Phthalocyanines on Surfaces

Monolayers, Films and Alkali Modified Structures

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Abstract

The Phthalocyanines (Pc’s) are a group of macro-cyclic molecules, widely investigated due to the possibility to use them in a variety of applications. Electronic and geometrical structure investigations of molecular model systems of Pc’s adsorbed on surfaces are important for a deeper understanding of the functionality of different Pc-based devices.

Here, Pc’s monolayers and films, deposited on different surfaces, were investigated by X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS) and Scanning Tunneling Microscopy (STM). In addition Density Functional Theory (DFT) simulations were performed.

For molecular films of Metal-free (H,Pc) and Iron (FePc) Pc’s, on surfaces, it is found that the intermolecular interaction is weak and the molecules arrange with their molecular plane mainly perpendicular to the surface.

Several monolayer systems were characterized, namely H,Pc and FePc adsorbed on Graphite, ZnPc on InSb(001)-c(8x2), H,Pc on Al(110) and on Au(111). For all the studied monolayers it was found that the molecules are oriented with their molecular plane parallel to the surface. The electronic structure of the molecules is differently influenced by interaction with the surfaces. For H,Pc adsorbed on Graphite the nearly negligible effect of the surface on the molecular electronic structure allowed STM characterization of different molecular orbitals. A strong interaction is instead found in the case of H,Pc on Al(110) resulting in molecules strongly adsorbed, and partly dissociated.

Modifications of the electronic and geometrical structure induced by alkali doping of H,Pc films and monolayers were characterized. It is found both for the H,Pc film on Al(110) and monolayer adsorbed on Au(111), that the molecular arrangement is changed upon doping by Potassium and Rubidium, respectively.

Potassium doping of the H,Pc films results in a filling of previously empty molecular orbitals by a charge transfer from the alkali to the molecule, with significant modification of the molecular electronic structure.

Keywords: Phthalocyanines, Surface Science, X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS), Scanning Tunneling Microscopy (STM), Density Functional Theory (DFT), Metal-free Phthalocyanine, Iron Phthalocyanine, Zinc Phthalocyanine, Gold, Graphite, Aluminium, Indium Antimony, Molecular adsorption, Monolayer, Film, Alkali, Geometrical structure, Electronic structure, Doping

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This thesis is based on the following papers, which are referred to in the text by their Roman numbers.

I  **Electronic structure of vapor-deposited metal-free phthalocyanine thin film**  
Journal of Chemical Physics, 122, 214723, (2005)

II  **Equivalent core-hole time-dependent density functional theory calculations of carbon 1s shake-up states of phthalocyanine**  

III  **The electronic structure of iron phthalocyanine probed by photoelectron and x-ray absorption spectroscopies and density functional theory calculations**  
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IV  **A STM study of Metal-free Phthalocyanine monolayer structures on Graphite**  
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V  **The adsorption of iron phthalocyanine on graphite: A scanning tunnelling microscopy study**  
VI  STM and XPS characterization of Zinc Phthalocyanine on InSb(001)
Submitted to Surface Science

VII  Characterization of Metal-free Phthalocyanine adsorbed on Al(110)
In manuscript

VIII  Potassium doped H$_2$Pc films: alkali induced electronic and geometrical modifications
In manuscript

IX  Rubidium doped Metal-free Phthalocyanine monolayer structures on Au(111)
In manuscript

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The following is a list of papers which I have contributed to but that are not included in this Thesis.

Excited-state charge transfer dynamics in systems of aromatic adsorbates on TiO$_2$ studied with resonant core techniques
Molecular ordering in isonicotinic acid on rutile TiO$_2$(110) investigated with valence band photoemission
J. N. O’Shea, J. C. Swarbrick, K. Nilson, C. Puglia, B. Brena, Y. Luo, V. R. Dhanak

Phase and molecular orientation in metal-free phthalocyanine films on conducting glass: Characterization of two deposition methods

Electronic and structural studies of immobilized thiol-derivatized cobalt porphyrins on gold surfaces

Comments on my own participation

The work presented here is the result of efforts made by a team of co-workers. The extent of my contribution to the papers has been different but in all cases I have participated in the experimental work and in the discussions regarding the studies. Paper II is mainly the result of a theoretical study, I contributed with the experimental work and data analysis. For paper IV, VI, VII, VIII and IX, I have been the main responsible person for the experiments, the data analysis and the preparation of the papers. However the STM work presented in paper VI has been performed by our collaborators Pål Palmgren and Mats Göthelid at Materials Physics, Royal Institute of Technology (KTH), Stockholm. The theoretical simulations have been performed by Barbara Brena, Mats Nyberg and Yi Luo at the Department of Physics, Uppsala University and Theoretical Chemistry, KTH, Stockholm.
## Contents

1 Populärvetenskaplig sammanfattning ........................................ 9  
   1.1 Våra byggklossar: ytor, atomer och ftalocyaniner ............... 9  
       1.1.1 Molekyl och yta: studier av modellsystem ............... 9  
1.2 Undersökningsmetoder .................................................. 10  
       1.2.1 Vakuum ......................................................... 10  
       1.2.2 Spektroskopi ............................................... 10  
       1.2.3 Mikroskopi ................................................. 11  
       1.2.4 Beräkningar ............................................... 12  
1.3 Resultat ............................................................... 12  

2 Introduction ............................................................... 15  
   2.1 Molecular phthalocyanine films .................................... 16  
   2.2 Monolayer studies .................................................. 16  
   2.3 Alkali doping of phthalocyanines ................................. 16  

3 Techniques ................................................................. 17  
   3.1 Photoelectron Spectroscopy ....................................... 17  
       3.1.1 X-ray Photoelectron Spectroscopy (XPS) ............... 18  
       3.1.2 Satellites ................................................... 19  
       3.1.3 Koopmans’ theorem and the sudden approximation .... 19  
       3.1.4 Electron escape depth ................................... 21  
       3.1.5 Ultraviolet Photoelectron Spectroscopy (UPS) ....... 21  
   3.2 X-ray Absorption Spectroscopy (XAS) ............................. 22  
   3.3 Scanning Tunneling Microscopy (STM) .............................. 23  
       3.3.1 Quantum Mechanical Tunneling ......................... 23  
       3.3.2 Imaging modes ............................................. 24  
       3.3.3 Principles of STM instruments ........................ 25  

4 Density Functional Theory ................................................ 27  

5 Experimental ............................................................... 29  
   5.1 Sample preparation and Ultra High Vacuum ....................... 29  
   5.2 Synchrotron radiation .............................................. 30  
       5.2.1 Beamline I511, MAX-lab, Lund .......................... 31  
   5.3 Home laboratories .................................................. 31  
       5.3.1 X-ray Photoelectron Spectroscopy ...................... 31  
       5.3.2 Scanning Tunneling Microscopy ......................... 31  
       5.3.3 Calibration of XPS, XAS and STM measurements ...... 32  

6 Substrates and adsorbates ............................................... 33  
   6.1 Substrates ............................................................ 33
1. Populärvetenskaplig sammanfattning

Allt som finns runt omkring oss består av atomer. De består i sin tur av mindre enheter: den positiva kärnan och de negativt laddade elektronerna som omger kärnan.

Atomer kan sammanlänkas till större enheter såsom molekyler och fasta kroppar, vilka alla har en yta. Den här avhandlingen handlar om molekyler som placerats på ytor av fasta material. Systemen, molekylerna på ytor, har studerats med olika experimentella metoder, detta bland annat för att förstå hur molekylerna och ytan påverkar varandra. En yta är i det här fallet precis vad det låter som, men ytorna som har studerats är extremt plana, rena och alla ytans atomer sitter regelbundet placerade.

De fysikaliska egenskaperna hos ett system bestäms framförallt av atomernas inbördes placering och av utbredningen och energin hos elektronerna i systemet. Det är därför den elektroniska strukturen (energiutbredningen) som undersöks här, vilken ger information om systemen.

1.1 Våra byggklossar: ytor, atomer och ftalocyaniner

Molekylerna som studerats i den här avhandlingen är ftalocyaniner (Pc) som består av kol, kväve och väte (metall-fri ftalocyanin). Molekylen kan även innehålla en metallatom (metall-ftalocyanin). Den här avhandlingen innehåller studier av både metall-fri (H2Pc) och av två metall-ftalocyaniner, zink (ZnPc) och järn (FePc). Dessa molekyler är intressanta bland annat för att de kan användas i en rad tillämpningar såsom solceller och molekylära elektronikkomponenter, dessutom användas de i katalysprocesser. Som katalysatorer påskynsar eller möjliggör de kemiska processer, något som är av stort intresse inte minst i industriella sammanhang.

Förutom att studera ftalocyaniner på olika ytor har alkaliatomer (kalium- och rubidiumatomer) placerats på den molekyltäckta ytan. Båda atomslagen är välkända för att lätt lämna ifrån sig en av sina elektroner. Målet här är att se om ftalocyaninen plockar upp en elektron och hur det påverkar systemtets elektroniska och geometriska struktur.

1.1.1 Molekyl och yta: studier av modellsystem

Ftalocyaniner har placerats (eller adsorberats, som man brukar säga) på olika ytor, bland annat på grafit, aluminium och indium-antimonid, vilka alla tre

1.2 Undersökningsmetoder
Två olika experimentella tekniker har använts för att uppnå resultaten i den här avhandlingen, nämligen spektroskopi och mikroskopi. Alla experiment som finns beskrivna i den här avhandlingen är gjorda i vakuum.

1.2.1 Vakuum
Det finns flera anledningar till att experimenten görs i vakuum, en av anledningarna är att då undviks föroreningar på provet, som bara ska innehålla de molekyler som undersöks. Ytorna som undersöks rengörs i vakuum, sedan adsorberas ftalocyaninerna på ytan, även detta i vakuum. Om mätningarna gjordes i luft (atmosfärtryck) skulle även annat fastna på ytan, i vakuum är det möjligt att studera just de modellsystem som intresserar oss.

1.2.2 Spektroskopi
Fotoelektronspektroskopi har använts för att förstå molekylernas växelverkan med ytan de är placerade på. Elektronerna hos en atom kan inte befinna sig var som helst runt atomkärnan, elektronerna finns i specifika orbitaler som visas schematiskt i Fig. 1.1. Detta betyder att elektronerna bara kan ha vissa specifika energier. I varje atomslag binds elektroner olika hårt, ju större atomkärnan är desto närmare kärnan finns (de starkast bundna) elektronerna. Näromtet till kärnan bestämmer vilken energi en elektron har och därmed också hur svårt det är att ta bort en elektron från atomen. Det går därför att bestämma av vilket slags grundämne en atom är genom att undersöka hur mycket energi man behöver tillföra atomen för att stjäla en elektron från den.

Små förändringar i energin bestämmer hur påverkade elektronerna i atomen eller molekylerna är av sin omgivning (s.k. kemiskt skift), detta illustreras schematiskt i Fig. 1.2. Det går alltså att bestämma både provets kemiska samman- sättning och hur olika delar av provet samspelar genom att mäta elektronernas energi.
I praktiken genomförs mätningarna genom att ett prov belyses med ljus, fotoner, som har en viss välbestämd energi. Elektroner hos atomerna i provet får då extra energi, de exciteras, och lämnar provet om de får tillräckligt mycket energi. Rörelseenergin hos elektronen som lämnar provet mäts och på så sätt går det att bestämma hur hårt bunden elektronen var i atomen.

Det finns många spektroskopiska tekniker och förutom fotoelektronspektroskop har absorptionsspektroskop använts. Provet belyses även här med ljus och elekronerna exciteras men får inte tillräckligt med energi för att lämna atomen. En molekyl har inte bara orbitaler som är fyllda med elektroner, de har även tommata orbitaler dit elektronerna kan exciteras (schematiskt visas detta i Fig. 1.1). Med absorptionsspektroskop gär det att kartlägga dessa tommata orbitaler.

1.2.3 Mikroskopi

Med ett sveptunnelmikroskop kan molekylerna på ytan avbildas. Det går att se hur molekylerna är placerade på ytan och att få information om hur molekylerna interagerar med varandra. En kvantmekansik effekt, så kallad tunnling, förklarar hur molekylerna avbildas: elektroner i molekylen kan flytta sig från molekylen och tunnla till en nål, som sveper över provet. För att detta ska hända förutsätts att det finns en elektrisk spänning mellan provet och nålen, samt att avståndet mellan nålen och provet är mycket litet. Om avståndet ökas kommer färre elektroner att tunnla (och inga alls om avståndet är för stort). Provet som undersöks är inte helt jämnt (t.ex. om en molekyl är absorberad på ytan) och för att det alltid, på varje punkt av provet, ska tunnla lika många elektroner till nålen så måste den flyttas upp och ner. Resultatet - bilden som fås, se Fig. 1.3 - är egentligen en karta över hur nålen har flyttats upp och ner. Men det är även en bild av hur (elektronerna i) molekylerna är arrangerade. Här är det alltså också elektronerna som ger information om systemet.
Atom 1: Kväve med väte- och kolatomer som grannar

Atom 2: Kväve med bara kolatomer som grannar

Elektronernas bindningsenergi ändras något beroende på vilka atomer som finns i närheten.

Energi

Intensitet (Antal elektroner)

Fotoelektronspektroskopimätning och till höger i figuren visas resultatet av mätningen. De båda topparna indikerar att elektronerna inte har samma energi i de olika kväveatomerna i molekylen, s.k. kemiskt skift.

Figur 1.2: Högst upp visas en ftalocyanin. I molekylen är två kväveatomer markerade (atom 1 och 2), de har olika atomer som grannar. Nedanför visas schematiskt att energin hos elektronerna är olika beroende på vilka atomer som finns i närheten, elektronernas energi i atom 1 och 2 är därför inte densamma. Detta bestäms med en fotoelektronspektroskopimätning och till höger i figuren visas resultatet av mätningen, de båda topparna indikerar att elektronerna inte har samma energi i de olika kväveatomerna i molekylen, s.k. kemiskt skift.

1.2.4 Beräkningar
Med hjälp av teoretiska beräkningar som simulerar systemen och experimenten går det att få extra information. I flera av artiklarna som presenteras i den här avhandlingen beskrivs även resultat från beräkningar, och jämförelser mellan experiment och simuleringar - sådana jämförelser ökar förståelsen för de experimentella resultaten.

1.3 Resultat
Experimenten som är grunden för den här avhandlingen har lett fram till en rad resultat. Några av resultaten fås från bilder som den i Fig. 1.3. Där kan man se att H₂Pc-molekyler ligger plant på en grafityta, med molekylplanet parallellt med ytan. Dessutom går det att se hur molekylerna interagerar med varandra, vilka atomer i en molekyl som placerar sig mot atomerna i grannmolekylen. I det här fallet är ytans påverkan på molekylen mycket liten - det går att avbilda olika molekylära elektronorbitaler i experimenten som sedan har
kunnat jämföras med teoretiska beräkningar för en fri, opåverkad molekyl, och överensstämmelsen är mycket bra.

![Diagram](image)


Mikroskopimätningarna har även visat hur ett monolager FePc (ett lager av molekyler) interagerar med en grafitytta. I den studien visas att placeringen av grafitytans atomer påverkar molekyllagrets formering, även om växelverkan med ytan är svag.

ZnPc har placerats på en indium-antimonidyta och mätningarna har visat att molekyllerna ligger plant på ytan och växelverkar svagt med den. Spektroskopiska mätningar visar dock att ytan påverkar ZnPc molekyllerna elektroniska struktur något.

Spektroskopimätningarna har gett information om hur den elektroniska strukturen hos H₂Pc påverkas av att kaliumatomer placeras på den molekyllära filmen. Som nämnts ovan har en molekyl inte bara orbitaler som är fyllda med elektroner, de har även tommar orbitaler dit elektroner kan exciteras. Här visas att en kaliumatom ger en av sina elektroner till ftalocyaninen, elektronen placeras i en av de tidigare tommar orbitalerna och molekylens elektronstruktur förändras. Dessutom har kaliumatomernas påverkan på molekyllernas geometriska struktur bestämts med absorptionsspektroskopi. Vidare har rubidiumatomers inverkan på molekyllära H₂Pc filmer undersökts.
2. Introduction

Highly organized molecular systems using organic building blocks introduces a new way to design novel functional materials. The attention towards these systems has therefore been massive in recent years and knowledge about ordered structures on the nano-scale have been sought. The electronic structure is a key to understand the physical properties and the functionality of molecular materials. In this thesis, X-ray Spectroscopy and Scanning Tunneling Microscopy techniques have been used to investigate Phthalocyanine (Pc) molecules adsorbed on different surfaces. With these techniques the electronic structure, the ordering of molecules within a monolayer, and to some extent, the ordering of molecules within molecular films have been characterized. Furthermore, structural changes of a Pc monolayer and a film, by alkali doping, have been investigated.

Phthalocyanine molecules are macro-cyclic compounds, extensively studied during many years. The large interest in Pc’s is due to several reasons, both the number of possible applications of Pc’s (for example solar cells [1], molecular electronics [2] and cancer therapy [3]) and due to the interest in molecular model systems. The phthalocyanines and the resembling porphyrins, with a chemical structure similar to the active sites of chlorophyll, hemoglobin and different enzymes, are very interesting in biomimetic applications such as catalyst for oxidation reactions [4, 5]. As a catalytic unit, the molecules adsorbed on surfaces, would enable or speed up a chemical reaction. Moreover, macro-cycles like metal phthalocyanines and metal porphyrins are also known to enable cathodic oxygen dissociation in fuel cells [6].

The functionality of such applications, as mentioned above, is dependent on the molecular film properties, which can be characterized by different techniques, among which those used in this thesis. In physics, models are often introduced to gain fundamental knowledge about certain aspects of more complex systems. The molecule-surface systems presented here, are regarded as being model systems for studying the interactions between molecular Pc films and different surfaces. A deeper understanding of such systems may possibly lead to an increased application range.

This work can be divided in three sections, which will be shortly presented here. These are molecular phthalocyanine films, monolayer studies and alkali doping of phthalocyanines.
2.1 Molecular phthalocyanine films
If a molecular film, consisting of several molecular layers, is characterized by weak intermolecular interactions, the film retains molecular properties. For phthalocyanines, it is known that the molecules interact only weakly, mainly by van der Waals forces. In this thesis, films of metal-free phthalocyanine (H$_2$Pc) and Iron phthalocyanine (FePc) have been examined. By X-ray spectroscopic techniques, both the occupied and unoccupied electronic structure have been mapped, which also have been compared to single molecule Density Functional Theory (DFT) calculations. Complementary to that, the ordering of molecules within the film can be investigated by the X-ray Absorption Spectroscopy measurements, showing organized growth of molecular Pc films.

2.2 Monolayer studies
For a molecular monolayer, the balance between intermolecular forces and molecule-substrate interactions is fundamental for the properties of the system. The effect of the substrate on the molecules and the intermolecular interactions have here been investigated. The aim has been to characterize the interactions present in the molecules-surface system, and to understand how the properties of the molecular overlayer are altered by different surfaces. Presented here are monolayer studies of H$_2$Pc, FePc and ZnPc on different substrates, namely Graphite (H$_2$Pc, FePc), Indium-Antimony (ZnPc), Aluminum (H$_2$Pc) and Gold (H$_2$Pc).

2.3 Alkali doping of phthalocyanines
By alkali doping the properties of the molecular films are modified, due to charge donation by the alkali. An important result from an earlier study was that a former insulating CuPc molecular film became metallic for a range of potassium doping levels [7]. Consequently alkali doping was proposed as a route for tuning of the physical properties of Pc films. Numerous studies have examined the influence of alkali doping on the molecular electronic and geometrical structure of different phthalocyanines [8, 9, 10, 11, 12, 13, 14]. Here H$_2$Pc have been doped by Potassium (H$_2$Pc film) and Rubidium (monolayer of H$_2$Pc) and changes of the electronic and geometrical structure have been characterized.
3. Techniques

To study material properties a range of experimental techniques may be used. Information about the electronic and geometrical structure is gained with the spectroscopy and microscopy techniques presented in the following sections.

3.1 Photoelectron Spectroscopy

The photoelectric effect, theoretically formulated by Einstein in 1905 [15], is the basis for photoelectron spectroscopy. In the experimental set-up a sample is irradiated by photons of well-defined energy and, photoelectrons are ejected from the sample. Since the energy of the system is conserved, the binding energy of the electrons in the sample ($E_B$) is obtained by measuring the kinetic energy ($E_{kin}$) of the ejected photoelectron, provided that the photon energy ($h\nu$) and the work-function ($\varphi$, the energy difference between the Fermi level and the vacuum level) of the sample are known [15]:

$$E_B = h\nu - E_{kin} - \varphi \quad (3.1)$$

The binding energy of electrons in different elements is unique and guarantees a chemical analysis of examined samples [16]. The photoelectron technique is therefore also known as ESCA, short for Electron Spectroscopy for Chemical Analysis. Nevertheless, slight changes of the electron orbitals as result of interactions among atoms or the presence of different chemical states can be detected as shifted spectral features, an effect also called chemical shift.

The information given by the intensity of different spectral features reflects to some extent the density of occupied states. The transition rate between the initial and final state is given by the Fermi Golden rule [17]

$$\omega = \frac{2\pi}{h} |<f|H^{int}|i>|^2 \delta(E_f - E_i - h\nu) \quad (3.2)$$

The initial and final states are denoted with $i$ and $f$. $H^{int}$ describes the interaction with the incoming photon, the delta function gives the energy conservation. The electron orbital symmetry in relationship to the polarization of the $E$ vector will influence the $<f|H^{int}|i>$ term, resulting in an angular dependence of the emission intensity.
3.1.1 X-ray Photoelectron Spectroscopy (XPS)

With X-ray Photoelectron Spectroscopy (XPS) the atomic core-levels may be examined. To probe the atomic core-levels X-rays are needed as excitation source. In this work the X-rays have been provided by a synchrotron facility or by a rotating anode in the home laboratory. For measuring the photoelectron kinetic energies a Scienta spectrometer has been used, consisting of an electron lens and a hemispherical analyzer. A schematic picture of the photoelectron spectrometer is shown in Fig. 3.1. The lens system focuses, retards or accelerates the electrons to the chosen pass energy before they enter the analyser hemisphere. An applied electric field between the two walls in the hemisphere affects the electron orbit, so that the electrons with a kinetic energy within a certain energy range hits the detector. The resolution of the spectrometer depends on a series of factors, the most important are the set pass-energy and the entrance slit of the spectrometer.

From the equation $E_B = h\nu - E_{kin} - \varphi$ (5.1) it is seen that the binding energy ($E_B$) can be obtained when the kinetic energy and the work-function are known. The energy position of the main feature in the spectrum is decided by the energy difference between the initial and final states. The main line often corresponds to the final state with the lowest energy, the most relaxed and/or best screened state. In addition satellite structures may be present, more about these in section 3.1.2. In Fig. 3.2 a schematic sketch of the photoelectron process is shown, together with the other processes described below.
3.1.2 Satellites

Often at higher $E_B$ than the main line in the XP spectrum, additional features called satellites can be seen. They can be regarded as different final states of a photoemission event. They are observed if, at the same time as the photoelectron is ejected, an excitation takes place in the molecular valence levels. Shake-up and shake-off satellites are due to excitations of valence electrons to bound and continuum states, respectively.

These valence level excitations require energy, whereby the ejected electrons will have decreased kinetic energy. Therefore satellites are seen as feature at higher binding energy than the main line in the XP spectrum. The excitations between the valence levels are monopole transitions between occupied and unoccupied states. This is theoretically further described in the following section.

3.1.3 Koopmans’ theorem and the sudden approximation

Koopmans’ theorem states that the ionization potential (IP) can be calculated for an occupied electronic orbital and that the absolute value of the IP is equal to the orbital energy [17].

This is based upon the assumption that the electrons remaining in the ionized system are not affected by the change in the potential when the core-hole is created, i.e. they are in a "frozen state". Within this assumption there would be only one final state and only one peak would be seen in the photoelectron spectrum, situated at the so called Koopmans’ energy.

However, for a more accurate description of the photoelectron spectrum, one has to introduce a relaxation term in the expression for the binding energy:
The relaxation term takes into account the response of the system to the new core-hole potential. The suddenly created core-hole leads to contraction of the electronic orbitals. Moreover, for molecular or solid systems screening of the created core-hole (by charge transfer to the core-hole site or by polarization) can occur to minimize the energy of the system. The relaxation of the remaining electrons leads to new excitations of valence electrons to bonded or continuum states seen as additional features in the XP spectrum.

The fact that additional excitations occur can be shown theoretically within the sudden approximation [18] which describes a fast (sudden) ionization process that occurs when the excitation energy is high enough. The system that is ionized is in the initial state, a N-electron system with wave function $\Psi_0(N)$, described by the Schrödinger equation

$$H(N)\Psi_0(N) = E_0^{N}\Psi_0(N)$$  \hspace{1cm} (3.4)

After the ionization event, a (N-1)-electron system persists:

$$H(N-1)\Psi_i(N-1) = E_i^{N-1}\Psi_i(N-1)$$  \hspace{1cm} (3.5)

$\Psi_i(N-1)$ describes a final state, a fully relaxed state that may have undergone additional excitations.

However, within the sudden approximation the (N-1)-electron system does not have time to fully relax and is therefore not in an eigenstate of the final ionic Hamiltonian, $H(N-1)$. The remaining electron system is instead in a $\Psi_R(N-1)$ state, a mixture of states that may be written as a linear combination of eigenstates of the ionic Hamiltonian $H(N-1)$ [18]

$$\Psi_R(N-1) = \sum_{i=0}^{\infty} <\Psi_i|\Psi_R> \Psi_i(N-1)$$  \hspace{1cm} (3.6)

The ionization therefore leads to several states, each with the probability

$$P_i = |<\Psi_i|\Psi_R>|^2$$  \hspace{1cm} (3.7)

which corresponds to the intensity of a certain satellite feature related to the ionization process. The energy positions of the satellites are instead determined by the eigenvalues $E_i(N-1)$. Then, a XP spectrum shows a peak at lowest binding energy (often the main line) corresponding to the most relaxed final state accompanied by several of these satellite features at higher binding energies. Since the relaxation minimises the energy of the ionized system, the main line will be situated at lower binding energy than the Koopman energy.
3.1.4 Electron escape depth

The photoelectrons emitted from a sample have a finite escape depth due to inelastic scattering. Only the electrons that are scattered elastically or not scattered at all are detected with their original kinetic energy. The inelastically scattered electrons loose some of their kinetic energy in the process and are therefore seen in the spectra at a higher binding energy, resulting in the continuous background in the spectra. The depth that electrons may escape without being inelastically scattered is dependent on their kinetic energy. This is shown by the universal curve, Fig. 3.3 [17]. Since the escape depth is 2-50 Å for kinetic energies between 1 and 1000 eV, photoelectron spectroscopy is a surface sensitive technique used to study the outermost atomic layers of a sample. In the case of adsorbed films, this fact might be used to secure that only the signal from the molecular film is studied.

3.1.5 Ultraviolet Photoelectron Spectroscopy (UPS)

In the case of XPS the core levels are examined, since the energy of the incoming radiation is high enough to probe these states. The core electrons are slightly affected by the interatomic interaction, even if they do not take part in the molecular bonding (core-level chemical shift). The shallow valence levels are responsible for the bonding, both with other surrounding molecules and in the case of adsorbate with the substrate. These states can be studied by ultraviolet radiation, used as excitation source in Ultraviolet Photoelectron Spectroscopy (UPS) measurements.
3.2 X-ray Absorption Spectroscopy (XAS)

The unoccupied electronic structure of materials can be probed with X-ray Absorption Spectroscopy (XAS). The samples are irradiated by a tuneable photon source (synchrotron radiation) that excites core electrons to unoccupied valence states. These core-hole states can decay either by emission of photons or by emitting Auger electrons. For elements with low atomic number $Z$, the Auger-like decay is dominating.

The cross-section for a transition between the initial ground state and the final excited state is described (in the dipole approximation regime) by [20]

$$\sigma_{XAS} \propto |< f | e \cdot p | i > |^2 \rho (E_f) \delta (E_f - E_i - h\nu)$$  \hspace{1cm} (3.8)

where $i$ denotes the initial state, $f$ the final state, $p$ linear momentum operator of electron, $e$ the unit vector (parallel to the polarization of the light) and $\rho (E_f)$ the energy density of the final states. The delta-function assures that the energy is conserved during the excitation.

The atom specific excitation into unoccupied states makes XAS a local technique. The intensity in the spectrum is proportional to the density of unoccupied states at the core-hole site, but this does not strictly correspond to the density of states (DOS) for the ground state since the unoccupied states are measured in presence of a core-hole.

However, the intensity of a feature also varies depending on how the molecules are oriented on a surface, i.e it is dependent on the polarization direction of the light. The dipole selection rule governs the absorption process and the intensity is dependent on the overlap between the electrical field of the light, $e$, and the linear momentum operator, $p$. This overlap changes with the polarization direction, directly leading to a intensity change. According to the dipole selection rule, electrons excited from a 1s state (which is the case in these studies) can only be transferred to states with a component of p-character ($\Delta l = \pm 1$) and the spatial distribution of those can be theoretically simulated. By measuring the change in relative intensity for different $\pi$- and $\sigma$-features as a function of the incidence angle of the polarized light, the orientation of the molecules on a surface may be determined.

The absorption spectra can be measured by collecting Auger electrons that are emitted when the excited atom decays. The number of ejected Auger-electrons as a function of the incoming photon energy gives the absorption spectrum and it is measured by a multi-channel plate or by a Scienta spectrometer.

The XA spectra can be recorded in three modes: partial, total or Auger electron yield. By the multi-channel plate detector in total yield mode all the electrons emitted from the samples are collected. In partial yield instead a bias voltage is set in order to collect only the electrons from a chosen Auger transition, filtering out electrons with too low kinetic energy. With a Scienta
spectrometer in Auger electron yield mode, spectra are recorded in a fixed kinetic energy window selected according to the Auger transition of interest. Since electrons originating from deeper lying layers in the samples have a larger possibility to be scattered, loosing energy, a filtration of low kinetic energy electrons enhances the surface sensitivity of the technique.

3.3 Scanning Tunneling Microscopy (STM)

Scanning Tunneling Microscopy was invented 1982 by Gerd Binning and Heinrich Rohrer [21, 22], who were rewarded the Nobel Prize for the invention in 1986. The technique uses the concept of quantum mechanical tunneling to obtain real-space images of surface structures, such as reconstructions and substrate adsorbates. An extremely sharp tip (in the best case monoatomic) is scanned over the examined surface at a distance of a few Ångström so that electronic tunneling between the tip and the surface can take place, enabling measurement of the distribution of electronic states at the surface.

3.3.1 Quantum Mechanical Tunneling

Electron tunneling is a quantum mechanical effect forbidden in classical mechanics. A particle with energy $E$ can tunnel through a potential barrier $\phi$ in the quantum mechanical regime, even if $E < \phi$.

For tunneling through a one-dimensional barrier, the tunneling current can be described by

$$I_{\text{tunneling}} \propto e^{-\frac{2\sqrt{2m\phi}}{\hbar} d}$$

where $d$ is the barrier width, in the STM case the distance between tip and surface, $\phi$ the local barrier height and $m$ the free-electron mass [23].

In STM, the wave functions of the tip and the surface overlap since their mutual distance is just a few Å, allowing electron tunneling from the one to the other. A bias voltage is thereafter applied between the tip and the surface, resulting in a misalignment of the respective Fermi levels as illustrated in Fig. 3.4. Depending on the sign of the applied bias, a tunneling current from the sample to the tip or vice versa is induced. Occupied and unoccupied electronic states near the Fermi level can be probed. As seen in equation 3.9, the tunneling probability exponentially decays with the surface-tip distance giving the high resolution of the technique, in fact even atoms can be resolved.

A detailed theoretical description of the tunneling process is troublesome, since it requires accurate descriptions of the substrate and tip wave functions as well as the interaction between tip and sample. Furthermore, the shape of the tip is most often unknown and likely to change under the experiment course. To describe the scanning tunneling process with higher accuracy than just considering two planar metal electrodes, Tersoff and Haman developed a model where the tip wave function is described as $s$-shaped, that is with spher-
**Figure 3.4:** The figure illustrates the tunneling event between two metals (e.g. substrate and tip) separated by the distance \(d\). Filled areas are occupied density of states. A positive bias (eU) is here applied to metal 1, resulting in tunneling of electrons from occupied states in metal 2 to unoccupied states in metal 1. The electron wave function overlap between the metals is indicated.

\[
I_{\text{tunneling}} \propto \sum_S |\psi_S(\vec{r}_0)|^2 \delta(E_S - E_{FT})
\]

where \(\psi_S(\vec{r}_0)\) is the substrate density of states, at the position of the center of curvature of the tip, and \(E_S\) the energy of the \(\psi_S\) state. Hence, the tunneling current measured at a given position of the tip is proportional to the surface local density of states at the tip Fermi level \(E_{FT}\), and the obtained image in constant current mode (see below) represents the contours of constant surface density of states. The Tersoff-Haman method is however only applicable for low bias voltages (in the order of 10 meV), for the sample-tip interaction to be sufficiently small to be neglected. Note that this condition is not fulfilled in the studies presented in this thesis.

As mentioned earlier, the image is a representation of the local density of states (see Fig. 3.5), at the position of the tip. For adsorbate systems, a convolution of the density of states of the adsorbates and the surface is observed as the microscope probes the adsorbate and the substrate both perturbed by their mutual interaction. Therefore, the adsorption site may influence the image of adsorbed molecules [25, 26, 27]. This effect can be as strong as to result in counterintuitive contrast. For example, an adsorbate such as Oxygen on a metal surface is imaged as a depression rather than a protrusion [28, 29].

### 3.3.2 Imaging modes

The STM can be used in different imaging modes, constant current and constant height mode [23, 30]. In the constant current mode, the tunneling current...
Figure 3.5: This schematically illustrates tunneling between a metallic tip and a metallic surface, separated by a distance $d$. A positive voltage $U$ is applied to the sample, resulting in tunneling from the tip to the surface. Filled areas indicate occupied states, unfilled areas unoccupied states. The tip electronic density of states near the Fermi level is nearly constant, and the density of states of the sample in the region $(E_{FT} - eU)$ is probed, indicated by the arrows.

is set to a specific value and held fixed by a feedback loop. At each probed point the tunneling current is kept constant, resulting in a measured height variation of the tip as compared to the surface when scanned over the substrate (see Fig. 3.6). The constant current mode is the most commonly used and all images presented in this thesis have been obtained in this mode.

In the constant height mode instead, the distance of the tip above the substrate is set, resulting in a measurement of the tunneling current variation at the specific tip height, illustrated in Fig. 3.6. The constant height mode measurement can be performed with a faster scanning speed compared to the constant current mode.

3.3.3 Principles of STM instruments

The resolution on the atomic scale and the local probing possibility are highly rated advantages of the STM technique. Crucial components of the STM instrument are the tip, the motors used for scanning and vibration isolation of the instrument. The tip is commonly fabricated from a thin wire of W or Ir/Pt alloy and is, as stated above, in the best case mono-atomically sharp [31]. Since the electronic density of states of the tip should be nearly constant close to the Fermi level, the choice of the tip material is important. The tunneling process between the tip and the sample is dependent of the metallic character of both the substrates and the tip. The three dimensional positioning of the tip relative to the sample is obtained by the use of piezoelectric scanner motors.
Figure 3.6: The principle of constant current and constant height mode. The tip is scanned in the x-direction, in the constant current mode the change of the tip-surface distance (z-direction) is measured while the tunneling current is fixed. In constant height imaging the tunneling current is measured while the tip height is kept constant.

The tip is scanned in the x (or y) direction by the motors, while measuring the change in the distance $d$ or the tunneling current $I_{\text{tunneling}}$, depending on the scanning mode. An inconvenience connected to the STM is the high vibration sensitivity of the instrumentation. To obtain resolution on the atomic scale, the tip-to-surface distance has to be stable on the sub-Å scale, and vibrations of the surrounding have to be compensated for by different vibration insulating components [23, 31].

By cooling the sample to low temperatures (in the studies presented in this thesis to about 70 K) vibrations and the mobility of adsorbates are minimized. Due to reasons as an un-sharp tip or vibrations, image artefacts can be observed and most often revealed by changing different measuring parameters such as scanning speed, scanning angle or bias voltage.
4. Density Functional Theory

Theoretical calculations have been used in several of the papers included in this thesis for interpretation of the experimental results. The theoretical results have been obtained with Density Functional Theory (DFT) [32, 33]. The calculations have been performed on a single, isolated H$_2$Pc molecule. XP and XA spectra have been obtained using DeMon [34] program. The valence band density of states (DOS) has been computed using the Gaussian 03 code [35].

For the XP spectra the binding energy is calculated according to the $\Delta$ Kohn-Sham ($\Delta$KS) procedure, as the difference in total energy between the core-ionized state ($E_f$) and the ground state ($E_i$):

$$E_B = E_i - E_f$$

(4.1)

where both states ($E_f$ and $E_i$) are energy optimized. Since the calculations have been performed on an isolated molecule, the theoretical binding energy is referred to the vacuum level and the spectra do usually need to be shifted in energy for the comparison with experimental data in order to account for the work function.

The XAS spectra have been calculated following the transition potential (TP) approach, where the electronic structure is calculated with a core hole of fractional occupancy on the excited atom. This simulates the relaxation of the valence levels. The absorption spectrum (i.e. the oscillator strengths) is calculated for the set of electronic levels obtained in the TP configuration.

Equivalent core-hole time-dependent density functional theory (ECH-TDDFT) has been used to simulate the shake-up structure of the C1s XP spectrum. This method combines the equivalent core-hole (ECH) or Z+1 approximation to describe the core ionized atom, with TDDFT to calculate the energy positions of the shake-up excitations. The Z+1 approximation simulates the core-hole state by adding an extra positive charge to the nucleus. The valence levels respond to this extra charge in the same way as if a core-hole is present. The TDDFT is widely used to study optical excitations in molecules. In our application, the excitation energy of the shake-up states are related to the optical excitation of a core ionized system.

The intensities of the shake-up transitions have been calculated on the basis of the sudden approximation, which states that the molecular orbitals do not have time to readjust during the photoemission process since the ejection of the electron is a fast event compared to the relaxation. In this framework, the intensity of the shake-up features is equal to the square of the overlap between
the initially occupied ($\Psi_i$) and the final excited ($\Psi_f$) valence states [18]

$$I_{\text{shake-up}} = |< \Psi_i | \Psi_f >|^2$$  \hspace{1cm} (4.2)
5. Experimental

This section includes a description of sample preparations and the experimental instruments used in the experimental work.

5.1 Sample preparation and Ultra High Vacuum

Surface science investigations are usually performed in a Ultra High Vacuum (UHV) environment, this is a necessity for obtaining clean surfaces and for keeping samples clean during the measurements. In normal atmospheric pressure a clean surface would immediately be covered by contaminants, while in UHV it can still be clean after few hours. The pressure in the different systems used for the studies presented here have typically been in the low \(10^{-10}\) Torr range. To reach UHV, pumps of different kind (as ion, titanium sublimation, mechanical and turbo pumps), together with the so called bake-out\(^1\) of the experimental system have been used.

In the studies presented here, several different substrates have been used, and different cleaning procedures have been performed.

The conducting glass substrates, used in papers I and II, have been cleaned \textit{ex situ} in a ultrasonic bath with ethanol, thereafter dry blown in Ar gas and inserted in the load-lock system connected to the UHV chamber.

In the case of Si(100), used in paper III, the substrates have been cleaned by direct heating to about 1070 K for several hours. Thereafter the Si has been flashed several times to about 1370 K while not exceeding a pressure of \(4 \times 10^{-10}\) Torr in the preparation chamber. The native oxide layer is removed in the heating procedure and the surface atoms are rearranged in an ordered structure (surface reconstruction).

The Highly Oriented Pyrrolytic Graphite (HOPG) surfaces, used in papers IV and V, have been cleaved in air before insertion in the vacuum chamber. Annealing of the substrates to about 1170 K resulted in that adsorbates were heated off and large, flat, clean areas have been observed in the STM.

The InSb(001) (paper VI), Al(110) (papers VII and VIII) and Au(111) (paper IX) surfaces have been cleaned by repeated sputtering and annealing cycles. During sputtering, the surfaces are bombarded with high energetic argon ions, accelerated from an ion gun towards the sample. This results in a clean

\(\footnote{\text{The instrument chambers are heated up to temperatures above } 120\text{°C to release and pump out molecules adsorbed on the chamber walls.}}\)
surface, free from contaminants, but corrugated due to the ion bombardment. The samples are annealed, whereby the surface atoms rearranges and flat surface areas are recovered.

The molecular depositions have in all cases been performed \textit{in situ}, either from a resistively heated tantalum pocket (FePc, H$_2$Pc) with a small hole (approximately 1 mm in diameter), warmed to a temperature of about 670 K or from an evaporator consisting of a quartz glass tube (with a hole of 3.5 mm diameter) with a tungsten wire winded around for heating (H$_2$Pc, ZnPc). In both cases the evaporation rate has been controlled by careful adjustment of the heating current. For the monolayers (ML) characterized by STM, the molecular films have been heated to about 670 K after deposition. But, this has not been the case for the monolayer studies of ZnPc/InSb(001) and H$_2$Pc/Al(110) (paper VI and VII, respectively) where the deposition rate of the evaporators have been carefully calibrated, before the presented data have been recorded.

The doping of alkali metals have been done from a SEAS getter source, activated in the UHV chamber.

5.2 Synchrotron radiation

Synchrotron radiation is generated when charged particles are accelerated in a magnetic field, \textit{i.e.} the particle linear trajectory is changed. If the particles have a speed close to the speed of light, the emitted radiation is strongly focused in the forward direction. Furthermore the radiation is intense, with a continuous energy spectrum, \textit{i.e.} the synchrotron radiation is a tuneable photon source.

Historically synchrotron radiation was only seen as an energy loss in particle storage rings [36]. However, the possibility of using the radiation for scientific investigations has resulted in facilities designed for generation of synchrotron radiation.

The synchrotron radiation facilities consists of a storage ring in which high energy electrons (or in principle positrons) are injected. The storage ring is under UHV to prevent the electrons from colliding with atoms or molecules. Synchrotron radiation is generated when the electrons pass the bending magnets or insertion devices (undulator or wiggler) [36].

In the studies presented here, synchrotron radiation has been used for spectroscopic investigations. The tuneable photon source is used for the X-ray Absorption measurements. In addition the possibility to choose a specific photon energy for the X-ray Photoelectron Spectroscopy measurement is used for surface sensitive measurements (see section 3.1.4).

The synchrotron radiation studies presented in this thesis have been carried out at the Swedish national laboratory MAX-lab in Lund. The measurements have been performed at MAX II, a 1.5 GeV third generation electron storage ring.
5.2.1 Beamline I511, MAX-lab, Lund

At MAX-lab the experiments have been carried out at the surface branch of beamline I511 [37] where linearly polarized light in the energy range of 100 to 1500 eV is provided. The beamline is equipped with a Zeiss SX-700 monochromator. The experimental end-station consists of two chambers; a preparation chamber and an analysis chamber. On the latter, a Scienta\(^2\) analyzer for X-ray Photoelectron Spectroscopy (XPS), an X-ray Emission Spectrometer for XES measurements, and an X-ray Absorption Spectroscopy (XAS) detector are mounted. The analysis chamber can be rotated around the light beam axis, implying that spectra can be measured at different emission angles with respect to the E vector of the light. Also the sample can be rotated, thereby the angle between the polarisation E vector of the light and the surface can be varied. The end-station construction results in that the incoming light is always shining on the surface at grazing incidence, thus the normal emission data is truly 7 degrees off normal. Measurements presented in paper I, III, VII and VIII have been performed at this beamline.

5.3 Home laboratories

5.3.1 X-ray Photoelectron Spectroscopy

In the ESCA 200 and 300 home laboratories [38, 39], photoelectron spectroscopy (XPS) measurements are performed. In both cases Al K\(\alpha\) radiation with the energy 1486.7 eV is produced by electron bombardment of a water cooled aluminium coated rotating anode. The monochromator focuses the X-ray beam onto the sample and the emitted photoelectrons are analysed with a Scienta SES-200 or SES-300 spectrometer, respectively. In both systems a separate evaporation chamber connected to the system has been used for \textit{in situ} film depositions. The ESCA 200 system is equipped with a sputter gun and a sample heating stage for annealing of the samples. The XPS measurements presented in papers I and II have been performed with the ESCA 300, the data presented in paper VI have been obtained with the ESCA 200.

5.3.2 Scanning Tunneling Microscopy

The STM measurements presented in this thesis are, with two exceptions, obtained with a Omicron variable temperature, UHV instrument in Uppsala, Sweden. The STM data presented in paper V has partly been performed using a home-built STM [31] in Aarhus, Denmark and the presented STM images in paper VI have been obtained with a Omicron STM at Royal Institute of Technology (KTH), Stockholm, Sweden.

\(^2\)A Scienta SES-200 exchanged in 2005 to a Scienta R 4000 analyzer.
The Uppsala instrument consists of a chamber with the STM stage and a preparation chamber. The latter is used for sputtering and annealing of the samples and is also equipped with LEED/Auger facilities. The molecular depositions on the substrates have been performed in an evaporation chamber connected to the preparation chamber. All STM measurements presented here have been performed in the constant current mode. Positive bias voltage has been used for probing unoccupied states, negative bias for probing occupied states. The STM stage can be cooled down using liquid helium, reaching sample temperatures of about 70 K.

5.3.3 Calibration of XPS, XAS and STM measurements
In XPS surface science investigations, the energy scale is most often referred to the Fermi level defined to be at zero binding energy. This is however only applicable for a metallic sample, in other cases the binding energy is referred to the vacuum level, or alternatively, to a XPS core-level with known binding energy. In the studies presented here the calibration has been done in different ways. In papers I and II the energy scale has been calibrated to the Fermi level of a Ag sample. For paper III the calibration has been done by referring to the Si2p feature at 99.7 eV. The XPS measurements presented in paper VI have been referenced to the In3d_{5/2} feature, at binding energy of 444.5 eV. For the measurements in paper VII, the Fermi energy of the Al(110) have been used for calibration. In the case of the doped films (paper VIII), the core-level spectra have been recorded using first and second order light to obtain the true value of the photon energy. The Fermi level of the clean sample has thereafter been measured, calibrating the kinetic energy scale of the spectrometer with chosen experimental settings (for example spectrometer slit and pass energy). In the same paper (VIII) the valence band spectra have been measured in a series during which all adjustable settings have been kept constant, thereafter the sample has been cleaned and the Fermi level, to which the binding energy scale of the spectra has been calibrated, recorded.

The energy scales of XAS spectra shown in this thesis have been calibrated by measuring the C1s photoemission peak with first and second order light.

The Uppsala STM instrument has been calibrated in the x and y direction using a HOPG substrate with a lattice constant of 2.46 Å as a standard. The STM used for measurements in paper VI has been calibrated by setting the distance of adjacent In rows to 18.3 Å.
6. Substrates and adsorbates

6.1 Substrates

Substrates with different physical properties, both metallic, semimetallic and semiconducting, have been used in the studies. In papers III, IV, V, VI, VII, VIII and IX molecules have been deposited onto highly ordered surfaces, characterized by a well defined atomic periodicity.

**Conducting glass (FTO)**

In the first two papers conducting glass, commonly used in displays and as back contact in view-through solar cells, has been used. This material is made of ordinary window glass, coated by a thin transparent conducting layer of tin oxide doped with fluorine, and is also known as FTO. In contradiction to the other substrates used in the experimental work presented in this thesis, these are cleaned *ex situ*. Moreover, the FTO is characterized by a large corrugation, as compared to other surfaces used in our experimental work.

**Al(110)**

The metal Al(110) surface structure is modified by a surface *oscillatory* relaxation [40] which results in a variation of the spacing between the outermost surface layers. Contraction and expansion of the interlayer distance is found for several layers, as compared to the distance between neighbouring layers in the bulk.

**Si(100)**

Silicon is a semiconductor, characterized by a band gap between the occupied and unoccupied levels, with the Fermi level situated in the band gap. The unreconstructed surface would have two broken bonds at the site of each surface atom and the Si(100) surface reconstructs in a (2x1) structure [41, 42]. Rows of dimers are thereby formed, lowering the number of broken bonds and the surface free energy.

**HOPG**

Highly Oriented Pyrolytic Graphite (HOPG) has been the substrate in the studies presented in papers IV and V. Graphite is a semimetal, *i.e.* it has a low density of states near the Fermi level [43]. The HOPG (0001) surface sheet has a hexagonal symmetry and consists of sp²-hybridized carbon atoms, whereas between parallel graphite sheets weaker π bonds are present [43]. The carbon
atoms are situated at two inequivalent sites, the $\alpha$ and $\beta$, illustrated in Fig. 6.1. The $\alpha$ has neighbouring atoms situated directly below in the deeper lying graphite sheet. This is not the case for the $\beta$ carbon atoms that, as seen in Fig. 6.1, do not have an atom directly below [44]. In STM images, only the $\beta$ atoms are observed, due to the fact that the STM measures a convolution of different electronic states [45] and the density of states close to $E_F$ is higher at the $\beta$ atom sites.

![Diagram of HOPG surface with $\alpha$ and $\beta$ atoms](image)

*Figure 6.1:* Schematic illustration of the HOPG surface with the so called $\alpha$ and $\beta$ atoms. To the left the graphite sheets are seen from the side, to the right from the top. The $\alpha$ atoms in neighbouring graphite sheets are placed directly above each other.

**InSb(001)**

The surface of the semiconductor InSb(001) can reconstruct in different ways, depending on the surface preparations [46]. The atoms in the bulk are arranged in a zinc-blende structure. The Sb atoms are placed on one fcc lattice, and the In atoms on another fcc lattice, but shifted compared to each other as seen in Fig. 6.2. The ideal (001) surface would consist of only one element, but the surface rearrange instead and this can result in a number of surface reconstructions, with different In and Sb surface concentrations. The most stable reconstruction is the c(8x2) which has a In-rich surface [46]. A model of the c(8x2) reconstruction, illustrated to the left in Fig. 6.2, has been proposed by Kumpf et al. [47]. As also observed by STM [48], In rows, about 18 Å apart, are formed along the [110] direction. Sub-surface dimers (not seen in the illustration) produces the (8x2) symmetry of the reconstruction in contrast to the (4x1) symmetry observed in the surface layer (and in Fig. 6.2) [47]. The InSb(001)-c(8x2) substrate has been used in paper VI.

**Au(111)**

An Au(111) surface reconstructs in a so called herringbone structure, also denoted ($\sqrt{3}$x22), with periodically distributed stress domains. The reconstruction has earlier been characterized by STM [49, 50], see for example the
Figure 6.2: To the left, schematic illustration of the surface layer of the InSb(001)-c(8x2) surface reconstruction, seen from the top and the side, according to the model by Kumpf et al. [47]. To the right the bulk structure of InSb is displayed.

study by Barth et al. [49]. In the surface plane 4% more Au atoms are found compared to a plane in the bulk. The surface can be described with a stacking-fault-domain model, which includes periodic sequences of areas with fcc-type and hcp-type stacking. These regions are separated by so called soliton walls where the Au atoms occupy bridging sites that appear brighter in the STM measurements, see Fig. 6.3. The fcc areas, having lower surface energy, are slightly bigger than the hcp- regions [50]. The soliton walls form a zig-zag structure to further minimize the surface free energy. At the so called elbow sites [50] the soliton walls change direction, the angle between two walls are about 120° [49]. In paper IX, Au(111) has been used as substrate.

Figure 6.3: STM picture of an Au(111) herringbone reconstructed surface. The soliton walls are seen as brighter lines, forming a zig-zag structure. Indicated are also the fcc and hcp regions. Bias = -3.9 V, I = 0.041 nA, 44.2 nm x 43.3 nm.
6.2 Adsorbates - Phthalocyanines

Phthalocyanines, the molecular adsorbates studied in this thesis, are macrocyclic compounds, extensively studied during many years due to different reasons, mostly for the possibility to use them in many different technological applications. Phthalocyanines can have chemical formulas MeC$_{32}$N$_8$H$_{16}$ or H$_2$C$_{32}$N$_8$H$_{16}$, that is metal-phthalocyanine (MePc, where Me stands for a metal atom) and metal-free phthalocyanine (H$_2$Pc) respectively. In this thesis H$_2$Pc, FePc and ZnPc have been characterized. The H$_2$Pc and FePc molecular structures are displayed in Fig. 6.4.

In films, these molecules are known to form molecular stacks which interact via van der Waals forces [51]. The interactions between neighbouring molecules within a stack are weak and mainly restricted to the first neighbours [52]. It is known that the Pc molecules self-organize into different phases, the two most well known are the $\alpha$ and $\beta$ phases [53], even though many others exist. Both the $\alpha$ and $\beta$ phases are formed by molecules with the molecular plane parallel to each other, but with the stacking direction tilted from the normal to the molecular plane with 26° and 45°, respectively, see Fig. 6.5.

Different phases are known to form by different deposition methods, for example sublimation [54], heat treatment [55] or solvent deposition [56]. For each phase the electron orbital overlap between neighbouring molecules is decided by the stacking direction and hence the electronic structure of the overlayers is distinct for each phase. The optical and photovoltaic properties are therefore different [57], and a tuning of specific properties might be obtained by controlling the film growth.

For monolayer formation of phthalocyanines on different substrates, it is in many cases found that the molecules are arranged with the molecular plane
parallel to the surface [58, 59, 60, 61, 62]. The characteristics of the adsorbate-substrate interaction, together with the adsorbate-adsorbate interaction, affect the molecular adsorption growth mode.

### 6.3 Adsorbate-adsorbate and adsorbate-substrate interactions

The adsorbate-substrate interaction can be of different strength, molecules can either be physisorbed or chemisorbed on the surface. There is however no strict distinction between physisorption and chemisorption.

In physisorption the overlap between the valence electronic levels of the adsorbates and the substrate is small and the molecule-surface interaction is weak. Often the interaction is mediated by van der Waals forces, which even if weak, are long range interactions [63] and the adsorbate-substrate distance can be relatively large. The bonding energy is small (in the order of about 0.1 eV [64]) and the adsorbate and substrate electronic structures are only weakly perturbed in case of physisorption.

In chemisorption on the other hand, the electronical states are significantly distorted and a chemical bond is formed between the adsorbate and the substrate [63]. Often the bonding is of covalent type [63] and electrons are shared by the two constituents. The bond distance is short and the bonding energy in the order of 1 eV [64]. In the case of chemisorption, a core-hole created by ionization of an atom in the adsorbate can typically be well screened by the substrate, since a charge transfer from the substrate to the adsorbate may occur.

Adsorbates can also interact via ionic bonding. In this case, an electron is transferred from one species to the other, resulting in a positive and a negative ion, attracting each other. In the periodic table of elements the group I, *i.e.* hydrogen and alkali metals, are known to easily donate their outer electron and to form ionic bonds with other substances.

Depending on the adsorbate-adsorbate and adsorbate-substrate interactions molecular growth can occur in different arrangements on the substrate. The growth are distinguished in three different modes, known as Frank-Van der
Merwe, Stranski-Kastranov and Volmer-Weber growth [19], illustrated in Fig. 6.6. In Frank-Van der Merwe growth the adsorbates are arranged in a layer-by-layer formation. In the case of Stranski-Kastranov growth a few monolayers are formed on the substrates before three-dimensional islands are formed [19]. Volmer-Weber growth are characterized by the growth of three-dimensional islands, and the surface may not be completely covered until a large deposition has been made.

![Image of different adsorbate growth modes](image)

*Figure 6.6: Illustration of the different adsorbate growth modes: Frank-Van der Merwe, Stranski-Kastranov and Volmer-Weber growth.*

The balance between molecule-substrate and molecule-molecule interactions also affects the formation of the molecular monolayer [65]. The adsorbate structure on the surface may coincide with the underlying substrate lattice. If every overlayer lattice point, *i.e.* adsorption site, overlap with a underlying substrate lattice point the adsorbed overlayer is commensurate with the substrate. Due to different interactions between the surface and the adsorbate, several different adsorption sites of the molecules may exist resulting in a coincidence or incommensurate adsorption. In the case of coincidence, a supercell (unit cell) for both the substrate and adsorbate can be defined. This is not the case for an incommensurate adsorption, where no unit cell for the whole system can be found. The formation of non-commensurate (coincidence and incommensurate) structures can be observed by the appearance of a Moiré pattern in STM pictures [65], due to the imaging of superimposed density of states of the substrate and adsorbates. The three different adsorption structures are the result of different adsorbate-adsorbate and adsorbate-substrate interactions. In the case of a commensurate adsorption the adsorbate-substrate interaction has a dominant role for the formation of the monolayer (ML), whereas for coincidence and incommensurate adsorption the adsorbate-adsorbate interaction plays a more significant role [65].

The spectroscopic and microscopy techniques used in this thesis provide detailed information regarding the molecule-molecule and molecule-surface interactions, as well as about the growth mode of adsorbates on surfaces. By XPS investigations modifications of the electronic structure, as well as the strength of the interactions can be characterized, whereas the microscopy studies can apply direct images of the adsorption geometry of adsorbates.
7. Summary of papers

Here follows a summary of the results that are included in the papers of this thesis.

7.1 Molecular phthalocyanine films
7.1.1 Electronic structure of metal-free phthalocyanine films

In papers I and II the electronic structure of metal-free phthalocyanine has been studied. Multilayer films of H₂Pc have been evaporated onto conducting glass (FTO) and characterized by core and valence photoelectron spectroscopy. The experimental data have also been compared with theoretical calculations.

**C1s with shake-up structure**

The shake-up structure of the C1s XP spectrum of phthalocyanines has been under debate for at long time [52, 66, 67, 68], since the relative intensity of the two peaks originating from the pyrrole and benzene carbons (see Fig. 6.4) does not correspond to the stoichiometry of the molecule. Instead, the pyrrole contribution to the C1s signal seems to be too large as reported in previous studies [52, 67], possibly explained by a shake-up feature, related to the benzene carbons, at the same binding energy as the pyrrole carbons [66]. To establish the existence, the energy position and the intensity of such satellite features a joint theoretical and experimental study has been done, presented in paper II. Equivalent core-hole time-dependent density functional theory (ECH-TDDFT) has been used to simulate the shake-up structure of the C1s XP spectrum. The positions of the shake-up features, relative to the main peaks, have been calculated for both states of \( \pi \) and \( \sigma \) symmetry and the valence transitions related to the photoemission of the benzene and pyrrole like C could be determined.

The C1s spectrum of a H₂Pc film is shown Fig. 7.1 (a). This is characterized by three major features due to the chemically non-equivalent C atoms, pyrrole and benzene. The ionization potentials of the non-equivalent carbon atoms and the energy positions of the shake-up features, as found by the calculations, are indicated as bars in Fig. 7.1. The shake-up structure is rather complex, but, to show their spectral contribution, these structures may be included as two additional features in the fit. The four-peak fit, seen in Fig. 7.1, leads to a
pyrrole contribution of 24% of the total intensity, in very good agreement with the expected value from the molecule stoichiometry. The agreement between the theoretical and experimental spectra is found to be excellent, as shown in Fig. 7.1 (b).

**N1s**
The N1s spectra of H2Pc, displayed in Fig. 7.2 (a), consists of two strong features (at about 398.9 and 400.4 eV), steaming from non-equivalent nitrogen atoms as resolved by the DFT calculations presented in paper I. It is shown that the main peak is due to excitations of the N2 and N3 atoms (see Fig. 6.4), the feature at about is 400 eV due to N1 atoms.

**Valence levels**
The valence level spectrum is displayed in Fig. 7.2 (b). The peaks, labeled by numbers between 1 and 8, are all present in the calculated spectra. In Fig. 7.2 (inset) the calculated components of the density of states (DOS) from all carbon and all nitrogen atoms are shown. The highest occupied molecular orbital (HOMO, peak 1) at about 1.7 eV, is a $\pi$ orbital formed by the C2p orbitals, the other orbitals are generally of mixed origin as shown by the C and N resolved simulations.

### 7.1.2 H2Pc and FePc films: Geometrical structure
As described in section 3.2, angle resolved XAS measurements can be used for investigating the molecular orientation with respect to the surface [20].

Figure 7.1: (a) A four-peak fit of the experimental C1s spectrum of H2Pc. The different curves used in the fitting procedure to simulate the main lines and the shake-up features are illustrated, together with the total fit and the experimental data (dotted curve). In addition the theoretical values (bar graph) are compared to the peak positions of the four-peak fit. (b) Convolution of the calculated intensities of the main lines and the shake-up features with gaussians of different FWHM (Full width at half maximum) in comparison with the experimental data (dotted curve).
Figure 7.2: (a) N1s spectra of H$_2$Pc. Bars indicating the DFT calculated ionization potentials of the non-equivalent nitrogen atoms. (b) Experimental data (dotted curve) and theoretical simulation (solid line) of the valence levels of H$_2$Pc. In the inset, the C and N contributions of the simulated spectrum are shown.

For H$_2$Pc experimental N1s XAS measurements have been performed with three different incidence angles of the radiation with respect to the surface plane, shown in Fig. 7.3 (a). In addition, the N1s XA spectra have been calculated for a single H$_2$Pc molecule, both resolving the spectral intensity along the x-, y- and z-axis (see Fig. 6.4) and resolving the contributions from the chemically non-equivalent nitrogen atoms, as seen in Fig. 7.3. The atom resolved spectra, Fig. 7.3 (c), shows that the second peak at 400.0 eV in the XA spectra contains contributions from all of the non-equivalent nitrogen atoms in the molecule, implying that the two features at low photon energy in the XA spectra are not only the result of the chemical shifted features seen in the XP spectrum.

The spatial resolved spectra of H$_2$Pc (Fig. 7.3 (b)) are used to determine an existing overall geometrical orientation of the molecule. In the experimental data the two $\pi$-states (at about 398.4 and 400.0 eV) are clearly dominating when the E vector is parallel to the sample surface, as compared to the geometry with the E vector perpendicular to the plane where the $\sigma$ features (around 410 eV) have the highest intensity, indicating that the molecules are predominantly oriented with the molecular plane perpendicular (or highly tilted) with respect to the surface.

In analogy, angle resolved XAS measurements of FePc films, presented in Fig. 7.4 (a), have shown that the FePc are mainly standing up on the Si(100) surface. This by comparing the XA spectra, showing that the intensity of the $\pi^*$ and $\sigma^*$ features dominate in different experimental geometries, with DFT calculations resolving the spatial distribution of the molecular orbitals. In Fig. 7.4 (a) the theoretical spectrum, simulating a molecule with tilt angle 60° with respect to the surface, is displayed together with the experimental data.
Figure 7.3: (a) The XA spectra of H$_2$Pc measured with the E-vector of the light parallel to the surface (top spectrum), with 45° between the E-vector and the surface (middle spectrum) and with the E-vector perpendicular to the surface (spectrum at the bottom). (b) Calculated XA spectra for a single H$_2$Pc molecule along the x, y and z directions, compared to the experimental data. (c) The calculated XA spectra resolving the spectral contribution from the chemically non-equivalent nitrogen atoms.

In the case of FePc, the molecular orientation within the film has also been found by combining DFT calculations with valence level measurements, recorded in different experimental geometries. The symmetry of different valence orbitals, also previously reported in ref. [69], has been deduced by our calculations. By investigating the variation of the intensity of $\pi$- and $\sigma$- type orbital features as the angle between the E-vector of the light and the sample is changed, it has been found that the molecules are mainly standing up on the surface. In Fig. 7.4 (b) the experimental spectra taken in two geometries are displayed, along with DFT simulated spectra where the angular dependence of the photoemission intensity of the C and N derived orbitals have been taken into account.

7.2 Monolayer Studies
For the formation of molecular monolayers, the balance between intermolecular forces and molecule-substrate interactions is fundamental, and the properties of the surface is of crucial importance. ML structures of different Pc’s on both metallic and semiconductor surfaces have been studied to characterize the present interactions.
Figure 7.4: (a) XA spectra measured in three experimental geometries, together with the simulated spectra of a molecule with the tilt angle of 60° with respect to the surface (bottom part). (b) The valence band of FePc. In the upper part are the experimental spectra recorded in two geometries, in the lower part are theoretical spectra where the angular dependence of the photoemission intensity of C and N derived σ and π orbitals, oriented parallel and normal to the molecular plane, have been taken into account.

7.2.1 Phthalocyanines on Graphite
Monolayer structures of H$_2$Pc and FePc have been investigated at low temperature with STM, as reported in paper IV and V. For the two systems, a post-deposition annealing of the samples to about 670 K resulted in islands of ordered, densely-packed structures of molecules oriented with the molecular plane parallel to the surface.

The similarities between the two systems are several. A weak molecule-substrate interaction is found for both molecules, and the intermolecular interactions are characterized as weak, of van der Waals type. As can be observed in Fig. 7.5 (H$_2$Pc) and Fig. 7.6 (b) (FePc) the molecules are arranged in unit cells of square symmetry, as also observed for PdPc on HOPG [70]. A Moiré contrast, see Fig. 7.5 (a) and 7.6 (d), is observed in a large number of images, indicating that the adsorption unit cells of the two molecules are not commensurate with the graphite lattice [65].

H$_2$Pc/Graphite
For H$_2$Pc molecular orbitals of a single molecule in the ground state have been simulated by DFT calculations. By bias dependent measurements, probing different electronic levels, images of different states have been obtained. In Fig. 7.5, STM images of two observed states are displayed along with simulations presenting the HOMO-2 and HOMO-4 orbitals. The observed state with a nodal line through the molecule (Fig. 7.5 (a)) have clear similarities with the HOMO-2 orbital, and the experimentally imaged state depicted in (d) have
Figure 7.5: H$_2$Pc/HOPG. The molecules are found to be adsorbed in a square unit cell. (a) A Moiré contrast is observed, ascribed to that the adsorption unit cell is not commensurate with the underlying graphite lattice. The STM image is obtained with bias = -1.93 V (0.067 nA, 14.2 nm x 9.7 nm). (b) HOMO-2 according to ground state single molecule calculation. (c) Experimental image measured with bias = -2.27 V (0.020 nA, 14.1 nm x 4.6 nm). (d) Image (c) with different contrast settings. (e) The HOMO-4 orbital. Clear resemblances between the state imaged in (a) and the orbital in (b) are seen, and the state observed in (e) have similarities with the HOMO-4 orbital (d). (All STM pictures can be seen in colour online.)

resemblances with the HOMO-4 orbital. The good agreement between the orbitals obtained in single molecule simulations and the STM images suggests a weak molecule-substrate interaction, only slightly perturbing the molecular orbitals.

FePc/Graphite
For FePc it have been found that upon deposition on samples kept at room temperature, molecules adsorb in three-dimensional islands. This is interpreted as a significant molecule-molecule interaction, dominating over the molecule-substrate interaction.

As described above, annealing of the samples results in islands of ordered ML structures. As indicated in Fig. 7.6 (a) the molecular islands are oriented with an angle of 30 degrees compared to each other. This indicates that the six-fold symmetry of the HOPG surface results in a preferential adsorption direction of the molecules, suggesting that the molecule-substrate interaction can not be neglected for the ML formation.

In addition to the square adsorption unit cell, presented in Fig. 7.6 (b), an adsorption unit cell of hexagonal symmetry is observed for FePc, as can be seen Fig.7.6 (c). This is however found only for a minor percentage of the cases (about 5 %).
Figure 7.6: FePc/HOPG. (a) Islands with densely-packed molecules are formed on the substrate. The islands are oriented at an angle of 30 degrees compared to each other. Hence, even if the interaction of the substrate is weak, the influence of the substrate on the ML formation is not negligible. Streaks due to highly mobile molecules are seen in the image. (1.9 V, 0.04 nA, 95 nm x 95 nm) (b) Molecules in the square unit cell. A molecular model from a single molecule calculation (paper III) is used to fit the STM image. As seen, the metal centre has a large contribution to the molecular electronic structure. (2.22 V, 0.19 nA, 4.8 nm x 4.8 nm) (c) In few cases (about 5 %) the molecules are found to be adsorbed in a hexagonal unit cell. (2.27 V, 0.42 nA, 9.5 nm x 9.5 nm) (d) Molecules in the quadratic phase, with the directions of the observed Moiré pattern indicated. (-0.38 V, 0.132 nA, 33 nm x 33 nm)

7.2.2 Zinc phthalocyanine on InSb

In paper VI, ZnPc is adsorbed on InSb(001)-c(8x2) have been studied by STM, LEED (Low energy electron diffraction) and XPS. As described in section 6.1, the c(8x2) reconstruction is characterized by In rows, about 18 Å apart, formed along the [110] direction. STM measurements, see Fig. 7.7, have shown that ZnPc adsorb with the molecular plane parallel to the surface, on top of the In rows as also found for H2Pc [61] and several MePc’s [60, 71, 62, 72] adsorbed on InSb(001)-c(8x2). The molecules are imaged as four protrusions around a dark centre, indicating contributions to the highest occupied orbitals exclusively from the molecular ring. In contrast to the other ML systems investigated by STM in this thesis, neighbouring Pc molecules are here found to interact with the benzene groups towards each other.
The geometrical match between parallel In rows and the molecular size (about 15 Å) result in an ordered overlayer after annealing, as observed by LEED. Molecules are adsorbed along the [110] direction, and a x3 LEED pattern (superimposed on the surface diffraction pattern) indicates a displacement of Pc’s with respect to neighbouring molecules on parallel rows.

XPS reveals that the molecular electronic structure is slightly influenced by the surface interaction, spectral features are broadened in the ML case as compared to the thicker film. As seen in Fig. 7.7, annealing to 640 K results in further spectral broadening, possibly due to an increased molecule-surface interaction.

7.2.3 Metal-free phthalocyanine on Al(110)

The H₂Pc adsorption on Al(110) has been investigated by spectroscopic techniques, the study is presented in paper VII. The multilayer data are in agreement with the results presented in paper I. In the case of ML coverage, substantial modifications induced by the substrate is observed both by the XP and XA measurements. For the ML, N1s XA angle resolved spectra reveal that molecules are found to be adsorbed with the molecular plane parallel to the surface, as compared to a standing or highly tilted orientation in the multilayer.
For this system, a strong molecule-surface interaction is found, evidenced by a significant perturbation of the molecular electronic structure upon surface adsorption. The ML N1s XP spectrum, Fig. 7.8 (a), suggests a dissociation of the central hydrogen atoms, indicated by the absence of a feature at about 400 eV (see section 7.1.1). The additional feature at low BE (about 396.6 eV) [73] is proposed due to a strong bond between N atoms and the Al substrate.

In the XA data, the broad low intensity shoulder in the photon energy region 396-399 eV, with respect to the multilayer results, is a clear evidence of a strong modification of the molecular empty levels due to the strong bonding to the surface. A charge redistribution, resulting from the creation of new states close to the threshold, can be identified by the modification of intensity of the π* features at low photon energy. Moreover, for the ML, the N1s XP binding energy is found on the threshold edge of the N1s XA spectrum (Fig. 7.8), as expected for molecules chemisorbed on metallic surfaces [74, 75, 20].

7.2.4 Metal-free phthalocyanine on Au(111)

ML formations of H2Pc on herringbone reconstructed Au(111) have been studied by STM at low temperature, the data are presented in paper IX. The ML has been formed by post-deposition annealing of the substrate, and as in previously reported studies of MePc’s on Au(111) (SnPc [58], NiPc [76], CoPc [59], FePc [76, 77], CuPc [78]), the molecules are found to be adsorbed
with the molecular plane parallel to the surface. The molecular unit cell is of square symmetry, as indicated in Fig. 7.9 (a), and molecules are placed with the benzene group of one molecule close to the N3 atom (see Fig. 6.4) in the neighbouring molecule, as observed on HOPG (see section 7.2.1).

The molecule-surface interaction has a significant influence on the ML formation, evidenced by the change in adsorption direction at the elbow sites of the surface reconstruction, as observed in Fig. 7.9 (b). This, together with the stable molecular adsorption and the less well-resolved imaging of the molecules as compared to the graphite substrate, indicates a significant molecule-surface interaction, stronger than in the case of H2Pc/HOPG.

7.3 Alkali doping of phthalocyanines

7.3.1 Rubidium doping of H2Pc monolayer on Au(111)

The structure of H2Pc monolayer adsorbed on Au(111) has been discussed in section 7.2.4. The STM data for this system is presented in paper IX, where also modifications induced by Rb doping is described.

Upon Rb doping, the molecular adsorption is significantly changed, and Rb-induced protrusions are observed on top of the molecular layer, as can be seen in Fig. 7.10. Doping results in a drastic alteration of the molecular adsorption unit cell. The undoped system is characterized by a unit cell of square symmetry, whereas an unit cell of hexagonal symmetry is observed for the co-adsorbed system, as indicated in Fig. 7.10 (a) and (b) respectively. Even though the molecule-surface interaction appears to be significant (as discussed in previous section), the intermolecular distances and interactions are considerably modified upon doping. In Fig. 7.10 schematic molecular models are added, displaying that the former arrangement, in which molecules in-
Figure 7.10: (a) ML of H$_2$Pc on Au(111). The molecules are adsorbed in a square unit cell with the molecular plane parallel to the surface. A molecular model from a single molecule calculation (paper I) is used to fit the STM image and white lines indicate the molecular adsorption unit cell. (-1.45 V, 0.17 nA, 10.4 nm x 10.4 nm). (b) Rb doped H$_2$Pc/Au(111). On top of the molecular layer Rb-induced bright protrusions are observed and the molecular adsorption unit cell is significantly altered, indicated by the schematic molecular models. (-2.62 V, 0.14 nA, 10.4 nm x 10.4 nm).

Interacted with benzene groups close to the aza-nitrogen atoms (N3, Fig. 6.4) in the neighbouring molecules, is altered and the benzene groups of adjacent molecules are closer to each other after doping. The Rb-induced bright protrusions are found to be aligned with the substrate reconstructed rows, indicating that the coupling to the underlying substrate is still significant.

7.3.2 Potassium doping of H$_2$Pc films

Multilayer films of H$_2$Pc, adsorbed on Al(110), have been doped with Potassium in increasing amount, up to 3.6 K atoms per molecule. The characteristics (i.e. electronic and geometrical structure) of the undoped film have already been described (see section 7.1/paper I and 7.2.3/paper VII). Upon K doping, significant changes are observed in both the XP and XA spectra, revealing modifications in the electronic and geometrical structure of the molecular film.

In previously reported studies of K doped Pc’s [9, 13, 14], the core-level spectra have been seen to be broadened and shifted upon doping. This is indeed the result also for K/H$_2$Pc, see Fig. 7.11. The spectral broadening may be ascribed to different effects. Our data are in-line with the observations by Giovanelli et al. [9] regarding K doped ZnPc, where different phases, due to adsorption of K atoms in different positions and stoichiometric ratio with respect to the molecules, have been found. In analogy with the study of ZnPc, we propose the presence of molecules with different additional charge, but also structural changes of the ordered molecular films, observed by XAS mea-
measurements (see below), may contribute to the spectral broadening. A charge transfer from the alkali to the molecule, evidenced by both valence and XA measurements, causes modifications of the core and valence levels. By a filling of initially empty states, the Fermi position is shifted in the density of states, resulting in observed binding energy shifts. For no doping level has intensity at the Fermi level been observed, demonstrating that there is no metallic phase for the K doses investigated here.

A filling of the previously empty LUMO level, by the alkali, is evident from the observation of a new feature in the valence spectra, see Fig. 7.12 (a). The filling of unoccupied levels by a charge donation results in a decreased intensity of the N1s XA threshold, as can be observed in Fig. 7.12. Modifications of other unoccupied levels are also observed. For the H2Pc film, the threshold feature (Fig. 7.12 (b)) has an asymmetric contribution at the low photon energy side, attributed to excitations from the N2 atoms (Fig. 6.4) as showed in Fig. 7.3 (c). After K doping, the asymmetry of the peak at threshold is no longer seen, indicating that the K doping affects significantly the N2 atoms.

The N1s XA spectra recorded in two experimental geometries (with the E-vector of the light parallel and perpendicular to the surface, respectively) are displayed in Fig. 7.12 (c) and (d). As previously stated, the charge donation results in a decrease of the π* features, at the threshold, seen in Fig. 7.12 (c). However, in the other experimental geometry, an intensity increase of the π* features relative to the σ* features is observed, indicating a change in the overall tilt angle of the molecules. This leads us to the conclusion that, upon K doping, the tilt angle of the molecular plane with respect to the the surface normal is increased.
Figure 7.12: K/H$_2$Pc/Al(110), with different K doses. (a) The low binding energy region of the valence band spectra, $h\nu = 130$ eV. The HOMO orbital are seen to be shifted upon doping, and an additional feature is observed at lower BE, due to a charge donation to the formerly unoccupied LUMO orbital. (b) N1s XAS recorded with the E vector of the light parallel to the surface, displaying the K induced changes to the $\pi^*$ features at threshold. (c) and (d) N1s XAS spectra measured with the E-vector of the light parallel and perpendicular to the surface, respectively.
7.4 Conclusions

The electronic and geometrical structure of the molecular H$_2$Pc and FePc films have been mapped. For both the FePc and H$_2$Pc, the excellent agreement between the experimental data and the calculations of a single molecule shows that molecules within the film interacts weakly, not disturbing the electronic states of the neighbouring molecules. In multilayers, H$_2$Pc and FePc are found to be oriented in a standing up or tilted orientation with respect to the surface. However, in monolayer coverage, the phthalocyanines studied here are found to be adsorbed with the molecular plane parallel to the surface, even though the adsorbate-substrate interactions are of different strength for the investigated systems. On the reactive Al(110) substrate, a strong, dissociative adsorption of H$_2$Pc is observed. The molecules are found to be oriented with the molecular plane parallel to the surface, but the molecular electronic structure (occupied and unoccupied levels) are strongly perturbed by the interaction with the substrate.

Although weaker molecule-surface interactions are found for the ZnPc/InSb(001), H$_2$Pc/Au(111) and Pc’s/HOPG systems, the substrate structure is clearly influencing the ML formation. In the case of Au(111), the molecular adsorption direction is found to change at the elbow sites of the substrate reconstruction (Fig. 7.9), evidencing how the surface plays a significant role for the formation of the ordered molecular arrangement.

Different molecular states have been resolved for H$_2$Pc/HOPG by bias dependent STM measurements and, due to the low perturbation of the substrate on the molecular orbitals, a good agreement between the experimental data and single molecule calculation is observed (see Fig. 7.5). For H$_2$Pc/Au(111), it has not been possible to resolve different states in the same way, most likely due to the stronger molecule-surface interaction. Even though the adsorbate-surface interaction is found to be weak for the Pc’s/HOPG, as suggested by the high molecular mobility and the possibility to image different molecular states, it is clear that the orientation of the densely-packed FePc islands are influenced by the substrate (Fig. 7.6). So, even if the molecule-surface interaction is found to be weak, the underlying surface structure is not negligible for the ML formation. For FePc/HOPG, the adsorbate-adsorbate interaction is found to be dominant over the adsorbate-substrate interaction and, as observed for several other systems [65], the dominating molecule-molecule interaction results in a molecular adsorption unit cell of FePc which is not commensurate with the underlying graphite lattice. This is observed in the STM measurements as a Moiré pattern, i.e. contrast modulation, very similar to the previously reported Moiré contrast for PdPc on HOPG [70]. The directions of the observed Moiré contrast modulation for FePc (see Fig. 7.6 (d)) and PdPc are however different. By comparing the two systems, it is clear that the central metal atom affects the molecular adsorption, since the molecular dimension are the same. The balance between the intermolecular and molecule-substrate
interactions is apparently influenced by the difference in metal ion, resulting in different adsorption parameters, and hence, Moiré patterns.

The effect of the metal centre on the molecular electronic structure of the FePc, PdPc, and H₂Pc, is also evident by studying a single molecule in the STM image. For H₂Pc, without central metal atom, a depression is observed in the molecular centre. For FePc, the contribution from the Fe3d orbitals of the metal center to the highest occupied and lowest unoccupied molecular levels is dominating, while for PdPc the depression observed in the molecular centre indicates that there is no contribution from the metal atom to the HOMO and LUMO orbitals [70]. Also for ZnPc it is observed that the metal centre does not contribute to the HOMO, confirming the previously reported data by Liao et al. [79]. As stated above, the studied surfaces clearly influences the Pc ML formation, this is also the case for ZnPc/InSb(001), since it is observed that ZnPc adsorb exclusively on the In substrate rows.

In the presented studies, for molecules in ML or in films, a weak intermolecular interaction, of van der Waals type, is suggested. However, as a result of the delicate balance between intermolecular and molecule-substrate interactions in the various systems, neighbouring molecules are found to be arranged differently as compared to each other on different surfaces. For ZnPc/InSb(001), it is found that the benzene groups of neighbouring molecules are close together, as also observed for other Pc’s on the InSb(001) surface [60, 61, 62, 71, 72]. On HOPG and Au(111) an arrangement with benzene groups close to the aza-bridging nitrogen (see Fig. 6.4) in the neighbouring molecule is observed, as also reported for other Pc’s on the same substrates [59, 70, 77]. But, as observed for the Rb/H₂Pc/Au(111) system, the intermolecular interaction and molecular arrangement are found to be significantly perturbed by the alkali doping. In fact, for the co-adsorbed system the balance between adsorbate-substrate and inter-adsorbate interactions result in a new molecular configuration, with an intermolecular arrangement somewhat resembling the one observed for Pc/InSb(001).

A geometrical rearrangement of the molecules is also the result of K doping of H₂Pc films. It is observed that the previously (almost) standing molecules are tilted, decreasing their tilt angle with respect to the surface by the K dosing. But, not only the geometrical molecular structure is modified by the alkali, also the electronic structure is strongly altered. As a result of the doping, previously empty molecular orbitals are filled by a charge donation from the alkali, displaying a charge acceptance of the H₂Pc. The filling of previously empty orbitals is observed both in the valence and XA spectra of K/H₂Pc, but is also evident from the decreased C1s shake-up intensity, which significantly contributes instead to the intensity of the undoped H₂Pc C1s spectrum.
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