Electronic and Geometrical Structure of Phthalocyanines on Surfaces

An Electron Spectroscopy and Scanning Tunneling Microscopy Study

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Abstract

Core- and Valence Photoelectron Spectroscopy (PES), X-ray- and Ultraviolet-Visible Absorption Spectroscopy (XAS and UV-Vis), Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) calculations are used to study the electronic and geometrical structure of a class of macro-cyclic molecules, Phthalocyanines (Pc), on surfaces. These molecules are widely studied due to their application in many different fields.

Multilayer and monolayer coverages of Iron Phthalocyanine (FePc) and metal-free Phthalocyanine (H_Pc) deposited on different surfaces are investigated in order to get insight in the electronic and geometrical structure of the obtained overlayers, of crucial importance for the understanding of the film functionality. Sublimation of molecular thick films on Si(100) and on conducting glass results in films with molecules mainly oriented with their molecular plane orthogonal to the surface. Ex-situ deposited H_Pc films on conductive glass show different molecular orientation and morphology with respect to the vacuum sublimated films.

We study the monolayer adsorption structure of FePc and H_Pc and compare our results with other Pc’s adsorbed on graphite. We find that the molecular unit cell and the superstructure is characteristic for each Pc adsorbed on graphite, even if the geometrical size of the compared molecules is the same. The PEs- and XA- spectra of FePc on graphite are essentially identical for the mono- and multilayer preparations, evidencing weak intermolecular and molecular-substrate interactions of van der Waals nature.

Furthermore, we characterize Pc’s on InSb (001)-(8x2). The substrate In rows are observed to be the adsorption site for Pc’s. We find that the growth of the two-dimensional islands of FePc is prolonged in the [-110] direction, in contrast to ZnPc adsorbed on the same substrate at room temperature. We interpret this result as an indication that the adsorption is controlled by the substrate corrugation observed at 70 K.

Keywords: PhotoElectron Spectroscopy (PES), X-ray Absorption Spectroscopy (XAS), UltraViolet-Visible absorption spectroscopy (UV-Vis), Scanning Tunneling Microscopy (STM), Phthalocyanine (Pc), Iron Phthalocyanine (FePc), metal-free Phthalocyanine (H2Pc), Zinc Phthalocyanine (ZnPc), Graphite (HOPG), Indium Antimony (InSb), Surface science

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Tanke nummer åtte: (inspirert av at jeg nettopp har bladd i National Geographic): An explorer is someone who goes to the edge of knowledge and brings back something new. Det er dit vi skal. The edge of knowledge. Dit og ingen andre steder.

‘Erland Loe ’L’

Till min familj, släkt och vänner. Tack för ert stöd. Till mamma som alltid trott på mig och stöttat mig och till pappa som tyvärr gick bort allt för tidigt, du finns alltid kvar i mina tankar. Og til den norske familie som mottatt meg så varmt i deres felleskap og till deg Mette, jag elsker deg.
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. Reprints were made with permission from the publishers.

I  The electronic structure of iron phthalocyanine probed by means of PES, XAS and DFT calculations

II  Electronic Structure of a vapor-deposited metal-free phthalocyanine thin film

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

IV  The adsorption of Iron Phthalocyanine on Graphite: a Scanning Tunnelling Microscopy Study
    (In manuscript)
V Electron spectroscopy study of the initial stages of growth of iron phthalocyanine on graphite
C. Isvoranu, J. Åhlund, E. Ataman, N. Mårtensson, J. N. Andersen, C. Puglia and J. Schnadt
(In manuscript)

VI A STM study of Metal-free Phthalocyanine monolayer structures on Graphite
K. Nilson, J. Åhlund, B. Brena, E. Göthelid, J. Schiessling, N. Mårtensson and C. Puglia
(Submitted)

VII STM and XPS characterization of Zinc Phthalocyanine on InSb(001)
(In manuscript)

VIII STM investigation of FePc on InSb(001)c8x2
(In manuscript)
Comments on my own participation

Science often requires teamwork, and the resulting gained knowledge is an effort of many people’s ideas and work. In paper I, IV and VIII I am the main responsible for the experiments, data analysis and writing. The STM work in paper VII are done by our collaborators Pål Palmgren and Mats Göthelid at Materials Physics, MAP, ICT, Royal Institute of Technology (KTH). The theoretical calculations are performed by our collaborators Barbara Brena, Mats Nyberg and Yi Luo, Theoretical Chemistry, Royal Institute of Technology (KTH) Stockholm and Department of Physics Uppsala.
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1. Populärvetenskaplig sammanfattning

1.1 Vad kan molekyler på ytor användas till?


Järn-Pc (FePc) är en viktig del i en del av en katalysatorprocess som används för att bland annat oxidera kolkedjor. Dessa reaktioner är viktiga i många industriella tillämpningar framför allt används de inom tillverkningen av plaster, mediciner med mera. Pc's och liknande molekyler är potentiella kandidater till att användas som katalysatorer i bränsleceller där en kemisk reaktion producerar elektrisk energi. Bränslecellen fungerar ungefär som ett batteri som tankas med en reaktant, vilket kan till exempel vara väte eller etanol.


1.2 Att mäta: Lantmätare och geologer, avstånd och energi

När lantmätaren ritar en karta så måste hon mäta hur höjdskillnaden är mellan två punkter, hur långt det är mellan de två punktarna, vilken
vinkel det är i förhållande till en sjö och så vidare. Genom att markera alla avstånd, vinklar och höjdskillnader i förhållande till varandra växer en karta fram. Den färdigritade kartan kan sedan användas till många ting, till exempel för att ge ut Motormännens Europa-vägatlas eller Svenljunga orienteringsklubbs karta, Ånebladet. Inom ytfysik/ytkemi finns liknande frågeställningar, men istället för mätutrustning som mäter avstånd i kilometer så används instrument som ger avstånd i Ångström (Å). 1 Å är 0.0000000001 m och är en passande enhet när man vill mäta avstånd på atomär nivå. Det finns tekniker för att mäta längder, höjder och vinklar i Å. En sådan teknik kallas sveptunnelmikroskopi (STM).


Figure 1.1: Kartan till vänster är en del av Ånebladet (publicerad med tillåtelse av Svenljunga orienteringsklubb). Ekvidistansen är 5 m vilket gör att det är ca 100 m i höjdskillnad mellan högsta toppen och en punkt längst ner i högra hörnet av kartan. Området är ungefär 1800x1800 m. Bilden till höger är en STM bild av ett ca. 95x95 nm stort område av grafit som är täckt av högar av FePc molekyler. Höjdskillnaden på bilden är ca 4nm (vit=högt, svart=lågt).
1.2.1 STM: Atomär kartproduktion

STM bygger på att en spets som befinner sig några Å över den yta som är provet. En spänning läggs mellan spetsen och ytan och strömmen mätts. Strömmen består av elektroner som förflyttar sig mellan ytan och spetsen genom ett kvantmekaniskt fenomen som kallas för tunnling. Om denna ström sätts till ett specifikt värde måste spetsen gå närmare eller längre ifrån ytan, för att just den strömmen ska behållas konstant. Genom att sedan flytta spetsen långs ytan, kan en kurva som beskriver spetsens höjdposition under förflyttningen erhållas. På så sätt fås en karta med linjer som påminner om höjdkurvorna på till exempel Ånekartan (Se Fig. 1.1). Kartan som STM:et producerar ger en bild av hur elektrontätheten är på ytan vilket kan översättas till hur atomerna är placerade på ytan.

1.2.2 PES: Hur hårt är en elektron fastklistrad?

PES är en spektroskopisk teknik där fotoner (ljus) med en bestämd energi (våglängd) används. Fotonerna skickas in i provet och slår då ut elektroner i en process som kallas den photoelektriska effekten (Fig. 1.2). Rörelseenergin i de fria elektronerna mäts. Varje atom häller olika hårt i sina elektroner (innerenerginivån är unika för varje grundämne), vilket innebär att det är möjligt att se vilket ämne (atomslag) som provet innehåller. Jämför med en kloss som är fastlimmad i en vägg. I vår modell har vi två atomslag/energnivåer: limstift och superlim. Om det går lätt att dra bort klossen så är det limstiftatomen som håller fast klossen (elektronen) och om det är tungt att dra bort klossen är det superlimatomen som håller fast klossen (Fig. 1.2). Om det inte går att dra bort klossen används för lite energi. Atomerna håller även olika hårt i elektronerna beroende på vilka andra atomer som de har i närheten av sig (s.k. kemiskt skift), vilket gör att man även kan dra slutsatser om vilka atomer som sitter bredvid varandra.

1.2.3 XAS: elektronbasket

I XAS belyses provet med ljus med olika energi. Ju kortare våglängd ljuset har, desto mer energi finns det i ljuset. Resultatet av mätningen visar vilka våglängder som absorberats av till exempel en atom. Våglängderna som absorberats motsvarar den energi som krävs för att atomens elektroner i en närmå insida energinivå ska kunna hoppa upp till en valensenerginivå (energinivån längst från kärnan) där det finns plats för elektronen, det vill säga en energinivå som inte är några av elektronen. En sådan energinivå kallas o-ockuperad. Om inte energin räcker till för att elektronen ska kunna hoppa hela vägen upp till en sådan nivå, så hoppar inte elektronen alls. Genom specifika regler, som kallas urvalsregler, kan man genom att ändra provets orientering i förhållande till ljuset
vinkelrät mot ytans indiumrader. En sådan utbredning ses inte i fallet ZnPc och en möjlig förklaring till skillnaden är att provet är kylt då FePc undersöks.

Figure 1.3: Schematisk skiss över vinkelberoende i XAS. Basketkorgen i övre delen av bilden vrids i förhållande till streckgubben. Streckgubben representerar fotonen (ljuset) och basketkorgen provets orientering i förhållande till ljuset. Förhållandet mellan basketkorgen och ljuset avgör om ljuset kan excitera elektroner eller inte. Förhållandet visas av stapeldiagrammet i mitten. En duktig basketstreckgubbe sätter 10 utav 10 bollar i en korg där öppningen är parallell med golvet, men bara fem utav tio bollar då korgen vridit sig 45°. Inga bollar eller fotoner kan exciteras om basketkorgen/orbitalen är vinkelrät mot fotonen.
2. Introduction

The field of surface science has emerged over some decades and provide techniques that can be used to study a variety of systems in different fields, such as in heterogeneous catalysis, nano-science, biomimetics, chemistry, magnetism and so forth. With the techniques used in surface science it is possible to probe systems at an atomic/molecular and electronic level as well as to monitor growth of atoms and molecules on surfaces. Using Scanning Tunneling Microscopy (STM), PhotoElectron Spectroscopy (PES) and absorption spectroscopies (X-ray Absorption Spectroscopy, (XAS) and UltraViolet-Visible adsorption spectroscopy (UV-Vis)) we have studied the properties of phthalocyanine (Pc) molecules and their interaction with different surfaces.

Pc’s and porphyrins are macro-cyclic molecules. Porphyrins have a wide variety of roles in nature such as oxygen transport (in Myoglobin and Haemoglobin [1]), electron transfer (cytochromes [2]), oxidation catalysts (cytocrome p450 [2]) and photosynthesis [2]. Thus Pc’s and porphyrines are good candidates for biomimetic applications. The broad range of functionality makes these macro-cyclic compounds used/candidates for use in an ever-expanding range of fields such as pigments, solar cells, gas and radiation sensors, electronic devices, medical applications, fuel cells and for catalysis.

A catalyst is a substance/material that speeds up a reaction and/or makes the reaction possible at lower temperatures or pressures. It is common to distinguish between homogenous and heterogenous catalysis. In homogenous catalysis the catalyst is in the same medium as the reactants and products. one of the big disadvantages in homogeneous catalysis is then the need of separation stages in order to extract the product from the catalyst. This is overcome in heterogeneous catalysis, since the catalyst is a surface or is immobilized on a surface. Aerobic oxidations of hydrocarbons to alcohols and epoxidation reactions, are catalytic reactions, where macrocycle compounds play an important role [3, 4, 5, 6]. These kinds of oxidation reactions can be used in a variety of applications ranging from fabrication of plastics to medicine/drug synthesis, testifying the importance of detailed studies of such molecules.

It has been shown that the functionality of macro-cycle compounds depends on the geometrical and electronical structure of the molecules on surfaces and in films [3, 7, 8, 9, 10, 11, 12] and of course on the central
metal of the metal-Pc [13]. Moreover, it has been suggested that macrocyclic compounds are a possible candidates for fuel cell applications for two reasons: firstly, since in the future they might replace the rare and expensive cathodic Pt catalyst [14, 15, 16, 17, 18, 19, 20, 21, 22] and, secondly, they might be used as anode additives to improve the CO tolerance of the standard Pt catalyst [23, 24].

Creating systems that model certain aspects of more complex nature is a key concept in physics. In the model the number of parameters is reduced in order to focus on few central aspects important to the understanding of the more complex system. The systems studied here are regarded as model systems in order to gain information about the electronic and geometrical structure of Pc’s in films and adsorbed on surfaces with particular interest in the characterization of the molecule-molecule and molecule-surface interactions. The information presented here can give insight in possible applications of Pc’s and improvement of already existing applications. A deeper understanding of the electronic and geometrical structures of Pc’s and porphyrines on surfaces and in films are therefore required in order to improve the turn-over rate in catalysis [7].
3. Concepts in spectroscopy

3.1 Introduction

A number of different spectroscopic techniques, which provide complementary information about the geometrical and the electronic structure of the studied system are used in this work. In core and valence Photoelectron Spectroscopy (PES) the occupied electronic levels are studied whereas X-ray Absorption Spectroscopy (XAS) and Ultra Violet Visible Absorption Spectroscopy (UV-Vis) use absorption of the light to probe the unoccupied density of states. A schematic one-electron picture of the different techniques is showed in Fig. 3.1 and a more detailed description of the techniques will follow in the next sections.

![Figure 3.1: A schematic one-electron picture of core and valence level PE, XA and UV-Vis processes. The black lines represent quantum energy states in a system, such as an atom or molecule. The picture is a one-dimensional graph having the energy (E) scale as a y-component. The wiggling arrows represent the light (hv). The black filled circles represent electrons and the unfilled circles represent missing electrons.](image-url)
3.2 Fermi’s golden rule

All of the above-mentioned spectroscopic techniques can be described by Fermi’s golden rule (Eq. 3.1) that provides information about the possible transitions and their relative intensity [25]:

\[ w \propto \sum_{s,k} |<f_s|\mu|i_k>|^2 \delta(E_f - E_i - h\nu). \]  

(3.1)

It is an expression of the probability, \( w \), of all transitions from initial states \( |i_k> \), (with \( k = 0, 1, 2, \ldots \)), to final states \( |f_s> \), (with \( s = 0, 1, 2, \ldots \)), when an atom or a molecule interact with electromagnetic radiation, described by the interaction operator \( \mu \). A delta function \( \delta(E_f - E_i - h\nu) \) gives the conditions for conservation of energy. The final state energy, \( E_f \), must be equal to the difference between the photon energy \( (h\nu) \) and the initial state energy, \( E_i \), in order for the function to be non-zero.

As shown in Fig. 3.1 the final states are different for the spectroscopic techniques used in this thesis. For PES the final state can be described by the photoelectron and the remaining ionized atom or molecule. For XAS and UV-Vis instead, the final state is an overall neutral atom or molecule with an excited electron.

The interaction operator describes the coupling between the incident photon and electron to be excited and is related to the so called dipole approximation. According to the dipole approximation the wavelength of the light used for a one-electron excitation has to be much larger than the radius of the atomic or molecular excited shell. For linear polarized light it is convenient to express the interaction operator as the scalar product between the unit \( \mathbf{e} \)-vector along the direction of the electric field \( \mathbf{E} \) of the radiation and the linear momentum operator \( \mathbf{p} \) as in Eq. 3.2:

\[ \mu = \mathbf{e} \cdot \mathbf{p}. \]  

(3.2)

This has important consequences for the polarization dependence of the transition intensities as it will be discussed in more details in the sections dealing with angle resolved PES (3.4.6) and the angle dependence in XAS (3.5.2).

3.3 The equivalent core- or Z+1 approximation

The equivalent core approximation is a method used to obtain information of the total energy of the core-ionized state [26]. According to this approximation the effect of the core hole on the valence electrons is the same as if the nuclear charge is increased by one, i.e. \( (Z+1) \). This is justified by the fact that the core orbitals have much smaller radius than the valence orbitals, e.g. the core electrons are localized inside the valence
electrons. This extra charge makes the valence levels above the core hole contract in order to adjust to the new potential.

3.4 Photoelectron spectroscopy

In PES [27] when photons with sufficiently high energy (X-rays\(^1\) or ultra-violet radiation\(^2\)) hit a sample electrons (called photoelectrons) are ejected from the sample. This process is called photoelectric effect, described by Albert Einstein in 1905 [28]. The conservation of energy implies that by knowing the photon energy \(h\nu\) and by measuring the kinetic energy of the photoemitted electron \(E_k\) the binding energy \(E_B\) of the electron can be calculated by (Eq. 3.3):

\[
E_B = h\nu - E_k - \phi.
\]  

\(E_B\) is the target of investigation and referred to the Fermi level. \(h\nu\) is the energy of the incoming monochromatic light that carries a momentum. \(E_k\) represents the kinetic energy of the electrons, emitted from the sample (and the energy measured by the spectrometer). \(\phi\) is the work function (the energy difference between the vacuum level, \(E_{\text{vacuum}}\), and the Fermi level, \(E_F\)).

Core level PES is a chemical specific technique since all elements in the periodic table have energetically well separated core levels, which will give distinct peaks in a core level PES spectrum. This means that the energy position of a peak is element specific. The intensity of the photoemission features is described by the ionization cross-section.

3.4.1 Ionization cross-section

PES can be used for quantitative analysis taking in consideration that the intensity of a peak depends on the concentration of that particular element in the sample. However, for quantitative analyses, comparing different elements, the cross-section must be taken into consideration. In PES the partial ionization cross section is used. It gives information about the probability of ionization from the different atomic shells of an element, giving information about the relative intensity of peaks in a PE spectrum [27]. The partial cross section is defined as the probability of a transition between an initial and final state under investigation and it can be considered as a modification of Fermi’s golden rule (Eq. 3.1), where the final state can be represented by the outgoing electron. Partial cross-

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\(^1\)The range of soft X-ray radiation is from 100 eV to about 1000 eV, which makes the Al K\(\alpha\) radiation a borderline case of hard X-ray radiation.

\(^2\)The UV regime ranges from a couple of eV to about 100 eV. (Visible light is between 1.8-3.1 eV)
section values for the different atomic electronic levels are given [29, 30], with respect to the excitation energy (photon energy) and they can be used when, for instance, comparing the PE Fe, C and N intensity ratio of the FePc molecule in order to study the stoichiometry of a film deposited on a substrate. However, the relative intensities in a PE spectrum also depend on the electron escape depth and diffraction effects.

3.4.2 Koopmans’ theorem

Koopmans’ theorem [27] is a first approximation used to estimate a binding energy for the photoemitted electron, by relating the kinetic energy of the emitted photoelectron to the initial state binding energy of the system, according to Eq. 3.3. The binding energy, $E_B$, of an electronic state in an N-electron system can be described by the Schrödinger equation as in Eq. 3.4:

$$H_N|i> = E_N|i>,$$

where $H_N$ is the N-electron Hamiltonian operator, $|i>$ is the eigenstate for the N-electron system and $E_N$ is its energy eigenvalue. $|i>$ can further be separated into the initial state wave function $\phi_i(1)$ of the electron which will be photoemitted and the wavefunction of the remaining N-1 electrons ($N - 1_{\text{remaining}}$) as in Eq. 3.5,

$$|i> = |\phi_i(1)> |N - 1_{\text{remaining}}>.$$

The final state, after the ionization, is described by the emitted (free) photoelectron and the remaining N-1 electrons. In Koopmans’ theorem these remaining orbitals in the final state of the atom or molecules are regarded as frozen, $N - 1_{\text{frozen}}$, i.e. the remaining orbitals are in the same state as in the initial state, thus are not effected by the photoemission. Within this model the binding energy of the photoemitted electron would be expressed by only one line in the PE spectrum at an energy $\epsilon_B$ called Koopmans’ energy (see Fig. 3.2).

3.4.3 Relaxed final state in PES

Koopmans’ theorem does not take relaxation of final states upon photoionization into account [27]. In reality the electrons of the ionized system reacts to the new potential of the core hole and relax as schematically illustrated in Fig. 3.2. The relaxation processes include both contraction of the atomic orbitals and, for solid or molecular systems, charge transfer to the core hole site (or polarization of the surrounding system) to minimize the energy of the system [26]. The relaxation will affect the value of the binding energy of the photoemitted electron $E_B$, which is
Koopmans' theorem, The frozen orbital approximation

\[ |\psi_i\rangle = |\psi_{i-1}\rangle = |\psi_0\rangle \]

Energy level diagram

Final state with relaxed valence orbitals

The sudden approximation

\[ |\psi_i\rangle = |\psi_{i-1}\rangle = |\psi_0\rangle \]

PES spectrum

Figure 3.2: A schematic illustration of different approximation models in PES. At the left: the one dimensional energy diagram is present as an illustration of the eigenvalue of the eigenstate represented by the bra and ket notation. At the right a sketch illustrating the effect of the relaxation in binding energy and number of peaks appearing. For the sudden approximation one shake-up and one shake-off state is illustrated. For a discussion of the line shape of the features see section 3.7.
more properly expressed as:

\[ E_B = \epsilon_B + E_{\text{relax}} + E_{\text{cor}}, \]  

(3.6)

where an energy relaxation term \( E_{\text{relax}} \) and an energy correlation term \( E_{\text{cor}} \) are added to the Koopmans' energy \( \epsilon_B \). The \( E_{\text{relax}} \) term takes into account the relaxation effects whereas the \( E_{\text{cor}} \) term has to be included for taking care of the electron correlation effects.

3.4.4 The sudden approximation, shake-up and shake-off effects in PES

The relaxed final state discussed above is a special case concerning the \( E_B \) of the main line of core level PES. The relaxation is dependent upon the kinetic energy of the photoelectron. If the energy is close to the ionization threshold the time scale for the ionization event is about \( 10^{-15} \) s and the valence electrons can rearrange to the new core hole potential during the photoemission event. This process is called adiabatic. If the electron is emitted using higher energies, such as X-rays, the time scale for the emission event is about \( 10^{-17} \) s and the valence electrons have no time to readjust to the new core hole potential under the ionization process. The process is then regarded as sudden.

\[ |N - 1_{\text{remaining}} \rangle = \sum_s <f_s|N - 1_{\text{remaining}}>|f_s>, \]  

(3.7)

where \( s \) is a running index, \( |f_s\rangle \) are the eigenstates of \( H_{N-1} \) with \( E_s \) eigenvalues. Every non-vanishing overlap \( <f_s|N - 1_{\text{remaining}}\rangle \neq 0 \).
between the eigenstates $|f_s>$ and the $|N-1>$ state of the remaining N-1 electrons after ionization will contribute to the spectra (see Fig. 3.3) with structures at energy position corresponding to the eigenvalues $E_s$. The eigenstate $|f_0>$ with the lowest energy eigenvalue $E_0$ corresponds to the most relaxed final state, usually the mainline in the PE spectrum. The $E_1, E_2, \ldots$ eigenvalues represent the energy position of the satellites (called shake-up or shake-off) seen at higher binding energies than the mainline. The shake-up can be regarded as a final state excitation when a valence electron is excited to a bound state, whereas a shake-off transition is an excitation of a valence electron into a state above the vacuum level.

The relaxation energy introduced in Eq. 3.6 then corresponds to the energy difference between the Koopmans’ energy and the binding energy of the main line. It is important to note that the main line will appear at lower binding energy than the Koopmans’ energy. According to a sum-rule the Koopmans’ energy represents the center of gravity of all photoemission features seen in the PE spectrum [32] (see Fig. 3.2). The sum-rule can be understood by examining figure 3.3. The initial state and final states will occupy the same area (considering there is an infinite number of final states, and not just the three depicted in the image), thus have the same center of gravity.

3.4.5 Chemical shift and final state effects in core level PES

Even if core electrons do not take part in the chemical bonding, as the valence electrons do, they are sensitive to the chemical environment that, for example, differs due to neighboring atoms, molecules or surface. This will cause a change in the core level binding energy, called “chemical shift”. When valence electrons take part in chemical bonding they change the charge distribution of the atom, which leads to chemical shifts. From the chemical shifts information about the electronic structure, the geometrical structure and the chemical stability of the system can be derived. The binding energy of a PE peak is a result of initial and final state effects, (see section 3.4.3). Due to relaxation effects the orbitals of the ionized atom are modified. For molecular or solid systems core hole screening can occur via charge transfer to the core hole site or via polarization of the surrounding molecules [33].

3.4.6 Photoelectron angular dependence in PES

The photoelectron intensity angular dependence in PES is seen in both core and valence level spectroscopy [34]. The photoemission angle dependence can be understood by examining the Fermi’s golden rule expression. The probability of a transition within the dipole approximation is given by:
This matrix element has to be non-zero to contribute to the PE spectrum. The final state in valence PES can be regarded as the emitted electron, specified by its kinetic energy and momentum. The initial state is given by the particular orbital to be ionized (according to Eq. 3.5), $e$ is the polarization unit vector and $p$ is the linear momentum operator. For a given polarization of the radiation, excitations from an initial state are only allowed to final states of particular symmetry, if the conditions in Eq. 3.8 have to be fulfilled. Allowed transitions are those that change angular momentum by $\pm 1$ due to conservation of angular momentum. Thus, the symmetry of the final states (the outgoing electrons) is expressed by the initial state and the direction of the light polarization $e$. As consequence of this, knowing the symmetry of the initial state and the polarization of the radiation it is possible to predict which emission angles of the photoelectron are allowed or forbidden. Then, considering the angle resolved valence data obtained for a certain system, it is possible to get information about the molecular orientation on a surface. For example: The $E$-vector has $p$ symmetry for linear-polarized light, which is the case in our experiments. For a core level with $s$ symmetry the photoelectron is mainly emitted as a $p$ wave in the direction of the $E$-vector.

3.5 X-ray Absorption Spectroscopy

3.5.1 Introduction

XAS probes the atom specific unoccupied valence states in presence of a core hole [32]. The photon energy is scanned in order to excite core electrons to unoccupied valence levels. The intensity of the transition is cross-section dependent and the transitions are governed by the dipole selection rules, thus only the dipole allowed transitions ($\Delta l = \pm 1$) are contributing to the spectra (as described by 3.1). Due to the created localized core hole the valence state adjust to the new potential by contraction [32]. This implies that XAS probes the partial density of states at the core-excited site in the system.

3.5.2 Angle dependence in XAS

In the case of polarized light the dipole operator gives rise to an angular dependence of the cross section, permitting to probe the molecular orientation of molecular films or adsorbates on surfaces. XA intensity is angle

---

< $f|e \cdot p|i > \neq 0$, (3.8)
dependent [32]. Fermi’s golden rule 3.1 can be applied in order to examine the XA peak intensity angle dependence, which can be evaluated according to symmetry arguments.

Here a simplified model determining the orientation of molecules on surfaces using $K$-edge XAS is presented. According to this model, in order to determine the geometrical orientation of a molecule with respect to the surface the intensity relation between the $\pi^*$ and $\sigma^*$ resonances of the XA spectra is compared. In $K$-shell XAS the initial state is an $s$ electronic state and the dipole transition promote excitations to $p$ components of $\pi$ and $\sigma$ final states. The intensity of the transition is obtained from the XA cross-section:

$$w \propto |\mathbf{e} \cdot <f|\mathbf{p}|i>|^2,$$

(3.9)

assuming linear polarized light in the direction of the $\mathbf{e}$ vector. Then, the polarization dependence of the matrix element can be expressed by:

$$w \propto \cos^2 \delta,$$

(3.10)

where $\delta$ is the angle between the polarization unit vector $\mathbf{e}$ and the direction of the maximum amplitude of the final state orbital. Take the $K$-shell XAS of a molecule on a surface as an example: The dipole transition promotes excitations to $p$ components of $\pi$ and $\sigma$ final states. The direction of the $\mathbf{E}$-vector with respect to the substrate surface is known in the experimental set-up and therefore it is possible to further assign the variations in intensity according to Eq. 3.10 to the molecular orientation with respect to the surface. For maximum intensity of $\pi^*$ zero intensity of $\sigma^*$ is expected in this (hypothetic, ideal) example, according to Fig. 3.4.

In the presented studies of molecular FePc- and a H$_2$Pc films density functional theory calculations simulating N 1s XA spectra are used to assign the atomic and symmetry related intensity contributions to the experimental spectra, pinning then the spectral contribution of the molecules on the surface for different sample orientations with respect to the $\mathbf{E}$-vector.

### 3.5.3 Monitoring XAS

The Auger electron decay process can be used to monitor the initial to final state transition in XAS. The Coulomb interaction between the core hole and the valence state leads to a decay in which the core vacancy is filled with a valence electron within $10^{-15}$s. Due to energy conservation the transition leads to the emission of a photon (florescence decay) or an electron (Auger decay) from the system.
Figure 3.4: Angle dependence of a molecule with a $\pi^*$ and $\sigma^*$-orbital (symbolized by there atomic contributions). In the left bottom figure $\pi^*$ is parallel with the E-vector and $\sigma^*$ is orthogonal. Thus the spectrum, illustrated in the top left figure, has maximum intensity for $\pi^*$ and no intensity for $\sigma^*$. In the middle figure both $\pi^*$ and $\sigma^*$ have equal intensity. At the right the $\sigma^*$ is dominating the spectrum. For a discussion of the line shape of the features see section 3.7.

The XA process can be monitored using total, partial or Auger yield mode. In total yield all electrons (not only Auger electrons, but also photoelectrons etc.) that hit the detector are registered. In partial yield, a retarding voltage in front of the XAS detector is set in order to cut-off low kinetic energy electrons. The voltage is set slightly below the energy of the Auger transition of interest. In Auger yield a hemispherical analyzer (such as a Scienta spectrometer) is used in an energy window (with a high and a low kinetic energy cut-off) defined by the energy of the Auger electrons expected for the defined transitions. Total yield measurements are most bulk sensitive, whereas partial and Auger yield are more surface sensitive.

3.6 Ultra-Violet Visible optical absorption spectroscopy

In UV-Vis spectroscopy light is used to populate the unoccupied electronic states of the system, thus the dipole selection rules are also here present (as the photon has an angular momentum of one), but unlike XAS, where the transition is from a core level to a unoccupied valence, the transitions measured here are between valence levels [35].

The basic principle for this type of spectroscopy is to irradiate the sample with a continuum spectrum of light with intensity ($I_0$) in the ultra-violet and visible region. The absorption of light ($I$), depends on the absorption coefficient ($u$) and the thickness of the sample ($x$), and it is a function of the wave length ($\lambda$). From the ration $I/I_0$, $u$ can be
obtained. An expression of the probability of an electronic transition at a certain $\lambda$ is given in Eq. 3.11:

$$\frac{I}{I_0} = e^{-ux}. \quad (3.11)$$

The UV-Vis spectrum can be used as a fingerprint tool, detecting the crystalline forms of the molecular films and determining the thickness of the same.

### 3.7 Line shape of spectral features

There are different contributions to the shape of a spectral line, such as lifetime, vibrations, inelastic losses and experimental broadening [36, 25]. The lifetime, of a core hole state, such that created during a PE or XA process, is typically in the femtosecond regime. Due to the decaying nature of the excited state the finite lifetime$^4$ of the core hole introduces a broadening of the spectral line described by a Lorentzian line shape [25]. As an example, the broader line shape of the $Fe2p_{1/2}$ with respect to the $Fe2p_{3/2}$ component in PES and XAS can be related to the shorter lifetime of the $Fe2p_{1/2}$ core hole state [37]. The core hole lifetime can be used to probe charge transfer processes in a femtosecond time scale [38].

The spectra can be further broadened by the presence of vibrational features [33], which often are the dominant contribution to the line shape. As an example the asymmetric line shape of C1s in benzene is largely due to vibrational features [39]. Often for adsorbates on surfaces the frustrated rotation and vibration modes give rise to new vibrational modes, which introduce a small broadening of the line with respect to a core line of gas phase molecules.

The experimental set-up, such as monochromator, slits, pass energy etc. give rise to experimental broadening, due to the finite instrumental resolution [40]. The experimental broadening contributes to the line shape in the form of a Gaussian function [33].

For solid samples a background is also present in the spectrum, which is due to ionization of core and valence levels and Auger transitions. These electrons have undergone several inelastic processes during their way through the material and will therefore be seen as energy broadening or energy loss tails [33].

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$^4$For tabulated values of life times see for example ref. [37].
4. Scanning Tunneling Microscopy

4.1 Introduction

Scanning Tunneling Microscopy (STM) [41, 42, 43, 44] was invented in 1982 [45]. It is a local probe that provides real space images of surfaces with resolution on the atomic scale. In the ideal case a monoatomic metallic tip is scanned over the sample surface at a distance of a few Ångströms (Å). STM is based on the electron tunneling (through a barrier) between a conductive sample and the atomically sharp tip.

4.2 Quantum mechanical electron tunneling

In the framework of quantum theory it is possible for a particle with energy $E$ to tunnel through a barrier of potential/energy $\phi$ ($\phi > E$) [25]. In the case of STM the particle is an electron, which can either tunnel from the sample to the tip or from the tip to the sample, depending on the bias voltage applied between the tip and surface. In this way, occupied and unoccupied states of the sample near the Fermi edge can be probed by STM. Since the technique is depending on the tunneling of electrons from the tip to the surface (or vice versa) the surface and the tip have to be conducting. Therefore STM can only be applied to metals and semiconductor materials, not to insulators.

A detailed treatment of the tunneling event requires an accurate description of the electronic states of the tip and substrate. Since the tunneling current can be evaluated from the overlap of the decaying wave functions of the tip and of the sample in the classical forbidden region, the knowledge of the electron potential within the barrier and of the wave function tails of the tunneling electron within the barrier would be necessary (see Fig. 4.1). The major difficulties in reaching such a detailed description are probably due to the poor characterization of the tip (of unknown shape and then to the wave function symmetry describing it) and of the unknown interaction between the surface and tip. This interaction can in some cases be so strong that the formulation of the tunneling current would require the description of tip, vacuum barrier and substrate as one system instead of weakly interacting separate systems [43]. Due to the enormous difficulties for having such a detailed
Figure 4.1: A schematic illustration of the wave function overlap in the classical forbidden region between two metal electrodes. A positive bias voltage $U$ is applied to metal (2) and the barrier height $\phi_1$ and $\phi_2$ are indicated. The tunneling occurs from the first metal (1) to the second (2) separated by a distance $d$. The grey area indicates occupied states.

description, different models and approximations have been introduced to explain and describe the physics of STM.

In order to simply describe the tunneling current through a potential barrier (classical forbidden region) we can consider the one-dimensional tunneling between two metal electrodes separated by a vacuum potential barrier, i.e. metal-vacuum-metal system. In early 1960’s Bardeen [46] described the transition probability for an electron through such a barrier neglecting the interaction between the two metals, assumed very weak [44, 41]. The application of a bias to the system causes a misalignment of the Fermi levels ($E_F$) of the electrodes, resulting in a tunneling current\(^1\) $i_{\text{tunnel}}$ described by:

\[
i_{\text{tunnel}} \propto e^{-2\sqrt{\phi/2m}d}
\]

where $m$ is the mass of the electron, $\phi$ the barrier height and $d$ the barrier width. From equation 4.1 it is possible to see that the current intensity has an exponential decay in the classical forbidden region, i.e. through the barrier. In the case of STM the barrier width would correspond to the

\(^1\)For electron tunneling through a potential barrier (classical forbidden region) it is required that there are occupied energy states at the side from which the electron tunnels and that there are unoccupied states at the side to which the electron tunnels. Moreover it is required that the tunneling barrier height is low, that the barrier width ($d$) is small to ensure a finite tunneling probability, and that the momentum is conserved in the tunneling process, for more details see ref. [47].
distance between the tip and the surface (z in the coordinate system used here). The exponential term explains the sensitivity of the STM since a displacement of one Å will result in a current decay of one order of magnitude. This allows measuring the surface corrugation on the atomic scale.

Figure 4.2: A schematic illustration of the tunneling between two metal electrodes (as in figure 1) here symbolizing the tip and sample. A positive bias voltage $U$ is applied to the sample and the barrier height (work function) $\phi_t$ and $\phi_s$ are indicated. The density of states for the metals are indicated by $\rho_t$ and $\rho_s$. In this configuration the tunneling occurs from the tip to the sample separated by a distance $d$. The size of the arrows in the gap indicates the probability for a tunneling event. The probability for a tunneling event is greatest at the Fermi level of the emitting electrode (here the tip).

It is important to mention that the tunneling current occurring by the application of the bias voltage $U$, is directly proportional to the density of states on the sample at the energy interval between $(E_F - eU)$, with $E_F$ being the Fermi level of the tip (according to the setup in Fig. 4.2) [48]. Assuming that the density of states does not vary significantly for the tip within this energy interval, we can express the $i_{\text{tunnel}}$ in terms of local density of states of the sample, $\rho_s(z, E)$ at the Fermi edge according to:

$$i_{\text{tunnel}} \propto U \rho_s(z = 0, E_F) e^{-2\sqrt{\frac{2m\phi}{\hbar^2}d}}. \quad (4.2)$$

with $z=0$ at the edge of the potential barrier and $z=d$ indicates the surface tip distance. This indicates that for low bias voltages, the STM probes the local density of state (LDOS) at Fermi edge at the tip position (in $x,y$).

In order to increase the accuracy of the theoretical description of the scanning probe technique, Tersoff-Hamann developed the model intro-
duced by Bardeen. The tip is here approximated by spherical symmetry and described by an s-wave. For this reason their model has been called s-wave approximation [49]. Although this method describes tunneling only for low voltages (V ≈ 10 meV), low temperature (or room temperature) and does not take any electronic coupling of the tip and surface wave functions into account it gives a conceptual illustration of STM. In the Tersoff-Hamann model a constant current image reflects the LDOS of the sample at the Fermi level, i.e. only sample properties would be mapped. Further, the resolution of the image can, in this model, be related to the radius of the tip [43, 44]. In fact in the Tersoff-Hamann model the apex atom of the tip dominates the electron tunneling process, explaining the high resolution in STM [43]. Within these models STM would only reflect sample properties neglecting the sample-tip interaction. However, the STM image is in reality a convolution between the electronic structure of the sample and of the tip. Other models have been introduced in order to describe the tunneling current taking in consideration the sample-tip interaction [50], of special importance when treating STM measurement of adsorbates.

For chemisorption it is possible to visualize the adsorbate as it modifies the local density of state of the substrate [43, 51, 52]. Lang showed that the Tersoff-Hamann model is also valid for adsorbates that are imaged as protrusions or depressions depending on the modification they induce on the LDOS at the Fermi level [43].

Since the STM image represents the convolution between the surface and the tip local density of states, the interpretation of the contrast should be done cautiously. Furthermore, when imaging an adsorbate on a surface the image can have contributions from both the adsorbate and the surface, both perturbed by their mutual interaction [43, 50].

A change in tip shape can change the appearance of the STM image [41] as shown for Sulphur on Re(0001) (both experimentally [53] and theoretically [54]) and for HOPG [55].

4.3 STM principles
As already mentioned, the STM presents atomically resolved images of surfaces using the phenomena of quantum mechanical tunneling. The elements used for operating the STM, such as tip and piezo motors that control the tip, make the STM set-up sensitive to vibrations and thermal drift [43]. A tip is scanned over the surface, (at a distance of a few Å) by piezo motors and the surface density of states is mapped and presented as an image².

²For a description of the STM set up see ref. [56] and Fig.1 page 1741 in ref. [43].

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The tip is usually constructed out of a thin metal wire of W or Pt/Ir. In order to achieve high resolution the tip must be mono-atomically sharp and stable. Moreover higher resolution is achieved by cooling the sample to minimize molecular vibrations and migration. The tip is mounted in connection with three piezo motors, one in each direction (x,y,z), controlling the tip movement. The x- and y-motors are in plane with the sample surface and the z-motor is perpendicular to the sample surface. The scan area (image) is built up by scanning x and y and plotting them as a function of z or i\textsubscript{tunnel} depending on the scan mode. It is possible to record images ranging from some Å up to µm areas.

![Figure 4.3: An illustration of STM scanning.](image)

- **A**: An atomistic picture of the surface and tip. On the surface an ad-atom is indicated by grey. A bias is applied. The distance between the surface and tip is indicated by d. Two arrows indicate the positions of the two scans seen in image B and C. B (constant current imaging), line scans of the surface are indicated along with the tip movement. For constant current imaging the tip moves in z to keep the current constant and the STM image is an expression in (x,y,z) of the tip movement.
- **B**: Line scans of the surface are indicated along with the tip movement. For constant height imaging the tip height is constant and the STM image is expressed in (x,y,i\textsubscript{tunnel}) coordinates.

*C* (constant height imaging). Line scans of the surface are indicated along with the tip movement. For constant height imaging the tip height is constant and the STM image is expressed in (x,y,i\textsubscript{tunnel}) coordinates.
A STM image can be acquired in constant current or constant height mode (See Fig. 4.3). For the experiments presented here the constant current mode has been used. Constant current mode presents the data as a function of $z(x,y)$, monitoring the height changes of the tip to keep the current constant during the scanning of the surface. For high electron tunneling probability the tip retracts from the surface, and for low electron tunneling probability the tip moves towards the surface.

By changing the scan speed, the direction of the x- and y-piezo motors and the loop gain (z-motor) it is possible to extract information of artifacts that can be present in an image like periodic vibrations and/or structure changes influenced by the tip scan direction.
5. Density Functional Theory

Quantum mechanical calculations are of great help when evaluating experimental results. In the present thesis single molecule Density Functional Theory (DFT) [57, 58], calculations of PES, XAS and molecular orbitals are used for that purpose, using the Gaussian 03 [59] and DeMon [60] programs. The obtained molecular orbitals are visualized using the MOLDEN viewing program [61]. A brief discussion concerning this type of calculations will follow.

DFT has become more and more popular in the last decade, due to its capability of computing large systems at a reasonable computational cost. Nowadays it is perhaps the most used approach in quantum chemistry, and it has obtained successful results also in the calculations of excited states.

The DFT method is based on the one to one correspondence between the energy of the system and its electron density. The energy of the system is in fact uniquely determined by the ground state electron density. However, the functional connecting energy and density is not exactly known, and the search for efficient functionals is still being carried on.

The electronic correlation \( E_{\text{cor}} \) (see Eq. 3.6) is automatically implemented in DFT calculations, which is a major advantage of DFT with respect to basic Hartree-Fock approach. However, it is possible to implement electronic correlation effects for the Hartree-Fock based methods as well, though, in general, at a larger computational cost.

In the PES experiment the kinetic energy of the photoelectron is measured and converted to binding energy according to Eq. 3.3. In the calculations, the binding energy is obtained from the difference in total energy between the core-ionized state \( E_f \) and the ground state \( E_i \) as shown in Eq. 5.1:

\[
E_B = E_i - E_f
\]

Both the ground state and the ionized state are energy optimized: in DFT this procedure is known as \( \Delta \text{Kohn Sham (\( \Delta \text{KS} \))} \). The resulting binding energy values are referred to the vacuum level. The calculated PE spectra need usually to be shifted in energy to fit the experimental spectra. The difference in the energy scale is due in general to polarization effects and to the work function.
The calculations of the XA spectra are done by the transition potential approach. In this method the electronic structure is calculated with half a core hole on the excited atom, in order to simulate relaxation of the valence band. This method has the advantage of being able to determine, in one single calculation, all the energetic levels of the system.
6. Experimental

In this chapter the experimental set-up’s used in this thesis for PES, XAS, UV-Vis spectroscopy and STM and sample preparation are discussed.

6.1 Sample preparation and Ultra High Vacuum

For cleanness Ultra High Vacuum (UHV) (approx. \(10^{-10}\) Torr) is often used in surface science in order to keep a surface clean for a time sufficiently long to enable data collection. A surface exposed to air (at one atmosphere pressure) is covered by one mono layer (ML) within a time of nano-seconds (ns) (assuming that the molecules in the air sticks on the surface with a sticking coefficient of 1), but the same surface at a pressure of \(10^{-10}\) Torr stays clean for about 3 hours [62].

It is common to distinguish between vacuum and ambient conditions – in-situ and ex-situ. The distinction is used for both sample preparation and experimental analysis. An ex-situ sample is here defined as a sample prepared outside vacuum and an in-situ sample is defined as prepared inside vacuum. It can be a specific interest to study ex-situ prepared samples to see, for example, the importance of the preparation method on the functionality and the structure of the obtained sample. In-situ samples are expected to be cleaner than ex-situ samples. In the papers presented here both ex-situ and in-situ preparations are used. In paper (II and III) ex-situ surface cleaning of conducting glass (Fluorine doped Tin Oxide, FTO) by ethanol washing is performed. Molecules are deposited on the surfaces either by ex-situ powder depositing using a stainless steel spatula (paper III) or by in-situ evaporation (paper I- VIII). In paper I the Si(100) substrate has been cleaned in-situ before the deposition of FePc molecules on the surface also performed in the UHV environment. By heating (annealing) the crystal/wafer to about 1370K it is possible to evaporate the outermost (oxide) layers of the crystal/wafer, leaving clean (bare) silicon. The heating of the crystal/wafer also makes the surface atoms mobile, often resulting in a reconstructed ordered surface. In-situ annealing was performed in the case of HOPG in order to heat off residual molecules adsorbed on the surface. Before inserting the HOPG sample into vacuum a fresh surface was created by cleaving the sample with the aid of tape (paper IV, V and VI).
For Indium Antimony (InSb) (paper VII and VIII) repetitive cycles of sputtering and annealing were used to clean the samples. Sputtering means that the substrate is bombarded with highly energetic ions (usually $\text{Ar}^+$ but other ions, like $\text{Ne}^+$, or electrons can be used). The molecules attached to the surface will be removed together with some of the atoms of the substrate. For this reason, after the sputtering procedure the substrate looks like a moon landscape and annealing is needed to recover a smooth surface. All of this is performed in UHV.

*In-situ* experiment is performed in vacuum, as in contrast to *ex-situ*, where the experiments are performed in air (at atmospheric conditions). When working with electron detection (as in PES and electron yield XAS) vacuum is needed in order to avoid scattering of photoelectrons by residual gas molecules. This would lower the resolution and the intensity of the spectra. In UV-Vis the absorption of the light through the sample is monitored and the measurements are usually performed *ex-situ*, since photons have a much larger mean free path than electrons. For STM experiments vacuum is not necessary. It is possible to run STM experiments from UHV up to atmospheric pressure and even in liquids. The reason for using UHV in STM is to have a controlled environment that protects the system from contaminants.

### 6.2 Home laboratory based PES equipment

The ESCA 300 [63, 64], and ESCA 200 [65] instruments are used in this thesis work for pre-characterization of the studied systems. Moreover, in paper II and III results obtained by the ESCA 300 spectrometer are shown and in paper VII the ESCA 200 is used. Both instruments consist of a fine-focus electron gun, a rotating anode producing $\text{Al K}\alpha$ radiation (1486.7 eV), a monochromator, an electron lens, a hemispherical analyzer, which in the case of the ESCA 300 instrument has a radius of 300 mm and in the case of the ESCA 200 instrument has a radius of 200 mm, and a channel-plates detector. The instruments also contain sample manipulators, which allow PE measurements at different Take Off Angles (TOA) of the photoelectrons. The ESCA 200 preparation chamber is also equipped with a LEED (Low Energy Electron Diffraction) analyzer, a sputter gun and a sample holder for resistive and direct heating of the sample.

### 6.3 Max- Lab synchrotron radiation facility

Synchrotron radiation [40] was first considered as a waste product in storage rings used for high-energy physics. Later, special laboratories
were built, focused on providing synchrotron radiation light for different types of experiments. The synchrotron facility consists of an injection part where particles are accelerated to relativistic speed and a storage ring made by straight sections and bending magnets. Light is produced if charged particles moving at relativistic speed are accelerated as when electrons are deflected by bending magnets or in insertion devices (wigglers or undulators) in the straight sections of the storage ring. In the present work the synchrotron facility is mainly regarded as a source of polarized light of continuum spectrum. This allows XAS measurements, where a tunable photon source is necessary and high-resolution PES measurements since the energy of the photons can be chosen according to different cross-sections for specific core levels. It is also possible to vary the electronic escape depth, thus the surface sensitivity, using different photon energies for one state [27].

MAX-lab synchrotron radiation facility is a Swedish national laboratory located in Lund. It consists of two storage rings, MAX I and MAX II [66, 67], with a third under construction (MAX III). MAX II stores electrons of 1.5 GeV. The ring is normally injected once a day with a beam current around 200 mA.

6.3.1 Beam line I-511

I-511 [68] is an undulator beam line located at the MAX II ring. An undulator is an insertion device consisting of a periodic set of magnets, which force the electrons in a motion of small harmonic undulations. Light is then produced each time the electrons are deflected. By changing the gap between the magnets different photon energies can be accessed. At beam line I-511 the light is made further monochromatic using a plane grating Zeiss SX-700 monochromator that has a spherical focusing mirror, gratings and a movable exit slit. At I-511 the range of photon energies span from 100 eV to about 1200 eV, however the intensity of the light in the high-energy range is quite low, which explain the poor statistics of the Fe 2p PE spectra presented in paper I.

When performing XAS measurements the photon energy is scanned by the monochromator (and the undulator is tapered: the gap differs in the front and rear end of the undulator) to produce a light spectrum of quite constant intensity over the scanned energy region (here the N K-edge).

The I-511 beam line has two end-stations, one for surface science and one for studies of gases and solids. The light is directed into either of the end-stations by turning a flip mirror.

The surface science end-station, used in our experiments, is a system including, an analysis and a preparation chamber, equipped by a fast entry facility (load-lock) for the samples. For the experiments an external
evaporator chamber is also mounted on the preparation chamber. The preparation system includes a gas dosing systems, a mass spectrometer, LEED and a sample holder which permits direct heating of the samples to approximately 1400K. The sample holder can rotate permitting to vary the orientation of the surface with respect to the polarization $E$-vector of the light. The analysis chamber can rotate around the axis of the incoming light that impinges the sample always at a grazing angle of approximately 7°. This special design permits to vary the polarization and the photoemission direction independently, allowing high-resolution angle resolved XAS and PES. The analysis chamber is equipped with a Scienta 200/R 4000 analyzer\(^1\) used for PES and Auger-mode XAS, a home built XAS detector and a Scienta X-ray Emission Spectroscopy (XES) detector.

6.4 Energy calibration for PES and XAS
For metallic systems the PE binding energies are usually referenced to the Fermi level of the system, defined as having zero binding energy\(^2\). In non-metallic systems there is however no distinct Fermi level in the spectra. Thus it is necessary to calibrate the energy respect to the vacuum level. Another quite common possibility to calibrate the binding energy scale for non-metallic or semiconducting materials is by taking a reference peak at fixed, known, binding energy. In our work we follow this procedure to calibrate the PE spectra taking the bulk Si 2p\(3/2\) peak, centered at about 99.6 eV, as a reference and calibrate the other photoemission peaks referred to this peak (paper I). For paper II and III the binding energy scale of the PE spectra is calibrated by the Fermi edge of an Ag sample. In3d\(5/2\) paper V the spectra were calibrated with respect to the onset of graphite states in the valence band. In paper VII the In peak of the substrate is used for calibration.

For XAS, photon energy calibration is usually performed by measuring a photoemission peak at 1\(st\) and 2\(nd\) order light.

6.5 Ultra-visible optical absorption spectroscopy
The UV-Vis spectroscopy measurements (paper III) have been performed at a commercial Hewlett Packard UV-Visible ShemStations 8453 at the Department of Physical Chemistry, Uppsala. This instrument is a single beam diode-array UV-Vis spectrophotometer with collimating optics of

\(^1\)The Scienta 200 analyzer was exchanged in 2005 to a Scienta R 4000 analyzer.
\(^2\)If the sample and spectrometer are in contact the term that represents the work function ($\phi$) in Eq. 3.3 can be neglected.
2 nm (nanometer) resolution, 0.5 nm wavelength accuracy, $5 \times 10^{-2}$ AU (Absorbance Units) photometric accuracy and a photometric noise below $2 \times 10^{-3}$ AU. The radiation source is a combination of a deuterium discharge lamp for the UV range and a low noise tungsten lamp for the visible and short wavelength near-infrared range (300 to 1100 nm).

For historical reasons, it is common to present the UV-Vis spectrum in wavelength units (nm). The wavelength units (nm) can be expressed in eV through the non-linear relation $E = h c / \lambda$, where $c$ is the speed of light and $\lambda$ is the wavelength.

6.6 Scanning tunneling microscopy

The STM measurements have been performed in Uppsala, Sweden, by a commercial Omicron variable temperature, UHV STM and in Aarhus, Denmark, by the home-built Aarhus UHV STM [43]. STM Experiments have also been performed by our colleagues in Stockholm on a Omicron STM, not described here.

The Uppsala instrument consists of a chamber for the STM stage in connection with a preparation chamber for sputtering and annealing of the samples, also equipped with a LEED/Auger facility. The molecular depositions has been performed in an evaporation chamber connected to the preparation chamber. It is possible to cool the STM stage by liquid He, reaching a sample temperature of about 70K. All STM images presented have been imaged in constant current mode, using a tungsten tip. Positive bias voltages has been used for probing the unoccupied states, and negative bias voltage, for probing the occupied states.

The Aarhus UHV STM [43] instrument consists of a chamber containing the microscope stage as well as surface preparation facilities and an evaporation chamber. The STM stage was cooled during the measurements by liquid nitrogen, resulting in a minimum sample temperature of about 90K. The measurements were carried out using a tungsten tip at negative bias voltage, thus probing the occupied states of the sample.
7. Substrates – Adsorbates

7.1 Substrates

The solid material used in surface science is called substrate. A solid material can be crystalline, polycrystalline or amorphous depending on the spatial order of the atoms, molecules or ions, which the material consists of. A crystal is described by the periodic repetition of a regular three-dimensional unit, called unit cell. However at the surface of a crystal, the atoms can rearrange themselves to form a structure with a different periodicity and/or symmetry than that of the crystal bulk. This process is called surface reconstruction and it is normally due to the reduced atomic coordination of the surface atoms with respect to those in the bulk of the solid. Polycrystalline materials consist of crystalline domains, which are however oriented in different way in the solid. Materials with no long-range order for the atoms/molecules or ions, which constitute the solid, are called amorphous.

In this thesis crystalline Indium Antimony (InSb(001)) with a \( c(8\times2) \) reconstruction is used in papers VII and VIII and Silicon (Si(100)) is used in paper I, high oriented pyrolytic graphite (HOPG) is used in papers IV, V and VI and amorphous conducting glass (fluorine doped tin oxide, FTO) is used as a substrate in papers II and III.

7.1.1 Graphite

The graphite (0001) surface displays no reconstruction with respect to the bulk. Graphite is a semimetal, i.e. characterized by very low density of states around the Fermi level [69, 70]. The graphite is built up of sheets of carbon atoms having an \( sp^2 \)-hybridisation, as benzene, and thus the carbon-carbon \( \sigma \)-bonding within the sheets are strong, with a C-C distance of 1.42 Å, in comparison with the weak \( \pi - \pi \) interactions between the sheets, mediated by the out of plane lone-pair \( p_z \)-hybridized orbitals. The distance between the sheets is 3.35 Å (Fig. 7.1).

The surface atoms can be divided into \( \alpha \)- and \( \beta \)-atoms (Fig. 7.1) [71, 72]. A \( \alpha \)-atom is located above an atom in the second layer whereas a \( \beta \)-atom is located in the center of a hexagonal ring structure of the second layer. Constant current STM measurements performed on graphite only resolves the \( \beta \)-atoms, since \( \beta \)-atoms have higher local density of states.
at the Fermi level than the $\alpha$-atoms. Thus the $\beta$-atoms are imaged as protrusions with a distance of 2.46 Å in STM [71, 72].

7.1.2 InSb

A semiconductor is characterised by a band gap between the occupied valence and unoccupied conduction band. The Fermi level is situated in the band gap. InSb (001) is a semiconductor and its surface presents many reconstructions, with the c(8x2) structure being the most stable. The reconstructions are annealing temperature dependent, the c(8x2) requiring annealing to about 675K. The c(8x2) surface structure of InSb has been studied by STM [73, 74] and surface X-ray diffraction [75] and a model for the reconstructed surface has been proposed (Fig. 7.2). According to this model the surface consists of In rows in the [110] direction, spaced about 18 Å apart. In STM the InSb (001) c(8x2) surface contrast changes for different voltage settings [74].
7.2 Adsorbates

Adsorption is the retention of gas molecules or atoms by a solid on a surface, as opposed to absorption when molecules or atoms penetrate into the bulk of the solid material. The interactions of the adsorbate with the surface can be week or strong. The organisation of the adsorbates on the surface is governed by substrate-adsorbate- and adsorbate-adsorbate interactions.

7.2.1 Physisorption and chemisorption

It is common to introduce two concept when discussing adsorption: physisorption and chemisorption [76, 77]. In chemisorption the valence levels of the adsorbate and the surface hybridize to form new chemical bonds whose strength can vary from tenths of an eV to over 1 eV [78]. In physisorption, on the other hand, the interaction between the adsorbed molecules and the substrate is rather weak, often mediated by van der Waals forces. The bond strength of physisorption is typically about 0.1 eV [78]. However, there is no absolute distinction between chemisorption and physisorption.

7.2.2 Substrate-Adsorbate- and Adsorbate-Adsorbate interactions

The resulting adsorption structure formed by the molecular overlayers on surfaces can be commensurate-, coincidence- and in-commensurate structures [79]. In commensurism each molecule of the overlayer adsorbes on symmetry equivalent substrate sites. This is not the case for coincidence- and in-commensurate structures. In a coincidence structure it is possible to form a supercell, a unit cell containing the substrate and molecular overlayer. In an in-commensurate structure it is not possible to create any unit cell containing both the substrate and the molecular overlayer.

Figure 7.2: A schematic illustration of the geometrical ordering of the surface atoms of InSb according to the Kumpf model [75].
For commensurate systems it has been predicted that the adsorbate-substrate interactions dominate over the adsorbate-adsorbate interactions \[79\]. For low interacting systems instead, adsorbate-adsorbate interactions can play a more dominant role in the ordering of the overlayer. The molecules occupy different adsorption sites on the surface and are often not commensurate with the substrate \[79\]. The overlayer is then either a coincidence-structure or it is in-commensurate with the substrate. The fact that the molecules occupy different sites on the substrate causes a Moiré pattern, often denoted superstructure. The Moiré contrast is the result of a superposition of two geometrical patterns on top of each other giving rise to a new pattern together. (Superstructures can also have an electronic origin \[80\].)

### 7.2.3 Molecular growth modes

The growth of layers of atoms or molecules on a surface is often described by three different mechanisms \[81, 82\]: Franck-van der Merwe growth (the ideal layer-by-layer growth) Volmer-Weber growth (with adsorption 3D island formation) and Stanski-Krastanov growth (which includes elements of the other two growth modes) see Fig. 7.3. In fact the Stanski-Krastanov growth initiates with one or a few adsorbate layers in a layer-by-layer fashion and after that 3D islands start to form. The growth mechanisms depends on several factors \[81\], such as deposition rate, surface diffusion rate, substrate temperature and strain between surface and adsorbate lattice. All plays a role in the growth mechanism and the result of a growth experiment can be hard to predict. However, a simple explanation for the different growth modes can be formulated in terms of interaction. In island growth the adsorbate is weakly bound to the substrate (physisorbed or weakly chemisorbed) whereas, in Franck-van der Merwe or Stanski-Krastanov growth, the adsorbate-substrate interactions are stronger than the adsorbate-adsorbate interactions \[82\].

\[\text{ABC}\]

**Figure 7.3:** Schematic illustrations of different growth modes of adsorbates on a surface \[81, 82\]. The substrate is indicated by a rectangle and the adsorbates are indicated with ellipses. A. Franck-van der Merwe growth, characterised by layer-by-layer growth. B. In Stanski-Krastanov growth the adsorbates initially grow in a layer-by-layer fashion and after one or a few layers adsorption islands start to grow. C. Volmer-Weber mechanism, characterised by island growth.
8. Phthalocyanines

8.1 Introduction

Phthalocyanine molecules (Pc’s) are macro-cycle complexes related to porphyrins [83, 84]. (They were first discovered in the laboratories in 1907 and 1927 [84].) The Pc’s (Fig. 8.1) are planar organic molecules that consist of four pyrrole units linked in a circular manner by nitrogen bridges (aza-bridges) and surrounded by four benzene rings, with either a metal atom (metal phthalocyanine, MePc, C$_{32}$H$_{18}$N$_8$Me) or two hydrogen atoms in the center (Metal-free Pc, H$_2$Pc, C$_{32}$H$_{18}$N$_8$H$_2$) see Fig. 8.1. In MePc’s the central atom is usually one in the first transition metals row [84].

![Figure 8.1: The molecular structure of FePc (left) and H$_2$Pc (right). The coordinate planes are indicated for each molecule, as used in the XAS calculations.](image)

The Pc’s are characterized by high polarizability and high chemical and thermal stability. The low vapor pressure of the molecules (10$^{-14}$ Torr at room temperature) makes them suitable for sublimation in UHV, allowing a controlled deposition onto the surface in a clean environment. In previous studies of Pc’s deposited at low coverages on different surfaces it has been reported that the first layers of Pc molecules in most cases lie parallel to the surface [85, 86, 87, 88, 89]. The molecular adsorption of Pc’s has been explained as dominated by the surface-molecule interaction for the first adsorbed layers, resulting mostly in molecules laying with the molecular plane parallel to the surfaces. The molecule–molecule interaction would instead govern the growth process for higher coverage,
resulting in films in which the molecules have the molecular plane essentially standing on the surface [85].

Pc’s crystallize by forming molecular stacks where the interaction between molecules is mediated by van der Waals forces [90]. These columns cohere to form a crystal. A number of different Pc polymorph structures are known (α, β, and many others) each characterized by a typical angle between the normal to the molecular plan and the stacking direction [91, 92, 90], as illustrated schematically in Fig. 8.2.

\[ \text{Figure 8.2: Illustration of } \alpha \text{ and } \beta \text{ polymorphs as discussed by G. Dufour et. al [92]}. \text{ Each line represents a FePc molecule with a Fe atom in the center. In the } \alpha \text{ polymorph } \phi \approx 26^\circ \text{ and in the } \beta \text{ polymorph } \phi \approx 45^\circ. \]

A difference in the molecular stacking is associated with a different intermolecular interaction within the stack. This results in a modification of the electronic structure, leading to optical and photoconductive properties that are characteristic for each polymorph [93]. Pc’s are reported to be both insulators and semiconductors [92, 94]. In order to improve the design and the performance of, for instance, molecular electronic devices, it is important to characterize/investigate the molecular stacking direction, which influences the carrier mobility [95] and electrical conductivity [96]. Different crystalline forms can be obtained by different deposition methods, such as sublimation [91], deposition by solution [97], heat treatment [98] or mechanical grinding [96, 99].

8.2 Phthalocyanine films

We have examined the geometrical and electronic structure of FePc and H$_2$Pc films. We find that the molecule orientation for evaporated films
are standing with the molecular plane quite perpendicular to the surface, while for the powder deposited (ex situ) film of H₂Pc the molecules are preferentially oriented with the molecular plane parallel to the substrate surface.

8.2.1 FePc Si(100): molecular orientation

We have used PE, XA spectroscopies and DFT simulations to characterise the electronic and geometrical structure of FePc in films grown on Si(100) surface (paper I). DFT calculations were carried out in order to interpret the experimental results. The very good agreement between these simulations carried on single molecule and our experimental data (obtained on deposited films) indicates that the intermolecular interactions within the film are weak.

By valence PES (Fig. 8.3) and XAS (Fig. 8.4) we could determine the orientation of the molecule with respect to the surface. In fact, the intensity variation of the valence PES features depending on the \( E \)-vector orientation with respect to the surface, can be assigned to the angular dependence of photoemission from the orbitals of \( \sigma \) and \( \pi \) symmetries of the FePc molecule (Fig. 8.3) [100].

![Figure 8.3: (Bottom part) Valence band simulations of FePc considering the angular dependence of the photoemission intensity of the C and N derived \( \pi \)- and \( \sigma \)-type molecular orbitals of the experimental results taken at two experimental geometries (upper part). For the experimental spectra a background has been set to zero at zero energy and the spectra have been normalized at 20 eV.](image.png)

The XAS measurements have been performed on the N K-edge at three different geometries: with the light polarization E-vector parallel, normal and at 45° angle with respect to the sample surface. The XA data
have been compared and interpreted by single molecule DFT calculations (presented in Fig. 8.4 A) that distinguish the intensities along the different x, y, and z axes (see Fig. 8.1 for the definition of directions). This has allowed to resolve the spectral features with respect to the symmetry character of the different molecular orbitals ($\sigma$ and $\pi$-type). We found, by XAS, PES and DFT, that the FePc molecules within the film were standing with the molecular plane quite perpendicular on the surface.

8.2.2 $\text{H}_2\text{Pc}$ on conducting glass: molecular orientation

In this section some results about $\text{H}_2\text{Pc}$ deposited on conducting glass (FTO) will be presented (paper II and III). We used PES, XAS and DFT to characterize the electronic and geometrical structure of $\text{H}_2\text{Pc}$ in films deposited on conducting glass (FTO) and UV-Vis to study the polymorph structures of the films. Also in this case the DFT calculations, carried out on a single molecule, reproduced the experimental spectra well indicating weak intermolecular interactions.

$\text{H}_2\text{Pc}$ films have been deposited on conductive glass via two different deposition methods: in-situ, via evaporation (VD) and ex-situ, via powder deposition (PD) by a stainless steel spatula. The PES data did not evidence any difference between films prepared by the two preparation methods used. UV-Vis and XAS have shown to be more suitable methods to characterized the geometric and electronic structure of the obtained films. By UV-Vis and XAS measurements we determined that the orien-
tation of the molecules with respect to the surface differs depending on the preparation method and that the evaporated film was a $\alpha$-polymorph while the smeared film was an $\alpha$-polymorph.

Figure 8.5: N 1s XA spectra for the $\text{H}_2\text{Pc}$ powder deposited (grey PD) and evaporated (black VD) films taken at three different incidence angles with respect to the light polarization $\mathbf{E}$-vector. Illustrated in the figure the $\mathbf{E}$-vector, the surface, and the vector $\mathbf{n}$, normal to the surface, for each of the different experimental geometries.

In Fig. 8.5 we compared XA results for $\text{H}_2\text{Pc}$ VD and PD films. The spectra were recorded with the light polarization $\mathbf{E}$-vector parallel, normal and at 45° angle with respect to the sample surface. The angular dependence of the N 1s XA spectra (Fig. 8.5) for the VD and PD films clearly indicate a different orientation of the molecules with respect to the surface for the two films. In the case of the XA spectrum of the VD-film (Fig. 8.5 dotted line), we have found that the molecules are oriented with the molecular plane preferentially orthogonal to the surface plane. In the case of the PD-film the angular dependence of the N 1s XAS spectra is reversed compared to the VD-film. Consequently, it can be concluded that the molecules in the PD-film are preferentially oriented with the molecular plane parallel to the substrate surface.

8.3 Phthalocyanine monolayers

8.3.1 Phthalocyanine on graphite

We have examined the geometrical and electronical structure of FePc and $\text{H}_2\text{Pc}$ and compared our results with other Pc’s adsorbed on HOPG [88, 101, 102, 103]. We have found that the molecular unit cell and the
superstructure is characteristic of each Pc adsorbed on HOPG even if the geometrical size of the compared molecules is the same, as seen in table 8.1.

<table>
<thead>
<tr>
<th>Square phase</th>
<th>$\beta$ (°)</th>
<th>Vector $b_1$ (nm)</th>
<th>Vector $b_2$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePc/HOPG</td>
<td>91.2(±1.5)</td>
<td>1.50(±0.11)</td>
<td>1.56(±0.11)</td>
</tr>
<tr>
<td>H$_2$Pc/HOPG</td>
<td>87.3(±1.1)</td>
<td>1.31(±0.02)</td>
<td>1.38(±0.02)</td>
</tr>
<tr>
<td>PdPc/HOPG</td>
<td>90(±2)</td>
<td>1.4(±0.1)</td>
<td>1.4(±0.1)</td>
</tr>
<tr>
<td>CuPc/HOPG</td>
<td>90.3</td>
<td>1.36</td>
<td>1.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hexagonal phase</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FePc/HOPG</td>
<td>60.4(±1.7)</td>
<td>1.29(±0.03)</td>
<td>1.32(±0.07)</td>
</tr>
<tr>
<td>H$_2$Pc/HOPG/8CB</td>
<td>60(±2)</td>
<td>1.30(±0.4)</td>
<td>1.30(±0.4)</td>
</tr>
</tbody>
</table>

**Table 8.1:** Presentation of the angle $\beta$ between the two vectors $b_1$ and $b_2$ of the molecular unit cell for different Pc’s on HOPG. For FePc and H$_2$Pc square phase a 95% confidence interval is used. PdPc and CuPc from ref. [101] and [102] respectively. The H$_2$Pc with hexagonal phase (H$_2$Pc/HOPG/8CB) was measured in octylecyanobiphenyl liquid crystal (8CB) and reported in ref. [104].

**FePc on graphite**

We have characterized the adsorption phases of FePc molecules on HOPG by STM (paper IV) and PES and XAS (paper V). For each different studied phase, our results have shown that the molecules adsorb with the molecular plane parallel to the surface. The photoemission and absorption spectra were found to be essentially identical for the mono- and multilayer preparations, which is evidence for a pure van der Waals nature of the adsorbate/substrate and intermolecular bonds (see Fig. 8.6).

![Intensity vs Photon energy for FePc/HOPG](image1)

**Figure 8.6:** N 1s x-ray absorption spectra of the FePc $\pi^*$ states for the indicated preparations. The molecular orientation is the same for all preparations.

Evaporation of FePc onto a HOPG surface kept at room temperature results in the formation of three-dimensional molecular islands on the substrate (See left image in Fig. 1.1). Annealing to about 670 K of low
initial coverage preparations of FePc leads to the formation of molecular chains whose orientations differ by approximately 60°, suggesting that the interaction between the substrate and the adsorbate cannot be neglected (Fig. 8.7 A).

Figure 8.7: FePc on HOPG. A. (46 nm x 46 nm) image (0.6 nA, 2.5 V, 90 K) typically obtained after a low dose deposition of FePc followed by annealing to about 670 K. The molecules are seen to form molecular chains. B. Overview (95 nm x 95 nm) acquired at 1.9V and 0.04 nA at 70 K. Both quadratic and hexagonal phases are present (For molecular unit cell dimensions see table 8.1). Note that islands with molecules arranged in the quadratic phase are oriented by ca 30° compared to each other. C. STM image (4.8 nm x 4.8 nm, 2.22V, 0.19 nA, 70 K) of a square adsorption island of FePc on HOPG. The molecular model used to fit the STM image is the result of a single molecule calculation as described in paper I.

STM investigations of annealed higher initial molecular exposures, show densely-packed monolayer islands on the surface with a square molecular arrangement. These monolayer islands are oriented by ca 30° compared to each other, again point to that the interaction between the substrate and the adsorbate cannot be neglected (Fig. 8.7 B). A Moiré pattern is seen for the square phase, indicating that the molecular adsorption cell is not commensurate with the substrate [79]. Occasionally regions with a hexagonal arrangement of the molecules are also observed (For molecular unit cell dimensions see table 8.1). For the square adsorption phase our STM measurements have identified that the molecules are oriented with the benzene rings towards the aza-bridge N of the neighbouring molecules in a more packed fashion than for the chain structure (Fig. 8.7 C). A comparison with other similar systems, underlines the importance of the central metal in the molecule-molecule and molecule-substrate interactions, which govern the adsorption geometry.

**H₂Pc on graphite**

We have examined the H₂Pc/HOPG system with STM and DFT molecular ground state calculations (paper VI). After annealing to about 670 K the H₂Pc molecules arrange in ordered two-dimensional island structures on the HOPG substrate (Fig. 8.8). The islands consists of quadratic
densely-packed H₂Pc. The molecules adsorb with the molecular plane parallel to the surface with the molecular unit cell dimensions as listed in table 8.1. For H₂Pc the molecular unit cell is somewhat smaller than for FePc, and comparable with the molecular unit cells of PdPc and CuPc.

![Image](318x611 to 432x649)

**Figure 8.8:** A: STM image of ML coverage of H₂Pc on HOPG (-1.93 V, 0.067nA, 14.2 nm x 9.7 nm). The picture clearly shows an electronic state with a nodal plane along a line through the molecular plane. B. Theoretical ground state simulation of the HOMO-2 state, similar in symmetry to the STM image displayed in A. C. ML coverage of H₂Pc on HOPG (-2.27 V, 0.020nA, 14.1 nm x 4.6 nm). D. a selected part (4.0 nm x 1.6 nm) of the picture in C is shown, clearer highlighting the contrast difference of two benzene groups which appear brighter than the other two. E. Theoretical ground state simulation of the HOMO-4 and HOMO-6 states, similar to the STM images displayed in C and D.

The high-resolution STM measurements permit a discussion about the occupied molecular electronic states of the molecule. By varying bias settings in the STM measurements different molecular orbitals have been probed and compared to ground state DFT calculations (Fig. 8.8).

### 8.3.2 Phthalocyanine on InSb

We have examined the geometrical and electronical structure of Pc’s on InSb. Earlier studies showed that different Pc’s forms ordered structures on the surface of InSb(001)-c(8x2). For InSb (001)-c(8x2) the In rows, with 1.8 nm spacing, seems to be the adsorption site for Pc’s. In fact, the diameter of a Pc molecule matches well with the lattice parameter of InSb (001) surface with a c(8x2) reconstruction [87, 105, 106].

**ZnPc on InSb**

In this paper the growth of ZnPc on InSb(001) has been studied with STM, LEED and PES (paper VII). We have found, using STM, that ZnPc adsorbs with the molecular plane parallel to the substrate surface.
The molecules are ordered along the [110] direction and can show a displacement with respect to the molecule adsorbed on the adjacent In row. The displacement result in a nx3 LEED pattern superimposed on the LEED structure of the c(8x2) surface.

![Figure 8.9: C1s spectra of ZnPc films of different thickness on InSb (001) as indicated. The spectra are normalized at the benzene feature to illustrate changes in the line-shape. Some of the curves stem from samples that have been annealed to 640 K. It can be seen that the valley between the pyrrole and benzene feature is enhanced with the thickness of the film. The sub-monolayers give rise to a very broad spectrum, which becomes even broader after annealing. A shift of about 0.1 eV is observed between the spectra that have been taken before and after annealing.](image)

PES results show that the electronic structure of the molecule changes with coverage. For sub-monolayer coverage the spectral features appear broadened with respect to the multilayer results due to the molecule-surface interactions as seen in the C1s spectra in Fig. 8.9.
FePc on InSb

We have studied the interaction and growth of FePc on InSb(001) with STM (paper VIII). The present system requires cooling to 70 K to get stable STM images. This is not the case for the above studied system of ZnPc on InSb(001), which was immobile at room temperature. We find that the molecule adsorbs with the center of the molecule on the indium rows of the InSb substrate. The four benzene rings of the molecule are facing the sides of the Indium rows, two in each direction for both as deposited as well as annealed molecules. This adsorption pattern is the same as ZnPc, PbPc, SnPc and H$_2$Pc, which also adsorb on the Indium rows [87, 105, 106]. The FePc molecule is always imaged with a protrusion in the center of the molecule, for different bias settings used in this study, related to the significant iron 3d contribution to frontier valence states. The growth of the two-dimensional islands of FePc is non-homogenous and that the islands are prolonged about the [-110] direction, indicating that the adsorption is controlled by the substrate corrugation observed at 70 K (Fig. 8.10).

Figure 8.10: A. 58 nm x 58 nm image of FePc on InSb (-2.2 V, 0.27 nA) taken at 70 K. B. 95 nm x 95 nm (-2.7 V, 0.27 nA). The coverage is about 0.5 monolayers. The two-dimensional islands is prolonged perpendicular to the [110], indicated in the figure. C. A close-up of figure A as indicated by a square. The contrast is adjusted to highlight structures in the substrate. Darker and brighter areas are seen, predominantly elongated in [-110] direction. A stripe-like feature (1) and two circular features (2 and 3) are marked with numbered arrows. D. The same area as in C in different contrast enhancement. The isolated molecules show a five-lobe structure and the molecular pair to the right in the figure has an extra circular protrusion between the two molecules in the pair.
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John Åhlund
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