

Chapter 1

Introduction

The continuing demand for smaller and smaller devices in microelectronics will ultimately lead the semiconductor industry to fabricate circuits near to the atomic scale, facing however severe and fundamental thermodynamic problems (for instance material break down or statistical fluctuation) [1]. It is therefore of fundamental importance to explore innovative solutions to implement electronic devices.

A conceptually new strategy in such direction, the so called molecular electronics, is based on the realization of electrical devices consisting of molecules [2, 3]. The idea that a few molecules, or even a single molecule, placed between two electrodes could perform the basic functions of digital electronics (rectification, amplification and storage), was first proposed in 1974 by M. Ratner and A. Aviram [4]. They demonstrated theoretically that a molecule with a donor-spacer-acceptor design would behave as a diode when placed between two electrodes. Although molecular electronics has been the subject of much interest and speculation over the past 30 years, single molecular devices have only in the last decade become accessible to experiments. Important works in this regard are for example the measurements by STM of the electron transport through individual molecules [5, 6] and the fabrication of a field-effect transistor consisting of a carbon nanotube connected to two metal electrodes [7].

For electronic applications, molecular structures offer several advantages: *(i)* their size scale (1-100 nm) combines benefit in cost and efficiency *(ii)* their fabrication methods can be provided by the system itself through self-organization (chemical recognition) [8–10], *(iii)* they can be tailored using chemical synthesis, which is nowadays able to vary their physicochemical properties for realizing new functionalities [11], and furthermore, *(iv)*

there is a large variety of molecules, which could realize basic operations like writing, storing, and transferring information [11].

In order to study the fundamental properties of molecular systems which could serve for molecular electronics, the low temperature scanning tunneling microscope (LT-STM) is a very powerful tool. It not only allows to image single atoms and molecules on surfaces, but also to manipulate them with atomic precision [12–14]. The techniques of manipulation have been intensely developed in the last decade [15–17]: Nanostructures have been fabricated atom by atom by STM manipulation [12] and atomic switches have been realized [18, 19]. Recent experiments have shown that conformational changes within a molecule can be mechanically induced by the STM tip and be used for realizing a molecular switch [20] or amplifier [21]. Moreover, molecular rotation [22, 23] and vibration [24–26] can be controlled by exciting molecules with tunneling electrons, while diffusion [27] or desorption [28] of molecules adsorbed on surfaces are induced by the intense electric field present between the STM tip and the sample surface. Furthermore, chemical reactions have been realized with single molecules by STM [29, 30].

This thesis focuses on the LT-STM study of single molecules interesting for future application in molecular electronics devices. The molecules chosen are organic systems which have been custom synthesized and present in the gas-phase special properties and functionalities. Adsorption and manipulation of such molecules was studied in detail, taking into account the interaction of the molecules with the substrate. The question, whether and how the molecular functionalities are affected by the substrate, was one of the central issue of this work.

To investigate the electronic properties of molecules, it is desirable to reduce their electronic interaction with a conductive substrate, which is used in STM experiments, since otherwise the charge flowing through a molecule would easily dissipate into the substrate. In order to solve this problem, in this work two different approaches are considered. On the one hand, molecules equipped with isolating spacer groups have been studied. On the other hand, the electronic isolation of a molecule is addressed by introducing decoupling oxide layers between a metal substrate and the adsorbed molecule, thus preserving the electronic properties of the molecule. For this aim, the study of the formation of thin vanadium oxide films on a metal substrate was performed.

Two basic molecular systems were studied in this thesis work: molecular wires and switches. A molecular switch requires at least two stable switching states. To be suitable for molecular electronics, the switch must be controllable, reversible, and readable at the molecular level. Many properties of molecules can be considered as they present bistability; examples include geometric changes (e.g. *cis/trans* isomerization and changes in coordination number), spin (e.g. 'up'/'down', high/low), and electron transfer (redox). Stimuli effecting the bistable state and enabling the writing and reading of the state include electromagnetic radiation (photons), applied magnetic or electric fields, and chemical reactions.

In this work, the mechanism of the *trans-cis* isomerization of an azobenzene molecule adsorbed on a gold surface was investigated. The goal was to adapt this molecular switch, known to work in the gas phase and in solution, to a solid-state device setting.

This thesis is structured as follows: in Chapter 2 the basic principle of scanning tunneling microscopy and spectroscopy as well as the STM manipulation are introduced. Moreover, the elastic scattering quantum chemistry (ESQC) approach, used for the simulation of STM images of adsorbates, is presented. The experimental set-up and its development are described in Chapter 3. The study of tip-induced lateral manipulation of Lander molecule, model system of a molecular wire on a stepped copper surface, is presented in Chapter 4. Chapter 5 illustrates the method of preparation of thin vanadium oxide films and reports on their formation and characterization. Additionally, it presents the study of the adsorption of pentacene molecules on these oxide films. Chapter 6 describes the study and realization of the reversible *trans-cis* isomerization of an azobenzene derivative on Au(111) by STM manipulation and the investigation of the switching driving mechanism. Finally in Chapter 7 some conclusions and outlook are given.

