electrochemical methods, “classical” as well as combined with other techniques, are focused on the study of the electrode reactions taking place on a working electrode (WE) as a function of its potential.

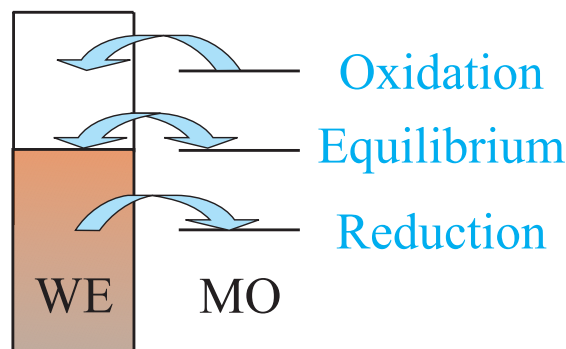


Fig. 2–6: Interfacial ET.

Two types of processes may occur at the electrode. The charge (typically electrons) could be transferred across the metal-solution interface causing the chemical transformation of substances. These processes are governed by Faraday’s law (Eqn. 2.24 on page 34) and are called faradaic. Besides interfacial ET *per se*, other processes such as adsorption/desorption on solid-liquid interfaces, and in particular the formation of the EDL (Sec. 2.3.3) may take place as

well. Here a current may flow when the potential or solution composition changes. The reaction of this type is often referred to as nonfaradaic one.

An interfacial ET (Fig. 2–6) occurs when a molecule with an accessible MO contacts the electrode. As it was discussed in Sec. 2.3.2, the equilibrium at the interface corresponds to the electrochemical potential of the electrode’s Fermi level $\bar{\mu}_F$ to be equal to that of MO $\bar{\mu}_{MO}$ and, by definition, the electrode potential is equal to the equilibrium value. When $\bar{\mu}_F > \bar{\mu}_{MO}$, the electrons tend to fill initially empty MO in a reduction process. The reverse process of oxidation occurs when $\bar{\mu}_F < \bar{\mu}_{MO}$. The energy difference is expressed as a displacement of the electrode potential from its equilibrium value and called overpotential¹⁰

$$\eta = E - E_{eq} = (\bar{\mu}_{MO} - \bar{\mu}_F)/F \quad (2.48)$$

The rate of the electrode reaction is expressed as the current per unit of the electrode surface j (see Sec. 2.1.2 on page 26). A particular $j - E$ response provides information about the properties of solution, electrode and reactions that occur on its surface.

Two important concepts were derived as a limiting cases of the interfaces’ behavior during the passage of current or the variation of the potential. No charge transfer occurs at an ideal polarizable electrode at constant applied potential. The potential of an ideal nonpolarizable electrodes doesn’t change upon passage of current, *i.e.*, it is an electrode of fixed potential. While no real interface can behave as an ideal one, some

¹⁰ Note that for the convenience the sign of overpotential is often reverted.

systems may approach the ideal polarizability/nonpolarizability in a limited range of potential/current.

The electrode reaction, in most cases, is a multistage process, which mechanism includes other steps besides ET. The most important additional stages are mass transport of reactants and/or products. Another complication could be due to the formation of a new solid phase, gas evolution, preceding and following chemical reaction and many other reasons. The overall rate of a reaction is determined by the kinetics of the slowest step or by an interplay of steps with a comparably slow rate.

Electrodes

The substrates used for experiments are described in details in Sec. 2.5, 3.4. The characteristics of many electrochemical processes is determined by the geometry of the electrode surface. Here I would like to specify that the further description is limited to solid electrodes with a uniform and constant area. Unlike in case of polarographic techniques employing dropping electrodes [31, Cha. 7], in our situation the current I flowing through the cell is just a product of current density and electrode area. The dimensions of the electrode is much bigger than those of the interfacial transitional structures relevant for the electrode reaction (EDL, diffusion layer). The latter are characterized by only one variable – the distance z to electrode, and considered to be uniform in the two other dimensions.

Mass transfer

In general, three types of mass transfer processes may occur during an electrode reaction [31]:

- diffusion – a movement of species under the influence of a gradient of the chemical potential, *i.e.*, concentration;
- migration – a movement of charged particles under the influence of an electric field;
- convection – a movement of particles with a flow of solution. It could be a natural convection caused by the gradient of solution density or a forced convection during stirring.

The overall 1D flux J (an amount of substance transferred through a surface unit per time unit) of mass transport along the axis z is determined by the Nernst-Planck equation:

$$J(z) = J_d + J_m + J_c = -D \frac{\partial c(z)}{\partial z} - \frac{ZF}{RT} D c(z) \frac{\partial \phi}{\partial z} + c(z) v(z) \quad (2.49)$$

where D is a diffusion coefficient and v is a velocity of a volume element in solution. Depending on the experimental conditions, one type may prevail in mass transport of the redox-active species.

The natural convection is poorly controlled and usually avoided. The experiments with a forced convection (*i.e.*, rotating disk electrode) are widely used in electrochemistry but beyond the scope of this work. The experiments discussed further assume measurement on a solid electrodes in a quiet solution, *i.e.*, in the absence of convection.

The diffusion of redox-active species emerges as a direct consequence of the electrode reaction. The surface concentrations of components of the redox pair are determined by the kinetics of the ET step, while that in the bulk of the electrolyte remains constant. The gradient of the concentration leads to the diffusion of reactants/products from/to the bulk and the creation of a transitional diffusion layer, where concentrations substantially differ from those in the bulk.

The mass transport by migration is a major contribution in the bulk of the solution, where concentration gradients are generally small. All charged species contribute to the migration current. To reduce the migration component in the kinetics of the electrode reaction to a negligible level, much larger concentrations of an inert supporting electrolyte are added to the solution. It is not participating in electrode reaction, but carries a major part of the current in solution.

By using aforementioned precautions, it is possible to restrict mass transfer of redox-active species to the diffusive mode. These situation is implied further.

2.3.5 Electrochemical measurements

Instrumentation

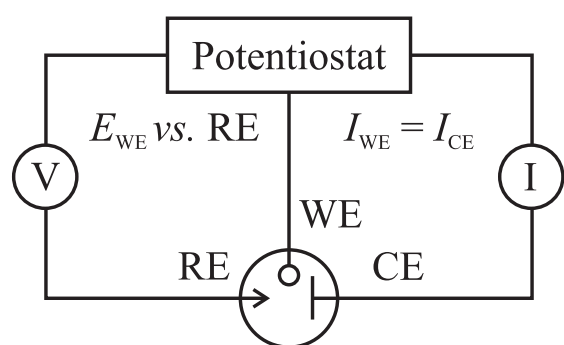


Fig. 2–7: The scheme of the potentiostat and three-electrode electrochemical cell.

The typical “classical” electrochemical experiment involves studies of relations between the parameters of the electrode reaction taking place on a WE: current flow I , electrode potential E vs. RE and their derivatives as a function of time, substrate and solution composition, sometimes also temperature.

It is clear from the intended purpose of the RE to have a constant potential, that it should be ideally nonpolarizable during the passage of current. For any real RE this condition would break provided that the passing current I is sufficiently big. Another complication is related to the passage of current is that the actual potential difference will differ from the applied external voltage V by the value of the Ohmic drop created due to the solution resistance R_{sol} :

$$|E_{WE} - E_{RE}| = |\phi_{WE} - \phi_{RE}| = |V| - |I R_{sol}| \quad (2.50)$$

A high Ohmic drop also leads to the increase of the electrical power dissipated in the cell and increase of the cell’s own response time in dynamic measurements. To circumvent uncertainties related to the passage of current through the RE, a three-electrode cell design is conventionally used in electrochemical experiments (Fig. 2–7). Here the potential of the WE is measured with respect to a RE. The latter has a high input resistance forcing all current to flow through the counter electrode (CE). An exact control/measurement of the potential/current is maintained by separating potential and current measurements into a RE and a CE loops. The electrochemical properties of the CE do not affect the WE. Typical CEs could be metals (Au, Ag, Cu, Hg, ...), highly oriented pyrographite (HOPG) or semiconducting materials. The only requirement for the CE is that the products of its interfacial reaction do not interfere with the reaction

on the WE. Frequently it is placed in a compartment separated from the one containing the WE.

The original approach to study dynamic electrochemical processes was to drive the current through the cell and to measure the created overpotential. An important advance in the technique of electrochemical experiments was achieved in the beginning of 1940th with the invention of the potentiostat [53]. The latter in combination with three-electrode cell is a standard electrochemical equipment allowing the precise control of the potential of the WE *vs.* the RE and measurement of the current between the WE and the CE. The actual function of the potentiostat is more complicated. It measures current and potential in the CE and the RE circuits. The potential difference between the WE and the CE is adjusted via a feedback loop in such a way, that the desired value of the electrode potential or the current is reached. Then the potentiostat provides information about the corresponding value of the current or of the potential attained. This procedure allows measuring the current as a function of potential or the potential as a function of current.

The instrumentation and cells used for the experiments described in this work are presented in the Sec. 3.5.2.

Supporting electrolyte

The experiments discussed further are carried out in the presence of high (0.01 – 1) M concentrations of a redox-inactive supporting electrolyte, typically salts of alkali metals and strong acids. The redox-active target species (if any) is used in much lower concentrations, seldom exceeding 10^{-3} M. The addition of supporting electrolyte has few consequences:

- controlling chemical composition of the solution (pH, ionic strength, ligand concentration, *etc.*);
- eliminating the contribution of migration to the mass transfer of the target species, leaving only the diffusion mode;
- decreasing of the solution resistance and of the corresponding Ohmic drop;
- building up and control of the EDL, which composition is not affected by the electrode reaction. The elimination of the migration by an excess of supporting electrolyte is equivalent to the EDL being much thinner than the diffusion layer.

The supporting electrolyte alters the medium in the cell, so that many properties of the solution differ from that of the pure solvent. This should be taken into account when comparing results obtained in the electrochemical experiments with those carried out by other methods, typically in pure solvent. Supporting electrolytes are used in large concentrations and their impurities can seriously interfere with a target electrode reactions, *e.g.*, by their own redox reaction, a reaction with the products, adsorption on electrode, *etc.* The supporting electrolyte is selected for specific experiment taking into account its chemical effect (pH, *etc.*), inertness, solubility and purity.

Types of electrochemical experiments

The types of electrochemical experiments are classified according to the parameters held constant, controlled and measured. I will only mention the experiments with

controlled current flow through an electrode [31, Cha. 8]. These techniques are called chronopotentiometric when E is determined as a function of time, or galvanostatic when the overpotential is determined as a function of a small constant current passing through the electrode. The types of experiments I will focus assumes the control of the electrode potential and measurement of the current.

An initial condition for the measurements implies the electrode's ideal polarizability, *i.e.*, the absence of current flow. The potential than could be varied in various ways. The simplest example is a potential step (chronoamperometry) experiments [31, Cha. 5]. Here the potential is varied stepwise from an initial value to a final one, at which a faradaic or nonfaradaic process takes place at an appreciable rate. The current-time response (transient) is then recorded until the current reaches its equilibrium ($j = 0$) or a steady-state ($j = \text{const}$) value. The potential could be stepped and held few times within one experiment.

In potential sweep experiments, such as chronoamperometry or voltammetry [31, Cha. 6], the potential is constantly varied with the time according to a predefined function. Most often it is a linear sweep with a sweep rate $r = |\Delta E / \Delta t|$ which ranges from $r = 5 \text{ mV} \cdot \text{s}^{-1}$ to $r = 1000 \text{ mV} \cdot \text{s}^{-1}$. The sweep rate is an important parameter to control the time scale of an experiment.

In a linear sweep voltammetry the potential is scanned once from an initial to a final value. In cyclic voltammetry (CV) the potential is ramped continuously between an upper and a lower value (Fig. 2–8A). Customary, in both methods the current density is plotted as a function of potential. In the first case this is completely equivalent to a $j - t$ characteristic, in the second the $j - E$ curve shows characteristic cycles, which overlap under steady-state conditions.

A much wider variety of the electrochemical methods (various pulse methods, application of the harmonic potential waveforms, to name only few) does exist, however, CV gained popularity as a simple and powerful electrochemical method for the initial characterization of electrode reactions, including those with rather complicated mechanisms [54]. In the next subsection I will describe this method in more detail and demonstrate few typical examples.

2.3.6 Cyclic voltammetry

Similar to other methods, the CV scan typically starts from an initial potential E_i within the range of the electrode's ideal polarizability, *i.e.*, from $j = 0$. E is ramped either in the positive or in the negative direction until the first return potential is reached. The scan direction is then reversed and E swept back to a second return potential. Further measurements are carried out with the potential E linearly varied between a lower (E_l) and an upper (E_u) return potentials, typically with the same rate r (Fig. 2–8A). Due to the nature of the processes driven, the positive and negative going scans are often referred to as anodic and cathodic half-cycles.

The CV ramp before the first return potential is completely equivalent to the linear sweep voltammetry. If an electrode reaction takes place in the covered range of potentials, the generation of products starts. Their stability and the reversibility of the ET are probed during the reverse scan. Typically during the few first cycles the $j - E$ curve varies until a steady-state is reached. Then the further cycles remain reproducible unless the system is perturbed by external factors.

Few examples of steady-state CVs obtained in our experiments are plotted in Fig.

2–8B. Here the potential scale is plotted relative to the center of the interval and the current is scaled for the convenience.

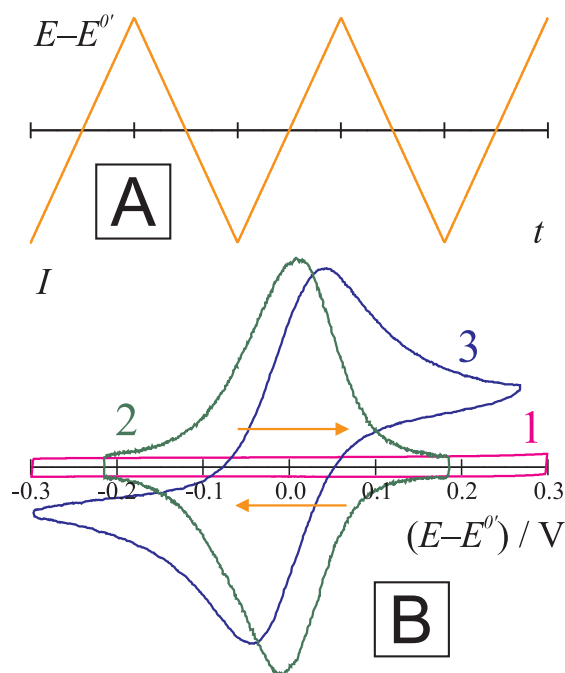


Fig. 2–8: Cyclic voltammetry: (A) potential sweep; (B) current response of (1) redox-inactive EDL; surface confined (2) and diffusing (3) redox-active species.

istics could be derived from the position (E) and height (j) of its cathodic and anodic peaks, their separation $\Delta E_p = E_{pa} - E_{pc}$ and dependencies of these parameters on the sweep rate r .

I will limit the description of the CV response to faradaic reactions of reversible or nerstian redox-systems. The latter were introduced during the description of the potentiostatic measurements (Sec. 2.3.2) as a half-reactions which potential is related to the activity/concentration of the components via the Nernst equation (Eqn. 2.36 on page 37). In a dynamic experiment, however, the latter is applied to the interfacial concentrations of the components:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{c_{z=0, \text{Red}}}{c_{z=0, \text{Ox}}} \quad (2.52)$$

Physically this condition implies that the ET step of the reaction is much faster than any other processes and the exact form of the CV (Fig. 2–8B, curves 2, 3) is determined by the other, non-ET steps of the reaction, such as mass transport. The presented $j - E$ curves are measured in such a way that the experimentally determined formal potential of the redox-pair $E^{0'}$ is located in the middle of the potential range.

Curve 2 (Fig. 2–8B) shows a typical CV for the redox-active molecule with both oxidized and reduced forms being confined on the surface. The system is characterized by the amount of substance per surface unit, the surface coverage

$$\Gamma = \nu/S \quad (2.53)$$

Both faradaic and nonfaradaic processes contribute to the current measured by CV. The major nonfaradaic contribution is the charging of the EDL. If the capacitance is constant, then

$$j = \frac{dq}{dt}$$

$$q = C_{EDL}(E - E_{q=0}) \quad (2.51)$$

$$j = C_{EDL} \frac{dE}{dt} = \pm r C_{EDL} = \text{const}$$

where the signs $+$ and $-$ corresponds to positively and negatively going scans respectively.

The resulting CV appears as two straight lines symmetric with respect to zero (Fig. 2–8B, curve 1). The constant current of the EDL charging often contributes to the CV as a background.

More complicated CVs may be obtained for various faradaic as well as nonfaradaic (*e.g.*, a structural transition in the EDL) electrode reactions. Its character-

The CV is characterized by the symmetric peaks during the positive and the negative going scans: $j_p = j_{pa} = j_{pc}$ and $E_p = E_{pa} = E_{ca} = E^{0'}$. The peak height is proportional to scan rate and coverage

$$j_p = \frac{n^2 F^2}{4RT} \Gamma r \quad (2.54)$$

The integration of the peak in the CV allows to evaluate the amount of charge per surface unit q transferred through the interface, after subtraction of EDL charging current. According to Faraday's law, it is proportional to the coverage of the substance:

$$q = nF\Gamma \quad (2.55)$$

The full width at half maximum (FWHM) ΔE_{FWHM} for non-interacting species is given by

$$\Delta E_{FWHM} = 3.53 \frac{RT}{nF} \quad (2.56)$$

Higher or lower values of ΔE_{FWHM} indicate repulsive or attractive interactions between neighbouring species. Very sharp peaks usually indicate a redox-reaction coupled with a phase transition and correspondingly to a significant change of the capacitance.

Curve 3 (Fig. 2–8B) demonstrates a typical CV for a fast oxidation-reduction process under diffusion control. The most pronounced feature of the curve is the shift between the formal potential of the redox pair $E^{0'}$ and the peaks of the CV E_{pa} , E_{pc} . I will explain the process in detail for a positively going scan.

The surface concentrations of the components of the redox pair follow the electrode potential (Eqn. 2.52), while those in the bulk of the electrolyte remain constant. The faradaic process starts when the electrode potential E approaches $E^{0'}$. The gradient of concentrations leads to the diffusion of reactants and products. As the potential passes $E^{0'}$, the surface concentration of the reactant drops to zero, *i.e.*, all molecules of the reactant reaching the surface immediately oxidize. Mass transfer of the reactant to the surface reaches a maximum. The simultaneous expansion of the diffusion layer and its depletion by the reactant leads to a decrease of the faradaic current. Reversing the direction of the potential sweep leads to a similar situation for the cathodic peak.

The exact mathematical treatment of the $j - E$ function of the CV [31, Sec. 6.2.1] is rather complicated and shall be omitted here. The separation of the cathodic and of the anodic peaks is given by

$$\Delta E_p = E_{pa} - E_{pc} = 2.3 \frac{RT}{nF} \quad (2.57)$$

and is independent of the sweep rate. The average of the two peak potentials is given by

$$E_{mid} = \frac{1}{2}(E_{pa} + E_{pc}) = E^{0'} + \frac{RT}{nF} \ln \left(\frac{D_{Red}}{D_{Ox}} \right)^{1/2} \quad (2.58)$$

There is generally a little difference in the diffusion coefficients of the reduced and of the oxidized forms of the reactant. Thus, E_{mid} could be used as an estimation of the formal/equilibrium potential of the studied redox pair.

The $j - E$ characteristics of a diffusion-controlled redox-process is given by

$$j(E) = nFc \left(\frac{nFD_r}{RT} \right)^{1/2} \pi^{1/2} \chi(E) \quad (2.59)$$

and its shape is determined by the auxiliary function $\chi(E)$. The tabulated values of χ as a function of $n(E - E_{mid})$ can be found in the literature [54]. The maximum value of χ is 0.446. The steady-state CV represents the superposition of two diffusion-controlled redox-processes.

The characteristic dependence of position and height of the peaks on the sweep rate r could be used to confirm the mechanism of the electrode reaction. The latter is linearly proportional to r for surface confined species (Eqn. 2.54) and to $\sqrt{r}$ for diffusion-controlled reactions (Eqn. 2.59). Surface coverage and diffusion coefficient of the species could be determined from the absolute value of the peaks.

So far I was considering only reactions with a very fast ET step. The time scale of electrode reactions in CV is governed by the potential sweep rate r . The latter is a basis for the determination of what is a “slow” and a “fast” ET in a particular reaction. The slow ET between electrode and surface-confined species results in a separation of the positions of the cathodic and of the anodic peaks, which increases with the sweep rate. If the rate of ET and diffusion are comparable, one refers to this situation as quasi-reversible process. It is characterized by the decrease and broadening of peaks and an increase of their separation with an increase of r . In principle, the peak separation in a quasi-reversible reaction can be used to determine the rate constant of an ET process [54]. If the reaction rate is determined by a very slow ET (irreversible process), the surface concentration of reactants and products could be taken to be equal to that in the bulk of the solution. In this case the $j - E$ characteristics is independent of the sweep rate (however, the contribution of the EDL charging is dependent) and could be determined from a series of measurements at constant potential.

2.4 Scanning Tunneling Microscopy

The technique of scanning tunneling microscopy (STM) was the first one which made the visualization of nanoscale structures such as atoms and molecules on surfaces possible. Invented already 25 years ago [55–57] in the IBM Zürich Research Laboratory, it quickly became a popular tool to characterize surfaces in UHV and at solid-liquid interfaces [58, 59]. The original inventors of the STM, Gerd Binnig and Heinrich Rohrer were awarded the Nobel Prize in Physics in 1986.

Modern applications of STM extend far beyond its original application as a microscopy tool [58, 60]. Here I will briefly describe the basics of STM.

2.4.1 Tunneling effect

The STM technique is based on the effect of electron tunneling, which is well known from quantum mechanics. Tunneling is also an important mechanism of ET at the nanoscale.

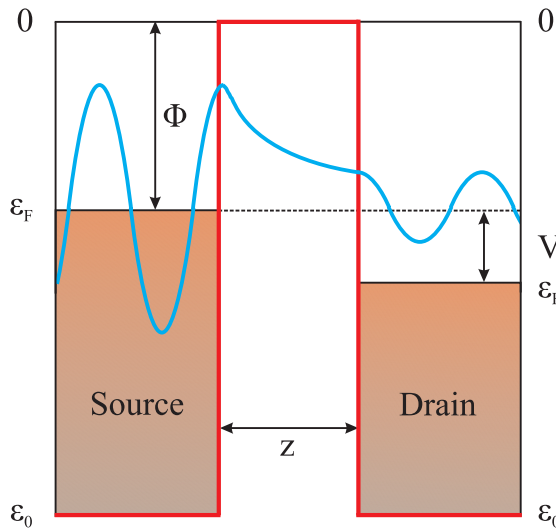


Fig. 2–9: Tunneling effect and tunneling in a one-dimensional source–gap–drain junction. The potential barrier is red line, the wavefunction is sketched blue.

Let us consider an electron which is “freely moving”, in other words its total energy is higher than the potential energy in that region (red line on the left part of Fig. 2–9). It may be represented as an oscillating wavefunction (blue curve). When it incidents an energy barrier of constant relative height Φ and width z (Fig. 2–9), it may penetrate through it with a probability

$$P(z) = \exp\left(-\frac{4\pi}{h}\sqrt{2m_e\Phi}\cdot z\right) \quad (2.60)$$

On the other side of the barrier (right part of Fig. 2–9) it again “moves freely” with a reduced amplitude. Thus, the probability of tunneling through the barrier exponentially decreases with barrier width z . The exponential decrease is proportional to square root of the barrier

height $\sqrt{\Phi}$. In order to distinguish the described mechanism from those involving tunneling mediation by the medium in the gap, it is further referred to as a direct tunneling. Direct tunneling has a non-vanishing probability up to the barrier width of a few nm.

2.4.2 Tunneling between metal electrodes

We consider two parallel metal electrodes separated by a nanometer-scale gap of vacuum or non-conductive media [61]. According to the convention introduced in Sec. 2.1.1, the potential energy of the electrons¹¹ in vacuum U is zero, in other media it is not necessary equal to zero but in any case the chemical stability of the metal in the media implies that $U > \epsilon_F$ and thus the tunneling barrier is $\Phi = U - \epsilon_F$.

¹¹ Again, it would be more correctly to use electrochemical potential instead of “energy”.

ET by means of tunneling may occur even when the Fermi levels of both electrodes are aligned, *i.e.*, if the bias is equal to zero. However, than the probability of the ET is equal in both directions and the net current is effectively zero. When a bias is applied across such a junction (Fig. 2–9), the population of energy levels of two electrodes is alternated and tunneling dominates in one direction: from occupied levels of the source to non-occupied energy levels of the drain. The current density j as a measure of the ET rate depends on bias determining the number of available energy levels and on the electron transfer probability. In a low-bias approximation [61]

$$j(z) = V \cdot \frac{3}{2z} \sqrt{2m_e \Phi} \left(\frac{e}{h} \right)^2 \exp \left(-\frac{4\pi}{h} \sqrt{2m_e \Phi} \cdot z \right) \quad (2.61)$$

When z is sufficiently big, the latter is equivalent to

$$j(z) \propto V \cdot \exp \left(-\frac{4\pi}{h} \sqrt{2m_e \Phi} \cdot z \right) \quad (2.62)$$

Thus, the tunnel current shows the same dependence on the barrier height and width as the electron tunneling probability (Eq. 2.60) and is proportional to the applied bias. When the applied bias is too big, additional effects (lowering of the barrier due to the shift of Fermi level, ET by field emission in a high electric field, etc...) may arise.

2.4.3 Scheme of STM

In STM a sharp metal tip, or probe, is brought into contact with a conductive surface (Fig. 2–10). The bias applied between tip and sample

$$V = (\phi_t - \phi_s)/e \quad (2.63)$$

causes ET by tunneling via the gap (left inset in Fig. 2–10). The tunneling current I_T is measured by the preamplifier with a high sensitivity and with a typical operational range of 1 pA to 100 nA. Transducers based on ceramics exhibiting piezo-effect (expansion or shrinking under an applied voltage) allow probe movement in the nanoscale. The tip is scanned across the surface with the help of a piezo element moving it in lateral directions while the tip-sample separation z is controlled by another piezo element [56].

Two operational modes of the STM are possible. In constant current mode the set-point I_T is kept constant via a feedback circuit by adjusting the z position of the probe (Fig. 2–10). The value of the set-point current is selected according to the application, typical values are between 0.01 – 10 nA. The information on vertical displacement of the tip as a function of the lateral position is recorded as an array of (x, y, z) data and may be presented as three-dimensional (3D) or two-dimensional (2D) image. In a 2D image the gradient of the color is associated with a vertical scale to represent topography. A brighter color typically designate higher feature (right inset in Fig. 2–10).

In constant height mode the vertical position of the tip is kept constant during the lateral scanning while the value of the tunneling current I_T is recorded as a function of the tip position. The array of (x, y, I_T) data provides information on surface topography and may be presented in a similar way as results of the constant-current mode STM.

STM allows resolution in the sub-nm scale. The resolution ability of the STM is due to the strong dependence of the tunnel current on the distance z between two electrodes, *i.e.*, tip and sample. With a typical barrier height of a few eV, an increase of z by the

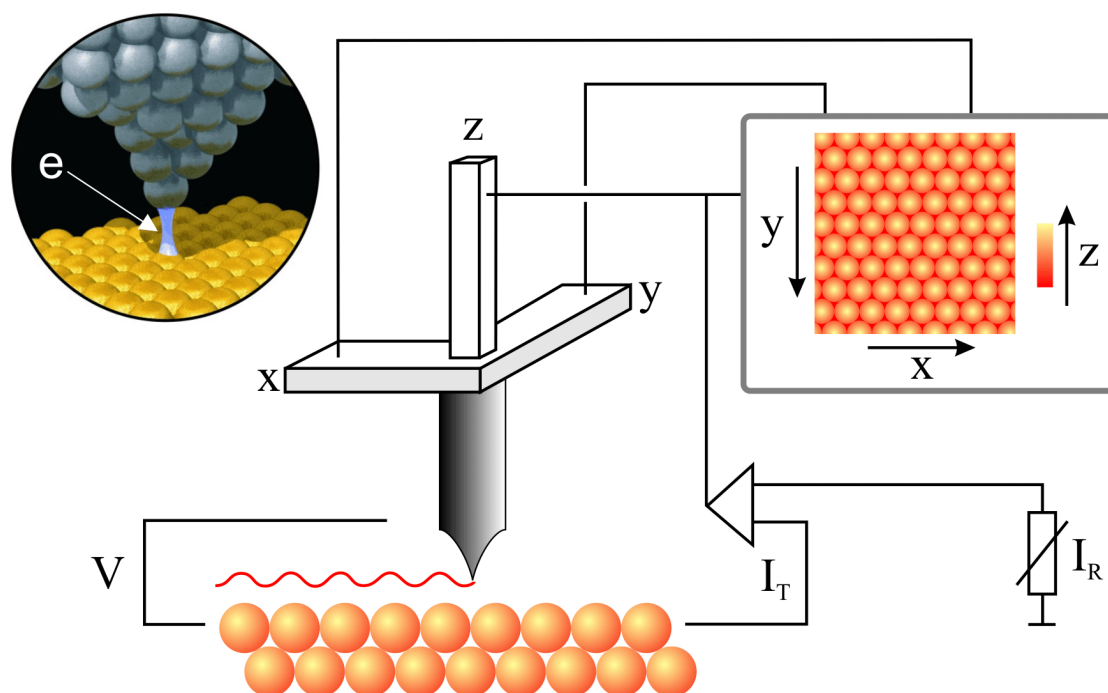


Fig. 2–10: Scheme of STM configuration (redrawn from [47]). Right inset – electron tunneling between tip and sample, left inset – obtained STM image.

size of a single atom of a metal (0.2 – 0.5 nm) decreases the tunnel current up to three orders of magnitude [56]. Thus, due to the distance sensitivity only the most protruding part of the sharp tip acts as a probe.

Despite of the name “microscopy”, the STM technique in constant-current mode is not providing direct information about the surface topography. Instead, it measures profiles of the constant tunneling current. In conventional application as microscopic tool it is common to assume that the constant tunneling current profiles and the surface topography coincide. However, the local variation of tunneling barrier as well as other processes (*e.g.*, the tunneling mediated by adsorbed specie) may lead to features in STM images not related to the surface topography. Another important limitation is that STM *per se* is not providing “chemical” information about the composition of the surface.

2.4.4 Scanning Probe Techniques

The invention of STM and its wide acceptance lead to the emergence of techniques based on similar technical realization and known under the general term scanning probe microscopy (SPM). One of the widely used techniques is atomic force microscopy (AFM) [62, 63]. Unlike STM, it is based on the force interaction of a probe (commonly referred to as a cantilever) with a sample instead of an electronic interaction as in STM. The realization of the scanning part of AFM is very similar to that in STM, and the two techniques may be combined in one system. AFM doesn’t require a conductive surface, but its resolution is typically worse than that of STM. It is possible to combine AFM scanning with current measurements by using a metal-coated cantilever and by applying a bias voltage. This realization is known as current probe atomic force microscopy (CP AFM). The latter features a decoupling between the probe positioning and current measurement. Both STM and AFM are widely used for surface studies and manipulation at the nanoscale.

2.4.5 Scanning Tunneling Spectroscopy

The term scanning tunneling spectroscopy (STS) is usually applied to the studies of tunneling current at fixed lateral position (x, y) . In this case I_T is determined only by the bias V and tip-sample separation z and may be described by equations such as 2.62. In order to study an intrinsic response of the interface, also the feedback mechanism has to be disabled. Although more complicated combined operational modes are also possible, the dependence of the current on one parameter at fixed value of another is typically measured. Therefore, two operational modes of STS are distinguished.

In current-distance, or $I - z$ mode the dependence of the tunneling current I on the distance z at fixed value of the bias V is studied. The absolute value of z is not always known¹², and a relative scale of z may be used. If the tunneling barrier is constant in the studied range of z , the dependence of the tunneling current on distance may be expressed as

$$\ln I(z)_V = a - b \cdot z \quad (2.64)$$

where a is a constant and $b = \frac{4\pi}{h} \sqrt{2m_e \Phi}$ (see Eqn. 2.62). In case of a non-exponential dependence of I_T on z due to the non-uniform structure of the media in the tunneling gap, it may be expressed as an effective tunneling barrier:

$$\Phi_{eff} = \frac{h^2}{32\pi^2 m_e} \left(\frac{\partial \ln I}{\partial z} \right)_V^2 \quad (2.65)$$

More complicated treatment of the $I - z$ spectroscopy results allows to make conclusions about the structure of the interface (Cha. 4).

In current-bias, or $I - V$ STS mode the dependence of the tunneling current I on bias V at fixed value of the separation z is studied. This mode is equivalent to the transport studies introduced in Sec. 2.1.3 with substrate and probe been either source or drain electrodes. The structure of the interface is complex and includes, for example, active molecules embedded into this gap. The $I - V$ characteristics of a particular interface strongly depends on its structure and electronic properties.

By using various STS modes, it is in principle possible to decouple structural and electronic factors on the tunneling current. The STS experiments may be performed in such a way, that $I - V$ scans are carried out at predefined fixed values of z . Both modes may be also used to locally modify the substrate surface via mechanical interactions with the probe or by application of large voltage pulses.

2.4.6 Electrochemical STM

Relatively soon after the invention of STM it was shown that it could be applied to solid-liquid interfaces as well [64–67]. The developed technique of electrochemical scanning tunneling microscopy (EC STM) became a unique tool for atomic-resolution, *in situ* structural studies of charged solid-liquid interfaces [47, 68, 69], which properties are controlled by the electrode potential.

The EC STM instrumentation combines that typical for electrochemical and *ex situ* STM experiments. The electrochemical cells used have to be miniaturized due to the limitations imposed by the geometry of the STM setup (Fig. 2–11). The sample is located at the bottom of the cell or, in many cases, actually forms it and acts as WE of the electrochemical cell. The liquid cell itself (not shown) is mounted atop of the sample and holds the solution. The electrode potential of both tip and sample must be

¹² For the approaches to the determination of absolute distance z see Cha. 5

controlled independently with respect to the RE, which requires a special device called bipotentiostat. The operational principles of the latter is similar to that of a potentiostat with effectively two WEs, the bias is determined as (*cf.* Eqn. 2.63)

$$V = E_t - E_s \quad (2.66)$$

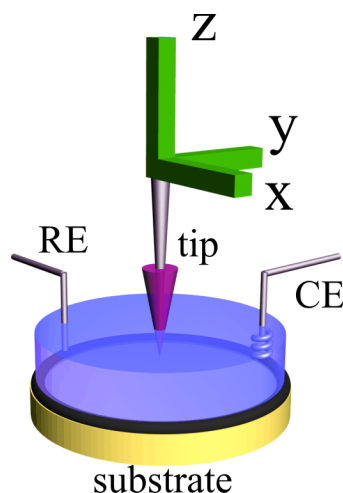


Fig. 2–11: Sketch of EC STM cell showing substrate, solution, coated tip, RE and CE.

Two wires employed as CE and RE (often QRE, see Sec. 2.3.2) accomplish the arrangement of the electrochemical cell. A real RE used in conventional electrochemical studies could be attached to the EC STM cell, however it makes the whole setup more complicated.

The major difficulty of the EC STM experiment is that it is not possible to distinguish between the tunneling current and that of an electrode reaction. Therefore, the electrochemical reaction on the tip should be avoided, essentially by taking care about two issues. First, the electrode potential of the tip should be held within the ideal polarizability range to avoid a significant amount of current flowing through the tip. However, with a macroscopic tip area even a minute current density results in a current much higher than that of tunneling. The current of the electrode reaction on the tip is reduced to the pA-level by the isolation of the whole surface immersed in solution, except of its very apex (Fig. 2–11). A wide range of materials was used as an insulation: Apiezon wax, glass, polymers, nail

polish and electrophoretic paint. The isolation procedure used in this work is described in Sec. 3.6.2.

A note should be given about the material of the tip (for the details see Sec. 3.6.2). Tungsten (W) probes are commonly used for UHV STM experiments due to their stiffness and sharpness. The procedure to prepare atomically sharp tungsten tips by direct current (DC) etching in concentrated NaOH solution is well known. Coated tungsten tips were also used in an electrochemical environment. However, their stability is limited to applications in acidic solution and only within a rather narrow potential range, which is a serious limitation for $I - V$ studies in an electrochemical environment. Alternative materials used are Pt-Ir alloys and Au. They benefit from the electrochemical stability / ideal polarizability, but are softer, less sharp and more difficult to prepare.

The “external” control of the potentials (*i.e.*, Fermi energy) of both tip and sample with respect to the RE results in two possible modes of current-voltage electrochemical scanning tunneling spectroscopy (EC STS). The first is fully equivalent to that in an *ex situ* environment: the potential E of one WE (typically, sample) is fixed, while that of the other (typically tip) is swept. It is referred to as a variable bias mode of current-voltage spectroscopy. The bias is determined by Eqn. 2.66. The second, fixed bias mode is unique for the electrochemistry (EC) environment. Here the potential of both the tip and of the sample are swept simultaneously, so that their difference (*i.e.*, bias) is kept constant. This mode allows to address in a controllable way the MO of molecules immobilized on surfaces, even at the single molecule level (Cha. 8).

The current-distance EC STS has its own peculiarities in comparison to an *ex situ* environment. The structure of the tunneling junction is complex due to the presence of two solid-liquid interfaces and the constituents of the electrolyte in the tunneling

gap. This may lead to deviation of the $I - z$ dependence from a simple exponential one, reflecting structure and electronic properties of the interface (Cha. 4).

Other SPM methods were successfully used in an EC environment as well. AFM in solutions doesn't require special instrumental modification, except of the isolation of the scanners from water and the usage of a liquid cell. The CP AFM in electrolyte requires the implementation of a bipotentiostat as well as an insulation of the probe.

The early EC STM experiments demonstrated atomic resolution of bare single crystal surfaces in various electrolytes, including the formation and lifting of the surface reconstruction [70]. Subsequently structure studies of ionic and organic adlayers were reported [71–74]. More recent applications of EC STM became an essential part of an “electrochemical nanoscience”, which go far “beyond imaging” [60] and include time-resolved kinetic studies, nanofabrication [75–77] and various transport studies.

2.5 Substrates and interfacial structures

In this subchapter I will describe in details the types of substrates used for experiments described in this work. The nanoscaled interfacial structures, which are the subject of the surface science, are created on certain substrates, which is in turn produced by the section of the solid body. These solid bodies and surfaces created from them are addressed in the first part of this subchapter, and part two describes general principles of self-assembly.

2.5.1 Single crystal metal surfaces

Bulk structure of crystal

Most of the solids have a crystalline structure, where its building elements (atoms or molecules) tend to arrange in a well-defined ordered way. The ideal crystal is an infinite 3D structure built by the translation of the basic unit cell. The latter is a parallelepiped in a general case (Fig. 2–12) and fully characterized by three distances a , b , c and angles α , β , γ . The axes of the crystallographic system of coordinates are oriented by the directions of unit cell. The translation of the unit cell by vector

$$\vec{t} = N_x \cdot a\vec{e}_x + N_y \cdot b\vec{e}_y + N_z \cdot c\vec{e}_z, \quad (2.67)$$

where $\vec{e}_i$ are unit vectors of the corresponding axes and N_i are integer numbers, allow to construct a periodic lattice.

The symmetry is a very important aspect of the crystal structure. It is determined by the symmetry of the unit cell itself, but also by the arrangement of crystal's building elements within the unit cell. Not going into details, I will stress that the majority of metals used in various fields of science and technology (Ag, Al, Au, Cu, In, Ir, Ni, Pb, Pd, Pt, Rh), as well as other more exotic elements, form a face centered cubic (FCC) type crystal lattice, which is relevant for this work. It is a cubic unit cell ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$) with additional atoms in the center of every face (Fig. 2–12) and one of the three lattices with the highest packing density possible for spherical atoms. It could be also represented by the three stacking hexagonally closely packed layers, which are recurring.

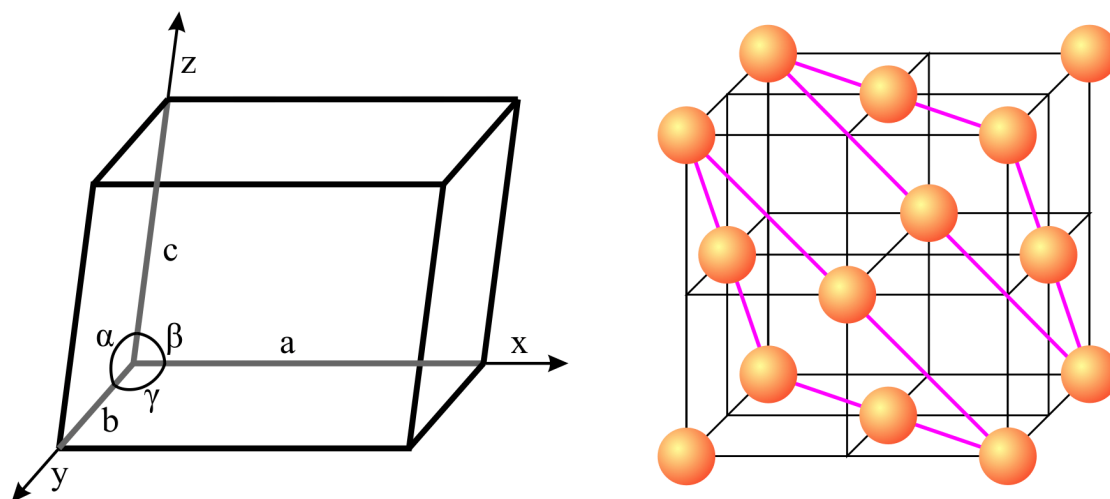


Fig. 2–12: Left: general unit cell of crystal with lattice parameters; right: unit cell of FCC lattice with hexagonal closely packed layers.

The real crystalline solids are formed during the growth from many nuclei and consist from many small crystallites. Special precautions should be taken in order to obtain crystals with a structure close to the ideal.

Crystal planes

The crystal planes are sections of the 3D crystal structure classified by unique Miller indices (hkl). These are the reciprocals of the intercepts (in units of lattice dimensions a , b , c) of the plane with the x , y and z axes. Small integer numbers are used, and parallel planes have identical indices. Considering the symmetry of the FCC unit cell, it is possible to derive the sets of six symmetry equivalent planes. They have the same structure and further one set of indices is used to designate all of them.

The low index faces of a FCC lattice are shown in Fig. 2–13. “Low” indicates that only 0 and 1 used as indices. The sections of FCC lattice corresponding to the planes (100), (110) and (111) are shown in the upper part of Fig. 2–13. They are particular important in FCC lattice due to the fact that only they pass through the atoms (marked by magenta color) and therefore have true atomically flat surfaces.

An example of STM images [78] of three low-index faces of a FCC metal (Ag) is shown in the lower part of Fig. 2–13. These ideally flat surfaces have 2D periodic structures, which, similar to crystals, could be represented by the translation of the parallelogram unit cell shown in red. The symmetry of the surface varies and corresponds to a square, rectangular and hexagonal arrangement of atoms in (100), (110) and (111) faces respectively. Among them the (111) has a highest packing density and corresponds to the hexagonal closely packed layer of atoms.

The single crystal surfaces are used as well-defined substrates for both electrochemical and STM experiments. One of the fundamental goals of modern electrochemistry is to establish relation between the surface structure of the electrode and its reactivity in processes like adsorption of ions and molecules, deposition of metals, redox reactions with a small molecules, *etc.* The usage of single-crystal substrates allows to control surface structures on atomic level. The high quality STM experiments with sub-molecular and atomic resolution also requires substrates with atomically controlled

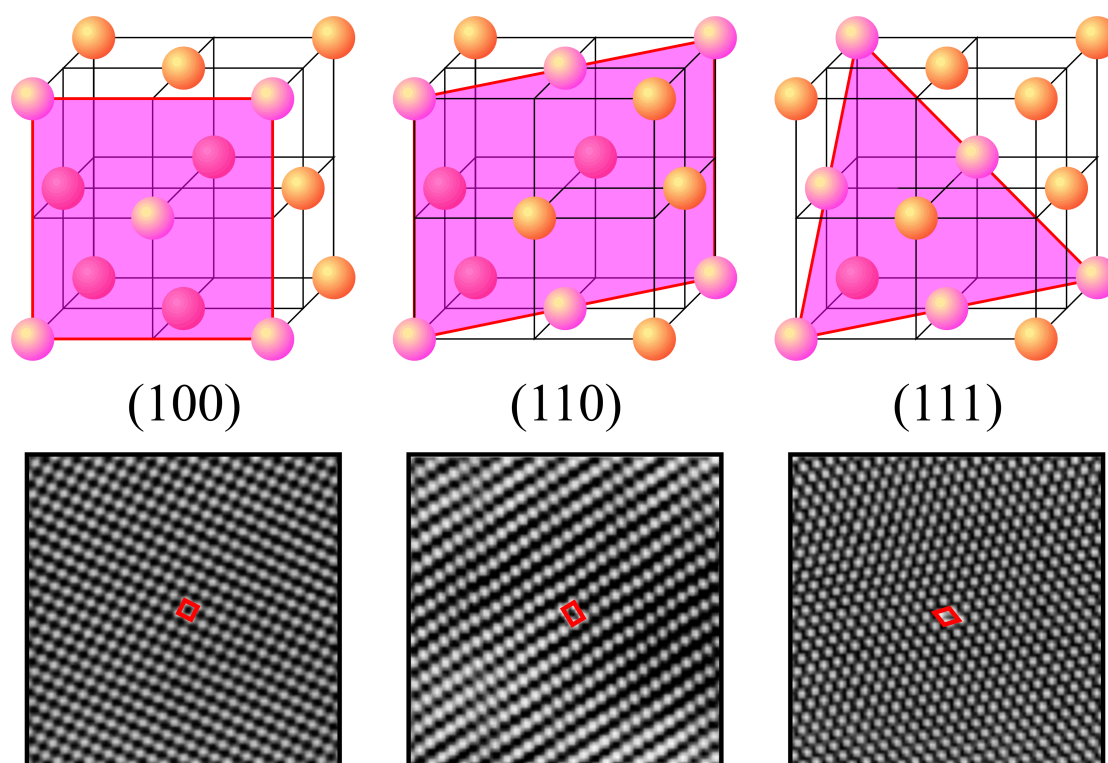


Fig. 2–13: Low index faces of FCC metal: sections and STM images of three low-index faces of silver single-crystal electrode in 0.05 M H_2SO_4 , 7×7 nm [78]. The surface unit cell is shown in each image.

structure, which are supported by the conductive single crystal surfaces.

Real solids and surfaces

Although many solids adopt crystal as a preferable type of structure, it is quite difficult to obtain single crystal, where a uniform single lattice spans over macroscopic dimensions. A conventional polycrystalline material consists of microscopic domains. Each of them constitute single crystal lattice formed during crystallization from a single nucleus of the new phase. A polycrystalline surface of such sample is formed by the randomly oriented and distributed sections of individual grains.

The preparation of single crystals requires controlled growth from a single nuclei (see further). The defects of the bulk crystal structure, such as point defects or dislocations are unavoidable. The crystal is then oriented, cut and polished to give single crystal surface with a desired structure. Due to technical limitations, each step introduces additional surface defects.

The single crystal surface is aimed to consist mostly of terraces. The terrace is an atomically flat up-most layer of atoms with one of low index orientations. An example is shown in Fig. 2–14 for the (111) orientation of surface and terraces, which is relevant for this work. The atomic layers protrude below each other forming a monoatomically high steps on their boundaries. The steps are mostly a result of a miscut due to a small misorientation during cutting and polishing. A miscut with respect to an orientation of a terrace could be done intentionally in order to form surfaces with terraces of predefined average width and nearly equidistant monoatomically high steps. The geometry of close-packed steps on a (111) surface could be (111) or (100), Fig. 2–14 displays (100)

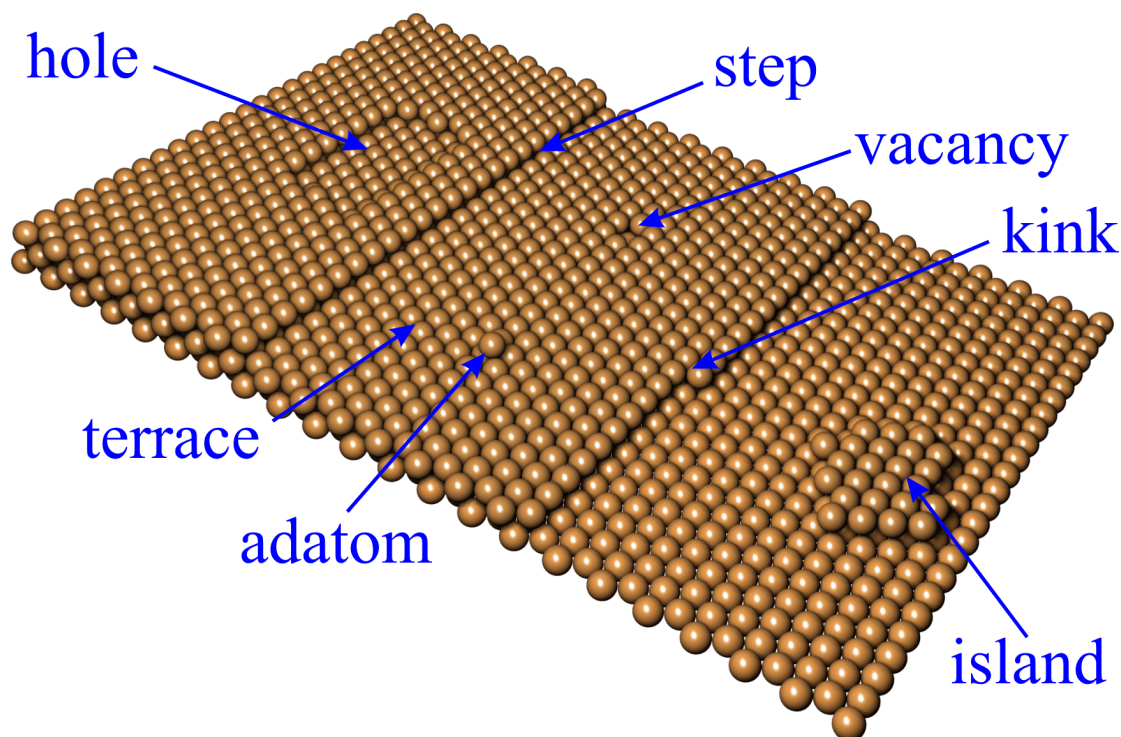


Fig. 2–14: Types of surface features for (111) surface of FCC lattice.

steps. Two steps at the boundary of an atomic layer may form an angle determined by the symmetry of the surface (*e.g.*, integer numbers of 60°). Additionally, the single step could have kink defects in the line of atoms.

While terraces and steps are essential features of the real single crystal surface, other defects could be created as well. Surface atoms are often displaced, *i.e.*, removed from the terrace or attached on top of it, during heterogeneous processes involving species strongly interacting with the substrate. The missing single atom and many adjacent atoms are known as a vacancy and as hole defects. On the other hand, the additional atom/adjacent atoms on top of the terraces form adatom and island defects. All these features have a vertical dimensions of one or a few atomic layers with respect to the terrace (Fig. 2–14) and could be healed in an annealing process (see further). Other defects have much higher vertical dimensions and may be considered as permanent ones. The region of steps separated by the terraces of a few atoms (step bunching), disordered regions and grain boundaries observed sometimes on a single crystal surface. They indicate poor quality of the crystal due to fabrication or handling [79].

Surface relaxation and reconstruction

The surrounding (coordination sphere) of the surface atoms deviate from that in the bulk of the crystal. In order to minimize the total energy, the surface atoms often adopts a geometry which differs from the one determined by the 3D crystal structure. Two types of behaviour are distinguished: surface relaxation and surface reconstruction [79].

The surface relaxation is an increase of the distance between the first and the second surface layer, which doesn't change the 2D atomic surface structure. In some cases also the lateral arrangement of the atoms may deviate from the one dictated by the crystal

plane. The reconstruction of the surface is often connected with a phase transition of its structure. The energetically favorable transition of an unreconstructed surface to a reconstructed one is often kinetically hindered at room temperature. The activation barrier could be overcome by thermal energy, *i.e.*, by annealing to create thermally induced reconstruction. Reconstruction of a metal surface is a well-known phenomenon in an UHV environment. Transition between unreconstructed and reconstructed metal surfaces could be also observed in an electrochemical environment [70]. In this case reconstruction and the reverse process of its lifting are tuned by the electrode potential and/or adsorbates. I will not go into details of the reconstruction phenomena, the experimentally relevant details are described in Sec. 3.4.6.

Crystal preparation

The procedures of single crystal preparation and characterization are well known at present time [79] and will be briefly described in this subchapter. A single crystal surface could be prepared in a laboratory by various techniques.

Vacuum evaporation on a suitable substrate under carefully chosen conditions allows to obtain thin metal film with a single crystal surface. The supported thin film may be used for electrochemical/interfacial studies as a substrate with high quality and low production cost.

Small spherical single crystals, known as bead crystals are prepared by melting one end of a high purity metal wire [80, 81]. When cooled, a drop of molten metal crystallizes. If the crystallization of the metal is slow enough, no nuclei of the solid phase is produced in the liquid. Instead, the existing crystallite in the solid part of the wire serves as a seed for a new phase. The new phase grows as a single crystal with a lattice following that of the seed. A well prepared bead is built by (111) facets in an octahedral configuration. These facets consist of large terraces separated by monoatomically high steps and virtually no other defects. Facets of the bead crystal with (111) orientation could be directly used for some types of studies. If a bigger area of a (111) surface or a surface with other crystallographic orientation is required, the small bead has to be oriented, cut and polished.

Massive metal single crystals are grown from a liquid phase using controlled cooling techniques as well. The technological processes involved are beyond the capabilities of the laboratory facilities and beyond the scope of this work. The consecutive treatment of grown single crystal is often more difficult than the crystal growth process.

First, a “coarse” cutting of the single crystal in a direction of the desired crystallographic plane is performed. A mechanical sawing, spark or electrical erosion or chemical erosion may be employed. The methods have varying accuracy, speed and mechanical impact on the crystal. The crystal is then fixed (*e.g.*, by epoxy resin) and oriented, *i.e.*, the direction of the desired crystallographic plane is precisely determined. X-ray diffraction is a main tool for the orientation of single crystals. A single crystal is mounted to the head of a goniometer, its orientation could be optimized by comparison of the Laue diffraction pattern with the known standard one (Greninger chart) [82, 83].

The next step of the preparation is polishing. The quality and accuracy of polishing is crucial for obtaining well-ordered surfaces. For purely mechanical polishing a silicon carbide emery paper is used at first. Afterwards a diamond paste (for hard materials) or aluminium oxide (for soft materials such as Au) with decreasing particles size in consecutive polishing cycles employed as polishing materials. A surface roughness of

better than 30 nm can be obtained. Finally, the residues of the polishing material are removed, *e.g.*, chemically, and the surface is smoothed in a few sputter and heating cycles or by flame annealing. The overall precision of the surface orientation within $< 0.1^\circ$ is possible, which corresponds to the terrace widths of several hundred nanometers.

Pretreatment

The single crystal substrates are typically pretreated before the experiment. The purpose of the final preparation is to heal the surface defects by allowing an increased mobility of surface atoms and to obtain a chemically clean surface.

A single crystal surface can be prepared in an UHV environment by cycles of Ar-ion bombardment (sputtering) and high temperature annealing. The surface structure and chemical composition of the interface can be simultaneously characterized by structure-sensitive interfacial techniques. Historically the UHV-based procedure for the final preparation of the single crystal surfaces was first employed in surface science. Experiments, based on the transfer of substrates prepared under UHV conditions into an electrochemical environment, have been developed in 1990th. The UHV data are very important for structure characterization of single crystal surfaces and, whenever possible, the results of electrochemical studies should be compared with that in UHV [39]. However, the UHV procedure of substrate preparation is rather expensive and time-consuming for regular electrochemical experiments.

In 1980 the group of Jean Clavilier have proposed a very convenient and cheap method of the crystal pretreatment without the need of a UHV technique based on flame annealing and consecutive quenching in pure water [80]. The CVs measured for Pt bead crystals treated in this way were found later to be in agreement with those obtained with clean and well-ordered surfaces prepared by UHV procedure. The flame annealing and quenching method was later used for the pretreatment of single crystals made from a wide variety of metals. In particular for Pt and Au, the flame annealing method offered the possibility to work with single crystal electrodes for many electrochemical groups all over the world.

Both reorganization of atoms and cleaning of the surface is achieved by annealing in a flame. Depending on the desired temperature and purity, a Bunsen burner or a hydrogen flame could be used. To achieve optimal conditions, several parameters can be varied: annealing time, temperature, use of oxidative or reductive zone of a flame. The annealing in the oxidizing part of the flame helps to remove organic contaminations. The duration of annealing ranges from a few seconds to hours. A long time is needed only for the initial treatment after polishing and/or healing of the disordered surfaces; few minutes is often enough, *e.g.*, to prepare the reconstructed surface.

The annealing in the presence of oxygen efficiently removes organic impurities, but as soon as the sample is cooling down it starts to collect contaminations from the environment until covered by the working solution. This process may be suppressed by intermediate protection of the surface, the exact method depends on experimental conditions. A very common strategy is to protect the working surface by a drop of ultrapure water. This is typically done by quenching, *i.e.*, immersing of the still hot crystal into water, often also purged with neutral (N_2 , Ar) or reducing (H_2) gases. The quenching after annealing is suitable only for small bead crystals with a diameter less than a few mm. When a bigger crystal used, the thermal shock may destroys the bulk structure and increase the amount of surface and bulk defects. The alternative solution

is to allow crystals to cool down in a clean gas atmosphere, with or without subsequent protection by water. The protection of the surface after thermal treatment is especially important for metals with an “active”, highly adsorbing surface, in particular Pt group metals. For less active metals such as Au or Ag it is not crucial provided that substrate after annealing is only treated for a short time in a clean environment.

I will only mention other procedures of annealing and surface protection. Instead of the flame, the metal crystal can be annealed by passing a current (resistive heating) or by circular currents induced by an alternating magnetic field (non-contact inductive heating). If needed, the sample could be immersed in a gas atmosphere during annealing. Instead of water, the sample could be protected by an adsorbate which can then be easily removed during the experiment to leave a clean surface. An example is the protection of the Pt surface by CO, which is easily stripped by oxidation to CO₂. Depending on the experimental requirements and conditions, the pretreatment of single crystal surfaces may strongly vary in details. The carefully chosen procedure of the final preparation allow to obtain well-defined substrates for further studies, using it either with a bare or modified surface.

2.5.2 Assembly and “bottom-up” approach

The assembly, or “bottom-up” approach to the fabrication of interfacial structures is the pendant of the more traditional for industry “top-down” material processing: *e.g.*, microfabrication or lithographic techniques, where big machines are used to prepare small structures. In bottom-up approach nanoscopic building blocks (atoms, molecules, metal nanoclusters) self-organize in a larger structure. The bottom-up approach of constructing complex architectures is a widespread principle in nature. Examples are inorganic minerals, crystals, clays and the whole world of living matter [84]. This approach requires a deep understanding of the molecular structures, their assemblies, and dynamic behaviors.

The self-organization of adjacent molecules is controlled by the intrinsic properties of these molecules (chemical complementarity and structural compatibility) and governed by weak intermolecular interactions [84]. Molecular self-organisation involves mostly noncovalent bonds, which are individually quite insignificant. Collectively these weak molecular bonds (hydrogen bonds, electrostatic interactions, van der Waals interactions, hydrophobic interactions, *etc.*) provide a mean for the formation of well-defined structures [84].

Self-organization, although possible in solutions, typically includes assembly of

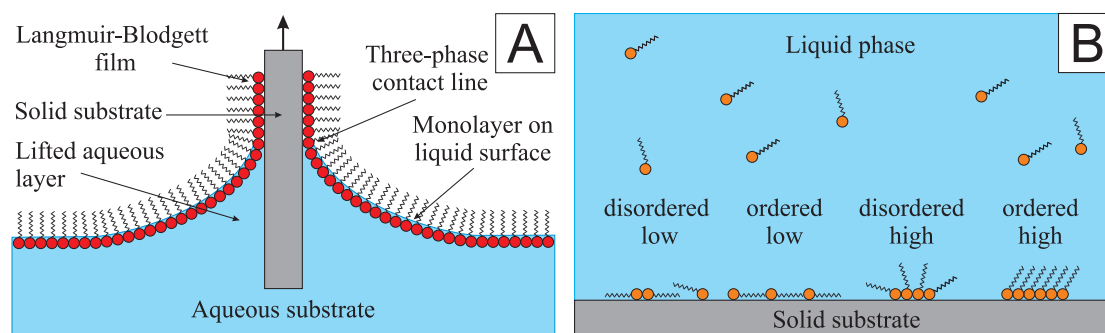


Fig. 2-15: Monolayer preparation technique: (A) LB technique (B) SAM with typical examples of the formed phases.

the molecular building blocks on the substrate. Assembly results in a thin film of molecules in a direct contact with the surface – a monolayer. Depending on the amount of molecules per surface area, the packing density may correspond to a lower or a higher coverage. The latter is the primary factor affecting the further self-organization and resulting structure of the interfacial phase.

The process of the assembly may be performed by various techniques. Historically, the first well established method to reproducibly prepare monolayers was a Langmuir-Blodgett (LB) technique [85–88] proposed by Katharine Blodgett after the studies of floating monolayers by Irving Langmuir. It is based on the interfacial properties of amphiphilic molecules (surfactants) consisting of two distinct parts: a hydrophilic head (polar group such as -OH, -COOH, -NH₃⁺ etc.) and a hydrophobic tail (hydrocarbon or other chain). Being dissolved in polar solvent, *e.g.*, water, they occupy positions on the water-air interface in such way, that the head is located “inside” the aqueous phase and the tail “sticks out” of it into the air. Depending on the amount of the molecules on the surface, different phases of the monolayer may be observed. The small surface concentration results in a well-separated, non-interacting molecules – surface “gas” phase. Intermediate concentrations obtained, *e.g.*, by compressing the film (constricting the surface) corresponds to the “liquid” phases with loosely packed, weakly interacting molecules. High concentration results in a solid monolayers of densely packed, strongly interacting molecules (Fig. 2–15A). Further compression leads to the collapse of the film into three-dimensional structures.

The LB film is prepared by the deposition of the “solid” monolayer preassembled on a liquid surface onto the solid substrate. The idea behind is that a solid substrate is pushed through the monolayer which “sticks” to it (Fig. 2–15A). The polar head are well bound to the hydrophilic solid substrate, due to the molecular orientation the latter must be lifted out of liquid phase. The tails of the surfactant are, in contrast, attracted by the hydrophobic substrate and LB films are prepared by dipping the substrate through the monolayer on a liquid surface. It is also possible to prepare multilayers with a controlled structure by this technique.

The self-assembled monolayer (SAM) approach is widely used in research and applications for various purposes [89–91]. Despite of the broad definition, SAMs are understood as monolayers formed due to the chemical bonding of the desired molecules to the substrate surface. The prototypical example is an adsorption of molecules bearing thiol (SH) “head”-groups on a gold surface (see Cha. 6). The SAM technique typically includes bringing the solid substrate into contact with the solution of the target molecules (Fig. 2–15B), although the evaporation of molecules on the surface in the UHV environment is possible and widely used.

Further self-organization of the molecules constituting SAM strongly depends on the factors such as the surface coverage by the molecules and reversibility of the process. For the “head-tail” design of molecules typically used to prepare SAM, the coverage is closely related to the orientation of the molecule on the surface. Low coverage SAM corresponds to the molecules “lying” on the surface, while high coverage SAM corresponds to the head-groups closely packed on the surface and “standing” tails. The incomplete monolayers as well as intermediate situation between two characteristic adlayers are also possible.

The reversibility of the adsorption process affects the ordering of the adlayer. The formation of ordered structures, as it was discussed above, is controlled by weak intermolecular interactions. The latter allows to achieve optimal packing of the molecules,

but only if they are allowed to move to occupy energetically preferred positions on the surface and/or adjust their orientation as well as conformation (*i.e.*, mutual orientation of the parts of the molecule). The adsorption in highly non-equilibrium conditions leads to the “frozen” molecules on the surface and results in disordered monolayers with a stochastic packing and less defined properties.

2.6 Electron transfer studies at the nanoscale

Studies of the transport properties of the single molecular junction (SMJ) – a MJ incorporating ultimately only one molecule – are of importance not only for molecular electronics, but for fundamental science as well. They challenge both experimental and theoretical branches of modern science. There are currently also advances in the studies of the architecture of hybrid IC incorporating molecules [92, 93, and references therein], however, I will not discuss this topic.

At this point I would like to describe the general characteristics of ET at the nanoscale in comparison with macroscopic conductance phenomena (Sec. 2.1.2). The qualitative difference (*i.e.*, quantum effects) appears as the characteristic dimensions of a junction approaches few tenth of a nm, *i.e.*, at the distances comparable with the size of an atom. The conductance of a macroscopic sample is determined by the properties of the material as well as by the geometry of the whole body (*cf.* Eqn. 2.12 on page 27). On the other hand, the transport characteristics of the circuit including nanojunction is determined solely by the properties of this junction. It is convenient to consider nanojunction as a number of conductance channels connecting two macroscopic metal source and drain electrodes. Once electron enters a conductance channel, it passes through it with a transmission probability $0 \leq T \leq 1$. The imaginable conductance channels usually corresponds to a “nanobridge” in the structure of the junction. The quantum theory of conductance predicts that conductance of such nanojunction is equal to

$$G = G_0 \cdot \sum T_i, \quad G_0 = \frac{2e^2}{h} = 77.5 \mu\text{S} \quad (2.68)$$

where G_0 is the maximal possible conductance of a single channel, a quantum of conductance. Here the factor of two accounts for electrons differing only by their spins (spin degeneracy). Thus, the conductance at the nanoscale is determined by the number and “transparency” of the conductance channels.

2.6.1 Types of nanojunctions

In this work I will consider three distinct types of nanojunctions. In the absence of a nanobridge connecting two electrodes (Fig. 2–16A) an ET by means of electron tunneling through empty space may occur. The properties of this tunneling junction were described in Sec. 2.4.

The logical and structural bridge between the macroscopic inorganic contacts and organic molecules in SMJ is provided by related system of quantum point contacts (QPCs) (Fig. 2–16B) [94–98]. This is a few atom wide metal junction connecting to macroscopic electrodes. A QPC could be also a suspended linear chain of metal atoms, which is known as atomic nanowire. The latter exhibit well-defined quantified ET (see Cha. 5), which characteristics are determined by the structure of the “thinnest part”

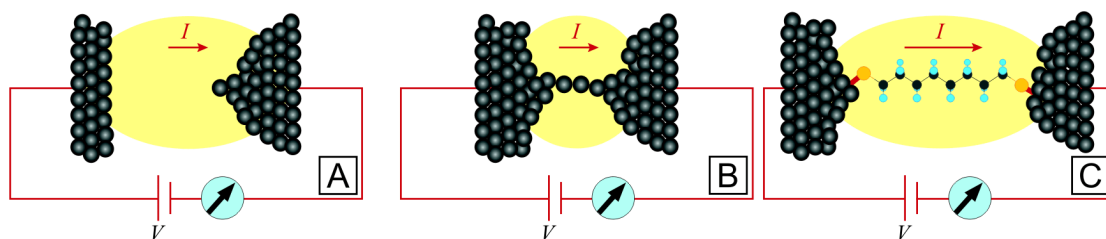


Fig. 2-16: Scheme of nanoscale junctions: (A) tunneling gap; (B) QPC / atomic nanowire; (C) SMJ (redrawn after [24]).

only. The experimental approaches developed for transport studies in QPC found their way to transport studies in SMJ.

The SMJ (Fig. 2-16C), as it is discussed further, consists of single molecule connecting two metal electrodes. I will also use this term for the junctions with a small number of molecules simultaneously acting as nanobridges.

2.6.2 Monolayer devices

For a long time the field of molecular electronics was limited by devices incorporating monolayer, *i.e.*, huge number of the functional molecules [14, 17, 18, 20, 21, 99–102]. The ET through the monolayers was first demonstrated by Bernhard Mann and Hans Kuhn [103]. They used LB films of the normal fatty acids $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOH}$ sandwiched between two metal electrodes and found that the conductivity of such junctions exponentially decrease with the length of the molecules. The results were attributed to the tunneling of the electron through the molecular layer (*cf.* 2.4.1). The simulations showed agreement with experimental $I - V$ curves and predicted general trend of the conductance dependence on the nature of the metal of the electrodes. Further, the functionality such as current rectification was demonstrated for measurements employing LB films as well as SAMs [14, 20, 21, 100, 102]. This technique is successfully reaching a production-ready state.

Devices employing monolayers of molecules allow to combine paradigms of both contemporary semiconductor technology and molecular electronics and as such may be considered as a prototype of hybrid technologies. However, the true molecular electronics devices are expected to feature individual molecule as a functional elements of the logic element [16, 99, 100]. This requires fundamental studies on the properties of the functional molecules.

2.6.3 Single molecule junctions

The primary question in studies of ET through SMJ is how to create the latter. To determine the transport characteristic of a molecule, one must first bring it into contact with at least two external electrodes. The contact must be robust, reproducible, and able to provide sufficient electronic coupling between the molecule and the electrodes [24]. Therefore, the measured response depends not only on the molecule itself, but also on the properties of the electrodes and the atomic-scale molecule-electrode contact geometry [104–109].

Probably the earliest experiments which may be considered as involving SMJ were transport experiments with CNTs. A CNT [110–112] is a unique robust structure con-

sisting of single or multiple sheets of graphite bent to a cylindrical structure. A single-wall CNT has a diameter of *ca.* 1.2 nm. The outer diameter of a multi-wall CNT may reach up to 20 nm with an inner hollow diameter of 1 – 3 nm. The interlayer distance corresponds to that of graphite (≈ 0.34 nm). The length of a CNT could be on the order of 1 μm and longer. Thus, the aspect ratio (length over diameter) is of the order of 100 to 1000. As a result of this large aspect ratio and of the small diameter, nanotubes are often considered as one-dimensional structures with respect to certain properties, for example their electronic structure.

The typical path to create SMJ with CNT is the following. After the synthesis or the deposition on an insulating surface (such as silicon oxide) between macroscopic metal electrodes, the surface is inspected by means of electron microscopy or AFM. Once a CNT is found, sub-micrometer size metal leads were patterned on the surface and connected to macroscopic metal electrodes. Two or four-electrode measurements [113–117] with single or multiple-wall CNT were demonstrated in the second half of 1990th. At present time conductive CNTs are used in a wide variety of application including electrochemistry and electrochemical biosensors [118, 119] and various analytical applications [120]. However, the approach used to study transport characteristics of CNT is not universal in the sense that CNTs are unique objects. The formation of SMJs incorporating individual small organic molecules are of more general interest and is still a challenge.

There is a number of experimental approaches developed to wire molecules between two electrical contacts. A nanometer-sized gaps can be prepared using contemporary electronic lithographic techniques, electromigration and metal deposition/dissolution on nanosized electrodes (see, *e.g.*, [121–124]). Stable nanogaps can trap single molecules stochastically. Alternatively, a nanopore can be used to assembly the SAM and manufacture a second electrode on top of it for further conductance measurements.

In mechanically controlled break-junction (MCBJ) experiments, first introduced in 1985 [125], two submicrometer-size metal electrodes are brought in mechanical contact. The electrodes are typically prepared by lithography and mounted on an elastic substrate in a three-point bending configuration with two fixed supports and one movable. The distance between the electrodes is controlled via the mechanical bending of the substrate. The MCBJ technique is often used to create QPCs and to study their transport properties during the variation of the interelectrode separation (Sec. 5.1). An atomically-sized gap is created upon breaking of QPC. A molecule from the surrounding can span the gap and create a SMJ, which conductance could be measured in the same manner as that of a QPC [126, 127]. The high stability of MCBJ and an excellent control of the electrode separation, especially in an cryogenic environment, allow to fix a single SMJ configuration for a detailed characterization.

The various SPM-based approaches are often used to form MJs [20–22, 24]. All of them are based on the fact that the SPM probe may be simultaneously used as a nanometer-sized electrode for transport measurements. The SAM on the conductive surface can be contacted by the SPM probe directly [106, 128–132] or via a tunneling gap [133–138] for two-electrode transport measurements. This method, however, suffers from the undefined contact geometry. Single “active” molecules could be embedded into a monolayer of “inactive” molecules [139–144] to allow addressing them individually. These methods could be accomplished by covalently attaching a metal (*e.g.*, gold) nanocluster to a SAM [145] or isolated molecules of interest [143, 146–149].

In recent years, a SPM-based method similar to a MCBJ was proposed [150]. Here the probe is used to mechanically contact molecules assembled on a surface and form probe|molecule|electrode SMJ. The molecules employed in these studies have two end groups which can bind to both tip and substrate electrodes. The strong binding allows to preserve a nanobridge configuration during stretching of the assembly, which is reflected as plateaus and abrupt drops in the $I - \Delta z$ characteristics. Advantages of this method include the simultaneous monitoring of the interface. A common SPM setup could be employed without complicated lithographic fabrication. The “SPM break junction” technique was employed in this work to study the conductance of SMJ assemblies (Cha. 6, 7); the detailed description of the experimental procedure is given in Sec. 3.7.4.

2.6.4 Electrochemical control of electron transport

Considering the details of the ET through MJ, one may state that the conductance strongly depends on the alignment of molecular states with the Fermi levels of the electrodes. By definition, in the absence of oxidation-reduction processes the electrode's Fermi energy is positioned between that of the HOMO and of the LUMO of the respective molecule (*cf.* Sec. 2.3.4). The alignment of energy levels is determined by the intrinsic properties of the molecule and the electrode. It can be evaluated by spectroscopic techniques as well as from STS data. The HOMO and LUMO of the molecule can be discretely varied by chemical modification [151–153]. In solid state field effect transistor (FET) the ET between source and drain electrodes can be tuned by the voltage on the gate electrode (*cf.* Sec. 2.1.3). In an electrochemical environment the Fermi energy of the WE is varied with respect to the RE (*cf.* Sec. 2.3.2). The control of the metal-molecule energy alignment (and, correspondingly, ET in the molecular junction) by the potential difference between the WE and the RE is often referred to as electrochemical gating [154]; the RE is correspondingly attributed as “electrochemical gate electrode”. The alignment of the electrode's Fermi level and of the molecular states corresponds to an electrochemical oxidation/reduction of redox-active molecules; the corresponding values of the electrode potential can be obtained by electrochemical measurements (Sec. 2.3.4).

The idea of an electrochemical gating was introduced into molecular electronics by the groups of Schönenberger and McEuen [155, 156]. According to first principle calculations by di Ventra *et. al* [27], the field in the EDL is close to the gate field required to significantly change the current through a molecule. Thanks to the long-existing experience of EC STM, the SPM-based experiments on electrochemical gating in SMJ seems to be the most advanced in comparison with other realizations. The control of the energy level alignment in EC STM was first demonstrated in 1996 by Tao [157]. Various redox-active molecules were shown to demonstrate electrochemical switching effects by different groups [158–170].

Using conventional precautions (Sec. 2.4.6), the SPM-based studies described above could be realized in EC STM configuration. Both symmetric and asymmetric SMJs could be created. The electrochemical gating was demonstrated by our groups using SPM break-junction method [171–173]. The independent control of the potential of SPM probe and sample in an electrochemical environment allows to employ various modes of current-voltage spectroscopy (Sec. 2.4.6, 3.7.3) either with variable or fixed bias. These techniques were used in our group to explore resonant enhancement of tunneling by redox-active molecules (Cha. 8).

Chapter 3

Experimental details

3.1 Materials and tools

3.1.1 Reactants

For all experiments described in this thesis Milli-Q water (Millipore) with a resistivity of 18.2 M Ω ·cm and a total organic carbon content (TOC) of 2 – 3 ppb was used both for cleaning and as a solvent for aqueous solutions. 98% mesitylene (1,3,5-trimethylbenzene) of analytical (*p.a.*) purity (Sigma-Aldrich) was used as solvent for specific STM experiments and assembly procedures. Absolute ethanol bought from KMF Laborchemie Handels GmbH (KMF) was used as a solvent for the assembly procedures. Isopropanol of *p.a.* purity (KMF) was used to rinse metal tools.

Ar of 99.999% purity (Messer-Griesheim) was used to dry crystals and utensils, for purging solutions and for creation of a protecting atmosphere.

The disk and bead single crystal gold electrodes were prepared from 99.999% Au as described below (see Sec. 3.4). 0.25 mm diameter wires of W (Goodfellow), Au (Goodfellow), Pt_{0.7}Ir_{0.3} (Heraeus), Pt_{0.8}Ir_{0.2} (Goodfellow) or Ir (Goodfellow) of 99.999% purity were used for the preparation of STM tips. Pt (99.999%, Goodfellow), Ag (99.999%, Goodfellow) and Cu (99.999%, Aldrich) wires of 0.5-1 mm diameter were used as RE in EC STM experiments. A Pt wire also served as a CE. Lab-built teflon liquid cells and Kalrez O-rings were used for STM experiments. CERAN plates (Schott) of 155×155 mm size were used as a support for disk single crystals during flame annealing and cooling. Parafilm (Pechiney) was used for the protection from ambient in various situations.

Concentrated ($\approx$ 96%) sulfuric acid H₂SO₄ of *p.a.* (KMF) and suprapure purity (Merck) was used for cleaning, including the preparation of caroic acid (Sec. 3.2.1) and the preparation of the working solutions respectively. A stabilized aqueous solution of 30 or 35 weight % hydrogen peroxide H₂O₂ (KMF) was used for the preparation of caroic acid. Suprapure aqueous HCl (36%, Merck) was used to prepare solutions for the lifting of the Au(111)-(22× $\sqrt{3}$) reconstruction (Sec. 3.4.4).

NaOH pellets (*p.a.*, Merck), ethanol (*p.a.*, KMF), HCl (*p.a.*, Merck) and CaCl₂·2H₂O (*p.a.*, Aldrich) were used to prepare solutions for tip etching (see Sec. 3.6.2). A commercially available polyethylene (PE) rods (“*Befüllung für Heißklebepistolen*”, various brands) served as a source of coating material for the probes used in EC STM experiments.

CuO of 99.9999% purity (Sigma-Aldrich) was used for the preparation of Cu-containing solutions (Cha. 4). The chloride ions were introduced by adding a small amount of suprapure NaCl (Merck).

Terminal alkanedithiols (S_nS) (Cha. 6) – 1,5-pentanedithiol (S5S), 1,6-hexanedithiol (S6S), 1,8-octanedithiol (S8S), 1,9-nonanedithiol (S9S) and 1,10-decanedithiol (S10S) were purchased from Alfa Aesar and used without further purification.

4,4'-bipyridine (44BP) (Cha. 7) of 99% purity obtained from Fluka was recrystallized twice before use. LiClO_4 (puriss. *p.a.*, Fluka) was twice recrystallized from ultrapure water. The pH of the solution was adjusted with NaOH (suprapure, Merck).

The viologen derivatives (Cha. 8) were synthesized (Alfred Błaszczuk) and provided for experiments in the frames of a scientific cooperation with the group of Prof. Marcel Mayor, University of Basel [171, 172].

3.1.2 Additional utensils and tools

The lab coat and gloves (polynitrile) were worn during all laboratory procedures. Goggles were taken when working with hazardous substances or solutions. Face mask were additionally used when working with clean single crystals (annealing, mounting).

The 3-electrode cells for electrochemical experiments (Sec. 3.5.1), flasks for solution purging and other smaller pieces of glassware were prepared by the workshop of FZJ. The standard laboratory glassware (Schott, Duran or FZJ) was used for solution preparation, monolayer assembly and for preparation of STM experiments.

Acid-resistant metal tweezers were used to handle glassware when working with caroic acid. Metal tweezers used to handle metal parts and dry glassware were rinsed by isopropanol and dried in an Ar stream before use. Alternatively, a butane flame was used to clean metal tools by annealing. Teflon and ceramic tweezers were used to handle disk single crystal STM samples at different stages of the preparation.

Eppendorf pipettes with a total capacity of 10, 100 and 1000 μl were used to handle liquids. Solid reactants were weighed on a balance with a precision of 1 mg or 0.1 mg (Sartorius) directly into the flask (working solutions) or on a clean paper first (etching solutions, *etc.*).

Hydrogen flame from hydrogen generator (Hot Flame 300, Elma) was used to anneal gold disk single crystals for STM studies. Metal containers (FZJ) were used for the thermal annealing of SAMs on Au(111) single crystals (Sec. 3.4.5) in the oven (Heraeus). Another oven of the same type was used to dry the glassware.

3.2 Cleaning procedures

3.2.1 Preparation of caroic acid

Caroic acid, or piranha is a very strong oxidizing agent used to clean glassware and other items from organic contaminations. It is prepared as a 1:3 mixture by volume of 30-36% aqueous solution of hydrogen peroxide H_2O_2 with concentrated sulfuric acid H_2SO_4 . The high activity towards oxidation of organic compounds is based on the formation of peroxysulfuric acids. The mixing of sulfuric acid and hydrogen peroxide solution is a strongly exothermic process, and an excess of heat can lead to the decomposition of H_2O_2 and peroxysulfuric acids. The heat should be quickly dissipated during preparation by intensive cooling with an ice-water mixture, constant stirring of the solutions and very slow (drop by drop) addition of sulfuric acid to hydrogen perox-

ylde solution. The typical sequence of actions taken to prepare caroic acid of a given amount (usually 600 or 2000 ml) is as follows.

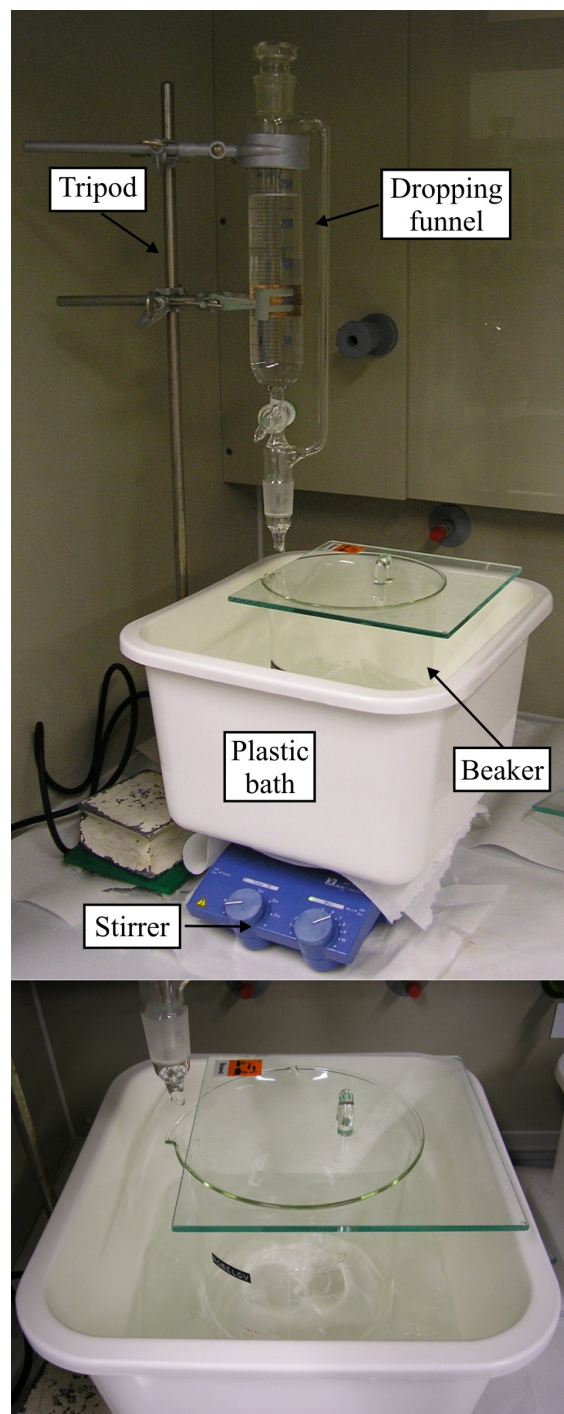


Fig. 3-1: Top: an apparatus for the preparation of caroic acid; bottom: caroic acid dropping into a beaker with a stirred H_2O_2 solution.

within *ca.* 1 min. Due to its hygroscopicity and usage for cleaning, the caroic acid is constantly diluted and should be prepared anew *ca.* every 3 months. Under no circumstances the old caroic acid should be mixed with waste sulfuric acid, but disposed separately.

A glass beaker (1000 or 3000 ml) is cleaned together with a stirring rod (small metal rod inside a Teflon coating) according to a standard cooking/rinsing procedure (Sec. 3.2.2). 150 or 500 ml of 30% H_2O_2 is added to a beaker, which is placed in a small plastic bath with high rims. The bath is filled with an ice-water mixture, so that it surrounds the content of the beaker. The plastic bath is positioned on magnetic stirrer close to a tripod (Fig. 3-1, top) and, if necessary, supported by a Laborboy (Rudolf Grauer AG, Switzerland). The dropping funnel is rinsed with Milli-Q water 3 times, once with conc. H_2SO_4 and mounted on the tripod. The glass funnel is rinsed with Milli-Q water several times and used for filling the dropping funnel with a conc. H_2SO_4 . The position of the dropping flask is adjusted on the tripod so, that the drops are falling on the wall of the beaker and slowly flowing down into the solution (Fig. 3-1, bottom). The beaker, except of the small opening for the drops, is covered by a flat glass lid. Now the magnetic stirrer is switched on and H_2SO_4 is added to the solution with a rate of approximately 3 drops per second. If necessary, the position of the dropping flask should be adjusted. The water-ice mixture and the sulfuric acid must be reloaded time to time, and small adjustments in the setup may be needed. Otherwise, a further process does not require permanent attention. The whole preparation procedure, depending on the amount of caroic acid, takes few days.

The oxidizing ability of caroic acid is tested by putting a drop of it on a paper towel. The drop should oxidize the paper producing a black spot and later a hole

3.2.2 Glassware

In order to clean the EC cells after receiving or when they were not used for a long time, they are kept overnight with concentrated sulfuric acid inside. Otherwise cells were kept with Milli-Q water inside. The standard glassware is soaked in caroic acid (Sec. 3.2.1) when not in use. Big beakers or flasks are filled with H_2SO_4 , caroic acid or Milli-Q water for initial cleaning.

The glassware used are typically vessels of different types, which should be cleaned inside prior to use. If an item cannot be filled with liquid, it should be put into a sufficiently big clean beaker with a lid and cleaned inside it as described further. Similarly, if a planned experimental procedure requires usage of many small glass utensils, they can be taken out separately and, after short initial rinsing, gathered in one beaker and cleaned together. Some items are soaked and rinsed only together. An example is a “double beaker”, which is a 10 ml beaker inserted into a 40 ml beaker. This pieces should not be separated, the inner one should not be touched during the cleaning. It should be handled carefully to not let the inner beaker falling down.

The filled vessels are emptied into a sink or a corresponding container for waste chemicals. The soaked glassware is carefully taken out of the caroic acid with a pair of tweezers. The tweezers should not touch the inner and grounded parts of the glass vessels as well as other sensitive zones. To remove the acid, initially both inner and outer parts of the vessel are rinsed with Milli-Q water. Afterwards only the inner part is rinsed by filling the vessel with water and pouring it out. The liquid from the outside wall, as well as occasional splashes of water, must not go inside the vessels. Therefore, the vessels should be tilted only with such an angle, that the water from the outer walls is not forming drops at the rim of the neck. When allowed to form, such drops may penetrate inside the vessel when it is turned upward and contaminate it. In general, when filling the vessels with water and pouring it out, one should watch carefully the direction of the water flow.

The vessel is filled with water and emptied at least 6 times. Even if water partially remains inside the vessel, this is enough to strongly dilute contaminations. Stoppers or caps (beakers, Erlenmeyer flasks, *etc.*) are cleaned immediately after the corresponding vessel in a similar manner, except that at the very end the water gathered at the outer wall are carefully sucked out by paper.

After rinsing, the vessel is put onto the heating plate for cooking. The stopper or cap should sit loose during heating of the vessel's content. At the end the water shouldn't boil, but a gentle cloud of steam should be visible. Hot water is removed completely and the rinsing procedure is repeated. The rinsing/cooking cycle is repeated 3-4 times. The cooking is known to be essential for the removal of residual sulfate ions. If it is not required, an extensive rinsing without cooking may be enough to clean glassware. Items used for non-aqueous solvents/solutions are additionally dried in an oven at *ca.* 105 °C after careful removal of residual water.

The glassware, which is carefully cleaned according to the outlined procedure must be clean enough to allow experiments without substantial surface contaminations. After use the glassware is emptied and rinsed with Milli-Q water. The vessels used for organic solutions are first rinsed with isopropanol. The water is allowed to pour out of the vessel completely, the outer surface is dried with clean paper. Some vessels (*e.g.*, dry, after alcohol or with a conc. H_2SO_4 inside) may be put into caroic acid after rinsing and drying of the outer surface only.

3.2.3 Eppendorf pipettes

The disposable plastic tips for Eppendorf pipettes are first soaked in concentrated sulfuric acid overnight inside a special vessel. Then they are cleaned by cooking/rinsing cycles similar to the glassware. One should ensure that during soaking and cooking the inner part of the tips are filled with the liquid. The plastic box for tips and its cover are carefully rinsed with Milli-Q water. After the last cooking and rinsing cycle, the water is poured out from the vessel. The tips are taken out and inserted into a box using annealed metal tweezers. The covered box with tips is placed in an oven and dried at *ca.* 105 °C. After cooling, the tips are stored in a box sealed from the ambient air by Parafilm.

3.2.4 Gas and liquid tubes

Stainless steel gas tubes are annealed before the experiment with a stream of Ar running through. Teflon gas and liquid tubes are placed inside a beaker, soaked in sulfuric acid and afterwards cleaned by the standard cooking/rinsing procedure with an additional pumping of water through the tube during rinsing.

A small amount of gas is released through the gas tubes before its further usage. Small glass tubes and funnels were attached to the gas outlets for drying and cooling of single crystals respectively. They are cleaned by heating with a flame (Bunsen burner) while a gas stream is running.

3.2.5 Tweezers

Acid-resistant metal tweezers were used to handle the glassware when working with caroic acid. They were kept in Milli-Q water, which was regularly exchanged. Metal tweezers used to handle metal parts and dry glassware were rinsed with isopropanol and dried in Ar stream before use. Alternatively, a flame from a butane Bunsen burner was used to clean the metal and ceramic tweezers by annealing.

3.3 Solution preparation

3.3.1 Aqueous solutions

Erlenmeyer flasks are used to prepare aqueous solutions for STM experiments. For less critical applications (some electrochemical experiments, etching) the solutions are often prepared in volumetric flasks. I will describe the procedure for preparation of clean solutions for STM experiments in an Erlenmeyer flask and point out the difference for the other solutions. In general the presented procedure of solution preparation is worked out to achieve a maximum purity of the solutions at the price of some inaccuracy in concentrations, volumes, *etc.*

Prior to final cleaning (Sec. 3.2.2), the Erlenmeyer flasks are soaked in caroic acid. The volumetric flasks are filled by sulfuric acid or water.

To add solid reactants, the cleaned Erlenmeyer flask with a small amount of water inside is dried by paper outside and put on the balance. The cap is carefully removed and after the stabilization the weight value is zeroed. The necessary amount of reactant is added directly from a container to the water through the wide neck of the Erlenmeyer

flask. This should be done quickly (water evaporation slowly changes the weight of the flask), but carefully. In case of overweight or spilling of reactant the flask must be emptied and rinsed again. After addition of the reactant the container and the flask should be immediately closed and sealed.

For a volumetric flask with a narrow neck a clean dry glass funnel may be used to add the reactant. The latter may be weighted on a weighting paper or in a separate vessel.

To add liquid components (*e.g.*, conc. H_2SO_4 or HCl) to the solutions, the following procedure is used. A “double beaker” (Sec. 3.2.2) is taken from carboxylic acid and cleaned simultaneously with a flask. The cleaned flask, cleaned double beaker, bottle with liquid and Eppendorf pipette (typically 1000 μl) with a mounted tip are conveniently arranged on the laboratory table. The tip of an Eppendorf pipette must not touch anything and has to be exchanged for a clean one if the latter happened. When not held in hand, the pipette lies at the edge of the table so that the tip “hangs out” of the table surface.

The double beaker is carefully emptied from water, the smaller beaker should not fall out. Small residual amounts of water are not critical for the procedure. A small quantity of liquid is poured into the bigger beaker aside of a smaller one, then continuously into smaller and again into the bigger beaker. In this way the possible contaminations from the brim of the bottle do not enter the smaller beaker. No drops should flow back into the bottle.

The tip of the Eppendorf pipette is first cleaned five times by sucking some amount (more than needed for the solution) of the liquid from the outer beaker and disposing it. The pipette is adjusted to a desired volume and cleaned once by sucking and disposing liquid from the smaller beaker. The liquid for solution is now taken by the pipette. While holding it in one hand, the Erlenmeyer flask is opened by another hand, the liquid is carefully added to the solution and the flask is closed. When cleaning the working place, the tips used for concentrated acids must be rinsed by tap water before disposing it in a general waste.

After addition of all solution components, the volume in the flask must be increased up to the marked value with Milli-Q water. Dilution of some solid components may require additional gentle heating of the solution (CuO) or sonication (salts). The caps are sealed by parafilm, the Erlenmeyer flasks are also placed inside a clean plastic bag. Solutions are stored in a refrigerator and may be used *ca.* one week after preparation.

The prepared solutions may be used for the further dilution. In this case the double beaker filled with water used to clean the tip of the Eppendorf pipette as described above. The cleaned Eppendorf pipette is then used to transfer the necessary amount of stock solution to the new flask.

3.3.2 Non-aqueous solutions

The non-aqueous solutions were prepared with ethanol or mesitylene and used for the monolayer assembly (Sec. 3.4.5) or STM experiments. The general preparation procedure is similar to that for aqueous solutions, but the excessive use of solvents, especially in an open vessels, is avoided.

Small volumetric flasks (5-20 ml) as well as conventional Erlenmeyer flasks are used. Small beakers (5-10 ml) are used additionally for various purposes. It is convenient to put these small pieces of glassware and a volumetric flask (with a cap) inside one big beaker and handle them together.

After cleaning by the cooking/rinsing procedure, the water is carefully removed from the vessels and they are then dried in an oven. Before usage, the glassware should cool down in order to not cause an evaporation or decomposition of organic compounds. The clean glassware is handled using metal tweezers annealed in a butane flame.

The solid reactants are added into a **dry** flask directly from container to the vessel on the balance as described above. To add liquid reactants, the Eppendorf pipette is used. Its tip is rinsed by the solvent poured from the bottle into a separate small beaker. The small volume of a reactant is added to another beaker, the necessary amount is taken by the Eppendorf pipette of a suitable size and transferred to the flask with a small amount of solvent inside. After addition of the reactants, the necessary volume of the solvent is added to the flask.

Similar to aqueous ones, it is sometimes necessary to prepare non-aqueous solutions by dilution. In this case the stock solution is handled as a liquid reactant.

The residual solvents and organic substances are properly disposed. Glassware is rinsed by isopropanol (except of beakers with pure ethanol) and soaked in carboxic acid for cleaning.

3.4 Au(111) substrates

Gold is one of the most commonly used electrode materials for electrochemical studies. The bare gold surface is chemically inert to air, water, acids (except *aqua regia*), alkaline solutions and ideally polarizable (*i.e.*, electrochemically inert) in a broad potential range. Among all pure metals, Au has the highest malleability and ductility. In combination with a relatively low melting temperature these properties allow a rather easy preparation of Au electrodes of different shapes and sizes by various techniques [79]. Au is an ideal substrate material for the assembly of the various molecules via physical interaction or covalent bonding. Besides EC STM studies, evaporated thin films of gold are commonly used as substrates in complementary spectroelectrochemical experiments [174].

Among the low index faces of Au, the Au(111) is most easily prepared and routinely employed for surface studies. The gold films with preferential (111) orientation of the surface can be grown or deposited on various substrates by different techniques. To exploit suitable and well-known properties of this surface, single crystal Au(111) substrates were used in all experiments described in this thesis.

3.4.1 Preparation

Massive Au(111) disk single crystals (Udo Linke, IBN-3, FZJ) with a nominal mis-cut below 0.1° were used for both STM and EC studies. The substrates for STM experiments were 10 mm in diameter and 2 mm height. The electrodes for complementary electrochemical experiments were single crystal cylinders of 4 mm height and 4 mm diameter with a wire attached to the rear for mounting purposes. Additionally, bead crystals [80, 81] were employed in some EC studies.

The major steps for the preparation of massive single crystals are outlined in Sec. 2.5.1. Commercially available gold single crystal rods of 99.999% purity prepared by zone melting techniques were cut using a spark erosion procedure. The obtained disks were oriented using the Laue diffraction pattern to monitor the orientation [82, 83] and

polished with Al_2O_3 particles with the size gradually decreasing to 30 nm.

After preparation the Au(111) crystals were soaked in diluted (*ca.* 20%) sulfuric acid overnight to remove residual aluminium oxide. The crystals were then rinsed and treated by multiple cycles of flame annealing (Sec. 3.4.3) and cooling in a stream of Ar in order to smoothen the surface and heal small surface defects of the polishing procedure.

The disk Au(111) crystals for STM were stored in a small Petri dish with conc. H_2SO_4 , the polished working surface on top. The crystals for EC studies were mounted on a holder and inserted into a glass tube or kept in a box with soft material inside. The single crystal must be handled carefully, the polished surface should never be touched.

Further I describe the procedures for the “big” STM samples and point out the difference for “small” massive or bead crystals used for EC studies.

3.4.2 Washing

STM samples are taken out of the H_2SO_4 using clean Teflon tweezers and are immersed in a clean Petri dish with some water inside. The water is poured into a Petri dish and partially poured out at least six times. One should be careful to not let the crystal fall down.

EC crystals mounted on a holder are rinsed in a stream of Milli-Q water before further procedures.

3.4.3 Flame annealing

The flame annealing of Au(111) single crystals (see Sec. 2.5.1) allows both to clean the surface by burning organic contaminations and to improve the surface quality by healing small surface defects due to the increased mobility of the surface atoms. The following sequence of steps is used to anneal the STM samples.

The crystal is washed as indicated above. The Petri dish with the crystal is brought to a hydrogen generator. The very gentle (slightly audible) stream of Ar used later to cool the crystal is switched on and allowed to run during the further procedure.

The hydrogen generator is switched on. If necessary, the water is added to it. When the pressure of the generated hydrogen/oxygen mixture reaches working value, the gas

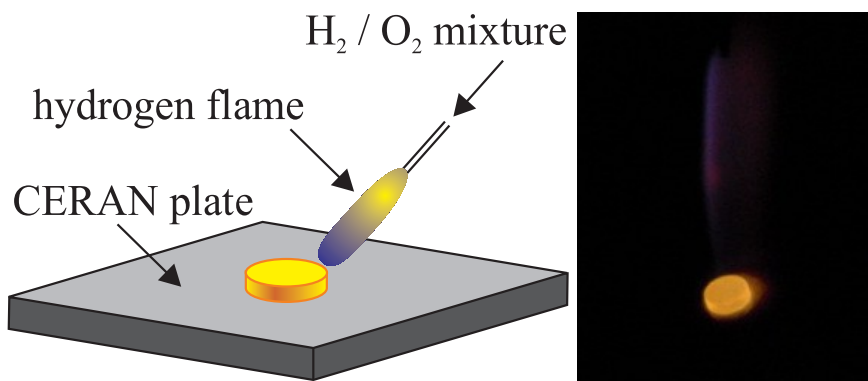


Fig. 3–2: Flame annealing of a Au(111) disk single crystal. Left: scheme; right: a photo of the Au(111) crystal at red heat.

valve is opened and a gas mixture is inflamed. The flame is directed down and towards the user at *ca.* 45° to the horizontal direction.

A CERAN plate is used as a support for the crystal during flame annealing. This material has a very small lateral heat conductance and may be held by hands while the hydrogen flame heats the plate 5 – 10 cm away. The CERAN plate is rinsed with Milli-Q water and dried in a stream of Ar. The plate is taken at the edge by two hands and preheated in the flame. It is moved in such a way, that the flame is uniformly distributed over the finger-free area (*ca.* 60 – 70 % of area). Water drops are condensed on the cold surface, the preheating continues until all water evaporates (1 – 2 minutes). After this a spot for the crystal approximately in the middle of the plane is heated, until the CERAN plate becomes slightly red.

The crystal is taken out of the Petri dish by Teflon tweezers, dried by a stream of Ar and placed on the CERAN plate at the preheated position. One should be extremely careful during this procedure and not drop the crystal. The annealing is performed in a darkened room. The color of the crystal allows to estimate its temperature. The temperature must be sufficiently high for the high mobility of surface atoms, but not high enough for the diffusion of bulk defects to the surface or melting of the crystal.

The CERAN plate is placed under the hydrogen flame. The flame is always moved around the crystal in circles in order to heat it uniformly. The temperature of the flame is controlled by the vertical distance from the nozzle to the plate and the distance between the flame tip and the crystal. To perform a slow heating, the plate is located lower and the flame circulates with a bigger radius. Then the plate is slowly lifted and the radius is gradually decreased. Finally the tip of the flame is directed close to the edge of the crystal, but shouldn't be directed on the crystal itself. The optimal annealing temperature is determined by the color of the crystal. It approximately corresponds to the red color, which should be reached in 3 – 5 minutes after annealing. It is difficult to exactly express desired color, the own experience is necessary. It is important to not overheat crystal, the latter is indicated by brighter and more yellowish color. The annealing time at the final temperature depends on the condition desired to be reached. For regular experiments it can be a few minutes. Longer time may be needed to heal out surface defects.

After major annealing, the crystal is slowly cooled down by lowering the plate and increasing the radius of the flame tip. This should take approximately the same time as the heating. The plate with a crystal is placed on the support and moved under a stream of Ar. A funnel attached to the gas outlet protects the crystal from the top. The crystal is allowed to cool there for 5 – 10 minutes and afterwards used for further treatment or mounted on the STM plate. The hydrogen generator is switched off, the excess pressure of the gas mixture is released.

To handle smaller crystals for EC studies during the annealing, they were mounted on a holder 3.5.1 which was held by hands. A butane flame with a lower temperature was used instead of a hydrogen flame. After partial cooling in a stream of Ar they were quenched in a flask with Milli-Q water. Thus, the surface was protected from contaminations before an electrode was brought into contact with the solution.

3.4.4 Lifting of reconstruction

The reconstructed Au(111)-(22 × √3) surface (see Sec. 3.4.6) is more stable at temperatures close to the melting point of the gold. It forms during thermal annealing of

Au(111) samples and remains kinetically frozen at room temperature. The reconstruction may be lifted to form a Au(111)-(1 × 1) surface *in situ* by applying a sufficiently positive electrode potential. However, sometimes it is necessary to ensure a (1 × 1) arrangements of the surface atoms before the experiment, *e.g.*, for further modification. This was done by immersing the Au(111) crystal into a solution containing chloride, which significantly increases the mobility of surface atoms.

A 0.05 M aqueous solution of HCl is prepared in advance (Sec. 3.3.1). A freshly annealed and cooled crystal is placed into a clean Petri dish. An amount of HCl solution, sufficient to cover the crystal, is added to the dish. The dish is covered to protect the solution. After 20 minutes, the Petri dish with a crystal is intensively rinsed with water in order to remove chloride. This is done by filling it with water and emptying it at least 50 times.

The EC samples are completely immersed into the HCl solutions and afterwards rinsed in a stream of water. The resulting surfaces are atomically flat with hundreds of nm wide terraces and very few large monoatomically high islands. After drying with Ar the crystal is ready for surface modification or use in STM / EC experiments.

3.4.5 Preassembly of thiol-terminated compounds

Gold single crystal surfaces covered with low or high coverage SAMs (Sec. 2.5.2) were used as substrates in some experiments. The concentration of the assembly solution and modification time affected the coverage, while the thermal annealing of adlayers promoted the formation of the well-ordered interfacial structures. The developed procedures allowed to reproducibly obtain adlayers with preset properties.

The solutions of organic compounds used for assembly were prepared as described above (Sec. 3.3.2) in advance or shortly before assembly. Typically ethanol served as a solvent, selected experiments were done with mesitylene-based solutions. Small beakers and glass containers used for thermal annealing were cleaned and handled in the same way as a glassware for the preparation of organic solutions.

Before assembly, the STM samples are dried by Ar or by immersing it several (3-4) times into ethanol. Two dried beakers filled with ethanol are used. The crystal is placed into one of them, the beaker is carefully shaken. Then it is transferred to the other beaker and treated similar. The ethanol from the first beaker is removed, it is refilled with a fresh portion of ethanol. The crystal is transferred from the second beaker to the first one and the procedure is repeated.

Low coverage adlayers were prepared by immersing the sample into a small amount of diluted (*e.g.*, 50 – 100 μM) solution of the target species poured in a small dry beaker. After an assembly (1 – 2 minutes) the crystal was taken and quickly rinsed 6 times by ethanol as described above. High coverage adlayers were prepared by immersing the crystal into a concentrated (*e.g.*, 1 mM) solution of the respective thiol for 10-12 hours. Adlayers prepared in this way are known to lack a long range ordering of the molecules on the surface. Thermal annealing was used to promote lateral movement of the molecules and allow their self-organization. The low coverage ordered adlayers are prepared by thermally annealing the crystal with preassembled molecules in pure ethanol. The high coverage ordered adlayers are prepared by thermally annealing the bare crystal in the concentrated (*e.g.*, 1 mM) solution of the target molecules.

A glass container is filled with ethanol or solution, the crystal is immersed in a liquid. The glass container with the liquid and the crystal inside is transferred into steel

container and closed by a cap. The steel container is deaerated inside by a gentle stream of argon and closed. The container is annealed in an oven at temperature of 70 – 90 °C for 10 – 12 hours. The tightly screwed lid prevents evaporation of the ethanol. After thermal annealing the container is removed from the oven and allowed to cool down. The crystal is taken out of the containers, dried with ethanol and Ar, and then used for STM/EC experiments.

3.4.6 Characterization of bare Au(111)

The Au(111) surface was used as a substrate in CV (Sec. 3.5) and STM (Sec. 3.6) experiments presented in this thesis. In this paragraph I will describe the typical characteristics of the bare Au(111) surface, which served as a reference for the experiments with a modified substrate.

The steady CV recorded in sulfuric acid in the potential range $-0.30 \text{ V} \leq E \leq 1.35 \text{ V}$ is shown in Fig. 3–3. The STM images illustrate the morphology of the gold surface

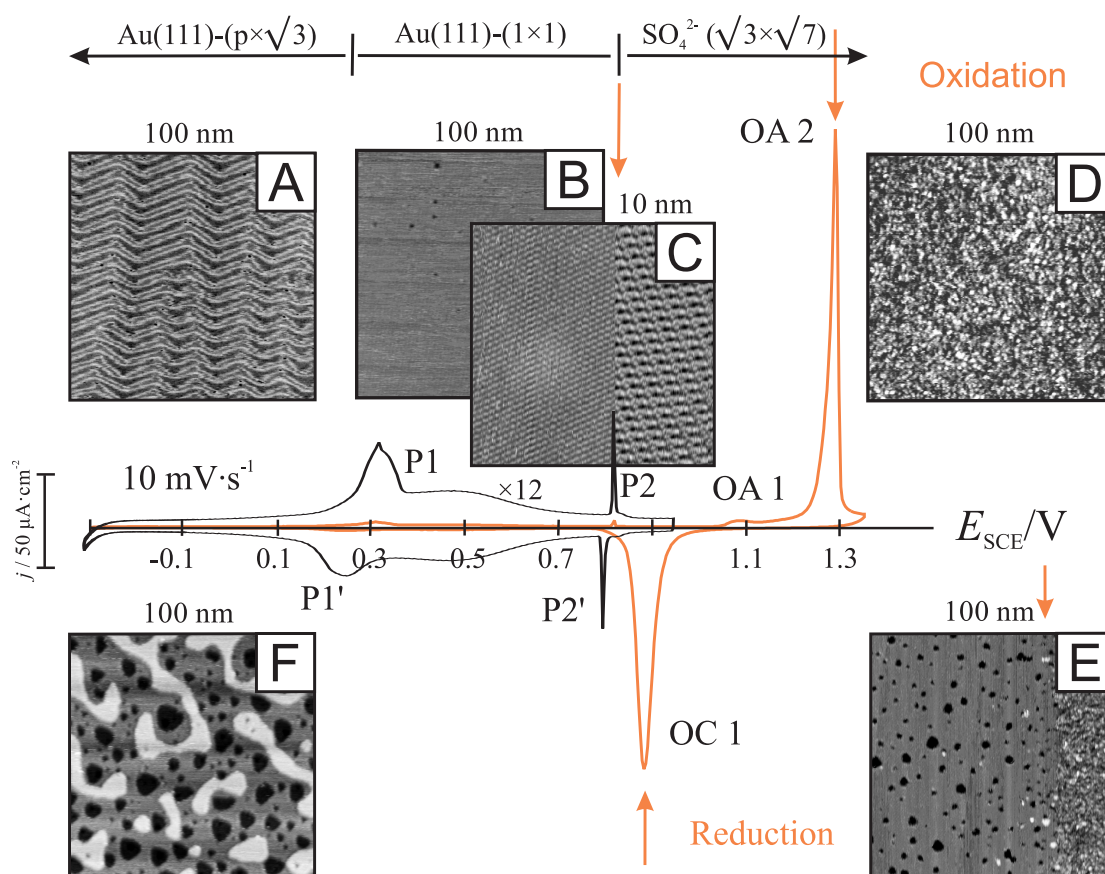


Fig. 3–3: CV of a Au(111) electrode in 0.05 M H_2SO_4 (yellow), scan rate $10 \text{ mV}\cdot\text{s}^{-1}$. The black curve represents a magnification (factor 12) of the steady CV recorded in the double layer region. The *in situ* STM images represent surface structures at various potentials: (A) thermally reconstructed Au(111)-($p \times \sqrt{3}$) surface, $E = -0.20 \text{ V}$, (B) Au(111)-(1×1) surface after lifting of the reconstruction, (C) transition between the disordered and the ordered sulfate overlayer ($\sqrt{3} \times \sqrt{7}$) $R19.1^\circ$, (D) oxidized gold surface, (E) transformation of the oxidized gold surface upon a negative-going potential scan, (F) gold surface with monoatomic deep holes obtained after 10 subsequent oxidation/reduction cycles.

in different potential ranges.

The CV experiment starts with the immersion of a freshly flame-annealed (Sec. 3.4.3) reconstructed Au(111) electrode in the electrolyte under potential control at -0.20 V. The potential is scanned towards positive values and then back. The voltammogram shows three pairs of current peaks (P_1/P'_1 , P_2/P'_2 , and $OA_{1,2}/OC_1$) corresponding to the substrate surface transition (lifting/formation of the reconstruction), the formation/dissolution of the $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ (hydrogen) sulfate overlayer and the oxidation/reduction of the gold surface.

Fig. 3–3A shows an STM image of the reconstructed Au(111)- $(22 \times \sqrt{3})$ surface. The thermally-induced reconstruction lines with the characteristic zig-zag pattern are clearly resolved. When scanning the electrode potential in positive direction, the passage of the current peak P_1 around the PZC [175, 176] (**other refs?**) results in the lifting of the surface reconstruction. A uniform unreconstructed Au(111)- (1×1) surface is obtained (Fig. 3–3B).

The disorder/order transition of adsorbed sulfate ions takes place around 0.80 V. The left part of Fig. 3–3C shows the atomically resolved gold surface and the right one shows the ordered $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ sulfate adlayer. Further increase of the electrode potential to 1.35 V causes the oxidation of the gold surface (Fig. 3–3D), which is represented by the current peaks OA_1 and OA_2 . Scanning the electrode potential towards negative values (passing OC_1) causes the reduction of the oxidized surface, which is often accompanied by the formation of monoatomically deep holes (Fig. 3–3E).

Repetitive oxidation/reductive cycles make the gold surface further textured (Fig. 3–3F) and decrease its quality. Unless performing specific investigations, one tries to avoid surface oxidation. The pH-dependent onset of the hydrogen evolution is observed at the most negative side of the potential range (black curve) and determines the second limit of the double layer region.

3.5 Electrochemical experiments

3.5.1 Instrumentation

The main experimental technique used in the presented work was *in situ* STM. The EC STM configuration, in principle, allows to perform typical electrochemical experiments such as CV, and those were carried out for some systems. However, the more reliable results may be obtained in the complementary EC experiments carried out with dedicated electrochemical setups. In particular, the EC cell is designed to keep an oxygen-free atmosphere, which is vitally important, much better than in the EC STM cell. The results of the EC experiments may be compared with that in the EC STM configuration, allowing to probe the integrity of the systems studied by the various experimental techniques.

Depending on the intended purpose, various setups were used for EC studies. An AutoLab (PGSTAT-30) potentiostat and a FHI (ELAB-200997) potentiostat were used for general single crystal experiments in an electrochemical cell. A lab-build potentiostat with current resolution below 10 fA (G. Mészáros [177]) was used for experiments employing nanoelectrodes.

A 3-electrode cells were used for electrochemical experiments (Fig. 3–4). The electrochemically characterized WE is a bead or disk single crystal. A connecting wire on the rear side of the electrode is inserted into a Teflon holder and fixed by a metal clamp

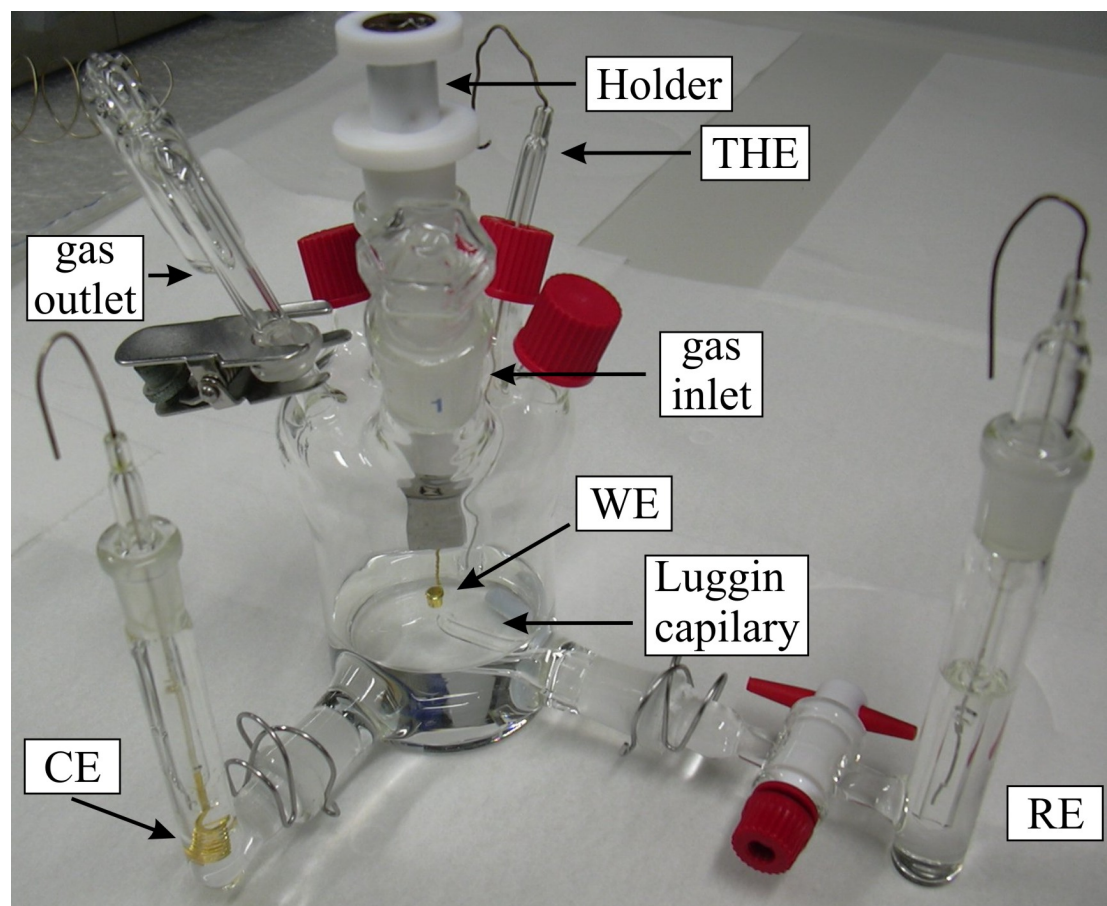


Fig. 3–4: Three-electrode cell used for electrochemical studies.

providing an electrical contact. To perform measurements, the holder with a mounted electrode is inserted into the cell body through a vertical opening on top of the cell. The outer stopper-like part of the holder is fixed, while the inner part moves vertically allowing to adjust the position of the electrode. The WE opening is closed by a glass stopper when not in use by the electrode holder. The RE is inserted into a dedicated side compartment or sometimes directly into the main cell. To keep a high input impedance and to minimize the uncompensated solution resistance, the RE compartment is connected to the main compartment through a Luggin capillary, which tip was put as close as possible to the WE. The CE is also located in a separate compartment. To protect the WE from interference with processes at the CE, the CE compartment is separated from the main cell by a glass frit or a Teflon tap. Both side compartments are filled with the working solution and fixed by a metal clamp. The gas inlet used (not shown) is inserted into the cell through a side opening.

3.5.2 Reference electrodes

The REs used in the EC experiments were SCE, mercury-sulfate electrode (MSE) or trapped hydrogen electrode (THE). Their standard potentials (see Sec. 2.3.2) are given in Table 3.1. The MSE and SCE are fabricated as a whole unit inside a glass tube with a membrane at the bottom and an electric contact on top, and inserted into the RE compartment.

Tab. 3.1: Reference and quasireference electrodes used in the work ($T = 25\text{ }^{\circ}\text{C}$).

Electrode	Half-cell composition	E^0 vs. SHE / V
SCE	Hg/Hg ₂ Cl ₂ /KCl saturated	0.241
MSE	Hg/Hg ₂ SO ₄ /Na ₂ SO ₄ saturated	0.64
THE or RHE	Pt in contact with H ₂ ($p = 1\text{ atm}$) and working solution.	$ca. -0.059 \cdot \text{pH}$
Cu wire	1 mM Cu ²⁺ Cu	0.248 V
Pt wire	H ⁺ Pt-H _{ads}	QRE !
Ag wire	AgO _x Ag	QRE

The THE was fabricated as a Pt wire in a glass tube. The tube has an opening from the bottom side and sealed from the top, the Pt wire goes from the hollow part through the glass and is then connected to a potentiostat (see Fig. 3–4). The hollow part of the THE is filled with the working solution before the electrode is inserted into the cell. The electrode is inserted into the RE compartment or directly into the cell body. Subsequently, after careful deoxygenation a hydrogen bubble is generated inside the hollow part of the THE by electrolysis with the Pt wire serving as a cathode. Thus, the THE is essentially a Pt wire, which is in contact with hydrogen at $p = 1\text{ atm}$ and the working solution. By definition, this arrangement is known as a real hydrogen electrode (RHE), which potential is pH-dependent. According to the Nernst equation (Eqn. 2.36 on page 37), the latter is

$$E_{RHE}^0 = \frac{RT}{nF} \ln a_{\text{H}^+} \quad (3.1)$$

or $ca. -0.059\text{ V}$ per pH unit at room temperature, while for this half-cell by definition $E^0 \equiv 0$ (Sec. 2.3.2).

The REs, used in the EC STM studies were Cu, Pt or Ag wire. The latter two are actually QREs which potentials have to be calibrated. Independent on the actual RE used during either EC or EC STM experiment, all electrode potentials are quoted further in the scale of the SCE. The latter was obtained by recalculating the potentials E vs. the arbitrary RE according to the following expression:

$$E(\text{SCE}) = E(\text{RE}) + (E_{RE}^0 - E_{SCE}^0) = E(\text{RE}) + (E_{RE}^0 - 0.241) \quad (3.2)$$

3.5.3 Experimental procedure

The electrochemical cells are cleaned as indicated above (Sec. 3.2.2). A stirring rod is kept inside the cell and cleaned together with it, the water is stirred during cooking. During rinsing the water is poured out through all outlets located at the bottom of the cell. All attached parts are also rinsed separately.

The solutions are prepared as described above (Sec. 3.3.1). The preparation of the substrates for the EC experiments includes flame annealing and optionally lifting of the reconstruction and the assembly of the monolayer (Sec. 3.4). The following steps were typically performed to mount the cell:

The water is removed from the cell and side compartments. Each side compartments is filled with the working solution without bubbles inside. The taps are closed to keep

the solution inside. The compartments are inserted into the cell and fixed by metal clamps (Fig. 3–4). The main compartment is filled with the working solution slightly above the level of the Luggin-capillary. The RE and CE (Pt or Au wire inside a glass capillary) are inserted into the corresponding compartments. If needed, the hydrogen is generated at the THE.

The gas inlet is inserted into the cell and connected to the gas line. It is designed to allow the Ar injection into or above the working solution. A water tap is connected to the gas outlet to prevent the back-flow of oxygen into the cell (see Fig. 3–4).

The solution is deaerated before each measurement by purging Ar under constant stirring. Typically it takes 30 minutes to purge a freshly added solution. After a quick exchange of the WE and the stopper 5 – 10 minutes of purging is sufficient to remove the oxygen.

The stirring is stopped. The Ar injection is switched from “into solution” to “above solution”. A slight gas flow is kept during all measurements. An inserted WE is contacted with the solution under potential control. To avoid edge effects, the WE is always fixed above the solution in a “hanging meniscus” configuration [178].

3.6 STM experiment

3.6.1 Instrumentation

A Molecular Imaging (MI) setup was used for STM experiments. A 25-pin cable was used to connect the PicoSPM measuring unit to the controller. During experiments the PicoSPM was assembled in a chamber for vibration isolation. The latter was mounted on a heavy granite plate freely hanging inside the metal rack. During preparation of the experiment the granite plate was supported by Laborboys to prevent its dangling. Experiments were done at constant room temperature.

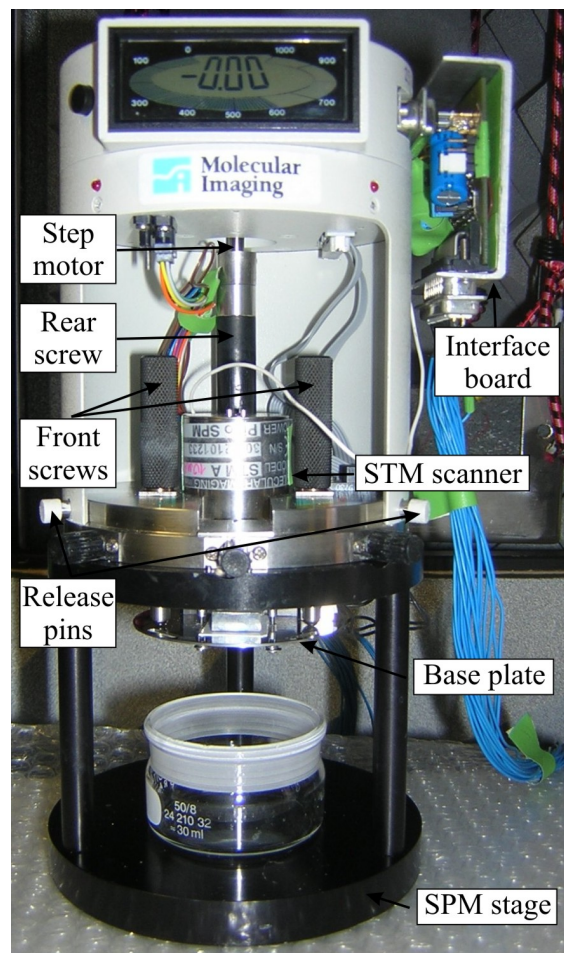


Fig. 3–5: PicoSPM measuring unit.

The environmental chamber (see Sec. 3.6.4) was designed and fabricated for experiments under strict environmental control.

A PicoSPM in a working configuration is shown in Fig. 3–5 as it is mounted on an SPM stage. When not in use, PicoSPM was kept mounted in a closed glass box. The STM scanner is inserted in the center of the PicoSPM, Fig. 3–5 displays a modified one. An interface board was used to connect an additional channel of the modified scanner to the oscilloscope.

The base plate with an assembled STM cell (Fig. 3–9 on page 89) is attached to the three screws with magnetic pegs below the main body of the PicoScan. The STM probe is inserted into the tubus of the scanner (not shown) above the STM sample. The coarse control of tip-sample separation is done by varying the vertical position of the

A PicoStat bipotentiostat was used to control the potential of both tip and sample (Sec. 2.4.6) in the EC STM experiments. The performance and response of the latter was tested in separate CV experiments and found to be satisfactory up to the voltage scan rate of $500 \text{ mV} \cdot \text{s}^{-1}$.

A generic MI STM scanners operating in the current range of ± 10 or ± 100 nA (gain is adjusted via the switch) were used. 16-bit preamplifiers employed in the scanners allowed 0.3 or 3 pA current resolution correspondingly. The scanners with modified double-channel preamplifiers (G. Mészáros [177]) as well as a digital oscilloscope Yokogawa DL 750 were used in some stretching experiments.

The used custom-made STM base plates were designed for the usage of single crystal disk electrodes (see Sec. 3.6.3). STM probes (Sec. 3.6.2) were lab-prepared from 0.25 mm diameter wires of W, Au, $\text{Pt}_{0.7}\text{Ir}_{0.3}$, $\text{Pt}_{0.8}\text{Ir}_{0.2}$ or Ir by etching and isolated by coating with PE. Pt, Ag and Cu wires of 1 mm diameter were used as RE in EC STM experiments, a Pt wire also served as a CE. The

base plate. The vertical position of the two front pegs is adjusted manually by rotating the corresponding front screws. The rotation of the rear screw by a stepper motor is software-controlled. The precise control of the tip-sample separation as well as the lateral tip movement is done by piezo elements located in the scanner.

3.6.2 STM probes

Etching of W tips

W tips are known to be mechanically stable and chemically inert in acidic solutions, with a well-known potential range of electrochemically inertness. They were conventionally used for high-resolution STM experiments.

A custom build setup was used for the electrochemical etching of W tips by the application of a DC voltage. Its main parts are a DC voltage source and a comparator allowing to switch off the voltage after the end of the etching (see further). The arrangement of the setup is shown in Fig. 3–6A. To avoid an interference from air flows, the etching setup was enclosed inside a Plexiglas box with access windows.

2 M NaOH solution used for etching is prepared in a volumetric flask (Sec. 3.3.1). The better results are known to be obtained with a solution preliminary cooled in a refrigerator overnight. The W wires are straightened in advance by tweezers. One can find out if the wire is straight by looking on it from the axial direction. A Pt ring (Fig. 3–6B) serves as a second electrode in the etching process. Before usage, it is aligned horizontally by tweezers. The ring is cleaned in place by rinsing with Milli-Q water and annealing in a butane flame. The carefully straightened W wire is fixed horizontally in the corresponding crocodile holder. It is centered inside the ring in order to obtain a uniform dissolution of W during the etching (Fig. 3–6B). A small amount of 2 M NaOH solution is placed in a 10 ml beaker. The ring and lower part of the wire is immersed into a solution by lifting of the beaker. After careful lowering of beaker, a thin film of liquid (lamina) is formed in the ring (Fig. 3–6B). The lamina is sensitive to vibrations and air flow, which should be avoided.

The lamina is illuminated by a lamp with a flexible neck. A telescope (Fig. 3–6A) is adjusted to see the area of contact between the wire and the lamina. By observing it in microscope, one could achieve a lamina film as thin as possible. Usually this is done by slowly lowering the beaker with the solution.

The voltage source is switched on. A DC voltage of *ca.* 2.7 V is applied between the W wire and the Pt ring serving as anode and cathode, respectively. During the whole etching process the applied voltage and current flowing through the electrochemical cell

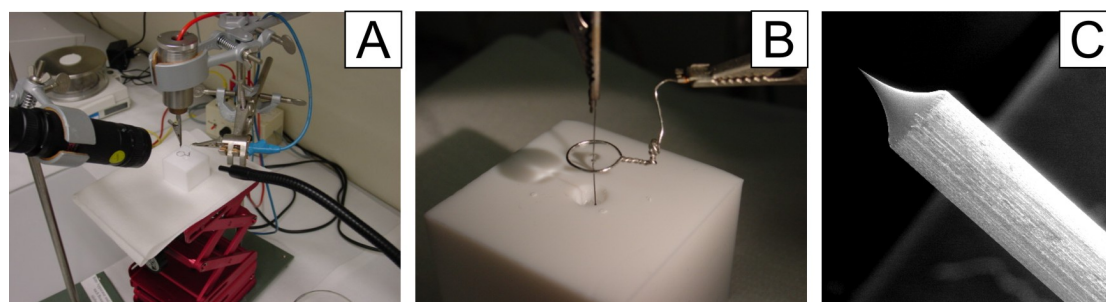


Fig. 3–6: (A) A setup for DC etching; (B) Tungsten wire wetted by a NaOH aqueous solution in a lamina; (C) TEM picture of an upper, uncoated W tip.

are monitored by multimeters. The voltage should be adjusted so that the current lies within 1 – 3 mA.

During etching, the W is oxidized and dissolved as WO_4^{2-} anions in solution. The wire becomes thinner in the contact region. The counter-reaction of hydrogen evolution takes place on the Pt ring. However, one must also avoid the gas evolution on the W wire. This process is an oxygen reduction, presumably promoted by the high concentration of tungstate and/or contaminations. The exchange of the lamina allows to prevent it.

The lamina should be exchanged if it breaks, if gas evolves on the W wire or the etching current drops below 1 mA. This is done as described above. After a new lamina is prepared, one must adjust the vertical position of the tip so that the same etched area is in the contact with the lamina again. This is critical for the preparation of tips with a short etched area. The tip position is adjusted by a screw on top of the crocodile holder with a simultaneous monitoring in a telescope.

As the contact area shrinks during the etching, the current steadily decreases. The breaking of the wire and falling of the lower part results in a sharp decrease of the current. This is detected by a comparator implemented in the etching setup, which ensures the immediate switching off of the applied voltage (response time $< 5 \mu\text{s}$). The further etching results in a removal of the sharpest part of the tip, *i.e.*, its apex, making the tip unsuitable for STM measurements.

The sensitivity of the comparator is adjusted by a knob on the etching setup. At the beginning it is set to a very low level to not interfere with the etching process and increased shortly before the end of the etching. If a false alarm occurred, the etching is restarted by pressing the button on the voltage source.

Shortly before the breaking of the wire, the lower part of the wire is inserted into a hole made in a teflon cube (Fig. 3–6B). After breaking, the upper part of the wire remains mounted, while the lower falls into the hole in upright orientation. Both upper and lower tips may be used in the STM experiments, although the former tends to be sharper and shorter. One should be careful when handling the tips, even a gentle touch of the sharp apex results in its destruction.

The prepared tips are rinsed in a stream of water and dried with Ar. The tips are stored in an desiccator filled with Ar and are used within one week. The Pt ring is rinsed from NaOH with copious amounts of water.

The quality of a tip is evaluated by the observation of its shape in an optical microscope. The tip apex must be straight, short and smooth. A transmission electron microscopy (TEM) image of a typical upper tip is shown in Fig. 3–6C. After coating the good W tips are used for EC STM experiments.

Etching of Au, Pt/Ir and Ir tips

Au, Pt/Ir and Ir used for STM experiments were etched by an AC voltage using a custom built setup (FZJ). Its main part is a AC voltage generator capable to produce sine, triangular and rectangular voltage waveforms with up to 80 V peak-to-peak amplitude and frequency $\nu = 50 - 5000 \text{ Hz}$. The setup is able to switch off automatically when the current reaches a predefined threshold value. The etched wire serves as one electrode, the second electrode is a glassy carbon (GC) rod. The amplitude and frequency of the AC etching voltage is monitored using a digital oscilloscope (Tektronix TDS 3034B). The current is measured by a multimeter in AC current mode. The pro-

cedure for the preparation of Pt/Ir or Ir tip is very similar, while for the Au tips it is significantly different.

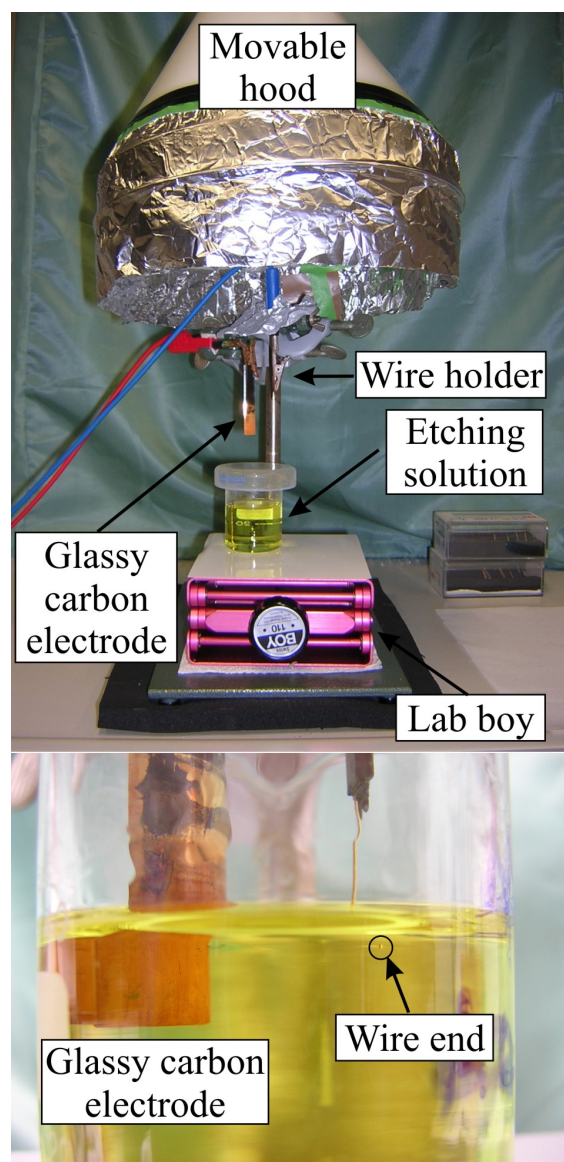


Fig. 3-7: Top: a setup for the etching with a AC voltage; bottom: Au wire immersed into a beaker with an etching solution.

The Ir wire is more brittle and should be handled with care. Stock wires used are rather straight and only small adjustments may be needed. It should be done carefully in order not to break it. Au wires are soft and can be straightened by rolling it between the palms. It should be straightened additionally if necessary.

To perform the etching, the setup, the oscilloscope and a multimeter are switched off. The contact to electrodes with a voltage applied may be dangerous, therefore the voltage generator should be active only when it is used, *i.e.*, during etching and adjustment of the parameters.

Two different GC electrodes are used for the etching of (a) Pt/Ir and Ir; and (b) Au wires. They are stored separately when not used. Before etching a corresponding GC electrode is rinsed with water and insert into the holder (Fig. 3-7).

A solution of 1 M $\text{CaCl}_2 + 0.25$ M HCl is used for the etching of Pt/Ir and Ir wires. It is prepared in a volumetric flask as described above (Sec. 3.3.1). CaCl_2 is used in form of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. It is weighted in a separate beaker and poured in a flask through a dry funnel without the usage of water. HCl is weighted in a beaker and added through the funnel as well. The beakers and the funnel are rinsed with water, which is then added to the flask. It is necessary to use the ultrasonic bath and turn the flask around from time to time in order to dissolve calcium chloride in a reasonable time.

The solution used to etch Au wires is prepared directly in a beaker by mixing concentrated (*ca.* 30%) HCl and absolute ethanol 1:1 by volume. After mixing, the beaker is covered by a Petri dish and homogenized for 2 – 3 minutes in an ultrasonic bath.

The wires are prepared and cut in advance. An etched wire should be long enough to be coated and inserted into the tubus of the STM scanner. The optimal length of the wire is 3 – 4 cm. If the etched apex of the wire is not good, one should cut it off and etch the wire again.

The Pt/Ir wires are straightened in advance by putting the load on the end of a hanging wire. This seems to also improve the mechanical properties of the wire. After cutting it into pieces, it is completely straightened by tweezers.

Tab. 3.2: Etching parameters

Tip	Pt _{0.7} Ir _{0.3}	Pt _{0.8} Ir _{0.2}	Ir	Au
AC voltage amplitude / V	55	80	80	27
I _{initial} / mA	200-250	200-250	200-250	300-350
v ₁ / Hz	50	140	500	4200
I _{switch} / mA	—	80	50	—
v ₂ / Hz	50	50	50	50
I _{end} / mA	5	2	5	10

Chlorine is known to evolve during the etching. It is sucked out by a small movable hood placed above the beaker with the solution and connected to the main ventilation system. However, a strong stream of air was found to perturb the etching process very much, so ventilation in the laboratory is switched to zero level during the etching and to the maximum after the etching. All other kinds of vibration should be avoided during the etching as well.

For Pt/Ir and Ir tips a fresh etching solution is known to work better. The black particles of the oxides are formed during the etching of Pt-Ir and Ir tips. Therefore, the solutions should be changed from time to time.

For Au wires the etching solution is used for long time. The presence of Au ions in the solution seems to improve the etching conditions. Usually, first attempts to etch the Au wire are not successful, but when solution become yellow, the results become much better. Moreover, Au is dissolved in this solution and there are no problems with the visibility of the wire.

For a single etching process the wire is vertically mounted in a crocodile holder. The length of the wire below the holder should be *ca.* 1 cm, otherwise it can vibrate during the etching. It should be finely adjusted to be strictly vertical.

The etching parameters (voltage amplitude and frequency) are adjusted according to the type of the wire etched (Table 3.2). A square waveform was found to be the best for all of them. The other optimal parameters are summarized in (Table 3.2), however they should be adjusted according to the results and experience. A two-step etching procedure was found to be successful for some types of wires. At the beginning the wire is etched with a higher frequency (v_1), and at the threshold value of the current it is switched to the lowest available value 50 Hz.

A beaker with an etching solution is placed on a Laborboy below the wire (Fig. 3–7). With the voltage source switched off, the beaker is lifted until *ca.* 1 mm of the wire is immersed in the etching solution (Fig. 3–7, bottom). One should adjust the wire according to the own experience. The movable hood is adjusted to cover the beaker and the wire without touching setup and cables.

The etching is started by switching on the DC voltage source. The value of the initial etching current reflects the area exposed to the etching solution. Its optimal values for different kinds of wires are summarized in Table 3.2. If the initial current is too small or too big, the voltage is switched off, the vertical position of the solution is readjusted and the etching is restarted. The soft gold wires are strongly affected by vibrations and formation of big bubbles. The etching voltage amplitude must be adjusted so that there is no buzzing noise during the etching and the gas bubbles have diameter of *ca.* 1 mm.

During the etching the current steadily decreases with time. Occasional sharp

increases of the current indicate instability of the solution level, the resulting tips are usually of bad quality. When the current reaches a predetermined switching threshold (Table 3.2), the DC voltage frequency is rapidly decreased. Afterwards, the current rapidly decreases to a final value, when the voltage source is switched off. The hood is removed, the tip is taken out and after rinsing inspected in a microscope. The bad tips are cut and etched again. When etching is finished, the beakers and GC electrodes are rinsed and dried.

Tip coating

The probes used for EC STM were coated with PE to decrease the area exposed to the electrolyte and to avoid a faradaic contribution to the measured tunneling current (see Sec. 2.4.6). PE is a clean and inert electrical insulator, the laboratory-designed coating procedure is simple and reproducible. The resulting tips have a residual non-tunneling leakage current below 10 pA.

The coating procedure is essentially the same for all types of tips used. However, one must pay attention to the fact that Pt/Ir and especially Au tips are much “softer” than those of Ir or W and should be handled with extra care.

The coating setup is shown in Fig. 3–8. The PE is melted on a Pt plate mounted on a soldering iron. The tip is inserted through the hole in the plate and covered by melted PE, which solidifies on cooling.

The PE rods are rinsed with Milli-Q water and ethanol, dried in Ar and stored in a glass beaker with a lid. Before coating, a rod is cut into slices with a clean scalpel, the outer parts of the slice cut off as well resulting in small, clean PE cubes. The Pt plate is cleaned by annealing to red in butane flame.

The tip is inserted into the hole on the plate and fixed in a holder of a micrometer screw (Fig. 3–8). The PE cube is cut in two halves, which are placed on the opposite sides of the tip. The initial length of the tip should be high enough to allow safe PE handling and at the same time short enough to let a complete dipping of the tip into PE. The light and telescope are adjusted and used to observe tip movement in PE.

The PE on the Pt plate is melted using a soldering iron by periodic heating and cooling cycles of *ca.* 10 sec. When PE is completely molten, the tip is lowered into the melt until it is completely covered. The relaxation of the liquid surface gives information about the actual viscosity. Driving the tip up and down, one follows the changes in the viscosity. A good coating may be obtained when the relaxation of the PE surface takes *ca.* 5 sec. When the optimal viscosity is reached, the tip is driven up from the melt and fixed. The PE should start to solidify at the upper part of tip almost immediately.

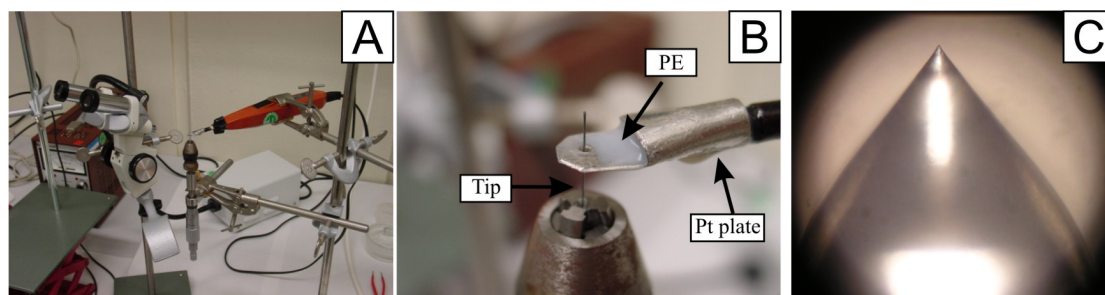


Fig. 3–8: (A) Setup for coating tips with PE; (B) Tip mounted on a holder and inserted into the hole in a Pt plate; (C) Coated Au tip as seen with an optical microscope.

Then the tip is taken by tweezers and removed from the holder. The length of the coated tips used for EC STM experiments is *ca.* 7 mm. An excess of PE is removed by first cutting the cover around the wire. This procedure is especially dangerous for soft wires. The tip is then pushed out from the rest of the coating with another pair of tweezers. The small residual PE are removed by a scalpel blade and the tip is inspected with a microscope. The rest of the PE is melted and removed by a scalpel before coating next tip.

Tip mounting

The bare or coated STM probe is inserted in the scanner of the PicoSPM operating unit (Fig. 3–5). The latter is mounted on the SPM stage and placed on a Laborboy in front of a camera connected to the screen. The upper part of the PicoSPM is released by pressing the corresponding pins and tilted back to allow easy access to the screws. All three screws are completely lowered.

The bare shaft of the tip is cleaned from the rest of PE by a sharp blade. The etched tip and the coating are rinsed with isopropanol and water and afterwards dried with Ar. The tip is slightly bent by two tweezers and inserted into the scanner from below. The distance between the coating and the tubus of the scanner should be *ca.* 1 – 3 mm.

The sample holder is mounted on the base plate as described in Sec. 3.6.3, the Au(111) disk single crystal is inserted into the holder after short rinsing and without annealing. The disk samples have varying height, so the same crystal should be used for tip mounting and the experiment.

The base plate is connected to the magnetic pegs with a tip approximately above the middle of the sample. The base plate is lifted up by manually rotating screw while maintaining the horizontal orientation of the plate. When the sample surface approaches the tip, a microscope and camera connected to the screen are used to monitor the tip–sample separation. The light source is adjusted allowing to see the tip reflection in a polished gold surface. In a used configuration, the separation between tip and its mirror image as seen on the screen at the highest magnification of the microscope should be *ca.* 2 – 3 cm, which corresponds to 40 – 60 μm of actual separation. The base plate should be slightly tilted backwards allowing the back screw to lift the plate into a horizontal position during the tip approach. After adjustment of the plate position, it is disconnected and disassembled. The PicoSPM with an inserted tip is mounted in a glass box and placed in a vibration isolation chamber.

3.6.3 Preparation of the STM experiment

The basic procedure to prepare the PicoSPM setup (Sec. 3.6.1) for the EC STM experiment as follows. The solutions are typically prepared in advance as described in Sec. 3.3.1, 3.3.2. The STM probes (Sec. 3.6.2) are inserted in advance and allowed to relax for *ca.* 12 hours before an experiment. The assembly and annealing of the monolayers (Sec. 3.4.5) are started in advance, otherwise the substrate is prepared before mounting (Sec. 3.4).

All glassware used at different steps of the preparation is soaked in caroic acid and cleaned as described above (Sec. 3.2.2). Two liquid cells and two O-rings used for the STM experiments are stored inside a 40 ml beaker and soaked in caroic acid. Two Teflon tweezers are stored in conc. H_2SO_4 . Before use they are taken out of the caroic

acid and cleaned inside the 40 ml beakers (Sec. 3.2.2).

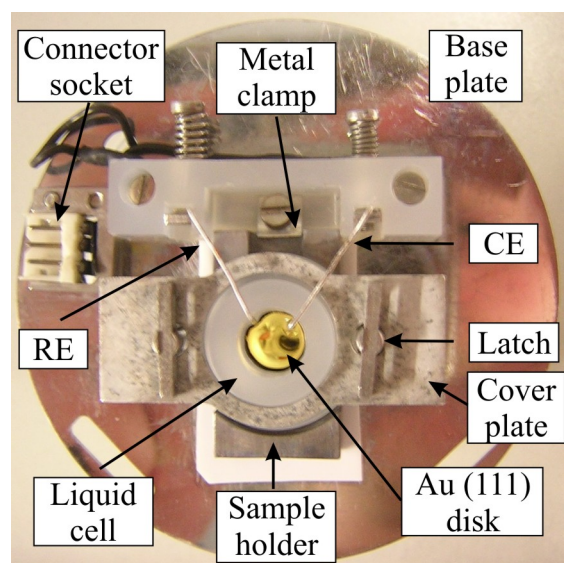


Fig. 3–9: EC STM cell mounted for experiment.

holder and the cover plate are taken out of the Petri dish, than rinsed by isopropanol and dried in Ar as well. The sample holder is mounted on the base plate. The electric connection between the former and a middle pin of the connector is tested by a multimeter. If there is a bad connection, the contact between the sample holder and the metal clamp must be adjusted. The latches holding the cover plate are placed vertically.

When the glassware is cooked 3 times and rinsed afterwards, the Au(111) sample must be already cooled down after flame annealing (Sec. 3.4.3) or thermal annealing of the monolayer (Sec. 3.4.5). The annealed ceramic tweezers are used to transfer the dry sample into the sample holder. The O-ring is taken with Teflon tweezers, dried in Ar and placed onto the sample. The liquid cell is also taken with Teflon tweezers, dried in Ar and mounted on top of the O-ring. The cover plate is placed on top of the liquid cell, the latches are pushed through the small holes on the cover plate. By lifting and turning the moving part of the latch, the cover plate is fixed to hold the liquid cell on top of the sample.

One should be careful to not touch the sample surface during the cell assembly. The O-ring must fit into the chute on the bottom side of the liquid cell. These parts should be dried from water with extra care if an experiment is to be carried out in a non-aqueous environment. The cover plate should not produce an excess pressure on the sample.

The described configuration is sufficient to carry out experiments without potential control. The wires of CE and RE should be additionally mounted for an EC STM configuration. These are two Π -bent wires of an appropriate material with a long middle part (1 – 1.5 cm) and short (5 – 8 mm) legs. The corresponding clamp is released by pressing on the metal screw, than an electrode is installed with one leg inside a clamp and another in solution. The electrode should be located close to the side of the liquid cell (Fig. 3–9), but does not touch neither sample, nor cell.

The Pt electrodes are cleaned by annealing at red color in a butane flame for 5 seconds. The Cu wires are prepared for every experiment from a stock wire. They are scratched from an oxide layer, cleaned by soaking in a hanging position in conc. H_2SO_4 for 1 – 2 hours before the experiment and rinsed with Milli-Q water before mounting.

A table flow box is used for the final cell assembly. To clean it, it is switched on 2 – 3 hours before the assembly. The STM setup, including a computer, is switched on 1 – 2 hours before the cell mounting. The PicoSPM is mounted on a stage and connected to a 25-pin cable. The electric connections are tested by connecting the dummy cell and running CV measurements.

The bare base plate is stored on a Petri dish covered by a glass lid inside a flow box. The metal sample holder and cover plate are kept together immersed in isopropanol inside a closed Petri dish. Before the cell assembly, the base plate is rinsed from dust by isopropanol and dried in a stream of Ar. The sample

The Ag wires are stored in a closed beaker and cleaned by cooking and rinsing.

150 – 200 μl of the liquid is added to the cell for measurements. The non-aqueous solutions are usually added into the cell immediately after mounting of the cover plate. A dry and clean Eppendorf pipette is used to take solution from the flask or a pure solvent added to a dry beaker. The cell is connected to the PicoSPM by inserting a cable from the latter to the corresponding socket. The aqueous solutions for EC STM experiments are added under potential control. The cell is connected and the bipotentiostat is switched on. The water is removed from the double beaker to expose the smaller one. The Eppendorf tip is rinsed 10 – 15 times by taking water from the small beaker and disposing it. Then the solution is taken directly from the Erlenmeyer flask and added to the cell. To avoid undesired potential jumps, the first drop must contact the RE and the sample surface and the CE is wetted later.

The base plate is slowly raised and attached to the magnetic pegs, so that the STM tip is located inside the liquid cell without touching its walls. The solutions should not reach the bare part of the coated tip and/or flow into the scanner. The PicoSPM with a mounted base plate is transferred into the vibration isolation chamber. The Laborboy supports are moved down to release the granite plate. The whole setup is allowed to relax *ca.* 1 hour.

After relaxation the plate is lifted by the step motor with a rate of $2\text{--}4\ \mu\text{m}\cdot\text{s}^{-1}$ until the preset tunneling current (10 – 20 pA) is detected. Further control of the tip-sample separation is done by piezo-motors.

3.6.4 Environmental chamber

An environmental chamber was designed for experiments in the absence of oxygen. After multiple trials, the configuration with a whole PicoSPM unit enclosed in a gas-tight glass chamber, which is filled with Ar, was selected as optimal.

The glass body is a cylinder of *ca.* 28 cm height and *ca.* 15 cm inner diameter open at the top (Fig. 3–10, top). It is covered by a metal lid locked by a ring clamp. A silicone O-ring is placed in the chute on the rim of the glass body to allow good sealing. The metal tubes of the gas inlet and gas outlet are connected to the tubes going through the lid. An additional metal tube going through the lid is used to insert a Teflon tube (see further). A sealed 25-pin socket is built into the lid allowing cable connection to the PicoSPM. The gas valves (Swagelok) are attached to the gas inlet and outlet. The Teflon tube is connected to the gas outlet from the inner part of the lid to deliver Ar to the bottom of the chamber.

After preparation, the glass body is cleaned from inside by filling it with conc. H_2SO_4 . The body is regularly wiped by a paper tissue sprinkled with isopropanol. The lid and the O-ring are rinsed by isopropanol and dried. The closed chamber is checked for leakages by immersing it into water while an excess pressure of *ca.* 2 bar is applied. The chamber is kept closed when not in use.

The environmental chamber could be used for experiments in the absence of oxygen in different media: gas (argon), organic solvent (mesitylene) and aqueous electrolyte. In the latter case the amount of oxygen may be estimated by CV measurements. The aqueous solutions are deoxygenated by purging it for *ca.* 30 min. with Ar in a flask with a gas inlet, a gas outlet and an additional mouth on the side. Mesitylene-based solutions contains less dissolved oxygen and may be used as prepared.

To carry out STM experiments, the PicoSPM is connected to the inner 25-pin cable, while the outer cable is connected to the controller. The cable connections are tested with a dummy cell before further procedures.

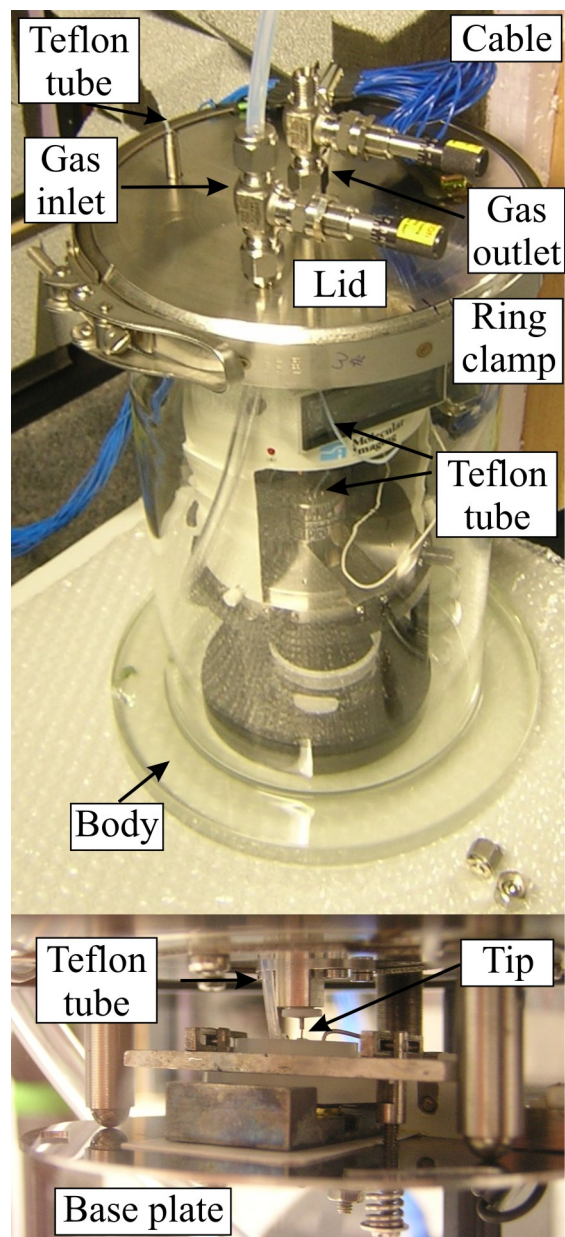


Fig. 3–10: Top: a PicoSPM inside the environmental chamber; bottom: mounted STM cell with a Teflon tube.

cooking and rinsing. The syringe is kept in a vial with water which is cleaned by cooking and rinsing. The syringe is cleaned inside by taking and disposing hot and cold water. The flask for purging is rinsed similar as a standard glassware (Sec. 3.2.2).

The STM cell is assembled on a base plate as for normal experiments (Sec. 3.6.3), including CE and RE electrodes. The base plate is mounted to the PicoSPM. To add aqueous solution, the thin Teflon tube is dried from inside and outside by Ar and pushed through the opening in the lid (Fig. 3–10, top). The Teflon tube goes through an opening in the STM scanner into the cell (Fig. 3–10, bottom). The PicoSPM is mounted into the chamber, the lid is closed. The chamber is purged with Ar at 2 bar overpressure for 10 minutes. At this step the major amount of air is removed through the tube opening. The deoxygenated solution is taken from the flask by a syringe and added through the tube into the cell. The amount of solution injected into the tube should be enough to fill the cell up to the wire electrodes, but does not flow out of the cell. The tube is pulled from the box, the tube opening is closed by the cap and sealed. The box is purged for additional 10 minutes with the gas going out through the gas outlet. After deoxygenation it is disconnected from the gas line and mounted into the vibration isolation chamber. The further experiment proceeds normally.

An Ar atmosphere for the measurements without the liquid and with non-aqueous solutions is created in the same way. The latter are added after assembly of the STM cell and can be additionally purged before. The tube is kept in an Erlenmeyer flask and cleaned inside it by

3.7 General measurement procedures

3.7.1 Cyclic voltammetry

The EC experiments were carried out using both a dedicated Autolab setup (Sec. 3.5) and a PicoSPM in a EC STM configuration (Sec. 3.6) with or without environmental chamber (Sec. 3.6.4). Although the existing setups allow carrying out various EC experiments, the series of CV measurements with varied voltage scan rate (Sec. 2.3.6) were mostly carried out at constant scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ or $50 \text{ mV}\cdot\text{s}^{-1}$. The detailed description of one such experiment is given in Sec. 3.4.6. Typical information extracted from the electrochemical results include:

- the potential range of the electrode/adlayer stability;
- the capacity of the adlayer;
- potentials of transitions between the interfacial phases;
- adsorption/desorption potentials;
- formal potentials of redox reactions;
- surface coverage of an adlayer, preferable orientation of the molecules in the adlayer;
- the oxygen content;

as well as others.

During the EC STM experiments the samples were typically characterized in a save potential range by CV at the beginning, in the course of the experiment and at the end. The STM tips were also characterized *in situ* by CV. The electrochemical response provided additional information about the current properties of the system.

3.7.2 STM experiments

The MI measuring setup was controlled by the PicoScan software, version 5.1. The STM images; CV responses of samples and tip; current-distance and current-voltage STS scans were recorded using standard PicoScan procedures. The external control of the tip movement was used in some stretching experiments.

All STM images were recorded in constant current mode as squares with a resolution of 512×512 or 256×256 points. The tip was moving always from left to right and from up to down with a lateral scan rate below $2000 \text{ nm}\cdot\text{s}^{-1}$. Brighter and darker contrast in the images represent higher and lower tip positions respectively. After flattening of the STM topography no further image processing was performed.

3.7.3 STS measurements

The current-distance and current-voltage STS and CV scans were recorded as single or multiple scans with a resolution of 1000 or 2000 samples in a selected potential or distance range. Prior to a spectroscopy scan, the imaging was stopped and the tip was stabilized via a current feedback. For the $I-z$ scans a vertical scan rate of $2-4 \text{ nm}\cdot\text{s}^{-1}$ was selected as an optimum between speed of the measurements and the stability of the system.

3.7.4 “Stretching” technique

Single atomic and molecular junctions were created employing the STM “stretching” technique [159, 179]. Sharp Au tips capable of nm resolution were used. The bare or adlayer-covered gold surface served as a substrate in this experiments. The following steps were taken to perform a single “stretching” scan (Fig. 3–11):

1. The surface is imaged by STM prior to the stretching regime. V and I_T are selected to ensure negligible interactions of the tip with the adlayer.
2. Lateral scanning is stopped on substrate terraces and the feedback is disabled at a tip-substrate distance z_0 . The latter is considered as a relative zero distance (Fig. 3–11A).
3. The tip approaches the surface for a distance z_{min} with reference to z_0 . This distance is selected according to the studied system. To form atomic junctions, the Au tip was brought in contact with the metal ($z_{min} < -2$ nm). SMJs were created by bringing the tip in contact with an adlayer and simultaneously avoiding its mechanical interaction with the gold substrate ($z_{min} = -1.5 \dots -1.1$ nm, Fig. 3–11B).
4. A 100 ms delay is applied to increase the probability of junction formation.
5. Current-distance characteristics are recorded upon retraction of the tip from z_{min} to $z_{max} > z_0$ (1 – 1.5 nm) (Fig. 3–11C).
6. The tip returns to z_0 and the feedback is switched on.
7. The cycle is repeated 10 – 15 times, than the surface is inspected by STM imaging.

The characteristic plateaus (see Cha. 5-7) observed in the retraction $I - z$ curves were attributed to the formation of stable atomic or molecular junctions. The statistical analysis allowed to evaluate the conductance of single junctions. The described technique was successfully applied to study the conductance of atomic and molecular junctions under various conditions.

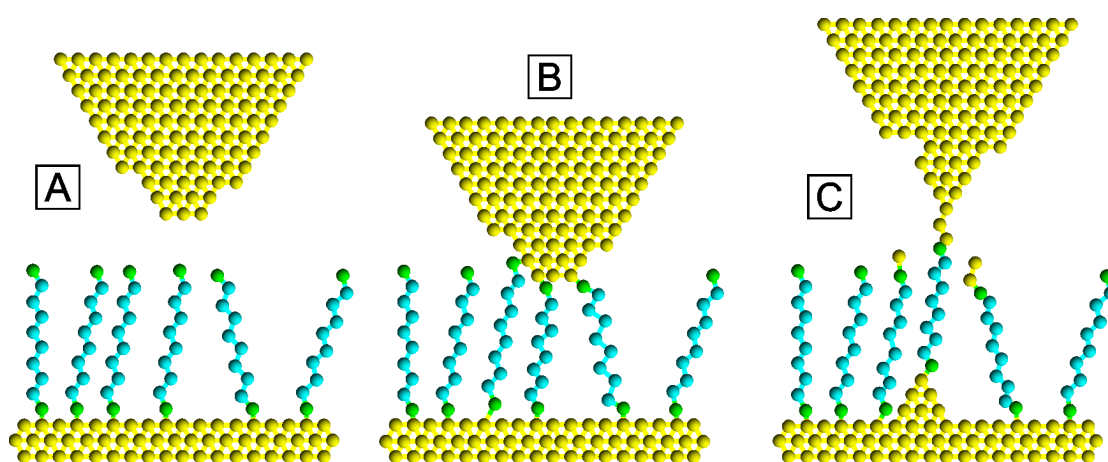


Fig. 3–11: Formation of metal-molecule-metal junctions in an STM configuration: (A) tip approaches the surface; (B) tip contacts the adlayer; (C) tip pulls away molecules from the surface.

3.8 System-specific details

3.8.1 STM and STS of Cu UPD adlayers

All measurements presented in Cha. 4 were carried out in aqueous solutions containing 1 mM Cu^{2+} and 0.05 M H_2SO_4 . The solutions were prepared in Erlenmeyer flasks. Cu as solid CuO and conc. H_2SO_4 were added to the solution as described in Sec. 3.3.1.

Experiments in the presence of chloride were carried out with $5 \cdot 10^{-5}$ M and 10^{-5} M NaCl. High and low Cl^- concentrations were employed for steady state STM measurements and for dynamic ones. The NaCl stock solution was prepared in an Erlenmeyer flask simultaneously with a $\text{Cu}^{2+}/\text{H}_2\text{SO}_4$ solution. Then an aliquot amount of NaCl containing solution was transferred between the flasks (Sec. 3.3.1). During the mounting of the EC STM experiment, the solutions were added under potential control.

A dynamic regime was used for the kinetic STM experiments. The upper part of the image was recorded under potentiostatic conditions and then a potential “step” was made by scanning the potential from the initial to the final value ($50 \text{ mV} \cdot \text{s}^{-1}$). In this mode, the movement down on the image also reflects the time-dependent evolution of the system. With a selected scan rate the whole image was recorded in approximately 2 minutes. The coverage was calculated from the STM images using the “Cover” tool in the “Filter toolbox” of PicoScan. If not stated otherwise, the coverage values are given with respect to the density of atoms on the Au(111)-(1×1) surface.

In order to prevent perturbation of the tip by the contact with an adlayer, current-distance EC STS experiments (Sec. 3.7.3) were carried out in the following way. During the topographic scan of the surface, the lateral tip movement was stopped. After a few seconds the vertical tip position was stabilized via a current feedback with a typical value of $I_T = 0.1 \dots 0.5 \text{ nA}$ at the initial tip-sample distance z_0 . Then the tip was first withdrawn out of the surface up to a distance $z_{\text{max}} > z_0$. A waiting period of 0.1 s was applied to let the tip relax. The current was recorded as a function of the distance during the movement of the tip to the position $z_{\text{min}} < z_0$. The scan range was selected so that $I_T(z_{\text{max}}) \approx 0$ and $|I_T(z_{\text{min}})| \leq I_{\text{max}}$, the latter was typically 100 nA for STS experiments. Only one distance scan was performed at every position, after that the topographic scan was continued and one could estimate the tip stability by the quality of the image. Only distance scans with accompanying images showing neither tip contact with the surface nor strong change of the surface pattern after the scan were selected for further processing. 5-10 scans were recorded for every set of conditions and averaged. The averaged scans are one dimensional and do not reflect the spatial distribution of the structural elements of the adlayer.

Tunneling barrier profiles were calculated from $I - z$ data using a program written by Gábor Nagy [180–182].

3.8.2 Conductance of Au QPC

The conductance of Au QPCs (Cha. 5) was studied using the stretching technique in three different environments: gaseous Ar atmosphere, the non-polar organic solvent mesitylene and an aqueous solution of 0.1 M H_2SO_4 at positively and negatively charged surfaces.

A low resistance preamplifier capable of measuring currents up to 100 μA (noise level is on the order of 1 nA) was employed for the STM / STS / stretching experiments.

Atomically resolved images of graphite were obtained with this scanner in a separate test experiment. Later another series of experiments was carried out using a double-channel preamplifier (Gábor Mészáros, [177]) having a current resolution of a few pA. The results did not differ.

Etched gold tips (Sec. 3.6.2) were used for STM and stretching experiments. For experiments in aqueous solution they were carefully isolated with PE (Sec. 3.6.2). Pt wires were used as QRE and CE in the latter case.

Special attention was paid to the presence of oxygen in the system. The purpose was to establish a technique of oxygen-free experiments. Solutions were deoxygenated before usage. During the experiment the whole MI PicoSPM setup was kept in a sealed chamber, filled with Ar (Sec. 3.6.4). The results of the CV experiments are presented in Fig. 5–1 on page 124.

3.8.3 Conductance of gold-alkanedithiol-gold junctions

The interfacial and ET properties of S8S (Cha. 6) were studied using CV, STM imaging and the stretching technique. Additional stretching experiments were also carried out with homological alkanedithiols (S5S, S6S, S9S, S10S). The pure substances used are volatile liquids with a fetid smell. In order to avoid cross-contaminations in other experiments, they were handled under the hood using dedicated glassware and tools.

Massive Au(111)-(1 × 1) single crystals were used as substrates for both electrochemical and STM studies. After flame annealing of the Au(111) sample (Sec. 3.4.3), the surface reconstruction was lifted as described before (Sec. 3.4.4). Low or high coverage SAMs of alkanedithiols were fabricated by the substrate modification in freshly prepared solutions of the respective alkanedithiols in ethanol (Sec. 3.4.5). One can reproducibly obtain adlayers with different properties by varying concentration, modification time or using thermal annealing at different temperatures [173]. Alternatively, the disordered high coverage SAMs on Au(111)-(1 × 1) were formed upon the loading of 1 mM solutions of the respective alkanedithiol in mesitylene into the STM liquid cell.

The high coverage SAM of S8S on Au(111) was electrochemically characterized by CV and in immersion experiments (by the courtesy of Rocio Aguilar Sanchez, [183]) in 0.1 M H₂SO₄ and 0.1 M NaOH. In the immersion experiments a dry SAM-covered sample is immersed in the solution under potential control. The EDL formation leads to the current flow at interface. Integration of the latter gives the EDL charge.

It is known that exposure of dithiol adlayers to the oxidants, in particular oxygen, leads to the dimerisation of the free thiol groups [184]. Precautions discussed above were taken in order to avoid the presence of oxygen in the system. Aqueous solutions were deoxygenated by Ar before usage. The STM / stretching experiments were carried out using a dedicated environmental chamber. CVs recorded in the STM cell demonstrated the absence of oxygen traces.

The SAMs of S8S on Au(111)-(1 × 1) were imaged using STM. Experiments were carried out with uncoated Pt_{0.7}Ir_{0.3} tips in pure mesitylene.

A conventional STM scanner allowing to measure currents up to 10 nA was used for stretching experiments. Etched gold tips (Sec. 3.6.2) were employed. For experiments in aqueous solution they were isolated with PE (Sec. 3.6.2), while a silver and a platinum wire were used as QRE and CE respectively.

3.8.4 Conductance of Au-44BP-Au junction

The conductance of Au-44BP-Au SMJs (Cha. 7) was studied by the STM stretching technique in an electrochemical environment. A coated Au STM tip and an annealed Au(111) samples were mounted in the EC STM setup. The latter was then placed in the environmental chamber. Aqueous solution of 0.05 M LiClO₄ + 3 mM 44BP was added under potential control. A silver and a platinum wire were used as QRE and CE respectively. STM scanners capable of measuring currents up to 10 and 100 nA were used in different experiments.

3.8.5 EC STS of viologen adlayers

The viologen adlayers for EC STS experiments (Cha. 8) were assembled on Au(111)-(1 × 1) STM sample as high coverage disordered adlayers (Sec. 3.4.5). The low coverage ordered phase was used in complementary imaging experiments [173]. The samples were mounted in the EC STM setup as described before (Sec. 3.6.3). The experiments were carried out in 0.5 M LiClO₄ aqueous solution adjusted to pH ≈ 8.5 by addition of NaOH. Silver and platinum wires were used as QRE and CE, respectively. An oxygen-free environment was created using an argon-filled environmental chamber enclosing the whole measuring unit (Sec. 3.6.4).

CV measurements in an EC STM configuration were carried out prior to the EC STS experiments and between series of measurements. The purpose was to estimate the oxygen content, quality and stability of the monolayer, as well as to evaluate the equilibrium potential of the viologen redox transition E^0 (Sec. 8.2.1) for a given conditions. The exact value of the equilibrium potential may vary due to nature and concentration of the supporting electrolyte, pH and other factors. The E^0 was assumed to be equal to the average values of the positions of the reduction and oxidation peaks as measured by cyclic voltammetry in the STM cell during the experiment (*cf.* Fig. 8–1C). The potential of the QRE was calibrated with respect to the SCE.

The current-voltage EC STS in a constant bias mode was carried out by fixing the bias voltage and cycling both tip and sample potentials with a rate of 0.5 V·s^{−1}. In the variable bias mode E_s was fixed and E_t was cycled in a wide potential range with a rate of 0.5 – 2 V·s^{−1}. In both cases the initial tip and sample potentials were sufficiently far away from E^0 . To record an STS scan, the lateral scanning was stopped and the tip was stabilized via the STM feedback loop. The tip–sample separation was controlled by selected initial values of the bias voltage V and of the tunneling current I_0 . The feedback was temporarily disabled while the tunneling current was recorded in a potential cycle. The experiment was repeated 5 – 10 times for every set of experimental conditions.

The EC STS experiments carried out require a high stability of the tip position. The lateral tip stability was checked by the drift of the scanned image. The vertical stability was checked by disabling the feedback loop and observing the evolution of the tunneling current. The EC STS measurements were carried out only if the tip displacement was negligible longer than the typical scanning time (1 – 5 sec). Only scans showing a return of I_T to I_0 at initial potential were selected for further analysis.

Comparative “blank” spectroscopy experiments were done to evaluate the contribution of the electrochemical current in the tip signal. The same voltage scan procedure was applied in the absence of the tunneling contact. In the presented experiments the faradaic contribution was negligible.

Chapter 4

Cu UPD on Au(111) in the sulfuric acid/chloride

4.1 Introduction

Structure–reactivity correlations in ET reactions, an important aspect of many processes, such as catalysis or a specific molecular recognition, may be assessed now by combining *in situ* STM and STS studies of molecular adlayers and individual molecules in a host-guest configuration. When the work on this thesis was started, there were already first results available on the formation of molecular bridges in the sample-molecule-tip configuration, studied by current-distance STS, which we wanted to develop. But in order to approach this task and to establish the experimental technique, I started from simpler systems and have chosen ionic adlayers.

As a first system to investigate by EC STM and STS a copper-sulfate adlayer on Au(111) was selected. It forms due to the so called underpotential deposition (UPD), when one or two layers of a metal are deposited on an electrode at potentials more positive than the equilibrium potential of bulk metal deposition. The Cu UPD is a first step of copper bulk deposition, which is a very important technological process. Copper with its high electric conductivity and low price is a standard metal used as a conductor. In particular, the copper is deposited in the etched trenches on chip to create interconnects in the ICs [185].

By taking into account the relative ease of Au(111) substrate preparation (Sec. 3.4), it is not surprising that among all UPD processes that of Cu on Au(111) in the presence of sulfuric acid is the one most intensively studied by methods of electrochemical surface science. The characteristics of this process were investigated by classical electrochemical methods [186–196] and the quartz crystal microbalance (QCM) [197–201] techniques. The kinetics and the mechanism of adlayer formation were analyzed using chronocoulometry (Sec. 2.3.5) [192–196]. The structure of the adlayer formed at moderately negative potentials (Sec. 4.3.2) was assessed by electron diffraction [202, 203], X-ray [191, 197, 204–209], infrared (IR) [195, 206, 210–212], Auger electron [213] spectroscopies; *in situ* STM [182, 214–223], current-distance STS [182, 220, 221] and AFM [224, 225].

The structure of this most addressed adlayer is completely resolved providing a good starting point for practicing and establishing a new technique. Extended studies based on the Cu UPD system included, to name only few: generation of Cu clusters on Au(111) and their spectroscopic probing [77, 226]; the exploring of catalytic properties of metal-ion adlayer [227, 228]; surface friction [229] and surface stress [230–232] experiments. The preparation of atomically thin metal films by replacing adsorbed copper with other metal cations [233, 234]; the preparation of ultrathin copper sulfide

film [235] and SAMs [236] are reported as well. A number of the theoretical methods allowing to evaluate structure and other properties of adlayers were tested on the Cu UPD system [213, 237–243].

The discussed system may be modified by introducing small amount of strongly adsorbing anions, *e.g.*, chloride. The effect of chloride on the Cu UPD on Au(111) was studied by voltammetry and chronocoulometry [190, 244–246], *ex situ* structure-sensitive methods such as low energy electron diffraction (LEED) [247] spectroscopy, *in situ* X-ray absorption spectroscopy [191, 246], *in situ* STM [182, 214, 217, 218, 223, 248–250] and AFM [225]. It was shown that the addition of even small amount of Cl^- in sulfuric [182, 191, 217, 218, 223, 225, 248, 249] and perchloric [190, 244–246, 250] acid changes significantly the properties of the metal-electrolyte interface. In the case of pure perchloric acid the deposition of Cu is known to be strongly kinetically hindered [200, 244, 250], and the evidences of the specific adsorption of ClO_4^- is better to be interpreted as being caused by the trace impurities of Cl^- [214, 215, 250, 251].

Summaries on studies of Cu UPD on Au(111) in the presence of sulfate and chloride can be found in [72, 73, 182, 252]. The previous results on this topic obtained in our group were already published in [182, 220, 221]. Here I will described and summarize my experiments done during my Ph.D. studies. The experimental details are presented in Sec. 3.8.1.

4.2 Electrochemical properties

The effect of Cu^{2+} and Cl^- ions on the interfacial properties of Au(111) surface in sulfuric acid was studied by CV (Fig. 4–1). In the absence of copper, the presented range of potentials corresponds to a negatively charged bare Au(111) surface [190]. Two characteristic pairs of peaks P_1/P'_1 and P_2/P'_2 separate 3 regions for each measured curves. Peaks are asymmetric, which represents the hysteresis of the voltammogram due to kinetic limitations [192]. The CV technique (Sec. 2.3.6) gives only general macroscopic information, while the structure of interfaces can be resolved by structure sensitive techniques.

In the potential range close to the PZC (area III) no ordered adlayer exists on the surface. A bare gold surface (phase III) can be imaged under these conditions (Sec. 4.3.1).

In comparison to the CV response of the Au(111) surface in sulfuric acid (Fig. 3–3), additional peaks appear at negative potentials in the presence of Cu^{2+} (Fig. 4–1, curve 1). The reconstruction of the Au(111) electrode surface is known to be lifted by the adsorption of copper in the whole potential range (I and II in plot) [206] and consequently no features of reconstruction formation/lifting are seen in the CV.

While scanning the potential in negative direction, the peak P'_2 is passed. In chloride-free solution it reflects the formation of an ordered loosely spaced Cu-SO_4^{2-} UPD adlayer (Sec. 4.3.2) with a surface coverage of Cu^{2+} and SO_4^{2-} equal to 2/3 and 1/3 respectively [188–190, 248]. At more negative potentials the peak P'_1 indicates the rearrangement of the adlayer due to an increased negative surface charge. The surface coverage of Cu^{2+} raises up to 1 [188–190, 248] and a phase with a structure isomorphic to Au(111) [225] forms. A simultaneous decrease of the SO_4^{2-} coverage (“partial desorption”) takes place [188, 248]. The hysteresis of the peak reflects a slow rate of the transition processes. The potential range I is narrow and limited from the left by the

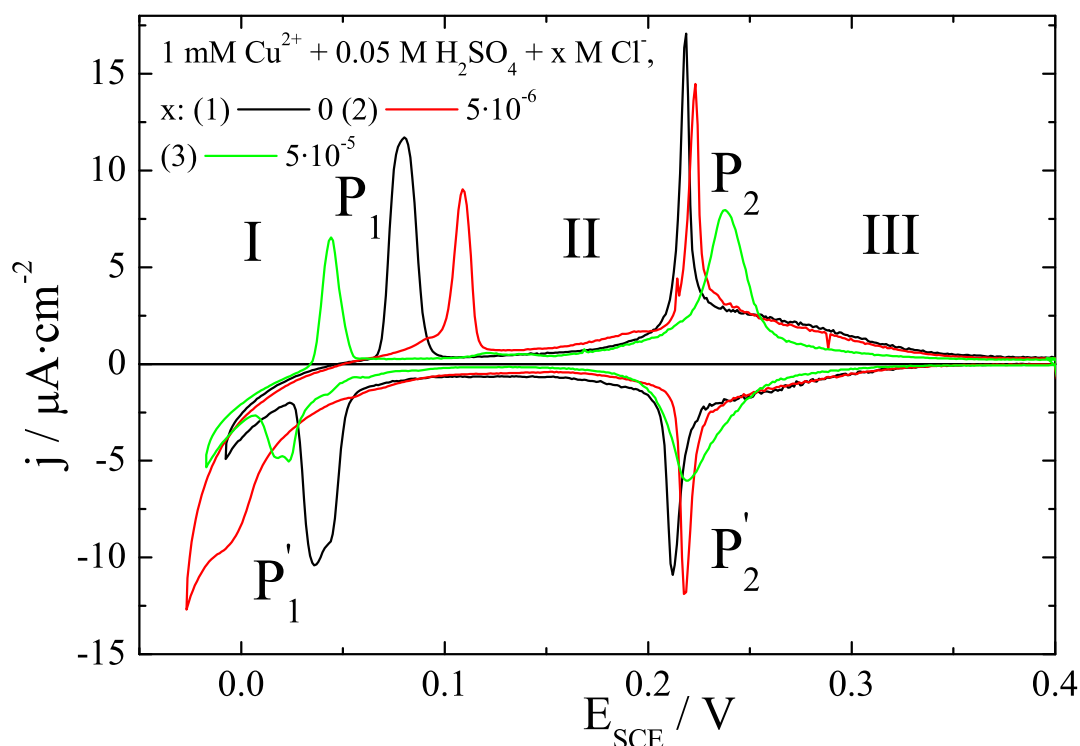


Fig. 4-1: Stationary CV of the Au(111) electrode in 0.05 M H_2SO_4 + 1 mM Cu^{2+} + x M Cl^- , scan rate $1 \text{ mV}\cdot\text{s}^{-1}$, x : (1) 0, (2) $5 \cdot 10^{-6}$, (3) $5 \cdot 10^{-5}$.

onset of the bulk copper deposition ($E^0 = 0.012 \text{ V}$) taking place before the hydrogen evolution (*cf.* Fig. 3-3). Bulk copper deposition leads to the desorption of sulfate anions [206]. On the return scan peaks P_1 and P_2 correspond to the gradual decrease of the Cu^{2+} coverage and the disappearance of the ordered adlayer.

An introduction of a small amount of Cl^- further modifies the interfacial properties of the studied system (Fig. 4-1, curves 2, 3). The onset of Cu adsorption is seen during a potential excursion from area III towards negative potentials [190, 245]. The formation of the Cu-Cl^- phase in potential region II and its dissolution on the reverse scan are reflected as peaks P'_2/P_2 . They systematically shift with the chloride concentration towards more positive potentials. This indicates that the Cu-Cl^- phase adsorbs stronger than the Cu-SO_4^{2-} , even at a concentration difference of 4 orders of magnitude. The thermodynamic surface excess data [190] demonstrate almost 0.1 V shift between the onset of SO_4^{2-} and Cl^- coadsorption with Cu^{2+} at equal concentrations of anions (here 10^{-3} M). These results reflect the difference in surface affinity. The surface coverage of chloride in the potential range II is higher than in the single-component solutions and close to 0.58 [190, 245]. This again suggests the primary role of cooperative adsorption (Sec. 4.3.3). The copper coverage in the same potential range was estimated as 0.75 [190]. At even lower chloride concentrations a splitting of the peaks P_2/P'_2 was observed [217], which was attributed to the separate formation of domains of Cu-Cl^- and Cu-SO_4^{2-} adlayers. The CV recorded in the solution with the highest concentration of chloride (curve 3) demonstrates a pronounced hysteresis between the peaks P_2/P'_2 even at a scan rate as low as $1 \text{ mV}\cdot\text{s}^{-1}$. This suggests kinetic hinderance of the adlayer formation and dissolution.

The position of the peak P_1 in curves 1-3 does not vary systematically with the concentration of chloride. Its counterpart P'_1 is clearly seen for chloride-free solution, van-

ishes at lower chloride concentration and reappears at a higher one. This non-systematic behaviour indicates the different nature of the peaks P_1/P'_1 in curves 1–3. Here I will briefly describe the corresponding interfacial processes [244, 250], the detailed STM studies are given further.

At the Cl^- concentration of $5 \cdot 10^{-6}$ mol the Cu-Cl^- structure introduced above transforms upon the decrease of the potential into another structure with a lower Cl^- content (Sec. 4.3.4). The transition of the Cu-Cl^- adlayer is slow and is not reflected as a pronounced peak in the CV [250]. This processes may be responsible for a small bump in the negatively tail of curve 2. The reverse transition is accompanied by the uptake of Cl^- anions from the solution, which is reflected as a sharp peak P_1 . The low Cl^- phase is stable until the very onset of bulk copper deposition [250], where the copper monolayer is formed.

At a Cl^- concentration of $5 \cdot 10^{-5}$ mol the behavior of the Cu-Cl^- adlayer is similar to that of Cu-SO_4^{2-} . The peak P'_1 corresponds to the formation of a full Cu monolayer and partial Cl^- desorption due to an increased negative surface charge ([245, 247] and similar results for Pt(111) in [253]). Again, the formation of a new surface phase almost overlaps with the bulk Cu deposition. The reverse transitions of the surface structure upon returning the direction of the potential scan are reflected as peaks P_1 and P_2 .

The transition between the two types of Cu-Cl^- adlayer behavior corresponds to Cl^- concentration of *ca.* 10^{-5} M [250]. We did not carry out CV experiments with a higher concentrations of Cl^- additives. It was shown that at concentrations above $5 \cdot 10^{-3}$ M the mechanism of bulk Cu deposition changes. Besides UPD formation, the reduction of Cu^{2+} to CuCl_2^- ions was observed in the potential range II [244]. Simultaneously, the peak of the bulk deposition shifts to more negative potentials due to the dominating CuCl_2^- discharge in the Cu-Cl^- adlayer.

It is necessary to note that EC STM experiments, presented in this chapter, were carried out in an open EC STM cell; thus, the presence of oxygen was not avoided. For the CVs of the Cu-SO_4^{2-} system measured in the EC STM cell the charge values were calculated from peaks P_2 and P'_2 . They are within 10% in agreement. The peak P_1 was mostly buried in the current response due to oxygen reduction. In the following I mostly concentrate on the results of the STM measurements in the potential ranges II and III, although oxygen was found to not affect the STM measurements, even at lower potentials [182, 217].

4.3 Steady STM results

The summary of the structural investigations of the adlayers existing in the studied system is presented in the Fig. 4–2. The names of the phases observed stand from the potential range of their existence (Fig. 4–1). Depending on the composition of phase II (Cu^{2+} coadsorbed with sulfate or chloride anions), additional indices “s” or “c” are used. For the sake of simplicity I reserve the name I for a full Cu monolayer coadsorbed with anions. Thus, there are two concurrent Cu-Cl^- UPD phases existing in range II. The first of them is promoted at the expenses of the second at higher chloride concentration, higher potentials and corresponds to higher coverages. To distinguish between these two phases, I will use additional indices “h” and “l” representing “high” and “low”.

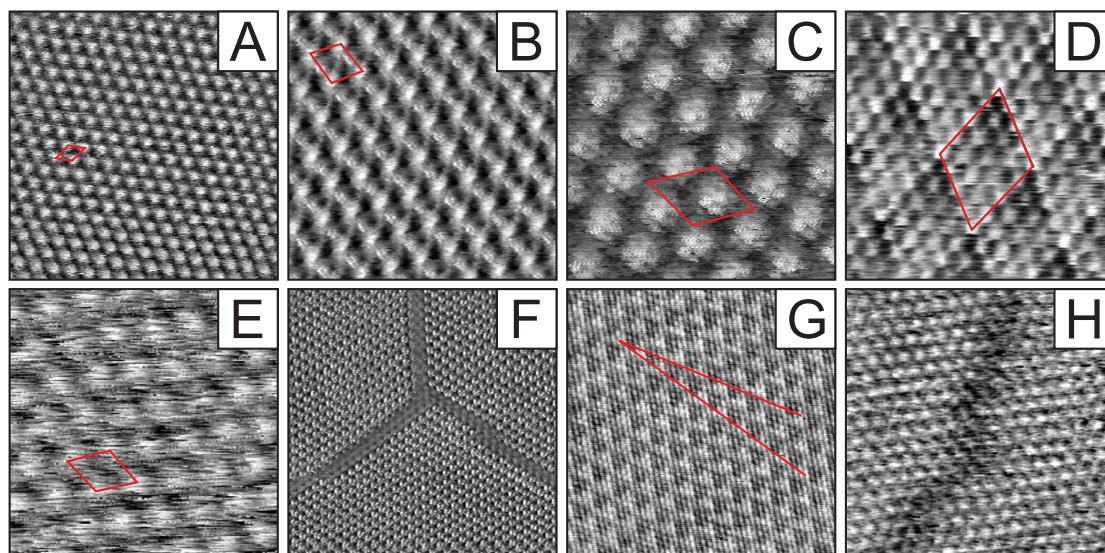


Fig. 4-2: A gallery of STM images of various adlayers. (A)–(E): high resolution images (4×4 nm) with a unit cell shown by the red rhombus; (A) Bare Au(111)-(1 $\times$ 1) surface III, (B) $(\sqrt{3} \times \sqrt{3})R30^\circ$ Cu-SO₄²⁻ UPD adlayer II_s; (C) (5 $\times$ 5) Cu-Cl⁻ UPD adlayer I [182]; (D) (5 $\times$ 5) Cu-Cl⁻ UPD adlayer II_{ch}; (E) (2 $\times$ 2) Cu-Cl⁻ UPD adlayer II_{cl}. (F) Domain boundaries in the phase II_s (B), 15 $\times$ 15 nm. (G) Moiré pattern of phase II_{ch}, 15 $\times$ 15 nm; the red lines show the misalignment between the translation vectors of the atomic features and the Moiré pattern. (H) Fuzzy domain boundary in phase II_{cl}, size 10 $\times$ 10 nm.

4.3.1 Phase III

No ordered adlayers were observed on the surface around PZC (potential range III) and one can image the bare Au(111)-(1 $\times$ 1) surface. Fig. 4-2A shows the latter as observed by STM. It exhibits the well known features with hexagonal symmetry (Fig. 3-3C). It was possible to resolve the atomic surface structure only when using a high tunneling conductance ($I_T/V > 20$ nS), *i.e.*, at a small tip-sample separation. The corrugation of the features does not exceed 0.03–0.04 nm. The value of the interatomic distance of $d_{Au} = 0.288$ nm was used to fine-adjust the calibration of the STM scanner.

4.3.2 Phase II_s

Images of the phase II_s (Fig. 4-2B) have a characteristic appearance of the bright features arranged in the hexagonal order with a corrugation of 0.05 to 0.07 nm. The nearest-neighbor distance between the features as estimated from the images, 0.49 ± 0.03 , nm is in agreement with the incommensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The existence of translational and rotational (forming angle 120° and 240°) domain boundaries (Fig. 4-2F) due to the mismatch of the occupied sublattices in different growth domains of the phase II_s supports this assignment.

The results of the STM experiments bear no information on the chemical nature of the adlayer and require complementary studies by other techniques. The presented phase was used as a reference for basically any structure-sensitive methods in electrochemical surface science and as a result it is studied in great details [72, 73, 252]. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of the Cu²⁺-SO₄²⁻ adlayers on Au(111) was resolved by electron diffraction spectroscopy in *ex situ* immersion-transfer configuration [202, 203]. First studies by *in situ* SPM were followed by a number of other investigations

[182, 216–219, 224, 225]. The symmetry and the dimensions of the unit cell suggested the geometry described above. An observation that the rows of bright features are rotated by 30° with respect to the direction of gold substrate atoms [224] supports this model.

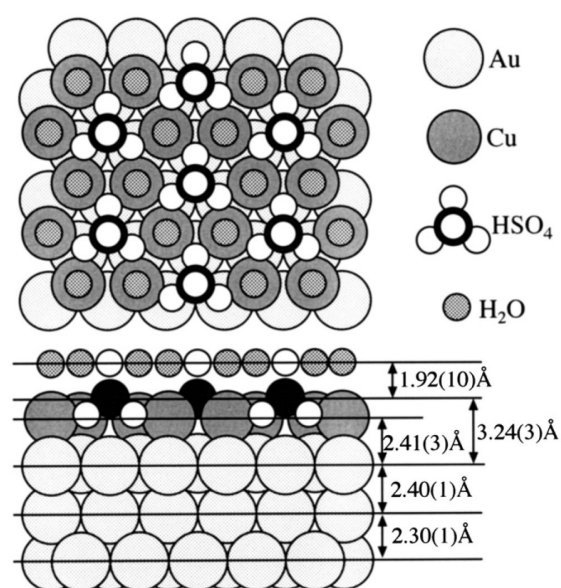


Fig. 4-3: The model of the structure IIs [212].

adsorbed in the center of every hexagon, which corresponds to a sulfate coverage of $1/3$. Only one S-O bond faces towards the electrolyte [191, 197, 204–206, 208]. The upper O atoms with coadsorbed hydroxonium ions form a hydrogen-bonded planar network, which constitute the outer boundary of the surface structure [210, 212]. Early X-ray based investigations suggested, that every of three oxygen atoms contacting a copper species just “touch” two atoms and sulfate in general is “above” the underlying layer [191, 197, 205]. However, later experiments [204, 206] demonstrated that the anion is located “inside” the hexagon. The centers of three O atoms of sulfate anion are close to the plane of the centers of adsorbed Cu atoms.

4.3.3 Phase IIch

An adlayer further referred to as IIch was observed in the presence of chloride in the potential region II. A typical intermediate size STM image of phase IIch, obtained at a sample potential of 0.110 V, is shown in Fig. 4-2G. One can see both atomic features and a Moiré pattern. These long order corrugations with hexagonal symmetry typically reflect a mismatch between substrate and adlayer. The observed Moiré pattern consists of interchanging triangles of darker and brighter contrast, forming a “chessboard”-like picture. The corrugation difference between brighter and darker spots is up to 0.05 nm. Often there is a bright spot seen in the middle of the dark part. The long-range superstructure was found to have a period of $d_M = 1.5 \pm 0.05$ nm.

Atomically resolved images of phase IIch were obtained only with a relatively high tunneling current [214]. Structures observed under these conditions exhibit Moiré pattern with a measured period 1.5 ± 0.05 nm as well. The distance between atomic features d was found to be 0.36 ± 0.01 nm (Fig. 4-2D) at $E = 0.11$ V and 0.39 ± 0.01 nm at $E = 0.21$ V. The contrast of atomic rows is not uniform with respect to the hexagonal

The observed features were originally attributed to the copper atoms [214, 216, 224]. Later results of the X-ray diffraction experiments [205] suggested the correct structural model of the phase IIs (Fig. 4-3). The latter corresponds to the of Cu and SO_4^{2-} coverages determined by the chronocoulometry [188, 189, 191].

According to the accepted model, copper atoms in the underlying layer occupy “hollow” positions and form a hexagonal network of honeycomb-like arranged Cu atoms with a coverage of $2/3$. The direct observation of the copper layer after manipulation with the sample potential and bias voltage was reported recently [219]. Sulfate anions are ad-

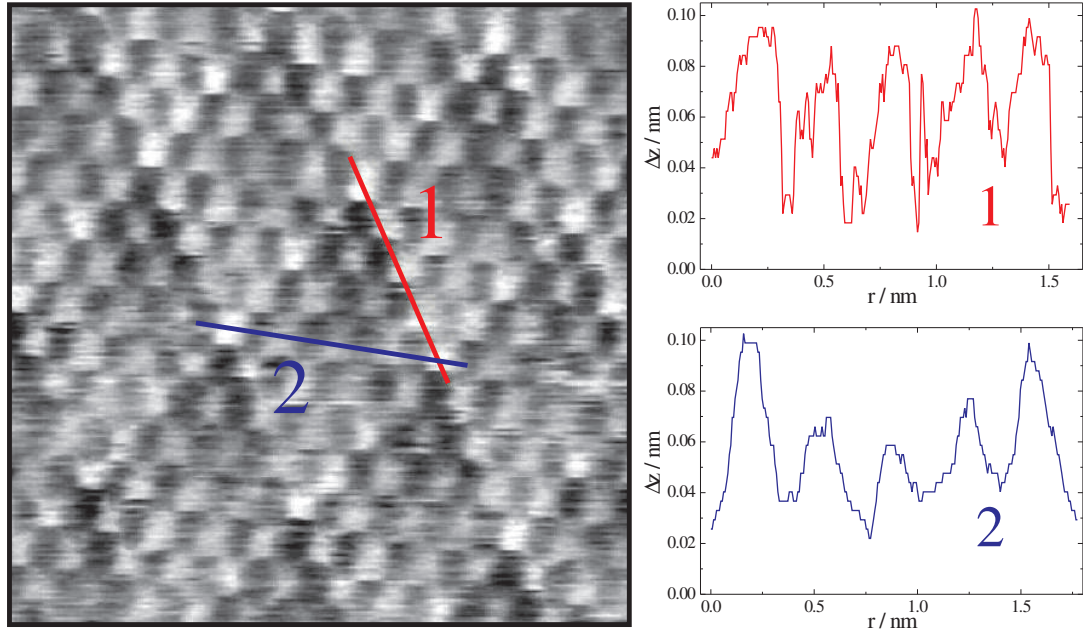


Fig. 4-4: High resolution image of the adlayer IIch (Fig. 4-2D) with two cross-sections.

symmetry. The image in Fig. 4-4 shows cross-sections of the adlayer in two hexagonal directions. On one of them (1, red) all atomic features have a similar corrugation height. For another direction (2, blue), the atoms “inside” the rhombus are lower. Similar to the other works, no domain boundaries were observed at any conditions.

From Fig. 4-2D one could make an apparent conclusion that the structure of the adlayer is (5×5) with the rhombic unit cell, drawn in red. This is a hexagonal lattice with $d = 0.36$ nm and $d_M = 4 \cdot 0.36 = 1.44$ nm [217]. The latter was derived from *ex situ* electron diffraction experiments [247] and assigned to the phase IIch in some SPM investigations [214, 225, 248, 249]. The assignment corresponds to the values of $4d = 1.44$ nm, $5d_{Au} = 1.44$ nm and $d_M = 1.5$ nm found in my experiments. However, the structure of the adlayer IIch seems to be more complicated, and a rather strong contradiction exists between results reported by various groups.

The information on surface coverage of Cu and Cl atoms in the adlayer equal to *ca.* 0.75 and *ca.* 0.58 may be considered as a certain one. It is also known from *in situ* X-ray absorption data [191, 246] that the adlayer is a Cu-Cl⁻ bilayer on the Au(111) surface, where the Cu layer contacts the substrate and Cl atoms are located in the second layer. The latter are actually observed in SPM experiments. The general pattern of the adlayer is in agreement with all SPM experiments reported. However, the quantitative properties of the adlayer vary between the existing publications.

The period of the Moiré structure $d_M = 1.5 \pm 0.05$ nm as determined in my experiments, corresponds to a value reported in [218]. In other works [182, 250], a value of 1.2 nm was determined. The authors of [217] reported “ d_M of between three to four times d ” and suggested that the (5×5) structure cannot be experimentally distinguished from the alternative one (1.29×1.29) . The latter has a quasi-hexagonal lattice, $d = 0.37$ nm and $d_M = 3 \dots 4d$.

The distance between Cl atoms at $E = 0.11$ V, $d = 0.36$ nm, is in agreement with all of the above mentioned SPM works. An increase of d with potential was mentioned only in [218]. In papers [225, 250], in which experiments were carried out in differ-

ent Cl^- concentrations and in the presence of perchloride, it was stressed, that there is no change of the interatomic distance in the whole potential range II. The same result was obtained in [225], although the experimental conditions of [218] were intentionally reproduced. The spacing difference is close to the error range, typical for distances determined from SPM images and, most probably, this question requires complementary studies by more geometry-sensitive methods.

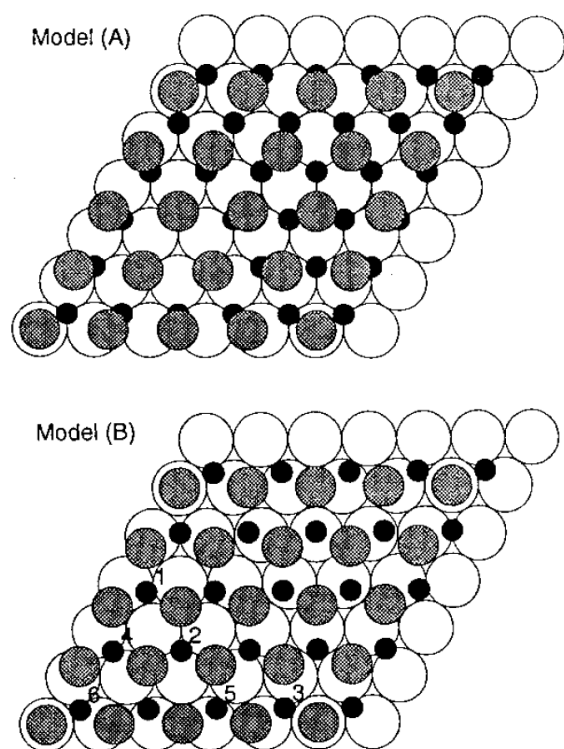


Fig. 4-5: The proposed (5×5) models of the Ilich structure [246]. White circle - Au, black circle - Cu and gray circle - Cl.

corresponded to the (5×5) and (4×4) arrangement of the upper Cl^- layer respectively. The modeling of the experimental spectra demonstrated, however, that no unique model could be ascribed to the adlayer. The results were explained by the “large degree of the static disorder” in the adlayer.

Rather similar conclusions resulted from STM experiments in [250]. The ratio of the periods found for the Moiré structure d_M to the spacing of atoms in the Au(111) lattice was estimated as 4.4. The slight dislocations and orientational changes of the long-range modulations were observed on a distance scale of a few tenth of nm. The observations were interpreted as an existence of “a number of different local lattice units which are sufficiently close in their free energy that they all contribute to the resulting adlayer structure”.

Indeed, the whole set of observations and conclusions described above may be rationalized by the assumption of coexisting local lattices. The distribution of coexisting structures can be readily affected by the preparation conditions such as nature and concentration of reactants, electrode potential, and generally by the “history” of the particular adlayer. The possible lattices may be those considered in [246], as well as others. However, the results of SPM experiments agree in the conclusion that the structure of

A mismatch in the directions of “short-range” and “long-range” corrugations was found in my experiments (Fig. 4-2G), the determined angle is $13 \pm 2^\circ$. The adlayer rotation of the same angle was described only in our previous work [182].

The calculated coverage of the (5×5) Cl^- adlayer, $16/25 = 0.64$, is higher than 0.58, which was determined by chronocoulometry. The structure of the underlying Cu layer is even more complex. The Cu coverage of 0.75 obtained from electrochemical experiments [190] contradicts the conclusion of [191] of Cu and Cl atoms being in registry. The latter was suggested in [191] based on the fitting of two models. The one where Cu atoms are in registry with the Cl^- layer was found to describe better the experimental data than the model of Cu atoms being in registry with the Au(111) substrate (Fig. 4-5). In the later work of the same group [246] five models of the Cu- Cl^- adlayer were considered. Two and three of them

the phase IIch may be well approximated as (5×5) , while a local unit cell may vary. By limiting the set of proposed lattices to those with (5×5) structures (Fig. 4–5), it is possible to account for the major characteristics of the IIch adlayer. Indeed, the models A and B corresponds to Cu coverages of 1 and 0.64 respectively (the complete set of parameters is given in [246], Table 2). A certain ratio of coexisting structures A and B may be responsible for the Cu coverage of 0.75. It is rather difficult to evaluate adlayer topography without special simulations, but model A seems to corresponds better to the observed contrast difference between two halves of the unit cell (Fig. 4–4). The experimental Cl^- coverage is slightly lower than predicted by both models A and B, which may be explained by coexisting patches of a (4×4) structure. Here I would like to note that the high resolution SPM measurements are carried out in the middle of terraces. Therefore, one may speculate that such patches with higher spacing between Cl atoms may exist in the vicinity of substrate defects, in particular nearby steps. The local lattices with a slight rotation of the adlayer with respect to the substrate may exist as well. At the moment I can only conclude that further experiments and simulation are needed to resolve the details of the phase IIch structure.

4.3.4 Phase IIcl

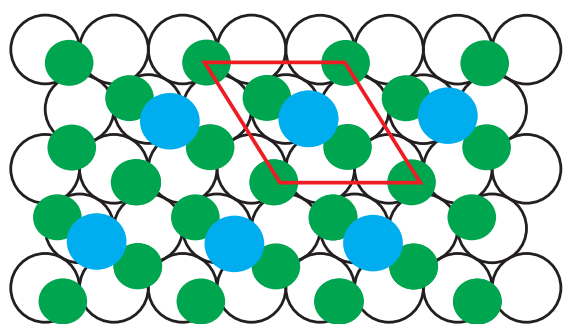


Fig. 4–6: Model of the IIcl structure [250].
White circle is Au, green circle is Cu,
blue circle is Cl, the unit cell is shown
in red.

At Cl^- concentrations of equal or lower than 10^{-5} M and at potentials below 0.11 V, the structure IIcl was observed (Fig. 4–2E). Unlike phase IIch, it displays clear domain boundaries (Fig. 4–2H) with angles of multiples of 60° and no Moiré pattern. No clear high resolution images of this phase were obtained. However, the estimated hexagonal geometry and period of 0.6 ± 0.02 nm, as well as other properties (see below) correspond well to a (2×2) mixed Cu– Cl^- structure (Fig. 4–6), observed in perchloric acid [250] at low potentials

and low chloride concentration.

The presented structure consists of a Cu layer residing on the Au(111) substrate and Cl^- anions coadsorbed on top of it. The Cu atoms are slightly displaced from the three-fold position of the Au(111) substrate. Three Cu atoms are incorporated in a unit cell with an area corresponding to four Au atoms, and the Cu coverage is 0.75. The structure is stabilized by a Cl^- anion coadsorbed in the center of the unit cell, as it is shown in Fig. 4–6. The Cl atoms with the coverage 0.25 are the features imaged by STM.

4.3.5 Phases Is and Ic

The phase existing in potential range I was not studied in these work. I only will described it here for completeness. The latter is a commensurate (1×1) monolayer of Cu atoms on Au(111), similar to the one formed under UHV conditions [203, 214, 215]. Anions are coadsorbed on top it.

The formation of the (1×1) adlayer Is in the presence of sulfate is reflected as the peak P'_1 in the CV (Fig. 4–1, curve 1), and was reported in [203, 207, 209, 219, 222–225]. The sulfate anions are believed to be disordered after the partial desorption. However, recent results [219] provided evidence for an ordered $p(2 \times 2)$ structure of sulfate on top of the Cu monolayer.

The structure Ic imaged in the presence of high concentrations (10^{-3} M) of chloride [182, 218] is shown in Fig. 4–2C. Its appearance is similar to that of the IIch structure, except of the less pronounced contrast. The latter is believed to be due to the lack of interfacial Cl atoms after their desorption [247] at potential below the peak P'_1 in the CV (Fig. 4–1, curve 3).

4.4 Phase transitions

The kinetics of phase formation and transitions in Cu-SO_4^{2-} adlayers on Au(111) were studied in detail by chronocoulometry [192–196] and STM [219, 222] and seems to be well understood now. According to a comprehensive description found in [222], the formation of IIs occurs via fast heterogeneous nucleation and lateral growth of domains. The transition into the phase Is occurs via instantaneous nucleation at the domain walls followed by the 1D growth of a new phase. The amount and distribution of defects is crucial for the phase transition mechanism [194].

Here I report detailed studies of phase transitions in the Cu UPD system in the presence of both sulfate and chloride. All investigated processes are classified as capacitive (non-faradaic) first order 2D phase transitions [254]. A chloride concentration of 10^{-5} M was found to be optimal for exploring these phase transitions by *in situ* STM. The aim of these studies is not only to evaluate the kinetics, but also to observe morphological changes during the phase transitions. The comparison of the STM patterns of the two phases with known geometries allows to elucidate the role of electronic contribution in the tunneling current.

Most of the transformations, studied in a dynamic mode, lead to changes of the Cu coverage as well as that of sulfate and chloride. However, I will not discuss the role of copper. The bulk concentration of copper is high enough and allows to neglect kinetic limitations due to diffusion of copper species to the surface. Their location between the Au(111) substrate and the anion layer does not allow to monitor directly the Cu atoms. However, one should bear in mind that the discussed phases are formed on a negatively charged gold surface due to the co-adsorption of the corresponding anions with Cu^{2+} cations.

4.4.1 Transition between phases IIch and IIcl

A transition between IIcl and IIch phases was observed after a potential step from 0.03 to 0.15 V (Fig. 4–7A). The phase IIcl, existing at the initial potential, is imaged as bright spots on the upper part of the image. After the potential step (red line on the image) patches of a new phase appear. It has slightly darker and more uniform contrast than phase IIcl, and a characteristic long range corrugation (Moiré pattern). The new phase is defined as a phase IIch. The patches of phase IIch are surrounded by “holes” with a darker contrast. The holes are up to 0.1 – 0.12 nm deep, and one can see the characteristic pattern of a chloride-free phase IIs inside the holes.

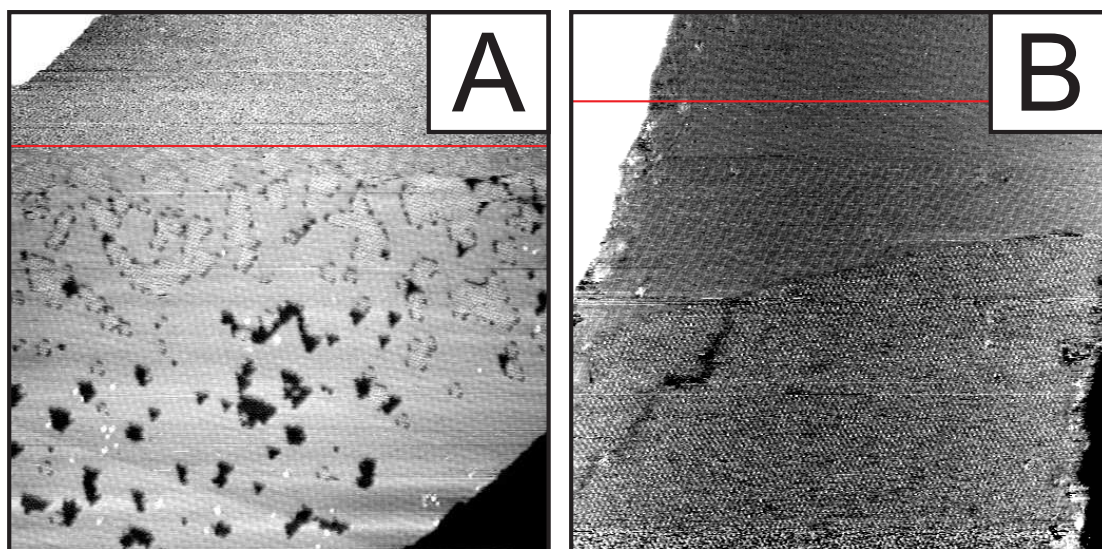


Fig. 4-7: Transitions between phases IIcl and IIch following a single potential step: (A) IIcl to IIch, step from 0.03 to 0.16 V, size 80×80 nm, $I_T = 0.33$ nA, vertical range 0.13 nm; (B) IIch to IIcl, step from 0.25 to 0.08 V, size 60×60 nm, vertical range 0.1 nm, $I_T = 0.27$ nA. The position at which the potential step was applied is indicated by the red line.

With the further evolution of the system, patches of phase IIch grow wider and cover the entire area observed. A simultaneous expansion of the holes occurs. Holes are healing out in a few minutes after disappearance of patches of phase IIcl. Only afterwards the whole surface is completely covered by phase IIch. The boundaries of growing islands and holes follow the hexagonal symmetry of the underlying substrate throughout the entire transformation.

A similar phase transition in chloride containing adlayer was also observed in the case of small chloride additives in perchloric acid [250]. Few comparative experiments were also carried out in sulfuric acid. According to those and our own observations, one concludes that the transformation proceeds in two steps. At first a fast potential-driven transformation of phase IIcl to phase IIch occurs. Only part of the surface will be covered by the new phase, leaving holes with the phase IIs formed inside. The second step is the slow healing out of holes. The latter are formed due to the fact that the phase IIch is more compact than the original phase IIcl. The lacking material is presumably chloride, as the solution concentration of chloride ions is much lower than that of the other components. Thus, the healing of the “holes” is kinetically limited by the chloride diffusion to the surface. The same conclusion was reported in [250].

It is necessary to discuss the possibility of a tip effect on the transitions observed [250]. The electrostatic field, induced by the tip, may affect the local potential at the interface. However, the bias voltage $V = 0.1$ V locally applied to the interface over a tip-sample distance of a few nanometers results in a electric field strength $X \approx 10^{-10}$ V·m⁻¹, which is one order of magnitude lower than typical electric fields existing in the EDL. A negligible electrostatic field effect was also concluded in [250]: the same potentials of transition between IIch and IIcl were derived from both CV measurements and STM observations. We also reject the possibility of a mechanical interaction between the tip and the adlayer. By studying the set-point dependence of the STM images, it was shown that $I_T > 50$ nA (small z) causes a distortion of the phase IIs

[182, 220, 221]. The I_T used here is at least two orders of magnitude smaller, and images were not perturbed. Another effect is the geometric shielding of the surface under the STM tip, which should hinder the diffusion of chloride. One may expect that the shielding may modify the diffusion rate and not affect the mechanism of the process. CV measurements with an enhanced mass transport were carried out to address the issue of the diffusion control in IIcl to IIch transition [244]. In contrary to the conclusion drawn in this work and in [250], no mass transport effect was found, and the authors of [244] suggested that the slow step of the adlayer transition is an ion rearrangement. The disagreement may be explained by the aforementioned hindering of the diffusion due to the surface shielding by tip in the STM configuration.

The reverse transition of IIch to IIcl was observed during the potential step from 0.25 to 0.08 V (Fig. 4–7B). Similar to [250], no hole formation was found in this case. During this phase transition a “smooth” phase IIch with a Moiré pattern is replaced by phase IIcl, consisting of many bright spots. Simultaneously, a domain boundary appears. The transition was typically observed to start from the upper step, like it is shown in this image. This process is accompanied by the desorption of excess chloride without any possible hindering of diffusion by the tip.

4.4.2 Replacement of sulfate by chloride

According to the CVs as well as based on surface excess data, the onset of deposition of both sulfate and chloride in the presence of copper is at *ca.* 0.26 V, and a maximum of surface excess occurs at $E \approx 0.1$ and $E \approx 0.15$ V respectively. The replacement of the sulfate phase IIs by the chloride phase IIch was observed by STM, but not studied in detail. It was shown that the replacement is very slow at the onset of copper deposition, but greatly enhanced at lower potentials.

I studied the replacement of sulfate on top of the Cu layer by chloride as well as the reverse process. A Cl containing phase is formed at substrate and adlayer defects (steps, domain boundaries), and even at potentials very close to the onset of the Cu UPD formation. The new phase was recognized by a brighter contrast of characteristic apparent height. After a potential step from 0.23 to 0.11 V (Fig. 4–8A), a lateral growth of existing patches of the Cl-containing phase was observed, as well as the formation and the growth of new nucleation centers. It is clearly seen that the growing phase reflects the symmetry of the substrate, forming triangular islands. A growing “rough” phase forming characteristic domains could be observed (Fig. 4–8 B–E), but after some time it was replaced (Fig. 4–8 F,G) by a “smooth” structure with a visible Moiré pattern (Fig. 4–8 H,I). Only small patches remained “rough” until they got incorporated into the bigger islands (Fig. 4–8 G–I). Finally, the last chloride-free areas transformed and a uniform structure with a visible Moiré pattern covered the entire observed area. No changes of the interfacial structure occurred after this.

The “rough” and “smooth” phases, as seen during the transition, possess the typical STM patterns of phases IIcl and IIch. This indicates that a replacement proceeds via the intermediate formation of the phase IIcl, which slowly transforms into phase IIch. Similar to the observations in the transition of IIcl to IIch, the latter is supposed to be a diffusion controlled process. Experiments with sulfate replacement by chloride performed at different final potentials showed that only at the E_{final} close to 0.11 V phases IIs, IIch and IIcl coexist on the surface (Fig. 4–9A). At lower potentials ($E_{final} \leq 0.08$ V) no IIcl to IIch phase transformation was observed, and phase IIcl remains stable

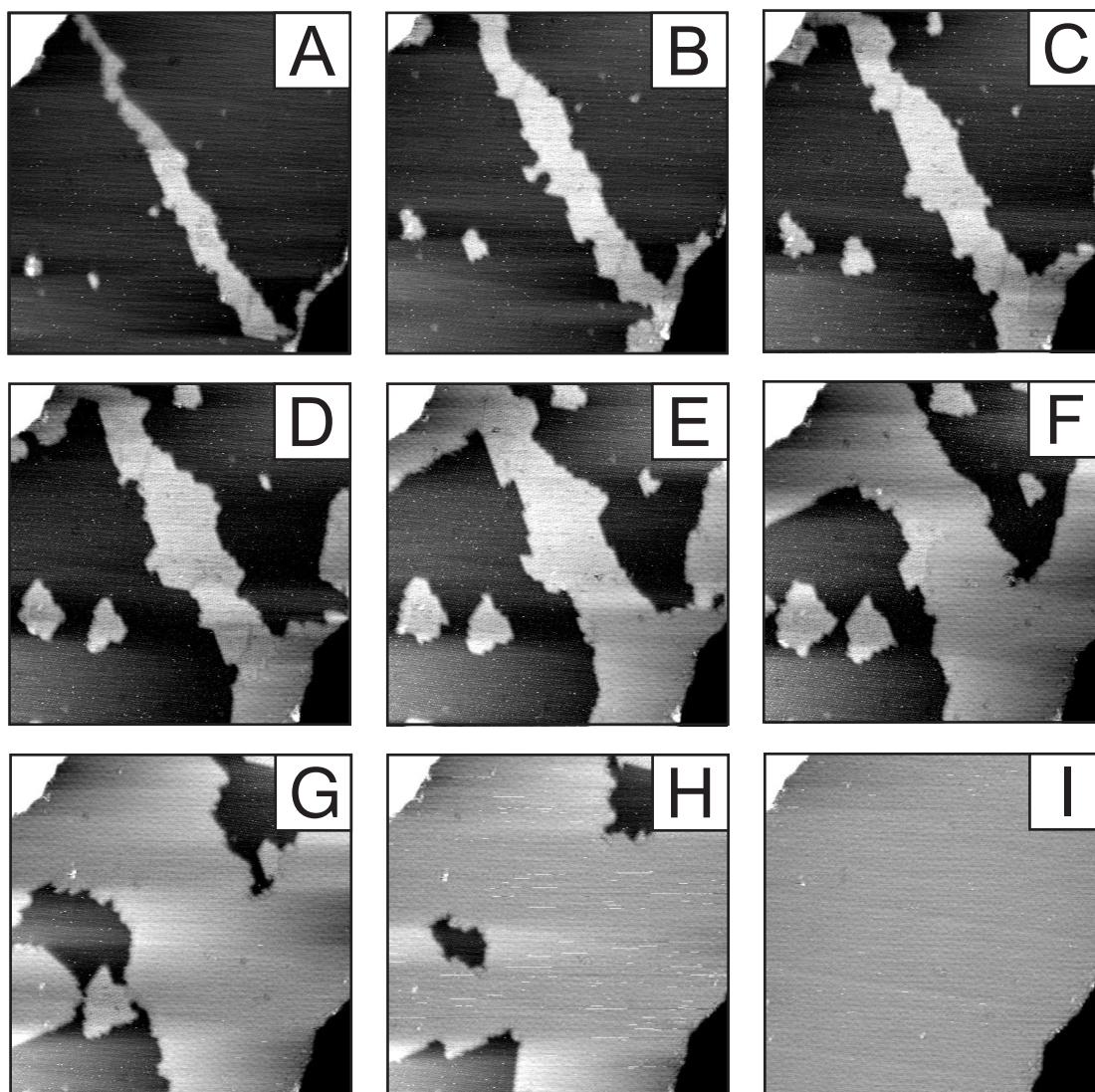


Fig. 4–8: A sequence of images showing the substitution of sulfate by chloride after a potential step from 0.23 to 0.11 V, size 65×65 nm, vertical range 0.15 nm, time / min: (A) 0; (B) 2; (C) 4; (D) 6; (E) 8; (F) 10; (G) 12; (H) 14; (I) 20.

(Fig. 4–9B). At $E_{final} = 0.135$ V a quick (within 2 minutes) phase IIcl to phase IIch transformation was observed. At $E_{final} \geq 0.14$ V no intermediate phase IIcl was seen. At even higher potentials, $E_{final} \geq 0.16$, a stable coexistence of phase IIs and phase IIch could be observed (Fig. 4–9C).

The kinetics of the phase transitions under discussion could be described in terms of the time dependent coverage. The latter was calculated from the sequences of images, such as shown on Fig. 4–8 as well as for similar sequences with the final potential of 0.08 and 0.16 V. A relative coverage of the chloride phase θ was estimated from each image as a ratio of the area occupied by this phase on terrace and the total area of the terrace. The time corresponding to the tip positioned in the middle of the imaged area was used as a temporal coordinate.

The results are shown in Fig. 4–10. Despite of the complicated transition mechanism, the shape of all kinetic curves was found to be close to the exponential one (Fig. 4–10). The corresponding time constants are indicated in the plot. As it was discussed above, the rate of the replacement process strongly increases with a decrease of the fi-

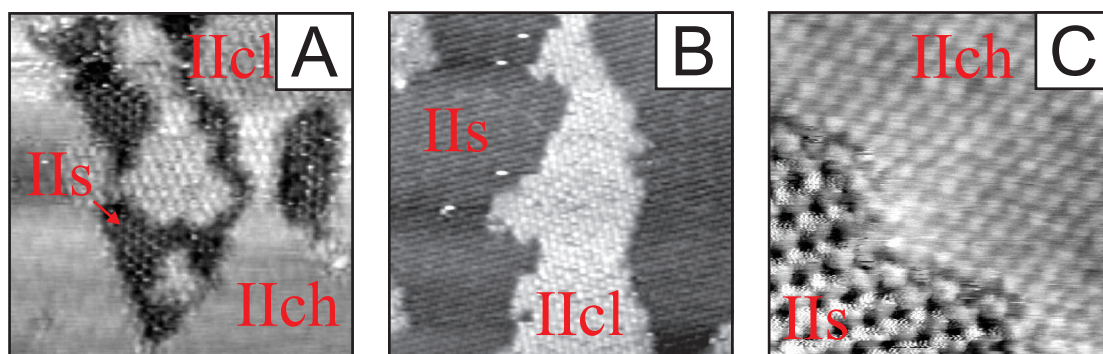


Fig. 4-9: Coexisting phases at different potentials: (A) 0.13 V, 15×15 nm, vertical range 0.2 nm; (IIs, IIch, IIcl) (B) 0.03 V, 20×20 nm; vertical range 0.2 nm (IIs, IIcl) (C) 0.26 V, 5×5 nm, vertical range 0.1 nm (IIs, IIch).

nal potential. The time required to reach (quasi)stationary conditions varies up to an order of magnitude. The maximum coverage is also potential dependent: an incomplete adlayer formation was observed at $E_{final} \geq 0.16$ V.

The exponential $\theta - t$ dependence may reflect two different mechanisms [254, 255]. The first of them corresponds to a kinetics controlled by an adsorption step. In the given system this corresponds to the slow anion replacement. The second mechanism is an instantaneous nucleation and a growth controlled by surface diffusion. The possible limiting step of Cl^- diffusion to the surface does not correspond to the exponential kinetic curves. Unlike in case of a fast transition between two Cu- Cl^- phases (Sec.

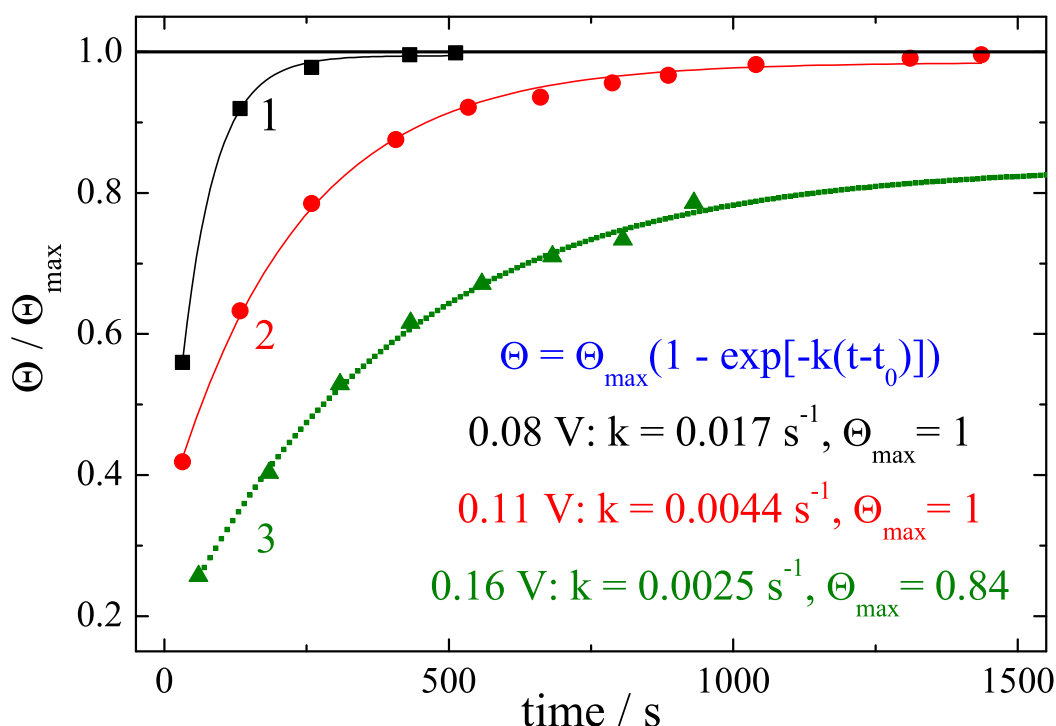


Fig. 4-10: Kinetics of the transition between phases IIs and IIc(h/l). Points show the experimental coverage data, and the solid lines are their exponential fits. The obtained parameters are given in the plot. The corresponding E_{final} / V are (1) 0.08, (2) 0.11, (3) 0.16.

4.4.1), the transition discussed here occurs on a much longer time scale. Thus, both the ion replacement and surface diffusion may be slower than the diffusion of chloride from solution. An additional argument is that the initially formed phase IIcl corresponds to a rather low Cl coverage (0.25). The transition of IIcl to IIch is a secondary process, which is not reflected in the presented curves.

Taking into account the experimental conditions and the observed details of the transition process, the slow adsorption mechanism may be selected as a preferable one. It is in agreement with the hysteresis of the CV peaks P_2/P'_2 (Fig. 4-1) corresponding to a slow formation of the Cu-Cl^- adlayer. The electrode potential corresponding to the equilibrium between Cu-SO_4^{2-} and Cu-Cl^- adlayers may be estimated as being located between the latter peaks and potentials of stable coexistence of phases IIs and IIch. Therefore, at least for the curves 1 and 2 of Fig. 4-10, the overpotential is very high, which facilitates the progressive formation of nuclei. Indeed, in contrary to the second mechanism, the formation of nuclei was directly observed after the potential step. And finally, it is rather difficult to assume a diffusion of the adsorbed species on the surface covered by the ordered adlayer.

The perfect structure of a Cu-SO_4^{2-} adlayer is disturbed by substrate defects, domain boundaries as well as boundaries between two phases. The bordering sulfate anions can be easier replaced by Cl^- than those inside the 2D network. This may explain an observed preferential growth at defects and a propagation of existing islands of the new phase. The evaluated rate thus corresponds to the substitution of sulfate anions by Cl^- ions located next to it.

4.4.3 Chloride replacement by sulfate

Chloride substitution by sulfate in the studied system was only possible for a freshly formed Cl-containing adlayer. To avoid an effect of chloride adlayer shrinking (*cf.* Sec. 4.4.1) interfering with a substitution, phase IIch was used as a starting substrate. The following sequence of images (Fig. 4-11) demonstrates the observed phase transition. The following sequence was anticipated:

- Quick formation of the Cl adlayer by selecting a low potential (Fig. 4-11A). In this potential range sulfate anions are substituted by Cl leading to phase IIcl as described above. The surface becomes completely covered by phase IIcl within 2-3 minutes.
- Formation of phase IIch by a potential step (Fig. 4-11B). Formation of “holes”, as discussed above, was observed. The holes were healed out in a few minutes.
- After formation of the complete adlayer of phase IIch and selection of a proper position, the potential was stepped to the onset of the Cu UPD stability range (Fig. 4-11C).

The formation of “defects” on the surface started immediately after the potential step (Fig. 4-11C) at steps and adlayer defects. The latter were seen as two lines within the IIch adlayer (Fig. 4-11C), which are most probably original domain boundaries of the IIs phase. Small growing patches of the sulfate phase IIs produce two clearly distinguishable lines along existing defects (Fig. 4-11D). They extend further, simultaneously keeping their triangular form (Fig. 4-11 G-H), and then merge (Fig. 4-11I).

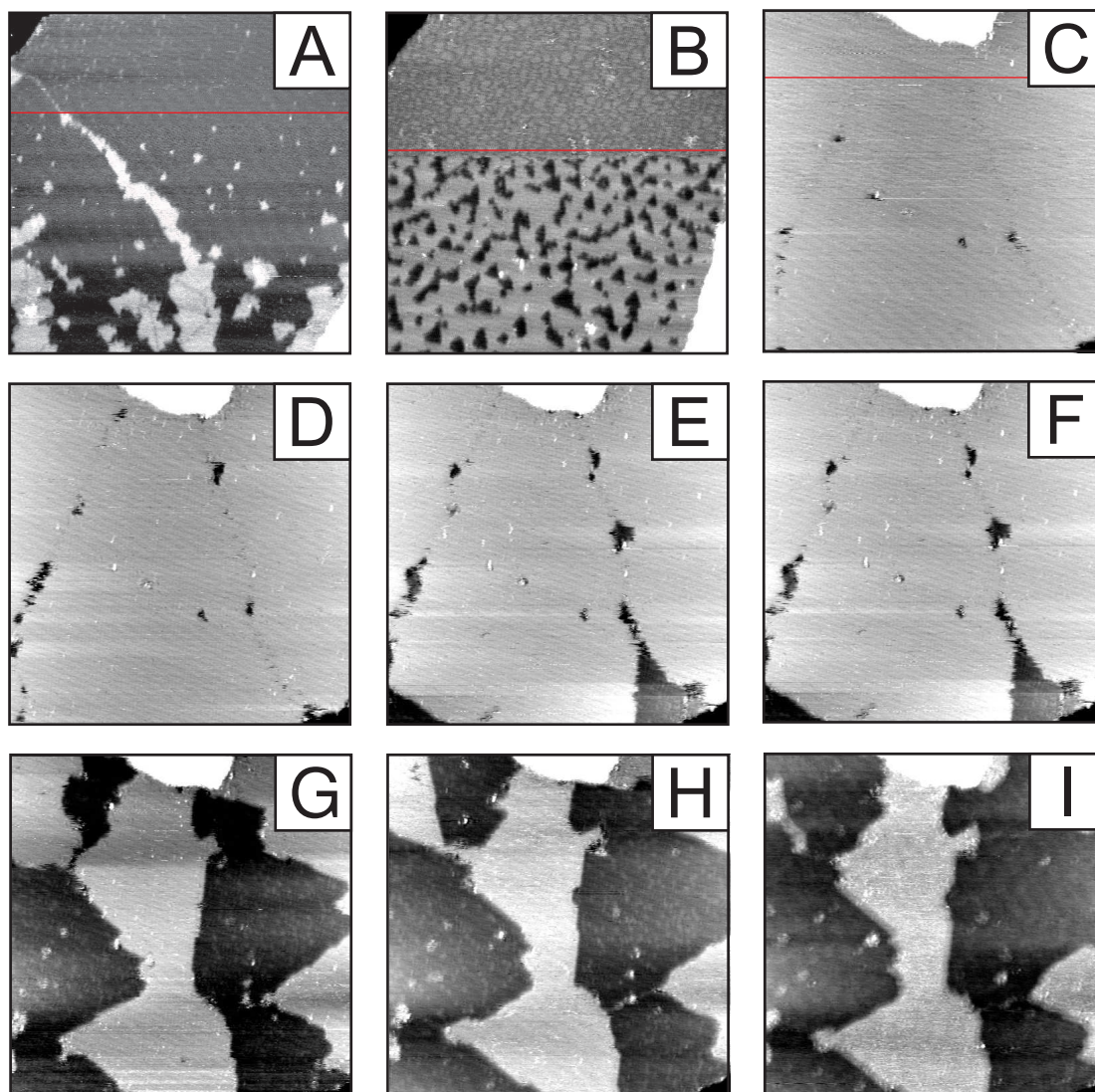


Fig. 4-11: A sequence of images showing the substitution of chloride anions by sulfate in a multiple potential step experiment. Size of the images 100×100 nm; vertical corrugation range is 0.15 nm. The positions of the STM tip at the time of the potential steps are marked in the STM images by red lines. The transitions are recorded in the following sequence: (A) Potential step from 0.23 to 0.03 V, which triggers a fast growth of phase IIcl; (B) Potential step from 0.03 to 0.16 V and the formation of phase IIch (*cf.* Fig. 4-7A); (C) Potential step from 0.16 to 0.24 V after the formation of phase IIch (Sec. 4.4.1). Panels (D) to (I) illustrate the evolution of phase IIch at 0.24 V as a function of time (minutes): (D) 2, (E) 4, (F) 6, (G) 8, (H) 10, (I) 20.

The replacement was accomplished after a period of a “quick” reaction (Fig. 4-11C-H). After 10 minutes no visible changes of the interfacial structure were observed (Fig. 4-11I). This demonstrates again that, under the given conditions, chloride is much stronger adsorbed on the gold than sulfate. In general, no complete substitution of chloride by sulfate was observed at chloride concentrations of 10^{-5} M, although there were some evidences of it at lower chloride concentrations.

The resulting kinetic curve, constructed as described above, is plotted on Fig. 4-12. There is an incubation period for the first 250 s, where the process is rather slow. After this time a “quick” transition starts up to the time of app. 700 s. Then the coverage

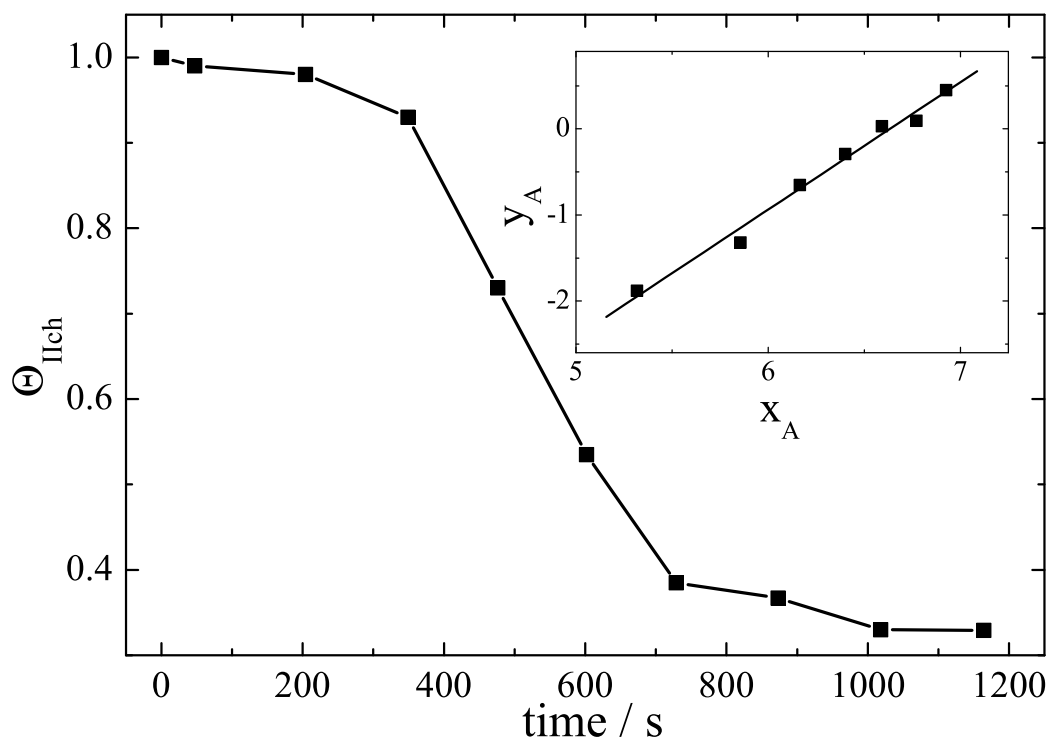


Fig. 4-12: Time dependence of the coverage of the IIch phase upon transition to IIs. Inset: data replotted according to the Avrami equation (Eqn. 4.1).

changes very slowly and, finally, after 1000 s no visible changes are seen anymore.

The morphology of the phase transition thus corresponds to a slow heterogeneous nucleation and lateral propagation of the formed patches. The Avrami equation [254, 255] was used to analyze the obtained time dependence of the coverage according to the models of nucleation and growth. The data in Fig. 4-12 were replotted in coordinates

$$y_A = \ln \ln \left(\frac{1}{1 - \theta(\text{SO}_4)/\theta_{\max}(\text{SO}_4)} \right) \quad \text{vs.} \quad x_A = \ln t \quad (4.1)$$

The result is shown in the inset of Fig. 4-12. The dependence is rather linear with a slope of *ca.* 1.5. The latter corresponds to an exponential increase of the number of nuclei with time and growth controlled by surface diffusion of the deposited species. A slow non-linear increase of the number of nuclei seems to be in agreement with the observations. However, the diffusion of point Cu-SO_4^{2-} “defect” to the bigger patches of the new phase seems to be very doubtful, as it is discussed above. The in-place substitution of Cl^- by SO_4^{2-} , however, is expected to result in a slope value close to 2. The disagreement of the simple model with the system properties may be due to the “macroscopic” and oversimplified character of the former.

4.5 Current-distance STS of the ionic adlayers

Dynamic STM experiments allow the simultaneous observation of coexisting phases (Fig. 4-9). The results indicate much darker STM contrast of the sulfate containing phase with respect to that of the chloride-containing ones. However, from the purely geometrical estimations one could expect a small height difference between the two

phases. This issue was addressed in a current-distance STS experiments carried out to probe the effective tunneling barrier on top of the interface. The measuring procedure is described in Sec. 3.8.1.

A current-distance response of the phases II_s and II_{ch} was analyzed with reference to that of the bare Au(111)-(1 × 1) surface (III). The results are summarized in Fig. 4–13. The tip-sample separation was normalized so that a maximum current $I_{max} = 100$ nA corresponds to zero. The current traces (Fig. 4–13A) appear significantly different. The response of the sulfate-containing phase (blue) features a step between the current values of 10–30 nA and a sharp increase of the current after 50 nA, while that of the chloride phase (green) exhibits only feature of the latter type. Comparative studies of tunneling response of the bare Au(111) surface (orange) demonstrated an exponential decrease of current. These results are in agreement with the previous studies [182].

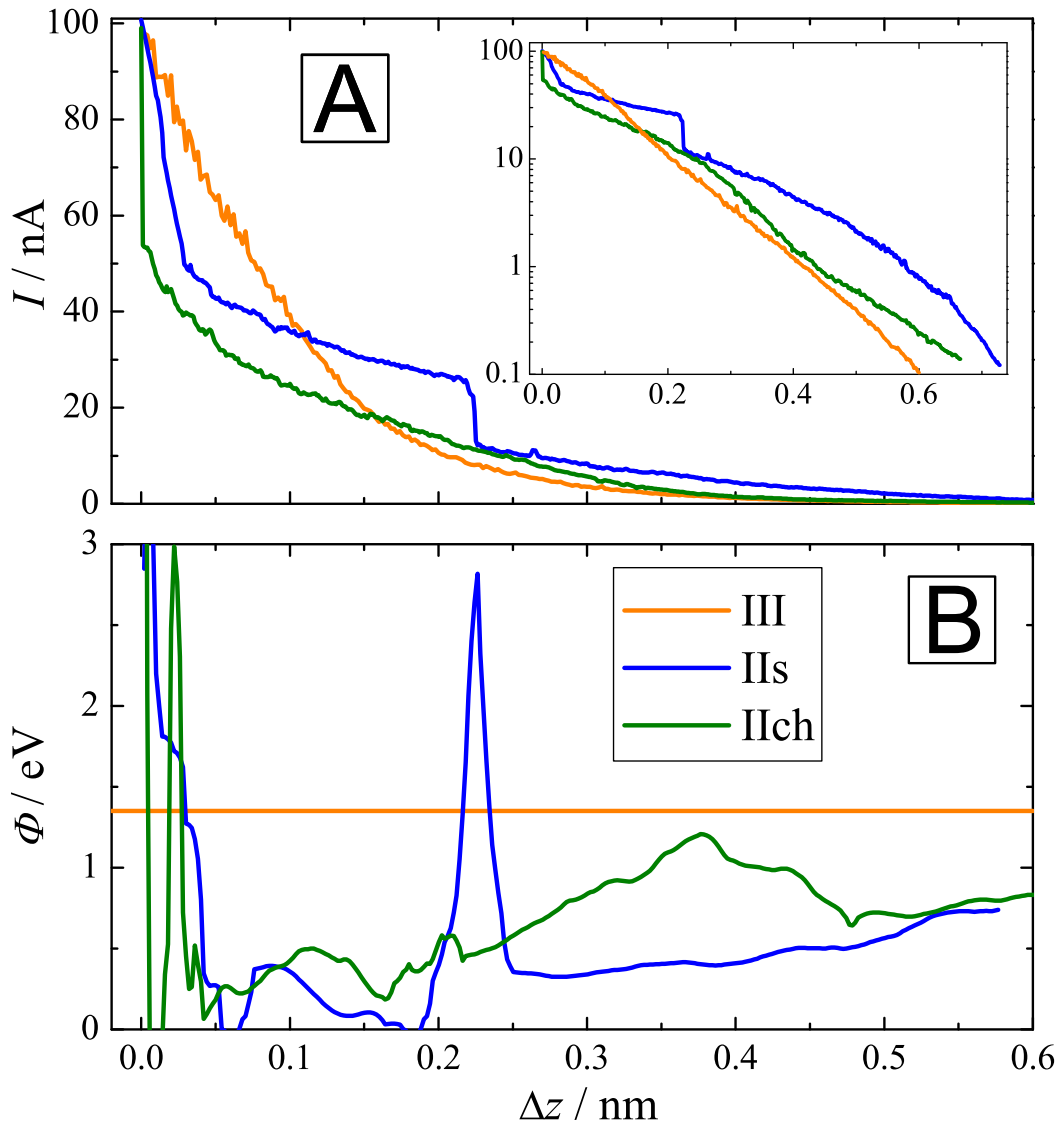


Fig. 4–13: Current-distance spectroscopy of adlayers III (orange), II_s (blue) and II_{ch} (green) (A) average of 10 scans, bias voltage $V = -0.1$ V. The inset represents the same data in a logarithmic scale; (B) tunneling barrier profile extracted from data on (A).

From the exponential current-distance response of the bare Au(111) surface a constant tunneling barrier of $\Phi \approx 1.35$ eV is estimated. For the two other, more structured current-distance scans, the fitting procedure presented in [180–182] was used to evaluate the profile of tunneling barrier Φ .

The tunneling barrier profiles (Fig. 4–13B, same colors) demonstrate pronounced differences for the two adlayers. Going away from the surface, the sulfate phase first exhibits a sharp decrease of Φ at distances 0–0.05 nm in a selected scale. Further away from the surface there is a region of small $\Phi \approx 0.1$ eV, with an occasional small peak up to 0.5 eV, extending up to 0.18 nm. A high peak reaching up to 2.8 eV is observed between 0.18 and 0.25 nm. Then there is a long tail of the tunneling barrier slowly increasing from 0.5 to 0.8 eV.

The Φ profile obtained for the chloride phase shows less features. There is a sharp decrease of Φ from $\Delta z = 0$ up to $\Delta z \approx 0.05$ nm, characterized by distinct fluctuations. It is followed by a slow steady increase of Φ up to a shallow peak at $\Delta z \approx 0.38$. Similar observations were reported in [182]. At higher distances Φ reaches *ca.* 0.8 eV.

Taking into account the experimental scatter, I will concentrate on the main features of the Φ profile, which are the sharp decrease around $\Delta z = 0$ nm. For the sulfate phase, an additional peak exists at $\Delta z = 0.25$ nm. The observed features of the tunneling barrier profile were correlated with the structure of the adlayer [182]. The peak in the tunneling barrier profile of the phase IIs was attributed to the penetration of the tip into the plane of the O-atoms on top of the adsorbed sulfate ions (Fig. 4–3). I would like to note that similar results were also obtained for the adlayer of sulfate anions only [182].

Due to the nature of the STM imaging procedure, which maps electronic properties rather than topographic ones, the former affects the images obtained. With typical set-point currents of 0.1...0.5 nA at bias values $V = 0.1 \dots 0.2$ V the tip is located at the tail of the $I - \Delta z$ dependence (Fig. 4–13A). The electronic orbital of the IICH phase is more compact than that of IIs, and the STM tip is located closer to the surface in case of the former adlayer under otherwise similar conditions. The data presented (see inset on Fig. 4–13A) suggest a difference of 0.09...0.13 nm. This seems to be opposite to the STM contrast observations.

However, the presented data are shown in a relative scale, where the zero position corresponds to the maximum of the measured current. The question of an absolute tip-sample position in a STM junction is an important one and not completely solved so far. The straightforward way would be to reach the point of tip-sample contact, *i.e.*, to form QPC (Cha. 5). Unfortunately, this requires certain modification of our equipment, which became available only recently [177]. After the strong mechanical contact between STM tip and a sample (“tip crash”), the adlayer would be disturbed due. Another approach is based on the assumption of a constant tunneling barrier up to the physical boundary of the substrate. Extrapolation of the exponential curves, such as shown on Fig. 4–13A for the bare Au(111)-(1 × 1) surface, up to the point of contact ($G = G_0$, Sec. 2.6) leads to an estimation. Employing this strategy, I found that the gold surface is *ca.* 0.6 – 0.7 nm away from the zero of the relative scale of Fig. 4–13. This estimation is in a reasonable agreement with the interfacial structure, but not accurate enough to evaluate the contrast difference of two adlayers. I note that this estimation cannot be applied for the strongly structured barrier profile.

Based on the correlations with the adlayer structure, the sharp increase of Φ at $\Delta z = 0$ is interpreted for both adlayers. The upper overlayer of structure IIs consists of loosely distributed (≈ 0.49 nm separation), well spaced “small” (with a small radius)

oxygen atoms. This is also reflected in the high STM corrugation of the features in phase IIs. H_3O^+ ions forming a hydrogen-bonded network with negatively charged upper O-atoms of the sulfate are not seen in the STM images. In the spatially averaged STS scans they are accounted for as one plane. The peak of the tunneling barrier for the adlayer IIs was attributed to the tip penetration into the plane formed by the upper O-atoms and H_3O^+ ions. Therefore, the second rise of Φ could be due to some inner structure elements of the adlayer, *e.g.*, the inner O or Cu atoms. Due to their proximity it is possible to assume them to be located in one plain. The distance between the initial rise and the peak in the barrier profile, $\Delta z \approx 0.22$, corresponds to the model of the phase IIs (*cf.* Fig. 4–3). The latter gives the distance between the centers of Cu and O atoms of *ca.* 0.19 nm.

There are no additional features at $\Delta z > 0$ for the adlayer IIch. Its upper layer consists of densely packed (≈ 0.36 nm separation) “big” Cl atoms. The corrugation of the individual atoms are small and they are difficult to resolve. This suggests a high and uniform electronic density at the position of the Cl atoms observed as a sharp rise of the tunneling barrier. Therefore, we can assign the “outer edge” of the Cl atoms to the zero of the relative distance scale.

The rough estimation of the difference between the two distance scales approaches the value of the diameter of a Cl atom. The latter is originally a single-charged anion, but may be partially discharged due to interaction with copper. From the values of atomic (0.1 nm) and ionic (0.167 nm) radii the difference in the scale may be 0.2...0.3 nm. Together with the interval estimated from the $I - z$ curves, this gives *ca.* 0.1...0.2 nm difference of the distance between the tip and the two adlayers at fixed I_T . This difference may explain the appearance of the two adlayers. Another factor which may affect the visual appearance of the two adlayers is the spatial distribution of the features in the upper layer. The adlayer IIch appears as a “solid” one, while IIs looks like small bright features separated by “empty” space. The size of the features may appear even smaller than the ionic diameter of the O-atoms due to the tip convolution.

4.6 Summary and conclusions

The interfacial structures formed due to the potential-driven coadsorption of Cu^{2+} cations with SO_4^{2-} and Cl^- anions on the Au(111)-(1 × 1) surface were studied using CV, steady state and time-resolved EC STM as well as current-distance EC STS.

The results of the CV for the studied systems were compared with that for the bare Au(111) surface. No features corresponding to the formation and lifting of the surface reconstruction were observed. Two additional pairs of peaks were attributed to the formation of ordered adlayers and their transformations. The three potential ranges observed correspond to two regions of ordered adsorbates (I and II) and to the bare Au(111)-(1 × 1) (III) surface.

The well studied interfacial structure of Cu cations coadsorbed with sulfate anions (IIs, $(\sqrt{3} \times \sqrt{3})R30^\circ$) was used as a tutorial system for mastering the EC STM experiments. The structure of the bare gold surface was successfully resolved in an electrochemical environment in the absence of adsorbed adlayers.

Two different concurrent phases of Cu coadsorbed with Cl^- ions were found in the potential range II. The atomically resolved images of the more compact phase (IIch, “(5 × 5)”) gave an additional clue to understand its structure. The available information

on the structure of the adlayer was analyzed. The previous suggestion [246, 250] about a complicated phase structure described as coexisting local lattices, is supported.

Atomic features of phase IIcl (lower coverage of Cl^- , (2×2)) were resolved. The latter phase is more stable than the more compact phase IIch at lower chloride concentrations and lower electrode potentials. The two Cl-containing phases observed are hardly distinguishable by purely electrochemical methods [244].

A pronounced difference in the STM contrast patterns of the studied phases allowed to observe their structure transitions in time-resolved EC STM experiments. On the images showing the coexisting phases the Cu-SO_4^{2-} phase always appears darker than any of the Cu-Cl^- ones, despite of the comparable geometric height. I was able to visualize the potential induced transformations between the Cu UPD phases containing either coadsorbed sulfate or chloride anions. Transitions between the two chloride phases were also resolved. During all transition processes the boundaries between the phases were seen to follow the hexagonal geometry of the $\text{Au}(111)-(1 \times 1)$ substrate.

Following a potential step to higher values, the Cl-poor phase IIcl quickly compresses to the Cl-rich phase IIch, leaving Cl-free patches on the surface. The slow healing of the latter was attributed to the slow chloride diffusion to the surface, which may be additionally screened by the STM tip. The reverse expansion of IIch to IIcl is not hindered by the chloride diffusion and proceeds in one quick step.

The replacement of the sulfate anions by chloride, after stepping potential to lower values, was studied in details. The nuclei of the new phase form at defects of the surface (steps, kinks) and of the initial adlayer (domain boundaries). Occasionally, I also observed nuclei on the smooth, defect-free surface. The nuclei formed are growing up to their coalescence. The features growing in the absence of nearby defects exhibit a distinct triangular shape. These observations correspond to a fast (instantaneous) heterogeneous nucleation and a directional lateral propagation of the new phase. The low Cl coverage phase (IIcl) was seen as an intermediate during the formation of the high Cl coverage phase (IIch). The latter was formed only after creation of sufficiently large domains of the former. Both, the rate of substitution and the reached maximum coverage, decreased at higher final potential.

The sequences of STM images showing transitions between sulfate and chloride containing adlayers were quantified to extract the time-dependent coverage of the two phases. The exponential kinetic curves were assigned to 2D phase transition controlled by the rate of anions' substitution. The latter is the only information about the phase transition, which may be extracted without direct observations of the transition. This example demonstrates an important role of the SPM techniques in studies of interfacial processes.

It was possible to observe the chloride replacement by the sulfate only for a freshly preformed phase IIch. The nucleation was seen only at substrate and adlayer defects. The substitution was not completed under the experimental conditions employed. The chloride coverage upon substitution by sulfate follows a sigmoid time dependence. The morphology of the phase transition suggests a slow heterogeneous nucleation and a lateral expansion of the created patches of the new phase. The analysis according to the Avrami equation predicts a mechanism of slow nucleation and a growth due to the surface diffusion of the created adlayer "defects". The disagreement seems to be due to the oversimplified nature of the macroscopic Avrami-type model.

Our results confirm a much stronger coadsorption of chloride with copper as compared to sulfate, even at concentrations 4 orders of magnitude lower. As sug-

gested before, the latter may explain the observation of structures different than the $(\sqrt{3} \times \sqrt{3})R30^\circ$ in the potential range II in earlier SPM experiments.

The current-distance STS responses of Cu-SO₄²⁻ (IIs) and Cu-Cl⁻ (IIch) phases were studied and compared with that of the bare Au(111)-(1 × 1) surface. Curves and extracted tunneling barrier profiles show pronounced features assigned to structural elements of the respective adlayers. The results suggest a more compact electronic cloud of the phase IIch in comparison with that of IIs. The brighter STM contrast of phase IIch compared to phase IIs was explained by the interplay of geometric and electronic effects.

Using the experience in EC STM gained during these studies of ionic adlayers, I started with the technically more complicated conductance studies in metal-metal and metal-molecule-metal junctions using STM.

Chapter 5

Conductance of gold atomic junctions

5.1 Introduction

Atomically-thin metal-metal junctions are known as quantum point contacts (QPCs) (Sec. 2.6.1). The mechanical and ET properties of QPCs are studied well. Among those the QPCs formed by gold, due to their unique properties, are the most explored ones and may serve as a reference system to establish techniques for conductance studies. In this introduction I outline the major concepts and results related to this work. A comprehensive review of the field is available elsewhere [98].

5.1.1 Experimental techniques

The question of how to make nanometer-scale contacts possessing specific “quantum” properties was first addressed as early as in 1980th. Before the so-called “spear-anvil” technique was used to study ballistic conductance in metal point contacts [256]. It essentially consists of bringing a sharp needle of a metal into a gentle contact with a metal surface. The typical conductance of these contacts ranged between 0.1 and 10 S, which corresponds to contact diameters between 10 and 100 nm [98]. Contacts of that type were used to study electron-phonon interactions in metals. They routinely exhibit non-linear current-voltage characteristics (Sec. 2.1.3), but not a quantified conductance (Sec. 2.6).

Soon after invention of the STM (Sec. 2.4), the opportunity of these technique to create stable tunneling junctions and atomic contacts without a feedback control was realized. The squeezable tunneling junctions approach [257–259] was a first proposed in solution. Here two flexible substrates are separated by evaporated thin-film spacers. The gap between the electrodes is adjusted by a squeezing force, so that a tunneling junction is stochastically created. The stability of the electrode separation in one direction was essentially achieved by sacrificing the control over the two other directions.

The development of this concept resulted in the MCBJ technique [125], introduced in Sec. 2.6.3. With further improvements [98, 260–264], this technique has proven to be particular suitable for the studies of QPC conductance, and a number of experiments were carried out [98]. The results of MCBJ studies may serve as a reference data for the SPM-based studies of QPCs.

Rather soon after invention of the STM, experiments on the surface modification by mechanical impact of the tip were carried out [265, 266]. It was also noted that the surface modifications induced may be simultaneously observed by imaging with the same tip. The idea of the nanoprobe usage both for an active manipulation and for a passive observation – provided that the probe remains intact after the contact with the

surface – resulted later in numerous applications.

The use of the STM to form QPC was demonstrated first in 1987 [267]. It was shown that upon an approach of the STM tip to the surface the transition between the tunneling and the conductance modes of the ET results in an abrupt jump of the conductance (jump-to-contact). As it will be shown further, this phenomenon is related to the force interaction between the metal SPM probe and the metal substrate.

Both SPM and MCBJ approaches are widely used to study transport properties of QPCs. The major drawback of the MCBJ technique compared to SPM is a lack of information on the contact geometry and on the surface evolution in the course of the experiments. Despite some attempts to implement a lateral STM-like imaging by one of the MCBJ electrodes, the badly defined “tip” geometry results in low resolution images, which are difficult to interpret [98]. As it is demonstrated further, the SPM approach is widely used to study the mechanical properties of the QPCs. The force, alone or simultaneously with a current, was measured in CP AFM or in combined STM/AFM configurations [98, 268–277].

5.1.2 Formation and breaking of QPC

The formation and the evolution of the QPC may be monitored by the observation of current through the junction. The strict exponential distance-dependence of the direct tunneling (Eqn. 2.62 on page 51) is observed when the tip is sufficiently away from the surface. Upon approach to the surface, two major effects may cause a deviation from the exponential dependence [98]. The overlap of the electron wave functions and an electron exchange between two metal electrodes becomes significant. The attractive metallic adhesion force pulls the probe and sample atoms together. The tunneling barrier decreases due to the image potential from two metallic surfaces. The decrease of the real barrier is expected even at a distance $z = 1$ nm. However, the distance-dependence of the real barrier is such, that the apparent tunneling barrier Φ , as measured from the slope of the $\ln I_T$ vs. z dependence, remains constant up to much smaller z [278–280].

The decrease of the Φ upon approach to the surface was reported at a distance $\Delta z < 0.3$ nm before the contact [267, 281] and attributed to the image potential effect. In other experiments [281–284] no distinct variation of Φ until contact was reported, and it was suggested that the image potential is compensated by a strong adhesive force [282]. MCBJ studies [285, 286], in turn, demonstrated an increase of the Φ , presumably due to the metallic adhesion. The latter result may be a more relevant one due to the higher stability of the MCBJ instrumentation [98]. However, the variation of the experimental conditions and in particular the geometry of the electrodes [287] may also be responsible for the existing disagreement.

The force interaction of the metal probe and the metal surface was studied both experimentally [273, 281, 288–298] and theoretically [298–309]. Complementary conductance-force measurements in a MCBJ configuration are also reported [287, 310]. The long-range probe-surface force interaction is dominated by the weak attractive van-der-Waals forces. Upon decrease of the gap, the attractive metallic adhesion overcomes the repulsive interatomic forces. The local elastic deformation of the surface leads and a “snap” of the tip to the surface. The latter is detected as a discontinuous current increase (jump-to-contact). The critical value of the probe-sample separation before jump-to-contact is estimated from the various simulations as 0.2 – 0.3 nm, *i.e.*, comparable with the size of a metal atom. The jump-to-contact occurs only between clean

metal contacts. When an adsorbate is located between two interacting metal surfaces, repulsive interatomic interactions dominate. The mechanical impact on the surface is observed instead of a coalescence of two metal parts [267, 292].

The jump-to-contact is typically considered as a sign of the transition between the tunneling and conductance modes of ET [94, 96, 98, 267, 281, 283–285, 287, 311–317]. However, some experimental [318–321] and theoretical [322, 323] studies suggested that, dependent on the material and the configuration of the electrodes, the transition may be also a smooth one. A spontaneous jump-to-contact and QPC formation was observed at high temperatures [324] and attributed to an alternative mechanism involving the “diffusion-to-contact” of the mobile surface atoms [325].

During jump-to-contact the conductance typically varies from $6 \cdot 10^{-6} \dots 3 \cdot 10^{-5} \text{ S}$ to $\approx 10^{-4} \text{ S}$ [98], *i.e.*, from $(0.1 \dots 0.4)G_0$ to $\approx 1G_0$ (Sec. 2.6). The smooth contact formation manifests itself as a continuous transition from the current increase to a plateau at $G \approx G_0$. Such contacts are typically attributed to a single-atom QPC. Pressing the tip further into the substrate results in an expansion of the contact area. The contact conductance increases in a step-like fashion. Upon the subsequent tip retraction, the constriction and the breaking of the metal neck results in a rapid conductance drops. Both contact expansion and shrinking proceed as a series of atomic rearrangements [94–96, 261, 269, 271, 312, 315, 326–330]. The last drop corresponds to the transition between the conductance and the tunneling modes. The pronounced hysteresis is typically observed between the positions of the transitions from one ET mode to another. The latter may be avoided by “training” the contact, *i.e.*, closing and opening the gap in a small distance range.

The formation of a thick “multiple-channel” contact between two electrodes and its subsequent separation are widely used to study the properties of QPC both in SPM and MCBJ configuration. The whole cycle of the tip-sample contact, the rearrangement of atoms upon driving the probe into and out of surface, the constriction and the breaking of a connecting neck was also investigated theoretically [303, 304, 331].

5.1.3 Conductance of a single metal atom

At low temperature a QPC or a tunneling gap can be held stable for virtually any desired time, either in a STM or a MCBJ configuration. At room temperature the diffusion of the surface atoms results in a spontaneous contact breaking or a rearrangement [332]. Fixed junctions built up by various superconducting metals at low temperature were extensively characterized in $I - V$ studies [125, 257, 258, 260, 312, 315, 333–340]. The $I - V$ curves were found to be highly nonlinear, and effects characteristic for the superconductors, such as a superconducting gap, multiple Andreev reflections, Josephson effect and a zero-bias peak [98, 312, 333], were observed.

Important conclusions were derived from studies of a superconducting subgap structure. The detailed investigations of the $I - V$ characteristics of tunneling between superconducting leads [333] demonstrated that the results are well described by the existing models [316, 341–347] considering a single conductance channel (Sec. 2.6). This is a natural assumption, because the various orbitals of the front atoms have different exponential decay length, and the orbital with a slowest decay dominates in tunneling [98]. The later studies of the $I - V$ characteristics of superconducting QPCs [334] demonstrated, that they do not correspond to the ET through a single conducting channel. A good description of the experimental data was possible only by the assumption of more

than one conducting channels per atom. Systematic studies of $I - V$ characteristics in superconducting QPCs for elements of different chemical valency [334–340] and the supporting theoretical treatment [348–351] resulted in a very simple concept: the number of conductance channels is determined by the number of valence orbitals of the atom. The same result was obtained from measurements of the shot noise [352, 353]. The transition from a one-channel tunneling to a five-channel conductance was observed for a superconducting Nb junction [336].

The transmission probability, associated with a single channel, is determined by the alignment of the orbital with the metal Fermi level and may be well below one. The existence of multiple conductance channels for single atoms has a remarkable effect on the current through a metal contact upon its rearrangement. However, only an overall transmission is measured as a conventional conductance. Thus, for a multiple-channel atom it may strongly deviate from G_0 or its multiple integer values.

5.1.4 Gold QPCs

Among the metals employed in QPC experiments, gold is an archetype. Au QPCs possess a unique combination of properties and are intensively studied. Irrespectively of the QPC formation, the clean and low reactive Au electrode by itself is a first candidate for virtually any kind of surface studies (*cf.* Sec. 3.4).

A single Au atom provides only one conductance channel with an electron transmission probability T close to one. It was demonstrated by $I - V$ characteristics of the Au QPC with induced superconductivity [335] and via simultaneous conductance and shot noise measurements [352]. The ET through Au QPCs was investigated theoretically as well. It was shown that a single conductance channel of Au arises mostly from the 6s orbitals. It is pinned to the metal Fermi level [327, 335, 348, 354–356] due to the charge conservation and provides almost perfect transmission. In general, the same situation is characteristic for the other *s*-metals studied, such as Cu, Ag, Li, Na, K.

The mechanical and transport properties of Au QPC during its formation and breaking were studied in much details. The Au QPCs are easily formed by bringing together two Au electrodes. A Au-coated cantilevers are routinely used for CP AFM experiments. Probes made of many other metals, *e.g.*, W [283, 357], are wetted by Au. Thus, after the first contact with a Au surface, the probe is covered by a thin layer of Au, which further acts as a Au electrode. When two Au electrodes are pressed against each other or pulled apart, the rearrangement of the contact area results in a step-like conductance increase. The conductance at every step is close to an integer number of G_0 [96]. The current plateaus are straight, without a positive or negative slope [283, 358].

Finally, a conducting chain of Au atoms may be stretched between two electrodes. The latter was observed as a long plateaus with a conductance close to G_0 [97]. A big hysteresis between the positions of the contact rupture and the jump-to-contact (return distance) [97] was attributed to the same phenomena. The preferential values of the plateau length were estimated from the statistical analysis [274, 359]. Their spacing is close to multiples of the Au–Au separation in the bulk (0.288 nm). The force measured simultaneously with the conductance during the pulling of Au nanowires [272] demonstrated a sawtooth-like dependence on the displacement. It was accounted for by the plastic deformations interrupted by the force relaxation. Moreover, the stretched Au nanowires were directly observed by electron microscopy [276, 360–363]. Au atomic wires have a conductance very close to G_0 and can be held stable at low temperature.

Besides Au, only Ir and Pt were found to form atomic chains during stretching [364–366] without stabilization by adsorbates. The stretching of Au QPCs is a very important process for the studies of ET through Au and Au-molecule-Au junctions.

The conductance of Au QPCs was studied by the repeated contact formation and breaking at cryogenic [96, 97, 269, 272, 275, 283, 310, 326, 330, 359, 364, 366–373] and room [270, 273, 276, 277, 329, 357, 360, 363, 368, 372, 374–377] temperatures in UHV; in ambient conditions [94, 271, 274, 372, 377–384] and in neutral liquid [385, 386] at room temperature using SPM [94, 96, 97, 269–277, 283, 357, 359, 360, 366, 368, 369, 372, 374–377, 380, 382, 385, 387–389] and MCBJ (or similar) [97, 310, 326, 329, 330, 359, 363, 364, 366, 367, 370, 371, 373, 378, 379, 381, 383, 384, 386] approaches. Despite of the broad investigations, only few experiments were carried out in an electrochemical environment [387–389]. Reports about stretching experiments under potential control for other metals just started to appear [390].

In this chapter I report studies of the conductance through the Au QPCs by the stretching technique. The experiments were carried out using a EC STM setup at room temperature in an aqueous environment (0.1 H₂SO₄) under potential control. Complementary experiments in Ar and mesitylene were carried out as well. The experimental details are described in Sec. 3.8.2.

5.2 CV and STM

Prior to STM imaging and stretching experiments in aqueous electrolyte the CVs were recorded in an EC STM cell (Fig. 5–1). The black curve corresponds to the sweep in the widest range of potentials available (*cf.* Fig. 3–3). The onset of the reduction process appears at potential around -0.13 V. This is *ca.* 100 mV more positive than observed in a cell dedicated for electrochemical studies (orange line in Fig. 3–3), while the concentration of sulfuric acid used is only 2 times higher. This suggests that the wave is due to the reduction of residual oxygen rather than due to the hydrogen evolution. However, the amount of oxygen is small and no oxygen effect is observed on the CV at $E > 0.05$ V. The peak of the Au(111) surface oxidation is seen during the potential scan in positive direction at $E \approx 1.40$ V. The corresponding reduction feature appears on the reverse scan at $E \approx 0.92$ V. These results are in agreement with the reference data in Fig. 3–3.

The red curve corresponds to a potential sweep in the double layer region. It shows features of the formation and lifting of the surface reconstruction, a broad pair of peaks due to the adsorption/desorption of disordered sulfate as well as a pronounced pair of current peaks attributed to the order-disorder transition to the $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ sulfate adlayer. The peaks are not as pronounced as shown in Fig. 3–3, probably due to the cycling with a rather high sweep rate and/or non-optimal geometry of EC STM cell. In general, there is good agreement between the CV data recorded in the EC STM setup and those obtained in a dedicated electrochemical cell.

An example of STM image recorded at negatively charged surface ($E = 0.115$ V, indicated by arrow) in the course of the experiment is shown in the inset of Fig. 5–1. The image displays typical features of a reconstructed Au(111)- $(22 \times \sqrt{3})$ substrate (Fig. 3–3A) and illustrates the good quality of the gold tips used in these studies.

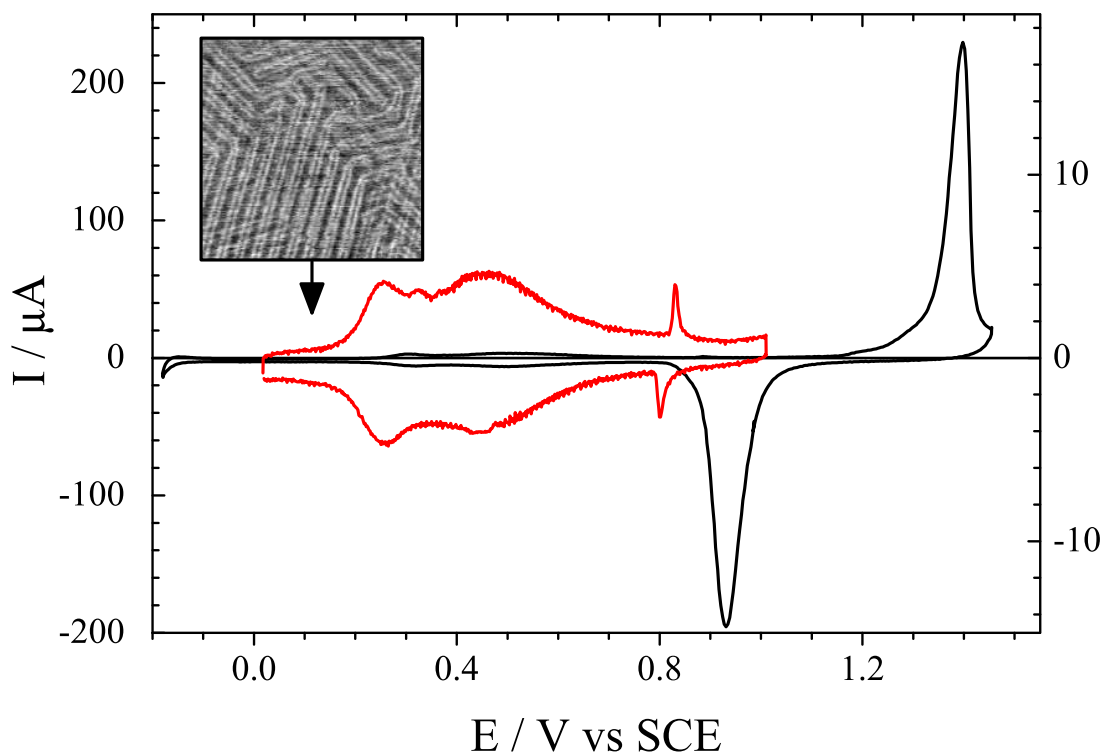


Fig. 5-1: CVs of Au(111) recorded in an EC STM cell in 0.1 M H_2SO_4 , $r = 50 \text{ mV} \cdot \text{s}^{-1}$ (cf. Fig. 3-3). The current scales for the black and red traces are on the left and right sides, respectively. Inset: STM image of the Au(111) surface, size $100 \times 100 \text{ nm}$, $E_s = 0.115 \text{ V}$ (indicated by arrow), $E_t = 0.015 \text{ V}$, vertical scale 0.055 nm .

5.3 Single stretching traces

Few typical current-distance traces recorded in electrolyte solution at a bare reconstructed Au(111) surface ($E_s = 0.115 \text{ V}$, $E_t = 0.015 \text{ V}$) upon tip retraction are shown in Fig. 5-2. The distance scale is displaced for different curves for better visibility. Unlike in case of approaching curves for the bare Au(111) surface (Fig. 4-13), demonstrating exponential response of the tunneling gap, the $I - z$ traces in Fig. 5-2 are non-exponential and demonstrate characteristic plateaus of a constant current. These plateaus are interpreted as being due to the constant current via stable configurations of QPC created between two electrodes. The observed decrease of the current is due to the constriction of Au QPC upon stretching and the sequential decrease of a number of conductance channels. The last step (*i.e.*, the one after which the current drops to zero) is typically located $1 \dots 1.5 \text{ nm}$ further from the surface than the initial tip position z_0 . It represents the pulling and breaking of a single-atom Au QPC.

At least 1000 curves were recorded for every set of experimental settings with a regular inspection of the surface by STM imaging. During the stretching characteristic Au clusters were created on the surface. An example is shown in the inset of Fig. 5-2.

The positions of the current plateaus are reproducible for many traces. However, a statistical analysis is required for the reliable determination of the conductance of single junctions and, as it will be shown further, this task becomes very critical in case of SMJ.

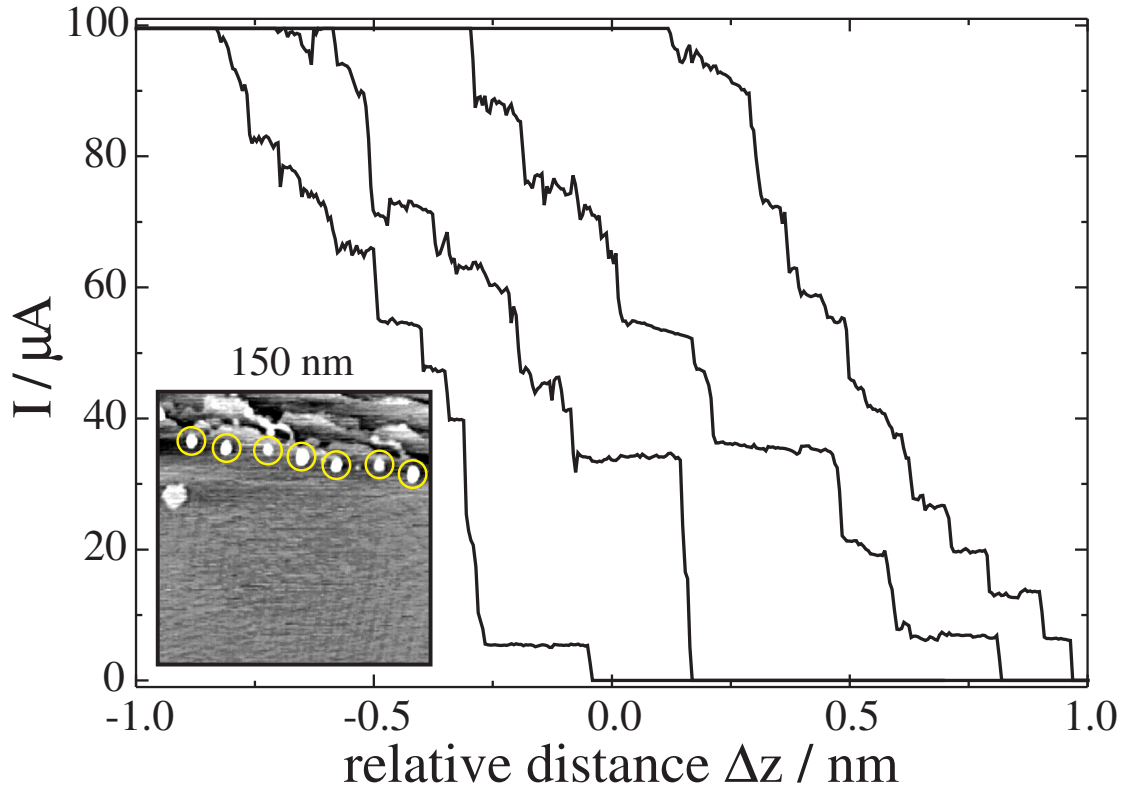


Fig. 5-2: Individual stretching curves exhibiting characteristic plateaus. Experimental conditions: 0.1 M H_2SO_4 , $E_s = 0.115$ V, $E_t = 0.015$ V. Inset: STM image recorded after stretching, size 150×150 nm, vertical scale 0.625 nm, E_s and E_t are the same. The Au clusters formed after stretching are marked by yellow circles.

5.4 Statistical analysis

In this section I summarize and categorize the existing approaches to the statistical analysis of the single junction (either QPC or SMJ) conductance. The data sets used for the statistical analysis consist of a big number (from few hundreds to few thousands) of stretching curves measured under the same experimental conditions and acquisition settings, such as the tip and the sample potentials, bias voltage, tip movement rate, resolution of x and y scales, *etc.* The data set presented in Sec. 5.3 is used further as an example. In general, the analysis procedures are based on the calculation of the statistical frequency of some representative variable (*e.g.*, current or conductance). The analyzed range of values is split into equal intervals (bins), and a number of occurrences falling into each bin is calculated [98]. The result is represented graphically as a histogram. The inspection of the histogram allows to determine statistically representative values of a junction conductance. As it is shown further, the details of the histogram construction strongly differ.

5.4.1 All-data analysis

This approach is based on the statistical analysis of all current data of the measured $I - z$ curves. It is the most straightforward procedure, but the results are often unclear. The manual preselection of the curves may be used before the analysis, however, this is a time-consuming and potentially subjective procedure. Alternatively, various automated filtering procedures may be applied (see below).

Linear histograms

In the simplest case all current values of the curves are used to construct the histograms of the measured current I in the studied range. This method was first introduced in the second half of 1990th [95, 285, 374, 391] and is widely used to determine the conductance of QPCs [95, 273, 285, 329, 355, 357, 368, 373, 374, 374, 377, 381–384, 391, 392].

An example of the all-data histogram in bar representation is shown in Fig. 5–3A. It was constructed for the data set described above using a bin width of 50 nA. The width of every bar on the plot is the covered current interval and the height is the number of current values (*i.e.*, points on the measured curves) lying within this interval. The histograms plotted in the same way for the stretching traces of Au QPC under other investigated conditions looked very similar. All histograms showed a most pronounced first peak at $I = I_1$, followed by a satellite peaks with positions close to integer multiples of the first: $I_n \approx n \cdot I_1$. The peaks indicate conductance values which occurrence probability is the highest in the surrounding. Several values of the bin width were tested for every data set. Although the exact appearance of the histogram varies with the bin width, no significant variation of the peak positions was found.

A detailed analysis of the shape of the pronounced peaks ($n = 1 \dots 3$) shows that they are symmetric with respect to the center. This suggests a symmetric distribution of the current with the position of the maximum (mode of distribution) been at the same time a mean and a median of the distribution. Conventionally, the position of the peak in the I scale is taken as the statistically most probable value of the current in a given junction. Further this value is often referred to as the “average” one.

In order to improve the statistical significance of the determined centers of peaks, the shapes of the whole peaks can be analyzed. One may argue that the formation of the junctions during the stretching are independent events and their distribution around an average value should be close to a Gaussian. Due to this reason, the positions of the peaks are often determined by fitting the histograms in a certain range by a set of Gaussian curves and taking their centers as peak positions¹. The width of the Gaussian peak may be used to estimate the error value according to well known properties of this distribution.

A series of Gaussian curves fitting the histogram is shown as blue lines in Fig. 5–3A. Their sum is shown as the red curve. The three first peaks are equally spaced and were interpreted as junctions with the currents I_1 , $I_2 \approx 2I_1$ and $I_3 \approx 3I_1$, corresponding to the configurations with one, two and three open conductance channels. There are also three pronounced peaks with a different spacing than the first three lower current peaks. We attribute these “high index” peaks to the integer multiples of a fundamental conductance, namely 5, 6 and 8, with the intermediate peaks being missing (see further).

The positions of the centers of the individual peaks are plotted as a function of the peak index in the inset of Fig. 5–3A. To determine the average value of I_1 , the peak current vs. peak index dependence was fitted by the line with a zero intercept. The obtained value of I_1 is indicated in the plot.

Besides the very pronounced peaks, the histogram shows a certain “background” amount of data points at any current value. Close inspection of the individual traces

¹ Although there are some evidences that the shape of peaks on QPC conductance histograms is closer to Lorentzian than to Gaussian one, the exact shape of the fitting function is not critical. Very similar peak positions are obtained with other symmetric peak functions.

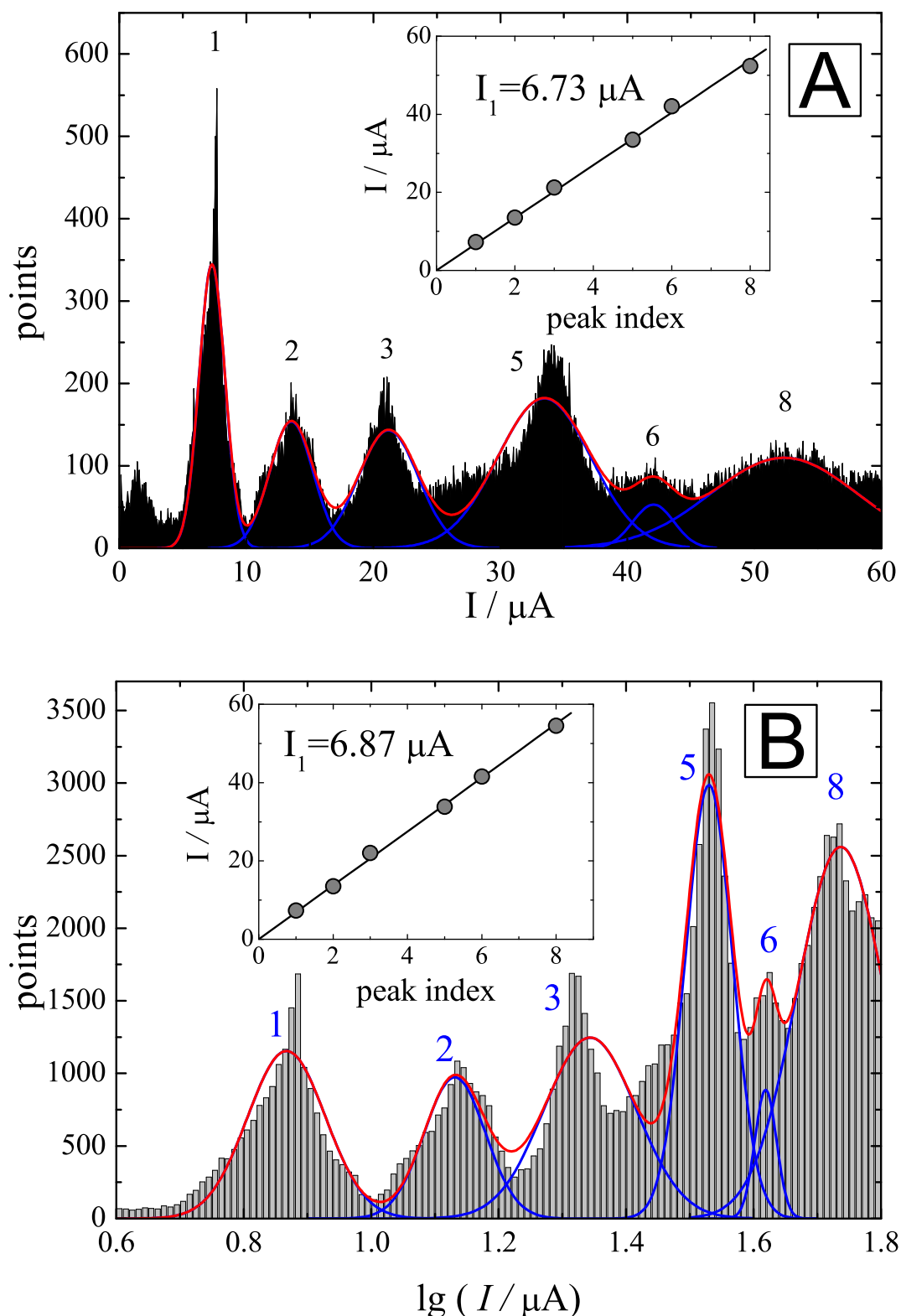


Fig. 5-3: Current histograms built from all current values of a set of 1000 individual traces: (A) linear scale, bin width 50 nA; (B) logarithmic scale, bin width 0.01. Blue lines – series of fitted Gaussian peaks labeled by the corresponding number of conductance channels; red line – sum of Gaussian fits. Insets: a position of the peak current vs. peak index and the corresponding linear fit. The indicated slope represents the estimated average current through a single junction I_1 .

suggests that in case of QPC stretching the observed background is mostly due to the current variation of the junctions formed, rather than to a significant amount of exponentially decaying curves (*i.e.*, traces with no QPC formed).

For the SMJs the contribution of the tunneling current often gives a featureless rising tail at the low current limit². The conductance peaks often appears on the top of the tail, which may be subtracted using various approaches.

In general, the all-data histograms allow to distinguish the preferred conductance feature only if there is a considerable amount of the well-pronounced junctions in the original data set. The latter is typically the case for the of QPC stretching traces, but seldom observed for the SMJ [393]. More advanced analysis procedures are used in the latter case, which shall be illustrated further.

Logarithmic histograms

Recently it was proposed by a few groups [127, 394–398] to use the logarithm of the current for the histogram construction. This is effectively equal to the current histogram with a “dynamic” bin width, which is small for low currents and big for high currents. The logarithmic representation allows to observe features with a very different conductance on the same plot. The abscissa of the histogram could be rescaled back to the linear scale of the current for a better visibility.

The histogram of $\lg I$ constructed using the bin width of 0.01 for the same data set is plotted in Fig. 5–3B. In comparison with the linear histogram (Fig. 5–3A), asymmetric and non-equally spaced, but essentially the same peaks are observed. Due to the “dynamic” character of the bin width, the peaks with higher indices are often higher and have a bigger area than the first one. The shape of the peak is slightly “skewed” towards higher current values. Here I would like to note that for an asymmetric distribution the mode (position of the maximum) differs from the mean/median value, in this case it is shifted positively. Therefore, one should be clear in definitions when talking about the “average” conductance values extracted from asymmetric peaks of a logarithmic histogram.

The logarithmic histogram was analyzed in the same way as the linear histogram. The position of the obtained peak was recalculated to linear current value. The resulting dependence (inset in Fig. 5–3B) is very similar to the one found in the inset in Fig. 5–3A. The difference between values of I_1 was found to be *ca.* 2%, which is much smaller than the typical width of the peak.

All-data histograms plotted in a logarithmic domain were found to be more useful for the analysis of the SMJ conductance [127, 394]. The latter has a conductance of 3...5 orders of magnitude smaller than G_0 . Logarithmic histograms allow not only to cover a wide range of current, but also to convert the background of the tunnelling to a constant offset. As I found, it is important to have a sufficient resolution of the used analog to digital converter at the lower limit of the current range to avoid the so called “biting” effect. If the resolution is insufficient, the very small current values after digitisation may have only certain discrete values. This results in a characteristic pattern of bins with a very high amount of datapoints separated by empty bins. Such logarithmic histograms may also exhibit spirituous peaks which positions depend on the bin width.

² It can be easily shown that for the exponential curve with equally spaced x samples the distribution of y values follows $N(y) \propto (1/y)$ [127].

5.4.2 Plateau position analysis

Another group of methods is based on the statistical analysis of the vertical position (*e.g.*, current) of the plateau rather than that of all measured data points. One counts the distribution of the plateau positions in a similar manner as that of the data points described in the previous section. The major question arising is, what is actually a conductance plateau? A certain selection criteria must be used in the analysis. However, consistent results are obtained within the carefully chosen limitations. The great advantage of the histograms constructed in this way is a lack of random data burying the conductance features [399], which is especially important for the SMJs.

The length of the plateau may be extracted simultaneously with the position. One can construct histograms using weighting a plateau contribution by its length during the histogram construction. Such procedure is more compatible with the all-data analysis, where the plateau contribution is effectively weighted by its length (*i.e.*, number of data points constituting plateau).

Manual analysis

The most straightforward way is to manually browse through the measured curves and record the positions (and, possibly, other data such as a length) of the conductance plateau. The selection may be subjective, however certain criteria such as minimum required length of the plateau, maximum allowed scatter of the current, an existence of abrupt changes at the ends of plateau and others may be applied. With carefully selected requirements this method gives histograms with the most clear features, but it is extremely time consuming.

For the molecular systems studied a selection of the plateaus with a maximum 5% current variation and a minimum 0.05 nm length gave straightforward and consistent results (see Cha. 6). The results obtained by the limited manual analysis may be used as reference data for other more advanced approaches.

Automated plateau position analysis

Basically every group coming across the problem of plateau selection develops its own analysis procedure. At the moment, there is no universal automated analysis procedure established. This drawback is probably due to the poor description of the procedures applied, lack of their systematic investigations, as well as different programming environments used. In this paragraph I will present few characteristic approaches described in the literature.

Probably the oldest automation analysis procedure is the one developed at Arizona State University and used in the groups of Prof. Nonjing Tao and Prof. Stuart Lindsay. It resembles in some sense the conventional all-data histogram procedure described above. Similar to the latter, a histogram is constructed using the current data of an individual curve [166]. Then, an algorithm finds peaks on the histogram. Providing that the peak width and the peak height are within the specified ranges, the position of the peak is taken as a current of plateau. After the analysis of a big amount of curves, the plateau position data are used to construct histograms. The peaks on the latter are attributed to the statistically averaged conductance through a conducting junction.

In an interesting approach proposed by the Columbia University group [393] the “quality” (*i.e.*, least square deviation) of the fitting of a single curve by a step and an

exponential decay function is compared. If the curve in a specified current range is better described by a step function, the position of the step is taken as a plateau current.

In an approach proposed by the Berkeley group [399] the current-distance curve is differentiated to find the drops of the current, which slope is higher than a predefined limit. Among those drops only a “last step” (*i.e.*, at highest distance from electrode) is taken for a further analysis. The last step presumably corresponds to the breaking of a true single junction. The histograms of the last step position exhibit a single peaks, which is attributed to the conductance through SMJ.

Plateau selection procedure

An additional plateau selection procedure was developed by me. Its principle is outlined in Fig. 5–4. The analysis program screens a single stretching trace for intervals of constant current. There are two selection criteria to be met. First, the current fluctuation around the mean value should not be larger than a certain threshold ratio. After several tests, 2% of the allowed current scatter was used for all systems studied so far. Another selection criteria is an allowed minimum plateau length (L_{min}). This parameter is adjusted for every system studied separately, and a value enabling to obtain the most pronounced histograms is selected. For the Au QPCs $L_{min} = 0.1$ nm was chosen. Optionally, original data could be smoothed before the major procedure, but the non-smoothed data was found to give the best results. The current is analyzed within the upper and lower limits. They are integrated into the analysis procedure and allow to avoid unwanted data related to the saturation or the noise level of the current.

The obtained set of plateaus is used to construct the histogram as for an all-data

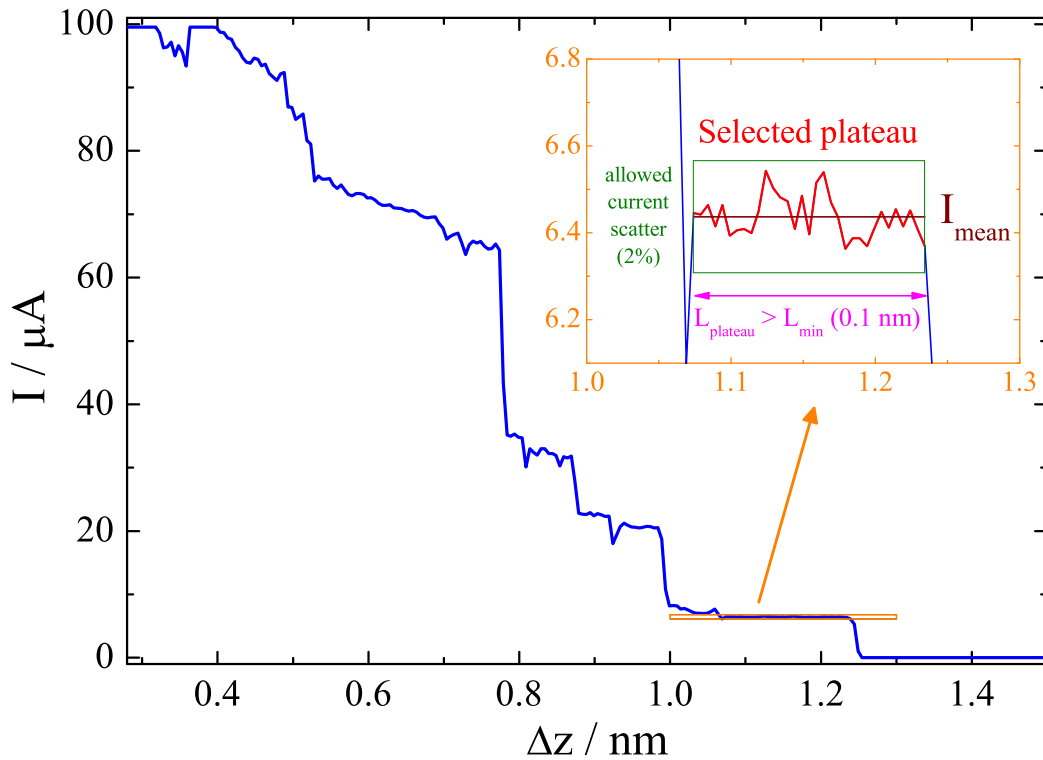


Fig. 5–4: Principle of the plateau selection procedure. The inset is a magnified part of the curve shown by the orange rectangle.

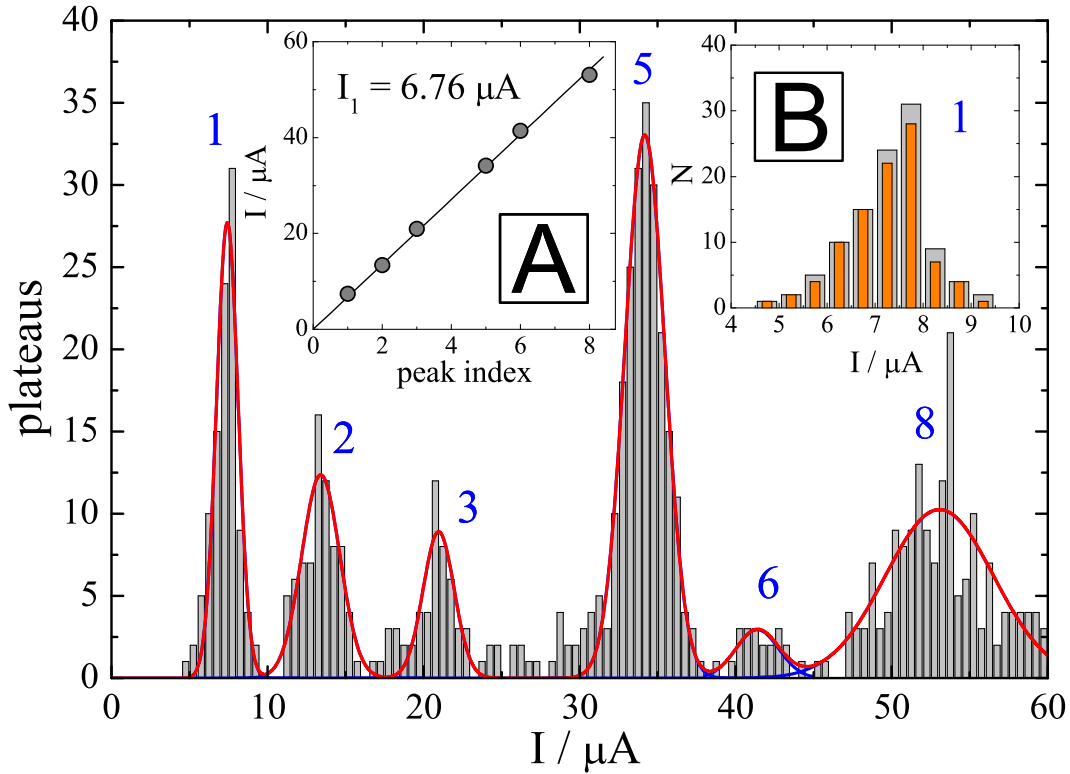


Fig. 5-5: Histogram of plateaus extracted from 1000 individual traces (*cf.* Fig. 5-3), bin width 500 nA. The blue lines represent a series of fitted gaussian peaks labeled by the corresponding number of the conductance channels; red line – sum of gaussian fits. Insets: (A) position of the gaussian peak current *vs.* peak index and their linear fit; (B) first peak of the histogram from the main plot (grey) overlaid by the one built from the last plateau only (orange).

procedure. An example is plotted in Fig. 5-5. Here each plateau is counted as one entry (*i.e.*, without weighting by the length). The major features of the histogram are essentially the same as in Fig. 5-3A. Unlike the latter, the peaks on the plateau histograms are well separated and there is basically no background. The effective elimination of the background is especially important for studies of the SMJ conductance, where the number of successfully created junctions is much smaller. The peak with index 5 is higher than the first peak. The same was often observed for high index peaks and will be discussed later. The calculated value of I_1 is essentially the same as it was obtained for the all-data histogram.

The procedure presented may be easily extended to select only the last plateau [399], *i.e.*, the one with the smallest current. The last plateau histogram is presented on the inset (B) of Fig. 5-5. This histogram indeed exhibit one peak, which corresponds to the first peak of the all-plateau histogram. However, this procedure implies the loss of satellite peaks, which are important for the data consistency check, or any additional series of peaks (Cha. 6).

5.4.3 General comments on the statistical analysis

In this paragraph I will summarize and add some general comments on the histogram construction and analysis. The latter are based on the whole experience of the

QPCs/SMJs conductance studies presented in chapters 5-6, and other experiments carried out in our group as well as on published data.

- The plateaus on the current-distance traces reflect stable junctions and lead to symmetric peaks in the linear current histograms (all-data, plateau, *etc.*).
- The peaks in the logarithmic histograms are slightly skewed towards higher values.
- The preferred conductance does not appear as a single peak, but it is accompanied by satellite peaks. The exceptions are procedures intentionally choosing only the last plateau.
- The first peak in a series is the highest and most pronounced one. Satellite peaks are progressively smaller and broader [357].
- The current distribution around an average value is well described by a Gaussian curve. It should be possible to fit the hole series with a set of Gaussian curves. Their centers are attributed to the average value of the junction conductance.
- For peaks in one series, the peak positions are the integer multiple of the first peak position (within the experimental error).
- The positions of the peaks are not affected by the variation of the bin width, although an exact appearance may differ. The systematic investigation of the current histograms upon the variation of the bin width is an essential part of the conductance histogram analysis.
- The conductance of single junction, as obtained from the histogram analysis, is constant in the range of small (up to few hundred mV) bias values.

This description may be rationalized in terms of the possible formation of multiple junctions (*i.e.*, a few atoms wide QPC or MJ embedding few molecules), while the single junction is the most probable one. The two last criteria allow to discriminate histogram features caused by the artifacts of the experiment or the analysis.

Typically 2-3, rarely 4 peaks of one set is observed on the conductance histogram. The high index peaks obtained for gold contacts is not a typical features and will be discussed further. The QPC/SMJ conductance is determined from the positions of the conductance peaks. One may take position of the first peak in a series, or use an average of I_{peak}/N_{peak} values, or apply another averaging procedure.

5.5 Bias and media effect

The linear all-data (Fig. 5-3A) and plateau (Fig. 5-5) histograms were constructed for all experimental conditions investigated. The difference of the peak positions in the two types of constructed histogram were within a few percents and considered as being negligible. Values of the single junction conductance were calculated from the positions of the current peaks in the histograms using the data for the low index (1-3) peaks only.

Besides the low index peaks, additional non-equally spaced peak are observed (see, *e.g.*, Fig. 5-3 and 5-5). The most reproducible indices of additional peaks were 5, 7

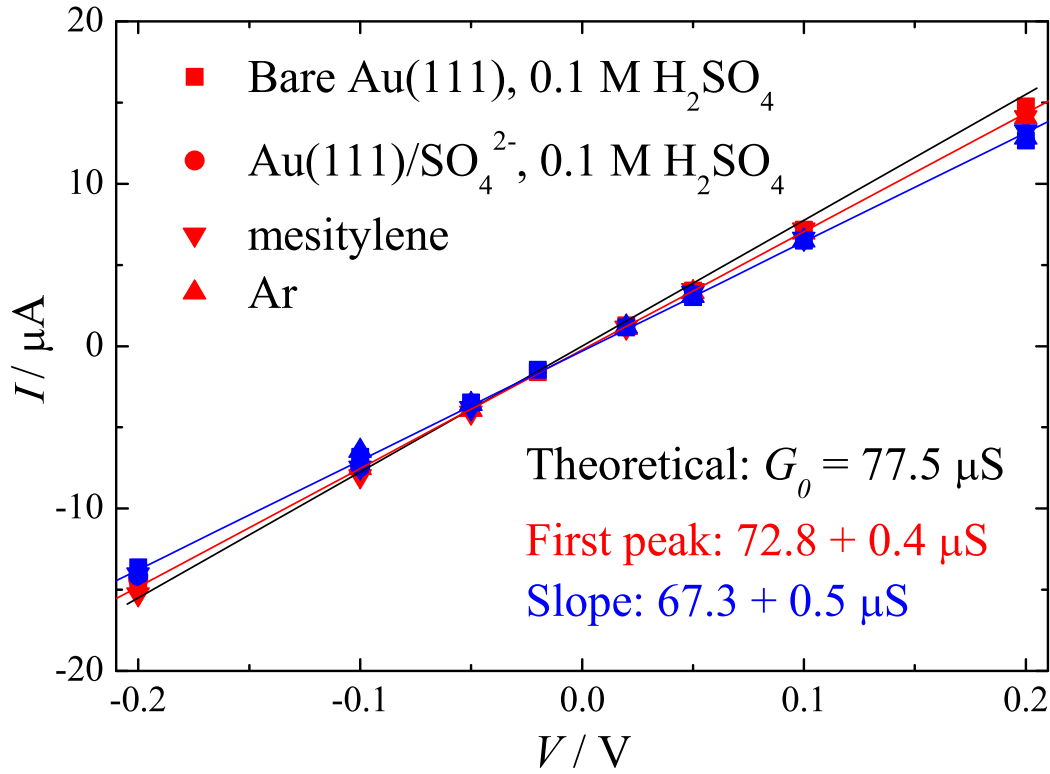


Fig. 5–6: Current-bias voltage dependence as obtained from the first peaks (red symbols) or the slope of the dependence peak position vs. peak index (blue symbols) of the respective histograms. The lines of the corresponding colors are linear fits of all experimental data points. The black line represents the current through a perfectly conducting channel ($G_0 \cdot V$). Conditions: circles – 0.1 M H₂SO₄, $E_s = 0.115$ V; squares – 0.1 M H₂SO₄, $E_s = 0.915$ V; triangles up – Ar; triangles down – mesitylene.

or 8, 10 or 11, and with a somewhat smaller confidence 14 or 15 and 18 or 19. These “magic numbers” reflects the enhanced stability of certain QPC configurations due to the electronic shell effect, reported in [385]. The preferable values 5 and 8 are also in agreement with the results of the histogram simulations [400].

The bias potential dependence of I_1 for all media is plotted in Fig. 5–6. The current of a single conductance channel was estimated using two approaches: from the position of the first peak (red symbols) and from the slope of the peak position vs. peak index plot (blue symbols). No media dependence of the single junction current was found within the same approach. The data for all studied media were included in a single current-voltage dependence (Fig. 5–6). The latter is linear in the studied range of bias voltages $|V| < 0.2$ V.

The resulting values of the conductance determined as a slope of the $I_1 - V$ dependencies vary between 72.8 and 67.3 μS , depending on the chosen method of analysis. They are up to 15% smaller than the expected theoretical value $G_0 = 77.5 \mu\text{S}$ (black line in the inset of Fig. 5–6). The difference is due to the fact, that the transmission of the Au QPC is not exactly 1. I would like to note that no correction for an empirical “serial resistance” was done for the data presented.

5.6 Length of the conductance plateaus

The analysis of the plateau positions presented above was extended to the plateau lengths. Information on the length of the plateaus may provide some insight into mechanic and structural properties of the created QPCs. The definition of the “plateau length” for a curves obtained by the stretching technique is probably even more unclear than that of the “plateau position”. In low temperature experiments [274, 359] the latter was determined from all-data histograms. The plateau length, in turn, was defined as an interval on the curve, at which the conductance changes from $G_{max} > G_0$ to $G_{min} < G_0$. The upper and lower limits were typically defined as $(1.1 \dots 1.2)G_0$ and $(0.5 \dots 0.8)G_0$ respectively. The results demonstrated the quantization of the plateau lengths obtained in this way. Such an approach to the evaluation of the plateau length is justified for the QPC stretching curves with a known conductance and abrupt drops of the current. However, it is hardly applicable to molecular systems with a conductance unknown in advance and less pronounced features.

In my approach instead of the length of the whole plateau, the length of the constant current interval is obtained simultaneously with the plateau position. These intervals are believed to cover the entire plateau.

The distribution of the plateau lengths was analyzed by constructing the corresponding histograms. The minimum plateau length $L_{min} = 0.1$ nm was used as one criterion for the selection procedures and, consequently, the resulting distributions were limited by this value. No histogram maxima were seen. Very few plateaus longer than 0.2 nm were observed in our experiments. No plateau length quantization could be determined.

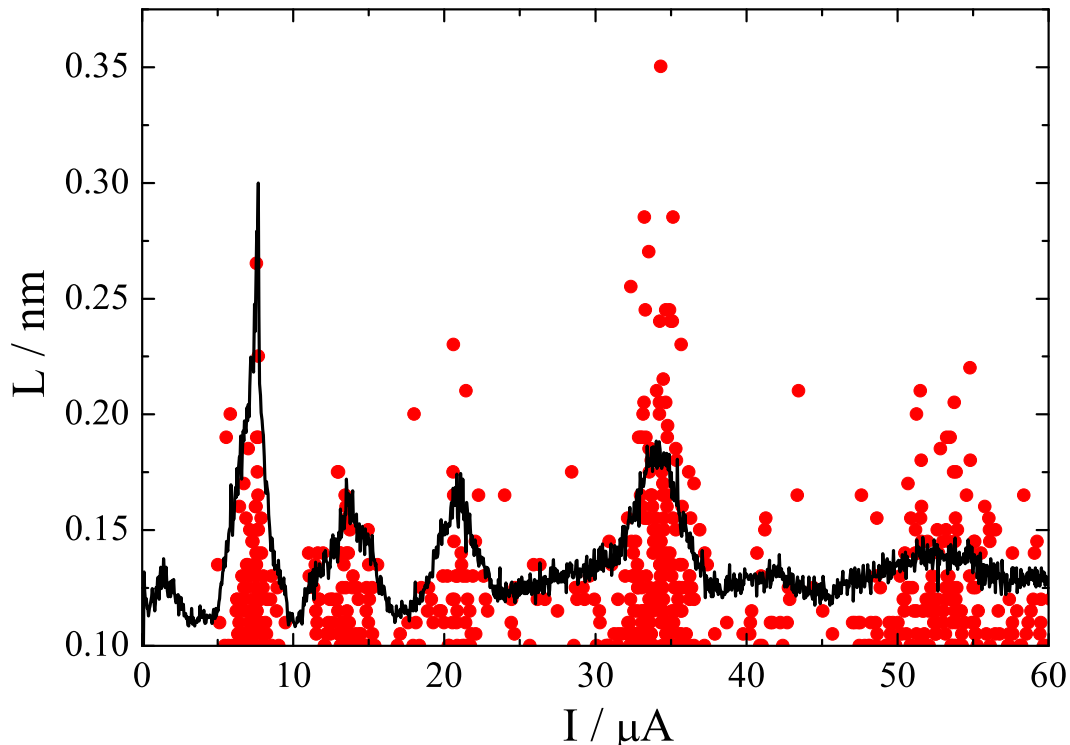


Fig. 5–7: Current (I) – length (L) correlation for the plateaus found on 1000 curves recorded in 0.1 M H_2SO_4 , $E_s = 0.115$ V, $E_t = 0.015$ V (red points). Every red point represents a single plateau (659 data points in the range shown). The black line represents the overlaid histogram obtained from the all-data histograms (Fig. 5–3A).

The plateau length histograms demonstrated an exponentially decaying distribution: $P(L) \propto \exp(-L/L_d)$. A factor L_d was determined as 0.02...0.03 nm independently of the applied bias potential and the environment. An average plateau length $L_{av} \approx 0.12 - 0.13$ nm was obtained. As it is expected for the exponentially distributed variable L with a minimum value L_{min} and a decay distance L_d , the average value of the plateau length $L_{av} = L_{min} + L_d$ is indeed obtained. The latter demonstrates the self-consistency of the results.

An intriguing picture was obtained upon construction the plateau current vs. plateau length correlation plot (Fig. 5–7). Here, every red point represents a pair of current (x) and length (y) values corresponding to a single plateau. Its appearance is similar to that of a current histogram. The points on the plot form distinct groups. Their “shape” correlates well with the peaks in the corresponding current histogram, overlaid as a black curve. For the junctions with the conductance close to that at the current histogram peaks, both amount and length of the plateaus increase. This indicates a correlation of the electrical and mechanical properties of the QPC formed: junctions having a conductance closer to integer multiples of the quantum conductance are more stable. This observation correlates with the results of simultaneous conductance and force measurements in Au QPCs [98].

5.7 Conclusions

The gold atomic junctions represent a well studied system with a known single junction conductance, which is a good tutorial system for conductance studies. The Au QPCs were formed between a Au(111) substrate and a Au STM tip. The experiments were carried out in Ar atmosphere, in mesitylene and in aqueous solution of 0.1 M H_2SO_4 at positive and negative surface charges. Individual retraction current-distance traces exhibit characteristic plateaus and steps corresponding to stable configurations of QPC and their breaking.

An overview of approaches used to statistically analyze stretching data was presented. The automated analysis procedure developed by me was introduced. One set of the experimental data was analyzed according to the procedures described. The same approaches will be used further to analyze the conductance of molecular junctions.

The pronounced peaks in histograms correspond to preferable currents through the junctions with an integer number of conductance channels open. Besides equally spaced low current peaks, I found additional peaks which could be attributed to “magic” numbers (5, 7 or 8, 10 or 11, probably 14 or 15 and 18 or 19) of a fundamental value of the current. The latter reflect the enhanced stability of QPCs with certain electronic configurations [385].

Currents corresponding to a single conductance channel were determined from the position of the first peak in the histogram and from the slope of the plot peak position vs. peak number using the low index peaks only. The current-bias voltage curves are linear in the studied range of bias voltages and show no significant medium effect. The results are in good agreement with other experiments and theoretical predictions.

For a chosen plateau selection criteria (same for all analyzed data sets) all histograms of the plateau lengths showed an exponentially decaying distribution with self-consistent values of the decay lengths and average lengths. No effect of medium or adsorbate on the mechanical stability of the contact was found. A correlation plot of

the plateau current *vs.* plateau length demonstrated an appearance similar to the current histogram. This reflects an enhanced mechanical stability of the junctions with current close to multiples of a fundamental value.

The results and procedures presented for the conductance studies of Au QPC are used as references for further studies of the conductance in molecular junctions.

Chapter 6

Conductance of gold-alkanedithiol-gold junctions

6.1 Introduction

One important aspect of molecular electronics is the formation of the contact between a molecule and a metal electrode. The natural properties of different functional groups to bind to metals could be exploited to create metal-molecule contacts. At present, the most widely used approach is to create a contact between a thiol (SH) group and gold. Studies of ET in molecular systems requires molecule “trapping” in a metal-molecule-metal junctions. In this case the formation of two contacts requires two terminal thiol groups. To establish a technique of conductance measurements in SMJs, I started from the investigations of a series of alkanedithiols, which are the simplest molecules with two terminal thiol groups.

6.1.1 Assembly of alkane(di)thiols on Au

Since it was first shown [401] that disulfides spontaneously form closely packed SAMs on Au, films of molecules attached by sulfur atom to a Au surface attracted great attention. Soon it was demonstrated [402] that disulfides adsorb dissociatively, while a molecular adsorption of thiols occurs. During the following two decades, adlayers of alkanethiols (nS) with different terminal groups on single crystal and polycrystalline Au surfaces were studied intensively and exploited for various purposes [89–91, 403, 404].

Strong binding of the thiol group to gold allows the deposition of SAM from both solution and gas phase [90]. Typically, simple immersion of the sample into an ethanolic solution of the adsorbate followed by rinsing ensures binding of the molecule to the surface. Alternatively, deposition from the gas phase under UHV conditions may be used.

Kinetic studies of the nS SAM growth from solution demonstrated an exponential (Langmuir-type, *cf.* Sec. 4.4.2) behavior with deviations, attributed to the multiple stages of monolayer formation and intermolecular interactions [89, 90]. For the typically used solutions of micromolar concentration two steps of monolayer formation were observed [405–407]. The first very fast step corresponds to the chemisorption of the thiol headgroup. It is well described by Langmuir kinetics with coverages typically reaching 0.8...0.9 of the maximum value within a few minutes. The second step can be described as a “surface crystallization” and is related to the straightening of the hydrocarbon chains and reorientation of the terminal groups.

Early investigations of long-chain nS on Au(111) employing infrared absorption spectroscopy (IRAS) [408, 409], TEM [410, 411] and helium diffraction [412] tech-

niques suggested a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of the adlayer. The *n*S adsorb in *all-trans* conformation with the molecular axis tilted by *ca.* 30° from the normal direction. This conclusion was supported by calculations [413]. A similar structure was proposed for terminally substituted 1-hexadecanethiol $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ [408], with a tilt angle of $28\text{--}40^\circ$. STM [414–416] and AFM [417] investigations confirmed the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of densely packed monolayers of *n*S.

Later helium diffraction [418], grazing incident x-ray diffraction [419] and STM [415, 416] studies demonstrated a $c(4 \times 2)$ superlattice with a basic $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, which appearance was attributed to the variation of the twist angle of hydrocarbon chains. Two different orientations of methylene chains were also observed by IRAS [420] at low temperatures. *Ex situ* AFM observations [421] on freshly modified samples revealed a $c(4 \times 2)$ superstructure on well-ordered islands during the ripening of the adlayer in the time scale from several hours to a few days.

A “striped” low coverage phase with flat oriented molecules was observed at the initial stages of adlayer growth, when diluted ($c < 1 \mu\text{M}$) solutions were used for the assembly [422–424]. Upon the coverage increase, a 2D phase transition leads to islands of the high coverage ordered phase. The same striped phase was observed in case of slow desorption of *n*S from a high coverage phase [425, 426]. Results of the chain-length dependence of the distance between the stripes suggest an orientation with fully stretched methylene chains and head to head orientation of the sulfur atoms on the surface.

In case of vapor deposition no kinetic features of adsorbed phase evolution (orientation or conformation changes) at fixed coverage were found [427]. At very low coverages the adsorbate behaves like a 2D gas. Islands of the ordered striped phase appear as the coverage increase. STM experiments [428, 429] demonstrated the existence of a few striped phases evolving with an increase of coverage. Striped domains slowly transform into a disordered liquid-like phase with further increase of coverage, which finally transforms to the high coverage phase described above.

CV studies of *n*S SAMs on Au(111) [409] demonstrated a capacitive behavior without any redox features. The limits of the electrochemical stability are defined by the oxidative and the reductive desorption at high positive and negative potentials [430]. A complete independence of the capacity on the electrolyte composition and the scan rate was observed for 1-undecanethiol $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$ and longer molecules [409].

The structure, electrochemical property and preparation procedure for the SAMs of terminal-substituted *n*S, in particular *Sn*S, on Au is similar to that of *n*S [403]. Structure [431–434] and electrochemical properties [430, 433–435] of *Sn*S on Au(111) were studied by various methods including CV [433, 434], impedance spectroscopy [434, 435], SPM in solution [433, 434] and under UHV conditions [431], X-ray scattering [432] and helium diffraction [432].

The kinetics of 1,8-octanedithiol (S8S) adsorption on a Au surface in ethanolic solution was studied by capacitance measurements [435]. Similar to *n*S, a two step adsorption procedure was suggested. Depending on the concentration, the first step of adsorption was described by the models of pure diffusion, diffusion controlled Langmuir and pure Langmuir kinetics. However, the rate constants estimated were higher than those for *n*S, which was accounted for by a geometric factor.

Depending on the preparation conditions, a high or a low coverage phases were observed for *Sn*S. The deposition of *n*S and *Sn*S on Au(111) from a vapor and solution was studied by UHV STM [431]. An ordered structure of vertically oriented molecules

was found for *n*S SAM deposited from the solution. For the SAM of *Sn*S prepared under the same conditions, no ordered structure was observed. The *Sn*S deposited from the vapor was seen to form a “striped” phase with a flat orientation of the molecules. Another multitechnique study [432] demonstrated a complicated structure of the S6S SAM on Au(111) with two uniaxial incommensurated phases.

No ordered structure of the high coverage *Sn*S SAM was observed by *in situ* STM as well. The striped phase appeared when the coverage was decreasing at the onset of reductive desorption or after oxidative readsorption [433, 434]. The reductive desorption peaks of S8S and S6S SAMs are shifted in a negative direction and have the higher charge compared to 1-octanethiol (8S) and 1-hexanethiol (6S), respectively. These phenomena as well as a lack of the long-range order were attributed to the random formation of disulfide bonds at the free end of *Sn*S, promoted by the ambient oxygen [434]. This conclusion is additionally supported by the observation of the oxidative formation of a *Sn*S bilayer [184].

The similarity between *n*S and *Sn*S allows to assume an almost vertical orientation of the latter at a full coverage. As it was mentioned above, in this case it is not possible to resolve the interfacial structure by STM. Therefore, an independent confirmation is needed. Most of the investigators come to the conclusion that the structure of the high coverage phase of *Sn*S is similar to that of the *n*S. It is supported by the existing similarities between adlayer capacities for homological *n*S and *Sn*S [433–435]. The small variation of the tilt angle of the alkane chain with different terminal group attached [408] allows to assume the same structure of the *Sn*S SAM.

6.1.2 ET through the methylene chain

The ET through the methylene chain was studied on the macroscopic, mesoscopic and single molecule levels. The access to the single molecule properties may be, in principle, provided by experiments with ensembles of the molecules. However, the fundamentals of the macro- and mesoscopic experimental approaches are not well transparent. A special attention must be paid to avoid experimental artefacts and to distinguish between single molecule and cooperative properties.

A summary of experiments under discussion was recently presented in [102, 436, 437]. All results obtained demonstrated an exponential decay of the ET rate constant *k* with the number of CH₂ units *n* or the length of the molecule *d*. The latter is calculated by referring to an estimated C–C bond length of 0.125 nm:

$$k = k_{0,d} \exp(-\beta_d d) = k_{0,N} \exp(-\beta_n n) \quad (6.1)$$

The exponential distance dependence is considered as an indication of ET following a tunneling mechanism. This experimental conclusion was supported by the simulations [105, 109, 438–441].

Electrochemical approach

Historically, first studies of ET through methylene chains were concentrated on the “blocking” of electrochemical reactions by the SAMs. Experiments employing *n*S SAMs on gold [442, 443] and mercury [444] electrodes were carried out. Here solution based redox-active species act as donors or acceptors of electrons. The rate of ET is

expressed as a rate of the electrochemical reaction on the modified interface. The absence of adlayer defects has to be ensured in order to assign the measured current to an ET step through an insulating film, rather than to the reactant penetration through the residual defects.

A decay constant β_n of 1.05...1.2 was found independently on electrode potential and redox couple used [442, 443]. Studies on expanded monolayers of *n*S on mercury allowed to estimate the coupling between adjacent hydrocarbon chains [444], *e.g.*, the ET between different molecules of the adlayer.

In a modified electrochemical approach redox-active assemblies were used. An example is ferrocene, bound to the terminal atom of *n*S as an electron “source” or “drain” [445–448]. Similar to the previous studies, an exponential decay of the rate constant was obtained with as $\beta_n = 1.1 \dots 1.2$ being independent on the temperature [447].

Metal-adlayer-metal assemblies

ET properties of macroscopic metal-adlayer-metal assemblies formed by *n*S were studied in so-called “mercury junction” experiments [449–453]. A *n*S SAM is formed on the surface of a small mercury drop. The latter is then brought in contact with a SAM-modified or a bare surface of another mercury drop, mercury pool or a solid metal electrode. These experiments led to β_n values ranging between 0.9 to 1.1.

Studies employing nanodevices [102, 398, 436, 454] with 500...1000 molecules allow investigations of SAMs of *n*S or *Sn*S in more defined mesoscopic junction. The chain lengths dependence of the tunneling current through SAM gave values of $\beta_n = 0.9 \dots 1.0$.

Scanning probe – SAM contact

The SPM approach to the creation of the MJs is outlined in Sec. 2.6.3. The contact created between the scanning probe and the SAM [106, 128, 130, 131, 136] allows to study the conductance of junctions formed by 50...100 molecules [437]. In most investigations CP AFM was used to control the contact formation independently of the measured current [437]. Otherwise a quite complicated data analysis is required to decouple “through-space” and “through-bond” tunneling [136].

SAMs of *n*S on gold were probed by gold-covered CP AFM cantilever at constant force. The exponential dependence of the conductance of such MJs on the molecule length gave $\beta_n \approx 1.15$ [131]. A similar approach [130] gave lower values of $\beta_n = 0.8 \pm 0.2$ after correction for the effects caused by interactions of the probe with the adlayer.

An interesting result was obtained during the studies of the ET through the S8S SAM upon its contact with an CP AFM probe [130]. Three different kinds of *I* – *V* curves were observed. Curves of the first type were often seen at first contact and are generally similar to that for the *n*S SAMs. Curves of the other two types were accompanied by a force hysteresis and found to be independent of the contact force. The low bias conductance was *ca.* 10 times higher than that for the curves of the first type. The different behavior was attributed to the formation of a “physical” and a “chemical” contact between the probe and the molecules.

Gold-*Sn*S-gold MJs with a small number of molecules were created by their incorporation into the insulating SAM of *n*S [147]. To facilitate the contact formation, a

Au nanoparticle (NP) was attached to the free thiol groups and contacted by CP AFM probe. ET studies in this assemblies gave $\beta_n = 0.57 \pm 0.03$, which is lower than typical values from other experiments.

Single molecule experiments

At present time the ET through the SMJ incorporating *SnS* is well studied in MCBJ [127, 393] and SPM [109, 146, 150, 177, 179, 393, 399, 455–465] configurations. The *SnS* molecules may be also embedded in molecular-sized metal gap, formed by electromigration or electrochemical dissolution/deposition [456]. The experiments of the latter type, however, are still under development.

The parameter β (Eqn. 6.1) can be estimated easily from various kinds of ET studies in a series of *SnS*. It was shown above that a very good agreement exists between values of β obtained from macroscopic and mesoscopic experiments. When the experiments described in this chapter were started, there was a pronounced difference between results on the single molecule level [127, 150, 159, 179, 455, 461], both in the absolute values of the single molecule conductance as well as in its dependence on the methylene chain length. We started our experiments hoping to resolve this contradictions.

6.2 Electrochemical characterization

The high coverage S8Ss SAM on Au(111)-(1 × 1) were characterized by CV and the complementary immersion technique (Sec. 3.8.3). The potential dependence of the EDL charge measured by the latter is shown as red circles in Fig. 6–1. The adlayer capacitance is estimated as $2.9 \pm 0.1 \mu\text{F}\cdot\text{cm}^{-2}$. Similar values ($2.5 - 2.7 \mu\text{F}\cdot\text{cm}^{-2}$) were found in [434, 435] from CV and impedance spectroscopy measurements.

The separate single sweep CVs were recorded using a scan rate $r = 10 \text{ mV}\cdot\text{s}^{-1}$ in 0.1 M H_2SO_4 (positive direction) and 0.1 M NaOH (negative direction) to explore the large potential window of Au(111) ideal polarizability in these two electrolytes. The results are presented in Fig. 6–1. Three characteristic areas of potentials can be distinguished. Close to the PZC a purely capacitive response of the adlayer is observed (Fig. 6–1, curves *a, b*). The SAM capacitance estimated from CV as $\approx 3 \mu\text{F}\cdot\text{cm}^{-2}$ is in agreement with the value obtained from the immersion experiments.

The CV recorded in 0.1 M NaOH (Fig. 6–1, curve *c*) exhibits a characteristic reductive desorption peak (negative-going scan) and a corresponding readsorption feature (broad peak on the positive-going scan). It is essential to use alkaline solutions in order to shift the onset of hydrogen evolution to more negative potentials. The position of the reductive desorption peak of -1.05 exactly matches results obtained in 0.1 M KOH [434]. The corresponding peak charges amount to $120 \mu\text{C}\cdot\text{cm}^{-2}$ and $109 \mu\text{C}\cdot\text{cm}^{-2}$ respectively. However, the one-electron reduction of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ -arranged adlayer on Au(111) would result in a charge density of *ca.* $77 \mu\text{C}\cdot\text{cm}^{-2}$. The excess charge is attributed to the simultaneous formation of ionic EDL upon the desorption of S8S [183].

A single electron reduction of the thiol linker is assumed to take place during the reductive desorption of *nS* [430], although the exact charge distribution between the Au and S atoms is still a subject of discussion. The comparison of the reductive desorption peaks for the SAMs of 8S and S8S [434] demonstrates a shift of the peak potential in the negative direction and an additional reduction charge. The latter was attributed to the

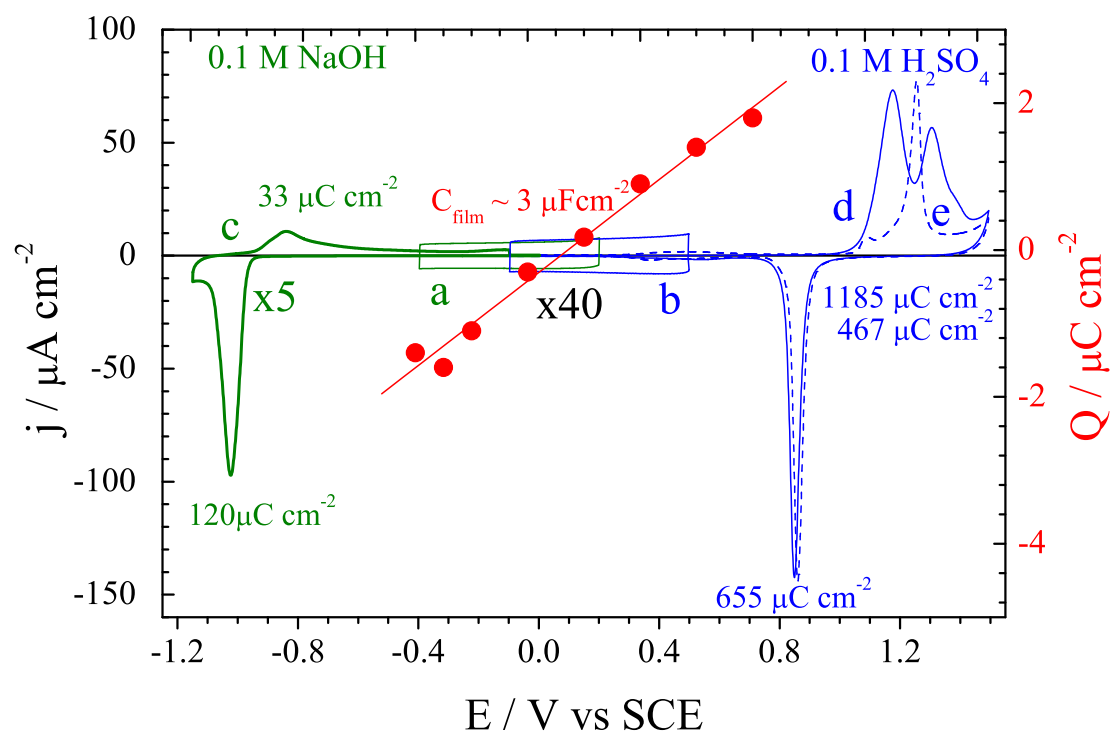


Fig. 6-1: CVs (scale on the right side) of a high coverage SAM of S8S on Au(111)-(1 × 1). (a) double layer region, 0.1 M NaOH, enlarged by 40 times; (b) double layer region, 0.1 M H₂SO₄, enlarged by 40 times; (c) reductive desorption, 0.1 M NaOH, enlarged by 5 times; (d) oxidative desorption, 0.1 M H₂SO₄, first scan; (e) oxidative desorption, 0.1 M H₂SO₄, second scan. Scan rate 10 mV·s⁻¹. The red circles (scale on the left side) indicate the EDL charge as obtained from immersion experiments (Sec. 3.8.3). Numbers indicate the surface charge obtained by the integration of the corresponding peaks (see main text).

formation of intralayer disulfides in the presence of ambient oxygen. An only slightly higher charge of the S8S reductive desorption peak confirms that our procedure yields monolayers with a comparable composition.

The broad peak of the oxidative readsorption has the characteristic shape of the CV response of a diffusion-controlled reaction. The peak maximum and charge were found to be -0.84 V and 33 μC·cm⁻², in comparison with -0.8 V and 55 μC·cm⁻² reported in [434]. I attribute the difference to the different scan rates (10 and 20 mV·s⁻¹).

The first scan toward positive potentials as recorded in 0.1 M H₂SO₄ (Fig. 6-1, curve *d*) shows a double peak with a higher maximum at 1.17 V and a lower one at 1.3 V. It is attributed to the adlayer's oxidative desorption superimposed by the gold surface oxidation [430, 433]. The total charge of the peak is 1185 μC·cm⁻². The subsequent sharp reduction peak at 0.85 V with a charge of 655 μC·cm⁻² is similar to that observed for other molecules with thiol linkers as well as for the bare gold surface [430, 433], and indicates the complete removal of the organic adlayer. The oxidation peak of the second positive going potential scan (Fig. 6-1, curve *e*) gives rise to a single maximum at 1.25 V with a charge of 467 μC·cm⁻² and corresponds to the oxidation of the bare disordered gold surface (*cf.* Fig. 3-3). Further potential sweeps did not change the CV.

The difference between the oxidation peak charges of the first and of the second scan amounts to 718 μC·cm⁻². It is attributed to the charge of the organic adlayer

oxidation and simultaneous EDL formation. The positive shift of the gold oxidation peak during the first scan and a small (≈ 10 mV) negative shift of the surface reduction peak with respect to that recorded during the second and each subsequent scan indicates an enhanced stability of the gold surface in the presence of the adsorbed monolayer. The charge of the adlayer oxidation is *ca.* 6 times higher than that obtained for a single electron reductive desorption and indicates the oxidation of the thiol group to a high positive oxidation state.

The oxidative and the reductive desorption processes determine the stability range of the organic adlayer.

6.3 SAM structure

Different S8S adlayers were formed on an unreconstructed Au(111)-(1×1) surface by variation of the preparation conditions (Sec. 3.4.5). A low coverage SAM was formed by a short-time exposure of the Au(111) substrate to the S8S-containing solution. Fig. 6–2A,B demonstrates its typical big scale STM images. Holes with a diameter of $4 \dots 9$ nm and 0.25 ± 0.01 nm depth are observed in the middle of large terraces. They are absent at the smaller terraces. The hole edges often resemble straight lines with an angle of 120° between them. The formation of holes and the alignment of steps is not observed in the absence of S8S, and could be therefore attributed to the assembly of the S8S-containing adlayers.

Characteristic brighter and darker “stripes” are observed on the terraces (Fig. 6–

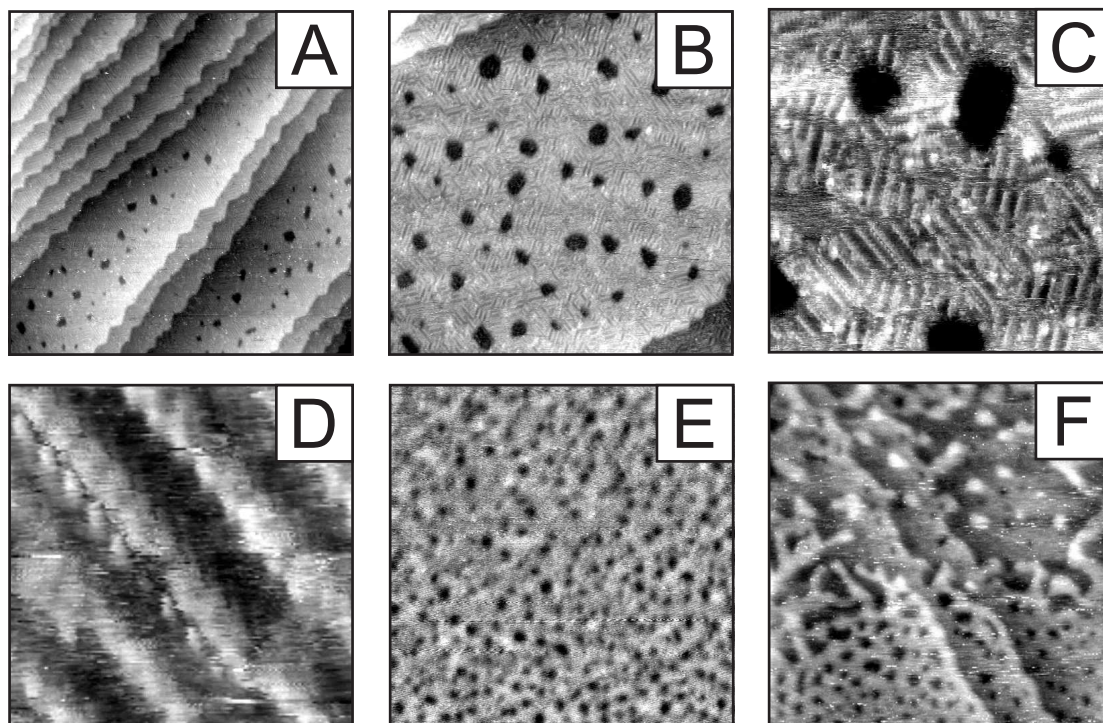


Fig. 6–2: STM images of S8S SAM on Au(111)-(1×1) surface: (A–D) Low coverage striped phase: (A) 200×200 nm; (B) 100×100 nm; (C); 30×30 nm; (D) 5×5 nm. (E–F) High coverage disordered phase, 100×100 nm, before and after the stretching experiments (different areas).

2B,C). The domains of the striped phase are rotated by 120° . The edges of terraces are aligned with respect to the orientation of the stripes. A closer inspection reveals that the same stripes as found on terraces, exist inside the monatomically deep holes. A striped phase with the same properties was created by the partial reductive desorption of a high coverage SAM [434] or by vapor deposition [431].

High resolution images (Fig. 6–2D) represent stripes as rows of round features with brighter contrast, separated by darker lines. The distance between the bright features is *ca.* 0.5 nm, which corresponds to $\sqrt{3}$ of the interatomic distances of Au(111). The distance between neighboring stripes is estimated as 1.1 ± 0.1 nm. A comparison of the observed SnS structures [431–434] demonstrates that the distance between stripes increases with chain length and correlates with the length of the SnS molecules. The distance between similar contrast spots within one row remains close to 0.5 nm. The bright stripes are attributed to pairs of sulfur atoms [432].

The high coverage phase (Fig. 6–2E) exhibit no long-range order [431, 433]. In comparison with the low coverage phase, the density of holes is higher. The holes are round with a diameter of 4...7 nm. As it was mentioned above, the lack of the ordering is due to the formation of disulfide bonds between the free thiol groups [434].

We did not carry out experiments on the transition between the high and lower coverage phases. However, the adlayer preparation conditions, as well as the experimental results reported by other groups, allow ascribing the observed surface patterns to high and low coverage phases with a coverage of $\theta \approx 1$ ML and $\theta \ll 1$ ML, respectively.

6.4 Stretching experiments

The conductance of Au-S8S-Au MJs was studied by the stretching technique. Four sample/medium combinations were used:

1. disordered high coverage SAM of S8S on Au(111) in 1 mM S8S solution in mesitylene;
2. disordered low coverage SAM of S8S on Au(111) in pure mesitylene;
3. disordered high coverage SAM of S8S on Au(111) in 0.05 M aqueous KClO₄;
4. disordered high coverage SAM of S8S on Au(111) in Ar atmosphere.

I will describe in detail one experiment carried out under conditions (1), and discuss than the differences due to the variation of experimental conditions.

6.4.1 Formation and breaking of SMJs

The scheme of the stretching experiment is described in Sec. 3.7.4. In all stretching experiments, the S8S molecules were attached to the sample. When S8S is dissolved in the solution (experimental conditions 1), the high coverage S8S monolayers assemble on both the Au tip and the Au(111) substrate surface.

After the tip approaches the sample, their configuration is fixed for a certain time. The molecules squeezed in between may spontaneously form a gold-thiol bond and bridge two electrodes [179]. Upon the tip withdrawing, characteristic plateaus, separated by sharp steps, are observed in the $I - z$ curves (Fig. 6–3). The plateaus typically

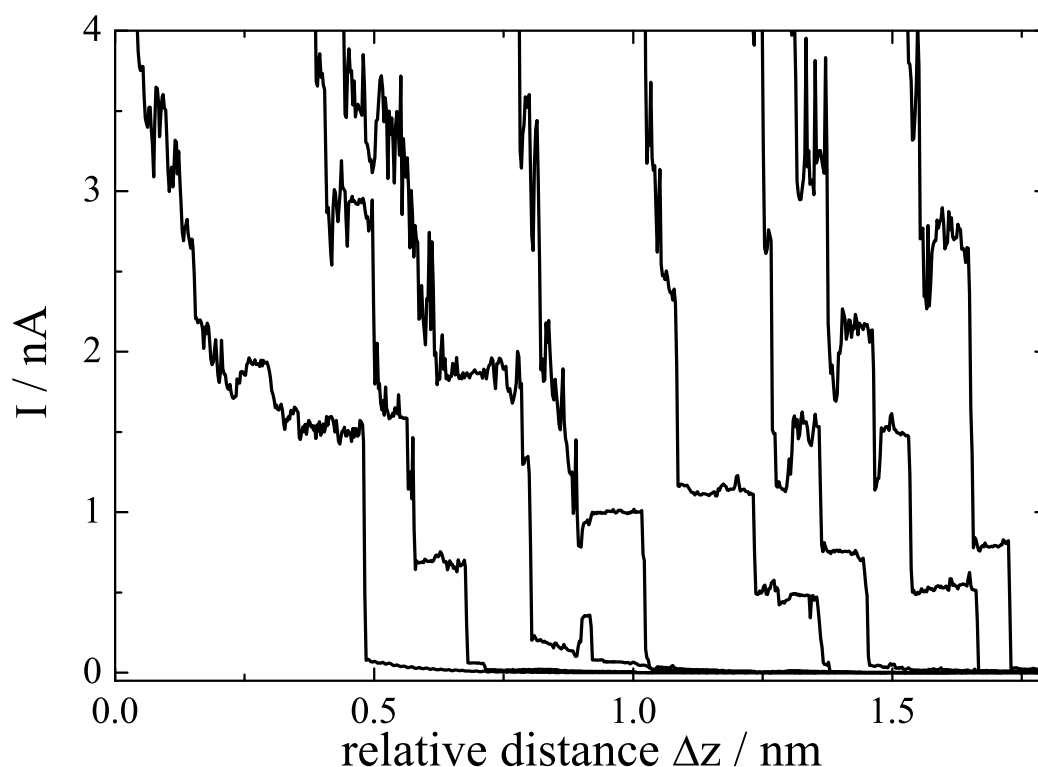


Fig. 6-3: Stretching curves recorded in 1 mM solution of S8S in mesitylene, bias voltage $V = 0.2$ V.

appear at tip-sample distances higher than that at the beginning of the stretching cycle. Under these conditions the tunneling current is negligibly small, and after a last plateau the current is decreasing to zero.

The shapes of the $I - z$ curves are similar to that obtained in the Au QPC stretching experiments (*cf.* Sec. 5.3). However, the values of the plateau currents are 3...4 orders of magnitude lower than those for the Au QPC. In order to clarify the origin of the “plateau and step” features on the tip retraction curves, the same procedure was employed in reference experiments. First, upon the tip approach to the surface (Fig. 3-11A), the $I - z$ curves are exponential in an accessible current range. The plateaus and the steps were not seen upon tip withdrawing after the approach to a bare gold surface or ionic adlayers. In other experiments reported [179], the steps on the stretching curves were observed only for molecules with two thiol groups. In case of experiments with S8S SAM and W or Pt/Ir tips, only very short plateaus were occasionally observed. Therefore, the plateaus and the steps were attributed to the formation of stable Au-S8S-Au SMJs and their breaking. The plateau current is thus taken as a current flowing through one or few SMJs.

Unlike in case of the “STM break-junction” approach [150], we are trying to explicitly avoid a mechanical interaction of the tip with the substrate, *i.e.*, QPC formation. The latter causes much stronger perturbation of the system than the gentle approach. For the robust SnS, the steps on the $I - z$ stretching curves were found to be similar in stretching experiments both with and without “tip crash”. [150, 171]. However, the situation may be different for other, more sensitive substances.

The evolution of the system in real time and space was followed by imaging the surface. After a series of stretching experiments, Au clusters were formed only occasionally. At the same time, the appearance of the adlayer changed. A typical STM

image recorded after multiple stretching experiments is shown in Fig. 6–2F. The appearance of the SAM suggests a removal of the S8S molecules from the adlayer during the “pulling” process without formation of a tip-surface contact. The former is also supported by the strong decrease of the amount of curves with pronounced plateaus and steps upon repetitive stretching at a fixed probe position.

6.4.2 Statistical analysis

The curves such as presented above were analyzed statistically in order to extract the values of the SMJ conductance. I used sets of typically 1000 or 2000 stretching curves for a given experimental conditions. Histograms build from all data points of the stretching curves (*cf.* Fig. 5–3A), gave no sign of peaks, despite of the regularly observed plateaus in the single stretching curves (Fig. 6–3). Therefore, only the values of plateau currents were used for the histogram construction. They were manually extracted from the original stretching curves. A minimum plateau length $L_{min} > 0.05$ nm and a current variation threshold of 5% were used as plateau selection criteria. The independent plateau selection was carried out by different persons, and the results did not differ.

Plateau position histograms were build without any weighting, *e.g.*, by the plateau length (Sec. 5.4). A histogram obtained for the experiment described above (Fig. 6–3) is shown in the Fig. 6–4. The average number of selected plateaus per stretching event was close to 0.5.

Histograms for all experimental conditions studied exhibit a pronounced first peak

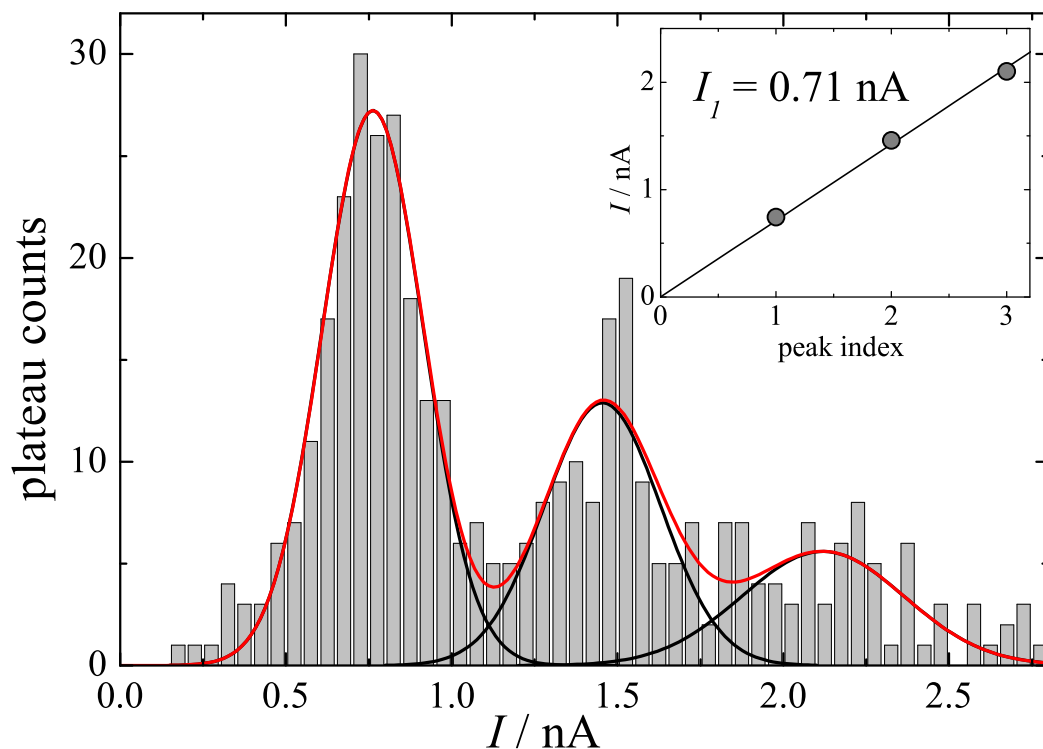


Fig. 6–4: Histogram built from the curves such as presented on Fig. 6–3, bin width is 0.05 nA. The red line represents the fit by a series of Gaussian curves (black lines). Inset: plot of the Gaussian peak position *vs.* peak index.

and few higher index peaks. The positions of the peaks were obtained from fits of the histogram with a series of Gaussian curves (Fig. 6–4). Two or three peaks were resolved for every set of data. The first peak in a series appears always as the highest one. The position of the first peak was attributed to the current flowing through a SMJ, while further peaks were assigned to an integer number of molecules connecting tip and substrate. Linear peak position *vs.* peak index dependencies were found. Their slopes were taken as an estimate of the current through the SMJ under the respective experimental conditions.

6.4.3 Media and bias effect

The currents of the S8S SMJ, as obtained for all experimental conditions studied, are shown in Fig. 6–5. They fall onto one line in the studied range of bias voltage $|V| < 0.2$ V. At a higher bias voltages, a non-linear current increase is observed. The results show no concentration (low or high coverage) or media (mesitylene, aqueous electrolyte, argon) effects. The SMJ conductance of 3.6 ± 0.1 nS was estimated from the linear fit of the all data points *vs.* bias voltage dependence.

The variation of the experimental conditions affected mostly the probability to form MJ during the adlayer contact step (Fig. 3–11B). The latter is determined by a number of factors, including the available time and geometry of the electrodes, but mostly depends on the amount of the molecules in the gap. This is in strong contrast with the QPC formation occurring at every approach of the tip to the sample.

The probability to form the SMJs was estimated as a number of selected plateaus per stretching curve. For conditions (1) this yield was 0.4...0.6, while a value of *ca.*

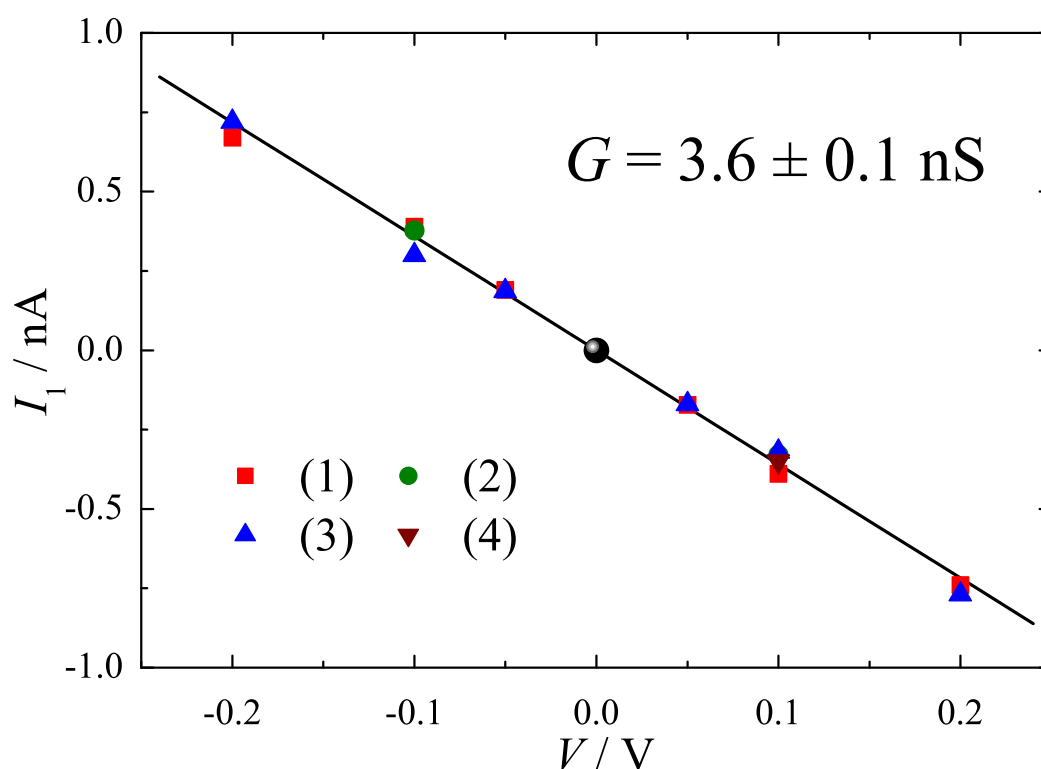


Fig. 6–5: Plot of the conductance current in S8S SMJ *vs.* bias voltage for different experimental conditions (see before).

0.1 and lower was estimated for other experiments. The exponentially decaying $I - z$ curves were often observed for conditions (2–3), but only few of them appear during the whole experiment under conditions (1).

The difference is clearly due to the presence of the high concentration of S8S molecules in the solution. The disordered high coverage SAMs are formed at both electrodes. Thus, a MJ may be formed by the molecules originally attached to either of them. Dissolved molecules may also form MJs or replace the molecules pulled out of the adlayer (Fig. 6–2F).

6.5 Chain length and junction geometry effect

Complementary stretching experiments with other alkanedithiols were carried out using only condition (1). The latter were selected due to the higher probability of the MJs formation, while the conductance of SMJs is unaffected by the variation of the experimental conditions.

In my original experiments, the results for S9S and S10S were similar to that for S8S. The values of the SMJ conductance were found to decrease with chain length. However, new features were observed in the S5S and S6S stretching curves. They exhibited two types of plateaus with pronounced differences in the current values. A few examples of stretching curves for S6S are shown in Fig. 6–6. Two types of plateaus give rise to two sets of peaks in the histograms (Fig. 6–7), which correspond to two values of the SMJ conductance.

The SMJ conductance determined for S8S, S9S and S10S and the higher values for

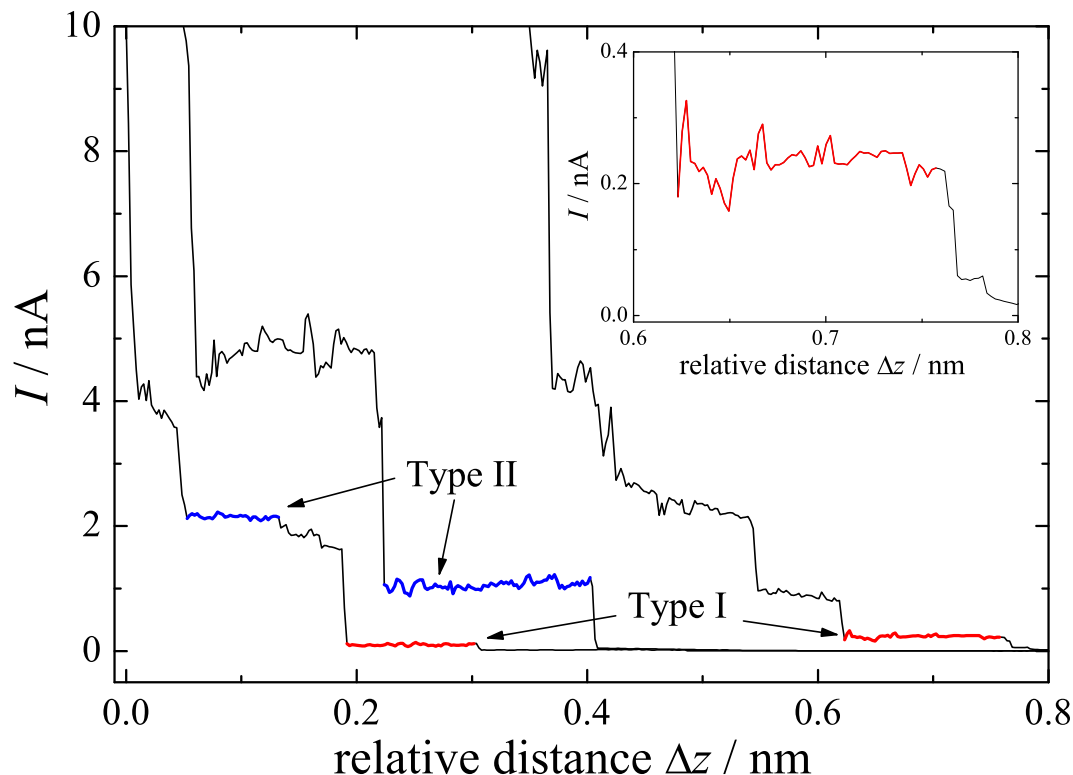


Fig. 6–6: Stretching curves of S6S SMJs, bias voltage is 0.05 V. The marked plateaus correspond to lower (type I, red) and higher (type II, blue) values of the SMJ conductance. The inset displays an enlarged plateau of type I.

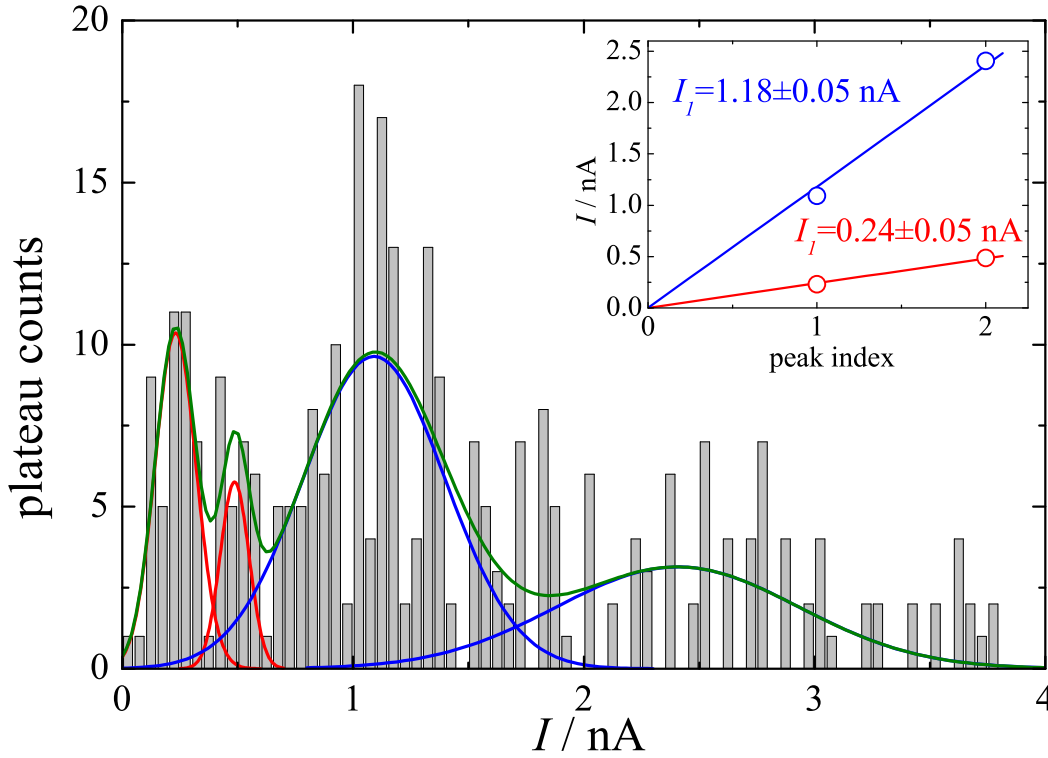


Fig. 6–7: Plateau position histogram built from curves such as in Fig. 6–6, bin width is 0.05 nA. The data were simultaneously fitted by a series of Gaussian curves, attributed to the SMJ of types I (red) and II (blue). The sum curve is shown in green. The inset shows the peak position vs. the peak index dependence for two series. The values of I_I are indicated by the corresponding color.

S6S and S5S, are very close to the “low” conductance values reported in [455]. The parameter β_n (Eqn. 6.1) estimated for this series as well as for a “high” conductance series in [150, 455] was determined as 1.00 ± 0.04 . The latter is in good agreement with the β_n values obtained in macro and mesoscopic experiments (Sec. 6.1.2). Significantly lower values of the SMJ conductance and $\beta_n = 0.52 \pm 0.05$ were reported in [179]. A similar value of the β_n was also reported from CP AFM experiments ([147], see Sec. 6.1.2). To add to the confusion, the S_nS SMJ conductance was reported to be (a) temperature dependent due to the temperature-dependent distribution of molecular conformations [460]; (b) temperature independent due to the ET by tunneling over the methylene chain [455].

To resolve the existing disagreement, we performed a detailed study of the conductance of S_nS SMJs. The experimental results were compared with the *ab initio* transport simulations (F. Evers, A. Bagrets, Institute of Nanotechnology, Forschungszentrum Karlsruhe) within the framework of an ongoing collaboration. The summary of the experiments and calculations [109] is given in Fig. 6–8.

The careful investigation of the SMJ conductance in a wide current range (Fig. 6–8A) demonstrated the existence of three conductance series, which are further referred to as “low” (L), “mid” (M) and “high” (H). The series H and M are exponentially dependent on the chain length with $\beta_n \approx 1$. Although the series L does not exactly follow an exponential dependence, $\beta_n \approx 0.55$ may be estimated.

The absolute values of the SMJ conductance were compared with those found in other single-molecule experiments. Our H series corresponds to the high SMJ conduc-

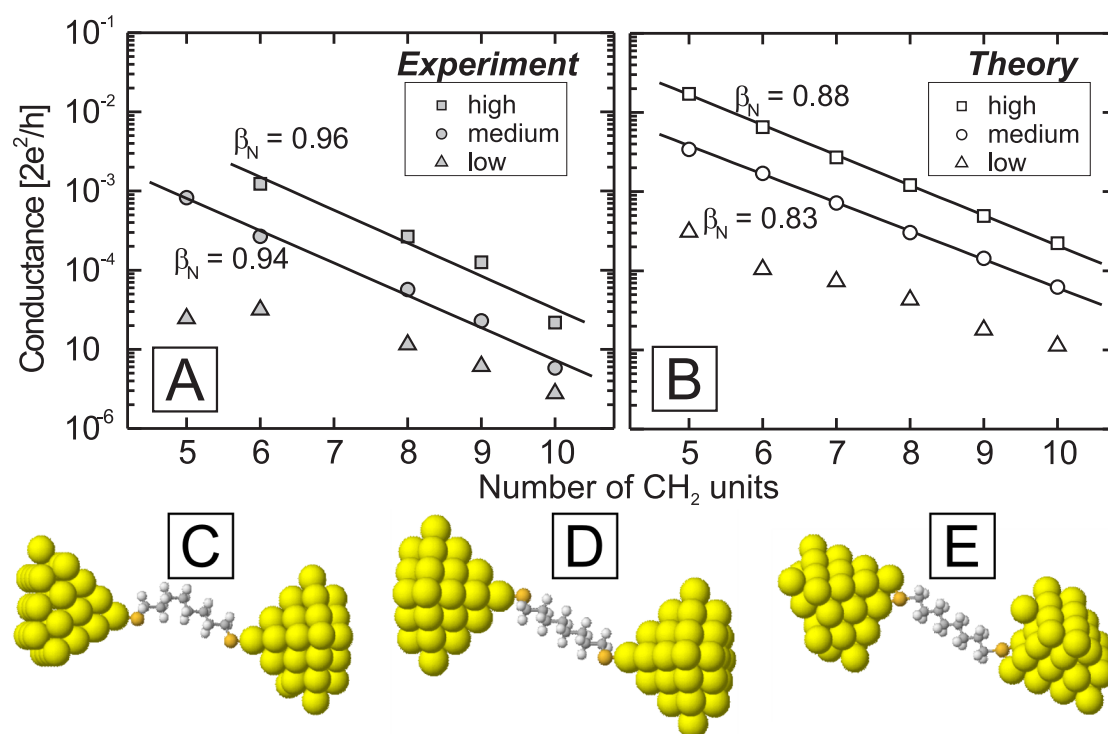


Fig. 6-8: Summary of stretching experiments and complementary simulations [109]. (A, B): Experimental (A) and simulated (B) chain length dependence of the conductance in the SnS SMJs. (C–E) The relevant SMJs configurations (see main text).

tance reported in [150, 455]. As it was mentioned above, the M series corresponds to the low conductance series of [455]. The L series, in turn, corresponds to the series reported in [179]. The difference between the conductance of SnS SMJ, as obtained by different groups, is within 10%. For comparison, the SMJs conductance, evaluated in the earlier experiments, varies up to a few orders of magnitude [437, 466]. The achieved agreement in the values of the SMJ conductance is thus a great experimental success.

It was already suggested [455] that the variation of the SMJ geometry may affect its conductance. *Ab initio* calculations of the SMJ conductance were employed to analyze the role of the junction geometry. The latter includes

- metal-molecule contacts at both side of the SMJ;
- the intrinsic geometry of the molecule, capable to adopt different conformations.

It is possible to consider the SMJ transmission as a product of transmission through each metal-molecule contact and a molecule itself

$$T_{SMJ} = T_{c1} \cdot T_m \cdot T_{c2}, \quad (6.2)$$

The representative SMJ configurations are displayed in Fig. 6-8 C–E. Typically, the same *all-trans* conformation as found in densely packed SAMs (Sec. 6.1.1), is assumed for the SnS molecule in SMJ (Fig. 6-8 D,E). The T_m over the fully stretched SnS molecule is determined by the tunneling between two S atoms. The chain length dependence of the latter gives $\beta_N \approx 0.85$, which is close to that for experimental M and L series¹.

¹ Due to the inherited limitations of the simulation procedure, the HOMO–LUMO gap, *i.e.*, a tun-

The strong Au–S coupling leads to an almost perfect contact transmission. Basically, it is possible to consider a S atom bound to a Au atom as an electron “source” or “drain” channel. The total transmission of each contact $T_{c1,2}$ is thus proportional to the number of Au–S bonds and determined by the contact geometry.

The top-top configuration (Fig. 6–8D) provides a single Au–S contact on each side. A small variation of the calculated conductance was found upon embedding the SnS molecules in short chains of gold atoms (extended top-top configuration). The bridge-bridge configuration (Fig. 6–8E) provides a 4-fold increase of the conductance due to the two Au–S bonds at each contact. The latter is in a good agreement with the experimental ratio of H to M conductances. Therefore, the M and H series were attributed to the conductance of the *all-trans* SnS molecules in top-top and bridge-bridge contacts respectively (Fig. 6–8B). The top-bridge contact geometry is believed to be experimentally indistinguishable from the two simultaneously connected molecules in top-top contact. Experimentally it was accounted in M series. Contact geometries involving “hollow” configurations of the sulfur on gold were considered, but found to be not relevant (see [109] for details).

The metal-molecule contact effect cannot account for the variation of the β value. To address this issue, the SMJs embedding SnS with one C–C bond in *gauche* conformation (Fig. 6–8C) were considered. The latter acts as a structural defect in otherwise uniform tunneling barrier and decreases T_m .

The simulation results were represented as conductance histograms (see [109] for details). For the SMJs with SnS in a *gauche* configuration, a few peaks were obtained on the histograms. Despite of the different origin, the latter are similar to the conventional picture of (almost) equally separated peaks corresponding to I_1 , $I_2 = 2I_1$, etc. The positions of the first high peaks in these histograms are attributed to the experimental L conductance. The overall effect of the molecular conformation and contact geometry leads to *ca.* 2 order of magnitude variation for T_{SMJ} (Fig. 6–8B).

The simulation results are in a good agreement with the existing experimental data. The different origin of the L and M / H conductance peaks on the histograms explains the existence of the temperature dependence for the former and the lack of it for the latter.

6.6 Summary and conclusion

The gold-alkanedithiol-gold molecular junctions represent the simplest system, which ET properties were addressed on the macroscopic, the mesoscopic and the single molecule level. At the moment, a good agreement between various experimental results is established on all levels.

The conductance of single Au-S8S-Au junctions was studied by the STM stretching technique in various media (mesitylene, Ar, aqueous electrolyte). The formation of SMJs was observed in all cases. The probability of the SMJ formation was the highest if the S8S molecules were not only adsorbed on the Au(111) surface, but also dissolved in the solution.

The results were analyzed by constructing histograms of the plateau current. Two to

neling barrier, is known to be underestimated. Thus, in comparison with experiment, the simulations are expected to give lower β and higher G . However, the simulation procedure may be improved to overcome this limitation [109].

three equally spaced peaks were observed in these histograms for all conditions studied. The peaks were used to determine the current through a SMJ. The conductance current is linearly dependent on the applied bias voltage in the range $|V| < 0.3$ V. A non-linear current increase is observed at higher bias voltages. No media or surface concentration effects on the conductance were found.

The single molecule conductance studies were extended towards a series of SnS ($n = 5, 6, 8, 9, 10$). After a careful analysis, three series of the SMJ conductance (low, mid, high) were found. The latter corresponded to the conductance values determined by other groups and explained the scatter of the reported conductance values.

It was already suggested that the variation of the SMJ geometry may affect its conductance. Comprehensive *ab initio* simulations (F. Evers, A. Bagrets) were carried out to understand the experimental results. The junction geometry is determined by the contact geometry and the conformation of the flexible molecule. The experimental “high” and “mid” conductance series were attributed to the SnS molecules in *all-trans* conformation, with a thiol groups bound to two and one Au atoms at each side, respectively. The “low” series was attributed to the interplay between SMJs embedding different SnS conformers with one C–C bond in a *gauche* conformation [109].

Using the alkanedithiol molecular junctions, we established and explored the limitations of the stretching technique and complementary data analysis. Our results represents an important contribution to the detailed understanding of the ET on molecular level.

Chapter 7

Conductance of Au-44BP-Au junction

7.1 Introduction

Historically, the thiol-gold bonds (Cha. 6) were the first used to create a metal-molecule contact. Still, it is the most widely used approach. However, it has certain drawbacks. The thiol-containing molecules, and especially the volatile ones, such as SnS , tend to contaminate the working environment. The SH groups oxidize and/or form dimers in the presence of oxygen. The SH-Au bond is mechanically strong, but non-selective. It was shown by a few comparative studies, that for the same molecule the MJ transmission may be enhanced by substituting SH with other anchoring group (see further). And finally, specific anchoring groups may allow controlling of the MJ formation by an external stimuli.

In this chapter I describe the transport experiments in SMJ supported by a non-conventional 4-pyridil end group. The effect of the anchoring group on the SMJ is described in the introduction. The properties of the studied system and results of the stretching experiments are presented and discussed further.

7.1.1 A relation between composition and conductance of the SMJ

To quantitatively describe the effect of the SMJ composition, I will consider the SMJs of the periodic type, very often used in experiments:

$$\text{Me}_1 - \text{B}_1 - \text{E} - \text{E} \dots \text{E} - \text{E} - \text{B}_2 - \text{Me}_2 \quad (7.1)$$

It is formed by a chain of n equivalent structural elements E, bound by the anchoring groups $\text{B}_{1,2}$ to metal leads $\text{Me}_{1,2}$. In general case $\text{B}_{1,2}$ and $\text{Me}_{1,2}$ may differ, although experimentally symmetric ($\text{B}_1 = \text{B}_2$, $\text{Me}_1 = \text{Me}_2$) SMJs are typically created.

The conductance of the SMJ as a function of n is described as

$$G_{SMJ} = G_c \exp(-\beta_d d) = G_c \exp(-\beta_n n) \quad (7.2)$$

(cf. Eqn. 6.1 on page 139), where G_c is a contact conductance. The latter is often expressed as a contact resistance $R_c \equiv 1/G_c$. Such dependence typically indicates the ET by means of the tunneling through the molecule. Tunneling through SMJ is considered to be temperature-independent [455, 467].

In Eqn. 7.2 the parameter β describes the distance dependence of the tunneling probability. The effective tunneling barrier Φ (cf. Eqn. 2.60 on page 50) is determined by the alignment of the HOMO/LUMO levels of the molecule with the Fermi level of the metal leads. The latter, as well as the experimentally determined values of β , are slightly affected by the variation of the anchoring group [167, 395, 467, 468].

The preexponent factor G_c , in turn, is determined by the properties of two metal-molecule interfaces, including

- the alignment between the MOs of the anchoring groups and the Fermi levels of the metal leads;
- the coupling of the anchoring group and the chain elements;
- the contact geometry.

Additional complications arise due to the conformational variation in a flexible chain [109].

The experimental contact conductance determined for the series of SnS in an *all-trans* configuration, bound to single Au atom at each side (series M in Fig. 6–8 on page 150) is estimated to $G_c \approx 10 \mu S$. For the contact geometries with a higher number of SH-Au contacts (*e.g.*, series H in Fig. 6–8 on page 150) β remains the same, while G_c is a few times higher. Similar results were obtained by experiments in condensed media, although UHV experiments [457] resulted in lower G_c values.

The comparison of the β and G_c values, obtained for other series of molecules connected with Au-SH bond, shows rather intriguing results. The conductance of SMJs formed by a series of SnS and linear α -helical peptides was studied by the STM stretching technique [459]. The β_l value determined for the peptides was lower than that for the SnS . However, an extrapolation of the experimental G vs. S–S distance to zero leads to the same value of $G_c \approx 20 \mu S$. A similar result was obtained in [469]¹. Thus, it is possible to conclude that the contact resistance in Au–S..S–Au junction is quite independent on the nature of the periodic chain. This conclusion is also supported by the conductance measured for a series of viologens (Cha. 8) with a variable length of thioalkyl spacers [172]. Similar G_c values were determined for two $G(n)$ series, corresponding to the two redox-states of the viologen core. In general, the simultaneous increase of G and the decrease of β is observed upon the redox-switching in various systems (see, *e.g.*, [167]). This agrees with a “fixed” value of G_c upon such variation of the composition of the SMJ. However, G_c , due to its nature, is strongly affected by the variation of the anchoring group [167, 467, 470].

7.1.2 The effect of the anchoring group

The ideas about the ability of certain functional groups to attach to metals are mostly coming from studies of SAMs [89, 91, 403] or metal-ligand complexes. Few types of groups capable of anchoring to Au were employed in single-molecule experiments so far. Further I briefly overview the most common ones.

The isocyanide/isonitrile (-NC) end group is known to form a strong “chemical” contact with Au, similar to that of the thiol group. It does not degrade in the presence of the ambient oxygen. The NC supported MJs were created and characterized in nanodevices [471], by contacting SAMs using a SPM probe [106, 468] and in STM-based stretching experiments with Au [395, 472] and Pt electrodes [473]. The experimental results reported are rather scattered, but in general absolute values of G [472], as well

¹ The SnS conductance data, plotted in original paper, correspond to H series (Fig. 6–8 on page 150). Thus, the contact conductance difference of *ca.* 4.3 may be attributed to the coordination effect, if the single Au-SH bond is assumed on both sides of the peptide SMJ.

as G_c and β [106, 468] do not vary strongly upon changing the anchoring group from SH to NC. It is interesting, that the isomeric cyano/nitrile (-CN) group basically does not bind to Au under otherwise similar conditions [472].

The binding of primary amines (-NH₂) was used to create SMJs in STM stretching [395–397, 470, 474–476] and MCBJ [477] experiments. The exponential chain length dependence of SMJ conductance was found in a series of terminal alkyldiamines. $\beta_n \approx 0.9$ [395] is slightly lower and $G_c \approx 1 \dots 2 \mu\text{S}$ is *ca.* one order of magnitude less than the respective parameters for the SnS SMJs.

The formation of a Au-NH₂ bonds occurs via donor-acceptor interaction, where a lone electron pair of the N atom couples with Au. According to the original statement [395], this type of weak binding leads to a selective bond formation. However, more recent experiments demonstrated that this seems to be not the case [476, 477]. The formation of Au-N bond may be controlled chemically. Thus, no binding was observed in case of secondary and tertiary amines [395]. The formation of ammonium-like ions in solutions with a low pH value is expected to prevent N binding to Au as well. However, the variation of the chemical composition or solution's pH is not a convenient way to control the bond formation in electronic devices.

The metal-molecule contact may be formed by an end group, which binding to the metal electrode is controlled by the electrode potential. An example is a 4-pyridine group (see Sec. 7.2). In this chapter I report the studies of conductance in SMJs formed by 4,4'-bipyridine (44BP) (Fig. 7–1A), the simplest molecule with two pyridine anchoring groups. Besides the potential-controlled binding, the 4-pyridine group has a rather unique combination of other properties. It is an intrinsically conjugated π -system. In first experiments the conductance of 44BP SMJ was found to be of the order of $0.01G_0 = 775 \text{ nS}$ [150, 456, 462], which is much higher than that for the majority of the molecules studied so far. For complex molecules of perylene derivatives, it was found that the 4-pyridine group provides a better electronic coupling to an “internal” π -system than a thiol [168, 478]. The anchoring groups itself is rigid, only rotation around the connecting C-C bond is possible (see Fig. 7–1A). And, finally, the 44BP was found to detach from a Au at moderate applied force [462], while the strongly bound thiol group pulls Au atoms out of the surface.

7.2 Interfacial properties of 44BP on Au(111)

Interfacial properties of 44BP adsorbed on the Au(111) surface were studied in our group employing CV, current transients, surface enhanced infrared reflection absorption spectroscopy (SEIRAS) and STM [479, 480]. The chemical structure of 44BP is drawn in Fig. 7–1A. It consists of two planar pyridyl rings, which are easily rotated with respect to each other. The rotation angle varies from 18.2° in a solid phase and 37.2° in a gas phase. In solution the rings are rotating almost freely.

Four different ranges of the potentials, separated by current peaks, are observed in CVs of Au(111) in 44BP-containing solution (Fig. 7–1). A pronounced hysteresis exists between the peaks recorded upon changing the potential sweep direction. The CV response of 44BP in neutral and slightly alkaline solutions is identical. In acidic solutions, the protonation of one or two N atoms of 44BP strongly modifies the CVs.

A monolayer of the densely packed 44BP molecules is formed in the potential range IV (Fig. 7–1B). The molecules are coordinated with one N atom to the posi-

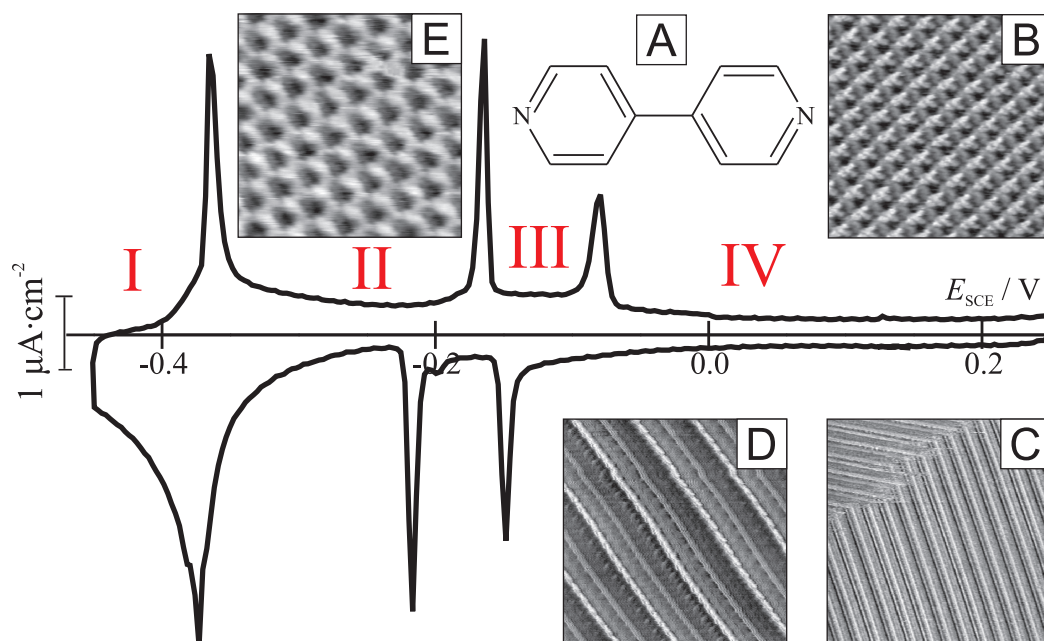


Fig. 7-1: Summary of the interfacial properties of 44BP on Au(111) [479, 480]. Main plot: CV of Au(111) in 3 mM 44BP + 0.05 M KClO₄, $r = 10 \text{ mV} \cdot \text{s}^{-1}$. The characteristic potential regions are labeled I-IV. (A) Structure of 44BP. STM images of 44BP adlayers existing in the corresponding potential ranges: (B) high coverage densely packed structure IV, $10 \times 10 \text{ nm}$; stacked structure III, $30 \times 30 \text{ nm}$ (C) and $10 \times 10 \text{ nm}$ (D); (E) loose stacking structure II, $10 \times 10 \text{ nm}$.

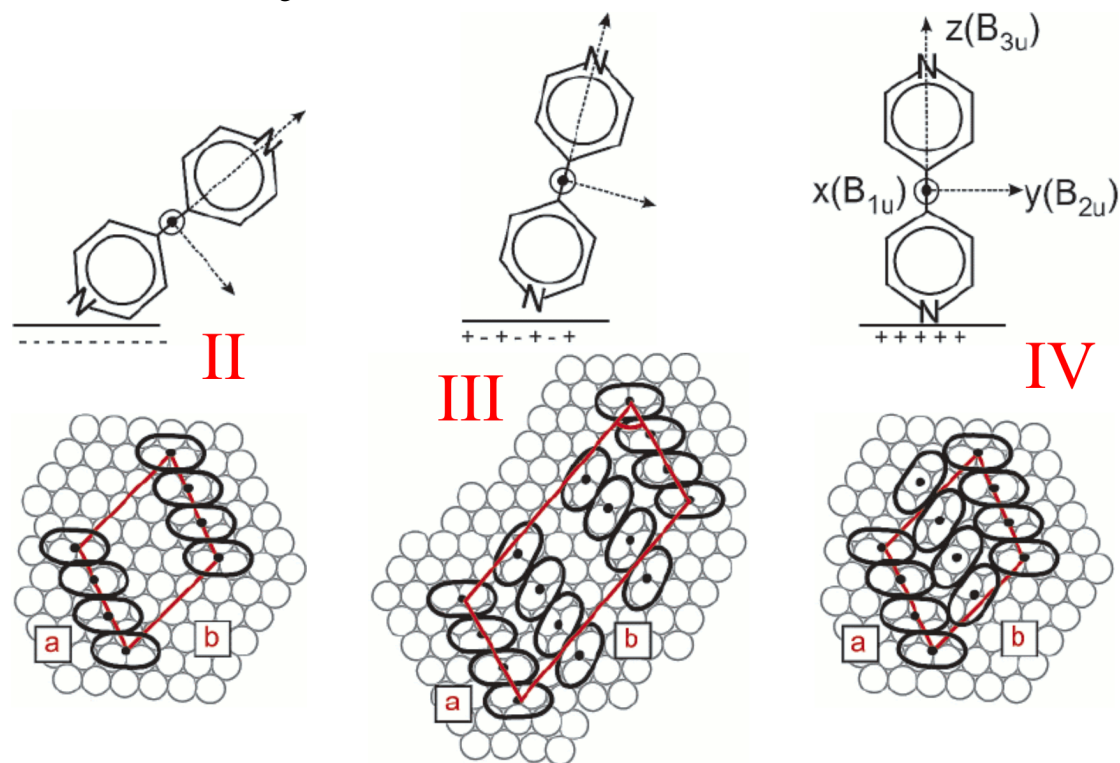


Fig. 7-2: Molecular orientation and models of 44BP adlayers [480].

tively charged substrate and oriented perpendicular to the surface (Fig. 7-2). The positions of the neighbouring molecules are determined by the competition between molecular and substrate coordination sites and intermolecular interaction of the π -systems

(π -stacking). The proposed structure includes “ribbons” of the π -stacked molecules. To accommodate more molecules and provide a good π -stacking, the pyridyl rings in neighbouring rows are twisted by *ca.* $\pm 16^\circ$ to the row direction (Fig. 7–2). The 44BP adlayer does not strictly follow the symmetry of the underlying Au(111) substrate, and its domains are quite fuzzy. These observations indicate a weak adsorbate-substrate interaction.

Upon a potential decrease, the densely packed phase IV transforms into the striped phase III (Fig. 7–1C,D). Translational domain boundaries and rotational ones with a characteristic angle of 120° are routinely observed. The stripes are attributed to parallel stacks of the single-coordinated 44BP molecules, which are tilted in an interchanging manner by *ca.* $\pm 25^\circ$ with respect to the normal axis (Fig. 7–2).

In potential region II we observe bright and dark spots, forming a regular rhombohedral arrangement on the surface (Fig. 7–1E). Rotational domain boundaries observed are characterized by an angle of 60° . The structure is attributed to widely spaced, parallel rows of π -stacked 44BP molecules, extending along the directions of the Au atoms. The molecules are more tilted compared to the adlayer III (Fig. 7–2). The variation of the coordination site on the Au(111) surface results in a brighter and higher appearance of the molecules in the STM image.

In potential region I the partial desorption and reduction of 44BP to an adsorbed anion-radical takes place. An extended residence time in potential range I causes irreversible changes of the interfacial properties.

The variation of the 44BP surface structure upon the decrease of the electrode is the result of a decrease in surface coverage. Polarisation at more negative potentials also corresponds to a decrease of the binding strength between the pyridyl ring and the Au surface. Simultaneously, the orientation of 44BP molecule on the Au(111) surface changes from the perpendicular to a more and more tilted one.

7.3 STM and stretching experiments

The conductance of Au-44BP-Au junctions was studied by the stretching technique in an electrochemical environment. The experimental detail are given in Sec. 3.8.4.

The studied system exhibits clear distinctions from previously studied Au-SnS-Au junctions, which were described before. The electrochemical conditions employed allowed the variation of the 44BP structure on Au(111) substrate (Sec. 7.2). Simultaneously, the 44BP binding to both substrate and tip was controlled.

Fig. 7–3C shows an example of the 44BP adlayer on Au(111) in region IV employing a medium quality gold tip. Characteristic double lines of the surface reconstruction (*cf.* Fig. 3–3 on page 77) are seen. The appearance of the reconstruction lines is rather uniform without a random noise. The latter often appears on adlayer-free Au(111) due to the spontaneous reorganisation of the water molecules in a tunneling gap. The areas free of reconstruction lines exhibit small regular corrugations. Despite of the lack of atomically resolved images, the latter were attributed to the densely packed adlayer of 44BP.

The different properties of the SnS and 44BP SMJs are also reflected in the stretching experiments. Firstly, clear stretching plateaus were observed in the $I - z$ curves only with the initial tip traveling distance of 1.5...2 nm. Compared to the stretching experiments carried out for other system under same conditions (bias voltage, initial I_T), the

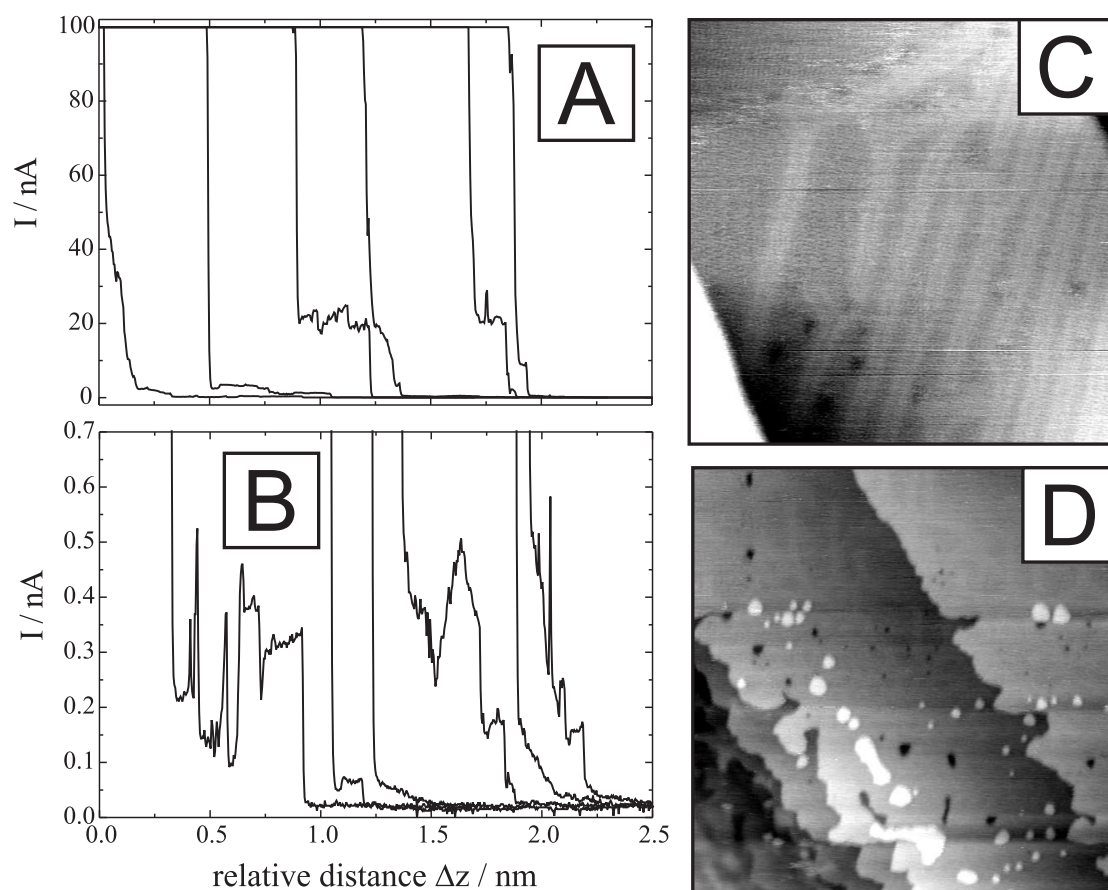


Fig. 7-3: Stretching curves for the 44BP on Au(111), $E_s = 0.1$ V (phase IV), $E_t = 0.2$ V. Current range: (A) 100 nA (B) 0.7 nA. Simultaneously recorded STM images: (C) Reconstruction lines and 44BP adlayer seen on the surface before the stretching, 80×80 nm; (D) Gold islands formed after stretching, 200×200 nm.

tip travel distance is higher than that for the SnS and close to the one used to create Au QPCs. Secondly, the appearance of the pronounced plateaus parallels with the creation of many gold islands on the surface (Fig. 7-3D). This observation may be attributed to the very low probability of SMJ formation upon the contact of the tip with the adlayer. Indeed, the kinetics of the 44BP adsorption on Au(111) is quite slow. The increase of the traveling distance leads to the QPC formation prior to the stretching step. Only upon its breaking the SMJ incorporating 44BP molecules may form. This situation is more closely resembles the original “STM break junction” approach (Sec. 3.7.4).

The stretching curves measured under the same conditions show plateaus with current values varying by few orders of magnitude. Selected examples are presented in Fig. 7-3. Fig. 7-3A shows the curves in the full range of the measured current, while Fig. 7-3B displays the same curves in a much smaller range of currents. The stretching experiments were repeated at different values of the sample potentials. The bias voltage was varied between 20 and 200 mV. Several thousands of curves were measured for every set of conditions.

7.4 Analysis and results

The obtained stretching curves were analyzed employing various approaches, as discussed in Sec. 5.4. I will describe in details the results for one set of the stretching curves, measured at $E_s = 0.1$ V and $E_t = 0.2$ (Fig. 7–3). These conditions correspond to the strongest possible binding of 44BP to the Au electrodes.

7.4.1 Manual analysis

First, 300 curves randomly selected out of total 2400 were analyzed manually. The plateau selection criteria were the same as employed for SnS SMJs: minimum plateau length 0.5 nm, maximum plateau current scatter 5%. The results exhibited few sets of conductance features in a series of linear histograms, obtained upon variation of the bin width. In order to present all conductance features in the same plot, a logarithmic conductance histogram was constructed. The $\lg G$ was calculated for each extracted plateau and a bin width of 0.05 was used.

The results are shown as light cyan columns in Fig. 7–4A. The most prominent histogram feature corresponds to the conductance of *ca.* 20 nS. Other features corresponding to *ca.* 2, 6, 60 and 500 nS were also observed in the linear histogram and appear in Fig. 7–4A as small features. The results of the manual analysis were used as a reference for the further procedures.

7.4.2 All-data analysis

The “all-data” analysis was also carried out for the experimental data sets. The linear histograms of the measured current exhibited a decaying $N(I)$ vs. I dependences without any distinguishable features. In turn, logarithmic histograms of the current demonstrated very broad peaks, which position scales roughly linear with the bias voltage. A typical result, obtained for the reference data set, is shown in Fig. 7–4 as a black line. It has a significant background and appears as an “envelope curve” for the light columns, with all fine structure smeared out into a single peak. The overall appearance of the logarithmic histograms is very similar to those reported for alkanediamines SMJs [395–397], while much clearer histogram peaks with a small background were obtained in case of alkanedithiols [127].

Similar broad peaks with the center at 50...60 nS were obtained for the other experimental conditions, when E_s and E_t were held in the ranges IV and III (see Fig. 7–1). In case of potentials in range II, no peak features were observed in the logarithmic histograms. However, the 44BP molecules are known to adsorb on Au(111). Both, characteristic stripes on the surface and plateaus in stretching curves, were observed during combined imaging/stretching STM experiments. This example illustrates the limitations of the logarithmic “all-data” analysis. The pronounced histogram peaks appears only in case of a sufficient amount of curves with stretching plateaus. The peaks cover a few order of conductance magnitude and may serve only as a rather rough estimation of the SMJ conductance.

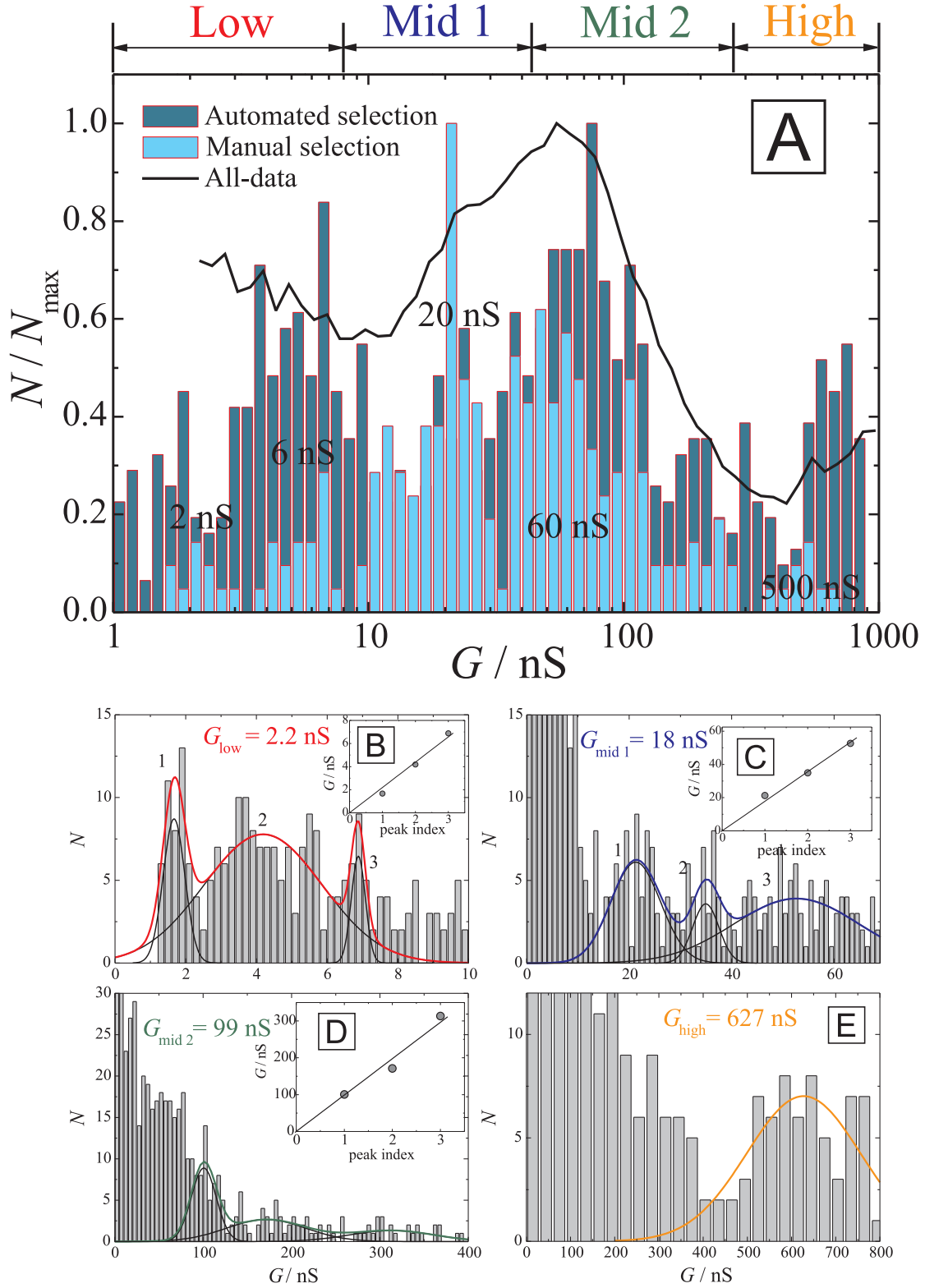


Fig. 7-4: Statistical analysis of the 44BP stretching curves such as shown in Fig. 7-3. (A) Histograms in log representation, the bin width is 0.05. Light and dark cyan columns are results of the manual and of the automated analysis, respectively. The black line is a logarithmic “all-data” histograms. Curves are normalized to the maximum value. (B-E) Results of the automated analysis (dark cyan columns in A) plotted as linear histograms, bin width / nS: 0.2 (B), 1 (C), 5 (D), 30 (E). Black and color lines are individual Gaussian curves and their sum. The low current features in plots C-E correspond to the contribution of plateaus with smaller conductance, which cannot be resolved at given bin width.

7.4.3 Automated plateau selection

The automated plateau selection procedure (Sec. 5.4.2) was employed to evaluate the SMJ conductance from the all stretching curves of the measured data sets. After some trials, the allowed scatter of 2% and the minimum interval of constant current $L_{min} = 0.02$ nm were used as uniform selection criteria. The obtained set of plateau positions was analyzed by constructing series of linear histograms with varied bin width.

Example histograms constructed for the reference data set are shown in Fig. 7–4B–E. Each of them exhibits a set of (almost) equally spaced peaks, which were fitted by a series of Gaussian lines (Sec. 5.4.3). The series were attributed to four different types of SMJs (*cf.* Sec. 6.5), further labeled as “low”, “mid1”, “mid2” and “high”. The average conductance of the SMJ was determined for every set of peaks by fitting G_{peak} vs. peak index dependence (see insets in Fig. 7–4B–E) to a line with an intercept fixed to 0. The obtained values are *ca.* 2.2, 18, 99 and 627 nS. The latter are close to the ones determined by the manual analysis. The conductance peak at *ca.* 6 nS did not appear as a separate one, but rather as a satellite peak of the feature at 2 nS peak. Fig. 7–4B displays the peak at *ca.* 4 nS as well. Therefore, we conclude that this is not a separate feature and its appearance during the manual analysis (Fig. 7–4A) is occasional.

The results of the automated analysis were also compared with a manual one by constructing a logarithmic conductance histogram (Fig. 7–4A, dark cyan columns). The histogram exhibit two broad peaks of almost equal height. In general, the features on the histograms constructed after the manual and the automated analysis are rather similar.

The logarithmic histogram of the automated analysis was compared with the individual linear histograms (Fig. 7–4B–E). Four ranges of conductance values may be separated rather well in a logarithmic scale. The latter corresponds to the “low”, “mid1”, “mid2” and “high” conductance described above.

It is interesting that, despite of the *decrease* of the peak height with the conductance in the linear scale (Sec. 5.4.3), an *increase* of the peak height is observed in the logarithmic scale. Obviously, this effect is related to the effective increase of the bin width with the current value in the logarithmic histograms. Therefore, one should be careful assigning the highest peak in the logarithmic histogram to a SMJ conductance. Indeed, the features appearing as equally spaced peaks in the linear histogram (Fig. 7–4 B–E) are displayed as a set of sharp peaks in the logarithmic histogram (Fig. 7–4A). It is also notable that the position of the peak in the “all-data” logarithmic histogram (black line in Fig. 7–4A) is close to the single broad peak in the histogram using automatically selected data.

7.4.4 Potential dependence

The potential dependence of the conductance of 44BP SMJs was studied by repeating the stretching experiment at different sample potentials. An automated analysis procedure was used to analyze the experimental data. The constructed linear histograms exhibited features similar to those in (Fig. 7–4 B–E). The latter, however, are not as pronounced as one typically finds for *SnS* SMJs. Therefore, to ensure the statistical significance of the results obtained, 2 to 5 data sets were recorded for every sample potential under different conditions (bias voltage, used scanner, experimental day).

The results are presented in Fig. 7–5A. Here the individual symbol type corresponds to the stretching experiments carried out in one day using the same bias voltage. Despite

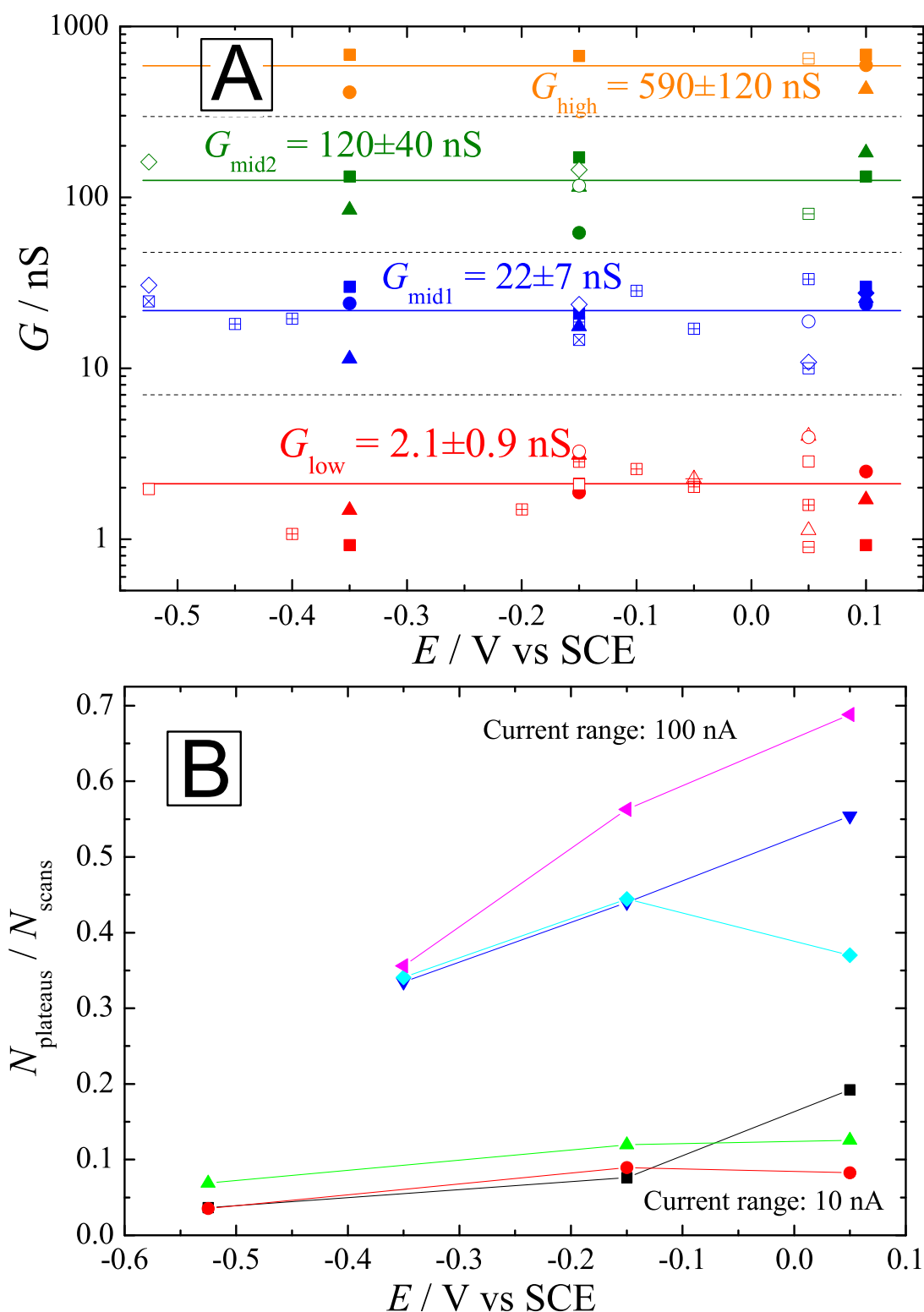


Fig. 7-5: Potential dependence of the SMJ conductance. (A) G , each data point style correspond to different experimental conditions. (B) Efficiency of junction formation. Series for two current ranges (10 and 100 nA) are shown. For every line the experimental conditions are the same, except of E_s .

of the moderate scatter, four group of the conductance values can be identified. The latter are indicated in Fig. 7-5A by color. The features in one group are assigned to the four types of SMJ, formed in the stretching experiments. No potential dependence

is observed for each group of conductance values. Therefore, the average conductance for each type of SMJs was calculated from all points of the corresponding group. The obtained results are $G_{low} = 2.1 \pm 0.9$ nS, $G_{mid1} = 22 \pm 7$ nS, $G_{mid2} = 120 \pm 40$ nS and $G_{high} \approx 590 \pm 120$ nS. G_{high} is rather close to the potential-independent conductance of 770 nS, reported earlier [150, 456, 462]. Otherwise, no multiple conductance values for 44BP and other molecules with 4-pyridyl linkers were reported so far.

Besides the conductance values, the efficiency of the SMJ formation was estimated from the results of the automated analysis. Fig. 7–5B demonstrates the ratio of the extracted plateaus per stretching curve as a function of the sample potential under otherwise similar conditions. The trend towards a decrease of the SMJ formation probability, while decreasing E_s , correlates well with the decrease of the 44BP coverage and the tilting of the molecules on Au(111) (Sec. 7.2). Therefore, it can be attributed to the weakening of the binding strength between 44BP and Au. It is also notable that a significantly higher ratio of plateaus per stretching curve was found upon the increase of the current range from 10 to 100 nA. The latter may be attributed to the contribution of the SMJs with “mid2” and “high” conductance. The latter were not accessible when the experimental current range was limited to 10 nA in order to increase the resolution in the low current limit.

7.5 Summary and discussion

The conductance of SMJs, created by the binding of 44BP to two gold electrodes, was studied by the stretching technique in an electrochemical environment. The SMJ conductance was evaluated using various analysis procedures (Sec. 5.4). Unlike previously studied alkanedithiols, the interaction of the 4-pyridyl anchoring group to gold is rather weak and may be described as “physisorption”. The latter has few consequences.

The binding of 44BP to gold may be controlled by the electrode potential. The probability to form SMJ upon the contact with the adlayer is found to be very low. It was enhanced by the preliminary creation of Au QPC between the tip and the sample and their subsequent separation in 44BP containing solution. The QPC formation was indicated by characteristic Au clusters, observed on the surface after stretching.

The low probability to form SMJ, even after breaking of the QPC, hinders the evaluation of its conductance. Thus, the linear “all-data” histograms exhibit no pronounced features. The logarithmic “all-data” histograms demonstrated a single broad peak with a strong background, which disappeared upon the potential decrease. The general shape of these histograms is similar to those found for the Au-NH₂ supported SMJs, while more pronounced peaks were obtained for SnS.

The SMJ conductance was evaluated using a more “sensitive” automated plateau selection procedure (Sec. 5.4.2). Both, the constructed histograms and the conductance values, scatters significantly. This effect may be related to the nature of the anchoring group as well. However, despite of the results’ variability, four group of the conductance values (“low”, “mid1”, “mid2” and “high”) were identified. They were attributed to the SMJs of different types. The conductance was found to be potential-independent for each SMJ type. The values of $G_{low} = 2.1 \pm 0.9$ nS, $G_{mid1} = 22 \pm 7$ nS, $G_{mid2} = 120 \pm 40$ nS and $G_{high} \approx 590 \pm 120$ nS were obtained. The last value is close to the single conductance value, reported for Au-44BP-Au SMJs [150, 456, 462]. In turn, the SMJ formation probability was found to decrease with the potential.

The experimental discovery of four different types of SMJ for Au-44BP-Au SMJs is quite surprising. Indeed, only three types of SMJs were determined for a flexible SnS molecules. For other molecular systems, even two types of SMJs are seldom resolved experimentally [166]. In case of 44BP, a molecule with only one rotational degree of freedom, the variability of SMJ conductance is higher. To clarify this aspect, I will discuss the existing theoretical results.

The conductance of 44BP incorporated between two Au electrodes was studied *ab initio* by our colleagues (A. Bagrets, F. Evers) [481]. The results are summarized in Fig. 7–6.

The pyridyl ring binds to Au by the formation of a donor-acceptor bond between a lone electron pair of a N atom and a free *s*-orbitals of Au atoms. The 44BP molecule is effectively discharged and forms a dication. The transport properties of SMJ are governed by the LUMO of the 44BP-dication, which position depends on the exact arrangement of Au atoms in the contact region (Fig. 7–6 A-C).

The coordination sphere of the nearest Au atom determines the coupling of the pyridyl to the electrodes. Two situations are possible. The *strong* coupling corresponds to the pyridyl ring attached to the surface Au atom. The latter is surrounded by other atoms, providing a good overlap between the LUMO of the 44BP π -system and of the Au states. The exact position of 44BP on the surface (coordination site) has a negligible effect on the coupling strength.

The *weak* coupling corresponds to the attachment of the nearest Au atom to a single surface atom. This atomic configuration resembles Au nanowires and is routinely created in stretching experiments. The additional atom between the 44BP molecule and the bulk Au electrodes significantly reduces the overlap between the LUMO and the metal states. A further extension of the Au nanowire (*i.e.*, introduction of another atoms be-

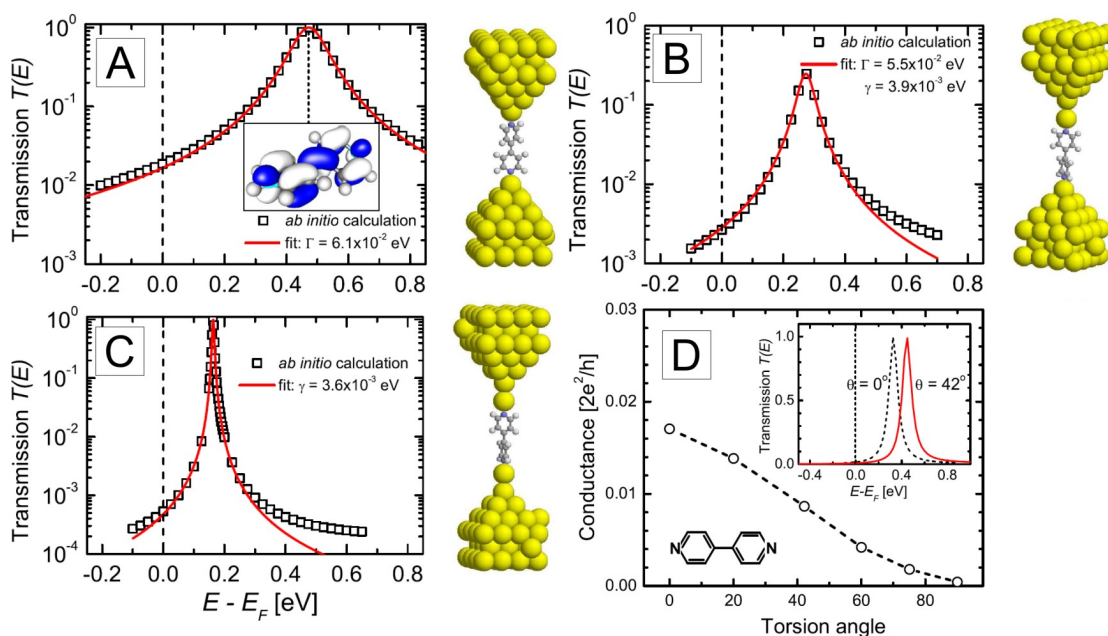


Fig. 7–6: Summary of the *ab initio* simulation of the conductance in Au-44BP-Au junctions [481]. (A-C) Transmission of three typical configurations illustrating the cases of (A) *strong-strong*, (B) *strong-weak*, and (C) *weak-weak* coupling. (D) Conductance in a *strong-strong* configuration as a function of the torsion angle between the pyridyl rings. The inset shows the transmission around E_F for the planar molecule (dashed line), and for the distorted one with the optimized angle of 42° (solid line).

tween the molecule and the electrode) does not modify the coupling significantly.

The difference in transmission probability between a *strong* and a *weak* coupling modes is *ca.* 10 times. Thus, depending on the geometry of both metal-molecule contacts, a conductance difference of up to 100 may be achieved (Fig. 7–6 A-C). This agrees qualitatively with my experimental results.

As it was mentioned above, the 44BP molecule itself has one rotational degree of freedom. The torsion angle between the planes of two pyridyl rings determines the coupling of their π -systems. The calculations described above were carried out with the 44BP in optimal geometry (torsion angle *ca.* 42°). The dependence of the SMJ conductance in the *strong-strong* configuration on the torsion angle was determined in a separate calculation. The coupling between rings and, respectively, SMJ transmission, monotonously decreases upon the transition from the planar to the perpendicular orientation of the rings (Fig. 7–6D). The overall difference reaches *ca.* 1 order of magnitude. Therefore, the existence of the preferable orientations of 44BP molecule in a SMJ may lead to an additional spread of the conductance values.

At present time, it is not possible to unequivocally assign the conductance values to certain SMJ configurations. The attribution of the “high” conductance to the 44BP molecule, strongly coupled to both metal electrodes (Fig. 7–6A) seems to be feasible [481]. Otherwise, additional experimental and simulation studies are required to address this issue in more detail. In particular, we are planning to study systematically the conductance of the pyridyl-supported SMJs as a function of the number of methylene spacers between two anchoring groups.

However, the existing experimental and simulation results allow to summarize the difference between the ET properties of SMJs, supported by the “chemisorbed” thiol and “physisorbed” pyridyl anchoring groups. In the first case, the transmission probability of the single metal-molecule contact is mostly determined by the number of the Au atoms, coordinating to the thiol anchoring group. The SMJ conductance is only slightly affected by the insertion of additional atoms between the Au-SH contact and the bulk electrode. In the second case, the contact transmission is rather independent on the coordination site of the molecule on the surface and drastically reduced upon the introduction of an additional metal atom between the molecule and the bulk electrode. The 44BP behavior may be better described by considering an “extended molecule”, formed by 44BP and two nearest Au atoms. Then, the coordination of the Au atom determines the contact transmission. And, finally, the intrinsic molecular geometry was found to strongly affects the SMJ conductance, independently on the nature of the anchoring group.

Chapter 8

Electron tunneling enhanced by a redox-active mediator

In this chapter I will describe experiments on the enhancement of the tunneling current mediated by the redox-active compound N-hexyl-N'-(6-thiohexyl)-4,4'-bipyridinium. The experiments presented here were carried out by Zhihai Li with my assistance and described in his PhD thesis [173]. The detailed analysis of the experimental results was done by me.

Two types of EC STS experiments were performed. In the constant bias mode the bias voltage was fixed, and both tip and sample potentials were swept to pass over the equilibrium potential E^0 . The tunneling resonance in the vicinity of E^0 resulted in a peak in the $(I - E_s)_V$ curves. In the second mode of the experiments E_s was fixed and E_t was swept over E^0 in a wide potential range. The resulting $(I - V)_{E_s}$ curves show a diode-like behaviour with an enhancement of the current in comparison to direct tunneling.

8.1 Introduction

8.1.1 Structure and application of viologens

The organic 4,4'-bipyridinium dication, also known under the trivial name viologen V^{2+} [482], is easily synthesized from the 4,4'-bipyridine (44BP) moiety. The interfacial and transport properties of bare 44BP were described in Cha. 7. The 44BP core is modified by alkylation of the lone electron pairs of each nitrogen atom, resulting in a quaternary ammonium-like configuration. An example of a viologen derivative is shown in Fig. 8–1A. Further I will use the following short nomenclature [483] for the family of substances constructed from the viologen core V combined with linear chain of alkyl spacers $(CH_2)_{m,n}$ attached to nitrogen atoms and optional end groups $E_{1,2}$: E_1mVnE_2 .

The dication of the viologen core V^{2+} is redox-active and may be easily reduced forming the radical-cation ($V^{+\bullet}$) and the neutral form (V^0) [482, 484, 485]. The redox transitions are accompanied by a change of color: the dication and neutral form of the viologen are colorless, while the radical-cation has an intense violet color [482]. The latter gave rise to the name “viologen”.

The oxidation-reduction $V^{2+} \rightleftharpoons V^{+\bullet}$ is particular known as a very fast redox-reaction involving organic molecules [484, 485]. Small alkyl-derivatives, *e.g.*, methylviologen CH_3-V-CH_3 (1V1), are used as standard redox reactants with known redox-potentials [482, 484, 485] in water, organic solvents or ionic liquids; as oxidation-

reduction indicators and as mediators for electrochemical reduction processes¹ [485]. The viologen core retains its redox activity upon further chemical modification of the side substitutes, including polymerization. Due to this property, the viologen derivatives have been used as redox-active components (*e.g.*, molecular scale ET mediator or electron acceptor in a DBA configuration) in various functional materials [486, 487]. Applications include redox-active polymers, biosensors, liquid crystals, photo energy conversion, complex-stabilized metal particles and luminescent materials. Further information on the research and applications of viologens can be found in the books and reviews [484–487] and the literature cited therein.

Redox-active molecular-thin films incorporating viologens have been prepared on various substrates using either LB or SAM techniques [486]. Gold-supported SAMs of alkylviologens modified with one or two terminal thiol groups HS_nVm(SH) were investigated by various electrochemical (see Sec. 8.2.1) and spectroscopic [171, 488–492, 492–507] techniques, contact angle measurements [490], ellipsometry [496], quartz crystal microbalance [490, 493, 508–512] and STM/STS [171, 501, 508, 513–515]. Unlike in case of alkane(di)thiols (Sec. 6.1.1), the redox-active monolayers [487, 497, 501, 509, 516] or multilayers [487, 517, 518] incorporating viologen derivatives were found to provide a pathway for electron exchange between the substrate and the species or the SPM probe located on top of the organic film. However, only few of the aforementioned experiments enjoyed the usage of well defined single crystal substrates, such as Au(111) [171, 496, 501, 513].

The electronic properties of viologens were exploited in functional nanostructures as well. The dithioalkylated viologens HS_nVmSH were used to covalently wire gold NPs into a single conductive network [519–527]. The resulting assemblies were shown to demonstrate photoconversion activity [519–521]. The light-harvesting proceeds by quenching of the viologen excited state by Au NP. The measured photocurrent is boosted by the fast ET from the viologen moiety to the NPs as well as by the fast ET from the NPs to the substrate via highly conductive viologen linkers [524]. The rectification of the ET between substrate and external aqueous species by HS_nVmSH/Au NP assemblies observed in [525] was attributed to the hopping through the MO of the reduced V⁺• core.

8.1.2 Single molecule studies

The pronounced and well known ET mediation ability of the viologen core make it a suitable model system for single molecule studies aiming to investigate relations between molecular structure and electronic properties. These experiments were pioneered by the Liverpool group [159, 169, 496, 501]. Our group carried out a comprehensive study of the self-assembly and of the ET-functionality of a series of symmetric viologens bound to gold via thioalkyl linkers [171–174, 498]. The SAMs of the target compounds were formed on three types of gold substrates (single crystalline Au(111) macro electrodes [171, 174], Au(111) film [171, 174, 498] and nanoelectrodes [171]) and characterized in electrochemical, SEIRAS [171, 174, 498] and STM[171–173] experiments.

Up to the present moment the conductance of SMJs incorporating thiolalkylated viologens was studied by *I* – *V* measurements of a monolayer and the sin-

¹ The compound, which cannot be reduced electrochemically, is reduced by electrochemically generated mediator.

gle molecule response [169, 496, 501] as well as the STM stretching technique [159, 160, 171, 172, 496] in the absence of potential control [159, 169, 496, 501] and in electrochemical environment [159, 160, 169, 171, 172]. In some studies, Au NP were attached to a viologen monolayer or single molecules isolated in a matrix of alkylthiols [169, 496, 501]. The observed asymmetry of the $I - V$ characteristics was attributed to a temporary population of the molecular redox state during the ET [169, 501] (see also Sec. 8.3). The conductance of SMJ was shown to be controlled by the electrode potential [159, 160, 169, 171, 172]. In all these studies an increase of the conductance was observed when the viologen core was electrochemically “switched” from the V^{2+} form to $V^{+\bullet}$. However, no current-voltage STS experiments involving viologen-functionalized molecules were reported so far.

8.2 Properties of the system

Here I report the detailed analysis of current-voltage EC STS characteristics of asymmetric Au–HS6V6|gap|Au junctions [173] demonstrating the enhancement of the tunneling current by the viologen core. Preliminary experiments with HS6V6 deposited on a Au tip in aqueous electrolyte were described in our paper [171]. The results presented in this chapter are based on a comprehensive experimental study, which was carried out later. The experimental details are given in Sec. 3.8.5. The chemical structure of HS6V6 used in the experiments presented is shown in Fig. 8–1A. The dithiolated modification of this compound (HS6V6SH) was used for some complementary studies [171, 172].

8.2.1 Electrochemical properties

The redox ET of viologens has been studied extensively employing electrochemical techniques both in solution [502, 503, 528] and immobilized on electrode surfaces [490–492, 494, 504–507, 510–512, 514, 515, 523, 529]. The thermodynamic redox potential is strongly dependent on the hydrophobic/hydrophilic environment and on the hydration capacity of the co-adsorbed anions [490, 494, 503–505, 507, 510, 511, 514, 515, 523, 528]. An ion-pair mechanism has been proposed in the presence of ClO_4^- as counter anions, leading to a rather complex charge transfer kinetics [490, 510, 511].

Fig. 8–1B and C show typical CVs of a HS6V6 monolayer on Au(111)-(1 × 1) in 0.05 M KClO_4 , adjusted to pH=10 by addition of KOH [174, 498]. Fig. 8–1B illustrates the first CV scan in a wide potential range. Contact with the electrolyte was established at $E = -0.700$ V. A subsequent potential excursion in the range of $-1.3 \text{ V} \leq E \leq -0.2 \text{ V}$ reveals three characteristic pairs of current peaks labeled P_1/P'_1 , P_2/P'_2 and P_3/P'_3 . The latter corresponds to the irreversible reductive desorption and a partial oxidative re-adsorption of a redox-active thiolate, respectively [433, 530] (*cf.* Sec. 6.2). The amount of charge required for viologen desorption (peak P_3) is considerably larger than typical values reported for the reductive desorption of alkanethiols [430]. The large overall charge and the sharpness of this current peak indicate parallel contributions from additional faradaic and/or charging processes [502, 506, 529, 531].

Restricting the potential range to $E \leq -1.05 \text{ V}$ results in two pairs of well-defined current peaks (Fig. 8–1C). P_1 and P'_1 are assigned to the one-electron reaction

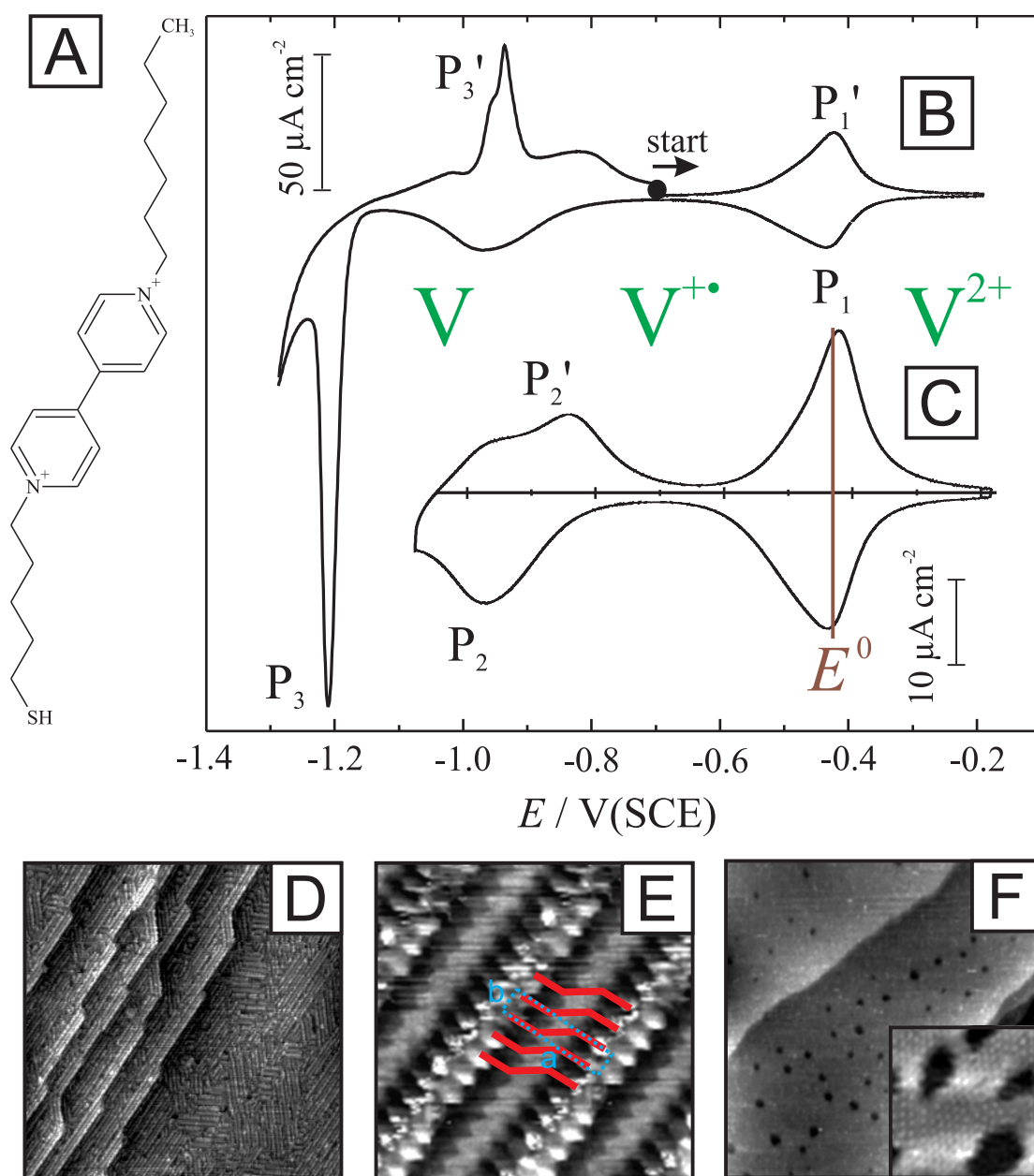


Fig. 8-1: Summary of the interfacial properties of HS6V6. (A) Chemical structure of HS6V6. (B,C) Cyclic voltammetry of high coverage HS6V6 assembled on Au(111) surface, sweep rate $50 \text{ mV} \cdot \text{s}^{-1}$, current density scale is indicated by vertical bars. STM images of HS6V6: (D) low coverage, $100 \times 100 \text{ nm}$; (E) low coverage, $7 \times 7 \text{ nm}$; the proposed arrangement of the molecules and unit cell are shown by red and blue color; (F) high coverage, $100 \times 100 \text{ nm}$, inset - $12 \times 12 \text{ nm}$.

$\text{V}^{2+} \rightleftharpoons \text{V}^{+\bullet}$ of surface-confined species [484, 485]. The migration of counterions and the reorganization of solvent molecules appear to be fast [503–505, 507, 514, 515, 528]. The peak-to-peak separation is rather constant up to $1 \text{ V} \cdot \text{s}^{-1}$, and the peak heights scale linearly with the scan rate. These observations indicate a fast reversible ET process (Sec. 2.3.6). The data extracted from CV were used to estimate the equilibrium potential of the redox-process E^0 as the midpoint between the anodic and the cathodic peak potentials (Sec. 2.3.6). An example is given in Fig. 8-1C.

The second pair of peaks, P_2 and P_2' , is assigned to the $\text{V}^{+\bullet} \rightleftharpoons \text{V}^0$ process [484, 485], which is less reversible. The broadening of the peaks P_2 and P_2' and the increase of the

peak separation indicates quasi-reversibility and a higher disorder within the adlayer attributed to the insolubility and/or aging tendency of the V^0 species [500, 531–533].

Au(111)-(1×1) electrodes modified with the dithiol form HS6V6SH gave results similar to those just described for the monothiol. In case of low coverage monolayers (see below) the electrochemical responses of the electrodes did not change qualitatively, except of a decrease of the currents of reductive desorption (peak P_3) and of the corresponding anodic counterpart P'_3 . The strict elimination of the oxygen exposure during the electrochemical measurement is extremely critical. Oxygen, even in trace amounts, is known to quickly oxidize the radical-cation form $V^{+\bullet}$ [482, 485], and therefore leads to the distortion of the redox response of the adlayer and to its degradation. Electrochemical experiments of similar quality were also carried out in our EC STM setup using an environmental chamber (Sec. 3.6.4). The careful removal of oxygen was one of the critical requirement for the EC STS experiments described in the next paragraphs.

8.2.2 Interfacial structures

A series of EC STM experiments was carried at potentials around the first redox peak to understand the 2D structure of these assemblies [172, 173]. Similar to the results obtained for alkanedithiols (Sec. 6.3), depending on the assembly conditions, distinctly different low coverage and a high coverage adlayers were obtained for both monothiol HS6V6 and dithiol HS6V6SH forms on Au(111)-(1×1).

Highly ordered low coverage adlayers feature regular arrays of parallel stripes covering the entire substrate surface (Fig. 8–1D). The stripes are not uniform. Bright and dark contrast patterns alternate. Individual domains extend from 10 to 50 nm. Neighboring domains with sharp boundaries are mutually rotated by multiples of 120° indicating registry of the adlayer with respect to the hexagonal substrate surface. This hypothesis is also supported by the faceting of steps (Fig. 8–1D). The steps are aligned with characteristic angles of 120° , and step edges are decorated by parallel molecular rows.

High-resolution experiments, such as shown in Fig. 8–1E, reveal more details of the molecular adlayers. The molecular rows composed of bright dots are separated by parallel rows of dark grey and light grey ellipsoid-like segments. Parallel rows of the same type are separated by (2.6 ± 0.3) nm. The axes of two types of rows exhibit characteristic tilt angles with respect to the main row direction, which were estimated to $(60 \pm 5)^\circ$ (light grey rows) and $(90 \pm 10)^\circ$ (dark grey rows). Cross-section profiles reveal a periodicity of (0.50 ± 0.05) nm between individual features of each type of row. The systematic studies of the assembly and surface structure of mono and dithiolated alkylated viologens with a variable length of the alkyl spacers [171–173] as well as SEIRAS studies [171, 174, 498] performed in our group allowed to deduce the surface structure of the low coverage “striped” phase. The proposed arrangement of the HS6V6 molecules on the surface is indicated by the red color in Fig. 8–1E. Here bright features forming double rows were attributed to the thiol groups, dark gray rows are methylene chains and light gray ellipsoidal features are the viologen cores (*cf.* Fig. 7–1C).

The high coverage phase is a poorly ordered adlayer with many atomically deep vacancy islands with a typical size of 2 – 5 nm in diameter (Fig. 8–1F). A $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ structure motif could be identified (inset in Fig. 8–1F). Similar to alkanedithiols (Sec. 6.3), the observed highly packed structure was attributed to a tilted orientation of HS6V6 on the surface, which is also supported by our recent SEIRAS

studies [174, 498].

8.3 Theoretical model

In recent years a number of experiments demonstrating the enhancement of the tunneling current by a redox-active ET mediator were reported under electrochemical conditions. The increase of the tunneling current at electrode potentials close to E^0 was observed in an asymmetric SPM configuration for compounds incorporating organic viologen moieties [171], ferrocenyl [129], organometallic complexes [137, 157, 483, 534–536] and metalloproteins [164, 165, 537–539]. Here and further I use the term “enhancement” in order to distinguish it from the electrochemical “switching” phenomenon in a symmetric configuration (Sec. 2.6.4). The latter is caused by the modification of active molecular unit as a result of the redox transition, while the former requires the coexistence of two redox forms of the reactant and vanishes as the electrode potential moves away from the equilibrium potential of the corresponding redox-pair [540].

Experiments on the tunneling enhancement, existing models and their application are nicely summarized together with a historical background in the review of Alessandrini *et. al* [539], which focuses on metalloprotein systems. The model of a two-step tunneling with a partial vibrational relaxation, developed by Kuznetsov, Ulstrup and colleagues [540–548, 548–551], is widely applied to rationalize the experimental observations on tunneling enhancement. However, no detailed analysis of experimental data according to this model was done so far, most probably due to the lack of high quality experimental data. With such data now available [173], I will try to address this issue.

Fig. 8–2 illustrates the model used. Here a molecule with discrete electronic levels is located between the metal sample and the probe electrodes, both providing continuously distributed electronic levels (*cf.* Sec. 2.3.4). The localized levels of the molecule are broadened by interactions of the redox-center with the surrounding electrolyte [552, 553], and with the substrate [554]. Fermi levels of both electrodes may be shifted independently by adjusting the electrode potentials of both tip and sample with respect to the RE (Sec. 2.4.6).

A direct (off-resonant) tunneling current is flowing between the tip and the sample independently on the relative positions of the molecular levels with respect to the Fermi levels of electrodes. Further I will describe the situation which leads to a strong enhancement of the tunneling current [539, 551]. For the sake of simplicity I will describe the situation involving the temporary occupation (reduction) of the initially empty molecular level and an enhanced ET from the left (negatively biased) electrode to the right (positively biased) one. The reverse situation is also possible.

The energy levels of the solvated molecule are constantly fluctuating due to the variation of the solvation energy up to the value of λ (Gibbs energy of the environmental reorganization) in both directions from the average position. The first step of the proposed mechanism is a situation where the Fermi level of the left electrode approaches the LUMO of the molecule due to the applied voltage, but is still located below it. The molecular LUMO may decrease its energy due to fluctuations and approach the Fermi level of the left electrode, causing the first ET.

Three scenarios of the second ET are possible. If the electron is transferred “immediately”, *i.e.*, without relaxation of the molecule and of the environment, the process is

referred to as a resonant tunneling [539, 555–557]. When a reduced center has sufficient time to vibrationally relax, two other situations are possible. In the diabatic limit (weak electronic coupling between the redox center and both adjacent electrodes) the ET rate is small and the reduced center is completely relaxed vibrationally before the second ET. The second step loses coherency with the first one, and the reaction must again overcome the Franck-Condon barrier. This scenario results in a small current enhancement, as basically only one electron is transferred per initial molecular fluctuation [541, 542].

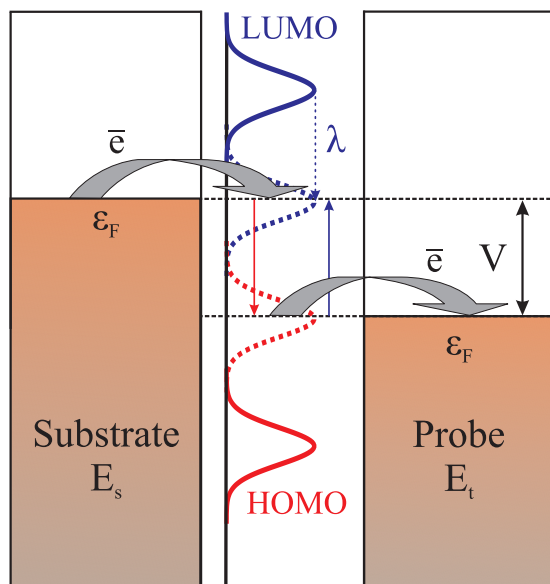


Fig. 8–2: Schematic electronic energy diagram of the two step ET mediated by the redox-active molecule. The electron is transferred from the Fermi level of the sample (left) to the LUMO of the molecule and after partial vibrational relaxation to the Fermi level of the probe (right).

I consider now the adiabatic limit (strong electronic coupling between the molecule and both adjacent electrodes) [543, 545, 550, 551] with fast ET between the molecule and the electrodes. It corresponds to an intermediate (partially coherent / partially vibrationally relaxed) case of two step ET. After the first step, the energy of the now occupied LUMO decreases due to the vibrational relaxation, but the second ET step occurs before the complete vibrational relaxation, and before the energy of the molecular level passes the Fermi level of the right electrode. The empty LUMO starts to relax towards higher energies and may accept another electron from the left electrode before it passes its Fermi level, thus repeating the cycle. The process comprises many cycles of consecutive molecular reduction and re-oxidation steps per single initial fluctuation of the molecular level. Thus, the high rate of interfacial ET is an important requirement for the

enhancement of the tunneling current.

After this qualitative description, I will describe the equations of the model. The master-equation is based on a two-step ET process and may be derived similar to standard equations of electrochemical kinetics. The total current I is given by

$$\frac{1}{I} = \frac{1}{I_1} + \frac{1}{I_2} \quad (8.1)$$

where I_1 and I_2 are the currents due to the first and the second ET.

$$I_1 = e\kappa_1\rho_1(eV)\frac{\omega}{2\pi}\exp\left[-\frac{(\lambda + e\xi\eta + e\gamma V)^2}{4\lambda kT}\right] \quad (8.2)$$

$$I_2 = e\kappa_2\rho_2(eV)\frac{\omega}{2\pi}\exp\left[-\frac{(\lambda + eV - e\xi\eta - e\gamma V)^2}{4\lambda kT}\right] \quad (8.3)$$

Here κ is the electronic transmission coefficient, and ρ is the density of the electronic levels in the metal near the Fermi level. ω is the characteristic nuclear vibration fre-

quency, ξ and γ are the model parameters describing the shift of the electrode potential at the reactive center with the variation of η and V respectively [543, 544, 546], ($0 \leq \xi, \gamma \leq 1$). The two latter parameters empirically describe the effective potentials at the redox site. They are introduced to account for the non-monotonic potential distribution in the tunneling gap due to the effects of the ionic atmosphere and of electrode screening.

Assuming the same values of κ and ρ for both oxidation and reduction processes of the redox-active molecule, one obtains

$$I = \frac{e\kappa\rho(eV)\frac{\omega}{2\pi}}{\exp\left[\frac{e}{4\lambda kT}(\lambda + \xi\eta + \gamma V)^2\right] + \exp\left[\frac{e}{4\lambda kT}(\lambda + V - \xi\eta - \gamma V)^2\right]} \quad (8.4)$$

Here λ is expressed, for convenience, in the units of volts and it is numerically equal to the energy in eV.

Equation 8.4 describes the dependence of the resonant tunneling current on the bias and the sample potentials at a fixed configuration of the tunneling junction. For the further analysis κ was assumed to be equal to unity, which results from the fully adiabatic limit. Using typical values of ω for an aqueous environment and ρ for gold electrodes, one obtains $A = e^2\rho \cdot \omega/(4\pi) = 9.1 \cdot 10^{-7} \text{ C}^2 \cdot \text{eV}^{-1} \cdot \text{s}^{-1}$ [534] and, therefore, it is possible to deduce a “numerical” version of Eqn. 8.4

$$I = \frac{1820 \cdot V}{\exp\left[\frac{9.73}{\lambda}(\lambda + \xi\eta + \gamma V)^2\right] + \exp\left[\frac{9.73}{\lambda}(\lambda + V - \xi\eta - \gamma V)^2\right]} \quad (8.5)$$

where I is in nA, V and η are in volts and λ is in eV.

Assuming low overpotential and bias values, *i.e.*, $V, \eta \ll \lambda$, one obtains

$$I = e\kappa\rho(eV)\frac{\omega}{4\pi}\exp\left(-\frac{e(\lambda + V)}{4kT}\right)\left\{\cosh\left[\frac{e}{2kT}(\xi\eta + (\gamma - 1/2)V)\right]\right\}^{-1}$$

$$I = 910 \cdot V \cdot \exp[-9.73(\lambda + V)]\left\{\cosh[19.4(\xi\eta + (\gamma - 1/2)V)]\right\}^{-1} \quad (8.6)$$

where $\cosh(x) \equiv [\exp(x) + \exp(-x)]/2$ is a hyperbolic cosine function and the assumed units are the same as in Eqn. 8.5.

The latter equations describe the peak-like shape of the tunneling enhancement observed in $(I - \eta)_V$ dependences. The experimentally accessible position (η_{peak}) and height (I_{peak}) of the peak are given by

$$I(\eta) = I_{peak}/\cosh[w(\eta - \eta_{peak})] \quad (8.7)$$

$$I_{peak} = e\kappa\rho(eV)\frac{\omega}{4\pi}\exp\left(-\frac{e(\lambda + V)}{4kT}\right) = 910 \cdot V \cdot \exp[-9.73(\lambda + V)]$$

$$\eta_{peak} = \left(\frac{1}{2} - \gamma\right)V/\xi$$

$$w = e\xi/(2kT) = 19.4 \cdot \xi$$

The parameter w represents the width of the resonance peak. Higher w results in narrower peak.

The model presented was chosen to describe our experimental data. Alternative models, which may be considered, are resonant tunneling [539, 555–557] and a vibrationally coherent two-step ET [558]. However, there is a simple criteria for the model applicability. According to the chosen model, the location of a resonance peaks in $(I - \eta)_V$ the curves at the low bias limit is close to the E^0 ($\eta_{peak} \rightarrow 0$ at $V \rightarrow 0$, cf. Eqn. 8.7). The two other models predict a maximum as well, but it is shifted from E^0 approximately by the value of the reorganization energy λ ($\eta_{peak} \rightarrow \lambda$ at $V \rightarrow 0$, [539, 543]). The latter has a typical values of few a hundred meV, and the shift may be clearly observed from experimental data. The stochastic adiabatic model [559] seems to predict a peak around E^0 as well, but doesn't provide an analytical solution and requires numerical simulations.

8.4 Constant bias spectroscopy

8.4.1 Experimental data

The data presented in this section were recorded by cycling both the sample and the tip potentials while keeping the bias constant (Sec. 3.8.5). There was no significant difference between the forward and the backward scans, so all forward and backward scans of the individual sweeps recorded under the same conditions were averaged. The

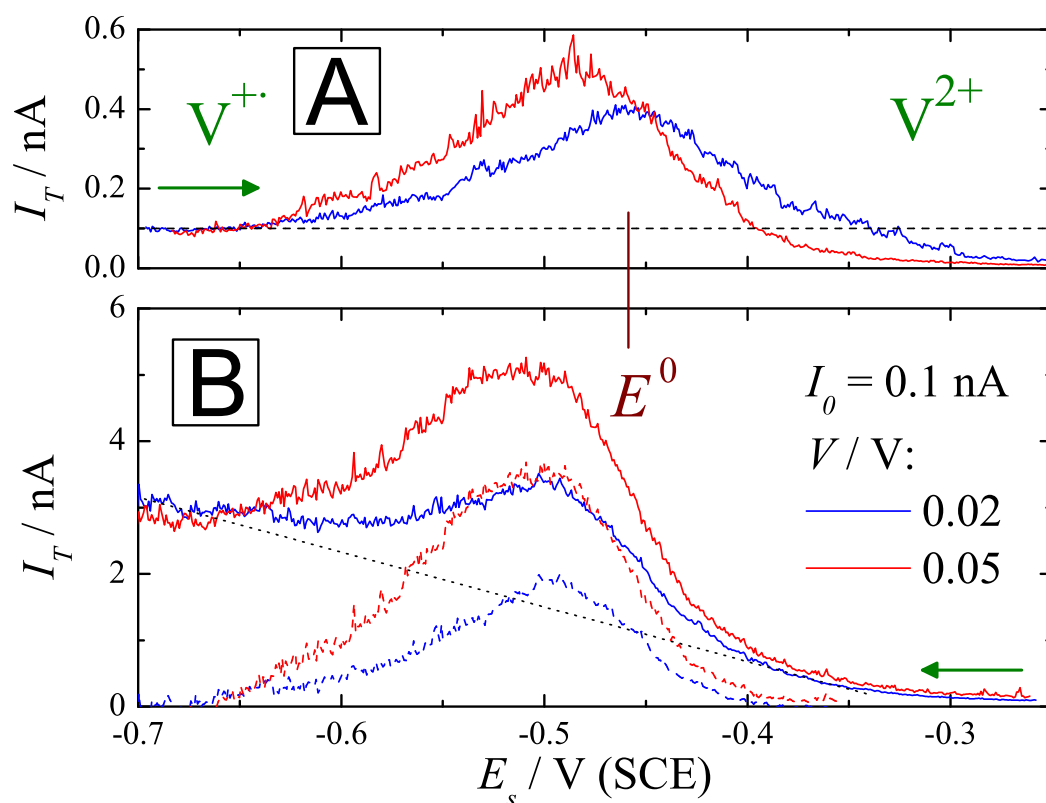


Fig. 8–3: Average curves recorded in constant bias spectroscopy. The sweep started left (A) or right (B) of the peak; bias voltage / V: 0.02 (blue), 0.05 (red); initial tunneling current $I_0 = 0.1$ nA.(B): the dotted black line is the base line for the solid blue curve, the dashed curves are solid curves of the corresponding color after base line correction. The mark on the voltage scale indicates $E^0 = -0.46$ V.

data are presented using the sample potential scale.

Examples of the averaged curves obtained in the constant bias mode are shown in Fig. 8–3. Depending on the initial potential, they correspond to the radical-cation $V^{+\bullet}$ (upper plot A) or the dication V^{2+} (lower plot B) initial form of HS6V6 at the interface. The initial part of the curves displays an interval of the constant current (see *e.g.* left part of Fig. 8–3A) due to the non-enhanced (off-resonant) direct tunneling. The current is constant at fixed tip-sample separation and bias and is equal to the initial set point, here 0.1 nA (dashed black line in the Fig. 8–3A). In the vicinity of the equilibrium potential E^0 an increase of the current is observed which then passes over the peak and again stabilizes at a constant value (see *e.g.* left part of Fig. 8–3B, solid curves). The height of the peaks varies up to one order of magnitude depending on the starting conditions: it is higher when the tip was initially stabilized at a potential positive of E^0 . It is also remarkable that, independently on the starting configuration, for a fixed gap geometry, the current is higher at the negative tail of the peak. The observed variation of the current away from the resonance peak suggests a higher “electronic transparency” (*i.e.*, lower effective tunneling barrier Φ) of the HS6V6 SAM in the radical-cation form $V^{+\bullet}$, in comparison with that of the dication form V^{2+} . The latter is in agreement with the results of current-distance STS carried out on top of the Au NP, which is wired to the substrate by a di(thioalkyl)viologen molecule [169]: the lowering of the tunneling barrier was observed when V^{2+} was electrochemically reduced. The reduction of the viologen core leads to the increase of the conductance in symmetric Au–HSnVnSH–Au junctions (Sec. 8.1.2) as well.

One should pay attention to the fact that the model presented in Sec. 8.3 describes an enhancement of the current on top of the direct tunneling. The similarities between the potential dependence of the tunneling current and of the transport current described above allow to assume a “switching” of the current of direct tunneling around E^0 as well (Sec. 2.6.4, 8.1.2). However, this effect cannot be investigated independently, at least in the experimental configuration used. One can assume that it will follow the same sigmoid potential dependence as a transport current [171], but the exact shape of this transition cannot be evaluated. Taking into account the experimental error, the task of the very accurate estimation of the potential dependence of the direct tunneling appears to be an excessive one. As an approximation for considering the effect of direct tunneling, the curves were corrected by subtracting the base line. An example is shown in Fig. 8–3B, where the dotted black line represents the selected base line for the blue curve and the dashed lines corresponds to the solid lines after correction.

An electrochemically controlled variation of the “electronic transparency” of the interface may explain the strong variation of the resonance peak heights in the two plots of Fig. 8–3. Indeed, the tip-sample separation and the tunneling current are not controlled independently in our measurements. The initial tunneling configuration corresponds to a constant tunneling resistance, rather than to a fixed geometry. Here a wider tunneling gap is expected for the more conductive interface at $E < E^0$, than in case of $E > E^0$. The observed difference in the peak height corresponds to a higher (even after baseline correction) resonance in case of a closer proximity of the tip to the sample, which is intuitively understandable. It is not directly described by the model, but, as it will be shown further, agrees with it.

The positions and heights of the resonance peaks are bias-dependent, and, as it will be shown in the next sections, the trends give a clue on the applicability of the considered model to our data as well as to allow the evaluation of model parameters.

8.4.2 Correlation analysis

Some simple correlations between the experimentally controlled parameters and the measured values are suggested by the Eqn. 8.6 for constant bias spectroscopy. As it was stated above, the latter is valid only in the limit of low bias and low overpotential values. However, the purpose of the correlations presented in this section is to demonstrate a simple and straightforward approach to compare our experimental data with the theoretical model on a qualitative and semiquantitative level. Taking into account this goal, we used as input data for the proposed correlation analysis only positions and heights of the resonance peaks as obtained from individual forward and backward scans of one potential sweep (without baseline correction). According to Eqn. 8.7, the slope of the E_{peak} vs. V dependence is equal to $(\frac{1}{2} - \gamma)/\xi$ with an intercept close to E^0 . The dependencies of the peak positions vs. the applied bias are linear, rather independent of the experimental conditions such as initial potential, set point current or scan direction. The results are reproducible from experiment to experiment.

The linear fit has a slope close to -0.5 and crosses zero bias at the potential $E = -0.47$ V, which is indeed near $E^0 = -0.46$ V. The expression for the slope of the dependence contains both ξ and γ . However, often one assumes in this case that $\xi \approx 1$ and $\gamma \approx 1$ [483].

The suggested dependence of the tunneling peak current on the applied bias (Eqn. 8.7) could be rewritten as

$$\ln(I_{peak}/V) = \ln\left(\frac{e^2 \kappa \rho \omega}{4\pi}\right) - \frac{e\lambda}{4kT} - \frac{e}{4kT}V = a - b \cdot V \quad (8.8)$$

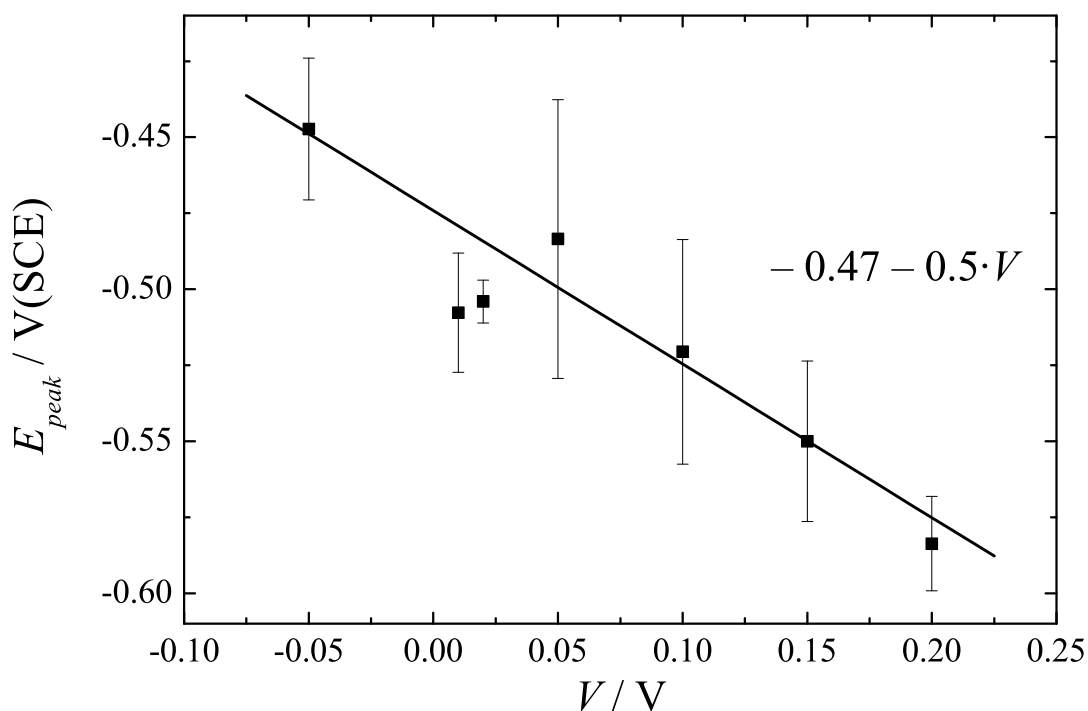


Fig. 8-4: Dependence of the position of the resonance peak on the applied bias. Each point is an average of all data for a given bias, the error margin is the standard deviation. The data for 208 scans are used. The line represents the linear fit of the data shown.

$$a = \ln\left(\frac{e^2 \kappa \rho \omega}{4\pi}\right) - \frac{e\lambda}{4kBT} = 6.81 - 9.73\lambda, \quad b = \frac{e}{4kBT} = 9.73$$

Equation 8.8 demonstrates that the slope of the $\ln(I_{peak}/V)$ vs. V dependence may be used to estimate the relation between the experimental data and the theoretical predictions, while the intercept allows to estimate semiquantitatively the reorganization energy λ . The set of data for the individual resonance curves (Fig. 8–5) clearly splits into two subsets corresponding to the different starting situations. The resonance peaks for the curves starting in the potential range where the dication is stable, are generally higher than for the ones starting from potentials, where the radical-cation is stable. Again, no dependence on the scan direction or the initial set point current I_0 was observed in this plot. Slopes of the two fitted lines $\ln(I_{peak}/V)$ vs. V are somewhat higher than the one predicted theoretically, but still in a good agreement with it. The corresponding values of λ are estimated from the intercept. For two sets of data, we obtained 0.2 ± 0.03 and 0.4 ± 0.03 eV, respectively. This result didn't change significantly when the data were fitted by a line with a fixed slope equal to the theoretical value. The latter values describe semiquantitatively the difference between the two starting situations in terms of the model.

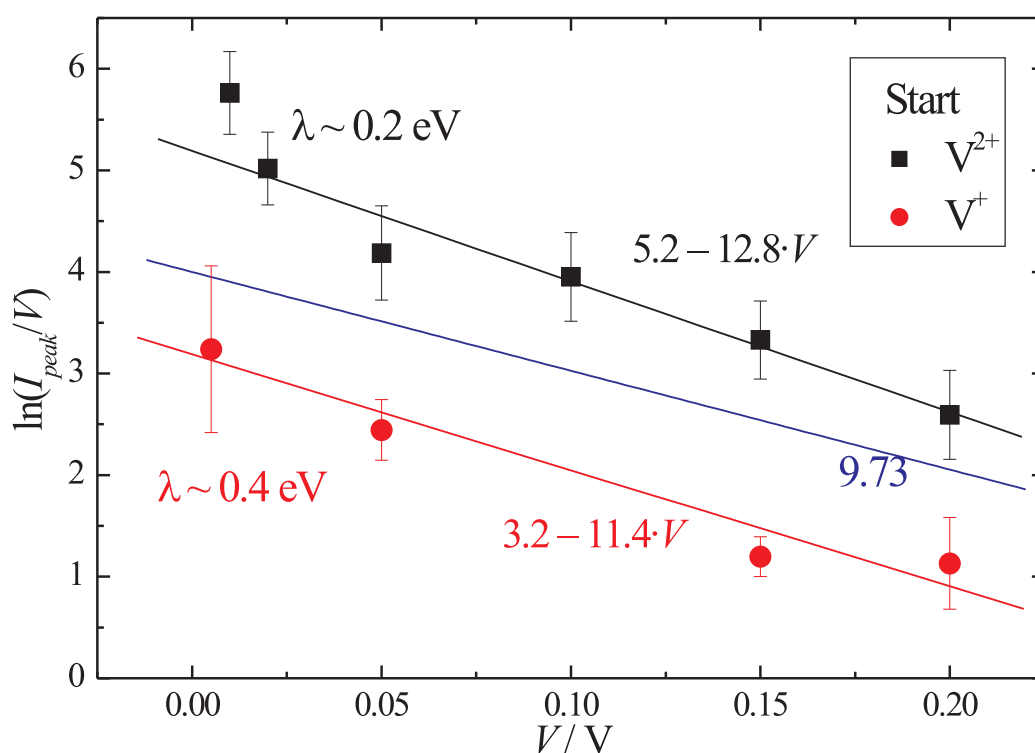


Fig. 8–5: Dependence of the height of the resonance peak on the applied bias. Each point is an average of data for individual scans starting from V^{2+} (black squares, 166 scans) or $V^{+•}$ (red circles, 48 scans) form. Black and red lines are linear fits of the corresponding sets of points with estimated value of λ (see text). The blue line is a guide line with a theoretically predicted slope.

8.4.3 Data fitting

For the fitting I used the averaged curves after a base line correction performed as demonstrated in Sec. 8.4.1. Peaks in these curves represent the enhancement of the tunneling only. The experimental curve may be described by the curves corresponding either to the “simplified” equation (8.6) or the “full” equation (8.5) using a non-linear fitting procedure. The simplified equation essentially represents the peak, which shape is determined by the somewhat non-conventional function $1/\cosh(x)$. The exact appearance of the peak (similar to other peak functions such as Gaussian or Lorentzian) is described by three parameters: peak position E_{peak} , peak height I_{peak} and peak width $1/w$. Fitting of this peak function to the experimental curves provides values of these

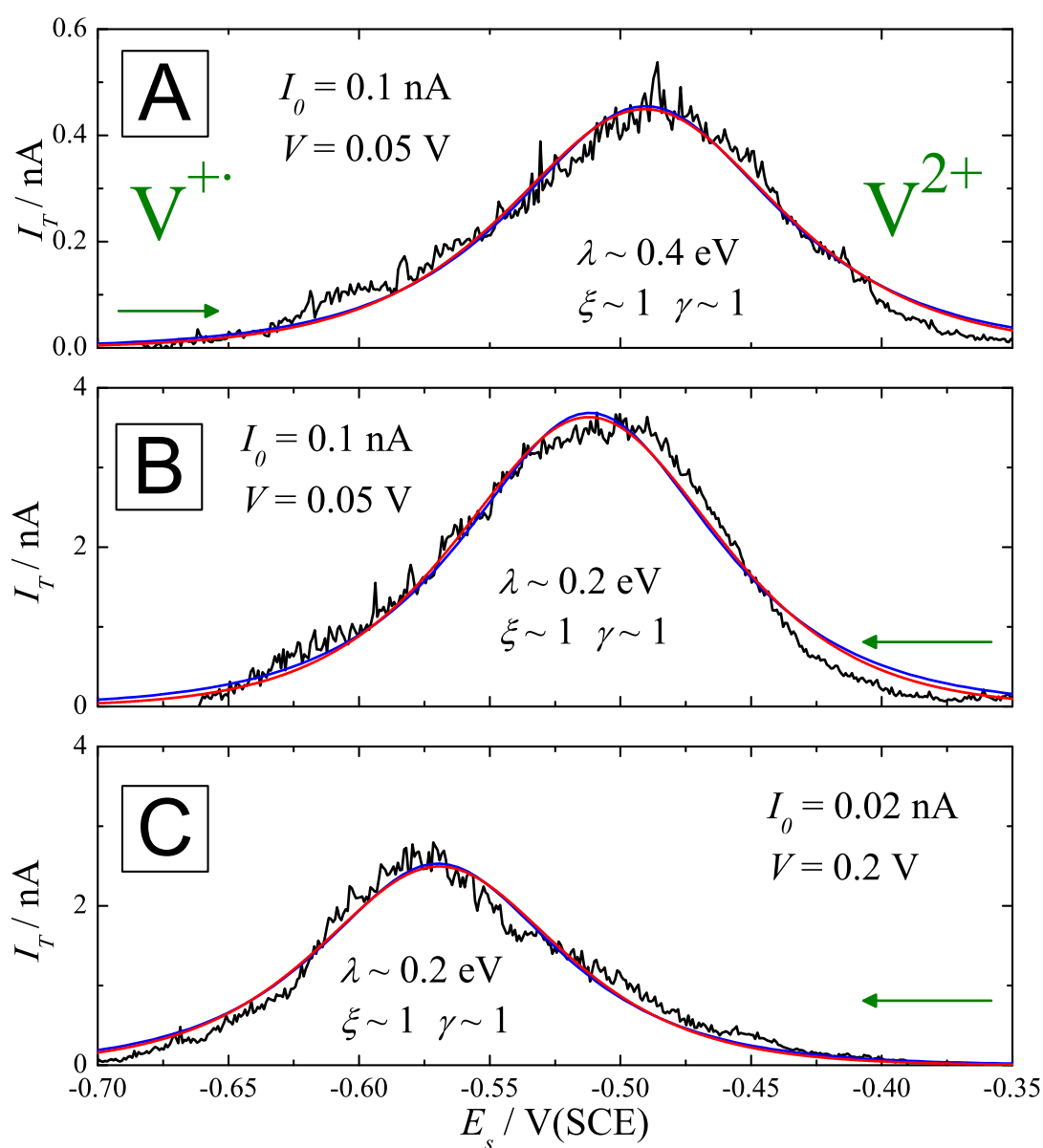


Fig. 8–6: Averaged constant bias spectroscopy curves after baseline correction (black, cf. Fig. 8–3). The sweep started from $V^{+•}$ (A) or V^{2+} (B,C) adlayers. Blue and red curves are fits using the simplified and the full equations of the resonance peak.

“empirical” parameters allowing the subsequent extraction of the model parameters λ , γ and ξ (Eqn. 8.7).

The experimental resonance curves, each of them is an average of 10–20 individual scans, were base-line corrected as described in Sec. 8.4.1 and demonstrated in Fig. 8–3. Examples are shown in Fig. 8–6. The fitted curves correspond to the simplified (blue) and the full (red) equations. The model curves describe the shape of the peaks rather well. Curves corresponding to the simplified and the full equations give almost identical results. However, the obtained optimal values of the model parameters differ between these two approaches.

The resulting values of γ_{simp} and ξ_{simp} obtained using the simplified equation are typically slightly higher than 1. Taking into account their definition, it physically corresponds to a value close to unity. The ones obtained using the full equation are also close to 1, but usually lower than γ_{simp} and ξ_{simp} , in some cases one obtains values between 0.8–0.9. These values correspond to the slope of -0.5 as obtained from the correlation plot (Fig. 8–4). The reorganization energy λ determined for the initial situations of V^{2+} and $V^{+\bullet}$ adlayers are similar to that obtained from the correlation plot (Fig. 8–5). Again, the use of the simplified equation leads to an overestimation of λ .

From the formal point of view, the sequence of plots in Fig. 8–6 (A–C) corresponds to an increasing deviation from the assumption used to deduce the simplified equation. For the plot (A) λ is almost one order of magnitude higher than V and $E_{peak} - E^0$. For (B) λ is smaller, and for (C) V is very close to the estimated λ . Consequently, there is a trend towards an increase of the difference between the parameters obtained using the simplified and the full equations. For example, $\Delta\lambda = \lambda_{simp} - \lambda_{full}$ is negligible for the data in plot (A), $\Delta\lambda \approx 0.002$ eV for (B) and $\Delta\lambda \approx 0.05$ eV for (C).

Based on these results as well as on their agreement with the correlation plots (Sec. 8.4.2), it is clear that the simplified equation can be used semiquantitatively to analyze the data obtained in constant bias spectroscopy, but one should bear in mind that this approach tends to overestimate ξ and γ , especially if λ is rather small. Additional trials on fitting the experimental curves without base line correction were carried out with both equations as well. The results do not differ significantly from those described above. The datasets of fitted I_{peak} and E_{peak} are very close to those determined empirically for every case and show exactly the same behaviour on the correlation plots as it is described in Sec. 8.4.2.

8.5 Variable bias spectroscopy

Complementary $I - V$ EC STS experiments were carried out in a variable bias mode. Similar to the constant bias spectroscopy, the tip was initially stabilized at a potential positive of E^0 . A tunneling current was recorded during the sweep of the tip potential over a wide range, while the potential of the sample was fixed (Sec. 3.8.5) at $E_s = -0.2$ V. The explored range of potentials was sufficiently far from the second redox transition of the viologen core (*cf.* Fig. 8–1B,C). The potential sweep rate r was varied in a range of $0.5\text{--}2$ V·s $^{-1}$.

The measured scans demonstrate a very pronounced asymmetry. Small hysteresis loops were found on the $I - E_t$ curves. In order to minimize its distorting effect, the forward and the backward scans of the potential sweeps measured under the same experimental conditions were averaged. No systematic effects were found in the ob-

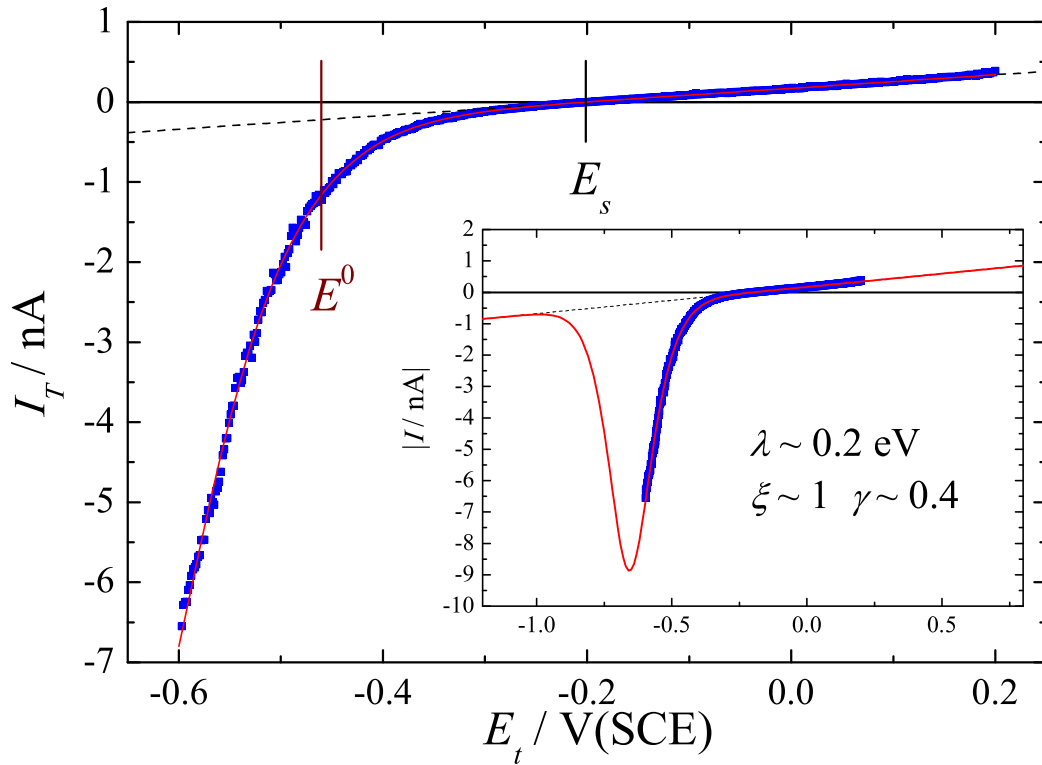


Fig. 8-7: Average $I - E_t$ curve recorded in variable bias spectroscopy (blue squares), an expected linear current response of the direct tunneling (black dashed line) and a fit of the tunneling enhancement (red line). The inset shows the same data and a simulated curve in a wide potential range.

tained average curves with the variation of r . The representative “master curve” (Fig. 8-7) was constructed by averaging curves representing different values of r . The data plotted correspond to 12 individual scans.

The resulting curve is highly asymmetric (Fig. 8-7). For $E_t > E_s$ ($V > 0$) and at small negative values V , a linear current response was observed, which is characteristic for the direct tunneling at fixed gap geometry. The fit of the linear part is shown by the dashed line in the plot. An enhanced exponential-like tunneling response is observed at $E_t \leq -0.25$ V. The on/off ratio between negative and positive branches of the $I - V$ curve is *ca.* 20 at $|V| = 0.4$ V.

Unlike in case of constant bias spectroscopy, I was not able to derive any kind of simple relations between the features of the recorded scan and the model parameters. The measured curve is quite featureless, in comparison with a peak-like characteristic in constant bias mode. The rising tail of the curve seems to be exponential, but its slope is not directly related to any single property of the system. Therefore, in order to obtain model parameters, the full equation 8.5 combined with a linear response of direct tunneling² was fitted to our experimental data. The linear baseline was evaluated by the extrapolation of the linear part of the experimental curve.

The fitted curve and the obtained parameters are shown in Fig. 8-7. Similar to the constant bias mode, the estimated ξ is close to 1, while $\gamma \approx 0.4$ is significantly

² Here we neglect the redox-switching of direct tunneling described in Sec. 8.4.1 and attribute the observed effect to redox-mediated tunneling only.

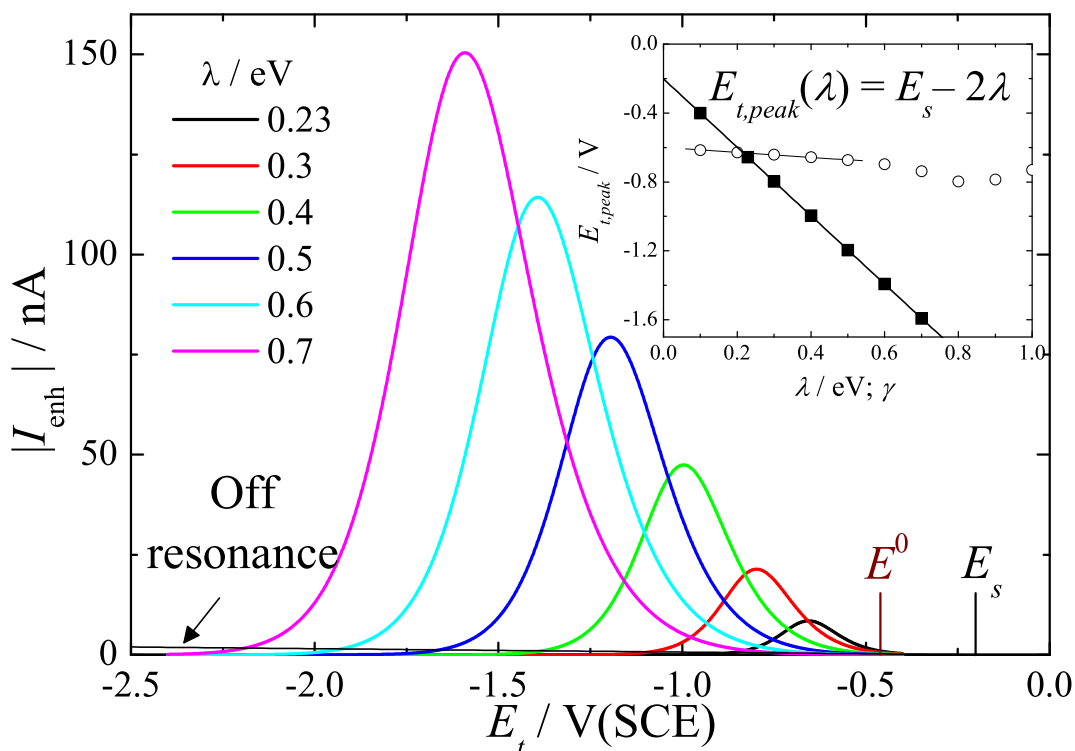


Fig. 8–8: Series of curves simulated according to Eqn. 8.5. λ was systematically varied while other parameters were the same as determined for the experimental data in Fig. 8–7. The inset shows a dependence of the peak position on λ (squares) and γ (circles).

smaller. The estimated value of $\lambda \approx 0.2$ is also in agreement with the one obtained for constant bias spectroscopy scans carried out with an initial tip stabilization at potentials positively of E^0 (see Table 8.1).

The important question concerning variable bias spectroscopy is a current behavior on the further extension of the bias window. The experimental requirements for the variation of the potential in a wide range are quite strict. The absolute limits of the accessible potential range are set by the oxidation/reduction of solvent and the samples, the resulting range may be insufficient. The issue of potential range may be resolved by using organic solvents or ionic liquids as electrolyte [535]. We currently elaborate this topic in our group. Other experimental complications includes, *e.g.*, distortion due to the presence of oxygen. Even the insufficient accessible range of currents may prevent experimental studies of the system behavior at very large bias. Actually, beside one experiment employing ionic liquids [535], no variable bias spectroscopy studies of redox-mediated tunneling was reported so far.

To address the issue of larger biases, I extrapolated the simulated curve describing our experimental $(I - V)_\eta$ dependence towards higher values. The result is shown in the inset of Fig. 8–7. After the onset of the enhancement at $E_{t,1} = -0.25$ V the tunneling current passes through a peak at $E_{t,peak} = -0.65$ V and vanishes around $E_{t,2} = -1$ V. However, the relation between tip position and other system parameters cannot be easily extracted from the model equations (*i.e.*, Eqn. 8.4, 8.5). To explore the dependence of the features in the predicted $I - V$ curves on the model parameters, I performed simulations by systematically varying a single parameter (*e.g.*, λ or γ) at fixed values of the other ones. Some results are summarized in Fig. 8–8. The current of the off-

resonance tunneling is given for comparison.

Both position and height of the peak are strongly affected by the value of λ . The dependence of the peak position on λ may be described by a simple linear relation $E_{t,peak} = E_s - 2\lambda$ (inset on Fig. 8–8). The assignment of the intercept to the sample potential was checked by varying its value. The simulated peaks were shifted correspondingly. Physically, the slope of 2 corresponds to the energy windows of 2λ accessible for the fluctuating molecular levels. Unlike in case of constant bias mode (*cf.* Eqn. 8.7), the increase of λ leads to an increase of the peak height in the variable bias mode. The latter may be also attributed to a wider energy window accessible for molecular levels. The type of dependence is not clear, for the simulated curves it seems linear at $\lambda > 0.3$.

The variation of the peak position with γ is much lower and non-monotonic. The linear dependence of $E_{t,peak}$ on γ with a slope of ≈ -0.143 V may be seen in the range $0.1 < \gamma < 0.5$. The current of the peak exponentially decreases with γ . The variation of overpotential does not affect the position of the peak, but leads to an almost exponential decrease of the peak height with η .

8.6 Summary and discussion

The SAM of N-hexyl-N'-(6-thiohexyl)-4,4'-bipyridinium (HS6V6) on Au(111) were comprehensively characterized by current-voltage STS techniques in an electrochemical environment. “Constant bias” and “Variable bias” spectroscopic modes were employed. The experimental data clearly demonstrated an enhancement of the tunneling current mediated by the redox-active viologen core. A very good agreement between the experimental data and the predictions of the model of two-step ET with a partial vibrational relaxation was found. The values of model parameters estimated from the two spectroscopic modes by various analysis procedures are in a good agreement as well (Table 8.1).

An interesting electrochemically controlled “switching” of the off-resonant tunneling through HS6V6 SAM was observed. At fixed gap geometry and bias a higher current of direct tunneling was measured for $E < E^0$ compared to $E > E^0$. This corresponds to an increase of the off-resonant ET rate during the transition $V^{2+} \rightarrow V^{2+}$. The same effect was demonstrated for the conductance of (di)thioalkylviologens $HSnVn(SH)$ incorporated in various assemblies (Sec. 8.1.2). A lowering of the tunneling barrier at the interface was observed from current-distance STS measurements for the asymmetric viologen-containing junction [169].

The peak-like current response in constant bias spectroscopy seems to be the most straightforward evidence of the tunneling enhancement. Simple correlations – dependence of position and height of the resonance peak on bias – allow to evaluate the

Tab. 8.1: Estimated values of model parameters.

Mode	Constant bias		Variable bias
Initial form	V^{2+}	$V^{+\bullet}$	V^{2+}
λ / eV	0.2 ± 0.05	0.4 ± 0.05	0.2 ± 0.03
ξ	1 ± 0.05	$\approx 1 \pm 0.05$	$\approx 1 \pm 0.03$
γ	1 ± 0.05	1 ± 0.05	0.4 ± 0.03

relation between the experimental data and the model predictions and to estimate the model parameters. The correlation of the first type (E_{peak} vs. V) is used virtually in every work exploring the tunneling enhancement by a redox-active center in order to demonstrate the applicability of the employed model (Sec. 8.3). To our knowledge, the correlation of the second type ($\ln(I_{peak}/V)$ vs. V), is described for the first time. Similar experimental dependencies of positions and heights of resonance peaks on bias were demonstrated for azurin in a series of constant bias spectroscopy curves by Alessandrini *et. al* (see [165] and Fig. 11 in [539]); however, no attempts to quantify these observations were reported. Correlations of the second type allows an easy estimation of the important model parameter, reorganization energy λ . It is well known to characterize nuclear dynamics of ET in solutions and may be evaluated by a number of experimental and theoretical methods.

The parameters estimated from the correlation plots are in a good agreement with results of the more advanced analysis (Table 8.1). The detailed analysis of the experimental curves was carried out according to both the “simplified” (8.6) and the “full” (8.5) equations. The former is typically used to analyze results of constant bias spectroscopy without going into the details of its applicability. I demonstrated that the simplified equation may be used even in case of deviations from the original assumptions ($\eta, V \ll \lambda$), but it leads to the overestimation of all three model parameters.

The variable bias spectroscopy experiments in aqueous environment is reported for the first time. This mode shows a strong enhancement of the tunneling signal when a molecular redox level is located between the Fermi levels of tip and sample. The same theoretical model describes the experimental $I - V$ dependence. Complementary numerical simulations demonstrated that, if the bias is sufficiently high, the used model predicts a peak on the $I - V$ dependence and a consequent vanishing of the tunneling enhancement. It was shown that the position of the peak follows a simple relation $E_{t,peak} = E_s - 2\lambda$, while its height is determined by various different factors.

The values of ξ and γ , as obtained from constant bias spectroscopy, are close to 1 independent of the starting potential. This result actually corresponds to the effective potential at the viologen site being equal to E_t [539]. The possible physical interpretation of such a surprising conclusion is that inside a tunneling gap the potential profile quickly drops at the sample and remains rather constant up to the tip. A more complicated picture arises when considering the effect of “Debye screening” [548, 560–562]. It is expected to be stronger at high electrolyte concentrations, which corresponds to our experimental conditions (0.5 M LiClO₄). It is not clear at the moment, what could be the effect of the monolayer / alkyl spacers on the potential distribution in the gap.

For the variable bias spectroscopy ξ is still close to 1, while γ decreased to *ca.* 0.4. This corresponds to the effective potential at the viologen core being equal to $E_s + 0.4V$ and may reflect an asymmetry in the experimental realization of this mode: the sample potential was fixed, while the tip potential was driven towards significantly higher values compared to the first experimental mode. Indeed, while a maximum value of the bias voltage of 0.2 V was used in constant bias mode, the very onset of enhancement in the variable bias mode is observed at $E_t = -0.25$ V ($V = -0.05$ V), and the measured range extends to $E_t = -0.6$ V ($V = -0.4$ V) (Fig. 8–7).

The experimentally determined reorganization energy λ was found to depend only on the initial gap geometry. We attributed this observation to the aforementioned lowering of the effective tunneling barrier at the interface when a SAM of HS6V6 was electrochemically “switched” from V^{2+} to $V^{+\bullet}$. Depending on the starting conditions,

λ is close to 0.4 and 0.2 eV correspondingly, with an error margin lying well within 0.05 eV. The same result was obtained for both spectroscopic modes.

The tip-sample separation was controlled via current feedback and corresponds to a constant tunneling resistance, rather than to a fixed geometry. Thus a wider tunneling gap is expected for a more conductive interface at $E < E^0$, than in case of $E > E^0$. The effect of a confined tunneling gap on λ was addressed theoretically [164, 539, 544]. Qualitatively, the smaller gap results in a smaller environment reorganization energy due to the exclusion of the water molecules from the surrounding of the redox center, which is in agreement with our observations. The dependence of peak height in constant bias mode on the initial set point I_0 illustrated by Albrecht *et. al* for Os organocomplex [536] agrees with our conclusions as well. We also observed a linear-type dependence of I_{peak} on the initial set point current I_0 in selected experiments, although it was varied in a much narrower range (0.05 – 0.5 nA).

We can conclude that all observations described in this chapter are in a good agreement with the model considered. However, there are inherited limitations in the presented version of the model. The equations used assume a strong (or at least equal) electronic coupling of the molecule with both electrodes, as reflected in the electronic transmission coefficient $\kappa \approx 1$. This is clearly not the case under our conditions. The tip is separated from the redox-active center not only by the “chemical” barrier of the alkyl spacer, but also by the “tunneling” barrier of the medium. It is possible to account for this asymmetry within the frames of the same model equations (8.1–8.3), but it would require special simulations, which are beyond the scope of this work.

Another limitation is an estimated absolute value of the factor $A = e^2 \kappa \rho \cdot \omega / (4\pi)$ (Eqn. 8.5), which corresponds to the adiabatic limit of each of the two ET steps. This is most probably not the case in the experimental configuration employed. The used value of A also corresponds to the ET mediation by a single redox-active center only. This does not imply that exclusively one redox group is trapped in the tunneling gap, but rather that at every moment only one redox center experiences a favorable fluctuation. The scatter between individual measured scans is quite high, and an averaged curve represents a statistically averaged picture. These curves may correspond to $n > 1$ simultaneously acting mediators. Taking into account the geometry of the tunneling junction, it is difficult to expect that n is higher than *ca.* 10. Fortunately, the overestimation of the transmission coefficient and the underestimation of the amount of active centers in the tunneling junction are compensating factors.

The robustness of the analysis presented to the variation of A is additionally supported by the pronounced exponential-like dependence of the resonant current on the reorganization energy λ , in comparison with the much weaker linear-like dependence on κ and n . The possible corrections taking into account precise values of $\kappa_{1,2}$ and n would be negligible with respect to the uncertainty of the results extracted from the experimental data. The presented suggestions may explain why, despite of some deviation of experimental conditions from those assumed by the model, our experimental data are well described by it.

The real limits of the model are probed in the tunneling experiments carried out at high values of the bias. The value of λ is a criteria of the bias magnitude. When V is comparable or higher than λ , the model may not be adequate. For example, in constant bias spectroscopy a plateau instead of a peak is expected in the limit $\lambda \ll V$ [539]. Some of our experimental curves, recorded at $V = 0.2$ V under conditions, corresponding to $\lambda = 0.2$ eV (Table 8.1), indeed demonstrated features more closely resembling

a plateau than a peak. However, we did not explore this issue in details. More critical for high bias limitations are experiments in variable bias mode. The current in the experimentally accessed bias range is well described by the model. Extrapolation of experimental data predicts a peak and a vanishing of the enhancement, and I deduced the empirical relations for the characteristic features of the curves. These attempts may have nothing to do with reality. The model as it is described above does not account for contribution of electrons from non-Fermi levels and the predicted features are similar to the “inverted Marcus region” in electrochemical kinetics. More advanced theoretical studies are required. In principle, the following two situations are possible [540]. A peak or a saturation in the $I - V$ curves may be observed depending on the properties of the system, and only further experiments could clarify this issues.

With the experimental data available for the viologens, a unique possibility of the comparison of ET at single molecule level in a symmetric and an asymmetric configuration arises. The intriguing question to be addressed is, why an electrochemical gating leads to the “switching” of conductance in the first case and a redox-mediated ET in the second case [540]. Clearly, the correct answer is based on properties of the nuclear subsystem. The concept of “soft gating”, as recently proposed by Ulstrup *et. al*, [160] is an example of the theoretical treatment of ET, deeply rooted in the nuclear motion modes of SMJ. There are many other interesting properties of redox-active SMJ, which are still to be addressed experimentally and theoretically.

Chapter 9

Conclusions and outlook

The techniques of EC STM and EC STS in combination with CV and other electrochemical methods were employed to study the interfacial structure and ET properties of five different systems. The samples used were:

- bare Au(111) substrates with and without reconstruction (Cha. 4, 5);
- ionic adlayers, formed by Cu^{2+} , SO_4^{2-} and Cl^- on Au(111)- (1×1) (Cha. 4);
- SAMs of alkanedithiols (SnS) on Au(111)- (1×1) (Cha. 6);
- adlayers of 4,4'-bipyridine (44BP) on Au(111) (Cha. 7);
- SAMs of a redox-active substance HS6V6 (Cha. 8).

For some systems, complementary experiments were carried out in air and mesitylene.

The technique of EC STM was mastered by using Cu UPD as a tutorial system. The results are described in chapter 4. CVs of an Au(111) electrode in aqueous solutions of Cu^{2+} and SO_4^{2-} with and without small additives of Cl^- demonstrated the adsorption of charged species at the solid-liquid interface. The bare Au(111)- (1×1) surface, as well as ordered adlayers formed by the coadsorption of Cu^{2+} with SO_4^{2-} or Cl^- were investigated in steady state EC STM experiments. The well known Cu^{2+} - SO_4^{2-} phase was resolved in the absence of Cl^- . Depending on the electrode potential and Cl^- concentration, two different Cu- Cl^- phases with different Cl^- packing densities were identified and described.

Sequences of the time-resolved STM images demonstrating potential-induced phase transitions were recorded and quantified to extract the time dependence of the respective adlayer coverages. The latter, together with the direct STM observation, allowed to suggest mechanisms of the transitions. The study demonstrated the important role of complementary imaging techniques and traditional electrochemical experiments.

The electron tunneling between the STM probe and the sample was investigated by current-distance STS for bare Au(111)- (1×1) , Cu^{2+} - SO_4^{2-} and Cu^{2+} - Cl^- adlayers. The results demonstrated significant differences of the STS responses for the systems studied. The latter was attributed to the interplay of the geometric and electronic properties of the adlayers.

Chapters 5–7 describe the studies of electrical conductance through single atomic and molecular junctions. The methodology of the experiments was developed in our group during the last few years. It includes

- preparation of sharp Au and Pt/Ir STM probes;
- a technique of an oxygen-free STM experiments;

- a STM “stretching” procedure;
- data analysis;
- hardware development.

The application of the developed complex of procedures to three archetypal systems is described in the presented thesis. Besides them, other experiments exploiting the same strategy are carried out in our group.

The study of conductance of Au QPCs is described in chapter 5. Various properties of this system were thoroughly investigated since a long time. However, very few experiments reported were carried out in an electrochemical environment. Nevertheless, the Au QPC conductance is governed by a single conducting channel with almost ideal transmission and found to be independent on the environment. The results of the stretching experiments employing Au QPC were used to introduce a new data analysis strategy. Besides the well known ones, two other properties of Au QPC were found. An enhanced stability of QPCs with certain electronic configurations (“electronic shell effect”) was observed. The results also suggested that the QPC configurations with conductance close to the multiple integer of a fundamental value are mechanically more stable than others.

The first molecular systems, which conductance was studied by the stretching technique, were alkanedithiols (S_nS) (chapter 6). The binding between gold and thiol groups is the most widely used approach to create metal-molecule contacts, while a methylene chain is the simplest possible molecular structure. SAMs of S8S on Au(111)-(1×1) were characterized by electrochemical techniques and STM imaging. The stretching experiments with S8S were carried out in various media. It was found that the probability to form a SMJ is the highest if the molecules are diluted in the working solution. The latter conditions were used to explore the chain length dependence of SMJ conductance. The detailed investigation demonstrated the existence of three types of SMJs for S_nS . Complementary *ab initio* calculation allowed to assign the observed variation of the SMJ conductance to the interplay of molecule-metal contact geometry and intrinsic molecular conformations.

The established technique of the stretching experiment was used further to explore the conductance of SMJs formed between Au contacts and 4,4'-bipyridine (44BP), a molecule with two pyridyl rings (chapter 7). The latter is an example of a weakly bound anchoring group. Like in case of a related amine anchoring group, a donor-acceptor bond is formed between a lone electron pair of the N atom and an empty *s*-orbital of Au. However, the pyridyl anchoring group is also an intrinsically conjugated, highly conductive π -system without conformational degrees of freedom, which binding to Au is controlled by the potential (*i.e.*, the surface charge) of the metal.

The conductance of 44BP SMJs was studied under electrochemical conditions. Four different types of SMJs were found after careful data analysis. The whole range of conductance values determined spans over more than 2 orders of magnitude. The conductance of each SMJ type is potential-independent, while the formation probability is strongly decreased upon the lowering of the potential. The latter is in agreement with the decrease of the coverage and a progressive tilting for 44BP molecules, known from other experiments. Complementary *ab initio* simulations demonstrated that the conductance of Au-44BP-Au SMJs is much stronger affected by the variation of contact geometry and molecular conformation (*i.e.*, tilt angle between two pyridyl rings), than

in case of SnS . The effects found may explain observed high variability of the SMJ conductance.

The last part of the thesis is devoted to the analysis of the ET enhanced by the redox-active mediator HS6V6 (chapter 8). The viologen core, which is essentially a 44BP molecule with alkyl spacers attached to N atoms, is particular known for fast electron exchange with metal electrodes. The current-voltage EC STS experiments were carried out by Zhihai Li with my help and described in detail in his Ph.D. thesis. They were carried out using a constant bias and a variable bias modes. I performed the analysis of the existing theoretical model of a two-step ET with a partial vibrational relaxation by Kuznetsov and Ulstrup, and adopted it to the experimental conditions. A new approach to the analysis of experimental data was proposed. A very good agreement of the theoretical description and experimental data was found. The values of two model parameters, obtained from different spectroscopy modes, are in agreement between each other. The difference between the evaluated values of the third parameter reflects the distinction of two spectroscopy modes. The limitations of the used model were discussed.

To summarize, in my thesis I demonstrated the power of the STM approach to ET studies at nanoscopic level in a variety of systems by a number of experimental methods. The theoretical descriptions of the studied processes were presented as well.

The work described in this thesis will be continued in several directions. After publications of the papers based on the results of the Ph.D. thesis (see appendix C), an extension of the experimental studies of anchoring group effect on the SMJ conductance are planned. In parallel, the experimental and analysis technique are to be developed further. The existing collaborations with experimental (N. Tao) and theoretical groups in the field of transport calculations (F. Evers) and ET in electrochemical systems (A. Kuznetsov, J. Ulstrup) will be continued to establish general correlations between molecules, respective junction composition, and ET characteristics. In this way, we hope to provide expertise for implementation in future device-type applications.

Appendix A

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A.3 List of Symbols

Symbol	Meaning	Units/Value
a	Thermodynamical activity	–
A	Model parameter (Sec. 8.3)	$9.1 \cdot 10^{-7} \text{ C}^2 \cdot \text{eV}^{-1} \cdot \text{s}^{-1}$
c	Molar concentration of species	$\text{M} (\text{mol} \cdot \text{l}^{-1}), \text{mol} \cdot \text{m}^{-3},$
C	Capacitance	F
C	Surface capacitance	$\text{F} \cdot \text{m}^{-2}$
C_{EDL}	Surface capacitance of EDL	$\text{F} \cdot \text{m}^{-2}$
D	Diffusion coefficient	$\text{cm} \cdot \text{s}^{-2}$
e	Electron (elementary) charge	$1.62 \times 10^{-19} \text{ C}$
$\bar{e}$	Electron (in chemical reaction)	–
E	Electrode potential	V
E^0	Standard electrode potential of redox-pair	V
$E^{0'}$	Formal electrode potential of redox-pair	V
$E_{q=0}$	potential of zero charge (PZC)	V
E_{cell}	Cell potential	V
E_{eq}	Equilibrium potential	V
E_i, E_u, E_l	Initial, upper and lower potential in CV	V
E_s, E_t	Sample and tip electrode potentials in EC STM	V
f_{FD}	Fermi-Dirac distribution function	–
F	Faraday constant	$96485 \text{ C} \cdot \text{mol}^{-1}$
$\vec{F}$	Force	N
g	Density of electronic states per volume unit	$\text{eV}^{-1} \cdot \text{m}^{-3}$
G	Conductance	S
G_0	Quantum conductance	$7.75 \times 10^{-5} \text{ S}$
G	Gibbs energy	J
$\bar{G}$	Electrochemical Gibbs energy	J
h	Planck constant	$6.626 \times 10^{-34} \text{ J} \cdot \text{s}$
I	Current	A
I	Amperometer (in schemes)	–
I_T	Tunneling current	A, nA, pA
j	Current density	$\text{A} \cdot \text{m}^{-2}$
J	Flux of species	$\text{mol} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$
k	Boltzmann's constant	$1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$
l	Distance, length	m
m	Mass	kg
m_e	Electron mass	$9.11 \cdot 10^{-31} \text{ kg}$
M	Molar mass	$\text{kg} \cdot \text{mol}^{-1}, \text{g} \cdot \text{mol}^{-1}$
Me	Metal	–
N	Concentration	$\text{particles} \cdot \text{m}^{-3}$
n	Integer number (various usage)	–
N_A	Avogadro's number	$6.022 \times 10^{23} \text{ mol}^{-1}$
Ox	Oxidized form of reactant	–
p	Pressure	Pa, atm
P	Probability	–

q	Electric charge	C
q_s	Surface charge	$C \cdot m^{-2}$
r	Sweep rate of CV	$V \cdot s^{-1}$
$\vec{r}$	Coordinates in space	$m \times m \times m$
R	Universal gas constant	$8.314 J \cdot K^{-1} \cdot mol^{-1}$
R	Resistance	Ohm
R_{sol}	Solution resistance	Ohm
Red	Reduced form of reactant	—
S	Surface, surface area	m^2
S	Entropy	$J \cdot K^{-1}$
t	Time	s
$\vec{t}$	Translation vector	$m \times m \times m$
T	Temperature	K, °C
U	Potential energy	J, eV
v	Velocity	$m \cdot s^{-1}$
V	Bias	V
V	Volume	m^3
V	Voltameter (in schemes)	—
W	Energy	J
w	Resonance peak width parameter (Sec. 8.3)	V^{-1}
$\vec{X}$	Electric field strength	$V \cdot m^{-1}$
x, y	“Lateral” coordinates on surface	m, nm, Å
z	“Vertical” distance to surface	m, nm, Å
Z	Charge number	—
ξ, γ	Model parameters (Sec. 8.3)	—
ε	Electron energy	J, eV
ε_F	Fermi energy of solid body	J, eV
ε_0	Minimum of electron energy of solid body	J, eV
ϵ	Dielectric constant	—
ϵ_0	Dielectric permittivity of vacuum	$8.85 \times 10^{-12} C^2 \cdot N^{-1} \cdot m^{-2}$
Γ	Coverage / Surface excess	$mol \cdot m^{-2}$
μ	Chemical potential	$J \cdot mol^{-1}$
$\bar{\mu}$	Electrochemical potential	$J \cdot mol^{-1}$
ν	Amount of substance	mol
ω_{eff}	nuclear vibration frequency	s^{-1}
ρ	Charge density	$C \cdot m^{-3}$
ρ	Density of the electronic levels (Sec. 8.3)	eV^{-1}
κ_d	Gouy-Chapman decay constant	m^{-1}
κ	electronic transmission coefficient	—
λ	Gibbs energy of the environmental reorganization	J, eV
η	Overpotential	V
ϕ	Electrostatic potential, work function	V
Φ	Tunneling barrier	J, eV
ψ	Electrostatic potential vs. that of solution	V
ν	Frequency	Hz
σ	Conductivity	$S \cdot m^{-1}$

A.4 List of Acronyms

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
44BP	4,4'-bipyridine
nS	alkanethiols $CH_3(CH_2)_{n-1}SH$
6S	1-hexanethiol $CH_3(CH_2)_5SH$
8S	1-octanethiol $CH_3(CH_2)_7SH$
AFM	atomic force microscopy
CB	conductance band
CE	counter electrode, also auxiliary electrode
CPU	central processing unit
CP AFM	current probe atomic force microscopy
CV	cyclic voltammetry, cyclic voltammogram
CNT	carbon nanotube
DAAD	Deutsche Akademische Austausch Dienst
DBA	donor-bridge-acceptor configuration
DFT	density functional theory
DC	direct current
EC	electrochemistry, electrochemical
EC STM	electrochemical scanning tunneling microscopy
EC STS	electrochemical scanning tunneling spectroscopy
EDL	electrical double layer
ET	electron transfer
FCC	face centered cubic crystallographic lattice
FET	field effect transistor
FWHM	full width at half maximum
FZJ	Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
GC	glassy carbon

HOMO	highest occupied molecular orbital
HOPG	highly oriented pyrographite
HS6V6	N-hexyl-N'-(6-thiohexyl)-4,4'-bipyridinium ion or bromide salt
IC	integrated circuits
IHP	inner Helmholtz plane
IUPAC	International Union for Pure and Applied Chemistry
IR	infrared
IRAS	infrared absorption spectroscopy
KMF	KMF Laborchemie Handels GmbH
LB	Langmuir-Blodgett (film, technique)
LEED	low energy electron diffraction
LUMO	lowest unoccupied molecular orbital
MC	Monte-Carlo simulation technique
MCBJ	mechanically controlled break-junction
MD	molecular dynamics
MI	Molecular Imaging Corp., 4666 South Ash Avenue, Tempe AZ 85282, USA
MJ	molecular junction, metal molecule metal assembly
MO	molecular orbital
MSE	mercury-sulfate electrode
NDR	negative differential resistance
NP	nanoparticle
OHP	outer Helmholtz plane
PE	polyethylene
PZC	potential of zero charge $E_{q=0}$
QCM	quartz crystal microbalance
QPC	quantum point contact
QRE	quasireference electrode
RHE	real hydrogen electrode

RE	reference electrode
SnS	alkanedithiols HS(CH ₂) _n SH
S5S	1,5-pentanedithiol HS-(CH ₂) ₅ -SH
S6S	1,6-hexanedithiol HS-(CH ₂) ₆ -SH
S8S	1,8-octanedithiol HS-(CH ₂) ₈ -SH
S9S	1,9-nonanedithiol HS-(CH ₂) ₉ -SH
S10S	1,10-decanedithiol HS-(CH ₂) ₁₀ -SH
SAM	self-assembled monolayer(s)
SCE	saturated calomel electrode
SEIRAS	surface enhanced infrared reflection absorption spectroscopy
SHE	standard hydrogen electrode
SMJ	single molecular junction, a MJ incorporating single molecule
SPM	scanning probe microscopy, a general term for AFM, STM and related techniques
STM	scanning tunneling microscopy, microscope
STS	scanning tunneling spectroscopy
TCNQ	tetracyanoquinodimethan
TEM	transmission electron microscopy
THE	trapped hydrogen electrode
TOC	total organic carbon content
TTF	tetrathiafulvalene
UHV	ultra-high vacuum with pressures lower than 10 ⁻⁷ Pa
UPD	underpotential deposition
VB	valence band
WE	working electrode

Appendix B

Curriculum Vitae

Personal background

Birth	September, 23, 1980, Saransk, Republic of Mordovia, Russia
Citizenship	Russian
Languages	Russian (native), English (excellent), German (good)

Educational and working background

09.1987–06.1989	Primary school #3, Saransk.
09.1989–06.1994	Primary and secondary school #38, Saransk.
09.1994–06.1997	Secondary and high school #4, Saransk (physical-mathematical lyceum).
09.1997–06.2002	Student, Chemical Department of Lomonosov Moscow State University, Moscow, Russia.
09.1997–12.1999	Education in the excellence program “Physical Chemistry”.
12.1997–06.2002	Student and junior researcher at the Electrochemistry Division of the Chemical Department, Moscow State University. Supervisors: Prof. Galina A. Tsirlina, Prof. Oleg A. Petrii.
19.06.2002	Graduated with honours. Title of the diploma work is “Electroreduction of Pt(II) chloroaquacomplexes at high overvoltage”.
06.2002–06.2003	Junior researcher at the Electrochemistry Division of the Chemical Department, Moscow State University. Supervisors: Prof. Galina A. Tsirlina, Prof. Oleg A. Petrii
10.2003–08.2007	DAAD Ph.D. Fellow at ISG/IBN-3, Research Center Jülich and Faculty of Mathematics, Informatics, and Natural Sciences, RWTH Aachen, Germany. Supervisor: Priv. Doz. Dr. Thomas Wandlowski.
since 10.2007	Ph.D. Fellow at the Department of Chemistry and Biochemistry, University of Berne, Switzerland. Supervisor: Prof. Thomas Wandlowski.

Appendix C

List of Publications

1. R. R. Nazmutdinov, **I. V. Pobelov**, G. A. Tsirlina, O. A. Petrii.
“Nature of the ‘current pit’ in concentrated solutions. Part I. Microscopic modelling of the interaction of Pt(II) aquachloro complexes with a mercury electrode”
J. Electroanal. Chem. **2000**, 491, 126.
2. **I. V. Pobelov**, M. I. Borzenko, G. A. Tsirlina, O. A. Petrii.
“Reduction of an ensemble of chloride aqua complexes of platinum(II): An analysis in the framework of phenomenological approach”
Russ. J. Electrochem. **2001**, 37, 233.
3. A. I. Danilov, E. B. Molodkina, A. A. Baitov, **I. V. Pobelov**, Yu. M. Polukarov.
“Initial Stages of Copper Electrocrystallization on a Glassy-Carbon Ring-Disk Electrode from Sulfate Electrolytes of Various Acidity: Potentiostatic Current Transients”
Russ. J. Electrochem. **2002**, 38, 743.
4. **I. V. Pobelov**, Z. V. Kuz'minova, G. A. Tsirlina, and O. A. Petrii.
“Reduction of an Ensemble of Platinum(II) Aquachloride Complexes: Dynamic Effect of the Solvent”
Russ. J. Electrochem. **2003**, 39, 828.
5. **I. V. Pobelov**, G. A. Tsirlina, O. A. Petrii.
“Correction for the Concentration Polarization for Simultaneous Reduction of Several Reactants: Platinum(II) Aquachloride Complexes”
Russ. J. Electrochem. **2004**, 40, 924.
6. Z. Li, B. Han, G. Meszaros, **I. Pobelov**, Th. Wandlowski, A. Błaszczuk, M. Mayor.
“Two-dimensional assembly and local redox-activity of molecular hybrid structures in an electrochemical environment”
Faraday Discuss. **2006**, 131, 121.
7. Z. Li, **I. Pobelov**, B. Han, Th. Wandlowski, A. Błaszczuk, M. Mayor.
“Conductance of redox-active single molecular junctions: an electrochemical approach”
Nanotechnology **2007**, 18, 044018.

8. G. J. Su, R. Aguilar-Sanchez, Z. Li, **I. Pobelov**, M. Homberger, U. Simon, Th. Wandlowski.
“Scanning Tunneling Microscopy and Spectroscopy Studies of 4-Methyl-4’-(n-mercaptoalkyl)biphenyls on Au(111)-(1 × 1)”
ChemPhysChem **2007**, 8, 1037.
9. G. Mészáros, C. Li, **I. Pobelov**, Th. Wandlowski.
“Current Measurements in a Wide Dynamic Range - Applications in Electrochemical Nanotechnology”
Nanotechnology **2007**, 18, 424004.
10. C. Li, **I. Pobelov**, Th. Wandlowski, A. Bagrets, A. Arnold, F. Evers.
“Charge Transport in Single Au|Alkanedithiol|Au Junctions: Coordination Geometries and Conformational Degrees of Freedom”
J. Am. Chem. Soc. **2008**, 130, 318.
11. N. Weibel, A. Błaszczuk, C. v. Hänisch, M. Mayor, **I. Pobelov**, Th. Wandlowski, F. Chen, N. Tao.
“Redox-Active Catechol-Functionalized Molecular Rods: Suitable Protection Groups and Single-Molecule Transport Investigations”
Eur. J. Org. Chem. **2008**, 136.
12. C. Li, A. Mishchenko, Z. Li, **I. Pobelov**, Th. Wandlowski, X.Q. Li, F. Würthner, A. Bagrets, F. Evers.
“Electrochemical gate-controlled electron transport of redox-active single perylene bisimide molecular junctions”
J. Phys.: Condens. Matter **2008**, 20, 374122.
13. **I. Pobelov**, Z. Li, Th. Wandlowski.
“Electrolyte Gating in Redox-active Tunneling Junctions – An electrochemical STM Approach”
J. Am. Chem. Soc. **2008**, submitted.
14. **I. Pobelov**, G. Nagy, Th. Wandlowski.
“Cu–SO₄^{2–} and Cu²⁺–Cl[–] UPD phases on Au(111): structure and transitions”
Electrochim. Acta, in preparation.
15. **I. Pobelov**, Th. Wandlowski.
“Statistical analysis of the single molecule conductance”
in preparation
16. **I. Pobelov**, Th. Wandlowski.
“Conductance of the single molecular junctions supported by Au–4-pyridyl bond”
in preparation

Appendix D

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