Modelling the Self-Assembly of supramolecular nanostructures adsorbed on metallic substrates

Settore disciplinare FIS. 03

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Bref, aborrezco los vanos circunloquios y contaré la historia *ab initio*, sin excluir, por cierto, la vigorosa ironía que invenciblemente sugiere el espectáculo moderno.

Senza perdersi in vani giri di parole, racconterò la storia *ab initio*, senza per altro dimenticare la pungente ironia che inevitabilmente suggerisce lo spettacolo del mondo moderno.

*Jorge Luis Borges, Adolfo Bioy Casares:*
*Seis problemas para Don Isidro Parodi*
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Introduction

The term Nanotechnology is used to describe a variety of techniques to fabricate materials and devices at the nanoscale. Nano-techniques include those used for fabrication of nanowires, those used in semiconductor fabrication such as deep ultraviolet and electron beam lithography, focused ion beam machining, nanoinprint lithography, atomic layer deposition, molecular vapor deposition, and the ones including molecular self-assembly techniques. All these methods are still being developed and not all of them were devised with the sole purpose of creating devices for nanotechnology.

A number of physical phenomena become noticeably pronounced as the system size decreases. These include statistical effects, as well as quantum effects, where the electronic properties of solids are altered if the particle size is greatly reduced. There are also effects which never come into play by going from macro to micro dimensions, while they become dominant when the nanometer scale is reached. Furthermore nanotechnology can be thought of as extensions of traditional disciplines towards the explicit consideration of all these effects. Traditional disciplines can be re-interpreted as specific applications of nanotechnology. Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices with atomic-scale control.

Modern synthetic chemistry has reached the point where it is possible to prepare small molecules of almost any (stable) structure. Methods exist today to produce a wide variety of useful chemicals. A branch of nanotechnology, relevant to the present thesis work, is looking for methods to assemble single molecules into supramolecular assemblies arranged in a well defined manner. These approaches use molecular self-assembly and supramolecular chemistry to automatically arrange the single molecules into interesting and potentially useful structures. The scanning tunneling microscope (STM) is a non-optical microscope that scans an electrical probe (the tip) over a conductive surface to be imaged. It allows scientists to visualize regions of high electron density at the atomic scale, and hence infer the position of individual
atoms and molecules on a material surface. STM is specially suited for the study of the self-assembly of molecules deposited on conductive substrates because it provides direct insight into the assembled structures. However, the STM images are often insufficient for a complete description of the phenomena, and computer simulations offer a complementary approach that can effectively integrate the experiments.

The theoretical investigation of the molecular self-assembly aims at the understanding of the mechanisms that are involved in the assemblies formation. In particular the atomistic simulation can provide information on the geometry of the stable structures, the nature and the intensity of the interactions as well as on the dynamical processes. In this thesis, a combination of first principles and classical molecular dynamics simulations is used to shed light on the self-assembly of some organic molecules deposited on noble metal substrates. Three cases are discussed, the self-assembly of TMA and BTA molecules on Ag(111) and the self-assembly of an oxalic amide derivative on Au(111).

When TMA and BTA molecules are deposited onto a silver surface at a temperature lower than room temperature they form a regular 2D honeycomb network featuring double hydrogen bonds between carboxylic groups. Even if this bonding makes the network very stable, when these systems are annealed to higher temperatures they undergo some irreversible phase transition into closer-packed supramolecular arrangements. Namely, the TMA has a transition from honeycomb to a high coverage “quartet” structure and the BTA has two transitions: from honeycomb to unidimensional stripes and from here to a closed-packed monolayer. A combination of experimental and theoretical techniques allowed us to identify the stepwise deprotonation of the carboxylic acid groups as the driving force driving the phase transitions.

Our theoretical investigation targeted the electrostatic interaction involved in the formation of the various phases revealing that a depolarisation of the molecular ions occurs as a consequence of the deprotonation process. Therefore, the repulsive contribution arising from the interaction of negatively charged molecules can be overcome by the attractive hydrogen bond interaction involving the deprotonated carboxylic groups, thus resulting in a stable closed-packed arrangement. Rather remarkably, this exemplifies how higher-coverage phases can be obtained at each step of a series of phase transitions in a supramolecular assembled system, despite the increasing temperature and the increasing electrostatic repulsive energy cost accompanying deprotonation.

The oxalic amide derivative molecules arrange themselves in linear chains both in the molecular solid and when adsorbed on a gold surface. However the intermolecular distance and the geometry of the chains are different in
these two cases. Various relaxed bonding structure between molecules in the chains have been calculated from first principles in the present work.

The rationale of the different linkage behaviour between molecules in the two situations described have also been investigated: the interaction with the substrate appears to be the main cause for the particular rearrangement observed in the chains. Both experimental observations and theoretical predictions indicate that a conformational change involving the rotation of the phenyl rings of the monomers is necessary for chain formation.
Chapter 1

The physical problem

1.1 A general introduction to Self-Assembly

Self-Assembly (SA) is the fundamental principle which generates structural organisation on all scales from molecules to galaxies. It is defined as a process in which pre-existing parts or disordered components of a pre-existing system form regular structures of patterns. Within this definition the self-assembly can be either static or dynamic. When the system is in equilibrium and does not dissipate energy the SA is static, while when the ordered state occurs with energy dissipation the SA is dynamic.

Molecular SA is the assembly of molecules without guidance or management from an external source. It can be classified as either intramolecular SA or intermolecular SA. Intramolecular self-assembling molecules are often very complex molecules with the ability to assemble from a random conformation into a well-defined stable structure, the protein folding is an example of intramolecular SA. Intermolecular SA is the ability of molecules to form supramolecular assemblies and is the subject of this thesis.

Also the SA is the name of the manufacturing method used to construct things at the microscale. The imitation of the strategies that biological systems use to aggregate into complex structures is its fundamental principle. Since the final structure is someway encoded in the building blocks, the SA is often referred as bottom-up manufacturing technique, as compared to lithography, a top-down technique, because the final structure has to be carved out from a large block of matter.

The function of a material depends both on the nature of its constituents and their mutual interactions and arrangement. The controlled fabrication, manipulation and implementation of nano-sized functional chemical entities into complex molecular architectures provide a wide range of potential appli-
cations with great value for science and technology. The supramolecular self-organization approach enables a high degree of structural organization within the nanoregime. Noncovalent bonds (mostly, hydrogen bonds) mediate the controlled assembly and hierarchical growth of instructed, fully integrated and connected operational systems. Thus an impressive variety of structural motifs employing various self-assembly protocols has been designed to date.

STM observations (Section 1.4.1) of noncovalent bonding and supramolecular self-organisation with simple organic building blocks at surfaces have recently became possible allowing for an unprecedented insight in complex molecular architectures. Theoretical atomistic simulations are an invaluable tool to complement STM observations.

1.2 Metal surfaces

1.2.1 Introduction

Metal surfaces are used to support the nanostructures for imaging with STM, and they play an active role in the assembly process. In this section a theoretical introduction to their properties will be given, with a particular interest for the noble-metal (111) substrates, which were used for the systems described in the following chapters.

1.2.2 The Jellium Model

The Jellium model is a good approximation for simple metals, and we report it as described in [2]. Within this approximation the lattice of positive ions is substituted by a uniform positive charge distribution \( n_+; n_+(r) = \bar{n} \) when \( z \leq 0 \) and \( n_+(r) = 0 \) when \( z > 0 \). In the case of the surface, the ionic lattice is semi-infinite, so the positive charge distribution terminates as a step function at the boundary. While the positive charge terminates abruptly, the electronic charge \( n(z) \) spills out of the boundary, giving rise to a surface dipole layer (Figure 1.1). To compensate for the sharp edge of the positive charge distribution, the electronic density oscillates to the asymptotic bulk value. These oscillations are known as Friedel oscillations and their wavelength is \( \pi/K_F \) where \( K_F \) is the Fermi Wavevector. The formation of a surface dipole layer yields a variation of the electrostatic potential when the surface is crossed.

\[
D = \phi(\infty) - \phi(-\infty)
\]

(1.2.1)

This potential step serves, in part, to keep the electrons inside the crystal. Within the jellium model an effective position of the surface can be defined.
Figure 1.1: Electron density profile of a metal surface described within the jellium model and plotted along the direction orthogonal to the substrate

\[ d_{||} = \frac{1}{n} \int_{-\infty}^{+\infty} dz \frac{dn(z)}{dz}. \]  

(1.2.2)

1.2.3 The workfunction

Figure 1.2: The workfunction (\( \Phi \)) is indicated with all the other quantities that are related to it, see text for more detail

The work-function of a crystal surface is defined as the minimum energy required to move an electron from the bulk to a macroscopic distance outside the surface. Considering the Figure 1.2 there are two potentials, the
electrostatic potential $\phi(z)$ and the effective one electron potential $v_{\text{eff}}(z)$ which includes the exchange-correlation potential. The workfunction $\Phi$ can be expressed as

\[
\Phi = \phi(\infty) - \mu = D - \bar{\mu}
\]  

(1.2.3) (1.2.4)

Where the $\mu$ and $\bar{\mu}$ are respectively the chemical potentials with respect to the bulk value of $v_{\text{eff}}(z)$, and $\phi(z)$. Thus the work-function is the result of the competition between a surface term $D$ and a bulk term $\bar{\mu}$. The surface part of the workfunction is of interest here because any change of the surface in terms of morphology or adsorption will also alter the value of the workfunction. The Helmotz formula [2] can be used to estimate work-function variation due to adsorption.

\[
\delta \Phi = -4\pi e \int dr z \delta n(r)
\]

(1.2.5)

where $\delta n(r)$ is the change in charge density that accompanies adsorption.

### 1.2.4 Surface State

When Schrödinger equation is solved for one electron at the surface, solutions that would have discarded in the bulk case, might instead be valid because of the different boundary conditions. This is the case of the Surface state (Schockley state), that is an electronic state confined within the surface. Along the surface plane it behaves like a two dimensional free electron gas, and it is scattered by defects and adsorbates (Figure 1.3), while it decays quickly inside the crystal. The energy of the surface state can be modified by the presence of adsorbates. For instance Hövel et al [5] studied the surface state energy variation due to the adsorption of Xenon atoms on a Ag(111) surface.

### 1.2.5 Ag(111) and Au(111)

In this work these two different surfaces have been used as support for the SA of the molecules. The (111) surfaces of Face Centered Cubic Metals are the flattest substrates available, since they are arranged in a closed packed triangular lattice (Figure 1.4a). The flatness of the substrates and the chemical inertness of gold and silver, which are the noblest among metals, were chosen to provide a high mobility of the molecules. The Au(111) exhibits a reconstruction (Figure 1.5), it spontaneously densifies along one of the three $\langle \bar{1}10 \rangle$ directions, resulting in a $n \times \sqrt{3}$ unit cell, $n \sim 22$. Domains
Figure 1.3: STM image of the Ag(111) surface state scattered by two carbon defects

Figure 1.4: a) The scheme of a FCC 111 surface, b) The STM image of a Ag(111) surface
with different stacking of the first three layers (FCC or HCP) alternate along the ⟨110⟩ direction. Furthermore there is a regular alternation of domains of two orientations of the $n \times \sqrt{3}$ cell, resulting in a striking herringbonelike pattern, with a domain width of about 150 Å. [7].

![STM images of the Au(111) surface reconstruction](image1.jpg)

Both the substrates exhibit a surface state, which, in the case of Au(111), is scattered by the reconstruction boundaries.

1.3 The selfassembly of molecules adsorbed on metal surfaces

1.3.1 Adsorption

Adsorption is a process that occurs when a gas or a liquid (called an adsorbate) accumulates on the surface of a solid, forming a molecular or atomic film. This process is operative in most natural physical, biological and chemical systems, and is widely used in industrial applications. According to the energy range of the interaction and the electronic behaviour, it is common use to classify the adsorption as physisorption or chemisorption. Adsorption of molecules often proceeds in two stages. In the first precursor stage the interaction is mainly physical and the molecule is in a metastable state that can lead to desorption or chemisorption. This transition to chemisorption
is irreversible and may result in the dissociation of molecules (dissociative chemisorption)

1.3.2 Chemisorption

When strong chemical bonds form between the adsorbate and the substrate, a chemisorption is said to occur. The whole system can be considered as an enormously large molecule with an electronic structure that is different from the one that the non-interacting molecules and substrates have. Charge transfer occurs between the two systems so that the bonds can have ionic or covalent character. In order to characterise the bond formation we shall observe that the adsorption energies are of the order of a few ev/atom and that preferred adsorption sites are present on the substrate. Unlike the bond formation in molecular chemistry, the case of adsorption is one between very different partners. The adsorbate comes with discrete energy levels and few occupied states, but the substrate has a near-infinite number of electrons. Thus the valence level of the adsorbate will interact with a semi-infinite continuum of levels $\varepsilon$. The location of the Fermi Energy is determined by the substrate. On a surface a description of the chemical bonding in terms of an elementary discrete level scheme has therefore to be extended: levels lying in the band region of the substrate receive a finite width. These broad levels are called adsorbate-induced resonances. Summarising the ideas expressed in [4], we illustrate a tight binding description of the adsorption of hydrogen adatoms. The $1s$ and $2s$ levels of free hydrogen are plotted in Figure 1.6 b, while the DOS of a transition metal is sketched in Figure 1.6 a. The broad and shallow s-band is superimposed with the d-band that is less extended, but higher. Different transition-metal substrates mainly differ in the width of the d-band, which increases from 3d to 4d to 5d; and they differ in the position of the Fermi level, which varies from the left to the right of the periodic table as follows: For the 4d series it is at the lower edge of the d-band for strontium, just below the top of the d-band for palladium, and above the upper edge for silver. In our example the Fermi level $\varepsilon_F$ is just below the upper edge. At first we consider the role of the substrate s-band. When the adsorbate and the substrate interact, the hybridization of the states gives rise to a broadening of the adsorbate levels, and the atomic levels will shift because the substrate Fermi level and the electron chemical potential of the atom become aligned. The latter will result in fractional electron transfer. When the mean value between ionisation potential and electron affinity is above the Fermi level of the substrate, the electron transfer is from the atom to the substrate, while if it is below the Fermi level, the electrons move from the surface to the adatom. The resulting broadened and shifted peaks are
Figure 1.6: Formation of adsorbate-induced peaks in the DOS. Panel a) sketches the DOS of a transition metal substrate before adsorption. b) shows the energy levels of the isolated hydrogen atom considered in the example. The interaction between the H 1s level and the substrate bands gives rise to a broadening and the formation of an antibonding and bonding levels that are plotted in panel c). Panel d) shows the bonding and antibonding levels due to the interaction of H 2s level with the substrate.
called *renormalized atomic levels* and interact with the localized d-states. Since d-band’s width is comparable to the interaction strength, the interaction will result in a splitting into bonding and antibonding states. Figure 1.6 c and d shows the bonding and antibonding peaks for 1s and 2s states.

### 1.3.3 Physisorption

The physical adsorption (*physisorption*) is a weak form of adsorption to a solid surface, since there is not a real chemical bond between the adsorbate and the substrate, and the interaction is driven by other kinds of forces, mainly Van Der Waals. These forces arise from the interaction of the polarisable solid with dipolar quantum fluctuations of the adsorbate’s charge distribution. At small distances these forces are balanced by repulsive interaction due to overlap of electronic orbitals. The typical adsorption energies involved are of order 50-500 meV/atom. In the first approximation instantaneous dipole of the adsorbate $P_{\text{adsorbate}}(\omega)$ generates a image dipole that can be expressed as $P_{\text{image}}(\omega) = \frac{1-\epsilon(\omega)}{1+\epsilon(\omega)} P_{\text{adsorbate}}(\omega)$ where $\epsilon(\omega)$ is the dielectric function of the substrate. The formation of a permanent dipole has been reported for physisorbed systems, [8] [9] and a consequent lowering of the workfunction down to 1eV. Although this phenomenon is not completely understood, at least for simple systems it seems to be a consequence of the Pauli repulsion. [10] [11].

### 1.4 Experimental techniques

#### 1.4.1 STM

The scanning tunneling microscope (STM), in Figure 1.7, is a non-optical microscope that scans an electrical probe (the tip) over a conductive surface to be imaged. A voltage (*bias-voltage*) is applied between the probe and the surface and the electrons tunnel from the tip to the surface (or vice-versa) thus producing a weak electric current that is measured. The intensity of the current is exponentially dependent on the tip-surface distance, and it is a function of the local density of electronic states. The STM allows scientists to visualize regions of high electron density and hence infer the position of individual atoms and molecules on the surface. A different approach is to use a servo loop to adjust the tip-surface distance in order to keep the current constant (*Constant Current Mode*) Although the STM provides real space topographies of surfaces at an atomic scale (0.2 nm) and for this reason is the natural choice for nanoscale investigations, the tip can also be used to
Figure 1.7: Scheme of a Scanning tunneling microscope.
manipulate individual atoms, trigger chemical reactions, or produce ions by removing or adding electrons from atoms or molecules. The STM images often need to be interpreted, and theoretical simulations at the quantum level of accuracy are an invaluable tool to help this interpretation.

1.4.2 STS

The STM is also used to perform the Scanning tunneling spectroscopy (STS). This technique gives information about the local density of electronic states (LDOS) on surfaces at atomic or molecular scale. While keeping the tip position fixed, the tunneling current (I) is measured from the variation in the bias voltage (V). As a result, the current-voltage (I-V) curve or the normalized differential conductance-voltage \((\frac{dI}{dV})/(\frac{I}{V})-V\) curve is obtained. Information about the surface LDOS \((\rho_s)\) can be obtained from the following relation which involves the Fermi energy of the sample \((E_F)\).

\[
\frac{dI}{dV} \propto \rho_s(E_F - eV)
\]  

(1.4.1)

1.4.3 XPS

X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopic technique. XPS spectra are obtained by irradiating a material with a beam of x-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the irradiated material. XPS as a surface chemical analysis technique can be used to analyze the chemistry of the surface of a material in its natural state, or after some treatment such as: fracturing, cutting or scraping in air or UHV. XPS is used to measure the elemental composition of the surface or the empirical formula of pure materials and it is particularly suited to detecting the impurities that contaminate the sample. The chemical or electronic structure of each element in the surface is revealed as well, this feature is useful for an accurate study of the electronic state of the adsorbates and for the investigation of bond formation between adsorbates and between adsorbate-substrate. A XPS spectrum is a plot of the number of electrons detected versus the binding energy of the electrons detected. Each element produces a characteristic set of XPS peaks at a characteristic binding energy. The number of detected electrons in each of the characteristic peaks is directly related to the amount of the element present. The XPS is not sensitive to the presence of hydrogen, thus its presence shall be guessed by the electronic state of the other elements.
1.4.4 NEXAFS

NEXAFS (Near Edge X-ray Absorption Fine Structure) is an electron spectroscopy technique with high sensitivity to bond angles, bond lengths and the presence of adsorbates. The great power of NEXAFS derives from its elemental specificity. Since the various elements have different core level energies, NEXAFS permits extraction of the signal from a surface monolayer and it can also determine the chemical state of the various elements. For this reason it is widely used in surface science, however it has also been used to study polymers and magnetic materials. NEXAFS is synonymous with XANES (X-ray Absorption Near Edge Structure) but NEXAFS by convention is usually reserved for soft X-ray spectroscopy. The fundamental phenomenon underlying NEXAFS is the absorption of an x-ray photon by a core level of an atom in a solid and the consequent emission of a photoelectron. The resulting core hole is filled either via an Auger process or by the capture of an electron from another shell followed by emission of a fluorescent photon. The difference between NEXAFS and traditional photoemission is that in photoemission the initial photoelectron itself is measured, while in NEXAFS the fluorescent photon or Auger electron or an inelastically scattered photoelectron may also be measured.
Chapter 2

Theoretical introduction

2.1 Introduction: Molecular Dynamics simulations

Molecular Dynamics (MD) is a form of computer simulation in which atoms and molecules are allowed to interact for a period of time under known laws of physics. Because in general molecular systems consist of a large number of particles, it is impossible to find the properties of such complex systems analytically. MD simulation circumvents this problem by using numerical methods. More formally, MD is a special discipline of molecular modelling and computer simulation. Based on molecular mechanics, it addresses numerical solutions of Newton’s equations of motion i.e. Hamiltonian mechanics on an atomistic or similar model of a molecular system to obtain information about its equilibrium and dynamic properties. The types of information that are required to perform a MD are the positions of atoms and the forces that are acting on them. Different types of MD calculate these forces in a variety of methods. Generally ab initio MD uses a quantum mechanical approach to calculate these forces while the classical MD derives them from empirical potentials. If the first family is generally more accurate, its applicability to large systems is strongly limited by the computational power currently available, the second family allows for much larger systems to be simulated with an accuracy that often is too low to give reliable predictions, because of the limited transferability of the potentials. It is clear that the choice of the right simulation tool has to take into account this trade-off. New hybrid methods are being developed to combine the classical and quantum approach: the high precision quantum approach is used only inside a zone (the quantum zone) where such an accuracy is required, while the rest of the system (the classical zone) is described with empirical
potentials. Among these methods we shall remind the QM/MM approach [13] and the LOTF method [12]. For the supra-molecular SA the embedding approach is not suitable since it is not trivial to split the system in quantum and classical parts. In fact the many molecules involved in the simulation should all be considered on the same footage with an high accuracy. For this reason we based our study on a combination of classical and quantum MD exploiting the good attitudes of the both methods and integrating them at a higher level. In this chapter the theoretical foundations of the applied methods will be introduced to give a complete overview to the reader.

2.2 Density Functional Theory

A fundamental paper by Hohenberg and Kohn (HK) [16] started the development of the Density Functional Theory (DFT), since which DFT has been applied successfully to a wide range of systems. HK demonstrated that the total energy of an electronic system in an external potential \( V_{\text{ext}} \) is uniquely determined by the electron ground state density

\[
n(r) = \langle \Psi | \hat{n}(r) | \Psi \rangle = \int dr_2...dr_n |\Psi(r, r_2...r_n)|^2,
\]

\[
E[n] = F_{HK}[n] + \int V_{\text{ext}}(r)n(r)dr,
\]

with

\[
F_{HK}[n] = \langle \Psi[n]|\hat{T} + \hat{V}_{ee}|\Psi[n]\rangle,
\]

where \( \Psi \) is the ground state of the system and \( \hat{n}(r) \), \( \hat{T} \) and \( \hat{V}_{ee} \) are the density, the kinetic energy and the electron-electron interaction operators respectively. It is important to realise that \( F_{HK}[n] \) is an universal functional, it is not explicitly dependent on the external potential. It includes all the complicated many body effects and, not surprisingly, is unknown.

Since \( V_{\text{ext}} \) and the number of electrons \( N \) fix the Hamiltonian, it turns out that the electron density is all we need to characterise the system. The main implication of this result is that the manybody wavefunction, that is a function of 3N variables is no longer necessary, and can be substituted by the electron density, that is a function of 3 variables ie a much simpler object to deal with.

HK proved a second theorem which states that the ground state density of the system is the one which minimizes \( E[n] \), and the minimum of \( E[n] \) is the ground state energy \( E_0 \). This result established a variational principle that can be used to find the ground states.
One year after the publication of the HK paper, Kohn and Sham (KS) published a reformulation [17] that was a major step towards the applicability of the method. They decomposed the charge density into a set of one-particle orthonormal orbitals.

\[ n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2, \]  

(2.2.4)

and recast the energy functionals as

\[ F_{HK}[n] = T_0[n] + E_H[n] + E_{xc}[n] \]  

(2.2.5)

where \( T_0[n] \) is the kinetic energy of an auxiliary system of non-interacting electrons, \( E_H[n] \) is the classical electrostatic interaction and the last term, the exchange-correlation energy, is implicitly defined by the relation above and is meant to contain all the many body effects.

Minimizing the total energy \( E[n] \) under the constraints of orthonormality for the single-particle orbitals of the auxiliary system, \( \int \psi_i^*(r)\psi_j(r)dr = \delta_{ij} \), one finds a set of single-particle schrodinger-like equations:

\[ -\frac{1}{2} \nabla^2 + V_{KS}(r) \psi_i(r) = \epsilon_i \psi_i(r), \]  

(2.2.6)

where the \( V_{KS} \) potential is

\[ V_{KS}(r) = V_{ext}(r) + \int \frac{n(r')}{|r - r'|} dr' + V_{xc}(r) \]  

(2.2.7)

\[ V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)} \]

The expression for the electron density can be rewritten considering the eigenvalues \( \epsilon_i \) and the Fermi energy \( \epsilon_F \).

\[ n(r) = \sum_{i} |\psi_i(r)|^2 \theta(\epsilon_F - \epsilon_i). \]

These are the famous Khon - Sham equations, since the potential \( V_{KS} \) depends on the density \( n \) they must be solved iteratively until self-consistency is achieved.

In principle the eigenvalues \( \epsilon_i \) do not have a direct physical meaning, however they are usually interpreted as estimates of excitation and electron removal energies. In the case of the highest occupied state, the KS eigenvalue is the exact ionization potential. For simple metals the KS formalism is
able to describe properly the band structure close to the fermi level \[22\], while in atoms with discrete energy levels and insulators the description is not so good \[22\]. Still even in insulators, the internal structure of the bands is quite accurate, the discrepancy is usually a rigid upward shift of the unoccupied levels with respect to the valence band. The success of this method relies in the good description of the kinetic and electrostatic terms (which are the most important in not strongly-correlated materials), and the appropriate description of the smaller exchange-correlation part via a suitable approximation.

2.3 Exchange and correlation energy approximations

Although the DFT formalism is exact for the ground state, it is not directly applicable, since the exchange-correlation functional is unknown. Thus an approximation for this functional must be introduced. The simplest approximation for the exchange-correlation energy is the Local Density Approximation (LDA) and it is obtained considering \( E_{xc}[n] \) to be a local functional of the density

\[
E_{xc}^{\text{LDA}}[n(r)] = \int \epsilon_{xc}^{\text{LDA}}(n(r)) n(r) dr, \tag{2.3.1}
\]

where \( \epsilon_{xc}^{\text{LDA}}(n) \) is the exchange-correlation energy density of a uniform electron gas with density \( n \). With this prescription, the form for the \( V_{xc} \) potential is

\[
V_{xc}^{\text{LDA}}(r) = \frac{d}{dn} \left( \epsilon_{xc}^{\text{LDA}}(n) \right) \bigg|_{n=n(r)} \tag{2.3.2}
\]

In practice, \( LDA_{xc} \) has been calculated using Quantum Monte Carlo methods and is available in a parameterized form \[20\], representing the basis for a full ab initio (i.e. parameter-free) description of real materials. Although this approximation appears to be questionable it is surprisingly accurate even when electronic charge density inhomogenities are big. The reasons for this unexpected success are still under investigation. Nonetheless, there are systems that are poorly described by the LDA, and many improvements have been attempted. The family of Generalized Gradient Approximation (GGAs) are able to partly correct LDA deficiencies with a modest increase in the computational load. They introduce an exchange-correlation term which depends also on the local variation of the electronic
density:

\[ E_{xc}^{GGA}[n(r), \nabla n(r)] = \int \varepsilon_{xc}^{GGA}(n(r), |\nabla n(r)|) n(r)dr. \] (2.3.3)

In this thesis we used LDA as well as the GGA formulation given by Perdew and Wang [24] [27]. Although in principle GGA should be a better approximation there are systems that are better described by LDA. There is not yet a recipe that can be blindly followed, but for every system the two alternatives should be considered accurately. In particular for the adsorption energies of physisorbed systems, with a predominant Van der Waalsic component, the LDA seems to be a better description than GGA, which strongly underestimates the adsorption energies.. [28].

2.4 local Spin Density Functional theory

The Density Functional Theory is, at least in principle, able to describe also magnetic systems using the density as the only variable. Nevertheless, the local approximations introduced for the exchange-correlation energy make the study of such systems problematic [22]. An effective solution to this problem is given by the spin-polarized version of the theory. In this scheme, separate densities of spin-up and spin-down electrons are used: \( n^\uparrow(r), n^\downarrow(r), n(r) = n^\uparrow(r) + n^\downarrow(r) \). Correspondingly, the exchange-correlation energy depends also on the spin-polarization, and the KS Hamiltonian contains different potentials for spin-up and down electrons. Thus the DFT equations are rewritten to include the two spin orientations \( \sigma = \uparrow, \downarrow \)

\[
\begin{align*}
[-\frac{\nabla^2}{2} + V_{KS}^\sigma(r)]\psi_i^\sigma(r) &= \epsilon_i^\sigma(r) \\
n^\sigma(r) &= \sum_i |\psi_i^\sigma(r)|^2 \theta(\epsilon_F - \epsilon_i^\sigma) \\
V_{KS}^\sigma(r) &= V_{ext}(r) + \int \frac{n(r)}{|r - r'|} dr' V_{xc}^\sigma(r) \\
V_{xc}^\sigma[n(r)] &= \frac{\delta E_{xc}[n^\uparrow, n^\downarrow]}{\delta n^\sigma(r)},
\end{align*}
\] (2.4.1)

thus accounting for a possible spin-magnetization of the system. The exchange-correlation energy is again taken from the exact results for a homogeneous gas for LDA (LSDA). GGA extensions are also available [29].
2.5 Periodic systems

When the system to be simulated has translational symmetry (a perfect crystal, for instance), the most natural choice is to work with a periodically repeated simulation box, with periodic boundary conditions. In this case the KS equations are translationally invariant

\[ V_{KS}(r) = V_{KS}(r + R) \]  (2.5.1)

where \( R \) is a direct lattice vector. Thus, according to Bloch theorem, the KS wavefunctions have the form

\[ \psi_i(r) = \psi_{nk} = e^{ik \cdot r} u_{nk}(r) \]

\[ u_{nk}(r) = u_{nk}(r + R), \]  (2.5.2)  (2.5.3)

and are labeled by the band index \( n \) and a vector \( k \) in the first Brillouin zone (IBZ) of the lattice. As a consequence, the computation of the electronic density and consequently of the energy requires an integral over the IBZ. The integral is recast over a discrete sum of finite elements below, in order to compute it.

\[ n(r) = \sum_k w_k \sum_n \theta(\varepsilon_F - \varepsilon_{nk}) |\psi_{nk}^2(r)|, \]  (2.5.4)

where \( w_k \) is the k-point weight. In principle, an infinite number of points should be included in the summation above. In practice, a finite set of k-points is used, chosen according to the symmetry properties of the system. Special point theory and the point symmetries are useful to greatly reduce the number of independent k-points needed in the calculation. In the case of metals, which have partially filled bands near the Fermi Energy, this procedure is not effective. The integration across the discontinuity at the Fermi surface, and the use of a reduced number of integration points gives a bad accuracy and, also, causes instabilities in the self-consistent cycle. In this work we have solved this problem using a technique due to A. De Vita et al. [30] [31], which involves a smearing of the Fermi function (somehow introducing a fictitious finite electronic temperature). For a given value of the smearing, it is possible to obtain a good integration in the IBZ without using a prohibitive number of k-points, and the convergence of the procedure can be checked reducing the smearing parameter.

Charged systems

When the considered system is charged the interaction between the periodic images of the system leads to the divergence of the energy. This is due to
the long range nature of the coulomb interactions. The standard solution is to include a jellium charge distribution that compensate for the charge state of the unit cell. This trick can influence the results of the simulation because of the interaction between the system and the jellium. However this interaction energy can be estimated for simple system as it is well described in [26]. In this thesis, when charged systems were considered, only energy differences with the same energy corrections were calculated, thus these corrections were not calculated.

2.6 Plane Waves and pseudopotentials methods

To solve numerically the KS equations it is necessary to expand the wavefunctions in a basis set, when periodic boundaries are used, the most common choice in ab initio calculations is Plane-Waves (PW) [32] [33], where

\[ \psi_{nk} = \sum_{G} e^{i(k+G) \cdot r} c_n(k + G), \]  
(2.6.1)

so that KS equations in reciprocal space read:

\[ \sum_{G'} \left[ \frac{1}{2} |k + G|^2 \delta_{G,G'} + v_h(G - G') + v_{xc}(G - G') + V(k + G, k + G') \right] c_n(k + G') = \varepsilon_{nk} c_n(k + G'), \]  
(2.6.2)

where all the potentials have been Fourier-transformed. The accuracy of the calculation is set by fixing the kinetic energy cutoff for the truncation of the basis:

\[ \frac{1}{2} |k + G|^2 < E_{cut} \]  
(2.6.4)

The self-consistent solution of equations 2.6.4 is the most time-consuming part of the calculation. The main advantages of the PW basis set are its translational invariance, the existence of one simple parameter to specify the accuracy and, very importantly, the availability of very efficient Fast Fourier Transform (FFT) algorithms to speed up calculations.

On the other hand, this basis puts the same resolution in every region of space so that it requires a huge number of PW’s to describe the oscillations of core electrons. The use of pseudopotentials is a well established method to overcome this problem, and has an accuracy comparable to other, computationally more demanding, methods. Starting from the consideration
that the core electrons are hardly influenced by the interactions with neighbouring species, it is reasonable to consider the core states as chemically inert, eliminating them from the calculation. The core-valence interaction is included in a pseudopotential, which is meant to accurately replicate the all-electron properties of the given atom. In particular, pseudopotentials are required to reproduce both the energy eigenvalues and the wavefunctions of the all-electron valence states outside the core region, while having nodeless pseudowavefunctions near the nuclei. The core radius is defined as the limit beyond which the pseudowavefunctions match the all-electron ones, with the constrain that the charge in the inner core region must be conserved (norm-conservation property [34]). The scattering properties of the atom must be preserved as well, thus imposing an upper limit to the value of the core radius. This approach permits us to perform the calculation with a manageable energy cutoff for the PW basis set. The use of non-local potentials, different for each angular momentum \( l \), is necessary to fulfil all the requirements. A fully non-local formulation of these potentials was introduced by Kleinmann and Bylander [35]. This technique works most successfully with s/p bonding type materials but, with strongly localized valence electrons, like oxygen 2p or transition metals d states, the norm-conservation constraint makes the pseudopotential still too hard to be described with an acceptable basis set. The PAW method, described in the section 2.7, is one of the solutions proposed for this technical problem. In this work we used norm-conserving pseudopotentials calculated within the Troullier-Martins scheme [25].

2.7 The Projector Augmented Wave method (PAW)

As its creator Peter Blöchl stated, *The Projector Augmented-Wave method is an extension of augmented wave methods and the pseudopotential approach, which combine their traditions into a unified electronic structure method* [36] [37].

In the atomic region near the nucleus, the kinetic energy of the electrons is large, resulting in rapid oscillations of the wave functions that require fine grids for an accurate numerical representation. On the other hand, the large kinetic energy makes the Schrödinger equation stiff, so that a change of the chemical environment has a little effect on the shape of the wave function. Therefore, the wave function in the atomic region can be represented well already by a small basis set. In the bonding region between the atoms the situation is the opposite. The kinetic energy is small and the wave function
is smooth. However the wavefunction is flexible and responds strongly to the environment. This requires a large and nearly complete basis set. If plane waves are used as a basis set to expand the complete wavefunction, a huge number of waves are required to describe properly the nodal structure in the proximity of the nuclei. According to the LAPW method, which is an ancestor of the PAW method, in the region close to the nuclei (augmentation region), the wavefunction is described by a localized basis set, while in the external region the wavefunction is expanded in plane waves. These two descriptions are matched at the zone boundaries, imposing the continuity of the wavefunction and of its first derivative. In the PAW method a transformation is applied to the wavefunctions $|\psi\rangle$ in order to map them to some auxiliary functions $|\tilde{\psi}\rangle$ that are much smoother in the augmentation region. These new functions are then easily expanded in plane waves and used to construct the true wavefunctions and the total energy functional. Thus we introduce the unitary transformation $\hat{T}$

$$|\psi_n\rangle = \hat{T}|\tilde{\psi}_n\rangle \quad (2.7.1)$$

An analogue of the Kohn-Sham equation can be obtained for these auxiliary wavefunctions, that can be solved in the usual way.

$$\hat{T}^\dagger\hat{H}\hat{T}|\tilde{\psi}_n\rangle = \hat{T}^\dagger|\tilde{\psi}_n\rangle\epsilon_n \quad (2.7.2)$$

where $\hat{H}$ is the standard Kohn-Sham Hamiltonian of the system.

The $\hat{T}$ operator has to change the auxiliary functions in the augmentation region while in the external region the structures are preserved. So we can write it as follow.

$$\hat{T} = 1 + \sum_R \hat{S}_R , \quad (2.7.3)$$

where the local operators $\hat{S}_R$ depend on the nuclei positions $R$, and give rise to the difference between the real and the auxiliary wavefunctions.

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_R \hat{S}_R|\tilde{\psi}\rangle , \quad (2.7.4)$$

In order to define the $\hat{S}_R$ we introduce in the augmentation region $|\phi_i\rangle$, a set of partial waves that are solution of the Schrödinger equation for isolated atoms. An auxiliary partial wave $|\tilde{\phi}_i\rangle$ is associated to each partial wave $|\phi_i\rangle$ such that

$$|\phi_i\rangle = (1 + \hat{S}_R)|\tilde{\phi}_i\rangle, i \in R , \quad (2.7.5)$$
this relation defines the local operator $\hat{S}_R$.

$$
\hat{S}_R|\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle.
$$

(2.7.6)

Since $\hat{1} + \hat{S}_R$ has to change the function only locally,

$$
\phi_i(r) = \tilde{\phi}_i(r) \quad \text{for } i \in R \text{ and } |r - R| > r_{c,R}
$$

(2.7.7)

the auxiliary wavefunction can be locally expanded in the auxiliary partial wave set

$$
\tilde{\psi}(r) = \sum_{i \in R} \phi_i(r) \langle \tilde{p}_i | \tilde{\psi} \rangle |r - R| < r_{c,R}
$$

(2.7.8)

which defines the projector functions $|\tilde{p}_i\rangle$ and holds only if $\langle \tilde{p}_i | \tilde{\phi} \rangle = \delta_{i,j}$ for $i, j \in R$.

The final expression for the operator is

$$
\hat{T} = \hat{1} + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i |,
$$

(2.7.9)

For the sake of precision, since the expansion in partial waves is truncated, there is a residual contribution of the plane wave expansion in the augmentation region. Outside of the augmentation region the real wavefunction and the auxiliary wave function are equal. The frozen core approximation is usually introduced to ensure that the density and energy of core electrons correspond to the values of isolated atoms.

Any observable expectation value can be calculated as follows

$$
\langle \hat{A} \rangle = \sum_n f_n \langle \psi_n | \hat{A} | \psi_n \rangle = \sum_n f_n \langle \tilde{\psi}_n | \hat{T}^\dagger \hat{A} \hat{T} | \tilde{\psi}_n \rangle.
$$

(2.7.10)

The PAW method has many advantages with respect to the pseudopotentials approach

- The control over approximation errors is improved, as well as the transerability;
- Since all the electrons are considered, the complete electron density can be calculated;
- The convergence of plane wave expansion is improved.
2.8 Hellmann -Feynman forces

The total energy, as function of the ion position can be thought of as the effective potential acting on a system of classical ions. The force components are the derivative of the energy with respect to the cartesian coordinates of the ions:

\[ f_\nu = \frac{dE}{dR_\nu} = \frac{\partial E}{\partial R_\nu} + \sum_i \frac{\partial E}{\partial \psi_i} \frac{\partial \psi_i}{\partial R_\nu} + \sum_i \frac{\partial E}{\partial \psi_i^*} \frac{\partial \psi_i^*}{\partial R_\nu} \]  

(2.8.1)

This expression can be simplified using the Hellmann-Feynman theorem, and the forces can be written as an expectation value over the ground state orbitals:

\[ f_\nu = \sum_i \langle \psi_i | \frac{dV_{ext}}{dR_\nu} | \psi_i \rangle \]  

(2.8.2)

When these forces are calculated the newtonian equation of motion can be solved to generate the dynamics. A common implementation of this scheme is the *Quench and Go* method: every timestep the ground state is found, the Hellmann-Feynman forces are calculated, the equations of motion are solved and the ions are moved. This method is very simple and robust, however it is really time expansive.

2.9 The Car-Parrinello method

In 1985 Roberto Car and Michele Parrinello [38] proposed an alternative to the *Quench and Go* method. They considered the wavefunction coefficients as classical degrees of freedom which evolve according to a fictitious dynamic. This dynamic is generated by the total energy functional, and controlled by a fictitious mass that is introduced as tuning parameter. As a consequence a kinetic energy contribute is associated to this new variables. This recipe is included in a unified Lagrangian.

\[ L_{CP} = \sum_{i=1}^N \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_{\nu=1}^n \frac{1}{2} M_\nu \dot{R}_\nu^2 - E[\{\psi_i\}; \{R_\nu\}] \]  

(2.9.1)

Initially the wavefunctions are set to some initial values (often randomly chosen). Keeping the ions fixed, the electronic dynamic is evolved quenching the associated kinetic energy to reach the ground state. Then the ions are allowed to move, so ionic and electronic dynamics are evolved simultaneously. During the dynamics the electrons are never in the ground state, however they oscillate around it so that the first order errors are averaged out. This method allows to perform molecular dynamics simulations very efficiently,
but it is important to ensure that electronic and ionic degrees of freedom do not exchange energy. To preserve this adiabaticity the ionic and electronic oscillation frequency ranges must be well separated. The ionic frequencies are known from the physical properties of the simulated material, while the electronic frequencies must be estimated from the following equation for their minimum:

$$\omega_{e}^{\text{min}} \approx \sqrt{\frac{E_{\text{gap}}}{\mu}}$$  \hspace{1cm} (2.9.2)

Where $\mu$ is the fictitious mass and $E_{\text{gap}}$ is the energy gap between occupied and unoccupied states. From this equation it turns out that, for systems with a finite gap an accurate choice of the fictitious mass may lead to the adiabaticity, while for systems with vanishing gap, i.e. metallic systems, the adiabaticity cannot be ensured and the energy can be transferred from the ions to the electrons. In practice the gap is never exactly zero also for metallic systems because the k-point sampling is discrete.

### 2.10 Car-Parrinello for Metallic systems

There is an additional problem that complicates the study of metals. In fact, during ion dynamics, a metallic system is in general characterised by frequent level crossing near the Fermi Level, that occurs when some electronic states close to the Fermi Level invert their energetic order. After the crossing the higher energy state lies in a unstable equilibrium condition that evolves towards a catastrophic accumulation of electronic kinetic energy. Many solution have been proposed in order to overcome these serious shortcomings, and a good review can be found in [14].

The following scheme was proposed by Vandevondele and De Vita [30] and then extended by Stengel and De Vita [31]. We start from the definition of free energy functional that is invariant for unitary transformations,

$$A[T, \psi_i, f_{ij}, R_I] = \sum_{i,j=1}^{m} f_{ij} \psi_i^* (\hat{T} + \hat{V}) \psi_j + E_{\text{Hxc}}[n] - TS[f_{ij}]$$  \hspace{1cm} (2.10.1)

In this expression we account for partially filled states, whose occupation is included in the occupation matrix $f_{ij}$. The electronic density can be expressed as

$$n(r) = \sum_{i,j=1}^{m} f_{ij} \psi_i^*(r) \psi_j^*(r)$$  \hspace{1cm} (2.10.2)
For the entropic term the following expression holds

\[ S[f] = -tr[ln f + (1 - f)ln(1 - f)]. \tag{2.10.3} \]

A unitary transformation rotates the electronic states and the occupation matrix simultaneously thus conserving the density. For the same reason the free energy functional is covariant. It can be shown that \([H, f] = 0\) when \(A\) is minimised with respect to \(f_{ij}\), so the Hamiltonian and the occupation matrix can be diagonalized simultaneously. A dynamic scheme can be constructed from this functional by introducing the equations of motion

\[
Q \epsilon_{ij} = -(\epsilon_{ij} - h_{ij} - \lambda \delta_{ij}) \tag{2.10.4}
\]

\[
\mu f_{ij}|\psi_l\rangle = -f_{ij}H|\psi_l\rangle + \sum_k \Lambda_{kl}|\psi_k\rangle \tag{2.10.5}
\]

The equation 2.10.4 is an harmonic oscillator that keeps the matrix elements of \(\epsilon\) close to those of the hamiltonian matrix, this sets a constraint to the possible first order perturbations that the wavefunctions can effectively undergo. \(Q\) is a parameter that regulates the frequency of the oscillator. Moreover it can be shown that this trick allows one to have electronic oscillation frequencies \(\omega\) that

\[
\omega_{ij} > \sqrt{E_{AG}/\mu} \tag{2.10.6}
\]

Where \(E_{AG}\) is an artificial energy gap corresponding to the range of eigenvalues with vanishing occupancies, and can be increased arbitrarily by including more empty states in the simulation. These empty states do not affect the evaluation of the total energy and consequently the dynamics, and the energy exchange between electronic and ionic degrees of freedom can be prevented by improving their number \(E_{AG}\). Furthermore this method has another good quality, it speeds up the convergence with the number of k-points.

### 2.11 Classical Molecular Dynamics

The Classical Molecular dynamics uses empirical potentials (known as forcefields) that either ignore quantum mechanical effects, or attempt to capture them in a limited way through entirely empirical equations. Parameters in the potential are fitted against known physical properties of the system being simulated, such as elastic constants and lattice parameters, and reproduce the basic aspects of the intermolecular and intramolecular interactions.
2.11.1 AMBER

AMBER (Assisted Model Building and Energy Refinement) is a family of force fields for molecular dynamics of biomolecules originally developed by the late Peter Kollman’s group at the University of California, San Francisco. AMBER is also the name for the molecular dynamics simulation package that implements these force fields [39] [40]. Among other codes that we used in this work, AMBER 8 was used to perform finite temperature MD simulations with the Generalised Amber Force Field [41] whose functional form is

\[ E_{TOT} = \sum_{\text{bonds}} K_r(r - r_{eq})^2 + \sum_{\theta} K_\theta(\theta - \theta_{eq})^2 + \]

\[ \sum_{\text{dihedral angles}} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)] + \]

\[ \sum_{i<j} [\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{R_{ij}}] \]  

The first and second terms describe the stretching and bending of the bonds, while the third takes into account the torsional degrees of freedom. The fourth term is a superimposition of Lennard-Jones potential and of a Coulomb potential and deals with long range interactions. AMBER is a large collection of programs covering all the aspects of the simulation from pre-processing to post-processing. Among the various features that are implemented in this code, we shall remember a few that were used in this work:

- it is possible to constrain the motion of some atoms to fixed position, by anchoring the atoms to the reference positions with harmonic potentials;
- canonic finite temperature simulations can be performed [42].

2.11.2 Matching the Forcefields to the ab-Initio results

In order to reproduce the interaction of molecules the electrostatic effects must be included in the forcefields. This can be done using effective point charges \( q_I \), positioned on the nuclei. From an ab-initio calculation we get the electronic charge density distribution \( \rho(r) \). From \( \rho \) the electrostatic potential can be obtained by solving the Poisson equation. The effective point charges are then chosen to fit this electrostatic potential. In the fit procedure the partial charges are substituted by gaussian charge distributions, centred around the atomic positions \( R_I \) and normalised to \( q_I \)

\[ \rho_I(r) = q_I \frac{\alpha^3}{\pi^{3/2}} e^{-\alpha^2(r-R_I)^2} \]  

(2.11.2)
It can be shown that the electrostatic potential has the following expression:

\[
V_{\text{mod}}(\mathbf{r}) = \frac{4\pi}{\Omega} \sum_{\mathbf{G}} \sum_{I} q_{I} e^{i \mathbf{G} \cdot (\mathbf{r} - \mathbf{R}_{I})} \frac{e^{-|\mathbf{G}|^2 4\alpha^2}}{|\mathbf{G}|^2} \quad (2.11.3)
\]

\[
= \sum_{I} q_{I} f(\mathbf{r} - \mathbf{R}_{I})
\]

The plane wave expansion can be applied since the electrostatic potential is periodic over the supercell, thus the expression 2.11.3 takes into account the interaction with periodic images. A cost function is defined which includes the electrostatic potential calculated ab-initio \( V(\mathbf{r}) \) and the one generated by the effective charges \( V_{\text{mod}}(\mathbf{r}) \).

\[
A(q_1, \ldots, q_N) = \sum_{J} \left( \sum_{I} q_{I} f(\mathbf{r}_{J} - \mathbf{R}_{I} + \lambda - V(\mathbf{r}_{j}))^2 + \beta (\sum_{I} q_{I})^2 \right) \quad (2.11.4)
\]

where \( \mathbf{r}_{J} \) are the points of the computational mesh in the fit region. The \( \beta \) is introduced to impose the neutrality constrain for the system. The \( \lambda \) parameter is free additive constant of the problem. By minimizing this cost function the effective point charges are calculated. The \( q_{I} \) are consistent with the geometry of the system that corresponds to the electron density distribution \( \rho(\mathbf{r}) \).

2.11.3 The Metals substrate in the classical MD

The metals are complicated quantum mechanical materials characterised by the presence of strongly delocalised electrons, thus their description within a classical potential is difficult. Among the many properties of a metal substrate it is possible to reproduce just a few.

- The geometric constraint that the metal surface imposes to the movement of the molecules,
- the screening effect due to the surface electrons.

When the molecules are known to lie flat on the surface the MD can be constrained to two dimensions, otherwise a fictitious substrate made of benzene can be introduced. To describe the screening of the adsorbate’s effective charges due to the substrate, their mirror images can be included in the calculation (Figure 2.1). The mirror plane coordinate \( d_{||} \) is the effective position of the surface described by the equation 1.2.2.
Figure 2.1: Illustration of the mirror images of adsorbate’s effective charges introduced to account for metal screening.
2.11.4 Preliminary calculations

Some preliminary calculation are required to evaluate the lattice constant. The experimentally measured and the calculated lattice constants often differ. Thus by using the experimental distances as a starting point for calculation, an amount of fictitious stress is introduced. The experimental geometries have to be adapted and rescaled in order to cancel this stress. The equilibrium lattice constant is found by measuring the system energy as a function of the crystal lattice and minimising it (Figure 2.2). The function

\[
E(V) = \frac{B_0 V}{B_0' (B_0' - 1)} \left[ B_0' \left( 1 - \frac{V_0}{V} \right) + \left( \frac{V_0}{V} \right)^{B_0'} - 1 \right] + E(V_0) \tag{2.11.5}
\]

where \( B_0 \) is the bulk modulus. In the table 2.1 the calculated values for the lattice constant and the bulk modulus are reported.

Figure 2.2: The Ag total energy as function of the lattice constant calculated with GGA PW91 and pseudopotential approximations
<table>
<thead>
<tr>
<th></th>
<th>Material</th>
<th>Lattice constant (Å)</th>
<th>Bulk modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>Ag</td>
<td>4.09</td>
<td>100</td>
</tr>
<tr>
<td>TM GGA</td>
<td>Ag</td>
<td>4.20</td>
<td>89</td>
</tr>
<tr>
<td>PAW GGA</td>
<td>Ag</td>
<td>4.14</td>
<td>90</td>
</tr>
<tr>
<td>Experimental</td>
<td>Au</td>
<td>4.05</td>
<td>200</td>
</tr>
<tr>
<td>PAW LDA</td>
<td>Au</td>
<td>4.08</td>
<td>220</td>
</tr>
<tr>
<td>PAW GGA</td>
<td>Au</td>
<td>4.14</td>
<td>137</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison of the experimental and theoretical values for the lattice constant and the bulk moduli of gold and silver. TM means that Troullier-Martins pseudopotentials are used while PAW means that the Projector Augmented Waves scheme is used.
Chapter 3

Hardware

3.1 Introduction

During the three years period of the PhD I have been greatly concerned with the contingent aspects of the computational sciences, that are strictly connected to the physical nature of computers. From computer maintenance to program development and debugging a big amount of time has been dedicated to a wide range of applications. Thus my PhD thesis would not be complete if a description of the the computational activity were lacking. However this chapter is not meant to be a complete and comprehensive description of this topic, instead it is a survey of the modern hardware available and of the machines used.

The attendance to schools and workshops such as the Summer School in High Performance Computing and the Machine Evaluation Workshop 2005 promoted respectively by the CINECA [43] and by the HPCX [44] has deeply improved my knowledge of these topics, and therefore influenced the PhD work.

State of the art machines for modern computer simulations use the paradigm of distributed computing to share workload among many different CPUs. These machines are referred to as parallel and allow for a big saving of time. In the following the structure of a parallel machine will be elucidated pointing the attention to the architectural revolutions that occurred in the last few years, and to their effect on programs and simulations.

3.2 Parallel Computers

A parallel computer is a set of Processing Elements (PE) that are able to work simultaneously and share the workload to reduce the computational
cost. The idea is based on the fact that the process of solving a problem usually can be divided into smaller tasks, which may be carried out simultaneously with some coordination. To share the workload these PEs have to communicate with each other. Some machines use the main memory to interconnect the PEs according to a paradigm known as shared memory, others use high performance network connections between PEs that use their own memory (distributed memory paradigm). The power of the PEs and the speed of the memory or interconnection strongly affect the efficiency of a parallel computer. Moreover different applications can take advantage in different ways from a parallel machine. The quality of the program, that has to be properly engineered to run in a parallel environment, is just one of the aspects. The nature of the problem also plays an important role: some problems can be solved parallely with a great efficiency others can not. Coarse-grained applications spend more time computing than communicating, while fine-grained applications must communicate often. Coarse-grained algorithms require less communications than fine-grained algorithms. Very coarse-grained applications that compute most of the time and communicate very little are referred to as embarrassingly parallel (or naturally parallel) applications.

Parallel computing systems can be categorized by the numbers of processors in them. Systems with thousands of such processors are known as massively parallel. Subsequently there are what are referred to as "Large scale" vs "Small scale" parallel processors. This depends on the size of the processor, eg. a PC based parallel system would generally be considered a small scale system. Parallel processor machines are also divided into symmetric and asymmetric multiprocessors, depending on whether all the processors are the same or not (for instance if only one is capable of running the operating system code and others are less privileged).

3.3 Network technologies

Interconnect performance directly affects the performance of the cluster as applications become finer grained. Two characteristics are important to consider: the latency between packets and the maximum bandwidth achievable on the network. High-latency protocols, such as TCP/IP, can degrade cluster performance as much as a network with limited bandwidth can. For fine-grained applications, the network needs to have low latency and high bandwidth. The text below compares the key performance characteristics of different interconnects.
3.3.1 Ethernet

A result of research done at Xerox Corporation in the early 1970s, Ethernet has evolved into the most widely implemented protocol today. Fast Ethernet increased speed from 10 to 100 megabits per second (Mbit/s). Gigabit Ethernet was the next iteration, increasing the speed to 1000 Mbit/s. Fiber gigabit Ethernet has recently been overtaken by 10 gigabit Ethernet which provided data rates 10 times that of gigabit Ethernet. Work on copper 10 gigabit Ethernet over twisted pair has been recently completed (July 2006). Even though it allows for high bandwidths, the high latency of this interconnect, 60\(\mu\)s makes it unsuitable for massively parallel machines.

Future developments

In late November of 2006 an IEEE study group agreed to target 100Gbps ethernet as the next version of the technology.

3.3.2 Myrinet

Myrinet is a high-speed local area networking system designed by Myricom [51] to be used as an interconnect to form computer clusters. Myrinet has much less protocol overhead than standards such as Ethernet, and therefore provides better throughput, less interference, and less latency while using the host CPU.

Myrinet physically consists of two fibre optic cables, upstream and downstream, connected to the host computers with a single connector. Machines are connected via low-overhead routers and switches, as opposed to connecting one machine directly to another. The Gbit/s. Newest ”Fourth-generation Myrinet” supports 10 Gbit/s data rate, and is interoperable with 10 Gigabit Ethernet on the physical layer (cables, connectors, distances, signalling).

Myricom supplies Myrinet components and software in two series: Myrinet-2000 and Myri10G. Myrinet-2000 is a superior alternative to Gigabit Ethernet for clusters, whereas Myri-10G offers performance and cost advantages over 10-Gigabit Ethernet. Myri-10G uses the same physical layers (PHYs: cables, connectors, signaling) as 10-Gigabit Ethernet, and is highly interoperable with 10-Gigabit Ethernet. The MPI latency is 2 – 3\(\mu\)s.

Future developments

The interoperability of Miry-10G and ethernet 10Gb is being used to realise wide area clusters without the use of the gateways. This approach is midway between a local cluster and a grid and is conceptually new.
3.3.3 Infiniband

Like many modern interconnects, InfiniBand is a point-to-point bidirectional serial link intended for the connection of processors with high speed peripherals such as disks. It supports several signalling rates and links can be bonded together for additional bandwidth. The latency is 1.29 - 2.68 microseconds. The serial connection’s signalling rate is 2.5 gigabits per second (Gbit/s) in each direction per connection. InfiniBand supports double and quad data speeds, for 5 Gbit/s or 10 Gbit/s respectively. Links can be aggregated in units of 4 or 12, called 4X or 12X. A quad-rate 12X link therefore carries 120 Gbit/s raw, or 96 Gbit/s of useful data. Most systems today use a 4X 2.5Gbit connection, though the first 5Gbit products are already entering the market.

3.3.4 Quadrics

QsNetII is the latest generation of Quadrics Interconnect family products. Quadrics QsNetII interfaces to the host computer through the standard IO PCI-X bus. The architecture of the network interface has been developed to offload the entire task of interprocessor communication from the main processor, and to avoid the overhead of system calls for user process to user process messaging. QsNetII is designed for use within shared memory systems - multiple, concurrent processes can utilise the network interface without any task switching overhead. A I/O processor offloads protocol handling from the main CPU. Local memory on the PCI card provides storage for buffers, translation tables and I/O adapter code. All the PCI bandwidth is available to data communication. Performance depends on platform used and configuration of the system, QsNetII MPI latency starts at 1.22 µs while its bandwidth 900 Mbytes/s. QsNetII uses a fat tree topology. This permits scaling up to 4096 nodes. The nodes themselves typically have multiple CPUs, permitting systems of > 10,000 CPUs to be constructed.

3.3.5 IBM

IBM [49] supercomputers use the proprietary High Performance Switch (HPS). HPS is IBM’s fourth generation switch and adapter technology. The MPI latency is about 3 – 4µs. The switch incorporates new link technology with peak performance of 2 GB/second in unidirectional and 4 GB/second of peak bi-direction bandwidth.
3.4 CPUs

The speed of processors is growing rapidly, and the choice for the best processor is one of the hardest. Every few months new processors are released with outstanding performances. In the commodity cluster market two companies fight for the leading position: INTEL [48] and AMD [47]. They produce processors that are highly compatible, although their architecture is rather different. The IBM probably is the only leader of the capability computer market. Although the computational power of the CPUs is steadily increasing because the working frequencies are growing, and the architectural complexities are improving, the main bottleneck to fast computing is the connection with the main memory (RAM). If the timescale of a modern processor is in the nanorange, a typical RAM memory can operate in the range of microseconds. Very small quantities of very expensive high speed memory (the caches) are introduced to bridge the gap, but the caches can have very different impacts on the programs. The future evolution in the computer design should look in this direction to have a big jump forward in performance, nevertheless in the last years two revolutionary changes have been introduced.

3.4.1 32bit to 64bit

The labels 64-bit, 32-bit, etc. designate the number of bits that each of the processor’s general-purpose registers (GPRs) can hold. So when someone uses the term 64-bit processor, what they mean is a processor with GPRs that store 64-bit numbers. And in the same vein, a 64-bit instruction is an instruction that operates on 64-bit numbers. The change from 32 to 64 bit registers has many consequences. In terms of memory limits this change is a big step forward. A 32-bit register means that \(2^{32}\) addresses, or 4 gigabytes of RAM, can be referenced. At the time these architectures were devised, 4 gigabytes of memory was so far beyond the typical quantities available in installations that this was considered to be enough headroom for addressing. The emergence of the 64-bit architecture effectively increases the memory limit to \(2^{64}\) addresses, equivalent to 17,179,869,184 gigabytes or 16 exabytes of RAM. Memory intensive applications that need to address more than 4GB per node can greatly benefit of the new limit. The presence of 64 bit registers should increase the performances for double precision floating point arithmetic, nonetheless the presence of vectorial FPU in the 32 bit processor family can compensate for this difference and the performance discrepancies are not always evident. A change from a 32-bit to a 64-bit architecture is a fundamental alteration, as most operating systems must
be extensively modified to take advantage of the new architecture. Other software must also be ported to use the new capabilities. For instance, old fortran programs often use integer variables (32 bit) as pointers. In a 64 bit environment this is not possible, and the code has to be modified in order to run. However the main disadvantage of 64-bit architectures is that relative to 32-bit architectures the same data occupies slightly more space in memory. This increases the memory requirements of a given process and can have implications for efficient processor cache utilisation.

The main 64 bit architectures are:

- Intel ia64, implemented in the Itanium processors;
- AMD 64 (previously known as x86 - 64) is an extension to standard x86;
- Intel 64 (previously known as EMT 64) is introduced for compatibility with AMD 64;
- IBM power and powerpc technology;
- SPARC 64 and ULTRASPARC;
- DEC ALPHA.

### 3.4.2 Multi-core processors

The application of advanced lithography techniques into the processors manufacturing technology leads to the construction of chips with an always growing density of transistors.

Today it is possible to include more cores in the same chip, this means that a processors is made of a set of independent PEs that can work simultaneously sharing the same memory and the same bus. This new approach is revolutionising the Information Technology market, since it is not only a technological advance but it has deep conceptual implications. By including more PEs on the same chip a certain degree of parallelism is introduced in the processor, therefore the operating system and the applications have to be designed to exploit this feature.

The multicore architecture is well suited for scientific computing:

- One double core processor costs less than two single core processors;
- The two cores can share the same memory, so there is no need to connect them with expensive high performance networks;
• The power consumption and the volume occupied are reduced.

However there are also some drawbacks that have to be considered. Since the cores share the same memory and the same bus the total bandwidth is limited and this can be a problematic for applications that are memory intensive, furthermore the optimised synchronisation of the internal parallelism (multicore) and of the external parallelism (network connection) is difficult to ensure.

Both AMD and INTEL have now multi-core processors as their top-level product, and many cluster have been built with these dual core processors (two PEs in a chip). In the last few months quad-core processors (four PEs in a chip) were released. IBM has introduced its first dual core processor, the Power 5, some years ago. SUN [50] is merchandising ULTRASPARC processors with up to 8 cores.

**Future developments**

Intel has produced a 80-core prototype. The chip is capable of transferring a terabyte of data per second. As Intel’s powerful dual core chips are able to transfer only 1.66 gigabytes of data per second, the proposed 80-core chip would represent a several hundred fold increase over the performance in today’s processors. This should be merchandised by the end of 2011. By the same year IBM expects to be able to produce silicon-germanium chips that should have a working frequency of 500 GHz. If these two predictions are exact, in a short time computational scientists will have extraordinary instruments to carry out their research.

### 3.5 Coprocessors

As the number of transistors per unit area increases the power consumption of a processor grows. In a world where the energy resources are limited, the real world, people realise that energy waste has to be minimised. For this reason the new supercomputers should be able to outperform aged machines without any further increase in power consumption. Unfortunately this is not the case, however new ideas are being attempted.

Coprocessors are chips designed for specific tasks which they are able to fulfill with a much higher efficiency than that of general use processors, furthermore their power dissipation is limited to 10-30 W. The main problem that oppose the diffusion of this interesting technology is that the programs need to be adapted in order to run efficiently. The effort to change the software is often too big, so scientists prefer to be conservative.
3.6 Programming paradigms

The standard for the development of parallel programs is the Message Passing Interface library (MPI) which is a set of procedures which control the exchange of information between the PEs. This approach can give very good performances if properly used, but on the other side it is difficult to use. Attempts have been implemented to automatise the distribution of the workload, but seldom the results were optimal. For shared memory machines the openMP paradigm seems to give discrete performances. It is a set of compiler directives which indicate the portion of the code that need to be parallelised. The compiler organise the distribution of the workload according to these directives, which unfortunately are compiler dependent.

Part of the scientific community feels the urge for new paradigms to be developed, that should simplify the distribution of the workload and the porting of the applications to different platforms.

3.7 Parallel computers used

3.7.1 Cineca

An agreement between the University of Trieste and the CINECA [43] was signed, according to it, from July 2003 to September 2007, an amount of 300000 CPU hours per year are available to the researchers and students of the University. The calculations have to be performed into two of the Cineca systems: CLX and SP5. Both have been used for the calculations described in the next chapters.
Figure 3.1: The SP5’s racks.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>IBM SP Cluster 1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processors</td>
<td>IBM Power 5, 1.9 GHz</td>
</tr>
<tr>
<td>Number of processors</td>
<td>512</td>
</tr>
<tr>
<td>Total Ram Memory</td>
<td>1216 GB</td>
</tr>
<tr>
<td>Number of Nodes</td>
<td>64</td>
</tr>
<tr>
<td>PE per node</td>
<td>8</td>
</tr>
<tr>
<td>Memory per node</td>
<td>16 GB or 64 GB</td>
</tr>
<tr>
<td>Network</td>
<td>HPS</td>
</tr>
<tr>
<td>Operative System</td>
<td>AIX 5.2</td>
</tr>
<tr>
<td>Scheduling System</td>
<td>Loadleveler</td>
</tr>
</tbody>
</table>
Figure 3.2: The CLX’s racks.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>IBM Linux Cluster 1350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processors</td>
<td>Intel Xeon Pentium IV 3 GHz</td>
</tr>
<tr>
<td>Number of processors</td>
<td>512</td>
</tr>
<tr>
<td>Total Ram Memory</td>
<td>1 TB</td>
</tr>
<tr>
<td>Number of Nodes</td>
<td>512</td>
</tr>
<tr>
<td>PE per node</td>
<td>2</td>
</tr>
<tr>
<td>Memory per node</td>
<td>2 GB</td>
</tr>
<tr>
<td>Network</td>
<td>Myrinet-2000</td>
</tr>
<tr>
<td>Operative System</td>
<td>Linux SuSE SLES 8</td>
</tr>
<tr>
<td>Scheduling System</td>
<td>OPENPBS, LFS</td>
</tr>
</tbody>
</table>
3.7.2 Rechenzentrum Garching

Because of our collaborations with the group of Klaus Kern we have access to some of the computational facilities that are stored in Garching [45]. Their Regatta system has been used by both myself and my colleagues.

Regatta

![Image of the REGATTA's racks.](image)

*Figure 3.3: The REGATTA’s racks.*

<table>
<thead>
<tr>
<th>Architecture</th>
<th>IBM eServer p690</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processors</td>
<td>IBM Power 4 1.3 GHz</td>
</tr>
<tr>
<td>Number of processors</td>
<td>812</td>
</tr>
<tr>
<td>Total Ram Memory</td>
<td>2 TB</td>
</tr>
<tr>
<td>Number of Nodes</td>
<td>27</td>
</tr>
<tr>
<td>PE per node</td>
<td>32</td>
</tr>
<tr>
<td>Memory per node</td>
<td>64 GB or 256 GB</td>
</tr>
<tr>
<td>Network</td>
<td>HPS</td>
</tr>
<tr>
<td>Operative System</td>
<td>AIX 5.1</td>
</tr>
<tr>
<td>Scheduling System</td>
<td>LoadLeveler</td>
</tr>
</tbody>
</table>
3.7.3 King’s College London

During the Phd I had many connections with the KCL [46] inclusive of a nice seven months visiting period aimed at the development of scientific collaborations. Contextually I had the opportunity to use their computational facilities. In the case of the linux cluster Archimedes, I followed thoroughly the purchase procedure by benchmarking and testing the candidates and, when eventually the machine was chosen, I had the honour to administer it.

Archimedes

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Streamline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processors</td>
<td>AMD Opteron DP 275 Dual Core</td>
</tr>
<tr>
<td>Number of PEs</td>
<td>32</td>
</tr>
<tr>
<td>Total Ram Memory</td>
<td>64 GB</td>
</tr>
<tr>
<td>Number of Nodes</td>
<td>8</td>
</tr>
<tr>
<td>PE per node</td>
<td>4</td>
</tr>
<tr>
<td>Memory per node</td>
<td>2 GB</td>
</tr>
<tr>
<td>Network</td>
<td>Myrinet-2K</td>
</tr>
<tr>
<td>Operative System</td>
<td>Suse 9.1</td>
</tr>
<tr>
<td>Scheduling System</td>
<td>SUN SGE 6.0</td>
</tr>
</tbody>
</table>
Chapter 4

The selfassembly of BTA on Ag(111)

4.1 Introduction and acknowledgements

Figure 4.1: Chemical structure of 4,4',4″-benzene-1,3,5-triyl-tri-benzoic acid (BTA).
In this chapter the selfassembly of 4,4',4''-benzene-1,3,5-triyl-tri-benzoic acid (BTA) is studied (Figure 4.1). This work was carried out in strict collaboration with many experimentalist, Mario Ruben and Aitor Landa from the Institut für Nanotechnologie, Karlsruhe, Dietmar Payer, Nian Lin, and Klaus Kern from Max-Planck Institut für Festkörperforschung, Stuttgart and Jean-Paul Collin and Jean-Pierre Sauvage from ULP/CNRS, Strasbourg. The initial part of the chapter is dedicated to the illustration of experimental results, while the following sections describe the theoretical and computational work done by me, Chiara Gattinoni and Alessandro De Vita in order to integrate and interprete experimental results. This work has been published in [52].

4.2 Experimental evidences

4.2.1 STM studies

The sublimation of the BTA molecules onto a Ag(111) surface held at 200-250 K followed by short annealing at 270-300 K resulted in the formation of a regular 2D honeycomb network (Figure 4.2a). However, holding the temperature of the Ag(111) surface above 320 K during the molecular deposition resulted in the evolution of a second phase of ribbons consisting of equal-spaced one-dimensional (1D) rows (Figure 4.2b). Alternatively, the phase I (the 2D open honeycomb network) can be transformed into phase II (the 1D ribbon structure) by annealing at a temperature of 320 K. Further increasing the Ag(111) surface temperature above 420 K resulted in the emergence of a phase III, in which a 2D close-packed adlayer with inherent three-fold symmetry could be observed (4.2c). All three phases are formed in extended domains on the surface. Both phase transformations were completely irreversible.

4.2.2 STS studies

To investigate the origin of the phase transformations, tunneling spectra were acquired at the three phases (Figure 4.3). The electronic structure of an adsorbed molecule is perturbed by the presence of the substrate electrons, and vice versa [53, 54]. For weak adsorbate-substrate interaction, the Shockley surface state (Section 1.2.4) present on the (111) surfaces of the noble metals Au, Ag and Cu is known to persist upon adsorption with modified band onset and electron/hole lifetimes [55, 75, 76, 77, 59]. An excess negative charge at the surface associated with the adsorption usually results in
Figure 4.2: The deposition of the BTA molecules onto a Ag(111) surface results in the formation of three different supramolecular hydrogen bonding motifs depending on the Ag(111) surface temperature: a) phase I (open 2D honeycomb network), b) phase II (1D ribbons), and c) phase III (closed packed 2D adlayer). Image size: 30nm x 20nm. Tunnelling current = 0.5nA, Bias voltage = 0.5V (applied to the sample).
an upward shift of the onset energy, [75, 77] whereas a downward shift is observed of electron-deficient adsorbates as alkali metals [60, 61]. Stronger adsorbate-substrate interactions can lead to substantial changes of the substrate electronic structure and even the quenching of the surface state.

Figure 4.3: $dI/dV$ tunneling spectra acquired at the three phases respectively. As a reference, the spectrum acquired at the pristine Ag(111) surface is shown, displaying the surface state onset at $-70$ mV. All spectra were taken at 5kHz. Setting parameters of measurements (tunnelling current and bias voltage before opening the feedback loop) are 0.2V and 1.5 nA, 0.2V and 0.7 nA, 0.6V and 0.5 nA, 1.0V and 1.0 nA, for acquiring spectra on clean Ag, phase I, phase II and phase III respectively. The magnitude of each spectrum is normalised according to the onset height of the clean Ag surface state taken with the same setting parameters. The curves are shifted along the y-axis for clarity.

Figure 4.3 shows the $dI/dV$ tunneling spectra of the three molecular phases along with the clean Ag(111) spectrum. The latter shows a sharp onset at $-70$mV. This step-like characteristic is modified by the adsorption of BTA in all three phases. In phase I a slightly broader onset at an energy of $-50$mV was observed (the onset position is defined by the half maximum
height). In contrast, phase II and phase III show onsets of remarkable broadening and upward shifting, $320mV$ and $770mV$, respectively. The spectra are independent of the position of the STM tip, i.e., STS mapping of BTA at various essential energies does not display submolecular contrast. This phenomenon suggests that the observed spectral features are not derived from BTA molecular orbitals [62, 63, 64], but rather from the Ag surface electronic states. Phase I consists of neutral BTA that weakly adsorbs at the surface, which only slightly alters the surface state onset [55]. The significant upward shift in phase II and III indicates the presence of negatively charged adsorbates at the surface, which are associated with deprotonated acid groups. The further shifting and broadening of the onset of phase III with respect to phase II reflects (and is possibly caused by) the development of the deprotonation processes, i.e., a stepwise increase of the number of deprotonated groups per BTA molecule [61], consistent with the irreversibility of the observed transitions.

4.2.3 Models

Based on these observations we propose the following models for the three BTA phases. The phase I represents a 2D open hexagonal network, which incorporates a regular array of cavities of 2.9 nm inner diameter and 3.1 nm periodicity (Figure 4.4a). The supramolecular interconnection of the BTA molecules is achieved by symmetric hydrogen bonds of carboxylic acid dimers, as shown in Figure 4.4b and 4.4c, whereby the oxygen-oxygen distance is estimated at a value of 3.1 Å, as expected for this type of bond. Structurally, the honeycomb phase I is similar to that of the related TMA systems, although the pore size is significantly enlarged to 2.95 nm [65, 66]. Very recently, the same hexagonal network structure of the unprotonated BTA was found at the solid/liquid interface (graphite/nonanoic acid or 1-phenyl octane), too [67]. Generally, two types of point defects can be observed: (i) Missing bricks within the hexagonal network and (ii) additional BTA molecules within the cavities. The latter defect suggests the possibility to achieve a controlled filling of the relatively large hexagonal cavities with different types of molecules. Phase II has a 1D ribbon structure, as shown in Figure 4.5a. Within the single rows, two BTA molecules are arranged in pairs forming a band of 1.70 nm width. The periodicity along the row is 1.55 nm and the row-to-row spacing is 2.18 nm. The orientations of the ribbons fall in three directions with a $120^\circ$ angle in between, reflecting the three-fold symmetry of the Ag(111) substrate. The structure of the phase III consists of close-packed BTA, with every end group pointing to the mid-edge of an adjacent molecule, as shown in Figure 4.6a. This phase has a C3 symmetry.
Figure 4.4: a) High resolution STM image of the phase I honeycomb network; b) Atomistic model proposed for this phase. c) The modeled double hydrogen bond between two carboxylic acid groups.

Figure 4.5: a) High resolution image of phase II ribbon structure. b) Atomistic model obtained for this chiral asymmetric structure. Each molecule is singly deprotonated, but still remains linked to neighboring molecules by hydrogen bonds between carboxylic acid pairs; c) Detail of the hydrogen bond linkage.

Figure 4.6: a) High resolution STM image of the phase III closely packed 2D adlayer structure. b) Atomistic model of phase III. The BTA molecules are doubly deprotonated in this model (the remaining proton is tilted backwards) with no residual H-bonds between carboxylic groups; c) Hydrogen bonds between one remaining protonated carboxylic acid group and the C-H protons of the phenyl rings of neighbouring BTA molecules.
and a 1.36 nm lattice constant.

4.3 Computational Modeling

4.3.1 Technical aspects

Computational Modeling: The structures revealed by the STM images were modeled by means of a combination of classical and ab-initio molecular dynamics techniques. First-principles calculations were carried out using the Car-Parrinello method (Section 2.9), with Troullier Martins norm-conserving pseudopotentials (Section 2.6) and a gradient corrected exchange-correlation functional (Section 2.3). The plane wave expansions were limited by a 70 Ry energy cut-off for gas-phase calculations and the Brillouin zone sampling was limited to the gamma point only. For metallic systems we introduced a 0.25 eV Fermi level smearing (Section 2.10). The classical constant-temperature simulations were performed using the AMBER package with the Generalized Amber Force Field and a Nose-Hoover thermostat (Section 2.11.1). As the AMBER package does not allow direct modelling of metal surfaces; we modelled the metal substrate by a planar “carpet” of benzenes constrained to fixed positions. However, electrostatic interactions between the molecules and the metal surface are not taken into account by this approach. To investigate this effect we used a home-made 2D molecular dynamics model where surface screening effects are described by introducing mirror images of the force-field partial Coulomb charges (Section 2.11.3).

4.3.2 Phase I

In order to investigate the stability of phase I, this phase was modeled with AMBER holding the system in a planar geometry. The resulted equilibrium structure is shown in Figure 4.4b. Although the benzenes surface model is probably less effective than the real metal substrate in stabilizing the structure, the network proved to be stable up to relatively high temperatures in the modeling. The structure consists of a network of molecules doubly bound to each other by hydrogen bonds of the carboxylic acid groups (Figure 4.4c) to form a honeycomb network structure.

4.3.3 Phase II

The ribbon phase II is far less immediate to model, as it presents molecules arranged in stripes that keep apart from each other (see Figure 4.5a).
AMBER package was next used to investigate the stability of the observed phase II ribbon structure. The simulations were carried out for different ribbon configurations imposing the same temperature, spacing and substrate initial conditions. The rows were made of BTA molecules with the carboxylic acid groups either fully protonated or singly deprotonated. It was found that in both cases the rows appear to be stable up to high temperatures (500-600 K in the simulations). However, neighboring rows made of fully protonated molecules tend to stick to each other, contrary to what was observed in the STM images. On the other hand, when partially deprotonated molecules are used, neighboring parallel rows remain apart from each other during the simulations, consistent with the experimental results. These results were obtained again using the molecular dynamics model which contains an image-charge description of the surface screening described in section 2.11.3. This all suggests that the observed behavior is due to the repulsive interaction between the neighboring rows containing negatively charged carboxylate groups on their borders. This electrostatic repulsion can not be overcome by hydrogen bonds between carboxyl groups of neighbouring chains, since all the available carboxyl hydrogens are involved in the internal linkage structure of the individual chains. Furthermore, the repulsion can be expected to be significant at short intermolecular distances even after taking into account the surface electrostatic screening, yielding stable structures with separated molecular ribbons at the experimental coverages. The most stable molecular structure identified for the phase II is the one shown in Figure 4.5b. It contains one deprotonated carboxylic acid group bound to two different protonated acid groups by two hydrogen bonds (Figure 4.5c). One of the hydrogen bonds is tilted backwards, yielding a chiral stepped structure for the assembled row. This structure was found to be more stable than any other structure we could produce with further modeling. Also, it is the structure in best agreement with the observed images. We note that while the honeycomb phase corresponds to the optimal hydrogen bonding geometry between fully protonated molecules, it would become relatively unstable if one carboxylic acid group per BTA were deprotonated, as this would imply couples of adjacent negatively charged mutually repelling oxygen atoms, located on the non-hydrogen-bonded side of facing carboxylic acid group pairs. We thus conclude that the observed phase II, which does not involve symmetric pairs of repulsive oxygens, would become more stable if deprotonation occurred. Although the lowered degree of direct carboxyl pairing does not in itself prove that deprotonation occurs, we note that the onset of deprotonation, which is known to occur in similar systems and temperature range, would be consistent with the tunneling spectra data, and with the irreversibility of the observed transition. We thus suggest that thermally initiated deprotonation
of the carboxylic acid groups is the driving force for the transition from phase I to phase II.

4.3.4 Phase III

When further deprotonation takes place at higher temperatures ($T > 420K$), as suggested by the tunneling spectrum taken at the phase III, even the phase II ribbon configuration becomes unstable, since at least two hydrogens are needed to bind together three carboxylic acid groups. Experimentally, the system changes into the 2D close-packed phase III upon further annealing, with all BTA molecules having the same orientation. This third phase does not contain hydrogen bonds between carboxylic acid groups, and the molecules stabilize in a triangular 2D lattice (see Figure 4.6a), in which every end group points to the mid-edge of an adjacent molecule. At first, it would seem reasonable to assume that complete deprotonation of the carboxylic acid groups were implied by such a structure. However, classical modeling carried out with the same MD packages used above indicates that the high density of negative charges left by complete deprotonation introduces an exceedingly large repulsive contribution to the cohesive energy of the supramolecular structure. Indeed, any attempt to reproduce a stable packed structure of fully deprotonated (-3e charged) molecular ions with classical codes failed, the repulsive energy term being too high for the system to remain stable.

Attractive interaction estimate

The attractive interaction between molecules was estimated by an ab-initio calculation modelling the bonding of a deprotonated benzoic acid with one BTA molecule in the gas phase. In equilibrium the molecules are coplanar and bind by hydrogen bonds involving COO oxygens and CH group hydrogens. The distance between the carbons and the oxygens is approximately 2.95 Å, the geometry is reported in Figure 4.7. Another calculation of the same molecules further apart in the same cell was performed to obtain the energy when the interaction is switched off. The comparison of the two calculations yielded a binding energy of 0.6 eV. Since each molecule binds to three different nearest neighbours the total estimated attractive energy is 1.8 eV per molecule.
Figure 4.7: The model used to estimate the attractive interaction, a deprotonated benzoic acid interacts with the phenyls of a BTA molecule.

Coulomb repulsion estimate

A simple estimate of the Coulomb repulsion energy can be obtained by approximating each negative carboxylic group (screened by the metal surface) with a standing electric dipole with a distance between the charge and its mirror image of about 6.0 Å. In Figure 4.8 the molecule are plotted as triangles of side $L = 15.7$ Å, and the dipoles are localised in the angles.

The system thus becomes a network of dipoles set on a regular triangular lattice with lattice parameter $L/2$, summing up the interaction of these dipoles gives a repulsive energy per molecule of 10 eV. The contributes of dipoles that belong to the same molecule have been removed from the summation since the self-interaction of molecules must not be included. The 10eV should be compared with the attractive interaction between molecules, that is 1.8 eV per molecule, i.e. much less than the repulsive contribution above. These results indicate that a fully deprotonated, fully charged system is unlikely to form, so that different states of charge or less than full deprotonation must be considered. We thus modeled the fully deprotonated system with an ab-initio simulation containing a single BTA molecule over 5 layers of Ag(111) in each periodically repeated cell of a triangular surface lattice. The chosen unit cell was a compromise between the experimentally measured dimensions and orientations and the constrains imposed by the periodic boundary conditions and by the DFT approximations. Namely the distance between two images of the same molecule have to commensurate
Figure 4.8: This scheme illustrates the arrangement of dipoles (coloured circles) in the lattice of molecules (yellow triangles) of the phase III. The blue circle is the reference dipole, while the other circles are its nearest neighbours (dark red circles), the second neighbours (mild red circles) and the third neighbours (pink circles). The dashed circles are the dipoles that belong to the same molecule of the reference dipole and have to be excluded. The circles form a triangular lattice with spacing $L/2$ where $L$ is the edge of a yellow triangle.
with the substrate periodicity. This periodicity is regulated by the calculated relaxed lattice parameter for silver.

After electronic and ionic relaxation, the electron density was integrated over the volume occupied by the molecule in order to evaluate its charge state. Our calculated value for the charge of the fully deprotonated adsorbed molecule is -1.97e, i.e. the model predicts that the molecule is less negatively charged than the previously considered -3e value. The repulsive energy can be estimated as before, but the smaller molecular charge must be taken into account. Assuming that the charge is homogeneously reduced in all the carboxylic groups, then all the sites of the triangular lattice (Figure 4.8) are charged -2/3e. Consequently the repulsive energy is reduced to \( (10eV \cdot \frac{2}{3}) \sim 4.5eV \) in this case.

We can conclude that the repulsive contribution is still too high to yield the close-packed configuration of the phase III. We then addressed the alternative hypothesis of incomplete deprotonation, implying e.g. that a doubly deprotonated system should be compatible with the geometry of the system. An ab-initio calculation revealed that the phase III arrangement is still compatible with the presence of protonated oxygens if the OH bond is tilted backwards. In such a system (see Figure 4.6c) the calculated ab initio value for the integrated charge of the molecule is -1.17e. If again we consider the charge homogeneously distributed over the sites, which are therefore -1.17/3e charged, the repulsive contribute is \( (10eV \cdot 0.152) \sim 1.5eV \), which is low enough to be compatible with the occurrence of a close-packed stable structure in which carboxyl groups are not facing each other. Thus, the phase III is rationalized by a structure containing doubly deprotonated BTA molecules. In this phase, both the two deprotonated carboxylate groups and the still protonated carboxylic acid group bind to the inner pocket of C-H protons of the neighbouring BTA leading to an intermolecular hydrogen bonding network, as shown in Figure 4.6c. In the equilibrium configuration the molecules lay flat on the surface, at a distance of about 3.1 Å from the first Ag layer. The oxygens in the deprotonated group are slightly tilted toward the surface. The main feature of the electronic structure of the phase III monolayer is the dipolar layer corresponding to the overall -1.17e charged molecule, screened by the metal surface. As discussed above, the main effect of the presence of the surface in mediating the interaction between deprotonated molecules is to define the long-range component of such an interaction as the lateral expulsion between negative standing dipoles.

To analyze the substrate - adsorbate interaction beyond dipole formation, we computed the displaced electron density on a vertical plane passing by an oxygen atom of a deprotonated carboxylate group (contour plot in Figure 4.9). To obtain this quantity, we first compute the electron density
Figure 4.9: Contour plot of the electron density displacement in a vertical plane containing an oxygen belonging to a deprotonated carboxylate group (see text). Electron density depletion is plotted in red-yellow, while the blue color palette denotes electron density accumulation.
of the phase III system. To this we subtract the electron densities associated to a gas phase -e charged deprotonated molecule and that associated to the +e surface unit cell, still assuming the phase III periodicity. As our choice of subtracted electron densities already approximately reproduces the final dipole structure of the interacting system (where the molecule is -1.17e charged and the surface is +1.17e charged) the displaced electron density as defined can be used to describe the local further density rearrangement occurring on the molecule and on the surface once the interaction between the two is turned on. The polarization of the oxygen atom in the negatively charged COO group and the screening response of the surface are visible in Figure 4.9 as a peak-through structure with a prominent electron accumulation lobe (in blue) located just below the Oxygen atom. This is screened by a corresponding depletion lobe (in red) located just above the Ag surface layer. No similar structure is found for protonated (neutral) carboxyl groups, and no appreciable structure is detected plotting the electron density displacement in the horizontal plane of the BTA adlayer, suggesting that the metal substrate does not significantly modify the electronic structure of the H bonding regions.

4.3.5 Conclusions

A 2D open honeycomb network with nanopores of an internal diameter of 2.95 nm was formed by the self-assembly of 4,4’,4”-benzene-1,3,5-triyl-tri-benzoic acid (BTA) on Ag(111) surfaces. Stepwise annealing of the initial phase resulted in two phase changes: the 1D ribbon phase II and the 2D close-packed adlayer phase III. The tunneling spectra acquired at the three phases suggested that the phase transformations are due to progressive deprotonation of the carboxylic acid functions of BTA, in agreement with the irreversible transformation. Theoretical modeling by classical force fields and ab initio calculations has been used to reproduce and interpret the experimental results. The emerging physical picture is that when one carboxylic acid group is deprotonated per BTA molecule, repulsion between facing carboxylic acid groups onsets and the first transition (phase I to phase II) takes place. If further deprotonation occurs the intermolecular links within the phase II, consisting of H-bonds between carboxyl acid groups, are progressively broken, and the second transition onsets. During these processes, stable hydrogen bonds connecting fully protonated opposite-facing carboxyl acid groups (phase I) are progressively substituted with lateral hydrogen bonds between partially deprotonated carboxyl acid groups (phase II) and finally by hydrogen bonds between carboxylic acid groups/carboxylates and phenyl C-H protons (phase III). In summary, our results indicate that deprotonation
can explain the occurrence of the self-assembled phases in the observed order. Rather remarkably, they also exemplify how higher-coverage phases can be obtained at each step of a series of phase transitions in a supramolecular assembled system, in spite of the increasing temperature and the increasing electrostatic energy cost accompanying deprotonation.

4.3.6 An application: Hierarchical Self-Assembly

Figure 4.10: a) Structure of the macrocycle molecule mt-33; b) STM image of the adsorption of the mt-33 on Ag(111).

The bottom-up generation of organization levels of increasing complexity, diversity and functionality relies on hierarchic self-assembly steps, where each step sets progressively the base for the next one. The nanocavities of the phase I honeycomb structure with 2.95 nm inner-diameter provide the space to bind a single molecule or a discrete number of guest molecules [68] [69]. Because its regular arrangement of nanocavities over extended domains, the phase I structure constitutes an ideal two-dimensional template to construct an ordered hierarchical systems with guest molecules. Furthermore the temperature-controlled phase transformation leads to a reorganization of the guest molecules(Figure 4.11). In order to test the possibility of hierarchical self-assembly, molecules of the macrocylic compound mt-33 (Figure 4.10) were chosen as guest molecules. mt-33 was deposited on top of the surface covered with the hexagonal 2D network of the phase 1. We found that single molecules of mt-33 were confined within the nanometer-sized cavities of the hexagonal network. STM measurements, as shown in Figure 4.12, which were taken at 5 K, clearly identified larger species trapped in the honeycomb cavities, as represented by the red rings in the schematic graph of Figure
4.12b. The appearance of these objects occurred exclusively after the de-
position of mt-33. The external size and the ellipsoidal shape indicate that
these objects are indeed molecules of compound mt-33 (see supplementary
material). In addition, the trapped molecules within the cavities exhibit a
donut shape, which advocates for a flat adsorption on the surface. In com-
parison, the small species, as expressed as yellow triangles in the schematic
view, are excess molecules of BTA trapped within cavities, which can be
easily distinguished from the macrocyclic compound mt-33. Figure 4.12 a
further reveals that due to the matching interior size of the cavity with the
molecule size of mt-33 only single species are accommodated in a cavity at
these particular deposition conditions. In any case, no double inclusion of
mt-33 could be observed. In more detail, the STM data also reveal that
the molecules are confined eccentrically within the hexagonal cavities con-
tacting the cavity inner wall, which might be explained by the attractive
interaction between the macrocycle outer rim and the cavity inner wall. The
preference of the adsorption sites also reflects the stereochemical misfit of a
C2-symmetry molecule mt-33 within a threefold-symmetric environment.

When annealing the phase I structure that included the trapped mt-
33 species to the phase transformation temperature of 320 K, the trapped
mt-33 molecules were released and formed dimers, trimers and tetramers
together with the close-packed phase II of BTA, as shown in Figure 4.13a.
The individual molecule appears as a donut-shape object, which reflects the
ring structure of mt-33. The high-resolution data in Figure 4.13b and c
elucidate an asymmetrically ellipsoidal shape of individual molecules of mt-
33 consisting of a broader 2,2',6',2''-terpyridine (denoted as head) part and
a sharper 1,10-phenanthroline part (denoted as tail). Within the aggregates,
the molecules form head-to-head arrangements for both the dimer and the
Figure 4.12: Trapping of single macrocycle molecules mt-33 in the nanocavities of phase 1 of BTA. a) STM image (18 nm x 11 nm) representing the hexagonal network of BTA with subsequently deposited mt-33. b) A scematic view of a.
tetramer. The inter-molecular interactions are attributed to hydrogen bonds between the nitrogen atoms and the protons of the aromatic rings of all-transoid conformers of neighbored 2,2',6',2''-terpyridine units, as proposed by the green dashed lines in Figure 4.13b and c. This nucleation behavior is identical to adsorption of mt-33 at a clean Ag(111) surface (Figure 4.10b).

Figure 4.13: a) STM image showing spontaneous clustering of macrocycle molecule mt-33 coexisting with the close-packed phase II of BTA. b and c) High resolution STM images of the dimeric and tetrameric aggregates with inscribed models.
Chapter 5

The self-assembly of TMA adsorbed on Ag(111)

5.1 Introduction and acknowledgements

In this chapter the selfassembly of TriMesic Acid (TMA) is studied. This work was carried out in close collaboration with many experimentalists, Dietmar Payer, Alexandre Dmitriev, Nian Lin, and Klaus Kern from Max-Planck Institut für Festkörperforschung, Stuttgart, Thomas Strunskus and Christof Wöll from Lehrstuhl für Physikalische Chemie 1, Ruhr Universität Bochum and Johannes Barth from Department of Chemistry and Physics and Astronomy, University of British Columbia, Vancouver. The initial part of the chapter is dedicated to the illustration of experimental results, while the following sections describe the theoretical and computational work done by Alessandro De Vita and myself in order to integrate and interpret experimental results. This work has been published in [70].

5.2 Experimental results

5.2.1 STM results

Figure 5.1a shows an STM topograph of the TMA structure after annealing the sample to 300K. The molecules are aggregated into the well known honeycomb-structure where every molecule is connected to three neighbouring molecules via carboxylic-acid dimer synthons between the carboxylic groups. This gives a hexagonal lattice with a lattice constant of 1.78nm and an O-O distance in the hydrogen bonds of 0.34nm, in agreement with previous results obtained with TMA on other substrates [71] [72] [73] [74].
Attempts to determine the registration of the honeycomb structure with respect to the Ag(111) surface were not successful because we could not resolve the Ag(111) atomic lattice and the honeycomb structure simultaneously. The presence of various oriented domains suggests that the honeycomb structure is non-commensurate to the Ag(111) substrate. After annealing the sample to 420K the open TMA honeycomb-structure is transformed irreversibly to a densely-packed structure as shown in the STM image in Figure 5.1b. The basic motif of this structure is a TMA quartet, a group of four closely packed TMA molecules in a rhombohedric arrangement with a side-length of 0.9nm and an angle of 68.4°. These quartet units are repeated in an oblique lattice with lattice-constants of 1.87nm, 1.77nm and an angle of 102°. Similar to the 300K structure the registration of the 420K structure with respect to the Ag(111) substrate could not be determined.

5.2.2 STS results

ST spectra acquired on the honeycomb structure show an onset at $-9.7 \pm 9.8$ meV and are broadened to $17.1 \pm 20.5$ meV with the flat plateau extending above 1500meV as shown in Figure 5.2. Because there is no significant difference between ST spectra taken at different positions of the TMA-honeycomb structure, we can rule out that the onset is a signature of TMA molecu-
Figure 5.2: ST-spectra acquired on clean Ag(111), the honeycomb structure and the quartet structure. The spectra were normalised to a constant onset height and shifted along the y-axis for better discrimination.
lar orbital. We attribute this onset to the surface state formed by a two-
dimensional electron gas, but shifted to higher energy and broadened by the
weakly adsorbed TMA molecules. It has been reported that weakly adsorbed
noble gas atoms have similar effects on the surface state of (111) surfaces of
noble metals [75] [78] [79]. We propose that TMA weakly binds to the Ag
surface, presumably van der Waals type like in the case of noble gas adsorp-
tion. This assumption is in agreement with the generally accepted picture
that planar aromatic hydrocarbons are weakly π-bonded with the benzene
rings parallel to the close-packed noble metal substrate [80] [81].

ST spectra acquired on the TMA quartet structure reveal pronounced
changes in the surface electronic structure. The spectrum reproduced in
Figure 5.2 shows a broad onset around 259.9±30.9meV with a width of 76.5±
23.6 meV. As no significant difference between various spots of the structure
is detected, we attribute the onset feature in the ST spectrum to the surface
electronic state. It is known that stronger adsorbate-substrate interactions
can lead to substantial changes of the substrate electronic structure and even
the quenching of the surface state. The observed significant deviation of the
ST spectrum of the 420K structure from the weakly bound neutral adsorbate
implies a noticeable impact of the TMA quartets on the surface electronic
state [75] [76] [77].

5.2.3 XPS and NEXAFS results

XPS- and NEXAFS-measurements provided complementary insight into
the chemical states and the bonding geometry of the TMA molecules in the
300K structure, endorsing the picture obtained by the STM-measurements.
The upper curve in Figure 5.3a shows the C 1s signal of the 300K structure
and the upper curve in Figure 5.3b shows the O 1s signal of the 300K struc-
ture. In the C 1s spectrum two well separated peaks are identified, a larger
one at a binding energy (BE) of 285.0eV which is assigned to the 6 carbon
atoms in the benzene ring and a smaller one at a BE of 289.1eV which is
assigned to the 3 carbon atoms in the carboxyl groups in accordance with
previous reports [82] [83] [86]. The fit of the spectrum with Gaussian shaped
peaks with a full width at half maximum (FWHM) of 1.4eV is improved by
adding a small additional peak with a BE of 287.3eV, which is assigned to
a small amount of carbon atoms of TMA molecules in a different chemical
state or it can be attributed to impurities on the surface like adsorbed CO.
The O 1s signal consists of a broad symmetric peak which is a convolution
of the signals of oxygen in hydroxyl groups (BE of 533.6eV) and in carbonyl
groups (BE of 531.5eV), in accordance with similar systems bound by hy-
dergen bonds between carboxylic acid groups [82]. The C 1s and O 1s XP

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Figure 5.3: (a and b) X-ray photoelectron spectra in the C 1s (a) and O 1s (b) regions, acquired on samples annealed to 300 K (upper graphs) and 420 K (lower graphs), respectively. (c and d) NEXAFS spectra of the 300K phase (c) and 420K phase (d) recorded at the C K-edge. Solid and dashed lines indicate spectra obtained at different angles of incidence of the synchrotron light (90°) means normal incidence to the Ag(111) surface.
spectra clearly show that after annealing to 300K the carboxylic groups of
the TMA molecules are still protonated, forming dimerized hydrogen bonds
between carboxylic groups. NEXAFS spectra of the 300K honeycomb struc-
ture are displayed in Figure 5.3c, where several pronounced \( \pi^* \)-resonances are
clearly discernible. The \( \pi^* \)-resonance at 284.6eV is assigned to transitions re-
lated to the carbon atoms of the aromatic ring, whereas the prominent peak
at 288.2eV and the shoulder at 290.0eV are assigned to transitions related
to the carboxyl carbons. At higher energy several \( \sigma^* \)-transitions located at
292.6eV, 296.4eV and 302.5eV can be identified. Both the \( \pi^* \)-resonances of
the benzene carbons and of the carboxyl carbons show a pronounced dichro-
ism with almost completely vanishing intensity for normal photon incidence
\( (90^\circ) \). The average tilt angles calculated from the observed dichroism are
\( 18^\circ \pm 7^\circ \) and \( 20^\circ \pm 7^\circ \) for the benzene and carboxyl part of the molecule, respec-
tively. These data indicate that the carboxylic acid groups are coplanar with
the benzene rings. There is a significant deviation of the obtained average tilt
angle from \( 0^\circ \) expected for perfectly flat lying molecules. Rather frequently
average tilt angles up to \( 10^\circ \), are observed in NEXAFS spectroscopy even for
perfectly flat lying aromatic molecules on metal surfaces [87] [88] [89]. The
tilting has been attributed to adsorption-induced aplanar intramolecular dis-
tortions, involving a bent of the CH-bonds out of the ring plane. Therefore
a plausible explanation of our data is that the vast majority of the molecules
are indeed adsorbed in a flat geometry and the larger average tilt angle is
caused by a small number of molecules deviating significantly from a flat
adsorption geometry. These latter molecules can be adsorbed at defects or
step edges.

A detailed analysis of the XPS measurements on the densely packed
420K structure showed a rigorous change in the chemical states of the TMA
molecules. The C 1s signal shown in the lower part of Figure 5.3a still con-
sists of two peaks, but the smaller one at a BE of app. 289.0eV is broadened
compared to the small peak in the 300K structure. The C 1s signal was fitted
by three Gaussian-shaped peaks with a FWHM of 1.4eV and the obtained
binding energies were compared to the results of the 300K structure and to
published data. The smaller peak has been deconvoluted into two peaks, one
for carbon atoms in the carboxylic groups at a BE of 288.7eV, in good agree-
ment with the 300K structure, and one for carbon atoms in carboxylate
groups in agreement with previous measurements [90] [91] [83] [84] [85]
[86]. Carbon atoms in the benzene ring are found at a BE of 284.6eV, also
in good agreement with the 300K structure. The relative peak areas, with
the total area of the spectrum normalized to the 9 carbon atoms in a TMA
molecule, were 5.9 for the benzene peak, 2.1 for the carboxylic acid peak and

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1.0 for the carboxylate peak. The areas of the carboxylic acid peak and the carboxylate peak sum up to 3 carbon atoms, implying that the carboxylate groups have its origin in the carboxylic acid groups. The O 1s signal (Figure 5.3b, lower curve) became asymmetric after annealing to 420K and could not be fitted anymore with two equal Gaussian shaped peaks. Instead, the signal had to be fitted by two or more nonequivalent Gaussians, clearly showing the formation of oxygen atoms in different chemical states in contrast to those found in the purely hydrogen bonded honeycomb arrangement [90] [83] [84] [85]. A quantitative interpretation of the O 1s signal is much more delicate than for the C 1s signal, as the chemical neighbourhood and therefore the number of different kinds of oxygen atoms in the 420K structure are not known. Therefore we refrained from a quantitative analysis of the fitted O 1s signal. In summary the appearance of new chemical states in the carbon and oxygen spectra is attributed to the often observed deprotonation of carboxylic acid groups upon adsorption on metal surfaces and the formation of carboxylate groups [92] [93] [94] [71] [95]. Based on the relative peak areas in the C 1s signal the number of carbon atoms in carboxylic acid groups is 2.1 and in carboxylate groups is 1.0. Considering the high symmetry of the structure we conclude that after annealing to 420K one out of the three carboxylic acid groups per molecule is deprotonated and changed into a carboxylate group. NEXAFS spectra of the 420K structure are displayed in Figure 5.3d. Upon warming to 420K and measuring the sample again at 300K the dichroism of the $\pi^*$-resonances remains very pronounced (cf. Figure 5.3d). The calculated average tilt angles are now $14^\circ \pm 5^\circ$ for the benzene rings and $23^\circ \pm 5^\circ$ for the carboxylic acid groups. This indicates that the molecules remain in an essentially flat-lying geometry on the surface. It seems that the carboxylic groups on average are now tilted by $5 - 10^\circ$ out of the plane of the benzene ring. Comparing the NEXAFS spectra obtained for the two phases one notices only small differences, in particular, the intensity of the carboxyl $\pi^*$-resonance is not much reduced relative to the $\pi^*$-resonance of the benzene ring. These changes are consistent with only a partial deprotonation of the carboxylic acid groups. For complete deprotonation we would expect a much more pronounced decrease of the carboxyl $\pi^*$-resonance as has been observed by us in a related system, i.e. TPA on Cu(100) [82].
5.3 Computational Modelling

5.3.1 Technical aspects

In our theoretical investigation we used a combination of classical and ab-initio molecular dynamics methods. All our first principle calculations were carried out using the Car-Parrinello method (Section 2.9), with Troullier Martins norm-conserving pseudopotentials (Section 2.6) and a gradient corrected exchange-correlation functional (Section 2.3). The metallic systems were treated within the scheme described in section 2.10, using a smearing energy width of $E_s=0.25\text{eV}$. The Brillouin zone sampling was limited to the gamma point only. The plane wave expansion was truncated at an energy cutoff of $50\text{Ry}$. In calculations including surfaces this cutoff was increased to $80\text{Ry}$. We initially performed ab-initio simulations of isolated molecules. The electron densities were used to determine a classical potential according to the well-established procedure explained in section 2.11.2.

5.3.2 Results

Evaluation of the charge state

The deprotonation of carboxylic acid groups upon adsorption on metal surfaces has been observed in many other systems but usually the oxygen atoms of the carboxylate groups bind to substrate atoms, tilting the whole molecule to an upright standing configuration [92] [93] [94] [71] [95]. In contrast to these results, our STM and NEXAFS measurements for the 420 K structure clearly provide evidence for flat lying TMA molecules containing one carboxylate group. This suggests that the carboxylate groups are engaged in lateral intermolecular binding forming ionic hydrogen bonds between charged carboxylate functions and neutral functions of the neighboring TMA-molecules. A fundamental and evident precondition for the formation of ionic hydrogen bonds is that the carboxylate group is still charged and the charge is not distributed over the entire molecule or compensated by the metallic substrate.

To gain information about the charge states of the partially deprotonated molecule, ab initio calculations were performed on a single TMA molecule containing one carboxylate group (denoted “deprotonated” TMA molecule in what follows). Then classical molecular dynamics calculations were performed to reproduce the quartet structure and to gain better understanding of the interplay between charged carboxylate groups and the neutral carboxyl groups.
Figure 5.4: The ball and stick model for the isolated TMA molecule adsorbed on a Ag(111) slab.
Figure 5.5: a) Charge-density variations upon deprotonation of a TMA molecule adsorbed on a slab of Ag(111). All quantities are integrated over the xy plane and plotted along the z direction. The blue dashed curve refers to the total charge density variation, which yields a negative surface dipole density profile. The electronic contribution to the total charge density variation is shown in the solid curve (see text). The red and gray filled circles correspond to the z positions of the adsorbed molecules and the first four layers of the metal substrate, respectively. b) The electron-density depletion (or positive charge-density accumulation) corresponding to the peak centered at \(z = -0.9\) Å is also visible as a green lobe located under the carboxylate group (the contour plot of the density difference is taken at \(z = -0.7\) Å).
We performed 0 K ab initio calculations of a single TMA molecule placed on a five-layer slab of Ag(111) (Figure 5.4). The solid curve in Figure 5.5a shows the response of the electronic charge density to deprotonation. This is computed from the electron densities $\rho_{\text{prot}}$ and $\rho_{\text{deprot}}$ of the protonated and deprotonated molecule systems as $-e(\rho_{\text{prot}} - \rho_{\text{deprot}})$. The atomic positions in both calculations are those obtained for the relaxed protonated molecule adsorbed on the metal surface. The electron density difference is integrated over the $xy$ planes and plotted as a function of the $z$ variable (the origin of the $z$ axis corresponds to the first atomic layer of the Ag surface). Deprotonation involves loss of a proton screened by release of some electron density to the surface, so that the net final charge of the molecular ion is a value $q$ between 0 and $e$. The release of electron density corresponds to the prominent positive (double) peak of the solid line centered at the position $z = -2.8 \text{ Å}$ of the adsorbed molecule (the relaxed adsorption geometry of the molecule was in all cases flat). A second, lower peak of the solid line is centered at about $-0.9 \text{ Å}$, that is, in the region between the molecule and the first surface layer of the metal substrate. This peak corresponds to a surface screening effect mostly localized under the missing proton (see also Figure 5.5b). As above, a positive peak here represents the loss upon deprotonation of some of the negative charge density originally screening the proton. The total charge-density variation upon deprotonation is simply the sum of its electronic contribution described by the solid curve in Figure 5.5a and the negative contribution due to the loss of proton charge (modeled by a Gaussian of width 0.3 Å centered on the proton site and normalized to $-e$). The total charge-density variation is represented by the blue dashed line in Figure 5.5a, and its overall shape is that of the charge-density profile of a negative surface dipole layer. To estimate the charge $q$ of the molecule after deprotonation we integrated the total charge density variation discussed above over the $z$ interval $\Omega_{\text{occupied}}$ by the molecule. This interval can be taken to start at any $z_0$ value located well inside the vacuum region where all densities are zero and end at an upper value $z_1$ located between the molecular plane and the first Ag layer. The value for $z_1$ was obtained by imposing the neutrality condition on the protonated molecule. The value of $q$ was then simply obtained by integration of the blue dashed curve in Figure 5.5a between $z_0 = -5.0 \text{ Å}$ and $z_1 = 1.48 \text{ Å}$. These calculations predict a total charge $q = -0.3e$ for the deprotonated TMA molecule. Note that in the calculations described so far and illustrated by Figure 5.5 the molecule/slab systems were in all cases neutral: in particular, one electron was subtracted from the overall system together with the proton to obtain the model used for the geometry in the deprotonated state. Imposing charge neutrality on the deprotonated system and repeating the calculation yields similar results, with a somewhat higher charge $q = -0.5e$. 78
associated with the adsorbed deprotonated molecule. Overall, these results predict the formation of a negative surface dipole layer on the Ag(111) substrate upon deprotonation, corresponding to the blue curve distribution in Figure 5.5a. We note that a physical picture of temperature-induced deprotonation with formation of a negative dipole lowering the electrostatic potential in the surface region consistent with the upshift of the surface-state energy level visible in the ST spectrum of Figure 5.2 [75, 76, 77].

Classical modelling

The classical MD force field can be used to model the presence of the charged surface species by appropriate modification of the partial coulomb charges set. This was done by simply adjusting the charges on the oxygen atoms of the carboxylic group after the removal of the hydrogen atom to achieve the overall calculated -0.5e total ionic charge. The partial charge values used are reported in Fig. 5.6a. As the TMA-molecules always adsorb in a flat-lying geometry on the surface, we performed two-dimensional classical MD simulated annealing runs, with the further constraint of describing the molecules as rigid bodies. The interaction between the molecules was modeled by a superposition of a Coulomb term obtained from the partial charges and of a short-range repulsive term designed to ensure that the molecules do not overlap. The electrostatic screening of the metal surface was taken into account by introducing mirror images of the partial point charges of the potential (Section 2.11.3). We then considered an isolated group of four molecules to find a stable candidate for a model-structure of the quartet units revealed by the experimental observations. Consistent with the XPS results and the high symmetry of the structure, we assumed that each molecule bore one carboxylate group. We explored the stability of different configurations by systematically changing the positions of the two remaining carboxylic protons of each TMA molecule in the unit cell. Furthermore, since the STM images showed a C2-symmetry, we limited the search to the different proton configurations that possess this symmetry, as shown in Figure 5.6b to Figure 5.6f. This cluster structure was thus used (with minor adjustments obtained by MD annealing) to produce a periodic pattern compatible with the experimental dimensions of the surface unit cell. The lowest energy structure found corresponds to the configuration shown in Figure 5.6f. The final equilibrium structure obtained in this way, shown in Figure 5.7a, is in good agreement with the experimentally observed structure. All charged carboxylate groups are bound to neutral carboxylic groups and furthermore two different kinds of carboxylate groups exist within the 420K-structure, highlighted in Figure 5.7a and magnified in Figure 5.7b and 5.7c. Figure 5.7b shows the first
Figure 5.6: a) Effective atomic point charges of a deprotonated TMA molecule. The total $-0.5e$ molecular charge (mostly localised on the carboxylate group) is consistent with the results of the ab initio charged calculation; b)-f) Balls and sticks models of the different investigated configurations of the quartet molecular unit are reported with indications of their stability (the interaction energy per molecule calculated with the classical forcefield is given in units of $10^{-4}$ a.u.). g) Model of hypothetical deprotonated honeycomb structure.
Figure 5.7: a) Calculated structure of the most stable configuration of the building block (Figure 5.6f). The two different kinds of ionic hydrogen bonds are outlined. b) Ionic hydrogen bond between one carboxylate group and one carboxylic group. c) Ionic hydrogen bond between one carboxylate group and two carboxylic groups.
kind of ionic hydrogen bond of this structure, stabilizing a TMA-dimer, in which the carboxylate group is bound to a single carboxylic group. Figure 5.7c shows the second kind of ionic hydrogen bond, in which the carboxylate group is bound to two carboxylic groups on different molecules. These different bonds to different molecules ultimately allow the dimers to assemble into the observed chain structure. The calculated O-O distance for both ionic hydrogen bonds was 0.256nm. In addition, the possibility of the formation of a honeycomb structure out of deprotonated TMA molecules was investigated, as shown in Figure 5.6g. We note that a honeycomb structure undergoing a single deprotonation per molecule as shown in Figure 5.6g would involve the same overall number of hydrogen bonds observed in the predicted stable structure of Fig.5.6f (as the overall residual number of hydrogens would be the same in the two structures). However, the hexagonal arrangement would imply couples of adjacent negatively charged and mutually repelling oxygen atoms, located on the non-hydrogen-bonded side of facing carboxylic group pairs. This cannot happen in the denser packing experimentally observed, where carboxylic group pairs are never facing each other and can thus be connected by at most one hydrogen bond. As one can see from the interaction energies reported in Fig. 5.6, the deprotonated hexagonal phase (honeycomb structure) is significantly less stable than the densely packed structure. Thus a structural transformation would presumably occur upon the deprotonation of the carboxylic groups. The preferred arrangement of the molecules upon deprotonation is determined by the concurrent need of maximizing the number of hydrogen bonds while minimizing the Coulomb repulsion between negatively charged deprotonated carboxylic groups. In this scenario, the honeycomb structure becomes unstable upon deprotonation and the system collapses into a more closely packed structure in which ionic hydrogen bonds play an important role. The phase transition is driven by deprotonation and is thus irreversible, consistent with the experimental findings.

5.3.3 Conclusions

In conclusion, our experiments and calculations suggest that intermolecular ionic hydrogen bonds offer a novel possible path to the assembly of supramolecular structures on surfaces. The so obtained supramolecular structures are still stable in the absence of counter ions (necessary in solvent phases to stabilize ionic hydrogen bonds) due to the presence of the metal surface charge screening.
Chapter 6

The Self-assembly of “Mosquito” on Au(111)

6.1 Introduction and acknowledgements

In this chapter the selfassembly of N,N-diphenyl-oxalamide is investigated (Figure 6.1). Because the phenyl rings resemble the wings of a fly this molecule will be called Mosquito, which is the tag name used by the group where it was synthesised. This work was carried out in collaboration with many experimentalists. Florian Klappenberger, Marta Esther Cañas Ventura, Sylvain Clair, Stéphane Pons, Uta Schlickum, Harold Brune, Johannes V. Barth and Klaus Kern from the Institute de Physique des Nanostructures EPFL Lausanne, Zhi-Rhong Qu and Mario Ruben from the Institut für Nanotechnologie, Karlsruhe and Thomas Strunskus and Christof Wöll from Lehrstuhl für Physikalische Chemie 1, Ruhr Universität Bochum. The experimental results are described in the first part of the chapter, while the second part is dedicated to the computational aspects. This work is still in progress at the moment of writing.

Figure 6.1: The structure of a N,N-diphenyl-oxalamide (Mosquito).
6.2 Experimental results

Solid state structure

Figure 6.2: The solid state structure as revealed by X-ray diffraction experiments. The solid state is an aggregate of chains. Panel (a) shows how the chains are orientated: each molecule represents a chain that propagates in the direction perpendicular to the plane of the picture. Panel (b) shows the internal structure of a chain.

In Figure 6.2 the solid state structure of the mosquito is elucidated as it was observed with X-ray crystallography experiments. The hydrogens have been removed from this picture for the sake of clearness. The main building block is the chain of hydrogen-bonded-mosquitos shown in panel (b). In the chain the intermolecular distance is 5.3 Å and the phenyls are rotated by 30° with respect to the inner group. The chains are arranged in
the solid as it is sketched in panel (a). In this picture each molecule represents a chain that propagates in the direction perpendicular to the plane of the picture. The $\pi-\pi$ interaction makes the chains stable in the solid structure, resulting in the characteristic herringbone pattern.

**STM**

Figure 6.3 shows a series of STM images for molecules deposited at different sample temperatures. Adsorption with the sample at 300 K (Figure 6.3 a) results in regular, self-assembled linear chains consisting of several molecular building blocks (bright dog-bone like features). A preferred nucleation at the elbow sites of the surface reconstruction leads to a regular distance between the chains. As the chains tend to avoid the hcp stacking regions of the surface the average chain length amounts to about 14 nm. The intermolecular spacing is 6.5 Å which is much larger than the distance of the molecules in the solid state. This indicates that the molecules rearrange upon adsorption. The high degree of order indicates that these lines represent the equilibrium structure of the system. Reaching this equilibrium is hindered when depositing the molecules at a T = 265 K (Figure 6.3 b). In this case molecules are seen to have different shape at the end of the chains as well as in the dimer structures which appear as four prominent lobes around a central one. Stabilizing the temperature at 160 K during deposition suppresses conglomeration of molecules as can be seen in Figure 6.3 c. The small bright spots represent single molecules, no chains are formed and dimerization is strongly suppressed. The fact that the individual molecules tend to stay isolated from their neighboring ones indicates that the diffusion length is smaller than the average molecule distance, in this case around 5 nm.

**NEXAFS and XPS**

The two opposed molecular phases, isolated molecules and chain structures, were studied with NEXAFS at the HE-SGM beamline in BESSY II in Berlin with an energy resolution of 0.4 eV. All the spectra were taken at 160 K. Details on data treatment are described elsewhere [97]. In the C1s spectra (Figure 6.4, left) the first $\pi^*$-resonance (binding energy EB = 285 eV) is connected with the phenyl ring $\pi$ system. The O1s edge (Figure 6.4, right) shows a $\pi^*$-resonance (EB = 531.2 eV) which originates from the two carbonyl double bonds in the molecular backbone. Taking into account that the central carbons are forming bonds within one plane, the carbonyl signal can be taken as an indicator for the inner group plane. Defining $\theta$ as the angle between the surface normal and the E-vector of the photon beam, an
Figure 6.3: a) A high temperature deposition (sample temperature $T = 300 \, K$) results in nanochains self-assembled due to H bonds. (bias voltage $V = -0.2 \, V$, tunnel current $I = 0.35 \, nA$) b) Metastable structures are found for $T = 265 K$. ($V = -0.05 \, V$, $I = 0.12 \, nA$) c) Adsorption at low temperature ($T = 155 \, K$) yields isolated molecules. ($V = -0.64 \, V$, $I = 0.28 \, nA$) The scale bar denotes 10 nm in all three cases.
Figure 6.4: Comparison of NEXAFS spectra of single molecules (upper row) with spectra of molecules in the chain structure. C1s edge (left column): The dichroism of the phenyl π*-resonance at 285 eV indicates essentially flat laying phenyl rings for single molecules (upper) and a tilt of 35° for molecules assembled in chains (lower). O1s edge (right column): The dichroism of the CO π*-resonance at 531 eV indicates an essentially flat lying inner group for single molecules (upper) as well as for molecules assembled in chains (lower).
ideally flat laying phenyl ring, resp. inner group, should result in a vanishing peak area for $\theta = 90^\circ$ for the corresponding peak. In the single molecule case, the phenyl ring signal (Figure 6.4, left upper) is strongly reduced when going from $\theta = 30^\circ$ (dashed curve) to $\theta = 90^\circ$ (solid line), indicating an adsorption almost parallel to the substrate surface. In contrast to this in the case of the chain structures the spectra (Figure 6.4, left lower) feature a remarkable intensity for $\theta = 90^\circ$. The angular dependence of the peak intensity corresponds to a rotation of the phenyl groups of about $35^\circ$. As in both cases the O1s edge indicates a flat laying inner group, the change of the phenyl orientation is a conformational change and can not be explained by a rotation of the whole molecule. The XPS measurements are still work in progress but the preliminary spectra for the monolayer and the multilayer indicate that the monolayer is less bound. The shifts in binding energy for the core electrons of the elements are 0.3 eV for nitrogen, 0.55 eV for carbon and 0.7 eV for oxygen. This suggests that carbon and oxygen are involved in the interaction with the substrate.

6.3 Computational Modelling

6.3.1 Technical aspects

In our theoretical investigation we used a combination of classical and ab-initio molecular dynamics methods. All our first principle calculations were carried out using the Car-Parrinello method (Section 2.9), with the PAW scheme (Section 2.7) and the LDA exchange-correlation functional (Section 2.3) which gives better results than GGA for the relaxed geometry of bulk gold, as can be seen in table 2.1. The metallic systems were treated within the scheme described in section 2.10, using a smearing energy width of $E_s=0.25eV$. The Brillouin zone sampling was limited to the gamma point only. The plane wave expansion was truncated at an energy cutoff of 28Ry. The normal mode analysis of a isolated molecule was carried out in collaboration with Filippo Zuliani with the Amsterdam Density Functional (ADF) code.

6.3.2 Gas Phase calculation

The presence of many $\sigma$ bonds along the backbone makes the mosquito a flexible molecule that can theoretically appear in many different configurations. In Figure 6.5 four alternatives are sketched. The models $a$ and $c$ refer to trans conformations while models $b$ and $d$ are cis conformation of
Figure 6.5: The four conformations of an isolated mosquito molecule, that have been studied ab initio in order to determine their stability. Each one can be obtained from the others with some rotations around the C-C and C-N sigma bonds that form the backbone.
the central inner group. The other difference in these models is the orientation of the adjacent NH and CO bonds. In models $a$ and $b$ these bonds are on different sides of the molecule, while in models $c$ and $d$ they lay on the same side. The stability of these structures were investigated \textit{ab initio} for isolated molecules. The $a$ structure is the most stable structure, at 0K the equilibrium geometry is flat. The $c$ structure is metastable, its equilibrium energy is 0.9 eV above the energy of structure $a$. The two cis-conformations, $b$ and $d$ are unstable in gas phase and evolve spontaneously to the structure $a$ as a consequence of the repulsive interaction between oxygens. The other asymmetric configurations that could have been considered are geometrically unsuitable as building blocks for linear chains. Moreover, when tested, they proved unstable and evolved to symmetric configurations. We then simulated a chain of molecules in periodic boundary conditions with variable intermolecular spacing. The equilibrium intermolecular distance is 5.1 Å, in good agreement with X-ray data obtained in the solid state. However the STM measured intermolecular distance for the self-assembled chains, 6.5 Å, is not compatible with this result. Thus we can conclude that the substrate has a significant influence on the chain dimension, either driving a conformational change of the molecules or forcing them to stick to some preferred adsorption sites.

6.3.3 The model chains

The chain structure is the key point to clarify. In Figure 6.6 the investigated hypotheses are reported. The panels I and II show the tentative model obtained by adapting the models for the solid phase chains to the geometries of adsorbed chains measured with the STM. In both cases the orientation of the molecules looks peculiar. In panel I the intermolecular bonding pattern shows oxygens involved in two unusually long hydrogen bonds. The model of panel II is worse still, exhibiting facing oxygens that are bound to repel each other. These two models are unsatisfactory and other hypotheses have to be considered.

\textbf{$\pi - \pi$ stacking}

In supramolecular chemistry, an aromatic interaction (or $\pi - \pi$ interaction) is a noncovalent interaction between organic compounds containing aromatic moieties. The $\pi - \pi$ interactions are caused by intermolecular overlapping of p-orbitals in $\pi$-conjugated systems, so they become stronger as the number of $\pi$-electrons increases.
Figure 6.6: The four hypothetical models considered for the arrangement of the adsorbed chains. The I and II models are obtained by adapting to the STM measures the geometry of the chains that are stable in the solid state. The model III is an alternation of opposite chiralities and gives a good description of the angles, while the model IV is made out of molecules in configuration c and exhibits an intermolecular spacing that is larger than in other models.
The $\pi - \pi$ interactions act strongly on flat polycyclic aromatic hydrocarbons such as anthracene, triphenylene, and coronene because of the many delocalized $\pi$-electrons. This interaction, which is a bit stronger than other noncovalent interactions, plays an important role in various supramolecular systems [99].

The possibility that the attraction between mosquito molecules is mediated by $\pi - \pi$ interactions involving aromatic phenyl rings has to be considered, even though the mosquito is not polycyclic. These kind of interactions are mainly dispersive, and are known to be badly described by DFT with LDA or GGA approximations [98], because of the local nature of these approximations. Thus we used AMBER, which is meant to simulate biological systems, and includes a description of the $\pi$-interactions that proved reliable in some cases [100, 101] We performed simulations of chains adsorbed on a fictitious surface made of benzenes (Section 2.11.3). The range of temperatures of the simulated chains was varied in the range 0 – 400K. All the simulations showed that the interaction were mainly driven by hydrogen bonds and that coherent movement of neighbouring phenyl rings was broken already at low temperatures (< 80K) as a consequence of the activation of low frequency phonons. Therefore the $\pi - \pi$ hypothesis seems incompatible with the experimental results that report the chain formation at annealing temperatures greater than 160K.

Although these simulations were not able to reproduce the geometries of the adsorbed chains, they gave some indications about the stability of the model chains of Figure 6.6. The attempted model I and II resulted in the same geometry of solid state chains with a spacing in good agreement with the experimental and ab-initio findings of 5.2 Å. The attempted model III resulted in a chain with an orientation that is closer to that observed in the adsorbed chains, but whose stability at high temperatures is lower. The model IV resulted in a stable chain with larger spacing (5.6 Å) and standing phenyls (Figure 6.7).

**The models III and IV**

Since the configurational change from the solid state to adsorbed chains cannot be rationalised with hydrogen bonds and $\pi - \pi$ stacking, the influence of the substrate has to be considered in more detail. The presence of preferred adsorption sites might act as a competitor to intermolecular hydrogen bonding forces, leading to the stretching of the chains and explaining the reduced number of chain orientation that have been observed. The model III exhibits a pairing of molecules with alternate chiralities that are bound by single hydrogen bonds. Although the presence of a single H-bond reduces the
stability to high temperature, an improved adsorption energy might stabilise the chain.

The model IV is made out of molecules in the configuration $c$ of Figure 6.5. In gas phase this configuration is metastable but strongly unfavourable. However, when adsorbed, the molecules might prefer this conformation to increase the adsorption energy. The orientation of the molecules in the chains looks reasonable, since the oxygens and the acidic nitrogen’s protons are facing each other with distances that are within the typical hydrogen bond range. The presence of a vibrational mode at 170K with an high adsorption peak can induce the configurational change that is necessary for the stabilisation of the chains in model IV. In this mode (Figure 6.8) the oxygens of the mosquitos turn around the molecule’s backbone in opposite directions, this can eventually evolve to a swap of their position, i.e. a configurational change from configuration $a$ to $c$.

### 6.3.4 Isolated molecules

The behaviour of isolated molecules on a gold slab has been studied to evaluate if the configuration $c$ is preferred when the molecule is adsorbed. The relaxed geometries revealed that in both cases the molecules lay flat on the substrate, consistent with the experimental findings. The configuration $c$ that in gas phase is metastable with upstanding phenyls (Figure 6.7) prefers to adhere to increase the interaction with the substrate. The adsorption ener-
Low frequency normal modes of the mosquito

Figure 6.8: Top Panel: adsorption intensities for low frequency normal modes of mosquito, the filled red circle indicates the mode at 170K which could drive a configurational change. This mode is illustrated in the bottom panel, the arrows show the motion of the oxygens that can eventually evolve to a swap of their position with respect to the backbone.
gies are comparable and about 1.5 eV. We conclude that unless the hydrogen bond energy is large enough to balance the energy cost of configurational change, the model IV is unlikely to be correct.

### 6.3.5 Results for the model chains

Some calculations of the chains comprehensive of the substrate in periodic boundary conditions have been performed to acquire detailed information on the systems. The dimensions and orientation of the substrate was chosen to be commensurate with the measured geometries. Unfortunately, the surface reconstruction could not be included because this would have required a far too big simulation cell. Figures 6.9 and 6.10 show the final structure for the chain models III and IV. In table 6.1 the energies for the two systems are reported.

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<td>III</td>
<td>2.90</td>
<td>0.34</td>
<td>-53195.680</td>
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<td>IV</td>
<td>2.55</td>
<td>0.37</td>
<td>-53195.598</td>
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*Table 6.1: Energies for the chain models including the substrate. The reported values refer to a unit cell containing two molecules(35,533),(784,690). The energetically preferred model is the III, since it has a higher configurational and adsorption energy.*

Therefore the preferred system is model III, which exhibits a higher configurational and adsorption energy. The strongest adsorption might be rationalised with an interaction between the inner group and the substrate. This is visible in Figure 6.11 as a clear redistribution of the electrons in the inner group involving carbon and oxygen atoms consistent with XPS data.

### The conformational change

In Figure 6.12 STM topography images (left column) are compared to the calculated models (middle row), all presented in the same scale. The single molecule (upper left panel) is imaged broader than the periodicity of the chain structures (lower left panel), indicating that there would be a steric hinderance, if the molecules stay flat in the chain structure. The molecules of the chain structure show a stronger difference between the apparent height at the phenyl ring and at the center. This is well explained by the tilted phenyl rings. The DFT calculations reveal that the chains are held together by one H bond per molecule, which forms between the amide groups of adjacent molecules (dotted line). The calculations agree with the NEXAFS results in
Figure 6.9: The final structure for the model chain III.
Figure 6.10: The final structure for the model chain IV.
Figure 6.11: Electron density displacement upon adsorption for model chain III; the red and blue lobes indicate electron accumulation and depletion respectively.

predicting a flat geometry for the single molecule (upper right panel) and a tilted phenyl ring for molecules within the chains (lower right panel). The tilt in the theoretical results is about 10°, thus remarkably smaller than the NEXAFS result. It is well known for the DFT recipe that was used here, that the phenyl system-metal substrate interaction is overestimated. Thus the theory predicts a flatter geometry than the one is found in the experiments. In summary, STM, NEXAFS, and DFT agree that the H bond driven formation of nanochains of N,N oxalic amide results in a conformational change of the molecular building block. In turn this conformational change allows to stabilize the chains through reduction of sterical hinderance and optimized H bond distances.

6.3.6 Conclusions

The unidimensional chains formed after the deposition and annealing are different with from the chains present in the molecular solid, the intermolecular distances and the orientation being the main differences. Classical simulations reveal that the $\pi - \pi$ interactions that play an important role in the solid, are not driving this change. Thus it is reasonable to assume that the substrate could be the main driving force. The competition between the
Figure 6.12: upper row: Comparison of a single mosquito as imaged by STM (left) with the equilibrium structure predicted by the DFT calculations (center). The calculations yield flat laying phenyl rings and a small angle for the inner group (right). lower row: The chain structure as recorded by STM (left). DFT calculations (center) indicate that the chains are bound by one H bond per molecule. The phenyl rings are tilted by 10°, the inner group is essentially flat.
interaction with the substrate and hydrogen-bond-mediated intermolecular interaction appears to drive the delicate interplay which leads to equilibrium in the stretched chains. Remarkably, our best model for the chains, consistent with the experimental geometries, features an alternation of molecules of opposite chiralities. A conformational change is associated to the chain formation. While isolated molecules adsorb in a flat geometry, inside a chain the molecules have rotated phenyl rings.
Conclusions

The use of the supramolecular self-assembly in technological application still appears to be a far and ambitious perspective. However the fundamental research of the physical and chemical mechanisms is a necessary step of paramount importance for its achievement. The rules that hold for biological systems may one day be exploited in a synthetic controlled environment, to design new powerful instruments and tools, to synthesise new drugs or produce new materials with extraordinary properties. This work was an attempt to investigate what contribution computational simulations can provide. It is currently possible to simulate the self-assembly of small molecules with a DFT and explicit inclusion of the substrate. Although the ever increasing computational power allows the simulation of ever larger and more complex systems, it is clear that some efforts to improve the present approximations should be attempted. In particular a more accurate description of the dispersive interactions should be included in the DFT calculations. Bengt Lundqvist and Stefano De Gironcoli showed in the last Total Energy Workshop some very interesting news about this topic.
Table of figures

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Table 6.2: The original web addresses of some of the pictures included in this thesis.
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