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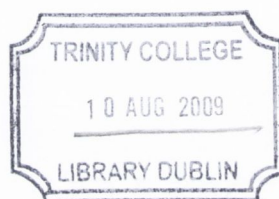
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An experimental investigation of metal phthalocyanine-germanium interfaces

A thesis submitted to
The University of Dublin
For the degree of
Doctor of Philosophy in Physics

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October 2008



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Abstract

Hybrid organic-inorganic devices present interesting possibilities for the growing field of organic semiconductors. The interface within these devices plays an important role in their performance, and as they decrease in size this becomes increasingly significant. This work investigates metal phthalocyanines (MPc), a potentially useful molecular organic semiconductor, on the technologically relevant Ge(001)-2×1, Ge(001)-2×1:H and Ge(111)-c(2×8) surfaces. The goal of this thesis is a characterisation of the physical, electronic and chemical behaviour of these interfaces.

Four different techniques are used in the characterisation: Near edge X-ray absorption fine structure (NEXAFS), which primarily provides information about molecular orientation; photoelectron spectroscopy (PES), which provides information about electronic and chemical structure; scanning tunneling microscopy (STM), which provides information about adsorption; and the computational technique of density functional theory (DFT), used in support of the experimental results.

The Ge(001)-2×1 surface is shown to interact strongly with the molecules. An apparent tilt, observed by NEXAFS, of molecules adsorbed on the surface is shown to be the product of a mixture of a degree of disordered molecules and flat-lying, but distorted, molecules. A model for the adsorption is given, showing a majority of molecules bonding across two dimer rows, and a minority along a single dimer row.

The strong interaction of the Ge(001) surface is drastically reduced on passivation with hydrogen. On this surface the molecules appear both electronically and structurally bulk-like from the first monolayer deposited. For PbPc the first layer appears to take the triclinic crystal structure, with a preference for forming a bilayer of molecules.

On the Ge(111)-c(2×8) surface the degree of interaction appears somewhere in between the two extremes of the Ge(001)-2×1 and the Ge(001)-2×1:H surfaces. STM of sub-monolayer coverages, PES of the molecular core levels and NEXAFS all confirm this. Despite this, for the first fraction of a monolayer, a distinct reaction is shown to occur that does not occur on the Ge(001) surface. It is shown that this reaction is only possible on defects in the Ge(111)-c(2×8) surface. This demonstrates a more passivating effect of the c(2×8) reconstruction in comparison to the 2×1 reconstruction of Ge(001).

On both the Ge(001) and Ge(111) surfaces a shift is observed in the core levels of the metal atom of the MPc. It is proposed that those molecules in which the metal lies close to the

substrate exhibit a shift to lower binding energy. Polarisation effects in both the initial or final state are excluded as possible causes for this shift. A loss of HOMO intensity in those systems exhibiting this shift demonstrates a link between initial state differences and the observed shift. From this, it is concluded that the shift is most likely to be the result of an initial state electron charge transfer into the metal atom of the molecule.

Underlying all of these conclusions is a demonstration of the difficulty of interpreting the results from the various experimental techniques employed. Although these techniques are powerful analytical tools, there are multiple possible mechanisms for any given result. This problem becomes increasingly severe with more complicated systems. This work shows that only through comparison of different experiments, and different experimental techniques, can the results be better understood.

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List of abbreviations

AES Auger electron spectroscopy	ML Monolayer
BR Branching ratio	MPc Metal phthalocyanine
CHA Concentric hemispherical analyser	NEXAFS Near edge X-ray absorption fine structure
DFT Density functional theory	PES Photoelectron spectroscopy
ESCA Electron spectroscopy for chemical analysis	PTCDA Perylenetetracarboxylic dianhydride
FWHM Full width half maximum	SOS Spin orbit split
GW Gaussian width	STM Scanning tunneling microscopy
HOMO Highest occupied molecular orbital	SXPS Soft X-ray photoelectron spectroscopy
HOPG Highly oriented pyrolytic graphite	UHV Ultra high vacuum
LEED Low energy electron diffraction	UPS Ultraviolet photoelectron spectroscopy
LUMO Lowest unoccupied molecular orbital	XPS X-ray photoelectron spectroscopy
LW Lorentzian width	XSW X-ray standing wave spectroscopy

Chapter 1

Introduction

Since the discovery of organic conductors and semiconductors about thirty years ago [1, 2] the field has grown to cover a vast range of organics, for many different applications [3]. Organic materials are cheap to produce and easily tailored to specific applications. For example light emitting organics can be modified to emit any colour of the visible spectrum. Moreover, they have the potential for dramatic size reduction in electronics with the realisation of single molecule devices.

On the other hand, inorganic semiconductors are the standard in industry, where the production and processing for device manufacture is very advanced. Inorganic semiconductors also display excellent electronic transport properties. Therefore, combining the potential benefits of both systems, to create hybrid organic-inorganic electronics, provides an interesting field of research with many potential applications [3].

The properties of the interface can have a significant influence over film growth, which in turn has a huge impact on device properties. As devices become smaller the electronic properties of the interface have a greater impact on the overall electronic character of devices. In the case of molecular electronics the device and the interface are no longer separable [4]. Therefore, a thorough understanding of any organic-inorganic interface is essential to device design.

This thesis follows work previously conducted within the research group. This work, primarily by G. Cabailh, focused on films of metal phthalocyanines (MPc) on the (001) surfaces of GaAs and Ge [5]. Characterisation of the interface between the phthalocyanines and GaAs was relatively straightforward, with no sign of strong interaction between the substrate and the molecules. However, the phthalocyanine Ge(001) interface was more interesting, with three major issues arising.

The first issue relates to an unexpected tilt of the molecules with respect to the substrate, as observed by a technique known as near edge X-ray absorption fine structure (NEXAFS). Although the work of Cabailh was focused primarily on organic films, some experiments were also conducted on the first monolayer of phthalocyanine deposited. These films show the same tilt for MgPc and SnPc on Ge(001) and SnPc on GaAs(001), but the reason for this observation

could not be determined. There are a number of instances in the literature where monolayers of small molecules also show an unexpected apparent tilt, with a number of proposed explanations [6, 7]. However, to date no comprehensive explanation has been found. Moreover, there is little evidence that the suggested mechanisms from these systems would apply equally to large molecules. Given the apparent contradictions in the literature and the numerous potential origins of the observed tilt, this is a question worth further investigation.

The second issue is an unexplained second state present in the soft X-ray photoelectron spectra (SXPS) of the core level of the metal atom in non-planar MPc-Ge(001) interface, not observed on GaAs(001). No similar observation of two states of the metal core level of MPc at the interface has been reported by any other research group. This is remarkable given that analogous systems have been studied by the same techniques. One possible reason for this is the difficulty inherent in the experiments employed. This effect only occurs at the interface, and as such can only be observed from a single monolayer of molecules. Without extreme care in sample preparation and data accumulation important spectral details can be easily overlooked.

The third and final issue is that there appears to be a unique adsorption site of the molecules on the Ge(001) surface. Cabailh obtained a single scanning tunneling microscopy (STM) image, which showed a few patterns of similar dimensions to flat lying molecules. Each of these looked identical, but did not appear consistent with other STM images of these molecules. It was concluded that these were molecules in specific sites, but the image was an enhancement of the substrate surface dimers, rather than an imaging of the molecule itself.

This thesis follows up these intriguing results and aims to provide a thorough characterisation of the interface between phthalocyanines and germanium. To this end three different surfaces of Ge have been employed, namely the Ge(001)- 2×1 surface, the monohydride passivated Ge(001)- 2×1 :H surface, and the Ge(111)-c(2×8) surface. The characterisation of the interfaces is achieved primarily through three experimental techniques: the two synchrotron based techniques of SXPS and NEXAFS as well as scanning tunnelling microscopy (STM). Some supporting simulations of the experimental results were also conducted in the framework of density functional theory (DFT).

Chapter 2 contains a summary of the background related to this work. First, a summary of the properties of the materials is given. This is followed by a review of the background literature of related interfaces. This background literature is broken down broadly into three sections, relating to the three issues arising from the work of Cabailh. Chapter 3 gives a description and theory of the techniques used, which is necessary for a qualitative understanding of the results presented in this thesis. This is then followed by three chapters, each of which deals with and expands upon the three issues arising from the work of Cabailh presented in the order as above. Finally, in chapter 7, the ideas from all three different aspects of the interface characterisation are summarised.

Chapter 2

Background

Organic materials, semiconductor surfaces and the interfaces between the two have been widely studied, but there are many important questions which remain unanswered. In the analysis of the orientation and interaction at interfaces the signal comes (generally) from a single monolayer of material, this limits the number of experimental techniques available. Furthermore, there may be various possible causes for a given result, introducing ambiguity. Therefore, it is only through combinations of different experiments and techniques that reliable conclusions can be drawn.

It is well established that many organics form well ordered interfaces on relatively weakly-interacting substrates, whereas on strongly interacting substrates the interfaces tend to be disordered [8]. These weakly interacting substrates provide an interesting means for determining molecular and thin film properties by minimising the influence of the interface. However, they are generally of less interest from a technological point of view. Unfortunately, on many of the semiconductor surfaces likely to be of more practical interest the interactions become much more complicated. Thorough understanding of the interaction in these cases could lead to a better approach for designing interfaces for specific purposes.

There is already a vast body of research on the properties of the materials and surfaces under investigation within this thesis, for example see refs. [9–12]. A brief summary of the relevant aspects of these materials is given in the first section of this chapter. This is followed by a review of the state of the art of organic/inorganic semiconductor interfaces in the second section.

2.1 Materials

In this thesis the interactions of metal phthalocyanines (MPc) are studied on two different faces of Ge: the (001) and (111) surfaces. As well as that, hydrogen passivated Ge(001), Ag(111) and highly oriented pyrolytic graphite (HOPG), where the molecule-substrate interaction is expected to be weak, are studied for comparative purposes. A range of MPc is studied to

investigate the effect of the configurational and electronic differences, which are the result of a different central metal atom of the molecule. This section details the relevant properties of the substrates, followed by a summary of the properties of the various phthalocyanines.

2.1.1 Substrates

The choice of germanium as a substrate for general investigation has three major rationales. First of all, germanium is a small band gap and high carrier mobility material, ideal for high performance devices [13, 14]. Furthermore, germanium is similar to the industrial standard semiconductor, silicon. Finally, from a practical point of view, it is much easier to work with than many other semiconductors. It oxidises more slowly with the ambient water, which is often unavoidable in vacuum chambers, and can be repeatedly cleaned. This avoids the need for regular sample transfer, which potentially involves a two to three day chamber recovery time. In synchrotron based experiments, where the chamber is often unfamiliar, time is of the essence and the quality of the vacuum is less certain, these considerations become very important.

2.1.1.1 Germanium

Germanium is an indirect band gap semiconductor with a band gap of 0.66 eV at 300 K. It has the diamond lattice bulk crystal structure as shown in fig. 2.1 with a lattice constant of 5.65 Å [15]. The electron mobility in Ge is approximately $3.6 \times 10^3 \text{ cm}^2/(\text{Vs})$ and hole mobility $1.7 \times 10^3 \text{ cm}^2/(\text{Vs})$, roughly three and six times the respective mobilities in silicon [9].

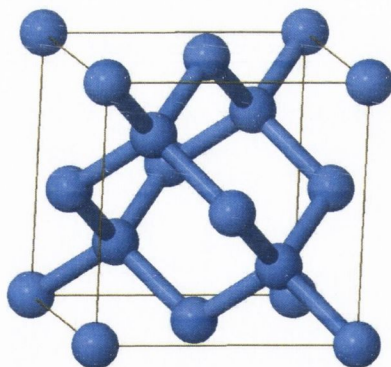


Figure 2.1: Diagram of bulk crystal structure for germanium. Each atom is bonded to four others in a tetrahedral arrangement.

The surfaces can be readily cleaned in UHV by bombardment of the surface with 500 eV argon ions with a dosage of approximately 7-10 $\mu\text{A.h}$. A high quality, atomically flat surface with the reconstructions discussed below can be formed by annealing the sample for 40 minutes at 550°C, followed by slow cooling at 10°C per minute until 400°C at which point the sample can be rapidly cooled to room temperature.

The two faces of Ge investigated in this thesis are (001) and (111). Relevant details about the reconstructions and surface properties are given below.

Ge(001) The (001) face of germanium, as with the (001) face of silicon, reconstructs with tilted dimers. At room temperature some of these dimers have enough energy to rapidly flip, as Si(001) dimers do, yielding a (2×1) reconstruction, however, around defects and step edges the dimers tend to get locked [16] producing the almost degenerate $c(4\times 2)$ and $p(2\times 2)$ reconstructions [17, 18]. The three different reconstructions, as shown schematically in fig. 2.2, are all based on tilted dimers, with differing configurations of the up/down elements of the dimer. Fig. 2.3 shows the LEED patterns for a clean Ge(001) surface for two different electron energies. At the higher electron energy of 42 eV, shown in fig. 2.3 (a), the 2×1 reconstruction which dominates the surface is the only visible reconstruction. Note that this image shows the two domains of the 2×1 reconstruction, rotated 90° with respect to each other, typical for the on-axis Ge(001) surface. At the lower energy of 22 eV shown in fig. 2.3 (b) the combination of a mixture of $c(4\times 2)$ and $p(2\times 2)$ becomes apparent, generating the faint lines between the half order spots of the (2×1) reconstruction.

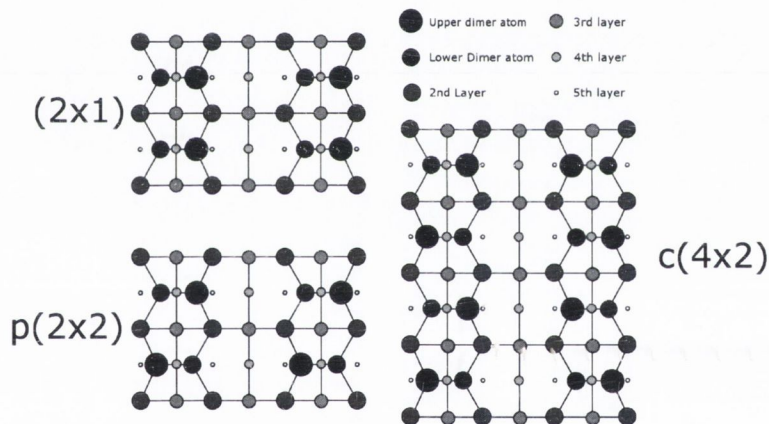


Figure 2.2: Schematic of the different reconstructions observed on the Ge(001) surface at 300 K.

For the purposes of NEXAFS, the main tool used in this work for orientation analysis, a two domain surface is four fold symmetric for which, as explained in section 3.4, all azimuthal information is lost. Therefore, for investigating the direction of tilt of a molecule adsorbed on the surface a single domain substrate is required. Taking a vicinal wafer miscut approximately 6° toward the $[110]$ direction creates a surface where forming double-atomic-layer steps is energetically favourable, giving a single domain over the entire surface [19–21]. The LEED of this shows clear half order spots relating to the (2×1) reconstruction, with only faint half order spots relating to the (1×2) reconstruction (not shown). This indicates that the surface is primarily of a single domain, with some small proportion of steps remaining as single steps, giving a minority of the second domain.

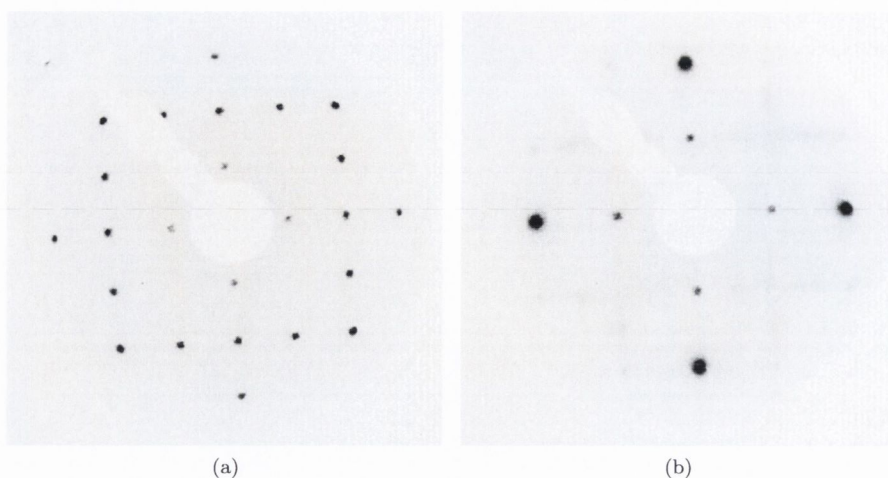


Figure 2.3: LEED of clean Ge(001) surface at (a) 42 eV and (b) 22 eV electron beam energy.

The photoelectron spectrum of the Ge 3d core level is used to track changes in the surface upon deposition of the phthalocyanine. This core level comprises four components in agreement with the literature [22, 23]. The four components are shown in fig. 2.4 and relate to bulk (B), “up” dimer (U) and “down” dimer (D) contributions, plus a feature assigned to the full layer below the dimers (S). See section 3.3.3 for more details of the fitting procedures applied.

It has been demonstrated both experimentally and theoretically that the Ge(001)-2×1 surface is partially metallic [24–27]. These states are predicted to be present for approximately 25% of the time as a result of thermal flipping of the 2x1 dimers. This is important as the degree of shift in adsorbate core levels in X-ray photoelectron spectroscopy is influenced by the density of surface states, in particular metallic surfaces can induce large shifts as a result of image charge screening.

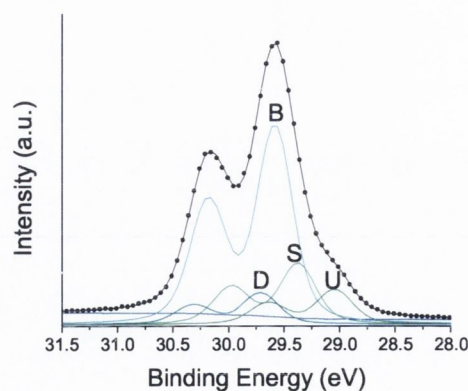


Figure 2.4: Fitting of the 3d core level of clean Ge(001). It is fit with four components and a Shirley background. See text for details of interpretation of the components.

Ge(111) Despite the similarities between Ge and Si, the (111) face reconstructs very differently for the two materials. Si(111) has a famous 7×7 reconstruction, whereas germanium typically reconstructs in a $c(2\times 8)$ pattern with four adatoms per unit cell as shown in fig. 2.5 [28]. Due to the three fold symmetric nature of this substrate no azimuthal information can be obtained from the NEXAFS of adsorbed molecules.

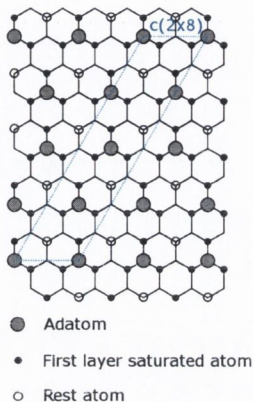


Figure 2.5: Schematic of the Ge(111)- $c(2\times 8)$ reconstruction.

Photoelectron spectroscopy of the Ge 3d core level for Ge(111) is described by fitting with four components [29,30]. As shown in fig. 2.6, these components are attributed to bulk atoms (B), adatoms (A), rest atoms (R) and second layer atoms (S). The intensity ratio A:R:S is 1:1:3 due to the number of each species present as seen in fig. 2.5. The assignment of adatoms and rest atoms is commonly reversed; however, more recent photoelectron holography experiments show that the shoulder at low binding energy is indeed the adatom contribution [31].

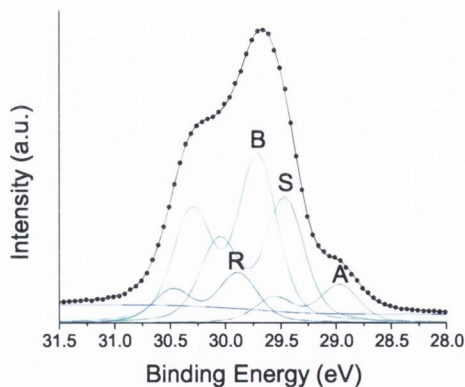


Figure 2.6: Fitting of the 3d core level of clean Ge(111). It is fit with four components and a Shirley background. See text for details of interpretation of the components.

Unlike the Ge(001) and the Si(111) surface the Ge(111) surface displays no metallic characteristic. However, for small coverages of hydrogen it has been demonstrated that metallic surface states arise as a result of passivation of the rest atoms and transfer of charge back to

the adatoms [32], again raising the possibility of metallic screening effects in the PES.

2.1.1.2 Non-Interacting Substrates

To determine certain details about the spectroscopies it is necessary to minimise the number of variables involved. Substrates where the molecules are known to be weakly bound provide the possibility of testing certain hypotheses with a minimum of unknowns involved. For this purpose three substrates where the molecules are weakly bound have been employed: a passivated version of the germanium surface (hydrogen passivated Ge(001)); a metal surface (Ag(111)); and a layered material (HOPG).

Hydrogen passivated Ge(001) The dangling bonds of the Ge(001)- 2×1 surface can be saturated with atomic hydrogen. Typical exposure is between 500 and 1000 L of molecular hydrogen, cracked by a tungsten filament held at approximately 1500°C, 5-10 cm from the sample. This gives a monohydride phase where the dimer bonds remain unbroken, but are now symmetric, with a single hydrogen on each atom in the dimer. To obtain a more uniform monohydride phase the surface is annealed at 150°C after exposure. Exposing the sample to significantly more atomic hydrogen leads to a dihydride phase in which the dimer bonds are broken, producing a 1×1 reconstruction and a roughening of the surface [33–35].

Ag(111) The (111) face of Ag has been shown to be non-reactive with organic overlayers. Moreover, as with many metal surfaces, STM shows that many molecules, including phthalocyanines, are able to move around the surface at room temperature [36]. As a result they can often form well ordered monolayers. The clean surface is prepared through cycles of argon ion bombardment. After entry from atmosphere the crystal can be typically cleaned by three to four cycles of 2-3 $\mu\text{A.h}$ exposure to 1 keV argon ions followed by 10 minute anneals at 500°C. This provides an oxygen and carbon free surface which displays a clear 1×1 pattern in LEED.

Highly Oriented Pyrolytic Graphite (HOPG) Graphite comprises layers of repeated six-membered carbon rings. The surface is non-reactive and stable in air, and the interaction with phthalocyanines is of the weak Van der Waals type via the conjugated π system. It is an unreconstructed, hexagonal lattice, and (0001) oriented. The surface is first cleaved ex-situ by attaching sticky tape then peeling it off taking a number of layers of the surface with it. The remnant crystal is immediately entered into the vacuum and annealed at approximately 500°C in vacuum to drive off any physisorbed molecules.

2.1.2 Phthalocyanines

Phthalocyanines are one example of the many commercially available organic semiconductors. They are an excellent candidate for study for a number of reasons. They have a vapour pressure of approximately 10^{-14} mbar, which makes them suitable for UHV experiments. They are

also thermally and chemically stable, with no sign of degradation, even in air, at up to 400°C. These two features also mean they can be readily deposited in-situ by thermal sublimation from Knudsen cells. Importantly, from an experimental point of view, the interaction of the various different metal phthalocyanines can be tracked to some degree from photoelectron spectroscopy of the central metal atom.

The molecule consists of a macrocycle of four isoindoline subunits, each of which comprises a benzene ring linked to a pyrrole ring. These isoindoline units are linked via bridging aza nitrogen atoms as shown in fig 2.7 (a). This macrocycle is an ion of charge -2 and forms a central cavity which can be satisfied in various different ways. This is commonly either two atoms of a charge of $+1$ (only hydrogen and lithium have a small enough ionic radius for this) or a single metal atom of charge $+2$, although many more elaborate variants also exist. In cases where the chemical species occupying the centre of the ring is large, steric repulsion can result in distortion of the phthalocyanine macrocycle [37]. This leads to two distinct structures of phthalocyanine, planar and non-planar as shown in fig. 2.7 (b).

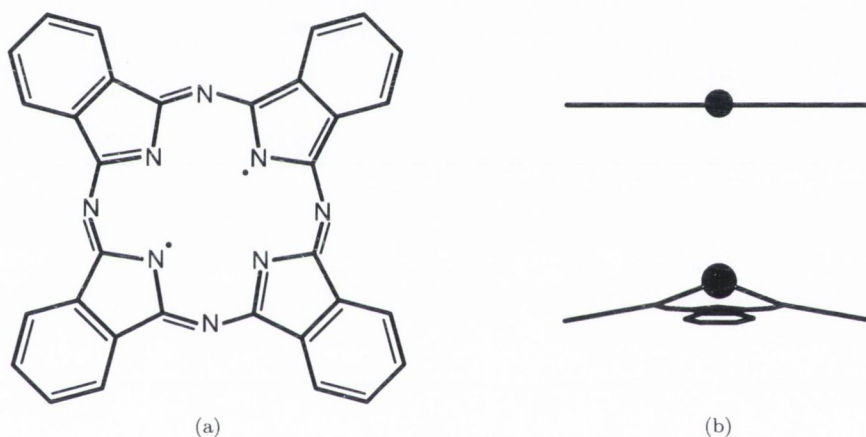


Figure 2.7: (a) Chemical structure of phthalocyanine molecule with (b) a side view of the difference between planar and non-planar phthalocyanines.

In this work, four planar and two non-planar phthalocyanines have been considered. The planar molecules under investigation are metal free (also called hydrogen) phthalocyanine (H_2Pc), magnesium phthalocyanine (MgPc), zinc phthalocyanine (ZnPc) and copper phthalocyanine (CuPc), although there is some argument from theoretical calculations that CuPc deviates slightly from planar [38]. The non-planar molecules studied are tin phthalocyanine (SnPc) and lead phthalocyanine (PbPc).

2.1.2.1 Crystalline structures

There are numerous reported crystalline structures of the different phthalocyanines, see ref [12] for some of these. Most dramatically there are distinct differences in the crystal structures of planar and non-planar Pc. For planar Pc there are two dominant crystal structures, both are monoclinic and are labelled α - and β -forms. Both forms are constructed of stacks of molecules

tilted with respect to each other as shown in fig. 2.8, with four molecules per unit cell in the α -form (two molecules deep in the c axis) and two for the β -form. The tilt angle, θ , is also different for the two crystal structures. The dimensions of the crystal structure are nearly independent of the central atom for all planar MPc.

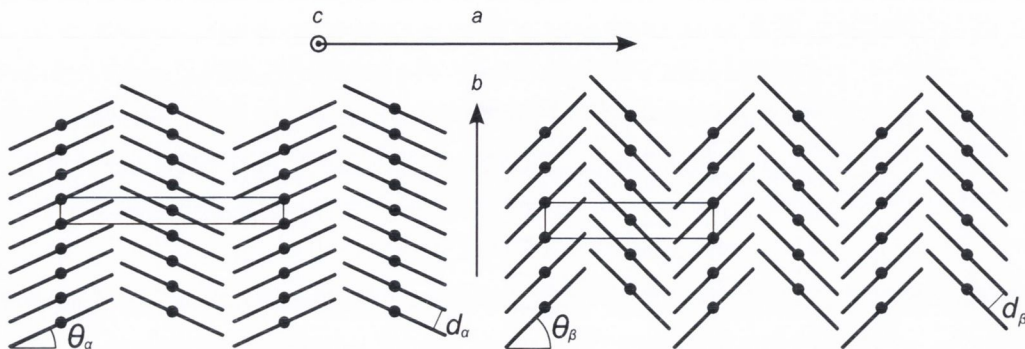


Figure 2.8: Schematic of the α (left) and β (right) crystal structures of the planar phthalocyanines. All planar phthalocyanines take these forms with $\theta_\alpha \approx 25^\circ$, $\theta_\beta \approx 45^\circ$ and $d_\alpha = d_\beta \approx 3.4 \text{ \AA}$. For the α form $a \approx 25.9 \text{ \AA}$, $b \approx 3.8 \text{ \AA}$ and $c \approx 23.9 \text{ \AA}$, and for the β form $a \approx 19.4 \text{ \AA}$, $b \approx 4.8 \text{ \AA}$ and $c \approx 14.6 \text{ \AA}$. Adapted from [12].

As with the planar phthalocyanines the non-planar PbPc shows two main crystal structures, a monoclinic phase and a triclinic phase. As seen in fig. 2.9, in the monoclinic phase the molecules stack directly on top of each other [37]. In the triclinic phase the molecules stack offset from one another with the protrusion alternating between up and down [39]. In this triclinic phase adjacent rows of molecules are almost perpendicular to each other as indicated in fig. 2.9. SnPc is only reported to exhibit a triclinic phase. This is similar to that of PbPc, but differs in that the adjacent rows of molecules are parallel to each other [40].

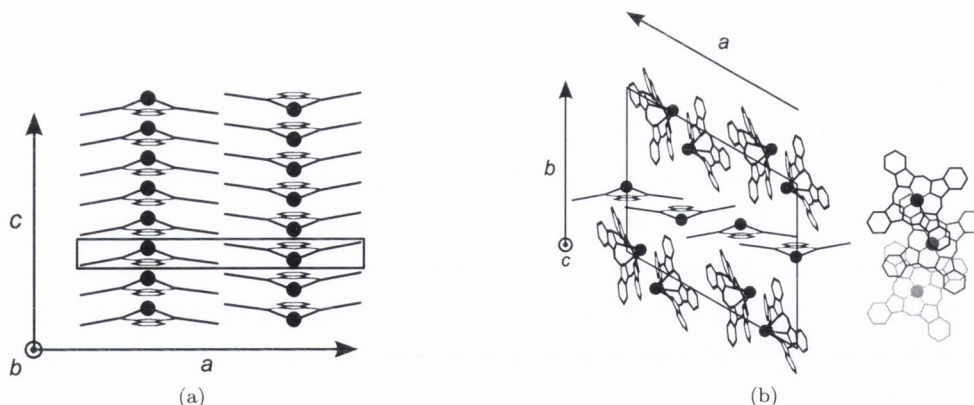


Figure 2.9: Schematic of (a) the monoclinic and (b) the triclinic crystal structures of PbPc. On the right of the triclinic structure the overlap of PbPc molecules in the stacking direction is shown. Adapted from [37] and [39].

These different crystal structures can have very different properties. For example, the two different crystal forms of PbPc [37,39] have been shown to exhibit several orders of magnitude difference in DC conductivity [39,41,42]. Thus the ability to generate the desired crystal

structure is very important. The crystal structure which forms depends largely on factors such as pressure, temperature and deposition rate [12]. However, the interface also plays a critical role. It acts as a template which defines the axis of crystal growth and strongly influences the quality of film produced.

Moreover, these different crystalline structures follow irreversible phase changes upon annealing [12]. This temperature of phase change depends both on the crystal structure and the molecule. For PbPc the phase change from monoclinic to triclinic has been seen at 130°C [43] and yet the H₂Pc α phase which converts to β upon annealing is stable up to 313°C [44]. This critical temperature is also dependent on the orientation and quality of the film. Vincett et al. [45] clearly demonstrate that for various α phase films of H₂Pc grown on glass at temperatures between -180°C and +50°C, films grown near a critical temperature of 5°C require higher temperatures to undergo the expected phase change.

2.2 Background literature of related interfaces

This work follows on from research conducted by Cabailh in which he was investigating MPc on Ge(001) and GaAs(001). Arising from this research there were three main unanswered questions about the MPc-Ge(001) interface: The first relates to NEXAFS results, which indicated an unexplained tilt at the interface; the second relates to shifts in the PES of the central metal core level; and the third relates to the specific adsorption sites of the molecules. This thesis looks at these three aspects of characterisation of the MPc-Ge interface and extends it to two other surfaces of Ge, the (111)-c(2×8) surface and the monohydride (001)-2×1:H surface. This section details important and relevant results from other authors, broken down into the respective issues mentioned above.

2.2.1 Molecular tilt

As mentioned previously there are dramatic differences in electronic properties depending on the ordering of molecules within the film [39, 46]. Knowing the geometry at the interface can also be important for other properties. For example, when employed in solar cells, charge separation can be dramatically improved by controlling the orientation with respect to the substrate [47]. Consequently, there is great benefit in understanding and controlling the ordering and orientation of molecules both at organic/inorganic semiconductor interfaces and in organic films.

In the work of Cabailh, the interfaces of Mg-, Sn- and PbPc on Ge(001) and GaAs(001) were investigated with NEXAFS. The first monolayer of SnPc apparently adsorbed on both substrates with the molecular plane at 25° to the substrate. MgPc also showed this same tilt on Ge(001), while data for a monolayer of PbPc were not presented [5]. These results are surprising given that STM of various phthalocyanines on various substrates, including metals and III-V semiconductors, indicates flat-lying molecules [36, 48–54]. On silicon the results are

not quite so clear-cut [55, 56], with line profiles across molecules, presented by Liu et al. [56], indicating the possibility of some degree of tilt. However, this is not enough to explain the angle observed by Cabailh [5]. The only STM of MPc on Ge(001) was taken with a low bias, which only imaged an enhancement of the dimers underneath the molecule. Although inconclusive this too seemed to indicate flat-lying molecules, at specific adsorption sites [5].

STM conducted on Si(001) clearly shows specific adsorption sites, one similar to that observed on Ge(001), whereas on the Si(111) surface, if specific sites are adopted, it is not observable through STM [57]. One NEXAFS study of phthalocyanines on Si indicates that CuPc molecules on Si(001) are completely disordered, in contrast to expectations from the STM results, whereas a strong dichroism is observed in CuPc on Si(111) [58]. In contradiction to this, another study indicates no angular effect of a monolayer of CuPc on Si(111) [59]. However, this disagreement could be the result of the different sample preparation procedure employed.

On most weakly interacting substrates the molecules are mobile over the surface at room temperature. These substrates create interesting possibilities for understanding the NEXAFS results further. By minimising the interaction between substrate and molecule, not only are the molecules able to arrange themselves parallel to the substrate, but any distortion in the electronic orbitals introduced by the substrate can also be minimised. However, to date there are no published NEXAFS results from a ML thickness on any such system.

InSb is a substrate on which long range ordering of flat lying molecules is observed, despite the fact that the phthalocyanine bonds to it strongly enough for individual molecules to become immobile at room temperature [54, 60]. Unfortunately NEXAFS of the PbPc on InSb system fails to clear up any of the confusion, with leading edge absorption features maintaining significant intensity at normal incidence for a single monolayer [61], where for flat lying molecules zero intensity would be expected (see section 3.4).

One possible explanation of these apparently contrasting STM and NEXAFS of molecules at the interface is that the observed tilt is an electronic rather than physical effect. For chemisorbed molecules the possibility exists for extra-molecular transition from a molecular core level into substrate related states [62]. This has been observed for small molecules on metallic substrates [7, 63], but no examples of this on semiconducting substrates could be found. Although this might contribute some intensity to the spectrum the onset of any intensity cannot occur below the PES binding energy of the relevant core level. Given this, it should not alter the intensity of the first π^* peak. Furthermore, this intensity should be step like, rather than the structured lineshape observed by Cabailh [5], which indicates transitions into molecular states. Therefore this alone is an insufficient explanation of the observed tilt.

A further possibility has been suggested by Mainka et al. [6]. An *apparent* tilt in the molecular plane of benzene was shown to be due to a bending of the hydrogens away from the molecular plane. For phthalocyanines two analogous possibilities present themselves: A bend in the C-H bonds on the benzene carbons; or a bending of the whole molecular plane. However, the only reported distortions of similar systems are minor, similar to that of the non-planar

phthalocyanines in gas phase. The bending is much less than the 25° tilt determined by NEXAFS [64,65].

Film growth beyond the interface becomes strongly dependent on the metal atom present. In the work of Cabailh the planar MgPc has an average tilt of 65° for a 60 Å film, consistent with the α -form with the b -axis parallel to the substrate. This change of tilt angle for planar phthalocyanines has been observed in a number of other systems, and through other experimental techniques [66,67]. The SnPc, on the other hand, maintains an angle of 25° , most consistent with the monoclinic phase with stacking perpendicular to the substrate. The PbPc NEXAFS for a 60 Å film is best fit with a molecular tilt of 45° , inconsistent with any simple configuration of either of its two known crystal structures with respect to the substrate, possibly indicative of a mixed polycrystalline structure.

Of some interest for further study is the influence the interface layer has on film growth. H_2Pc is observed to grow with the b -axis perpendicular to the Ag(111) surface, but parallel with the Ni_3Al surface [68], despite the fact that in both cases the molecules are aligned parallel with the substrate at the interface. Similarly, CuPc, which has a crystal structure almost identical to that of H_2Pc and other planar MPc, is observed to orient with the b -axis parallel to the HOPG surface in one preparation [66] yet perpendicular in a different preparation, where the conditions were nominally the same [69]. This is despite the fact that the first monolayer appears well ordered and flat lying in both cases, as expected from all other experiments [48,50,70].

One possible explanation for these non-intuitive results arises from studies of phthalocyanines grown on a template layer of perylenetetracarboxylic dianhydride (PTCDA). Planar phthalocyanines on SiO_2 grow in bulk crystals of upright molecules, but with just a single monolayer of PTCDA as a “template” they grow in a flat-lying configuration [71]. Calculations of this system show differences in the energy of only a few percent between the flat-lying and upright configurations [72]. As a result, the structure of each subsequent layer depends on small differences in the layer beneath. Different phases of MPc on weakly interacting substrates, observed to form for small variations in sample preparation [50,51,73], could potentially facilitate the same effect. The dramatic effect for bulk crystal growth of small changes at the interface implies a need for careful characterisation of the interface.

Given the dramatic difference in crystal structures for subtly different systems and the large influence crystal structure has over the electronic properties of the film, a firm understanding of the interface is necessary for optimum device design. Due to the nature of the interaction at the interface and the variety of possible causes of an observed result there is significant uncertainty in the interpretation of the NEXAFS results. However, the alternative techniques employed for this purpose such as metastable atom electron spectroscopy (MAES) [74], angle resolved ultraviolet photoelectron spectroscopy (AR-UPS) [75], ellipsometry [76] and STM [67] all have their own associated limitations. This makes conclusive analysis of such systems difficult and comparison between different systems and techniques becomes necessary.

2.2.2 Non-planar MPc metal ion core shifts

This section discusses elements of electronic structure at the interface, primarily related to possible effects causing the “up/down” influence of the metal core level observed by Cabailh.

There are currently no examples of such an effect in the literature, other than that of Cabailh [5, 77]. Because of this, this review starts with literature of similar systems where *no* such effect is observed. There are a handful of publications investigating the interfaces of non-planar phthalocyanines on semiconductor surfaces. For PbPc on Si(001) and Si(111) the Pb 4f core level of a monolayer of phthalocyanine has shown no such double state [55]. Likewise, a number of studies of the interface of non-planar phthalocyanine with III-V semiconductors also show no such effect. This includes SnPc and PbPc on GaAs [5] and PbPc on and InSb [78]. PES results of PbPc on InSb indicate a possible interface state, but with no spectra of less than a three ML coverage the nature of this state is unclear [79]. Moreover, energy difference between the two spectral components observed here is nearly twice that of the PbPc-Ge(001) interface indicating it is likely to be of some other origin.

There are only two articles of PES from monolayer films of non-planar phthalocyanines on metal substrates. One is of PbPc on Pt(111) [80] and the other is of SnPc on polycrystalline Fe [81]. Both of these show an apparently similar effect to that observed by Cabailh, i.e. a second state is seen to lower binding energy. However, in these cases this is related to a reaction in which the metal atom is stripped from the molecule. Consequently, it is unlikely the shift observed by Cabailh would be possible in either case.

Photoelectron energy shifts can be broken down into differences in the initial state of the electron or of the final state. The dominant initial state effects are due to charge transfer or an intrinsic polarisation. The final state effects are due to a relaxation of orbitals due to the photohole, and are also typically either by charge transfer or polarisation of the surrounding medium. Determining exactly which of the above factors is the source of a given shift is a difficult prospect.

Molecular dipoles are expected to introduce equal shifts in all PES peaks. Various ultraviolet photoelectron spectroscopy (UPS) studies of non-planar phthalocyanines on weakly interacting substrates show two states in the HOMO level of the valence band, attributed to molecular dipoles. Titanyl phthalocyanine (TiOPc) on ZnO(0001) shows two peaks in the HOMO region, 0.8 eV apart [82]. This is similar to the energy separation of the Pb 5d and Sn 4d core levels of PbPc and SnPc on Ge(001), observed by Cabailh. On HOPG similar but smaller shifts have been observed for vanadyl phthalocyanine (VOPc), TiOPc and PbPc [83–86]. This provides one potential explanation for the two states observed in the metal core level. However, it is also possible that the doublet states of the HOMO are not the result of a molecular dipole at all, instead being the result of splitting due to dimerisation of the molecules [87].

Charge transfer is commonly assumed to be the sole mechanism of chemical shift. In systems where the photohole is expected to be “completely” screened by transfer of one electron this assumption can be near to the truth [88]. However, in molecular or insulating systems it

often breaks down and the final state effects play a significant role. In general PES of metal phthalocyanines on the (001) surfaces of Si and Ge tend to indicate an increase in binding energy of substrate surface core levels, and a decrease in binding energy of molecular core levels [5, 89] indicative of transfer of electrons from the substrate to the molecule. Likewise for MPc on the Si(111) surface there are indications of electron charge transfer from substrate to molecule [58, 90]. However, there is no indication in any of these cases of charge transfer into the metal atom itself, only the macromolecule.

Work on the effect of dielectric screening by the substrate shows significant shifts for gas molecules adsorbed on metal substrates [91–93]. However, these effects are expected to be smaller where the molecule provides better self-screening, and where the substrate screens less effectively than a metal. On HOPG it has been shown that such dielectric screening does not occur [94]. Despite this, there is some expectation that Ge would make an effective substrate for screening due to metallic surface states [24, 26, 27].

Finally, there is the possibility of charge transfer in the final state as a mechanism of the observed shift. This is a very difficult process to separate from any other form of chemical shift. There are a few examples of the influence of final state charge transfer for adsorbed gases such as N_2 and CO on Ni(001) or Ar on Pt(111) [88, 95]. The charge transfer for these systems of small molecules can to some extent be understood by application of the $Z + 1$ hypothesis. This states that the core ionised atom is similar to the next atom in the periodic table, i.e. the atom of atomic number $Z + 1$ where Z is the atomic number of the photoionised atom. Comparison of the adsorption energies of the target molecule and the molecule created by replacing the photoionised atom with its $Z + 1$ counterpart can then give some indication of the final state energy [95]. However, for most systems, in particular those with larger molecules, this is generally not possible to determine experimentally. In this case theoretical approaches can provide valuable insight, but due to the large systems involved are computationally taxing.

2.2.3 Molecular adsorption

There is no literature of the specific bonding involved for phthalocyanines on Ge(001) or Si(001). However, the primary adsorption site of MgPc on Ge(001) is shown to be across two dimer rows, although only a modification of the substrate atoms has been observed [5]. On Si(001) CoPc occupies three different adsorption sites, two straddling two dimer rows and one centred on a single dimer row [56], similar to CuPc on the same surface [96, 97].

No results exist for STM of phthalocyanines on the (111) surface of Ge. On the Si(111)- 7×7 surface a few studies have been conducted, none of which clearly show specific adsorption sites for the phthalocyanine [55, 57, 96]. The indication from these papers is that imaging of the molecules is much more difficult on the (111) surface than the (001).

Beyond the STM results, PES of various phthalocyanines on Si(111) shows a reaction, not observed on Si(001), in which the metal is removed from the molecule. In one example, a significant fraction of the metal is found to be in a neutral state for CuPc and F_{16} CuPc deposited

on Si(111), rather than the expected +2 state [58,96,98]. However, there is some confusion in this issue, with the recent work of Wang et al. indicating a +1 state of Cu from CuPc on Si(111) [59]. These contrasting results highlight the challenges involved in these experiments. Similar reactions have been observed for MPc on metal substrates [80,81].

As a consequence of the lack of substantial work in this area for phthalocyanines, it is worth looking at research related to the functional groups making up the molecules. The (001) surfaces of the group IV elements silicon and germanium exhibit similar chemistry to carbon, the building block of all organic chemistry [99]. This is due to a π bond which occurs between the dimers on the surface, analogous to carbon-carbon double bonds. This provides useful insight into the types of chemistry that can occur at these surfaces. Unfortunately, on Ge(111) there are no π like bonds in the surface. The reconstruction on this surface does not have a useful analogue in organic chemistry, making discussion of adsorption possibilities more difficult.

In consideration of possible reaction of the benzene functional groups of the MPc there are two major types of reactions likely with the Ge(001) dimerised surface. They are both cycloaddition reactions called $[2+2]$ and $[4+2]$, where the numbers indicate the number of π -electrons involved in bond formation. Fig. 2.10 shows these two processes schematically.

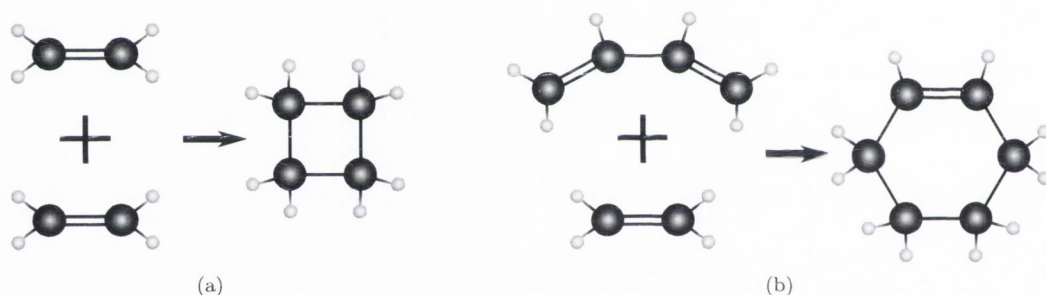


Figure 2.10: Schematic of (a) the $[2+2]$ and (b) $[4+2]$ cycloaddition processes.

In organic chemistry the $[2+2]$ reaction is not expected to occur without significant activation energy due to symmetry considerations. However, on Ge and Si these reactions can progress due to the asymmetry of the dimers, although generally through intermediate pathways [99,100]. This fact highlights the potential limits of using organic chemistry analogues.

On Si benzene is seen to bond exclusively via the $[4+2]$ reaction, with three different adsorption geometries [100]. Two of these are depicted in fig. 2.11 (b) and (c), the third bridges two dimers with four adjacent carbons, but only occurs at what are known as type C defects. Although on Ge less work has been presented than on Si, the $[4+2]$ product has been clearly shown, and as for Si(001) there is no indication of the $[2+2]$ cycloaddition product [101]. In this case the molecule bonds primarily through two opposite carbons of the ring as depicted in fig. 2.11 (b), although it is uncertain whether the bridging product could also exist. These bonds are relatively weak and benzene desorbs from Ge(001) at room temperature [101].

Also of interest is the relative bond strengths of these cycloaddition products for different

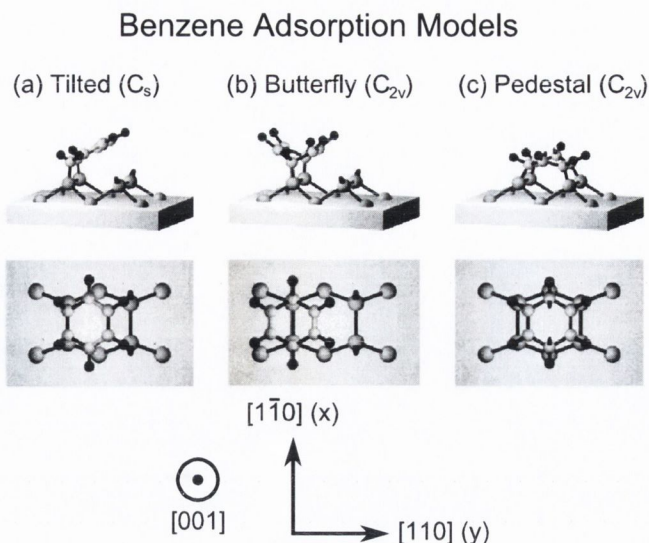


Figure 2.11: Models of different possible adsorption sites for benzene on the Ge and Si (001)- 2×1 surfaces. The $[2+2]$ product in (a) does not occur on either surface at room temperature, the $[4+2]$ product in (b) occurs on both substrates, and the bridging structure in (c) occurs on Si(001). Adapted from Fink et al. [101].

group IV elements. The trend in bond energy is $C-C > C-Si > C-Ge$. Consequently benzene is seen to desorb from Ge(001) on heating to 275 K, whereas it remains stable on Si(001) until over 500 K [101]. Other small molecules that form $[4+2]$ cycloaddition products with Si(001) decompose on heating and form carbides on the surface, while these reactions are reversible on Ge(001) [100]. This reversal occurs for butadiene at 570 K, near the temperature at which phthalocyanines sublime [102].

Where there are non-carbon atoms in the functional group, such as the pyrrole groups of MPc, electrophilic/nucleophilic reactions can occur. Where one atom has an excess of electron charge, which generally occurs for nitrogen due to a lone pair, and another has a lack of electron charge, a bond known as a coordinate covalent, or dative bond can occur. The asymmetric nature of the bond in the Ge(001) dimer results in transfer of electron charge from the lower to the upper dimer atom, making them electrophilic and nucleophilic respectively, as shown in fig. 2.12. This opens the possibility for dative bonding of pyrrole groups with the lower dimer atom.

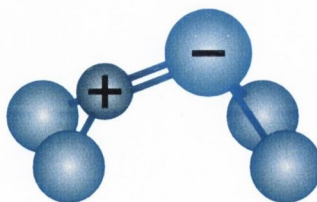


Figure 2.12: Cartoon of a charge distribution in a dimer on the Ge(001) surface.

For the most simple N containing organic molecules, the methylamines, dative bonds occur

on both Si and Ge at very specific sites [103, 104]. The 6-membered aromatic ring pyrimidine, which has two nitrogens is also seen to bond datively through one or both nitrogens to one or a pair of down dimer atoms [105]. Finally pyrrole, which makes up the inner 5-membered ring in phthalocyanines also follows dative bonding reaction pathways on Ge(001) [106]. However, unlike other N containing organics, the aromatic nature of pyrrole means that the dative bond can occur through the carbons as well as the nitrogen. This results in final products in which there is no dative bonding, despite the initial bond formation being dative. For the majority of pyrrole on the Ge(001) surface, hydrogen bonds dissociatively to one dimer atom, while the pyrrole ring bonds covalently to the other [106].

Finally, as with the cycloaddition products, the small datively bonded organic molecules can be desorbed without decomposition on Ge(001). In the case of trimethyl-amine this desorption occurs at approximately 360 - 400 K [104].

The last surface under investigation in this thesis is the Ge(001)- 2×1 :H surface. The passivation is expected to dramatically reduce the interaction with any adsorbed molecules. Although no work has been conducted on organics adsorbed on this surface it is likely that it will behave similarly to other weakly interacting substrates. Where the interaction with the substrate is weak the adsorption arrangement is dominated by intermolecular interactions. However, there is still an influence of the substrate in many cases, with slightly different unit cells observed on different substrates [36, 48, 54]. The first monolayer in these systems is typically flat-lying [50–53]. The structure formed often depends on coverage, with different loosely and densely packed monolayer structures commonly observed [49]. Due to the high mobility of molecules on these surfaces imaging in STM is generally only possible at very low temperatures or when large domains of molecules form, stabilising themselves.

2.3 Summary and plan

Although the materials involved in the interfaces under investigation here are well understood there are significant gaps in the literature of these and related interfaces. STM shows flat-lying MPc in most cases, yet *no* NEXAFS has been reported to show these as flat-lying. Different results are obtained for different phthalocyanines and different surfaces, but comparison between these results is difficult. In some cases the results even seem to contradict one another. Chapter 4 of this thesis presents a more comprehensive study of possible tilt, comparing different interfaces and testing the basic assumptions of the analysis, as required.

There is also insufficient literature to explain the particular shift in the core level of the metal ion in non-planar MPc, observed by Cabailh. In this case no directly comparable shifts have been observed. There are a number of different mechanisms by which this shift could occur. The possibility of this shift resulting from a molecular dipole seems promising, with results showing significant shifts in the HOMO of non-planar MPc. However, it has also been suggested that these HOMO shifts are actually splitting due to dimerisation of the molecules.

Similarly, dielectric screening by the substrate is a possibility, with the Ge surface displaying the high density of states necessary for such screening. For simple gas molecules adsorbed on metal substrates this is shown to cause large shifts, enough to explain the observations of Cabailh. The other possibilities relate to charge transfer. But, although PES shows electron charge transfer *from* the substrate, this adds little value as it is found to be the same for both planar and non-planar MPc. In chapter 5 of this thesis the dataset is expanded to other systems likely to exhibit the shift and the various mechanisms are more fully explored.

In the case of molecular adsorption there are a few useful STM studies of similar systems. More importantly there is a large body of work of simple molecules adsorbed onto the Si(001) and Ge(001) surfaces. These provide a good starting point for an understanding of how the MPc molecules may interact with the surface. Unfortunately, for complicated molecules the number of possible interactions increases, making determination of the actual interactions more difficult. An example of this is the multiple adsorption sites observed for MPc on Si(001). There are no reported adsorption studies of organics on the H-passivated Ge(001) surface, which is expected to dramatically reduce interaction with the substrate. In systems where the interaction is weak the molecules tend to be mobile and the arrangement is dominated by intermolecular interactions. There are also no published results for MPc on the Ge(111) surface, but indications from the related Si(111) surface lead to an expectation of strong interaction and the metal atom is removed from the macromolecule for a portion of the molecules. STM shows immobile molecules on the terraces but with only poor resolution, preventing the determination of any specific sites. In chapter 6 the adsorption on these three surfaces is investigated and compared, primarily via STM, but also drawing on PES and NEXAFS.

Chapter 3

Experimental Techniques

To accurately characterise the various surfaces and interfaces involved in this work, a number of different experimental procedures are required. This section contains a brief description and supporting theory of all of the experimental techniques that were employed for this thesis. The three primary techniques used in this work are near edge x-ray adsorption fine structure (NEXAFS), photoelectron spectroscopy (PES), and scanning tunneling microscopy (STM). This is supported by the secondary techniques of low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Finally, the interpretation of the experimental results was assisted by the use of the computational technique, density functional theory (DFT).

Determination of a well prepared substrate surface is of critical importance to all experiments relating to the chemical and electronic properties of interfaces. High quality and repeatable results require high quality and repeatable surface preparation. This was achieved by combining the ability of PES or AES to detect the presence of impurities and LEED to determine the form and quality of surface reconstruction.

The issues discussed in each of the next three chapters are each focused primarily around one experimental technique. However a comparison of results from the different techniques is required for more complete analysis. The molecular tilt is investigated primarily through NEXAFS, with supporting information from DFT. The interface states of the metal core level of non-planar MPc is investigated primarily with PES. The adsorption of the MPc with the three substrates was investigated by a combined STM and PES study.

3.1 Low Energy Electron Diffraction

LEED is a technique commonly used in the determination of surface structure in ordered systems. A diffraction pattern generated by back scattered electrons relates to the reciprocal space interpretation of the surface symmetry. However, this is limited to the symmetry and gives no information about surface atom position; for example, if all surface atoms are uniformly shifted relative to the bulk, no change would be observed in diffraction pattern *positions*. To

reveal more information, the more in-depth techniques of spot profile analysis LEED (SPA-LEED) and/or intensity-voltage LEED (IV-LEED) are required. However, these still require long range order of overlayers, and would provide no information in the systems under discussion here, where this is not the case. Consequently, details of these are not included here.

The wavelength of an electron is defined by the de Broglie relation:

$$\lambda = \frac{h}{p} \approx \left(\frac{h^2}{2meV} \right)^{1/2} \approx \left(\frac{150}{E(\text{eV})} \right)^{1/2} (\text{\AA}) \quad (3.1)$$

For an electron wavelength of 4.0-0.5 $\text{\AA}$ similar to the typical surface lattice spacings required for diffraction, the electron energy must lie in the range of approximately 10-600 eV. Electrons with energy in this range have a mean free path in the order of $\sim 5\text{-}20 \text{\AA}$ in solids. This quality makes LEED a strongly surface sensitive technique for determining surface symmetry.

A typical experimental set-up is given in fig. 3.1. The apparatus consists of a monochromated electron source directed at normal incidence to the sample with a spherical phosphorescent screen to display the back-scattered diffraction pattern. In front of the screen there are a series of grids, the first connected to ground, with the grid behind at a negative voltage generating a retarding field. This prevents any inelastically scattered electrons from penetrating through to the screen. The screen is held at a high voltage (typically 4-6 kV) to accelerate all remaining electrons toward the screen to provide the required phosphorescence.

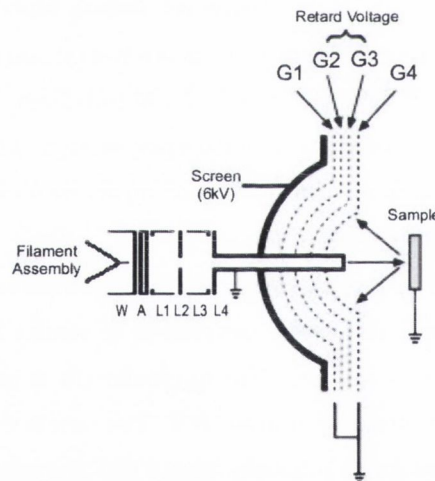


Figure 3.1: Diagram of a typical LEED experimental set-up. The filament assembly, Wehnelt (W), anode (A) and lens elements (L1 - L4) make up the electron gun. The four grids (G1 - G4) and the screen make up the detector.

The electron gun consists of various lens elements which define the spatial resolution; typically the spot size is in the range 0.5 - 1 mm. The energy resolution is primarily defined by the temperature of the filament. Thermionically emitted electrons have energy $E = \frac{1}{2}kT$, which yields an energy spread of 0.1 eV at 1000 K (typical for LaB_6 filaments) or 0.3 eV at 2500 K (typical for W filaments).

The production of a diffraction pattern relies upon a coherent electron beam. In reality, due to both the energy and spatial spread of the electron beam, it is not coherent over the entire spot. To describe the spot more accurately the idea of a coherence length is introduced. Although over the area covered by the spot the beam is incoherent, over very short range (~ 100 Å) it can be considered coherent. The observed diffraction pattern is an incoherent sum over the contributions from these areas.

Many LEED images are not a simple reciprocal space interpretation of the surface symmetry. The diffraction pattern generated is a sum of diffraction patterns created by local surface symmetry. Many surfaces reconstruct such that there are multiple domains of the particular reconstruction rotated with respect to each other, which results in diffraction patterns from all domains superimposed on one another. Ge(001) generally has two distinct 2×1 surface reconstruction domains rotated 90° to each other. For the Ge(111) surface, which has 6-fold symmetry before reconstruction, the LEED shows a superposition of three different reconstruction domains rotated 60° to one another.

The LEED system mostly used in this study is an Omicron SpectraLEED. This is a rear view system, with a camera attachment and a LaB₆ filament in the electron gun.

3.2 Synchrotron Radiation

Synchrotron radiation refers to the light emitted by charged particles as they trace a curved trajectory. Synchrotrons employed as radiation sources use electrons with relativistic velocities. The total power spectrum of the radiation produced in this case is proportional to γ^4 with

$$\gamma^{-1} = \sqrt{1 - \frac{v^2}{c^2}} = \frac{mc^2}{E} \quad (3.2)$$

where v is the velocity of the particle, m its rest mass, E its energy and c is the speed of light. Thus, it is proportional to the fourth power of particle energy, and to the fourth power of the inverse of the particle mass. This is the reason high energy sources are required and why electrons are typically used. The radiation emitted by a charged particle of low velocity has a $\sin^2(\theta)$ distribution, where θ is the angle between the observation direction and the orbital radius. At relativistic speeds the observed radiation becomes strongly directed along the tangent of motion, with angular distribution proportional to γ^{-1} . Radiation produced in this way is strongly polarised in the plane of the particle motion.

A typical synchrotron storage ring is made of straight sections of vacuum tubing linked by curved sections set within bending magnets, as shown in fig. 3.2. Various arrangements of magnets are also used to surround the straight sections of tubing to provide other characteristic spectra such as wigglers, undulators and shifters. The only one of these utilised for experiments contained within this thesis is known as an undulator. This is a series of magnetic dipoles (up to 100) which operate at low field, generating interference patterns in the radiation produced

from the sequential oscillations of the electron motion. This results in a high intensity, relatively narrow bandwidth spectrum of radiation. The light generated by undulators is almost 100% polarised in the plane of motion, compared with a typical value of 85-90% in the case of bending magnets.

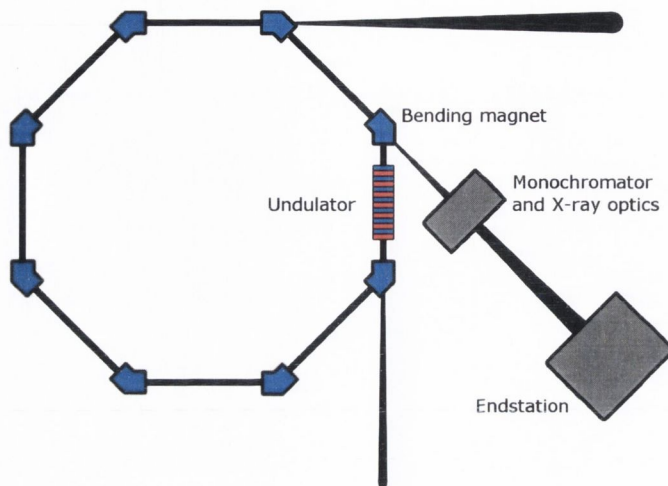


Figure 3.2: Schematic of the basic features of a synchrotron radiation facility.

X-ray optics are then used to produce the usable beam. The light generated is monochromated with a movable diffraction grating in tandem with entrance and exit slits. It is then focused to minimise spot size on the sample. In undulator experiments the gap between magnets is also varied to tune the energy at which the peak intensity occurs. The result of all this is a high intensity, well focused, polarised, tunable radiation source.

3.3 Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is a well established technique which yields information about electronic structure and bonding at surfaces and in the near surface bulk. The energy spectrum of electrons emitted by the photoelectric effect, due to absorbed monochromatic photons yields information about the bound state of these electrons. PES is often divided into two main categories depending on the energy of photons used. When conducted with low energy photons it is typically called ultra-violet photoelectron spectroscopy (UPS), providing a tool for analysis of the loosely bound valence states. With higher energies it is typically called X-ray photoelectron spectroscopy (XPS) or, historically, electron spectroscopy for chemical analysis (ESCA). This allows for the analysis of the tightly bound core states, and provides a elementally sensitive technique for analysing surface and bulk electronic states. When conducted with synchrotron radiation it is commonly referred to as soft X-ray photoelectron spectroscopy (SXPS).

In this work both synchrotron and lab based PES have been employed. Lab based sources provide fixed energies depending on the type of source used, in this case He I emission (21.2

eV) and Mg- and Al- $K\alpha$ emission (1253.6 and 1486.6 eV respectively). The use of tunable synchrotron radiation introduces an extra dimension to the basic PES process. By selecting specific photon energies the surface sensitivity can be dramatically altered by tuning the electron kinetic energy, as can the intensity due to cross section.

This section details the important aspects of the theory of photoelectron spectroscopy, a basic description of the equipment and an explanation of the processes used for analysis of photoelectron spectra.

3.3.1 PES Theory

There is a large body of theory related to PES, much of which, although required for calculation of spectra, is unnecessary for interpretation of experimental data. The following section contains the basic theory required for an appropriate understanding of results presented in this work. For more information see references [107, 108].

The most critical theoretical result for the purposes of these discussions is understanding the probability of a particular excitation occurring. The probability of transition P_{if} of an electron from an N-electron initial state Φ_i to the N-electron final state Φ_f assuming some perturbation, defined by the interaction matrix $\mathbf{H}_{\text{Int}}$, is given by Fermi's Golden Rule as [108]

$$P_{if} = \frac{2\pi}{\hbar} |\langle \Phi_f | \mathbf{H}_{\text{Int}} | \Phi_i \rangle|^2 \delta(E_f - E_i - h\nu) \quad (3.3)$$

where the delta function takes into account the energy conservation due to absorption of a single photon with energy $h\nu$. The general form of $\mathbf{H}_{\text{Int}}$ is

$$\mathbf{H}_{\text{Int}} = \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) - e\phi + \frac{e^2}{2mc^2} \mathbf{A} \cdot \mathbf{A} \quad (3.4)$$

where $\mathbf{A}$ is the vector potential of the incident radiation, $\mathbf{p}$ is the momentum operator ($i\hbar\nabla$), ϕ is the scalar potential and e , m and c are the electron charge, rest mass and the speed of light respectively.

This expression can be simplified, while retaining the essential details for most cases. Applying the commutation relation gives $\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A} = 2\mathbf{A} \cdot \mathbf{p} + i\hbar(\nabla \cdot \mathbf{A})$, and under the assumption of translational invariance at the site of core hole creation $\nabla \cdot \mathbf{A} = 0$. Furthermore, if one assumes that only single photon processes are involved, the term $\mathbf{A} \cdot \mathbf{A}$ can be ignored. Finally, if the Coulomb gauge is used $\phi = 0$ and $\mathbf{H}_{\text{Int}}$ is reduced to

$$\mathbf{H}_{\text{Int}} = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \quad (3.5)$$

This is generally referred to as the *dipole approximation*.

This can be further simplified because, except at very high energy, the wavelength of light is large in comparison to the electron wavefunction, so can be considered as a constant $A = A_0$. Combining eqs. 3.3 and 3.5 gives us

$$P_{if} \propto |\langle \Phi_f | \mathbf{p} | \Phi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.6)$$

Due to the rapid nature of the photoemission process, a common assumption known as the *sudden approximation* is employed. It is assumed that the electronic transition is essentially a single electron event because it is “sudden”, so that the other electrons of the target system do not have time to relax. In this case, the transition matrix can be separated into the one electron event, and overlap integrals of the initial and final states of all other electrons in the system, i.e.

$$\langle \Phi_f | \mathbf{p} | \Phi_i \rangle = \langle \phi_f | \mathbf{p} | \phi_i \rangle \langle \Phi_{f,R} | \Phi_{i,R} \rangle \quad (3.7)$$

where $\Phi_{i,R}$ and $\Phi_{f,R}$ are the N-1 electron initial and final state wavefunctions of the remaining electrons after photoionisation, and ϕ_f and ϕ_i are the final and initial wavefunctions of the photoexcited electron.

The following discussions utilise these simplifications to clarify elements critical to the energies and intensities of the observed spectra.

3.3.1.1 Energy Spectrum

The energy spectrum observed is generally separated into two parts, core levels and the valence band. The spectrum of core levels is element specific and is a superposition of: the core-level emission lines; satellites of these; auger spectra; and a background of inelastically scattered electrons. The valence band provides information about the electrons involved in bonding and is difficult to understand directly as the peaks are due to combinations of valence electrons.

Photoexcitation spectra The most basic theoretical treatment of transition probability given above is to assume $\Phi_{f,R} = \Phi_{i,R}$ in eq. 3.7. This leaves only the single electron transition matrix element, resulting in a kinetic energy given by

$$E_K = h\nu - E_B - \phi \quad (3.8)$$

where $h\nu$ is the photon energy, E_B is the (Koopmans') binding energy of the electron before photon absorption, relative to the Fermi energy E_f , and ϕ is the work function of the surface. This simplification is usually sufficient for chemical analysis, and tends to characterise well the major photoemission lines. However, this is often not a valid assumption as the electrons remaining after photoexcitation will tend to relax to minimize the energy. This results in final state wavefunctions which are sometimes distinctly different from the initial state.

The overlap integrals between these initial and final wavefunctions leads to several possible excited states giving a spectral output. One version of this is seen commonly in metals resulting in an asymmetric lineshape, originally described by Doniach-Sunjić [109], then more rigorously expressed by Mahan [110]. This appears as an elongated tail on the low kinetic energy side

of the peak. In the case of phthalocyanines, and many other organic molecules, the overlap between initial and final states results in what are known as shake-up peaks. These give a spectral output for a single core level which is related to intrinsic plasmons, or excited states of the molecule, generated as part of the photoemission process.

Another source of satellite that has to be considered is the generation of extrinsic plasmons. These result in energy loss features due to generation of excited states by scattering of photoelectrons either in the bulk or at the surface. These also appear at lower kinetic energy, but tend to be much broader features. Given that these extrinsic loss features are not part of the primary emission spectrum, they are often treated with the background.

Auger spectra The second feature of the overall energy spectrum to be considered is that of Auger electrons. Photoelectron emission results in atoms in an excited state. When this hole is refilled with an electron from a less tightly bound orbital it releases energy. This energy can be transferred to another electron which is then emitted from the material. This process is known as Auger emission. Fig. 3.3 shows a schematic of an example of this process.

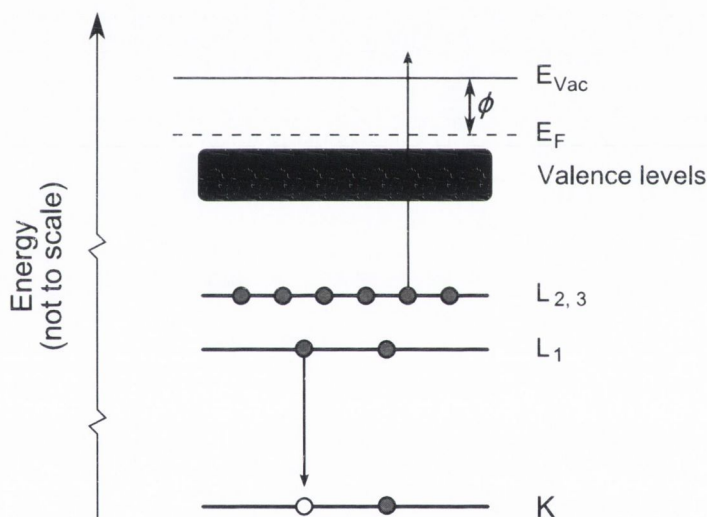


Figure 3.3: Schematic of the process involved in creation of an Auger electron.

The kinetic energy of the $L_{2,3}$ electron emitted in this example is approximately determined by

$$E_{Auger} = E_K - E_{L_1} - E_{L_{2,3}} - \phi \quad (3.9)$$

where E_K is the binding energy of the initial core hole, E_{L_1} and $E_{L_{2,3}}$ are the binding energies of the two outer shell electrons involved in the Auger process and ϕ is the work function of the surface. This equation neglects the effect of electronic rearrangement resulting from ionisation. However, it demonstrates the important result that the original photon energy has no role in determination of the electron's kinetic energy. The emission energy is purely determined by the material itself. This provides the simple technique of distinguishing between photoemission

peaks and Auger peaks by changing the photon energy. It also means that the photon energy for a particular experiment has to be carefully chosen to ensure that overlap of photoemission and Auger peaks does not occur.

Background The background spectrum is generated by inelastic scattering of excited electrons due to electron-electron or electron-ion collision. In a general form this is given by

$$B(E) = \int_{E' > E} \lambda(E) S(E, E') P(E') dE' \quad (3.10)$$

where $\lambda(E)$ is the mean free path at energy E , $S(E, E')$ is the scattering function and $P(E)$ is the spectrum. $\lambda(E)S(E, E')$ gives the energy loss function. Determining this loss function accurately is a difficult prospect, whether experimentally or by calculation. It can be done through Electron Energy Loss Spectroscopy (EELS) [111], but this is generally not possible.

Two methods are commonly used to circumvent this problem. The first is to assume the scattering is constant; this results in what is known as the Shirley background [112]. This is only a rough approximation of the background, but when applied to short energy ranges $E_1 < E < E_0$, as in the fitting of a single peak, it is often sufficient. This gives the formulation of eq. 3.10 as

$$B_S(E) = A \int_{E' > E}^{E' < E_0} (P(E') - P_0) dE' \quad (3.11)$$

A is a constant fitted to the experimental data and P_0 is the background intensity at E_0 , a point on the high kinetic energy side of the peak at which the intensity of the tails of the peak is approximately zero. This first method is by no means a rigorous solution. It is known that in the case of metals it often yields an inaccurate result [108]. In this case, a second method commonly used is to employ a “universal” energy loss function [113]. This is generally referred to as the Tougaard background. The energy loss function suggested by Tougaard from empirical results is

$$\lambda(E)S(E, E') = \frac{A(E - E')}{(B + (E - E')^2)^2} \quad (3.12)$$

with $A = 1643 \text{ (eV)}^2$ and $B = 2866 \text{ (eV)}^2$, although in practice A is often left as a variable in the fitting of the data. For more information regarding the practical application of these backgrounds see section 3.3.3

3.3.1.2 Line Intensity

The spectral line intensity (measured as the area of a given peak) is essentially the result of five main factors: Equipment related intensity; occupancy of the given emission line; escape depth (or mean free path) of electrons; cross section of the given orbital; and transmission of electrons through the surface. Unfortunately, most of these factors are complicated to calculate or to measure independently. With compounding of errors associated with each of these factors

quantitative measurement is very difficult and could be expected to result in a total error in the range of $\pm 30\%$. The accuracy depends significantly on the core-level lineshape; those with a single, symmetric lineshape (few satellites or energy loss features) will provide much more accurate results.

Equipment related effects Depending on the photon flux incident on the sample, the energy analyser used, the operating conditions of the analyser and the exact geometry of the experimental equipment the intensity of spectra will vary greatly. However, the intensity variations related to equipment are generally uniform over the entire spectrum, affecting all peaks in the same fashion, therefore, for the purposes of relative intensity they can be ignored. The analyser is a fixed parameter for any given chamber, but in selecting the operating conditions, one generally has the choice of trading resolution for intensity. For each experiment an appropriate balance between resolution and signal to noise must be reached. The main variable of interest, related to the physical set up, is the geometry. For an increased angle of emission the intensity of electrons emitted toward the analyser is unchanged but they must travel $\frac{1}{\cos^2(\theta)}$ times further through the solid to reach the analyser. Given the exponential decay in intensity relative to thickness (see the following section on escape depth), this gives a higher proportion of the signal from the surface, increasing surface sensitivity. Two other factors related to the geometry also influence intensity: The emission intensity decays away from the polarisation direction; and diffraction effects on the photoemitted electrons produce an angular dependent variability which depends on photoelectron energy.

Occupancy Here the word occupancy is used to indicate the total number of electrons present in a given core-level. The line intensity is simply proportional to this occupancy.

Given that XPS is a core-level spectroscopy, all probed orbitals are fully occupied, i.e. 2, 6, 10 and 14 for s, p, d and f orbitals respectively. However, for orbitals with quantum number $l \neq 0$ spin-orbit coupling splits this into two peaks. The total angular momentum $\mathbf{G}$ is given by

$$\mathbf{G} = \mathbf{G}_l + \mathbf{G}_s \quad (3.13)$$

where $\mathbf{G}_l$ is the total orbital momentum and $\mathbf{G}_s$ is the total spin momentum. This can be shown to obey the rules of spatial quantisation [114] for orbital and spin momentum. This results in a quantum number j , with

$$j = |l \pm s| \quad (3.14)$$

denoting the total angular momentum for a given electron with magnitude $\hbar\sqrt{j(j+1)}$ and components in any specified direction of $\hbar m_j$, where $m_j = j, (j-1), \dots, -j$ [114]. This gives a total of $2j+1$ degenerate states.

The ratio of occupation between the two spin orbit peaks is therefore

$$\frac{2(l + 1/2) + 1}{2(l + 1/2) - 1} \quad (3.15)$$

The different states are typically denoted by the symbol

$$n^\rho X_j$$

where n is the principal quantum number, ρ (sometimes left out) is the “multiplicity,” which is given by $(2s + 1)$ where s is the total spin number, X denotes the subshell S, P, D or F for $l = 0, 1, 2$ or 3 respectively and j is given by eq. 3.14. For a single electron s is $1/2$, therefore ρ is always 2 in photoemission. The X is also generally written in lower case. For example $3d_{5/2}$ would refer to the electron of quantum numbers $n = 3, l = 2, j = 5/2$.

Escape Depth The electron escape depth, or mean free path, normally denoted by λ , is a measure of how far electrons travel before undergoing inelastic scattering. The probability of an electron escaping without undergoing inelastic scattering is proportional to $e^{-x/\lambda}$, where x is the distance traveled through the solid. Integrating over the entire depth of the sample gives intensity $\propto \lambda$.

Cross Section The cross section of a given core level is a measure of how likely it is for that electron to absorb a photon. It is strongly photon energy dependent. Obviously for photon energies lower than a certain threshold no excitation is possible, beyond that point the cross section tends to decay towards higher photon energy. But, for $h\nu$ only slightly above threshold, there are significant changes in cross section, which are characteristic of the orbital, e.g. 1s core levels decay monotonically, whereas 2s core levels tend to increase slightly before decaying.

Most notable amongst the features occurring above the threshold is the Cooper minimum. It is a dramatic drop in cross section above threshold which can occur in any core level for which the wavefunction has a radial node ($n - (l + 1) > 0$). It is an effect that arises from a first order approximation of the transition matrix, which is essentially the result of a cancellation of positive and negative parts of an integral over the wavefunction [115, 116]. This gives a minimum in cross section of zero for this first order approximation. However, in reality the cross section is reduced to finite values due to higher order effects.

To get manageable signal to noise in experiments, careful selection of photon energy to optimise cross sections is critical. A comprehensive set of calculated cross sections for all elements has been produced by Yeh and Lindau [117] which are ideal for this purpose.

Transmission of Electrons through surface For XPS where the electron energy is significantly above the ionisation threshold the transmission probability approaches 1 for all electrons propagating toward the surface and tends to be ignored. For valence band spectroscopy, where low photon energies are often used, to achieve any significant understanding of the intensity of the emission features these transmission factors have to be calculated from the components of

the final state wavefunction propagating toward the surface. This goes beyond the scope of this thesis; for more information see [107].

3.3.1.3 Chemical Shifts

Although the binding energy of core levels is characteristic of the particular element, small shifts in this energy result from different chemical environments. This allows core-level photoemission to be used as a chemically sensitive method for determining bonding and other electronic interactions. The shifts are the result of two effects: first the initial state binding energy depends on the electronic environment of the photoemitting atom; and second the final state relaxation depends on the type of bonding and nearest neighbour atoms of the target.

The chemical shift related to the initial state depends on the valence charge of the atom. The charge of the atom creates a potential, which gives the change in energy for all charges within that potential. This is the sum of two components, a term related to the potential of the atomic charge and a term related to the Madelung potential of that atom [108]. The potential difference for a transfer of charge is then approximately

$$\Delta V = \frac{\Delta Q_i}{4\pi\epsilon_0 r_v} + \sum_{j \neq i} \frac{\Delta Q_j}{4\pi\epsilon_0 d_{ij}} \quad (3.16)$$

where ΔQ_i is the change in charge on atom i and r_v is the average valence shell radius. The Madelung potential is the potential of the surrounding lattice. It is calculated by an infinite sum over the change in charge (ΔQ_j) of atom j a distance d_{ij} from atom i [107, 108]. The potential energy is in the order of 12 eV per electron transferred and the Madelung energy is in the order of 10 eV per electron transferred. The two energies are of opposite sign, which results in a total shift in the order of 2 eV per electron transferred.

The measured energy of the electron depends also on the final state energy of the system. Changing the chemical environment of an atom can also significantly effect the relaxation energy of the final state orbitals. This is done by a polarisation of the surrounding environment or charge transfer. Relaxation due to polarisation can, with some assumptions, be treated as classical dielectric screening as discussed below. Charge transfer in the final state is more challenging and can only be calculated using full energy calculations [88, 118]. Qualitatively this screening due to charge transfer is generally greater for larger molecules, due to significant contribution from atoms further than the nearest neighbour [88]. It is also generally greater for molecules chemisorbed onto surfaces [118].

The core levels of atoms at the surface of materials are often shifted in energy from the bulk by an analogous process. The top, unterminated layers rearrange themselves, altering their electronic environment. As a result the photoelectron spectrum of a substrate core level often comprises surface components at different binding energy to that of the bulk component. This effect is used in conjunction with LEED and PES of potential contaminant core levels as a means of determining cleanliness and quality of surface preparation.

3.3.1.4 Dielectric Screening

The term screening is interchangeably applied to either dielectric screening (also called image charge screening) as discussed here, or to intrinsic plasmon satellites. In this thesis all intrinsic plasmon effects are referred to as shake-up effects, with the term screening only used in relation to dielectric screening. Dielectric screening refers to the energy change of the photoemitted electron resulting from a polarisation in the surrounding environment as a result of the positive charge on the photoionised atom.

It has been demonstrated that treating dielectric screening classically is a reasonable approximation, giving shifts in fairly close agreement with experimental results [91]. Due to the tightly bound nature of the core electrons, core holes can be reasonably approximated by a point charge. In the simple case of a point charge above a dielectric substrate, this screening energy is given by $-\frac{\varepsilon_R - 1}{\varepsilon_R + 1} \frac{q^2}{16\pi\varepsilon_0 z}$ where z is the distance from the image plane, q is the charge and ε_R is the relative dielectric of the substrate [119]. This is equivalent to the energy of the system where the dielectric is replaced by a point charge of $-\frac{\varepsilon_R - 1}{\varepsilon_R + 1} q$ a distance z behind where the boundary was, as an “image” of the real charge.

In the case of a point charge generated in a film on a substrate the situation becomes more complicated. Here there are two dielectric boundaries, both of which have an image charge effect. In this case the total screening can be expressed as the influence of an infinite sum of point charges. No theory has been published that is suitable to the systems investigated here, but for two related forms of a two-dielectric boundary system an appropriate expression has been determined [91, 119].

3.3.2 Experimental Apparatus

The general configuration of an XPS experiment is as shown in fig. 3.4. For energy calibration the sample voltage must be known with respect to the analyser (typically both are grounded). The analyser depicted in the diagram is known as a concentric hemispherical analyser (CHA), this is by far the most common type of analyser used for high resolution PES.

When a negative potential exists on the outer hemisphere with respect to the inner there is a well defined energy of electron that will follow the semi-circular path between the entrance and exit slits of the analyser. This electron energy is known as the pass energy (E_P) of the analyser and is given by

$$E_P = \frac{eV}{\left(\frac{R_1}{R_2} - \frac{R_2}{R_1}\right)} \quad (3.17)$$

where V is the voltage between the hemispheres, R_1 and R_2 are the radius of the outer and inner hemispheres respectively. Due to the finite size of entrance and exit slits and incident electron angle there exists some finite range of electron energy which pass through the analyser. The energy resolution (ΔE) of an analyser is typically defined by the full width at half maximum

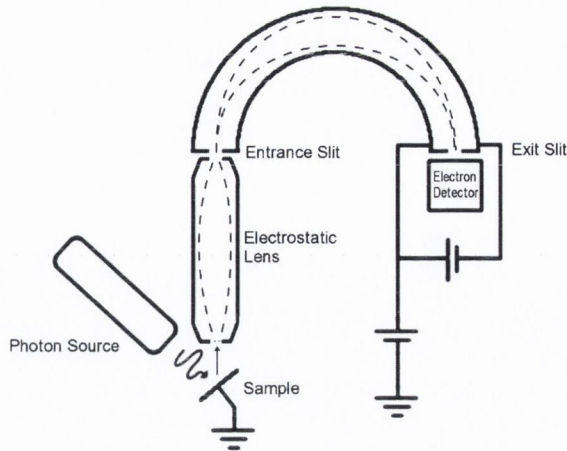


Figure 3.4: Schematic of the typical experimental arrangement for a basic photoemission spectroscopy.

(FWHM) of electron energy distribution passed. More commonly quoted is the resolving power of the analyser which is given by the inverse of

$$\frac{\Delta E}{E_P} = \frac{S}{2R_0} + \alpha \quad (3.18)$$

where R_0 is the mean radius, S is the slit width and α is a term to take into account angular effects.

There are two modes of operation available for energy selection. Obviously varying the potential given in eq. 3.17 will vary the pass energy of electron; this is known as constant retard ratio (CRR) mode. However, as seen in eq. 3.18, the energy resolution is proportional to pass energy hence this will give very low resolution at high energies. The second mode of operation, which is used almost exclusively, provides a solution to this. In this case the pass energy is kept constant and a retarding field at the entrance slit is varied to provide the energy selectivity. This is generally called constant analyser energy (CAE), or fixed analyser transmission (FAT) mode.

Before the entrance of the hemispheres is a set of lens elements. These focus the electrons from the sample in a way that is dependent on the experiment being conducted. For angle integrated spectra the lens attempts to collect as many electrons as possible, which in lab experiments means collecting from a large area. For the small spot sizes used in synchrotron experiments (or Auger spectroscopy where a focused electron beam is employed) a maximum angular dispersion is focused from a small area of the sample. For angle resolved spectra a narrow solid angle of acceptance is used, trading intensity for angular resolution.

There are various different detectors used in analysers. All rely on electron multipliers,

which utilise secondary emission of electrons. Typically, these are insulating tubes coated with a conductive material that emits a few low energy secondary electrons for an incident electron. By applying a high voltage along the length of the tube the electrons are accelerated as they pass through it, generating many successive secondary emission events. Typically, a single electron in yields in the order of 10^7 electrons out. A single electron multiplier (or channeltron) is the most basic form of detector, although in some cases a number are employed along the slit length. Many of the larger analysers use a channel plate, which is a two dimensional array of holes, each of which is an electron multiplier. The output from this is then typically detected via a CCD camera on a phosphorescent detector. Using this latter arrangement gives an image of the exit plane, which can give both energy and momentum information in a single snapshot, but it introduces difficulties with normalisation.

3.3.3 Core-level analysis

As mentioned in section 3.3.1.3 one source of multiple peaks for a given element is if that element exists in different chemical environments. This occurs commonly at surfaces and interfaces, as well as in molecular materials. The other major source is that of final state effects as mentioned in section 3.3.1.1. Final state effects can take the form of shake up or shake off peaks, giving multiple peaks for a single core level, or screening effects which can shift the peak associated with a particular atom. Analysing these core-level spectra is then a process of trying to extract and assign all components of a single core level making up the acquired spectrum.

In practice the peaks are often not clearly separated, and to complicate matters further they lie on a non-zero background. This means the task of distinguishing all individual components is not a simple one. Fitting peaks to spectra with any meaning is a process of applying numerical fitting algorithms based upon available theory and testing probable hypotheses. Due to the numerical nature of the fitting, an accurate fit can always be obtained by introducing many peaks, but the result loses all physical meaning. To obtain real information the data would usually be represented with the minimum number of components possible, only adding components where there is some physical meaning to be attached to them.

Each core-level component is typically expressed as a convolution of the Lorentzian linewidth associated with lifetime broadening and Gaussian linewidth associated with all experimental broadening and broadening due to sample inhomogeneity. This is known as a Voigt profile and is defined as

$$V(E; \sigma, \gamma) = \int_{-\infty}^{\infty} G(E', \sigma) L(E - E', \gamma) dE' \quad (3.19)$$

with the Gaussian component

$$G(E; \sigma) = \frac{e^{\left(\frac{-E}{2\sigma^2}\right)}}{2\pi\sigma} \quad (3.20)$$

and Lorentzian component

$$L(E; \gamma) = \frac{\gamma}{\pi(E^2 + \gamma^2)} \quad (3.21)$$

However, for the case of metallic core levels, or core levels screened by a metallic surface, an asymmetric tail due to relaxation in the final state as explained in section 3.3.1.1 has to be accounted for. The Doniach and Sunjic lineshape

$$DS(E; \alpha, \gamma) = \frac{\cos \left[\frac{\pi\alpha}{2} + (1 - \alpha)\tan^{-1}\left(\frac{E}{\gamma}\right) \right]}{(E^2 + \gamma^2)^{(1-\alpha)/2}} \quad (3.22)$$

is typically used to fit this. Although the integral of this lineshape diverges, which is clearly unphysical, it yields results almost identical over the range of interest to the lineshape derived by Mahan [110], which has a convergent integral. Since the Doniach and Sunjic lineshape is implemented in more fitting packages it is more commonly used.

Depending on the nature of the background, different procedures are required. If the background contains features relating to the substrate, difference spectra between post- and pre-deposition of adsorbate are taken. The remaining background is typically fitted numerically, while fitting the associated core levels. For semiconducting substrates the Shirley background is generally used (see 3.3.1.1). For metallic surfaces a better fit is obtained with the Tougaard background, where the A parameter as given in section 3.3.1.1 should be allowed to vary. On top of this a polynomial of first or second order is often required to account for the background related to inelastically scattered electrons from core levels of lower binding energy in the spectrum.

To obtain a unique fit with some physical meaning, careful restrictions have to be applied. In the spectra within this thesis the components related to a single core level are generally assumed to have the same Lorentzian and Gaussian broadening. This assumption will not always hold true if components have different decay mechanisms, or are in distinctly different chemical environments. For example, many semiconductor oxides are distinctly broadened relative to a crystalline non-oxide. However, for all core levels considered in this thesis, except where explicitly discussed, it is a reasonable assumption. Where present, both the spin orbit splitting and intensity ratio between the two spin orbit components (the branching ratio) are assumed to be identical for all components of a given core level. Although the branching ratio can vary slightly, due to diffraction effects, these are expected to be weak due to the small energy differences involved and the use of angle integrated analysers. Finally, the lifetime broadening, spin orbit splitting and branching ratio from interface layers of the phthalocyanines investigated are assumed to be the same as that of the bulk material and have been determined experimentally by fitting the photoelectron spectra of the bulk materials, except where otherwise mentioned.

3.4 Near Edge X-Ray Absorption Fine Structure

Near edge X-ray absorption fine structure (NEXAFS) is the spectroscopy of photoexciting an electron from a core level into the low lying unoccupied states. In doing so, it reveals information about the density of unoccupied states near the Fermi level. A schematic demonstrating the energy alignment is given in fig. 3.5.

The spectrum has three major parts: for photon energies lower than the absorption threshold there is no signal from that particular core level; just above threshold there are sharp peaks associated with energy transitions between the core level and bound, excited states; and lastly is the above threshold spectrum which consists of a step increase in intensity due to the continuum of states in vacuum (also known as the step jump) plus peaks associated with molecular states above the vacuum level.

Experimentally NEXAFS is a process of scanning the photon energy over a range near the binding energy of the probed core level. The absorption is then quantified by measuring the yield of secondary electrons, emitted as a result of photoexcitation. The emission is either measured directly with an electron detector in the chamber, or through an external measure of the current required to replace them.

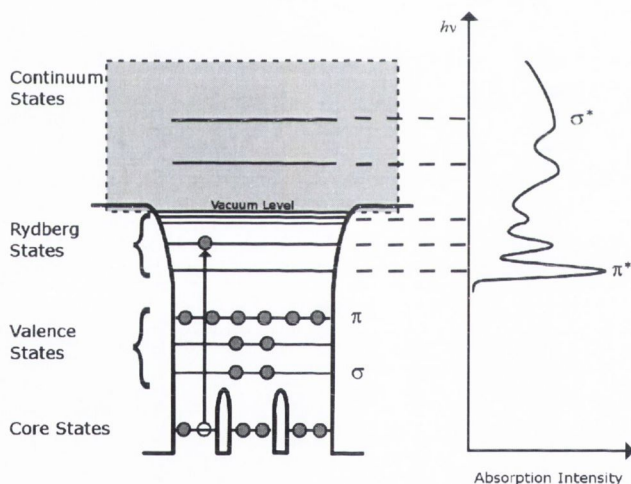


Figure 3.5: Schematic potentials and NEXAFS spectrum of a molecule. Discrete Rydberg states are seen below the vacuum level, with a continuum of empty states and some unoccupied molecular states above the vacuum level. The unoccupied states are denoted with an asterisk.

The possibility of a transition occurring is governed not only by the density of unoccupied state, but also by symmetry selection rules. This reveals information about the symmetry of the unoccupied states, or in the case where this symmetry is known before hand, reveals information about the orientation of particular orbitals.

The filled states of molecules are typically labelled with σ or π symmetry and unfilled states are similarly labelled with an asterisk. Phthalocyanines, like many planar organic semiconductors, have well defined unoccupied π^* orbitals directed out of the plane of the molecule and σ^*

orbitals in the plane of the molecule. Fig. 3.6 shows a schematic representation of the symmetry directions for the basic orbitals critical to phthalocyanines. As a result of this NEXAFS can be used as a means of determining molecular orientation.

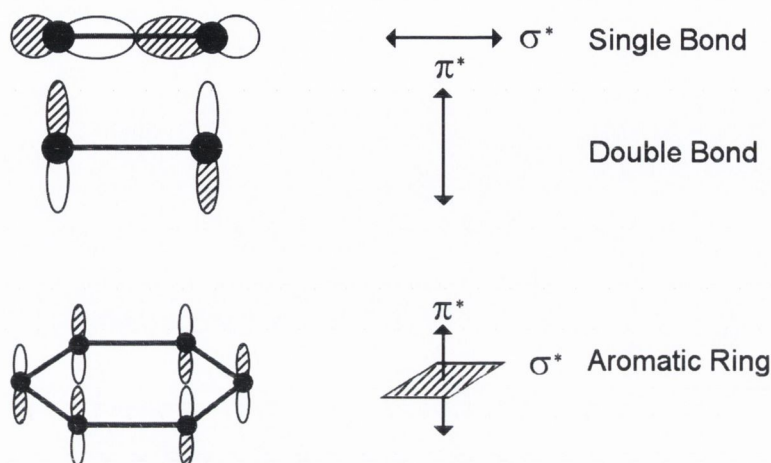


Figure 3.6: Schematic of the directions of maximum intensity for the main orbitals involved in phthalocyanines. For multiple orbitals in a plane where three-fold or more symmetry exists the maximum intensity spans the entire plane. Adapted from [62].

In the case of metal free phthalocyanine the unoccupied molecular orbitals just above threshold are all π^* orbitals, perpendicular to the plane of the molecule, and above the vacuum level are σ^* orbitals, in the plane of the molecule. For metal phthalocyanines these orbitals still dominate, although some subtle variation is introduced by the bonding associated with the metal atom. This means that the carbon and nitrogen NEXAFS spectra have strongly oriented character. When the polarisation of light is parallel to the plane of the molecule the π^* character is suppressed and the σ^* orbitals are probed, when the light is polarised perpendicular to the plane the converse is true.

The intensity of a given resonance for a K-shell excitation follows the relation [62]

$$I \propto \cos^2(\beta) \quad (3.23)$$

where β is the angle between the polarisation vector and a vector in the direction of the maximum amplitude of the final state. For σ^* states this gives a maximum in intensity for polarisation in the direction of the bond axis, for π^* states it is perpendicular to this.

To determine the orientation of molecules relative to a surface a coordinate system needs to be defined. A schematic of the coordinate system which most simplifies the equations is given in fig. 3.7. For this analysis the electric field vector is described by two components, the dominant component in the plane of the ring ($E_{\parallel}$) and a smaller component orthogonal to that ($E_{\perp}$). The principal axes are defined as: the sample normal (z); parallel to the sample surface, normal to the dominant plane of polarisation (y); parallel to the sample surface, parallel to the

dominant plane of polarisation (x). The origin is defined as the point where the light hits the sample surface. If the sample is mounted such that $E_{\parallel}$ is in the xz-plane, as is the case in most chambers, the equations are further simplified by $E_{\perp}$ always lying in the plane of the surface.

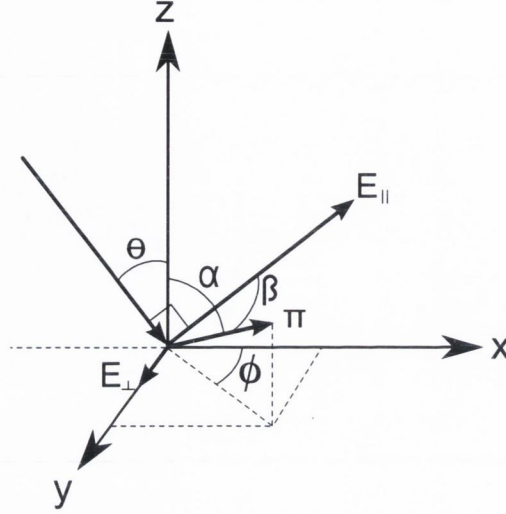


Figure 3.7: Diagram of the coordinate system and angles involved in the analysis of NEXAFS intensities. The orientation of the incident light is defined as being in the x-z plane with the main component of polarisation at angle θ from the surface normal and the perpendicular component of polarisation in the y-axis. The molecule normal (M) is defined by the azimuthal angle ϕ , and polar angle α .

In this coordinate system the molecule normal direction is defined as

$$\Pi = x \sin(\alpha) \cos(\phi) + y \sin(\alpha) \sin(\phi) + z \cos(\alpha) \quad (3.24)$$

and the electric field vector directions are defined by

$$\frac{E_{\parallel}}{|E_{\parallel}|} = x \cos(\theta) + z \sin(\theta) \quad (3.25)$$

and

$$\frac{E_{\perp}}{|E_{\perp}|} = y \quad (3.26)$$

Combining eq. 3.23 with the vector described by eq. 3.24 and the electric field described by eq. 3.25, the intensity from an orbital normal to the molecular plane due to $E_{\parallel}$ is described by

$$I_{\parallel} \propto \sin^2(\alpha) \cos^2(\phi) \cos^2(\theta) + \cos^2(\alpha) \sin^2(\theta) + 2 \sin(\alpha) \cos(\alpha) \cos(\phi) \sin(\theta) \cos(\theta) \quad (3.27)$$

and similarly using the electric field described by eq. 3.26 the intensity due to $E_{\perp}$ is given by

$$I_{\perp} \propto \sin^2(\alpha) \sin^2(\phi) \quad (3.28)$$

Where the surface displays symmetry the equations for intensity can be simplified. In the

case of two fold symmetry $I_{\perp}$ remains unchanged and $I_{\parallel}$ simplifies to

$$I_{\parallel} \propto \sin^2(\alpha) \cos^2(\phi) \cos^2(\theta) + \cos^2(\alpha) \sin^2(\theta) \quad (3.29)$$

In the case of three-fold or greater symmetry the equations further reduce to

$$I_{\parallel} \propto \frac{1}{2} \sin^2(\alpha) \cos^2(\theta) + \cos^2(\alpha) \sin^2(\theta) \quad (3.30)$$

and $I_{\perp}$ reduces to

$$I_{\perp} \propto \frac{1}{2} \sin^2(\alpha) \quad (3.31)$$

It is important to note that for three fold or greater symmetry all azimuthal (ϕ) contributions are eliminated. Since the signal is averaged over an area much greater than typical domain sizes two domains of a two-fold symmetric substrate effectively give a four-fold symmetric surface. Therefore, to determine any azimuthal preference for molecular adsorption single domain, two-fold symmetric substrates are required.

Summing over the two polarisation directions gives the normalised intensity for a particular orbital as

$$I = C(P I_{\parallel} + (1 - P) I_{\perp}) \quad (3.32)$$

where P expresses the degree of polarisation and is defined as

$$P = \frac{|E_{\parallel}|^2}{|E_{\parallel}|^2 + |E_{\perp}|^2} \quad (3.33)$$

This is then normalised by $I_{norm} = \frac{I}{C}$. For a two fold symmetric case this gives

$$I_{norm} = P \left(\sin^2(\alpha) \cos^2(\phi) \cos^2(\theta) + \cos^2(\alpha) \sin^2(\theta) \right) + (1 - P) \sin^2(\alpha) \sin^2(\phi) \quad (3.34)$$

and for three-fold or higher

$$I_{norm} = P \left(\frac{1}{2} \sin^2(\alpha) \cos^2(\theta) + \cos^2(\alpha) \sin^2(\theta) \right) + (1 - P) \frac{1}{2} \sin^2(\alpha) \quad (3.35)$$

From these equations come important normalisation results for each symmetry situation. Setting $\frac{dI_{norm}}{d\phi} = 0$ in the two-fold symmetry case reveals that there is a certain incidence angle where the intensity is independent of azimuthal angle. This is given by

$$\theta = \cos^{-1} \sqrt{\frac{1 - P}{P}} \quad (3.36)$$

and setting $\frac{dI_{norm}}{d\alpha} = 0$ in the three-fold symmetry case gives an angle at which the intensity is independent of the tilt angle, given by

$$\theta = \cos^{-1} \sqrt{\frac{2}{3} - \frac{1-P}{3P}} \quad (3.37)$$

A typical case for a bending magnet beamline would be polarisation of ~ 0.90 , this yields no azimuthal dependence for two-fold symmetric surfaces at 70.5° and no polar dependence for three-fold symmetric surfaces at 37.5° .

Using the above results provides a method for normalisation of the NEXAFS spectra. First the spectra must be measured for various different angles, then the background should be removed and the intensity scaled such that all spectra are equal before the leading edge and after the step jump. The π^* intensity can then be measured from the spectrum and plotted as a function of angle, using a least squares fit of the data to eq. 3.32. In the case of a three-fold or higher surface symmetry the constant C is simply determined by setting θ in eq. 3.35 to the angle determined from eq. 3.37.

For two-fold symmetric surfaces a minimum of two curves in different azimuths, each fit with eq. 3.32, are required. The largest difference occurs between the two perpendicular azimuths in the directions of surface symmetry. Assuming these are the two measured azimuths gives two equations with the azimuthal angles of ϕ and $\phi + 90^\circ$. Setting $\theta = 0$ in each of the two equations and $\theta = \sin^{-1} \sqrt{\frac{1-P}{P}}$ gives a set of three simultaneous equations from which C , α and ϕ can be determined.

3.5 Scanning Tunneling Microscopy

A scanning tunneling microscope (STM) works by measuring the current between a sharp metal tip and the sample surface. This current arises through quantum mechanical tunneling through a potential barrier between tip and sample. Due to the nature of wavefunctions decaying into vacuum the probability of electron tunneling decays exponentially with tip sample spacing, approximated by

$$T \approx \exp \left(-2d \sqrt{\frac{2m\phi}{\hbar^2}} \right) \quad (3.38)$$

where d is the sample-tip spacing, ϕ is the average of tip and sample work functions and m is the electron mass. This equation assumes the barrier is to be square and of height ϕ , which is only reasonable for low bias conditions. For a typical work function the current decreases by a factor of approximately ten per $1 \text{ \AA}$ change in d [120]. This enables a vertical resolution of as little as $0.1 \text{ \AA}$. The lateral resolution is limited by both this decay and the tip dimensions. Where the tip-sample spacing is small the tip dominates resolution, while for larger spacing the decay plays an important role. This results in a lateral resolution typically on the order of $1 \text{ \AA}$.

A schematic of the basic components of an STM experimental set up is given in fig. 3.8. The tip is rastered over the sample using piezoelectric crystals. There are two typical methods of operation for the basic microscopy experiments, constant current and constant height modes. In constant current mode the measured current is fed back into the system and the vertical

position is adjusted to maintain a desired set current. The vertical position is then given as a function of the vertical piezo voltage. This is the technique exclusively employed for this thesis. For constant height measurements a fixed z dimension is selected and the current as a function of x - y position is measured. An intensity map is then given typically as the log of the measured current.

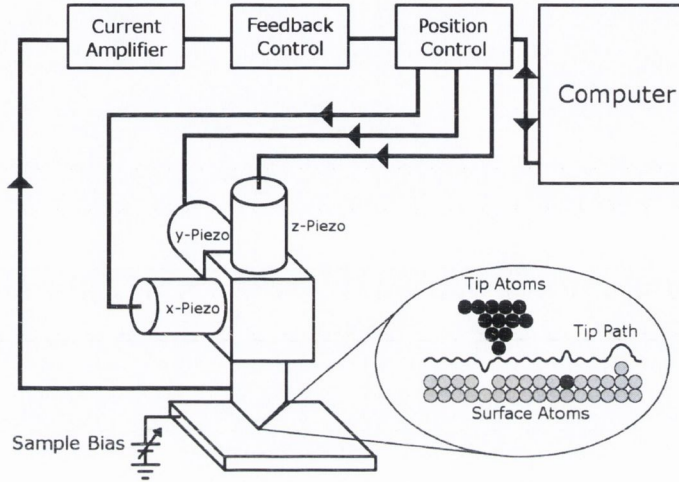


Figure 3.8: Diagram of the basic experimental set up used in STM.

The probability of electron tunneling is only one component of the current measured. The other main element is the density of electron/hole states that overlap in the tip and sample at the set bias voltage. This means that the height of a given image point is a function both of geometry and electronic character, for example atoms will not be imaged at voltages for which they have no density of states. Using the tunneling probability given in eq. 3.38 the total current can be approximated by

$$I \propto \int_{-eV}^0 \rho_t(E) \rho_s(E + eV) T(d) dE \quad (3.39)$$

where ρ_t and ρ_s are the local density of tip and surface states respectively. In this thesis the bias voltage refers to the sample, therefore a positive bias involves tunneling into empty states of the sample and a negative bias into the filled states.

In the ideal case of a metallic tip the density of states can be reasonably approximated as a constant near the Fermi level. This means that the current is merely proportional to the density of states of the sample. When dealing with loosely bound adsorbates extreme care with tip preparation must be taken. In these systems adsorbates can be picked up and information about the sample can be distorted via convolution with the local density of states of a molecule adsorbed on the tip.

3.6 Density Functional Theory

Density functional theory (DFT) is a powerful tool for computation of the electronic properties of materials. It is a well established theory about which many books have been written. For an excellent explanation of the theory and comparisons with experiment see ref [121]. The theory is based on two important principles stated in the Hohenberg-Kohn theorems: The first states that all ground state properties of any material can be uniquely determined by the electron density; the second asserts that the ground state is the lowest energy configuration, i.e. $E[n] > E[n_0]$ where n_0 is the ground state density and n is any electron density $n \neq n_0$.

The most common approach to minimising the energy, and thereby determining the density and all ground state properties, lies in what is known as the Kohn-Sham approach. This breaks the energy down into four parts as a functional of density with

$$E[\rho(\vec{r})] = T_S[\rho] + J[\rho] + E_{Ne}[\rho] + E_{XC}[\rho] \quad (3.40)$$

where T_S is the exact kinetic energy of a *non-interacting* system of electrons, J is the classical Coulomb energy, E_{Ne} is the potential energy due to nuclei-electron attraction and E_{XC} is the exchange-correlation energy. All components of eq. 3.40 have an exact form except the exchange-correlation energy. If the exact form of this could be determined then it would yield the exact ground state system.

The most basic form of E_{XC} is to assume that it is a functional of the density at any given point in space, using what is known as the local density approximation (LDA). This already gives reasonable results for certain details such as molecular geometries, but has significant limitations in the calculation of electronic properties. For molecular systems it is more common to use the generalised gradient approximation (GGA) in which a component of the density gradient is also included. This has a significantly better match to experiment for most electronic properties.

This electron density calculated as described above is only strictly true for the ground state. Moreover, these calculated values give only the filled state orbitals in a strictly correct manner. Despite this, for many systems the calculations give fairly good agreement for the unoccupied states near the Fermi level (apart from a systematic problem of miscalculating the band gap). They also often yield close agreement to experiment for valence ionised systems.

Due to the limitations of the theory, simulating any excited-state spectroscopies requires some further assumptions. To deal with the influence of the final state of the system two methods are commonly employed. The first is known as the $(Z + 1)$ approximation. This assumes the final state to be the *valence* ionised state of the system in which the *core* ionised atom is replaced by the next atom in the periodic table [108]. The second approach is known as the transition state approach. Here the calculation is performed for the system in which half the core electron is removed [108]. Both assumptions are limited, giving significant errors in exact energy, but for energy shifts or differences they often yield close agreement with experiment.

Chapter 4

The origin of observed tilt in NEXAFS

The theme of this chapter follows the work of Cabailh on MPc-inorganic semiconductor interfaces using NEXAFS. He investigated MgPc and SnPc on both GaAs(001) and Ge(001), and PbPc on Ge(001), although the latter only for a 40 Å film. That work showed that on the surfaces of Ge(001) and GaAs(001) SnPc has an apparent molecular tilt angle of 25° to the substrate, with a similar result for MgPc on Ge(001) [5]. An example of the spectra from this work is given in fig. 4.1. Fig. 4.1 (a) shows the spectra after background removal and normalisation for various different polar angles of the sample with respect to the incident light. Fig. 4.1 (b) shows the normalised intensity of the lowest energy peak, fitted according to the procedure outlined in section 3.4. This peak results from a transition from the N 1s core electron into the LUMO, which has π^* symmetry.

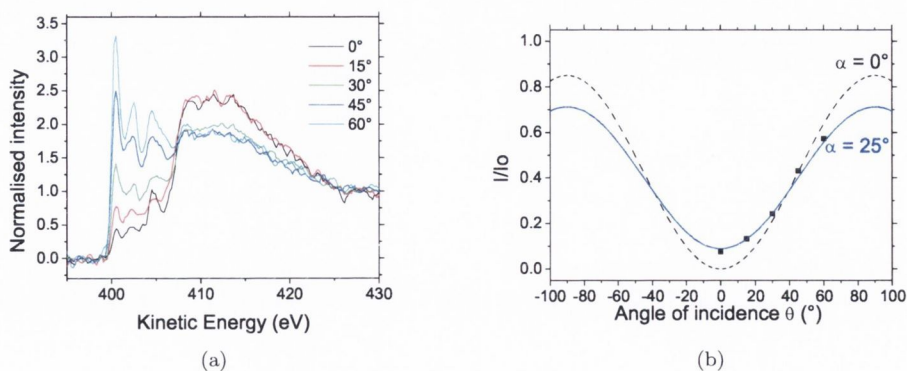


Figure 4.1: (a) Normalised NEXAFS spectra at the N1s absorption edge for 3 Å SnPc deposited on the Ge(001)-2×1 surface. Spectra were taken using a partial yield detector. (b) Evolution of the π^* peak intensities versus the angle of incidence. Expected curves for an average molecule tilt angle of 0° and 25° are plotted alongside the original data assuming a polarisation factor of 0.85 (experiment carried on a bending magnet beamline). Adapted from [5]

It is expected that a monolayer of planar organic molecules will lie flat on substrates where they are weakly bound, as has been observed by STM for phthalocyanines [36,48,49,51,122,123], with a few exceptions [124]. The STM that has been conducted of phthalocyanines on both III-V semiconductors [54, 60] and group IV semiconductors also seems to indicate flat-lying molecules [55–57, 96, 125], although it is less clear in these cases. Given this expectation from STM studies of flat lying molecules, the observation of a significant tilt in the NEXAFS is an interesting result requiring further investigation.

Due to the nature of the spectroscopy there are multiple possible explanations for such an observed tilt:

- (a) Uniform tilt of the molecules with respect to the substrate.
- (b) An intrinsic in-plane contribution to the spectrum in the energy range of the π^* features.
- (c) An extrinsic in-plane contribution to the π^* energy range. This could result either from distortion of the shape of the molecule upon adsorption or from a distortion of the probed orbitals due to interaction with the substrate.
- (d) A mixture of a majority of flat-lying molecules with a minority of non-flat molecules.

This chapter details an investigation of these possible causes of the observed tilt. A discussion of the influence of polarisation is given in the first section. This is followed by experiments which address the different possible causes of tilt as outlined in the list above.

4.1 The effect of incomplete polarisation

The degree of polarisation of light from different beamlines is not consistent. In the case of undulator beam lines the polarisation is near to 100%, but for bending magnet beamlines it can be significantly lower. Unfortunately, in these cases it is poorly defined. This introduces a problem in the analysis of NEXAFS data. The normalisation procedure for NEXAFS relies on fitting a sinusoid to the measured intensities. The sinusoid depends on both the tilt and polarisation. A simple measure of the sinusoid is the ratio of the π^* peak intensity at normal and grazing incidence. Fig. 4.2 (a) gives this ratio as a function of molecular tilt angle for 100% and 85% polarisation. It is obvious from this plot that, for low angles of molecular tilt, the polarisation has little influence. However, for molecules tilted close to perpendicular to the substrate, any inaccuracy in the treatment of polarisation has a significant influence on the calculated tilt.

Fig. 4.2 (b) shows the error in tilt calculation if 100% polarisation is assumed, but measurements are made with 85% polarisation. This shows that for tilt less than 45° the assumption of 100% polarisation yields less than 1.5° error in molecular tilt. Given the uncertainty in polarisation and the little error it introduces for near flat-lying molecules, all spectra are treated as if taken with 100% polarised light, with the expected errors treated in the discussion.

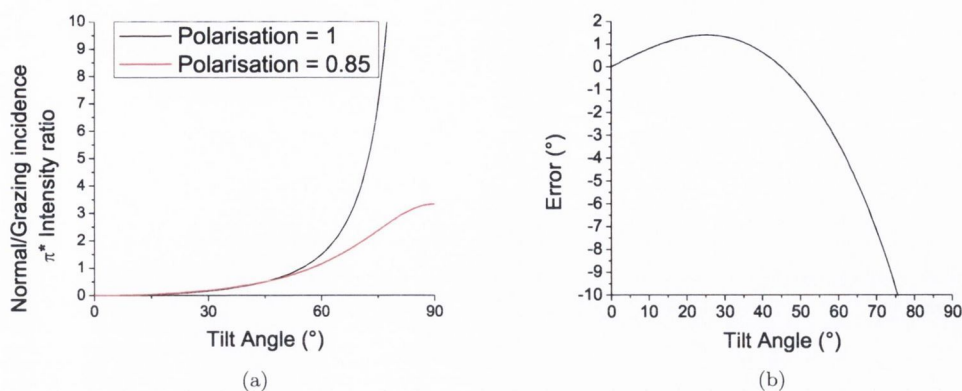


Figure 4.2: (a) The intensity ratio between the normal and grazing incidence π^* peaks as measured by NEXAFS for a polarisation of 100% and 85%. (b) The error in calculated tilt for 85% polarised light, under the assumption of 100% polarisation.

4.2 A uniform molecular tilt?

STM of the planar MgPc on Ge(001) presented by Cabailh [5] shows a distinct adsorption site of the molecule on the Ge(001) surface. Results presented in section 6.1.1 show this more clearly and, in addition, that it applies also to other phthalocyanines. Therefore, if the observed tilt is a result of a genuine, uniform tilt of the molecule, it could be expected that this tilt would have a defined orientation with respect to the surface reconstruction. In other words, this tilt would most probably be in a particular azimuth. However, for any surface of three-fold or greater rotational symmetry all information about the azimuthal direction of the molecular tilt is lost. The two orthogonal rotational domains of the typical Ge(001)- 2×1 surface effectively render it a four-fold symmetric surface, from which no azimuthal information of the tilt can be obtained. By utilising a Ge(001) wafer, miscut 6° towards the [110] direction a single domain Ge(001)- 2×1 surface can be prepared. This has now only two-fold symmetry, for which an azimuthal preference of the molecular tilt could be determined.

Shown in fig. 4.3 are the NEXAFS of CuPc on the single domain Ge(001)- 2×1 surface. This plot shows the angular dependent NEXAFS taken in two orthogonal azimuths, one probing the 2×1 direction of the surface, the other probing the 1×2 direction. The fit shown is calculated as per eq. 3.34. For the presented figures the normalisation is carried out under the assumption of 100% polarisation. This leads to the restriction that the two curves must be equal at 90° incidence. Note that the data for the azimuth parallel to the dimer rows is offset in polar angle to accommodate the offset of the sample in this direction.

The fits presented in fig. 4.3 demonstrate that there is no significant variation in the NEXAFS of the two different azimuths. Under the assumption of a uniform molecular tilt, the calculated azimuth of the tilt is 43° . Within the error of the measurement, this is equivalent to azimuthally disordered, or potentially higher order symmetry of the tilt, which could be the case if the observed tilt is a result of a four-fold distortion of this four-fold symmetric molecule.

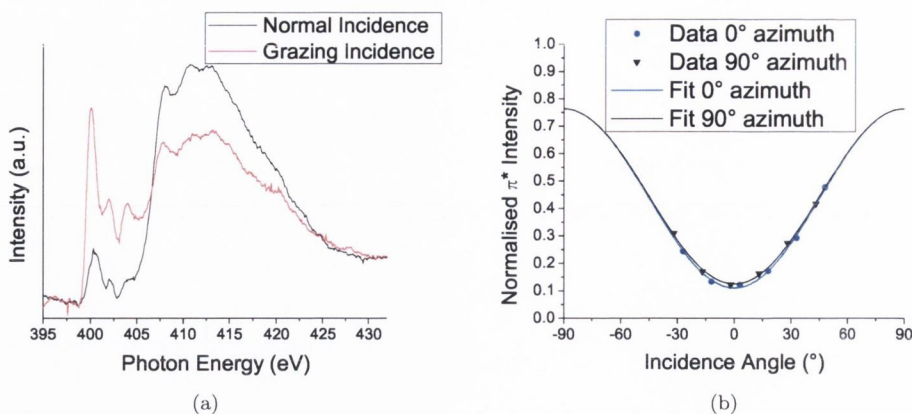


Figure 4.3: Angular dependent NEXAFS spectra of a monolayer of CuPc on single domain Ge(001), panel (a) shows spectra of the most extreme angles measured in the 0° azimuth, and panel (b) shows the normalised intensity of the leading π^* feature as a function of angle for both azimuths.

The best fit of the molecular tilt angle is 29°, slightly greater than the 25° observed for SnPc and MgPc on the two-domain Ge(001)-2×1 surface.

These values were calculated under the assumption of perfectly polarised light. However, these spectra were taken at a bending magnet beamline. Recalculating the azimuthal and tilt angles with the assumption of 85% polarisation, the expected minimum for a bending magnet beamline, yields less than a 1° difference, with the azimuthal angle still 43°, and the tilt angle reduced to 28°.

These results demonstrate that the observed tilt is unlikely to be the result of a uniform molecular tilt. Further than that, it indicates the tilt is unlikely to be the result of mixed, ordered adsorption sites. There is some indication from STM, to be discussed in section 6.1, that a second minority adsorption site of phthalocyanine on the Ge(001) surface exists, and similarly three adsorption sites have been observed for CuPc on the related Si(001)-2×1 surface [57]. However, if the observed tilt results from mixed, ordered molecules the tilt would still be expected to display an azimuthal preference, except in the unlikely case where the mixed tilts are such that the sum of their signal presents an equal intensity for any azimuth of measurement.

4.3 An intrinsic in-plane “ π^* ” contribution?

The occurrence of a 25° tilt on both Ge(001) and GaAs(001) is an interesting coincidence. Since these surfaces demonstrate noticeably different degrees of interaction with MPc as observed by PES [5], any tilt resulting from interaction with the substrate could be expected to be different. Therefore, the identical observed tilt on both surfaces perhaps suggests that the mechanism by which there is a finite intensity for normal incidence is intrinsic to the spectroscopy of this molecule.

On the other hand, a finite intensity in the π^* features for light normal incidence to these

molecules is inconsistent with theory. Theoretical approaches lead to the expectation that the low energy features of the NEXAFS are out of the molecular plane for most MPc [62, 126] with the known exception of FePc [127]. Even in this case, the shape of the low energy peaks should be spectroscopically distinct for polarisation in the molecular plane and perpendicular to it. This would allow for determination of tilt by using a fitting procedure on the low energy range of the spectrum, which is not the case in the work of Cabailh.

Despite the theory there are no examples in the literature of flat-lying MPc as observed by NEXAFS. The smallest observed tilt presented in the literature of NEXAFS of phthalocyanine is 10° for the system of H₂Pc on Ag(111) [128], whereas for other organics complete suppression of π^* features at normal beam incidence has been observed, as expected for flat lying molecules [129, 130].

To determine whether this observed tilt is intrinsic to the molecule, the spectroscopy would be ideally carried out on a precisely oriented single molecule. This is obviously not possible, but by conducting the NEXAFS of a monolayer thickness film of weakly bound phthalocyanine, where the molecule is thought to lie flat, a reasonable approximation can be approached. In this section the planar CuPc on highly oriented pyrolytic graphite (HOPG) and the non-planar SnPc on Ag(111) are used to this end.

Fig. 4.4 (a) shows the NEXAFS of CuPc on HOPG for normal incidence and grazing incidence X-rays. At normal incidence a single peak appears in the π^* energy range of 399 and 405 eV, specifically at an energy of 400.2 eV. At grazing incidence, there are three peaks in this range, at 399.6, 401.7 and 403.6 eV respectively, associated with out of plane orbitals in the molecule. None of the peak positions of the out of plane orbitals match the position of the peak at normal incidence. The intensity of all π^* orbitals is expected to vary as a simple sinusoid, symmetric about 0° . This means the spectroscopic differences in the π^* region between normal and grazing incidence must be related to an intrinsic in-plane transition in this energy range.

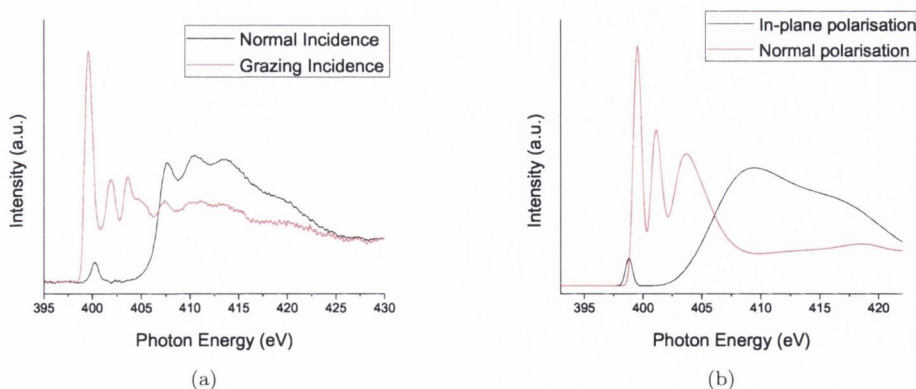


Figure 4.4: Angular dependent NEXAFS of CuPc. Panel (a) shows the spectra of CuPc on HOPG for both normal incidence and grazing incidence and panel (b) shows theoretical spectra of the in plane and out of plane NEXAFS spectra.

To understand this experimental result a density functional theory (DFT) calculation of the NEXAFS of a molecule in gas phase was conducted. The results of this calculation are presented in fig. 4.4 (b). From this calculation is clear that for light incident normal to the CuPc molecule a non zero signal is expected at an energy similar to that of the first π^* feature. This intensity relates to a mixing of the inner (pyrrole) N $2p_x$ and $2p_y$ orbitals with the Cu $3d_{xy}$ orbital. The small error in the energy at which the normal incidence peak occurs is probably related to the difficulties involved in calculating the excited state involved in the spectroscopy in DFT, which is strictly speaking a ground state theory.

The occurrence of a single peak for polarisation in the plane of the molecule from both the calculation and experiment demonstrates the validity of both. It also demonstrate the importance of an understanding of the symmetry of the unoccupied energy levels observed in NEXAFS for analysis of molecular orientation. Consequently, for a practical analysis the π^* features of CuPc must be fit to take into account the in-plane contribution. Within this thesis all CuPc spectra are fit with four components in the range of 397-404 eV, three of which take into account the π^* features and one for the in-plane Cu related feature.

On fitting these spectra, zero intensity is obtained for the π^* features at normal incidence. This result demonstrates that on a weakly-interacting substrate complete suppression of the π^* features can occur for planar phthalocyanines as expected for flat lying molecules. Consequently, the calculation of tilt for this system from the NEXAFS agrees with the expectation from STM. Furthermore, it shows that there is no intrinsic in-plane π^* features, even although in this case there is an in-plane orbital in this energy range.

The experiments of SnPc on Ag(111) were conducted on two distinct preparations of the SnPc monolayer, which yield two different phases of well ordered, flat-lying phthalocyanines following the procedures of Lackinger et al. [36]. The first is a simple deposition of the equivalent of 0.75 ML at room temperature, resulting in a film commensurate with the substrate. The second surface is prepared by deposition of approximately 10 ML, followed by annealing at 290°C, which yields a close packed monolayer, incommensurate with the substrate. For both preparations the NEXAFS results are identical, therefore only results from the first are included here.

The NEXAFS of the monolayer of SnPc on Ag(111), shown in fig. 4.5 (a) and (b), again shows complete suppression of the π^* features for the monolayer film. This is somewhat surprising given a prediction from the DFT calculations of finite intensity in the π^* peaks even for normal incidence as shown in fig. 4.6. The expectation of in-plane intensity in the π^* peaks is due to the fact that the Sn sits out of the molecular plane. This essentially tilts the orbitals around the inner (pyrrole) nitrogens.

There are two possible reasons why this in-plane intensity is not observed in the NEXAFS. The first is that the optimised geometry used in the calculation has the Sn atom further out of the molecular plane. The distance above the inner nitrogens is 1.14 Å in the calculation, significantly more than the 0.6-0.9 Å measured by X-ray standing wave (XSW) experiments [73]. Due to the $\sim \frac{1}{2} \tan^2$ dependence on orbital tilt of normal to perpendicular incidence intensity

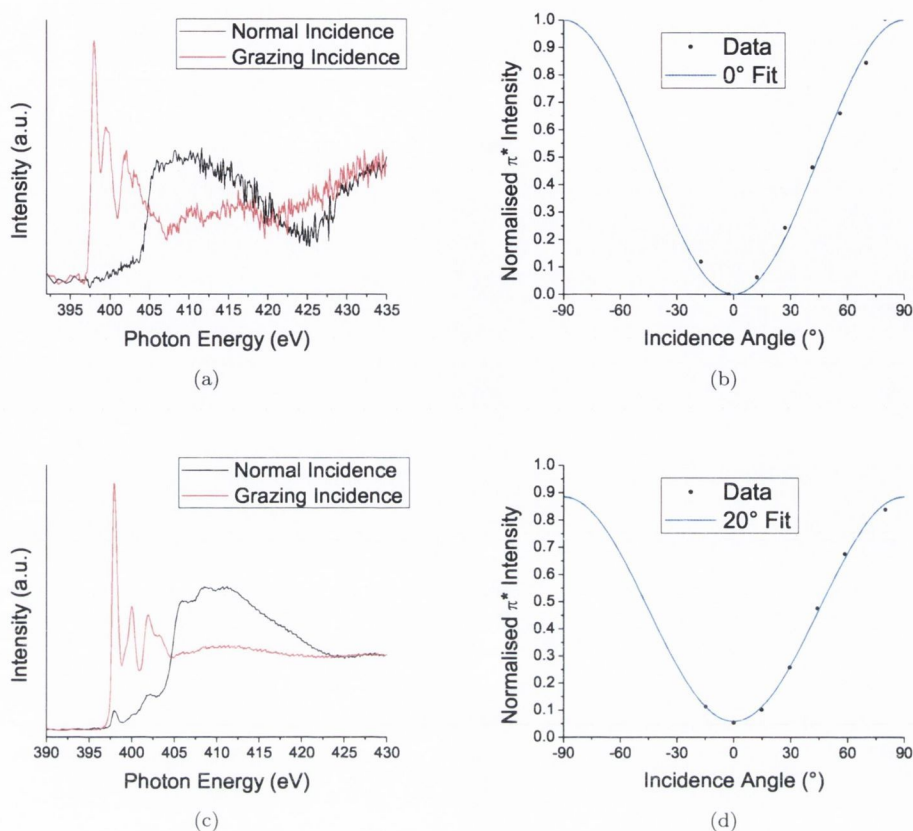


Figure 4.5: Angular dependent NEXAFS of SnPc on Ge(001). The upper two panels show the results for a monolayer film and the lower two show the results for a 40 Å film. (a) and (c) are example spectra of the most extreme angles measured for and (b) and (d) show the normalised intensity of the leading π^* feature as a function of angle.

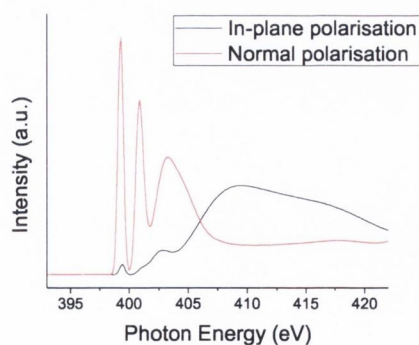


Figure 4.6: Simulation of the angular dependent NEXAFS of SnPc using DFT. The spectra are calculated with the optimised geometry configuration.

ratio (shown in fig. 4.2) it is possible that a genuine tilt of a few degrees would not be noticeable against the background noise. Based on these geometric arguments, and assuming the π^* orbital bisects the Sn-pyrrole N angle, fairly close agreement is achieved with the optimised geometry DFT calculation. Applying this then to the XSW geometry the intensity in the π^* feature at normal incidence could be less than 1% of its intensity at grazing incidence.

The second possibility arises from XPS experiments, which show an apparent filling of the lowest unoccupied molecular orbital (LUMO) of various organics on Ag(111) [131, 132]. If the LUMO states associated with the inner nitrogens are filled then they would obviously no longer appear in the NEXAFS spectra. It is primarily these inner nitrogen states that make up the expected in-plane intensity

Fig. 4.5 (c) and (d) show data for the 40 Å thick film of SnPc on Ag(111). Here the best fit of tilt to the data is 20°, under the assumption of no in-plane intensity in the π^* features. However, some intensity could be due to the molecular distortion as predicted by the calculation, meaning that the actual tilt could be significantly less than 20°. Regardless of the error introduced by this assumption, the tilt here is distinctly less than the 25° of SnPc on Ge(001) calculated based on the same assumption. This indicates that the differences in the first layer on the two substrates has a noticeable effect on the film growth beyond the first monolayer.

In summary, two different systems where the molecules are thought to be flat-lying have been examined. The CuPc on HOPG system shows an intrinsic peak in the π^* region of the NEXAFS spectrum. This is because it is an open-shell MPc, and a similar effect is not expected for any of the other MPc dealt with in this thesis. After taking this into account through an appropriate fitting procedure complete suppression of the π^* peaks for normal incidence light is demonstrated, yielding the expected result of flat-lying MPc on this surface.

The second system, SnPc on Ag(111), similarly shows a complete suppression of the π^* features for normal incidence light. However, in this case the result is somewhat more surprising. From the DFT calculations an in-plane π^* intensity is predicted due to the distorted geometry of this non-planar phthalocyanine. An examination of the energies of the π^* peaks shows that they are slightly different from those of the bulk. Most noticeably, the second peak is shifted to lower energy. It is suggested that the lack of π^* intensity at normal incidence is due to an extrinsic *suppression* of these peaks. This occurs even in a system where the molecules are mobile across the surface, and appear more weakly bound than on inorganic semiconductor surfaces.

Most importantly, these results show that the observed tilt is indeed related to the substrate and that both intrinsic and extrinsic influences on the intensity of peaks in the π^* energy range are possible.

4.4 An extrinsic in-plane “ π^* ” contribution?

The third possibility to be investigated as the cause of the observed tilt is an extrinsic contribution to the intensity in the π^* energy region for polarisation in the plane of the molecule. This could be the result of two factors: Either it could be a physical distortion of the molecules which induces a distortion of the orbital symmetry, or it could be a purely electronic distortion. These two possibilities are difficult to separate and are consequently discussed together. First the range of phthalocyanines on Ge(001) is expanded, followed by a comparison of the effect of depositing on Ge(111) instead. Finally the effect of specific distortions to the molecule is investigated computationally.

4.4.1 Phthalocyanines on Ge(001)

The two previously studied MPc on the Ge(001)- 2×1 surface both exhibited the same tilt in the molecular plane observed by NEXAFS. It is demonstrated in the previous two sections that the observed tilt is not a fundamental limit of the spectroscopy of these molecules and that it displays no observable azimuthal orientation. Moreover, CuPc on the single domain Ge(001) surface was shown to exhibit a slightly *greater* tilt than the previously studied MPc. However, this difference is on the limits of the accuracy of the experiment, and could further be influenced by the greater step density of the single domain substrate. This section provides a more in-depth and extended analysis of various phthalocyanines on this Ge(001) surface in an attempt to better understand the nature of the observed tilt.

4.4.1.1 PbPc on Ge(001)

The previous study of Cabailh [5] examined NEXAFS of a 40 Å film of PbPc on Ge(001), but the spectroscopy of a single monolayer was not performed. Presented in fig. 4.7 are the NEXAFS spectra of 1 ML and 40 Å films of PbPc on the Ge(001)- 2×1 surface; the results for the 40 Å film, shown in the lower two panels of fig. 4.7, were conducted at only two polar angles, merely as a confirmation of the result of Cabailh [5]. In agreement with Cabailh the best fit angle obtained from the NEXAFS of the 40 Å film is 45° . This is inconsistent with any of the known crystal structures for PbPc in any registry with the substrate and, like in the previous work, it is concluded that this is a result of mixed crystal structures in the film.

The monolayer coverage is somewhat more interesting. There is a distinct change in the spectral shape at the interface, when compared with the bulk, indicative of interface states created as a result of bond formation between the Pc and the Ge. The main differences between the interface and bulk-like phthalocyanine spectra are a reduction in the valley depth and a clear change in the intensity ratio of the first and second π^* peaks. Furthermore, there is a distinct difference in the shape of the spectrum in the π^* region (398-402 eV) for the normal incidence and grazing incidence spectra of the monolayer coverage. As confirmation of these results this normal incidence spectrum has been repeated four times, measuring two locations

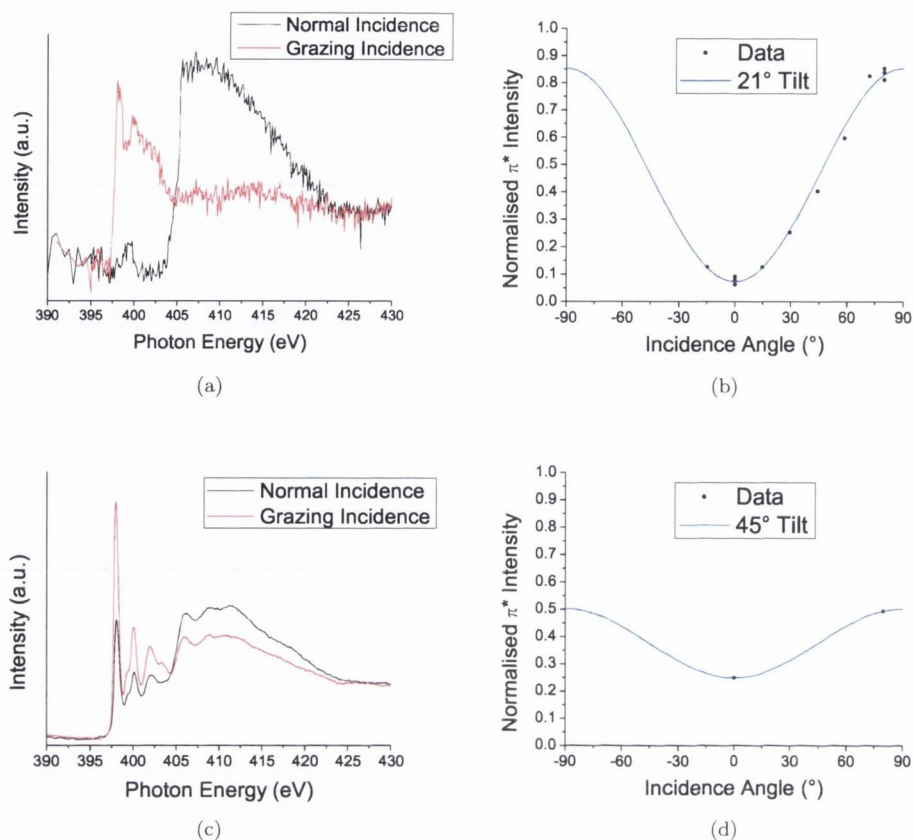


Figure 4.7: Angular dependent NEXAFS of PbPc on Ge(001). The upper two panels show the results for a monolayer film and the lower two show the results for a 40 Å film. (a) and (c) are example spectra of the most extreme angles measured for and (b) and (d) show the normalised intensity of the leading π^* feature as a function of angle.

on each of two separate preparations of the sample. The spectrum at grazing incidence was also repeated four times.

The difference in spectral *shape* between grazing and normal incidence indicates an in-plane character of some of the low energy unoccupied molecular orbitals. If all orbitals giving rise to the peaks in the region between 398 and 402 eV were out of the plane of the molecule, as expected from DFT calculations of the molecule itself, the changing angle of observation would merely change the intensity of these features. Most notable is the peak in the normal incidence spectrum at 399.5 eV, 1.4 eV higher than the leading edge. This peak is not reproduced in the DFT calculations. Furthermore, it is not observable as any difference in the bulk spectrum upon comparison of the suitably scaled π^* region of the two angles of measurement. As such it is concluded to be of extrinsic origin.

To take the peak at 399.5 eV into account, the π^* region of the spectra is fitted with peaks at 398.1, 399.5 eV and 400.0 eV, with the intensity of the lowest energy peak used to determine tilt angle. The result of this is shown fig. 4.7 (b). This procedure gives a tilt of 21°, clearly less than the 25° observed by Cabailh for both MgPc and SnPc. Moreover, this is a conservative estimate

of the tilt as the spectrum in the range of 400-403 eV seems to show complete suppression of any features, leaving open the possibility that the small peak fit in the normal emission spectrum at 398.1 eV results from a finite in-plane intensity, like that of the peak at 399.5 eV. These data were collected at an undulator beamline, and as such the assumption of 100% polarisation used here is considered reasonable.

These PbPc NEXAFS results show that interaction at the interface can have a significant influence over the spectrum produced by the molecules. This makes an accurate assessment of tilt by NEXAFS more difficult than the simple assumption typically used.

4.4.1.2 H₂Pc on Ge(001)

H₂Pc is the simplest of the phthalocyanines, having no metal atom present. This provides a case against which the influence of the metal atom can be better determined. Fig. 4.8 shows the spectra from normal- and grazing-incidence NEXAFS of both a ML and 40 Å coverage of H₂Pc on Ge(001). The ML coverage spectra display large error due to fluctuations in signal intensity at the beamline at which they were taken. To deal with this each spectrum was repeated a number of times. The critical normal incidence ML spectrum presented in fig. 4.8 is a compilation of twenty repetitions of the same spectrum, the grazing incidence as a compilation of six repeats and spectra for all other angles a result of a compilation of four repetitions. Due to the occasional large fluctuations in the signal intensity due to equipment related effects a simple average of the data was significantly distorted. To resolve this, a procedure of outlier exclusion was used on the set of twenty values for each point in the normal incidence spectrum to achieve the presented spectrum.

The normal incidence spectrum of the monolayer, shown in fig. 4.8 (a), shows the changes most clearly. Similar to the PbPc, there is a peak at 399.5 eV in the π^* region (398-402 eV) with in-plane character. Although the nature of the changes in the grazing incidence spectrum are less clear due to the greater error, it exhibits significant differences in comparison to the bulk spectra. Most noticeably, the intensity ratio of first to second π^* peaks is dramatically reduced as for PbPc on Ge(001).

Despite the poor signal to noise ratio, clearly non-zero intensity is observed in the π^* region of the normal incidence spectrum. In this case, after fitting to exclude the contribution of the peak at 399.5 eV, the best fit is achieved with a 21° tilt of the molecule with respect to the substrate. Within the errors of this experiment, this is indistinguishable from any one of the previously investigated phthalocyanines. These spectra were taken at a bending magnet beamline, but due to the near-flat nature of the monolayer film the assumption of 100% polarisation should introduce a maximum of 1° error.

For the 40 Å film, as with the planar MgPc previously investigated, the molecules are tilted near perpendicular to the substrate, most consistent with an α -form crystal structure with the b-axis parallel to the substrate. However, because the molecules in the film are near perpendicular to the plane of the substrate, the influence of the polarisation becomes rather

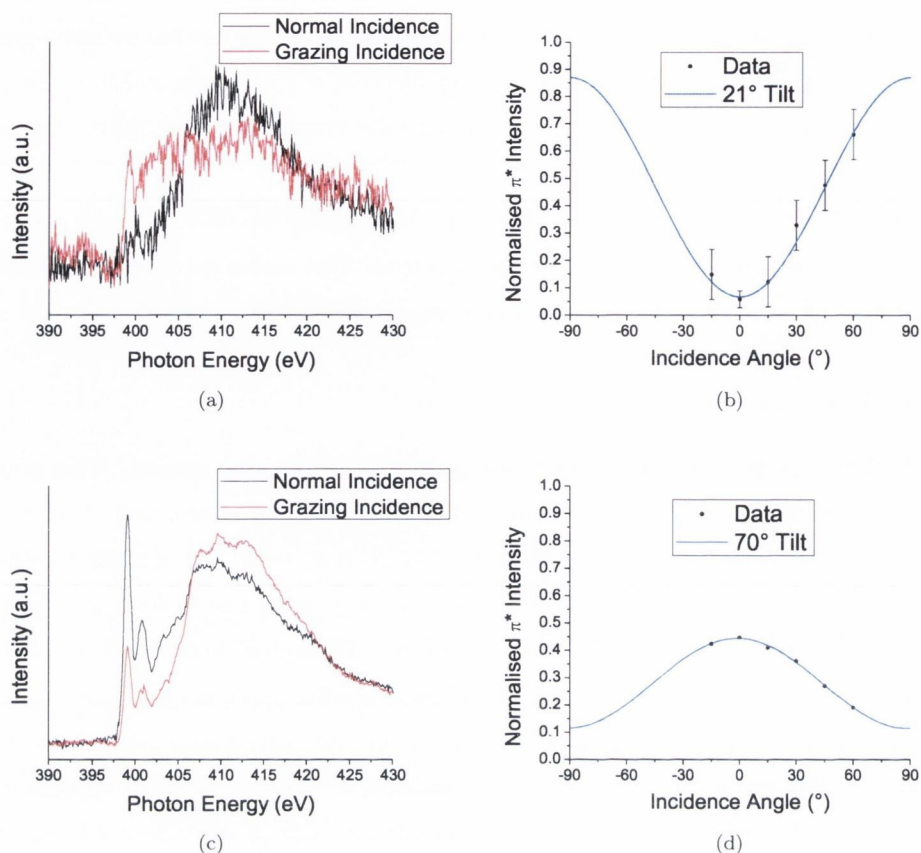


Figure 4.8: Angular dependent NEXAFS of a H_2Pc on $\text{Ge}(001)$. The upper two panels show the results for a monolayer film and the lower two show the results for a 40 Å film. (a) and (c) are example spectra of the most extreme angles measured for and (b) and (d) show the normalised intensity of the leading π^* feature as a function of angle.

significant. If the polarisation were as low as 85% this real tilt could be as much as 77° . This indicates molecules significantly closer to upright than observed for MgPc . This tilt is greater than that expected for an α -form crystal with plane of the b- and c-axes parallel to the substrate, as concluded for MgPc in the work of Cabailh, yet less than an α - or β -form crystal with plane of the b- and a-axes parallel with the substrate. The most likely explanation is that the film is polycrystalline, with a majority of domains aligned with b- and a- axes parallel to the substrate and other domains aligned differently, although exact determination of these other domains is impossible from NEXAFS.

4.4.1.3 CuPc on Ge(001)

NEXAFS of both ML and 40 Å films CuPc on the two-domain $\text{Ge}(001)$ - 2×1 surface is presented in fig. 4.9. As with all the phthalocyanines on $\text{Ge}(001)$ investigated so far, the molecules tend to lie predominantly flat at the interface. After taking into account the intrinsic contribution, the angle of tilt that best fits the progression of π^* intensity is 28° , as shown in fig. 4.9 (b). This is slightly greater than that observed for other phthalocyanines, similar to that observed for CuPc

on the vicinal Ge(001) substrate. Here the spectral shape at the interface is not dramatically changed when compared with that of the bulk, as is the case for MgPc and SnPc, although it is difficult to determine more precisely due to noise. However, this conclusion is strengthened by a look back at the CuPc on vicinal Ge(001) in section 4.2, which similarly shows no change at the interface.

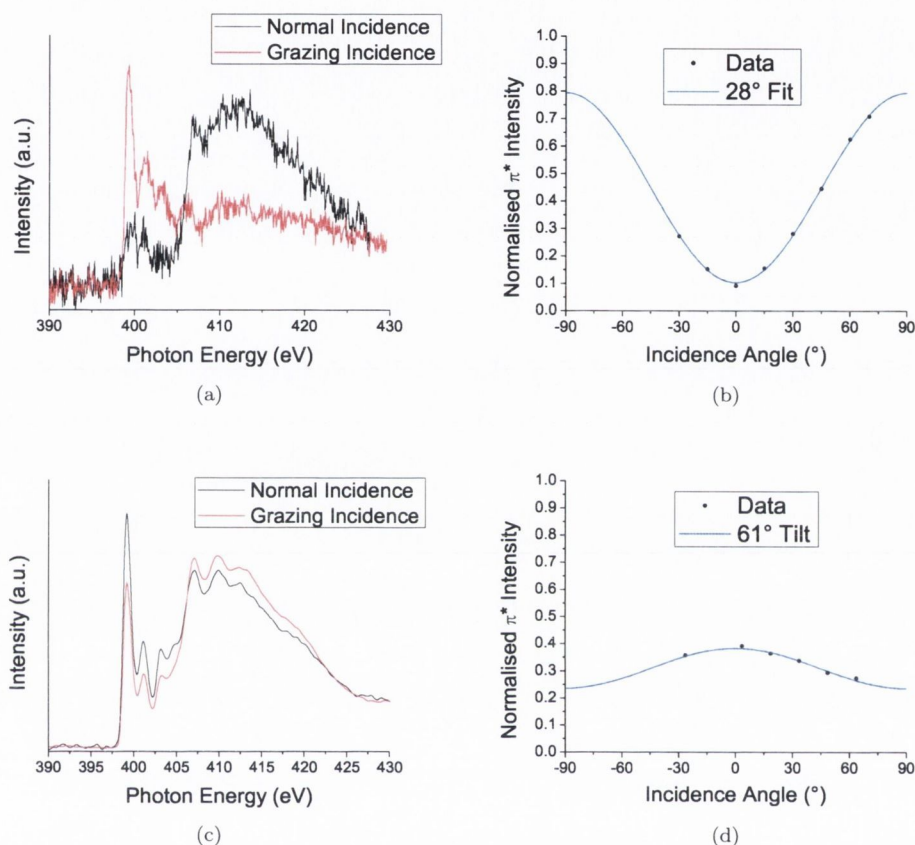


Figure 4.9: Angular dependent NEXAFS of a CuPc on Ge(001). The upper two panels show the results for a monolayer film and the lower two show the results for a 40 Å film. (a) and (c) are example spectra of the most extreme angles measured for and (b) and (d) show the normalised intensity of the leading π^* feature as a function of angle.

The behaviour of the 40 Å film is similar to that of the planar H₂Pc and MgPc on Ge(001) [5], and of CuPc on other substrates [58, 59, 133]. As the coverage increases, the molecules orient themselves close to perpendicular to the substrate, as seen in fig 4.9 (c) and (d), with the best fit tilt of 61° with respect to the substrate in this case.

Again these data were taken on a bending magnet beamline, therefore polarisation effects have to be taken into consideration. As discussed previously the polarisation has little influence over the tilt determined for the 1 ML film. However, for the 40 Å film where the molecules are close to upright, it can have a more significant influence. In this case, the angle determined for a polarisation of 85% could potentially be as much as 65°. This is consistent with an α -form crystal structure with the b- and c-axes parallel to the substrate, but following the discussion

of the H₂Pc results, is more likely the result of a polycrystalline film.

4.4.2 CuPc on Ge(111)-c(2×8)

One final system was investigated with respect to understanding the unexplained tilt observed by NEXAFS. The different reconstructions of Ge(001) and Ge(111) yield surfaces which display significant differences in their degree of interaction with MPc, as will be demonstrated in chapter 6. The greater mobility of the molecules on the Ge(111)-c(2×8) terraces should lead to the intermolecular interactions playing a larger role in molecular ordering in comparison to the Ge(001) surface.

The ML spectra presented in fig. 4.10 (a) and (b) show similarly flat lying behaviour when compared with the results of Ge(001). However, a significantly smaller angle of 21° provides the best fit of molecular tilt with respect to the substrate. Given that CuPc, as most other MPc, tends to form flat lying monolayers in cases where molecule-molecule interaction dominates the ordering, this result is consistent with the greater mobility of the molecule on the Ge(111) terraces in comparison to the Ge(001) terraces. The spectral shape in this case is nearly identical to that of the bulk CuPc, again consistent with a lower degree of interaction in this case.

Fig. 4.10 (c) and (d) show the results from the 40 Å film. In general terms this shows the same result as observed for the 40 Å film on Ge(001), i.e. the molecules tilt almost perpendicular to the surface. However, in this case there is a slightly increased observed tilt angle of 68°, even when assuming 85% polarisation for Ge(001) result. In this case the data were taken at an undulator beamline, for which the treatment of data assuming 100% polarisation is reasonable.

4.4.3 Simulated NEXAFS

Two different tests were performed using DFT of an isolated molecule to determine the expected effects of geometric changes in the molecule when adsorbed on a surface. There are two changes considered likely for these molecules. The first distortion relates to the hydrogens surrounding the benzene rings of the molecule. The plane of benzene molecules is known to lie parallel to many metal surfaces, but the hydrogen atoms at the outside of the molecule are tilted at an angle of up to 40° with respect to the plane [6]. This distortion in the hydrogen generates a finite intensity in the π^* region of the NEXAFS for normal incidence light. The second distortion in the molecule is a bending in the wings of the molecule. This is seen to some degree in the non-planar phthalocyanines already and it seems possible that bonding with the substrate could induce a similar effect.

Fig. 4.11 shows the results of DFT based NEXAFS simulations for the first case. Panel (a) shows the results for a geometry optimised H₂Pc molecule and (b) shows one in which the outer hydrogens are bent to 45° from the molecular plane, with the bond length maintained from the optimised geometry. The main effect of this distortion is a reduction in intensity of the π^* features. However, it is clear that even a large distortion in the outer hydrogens such

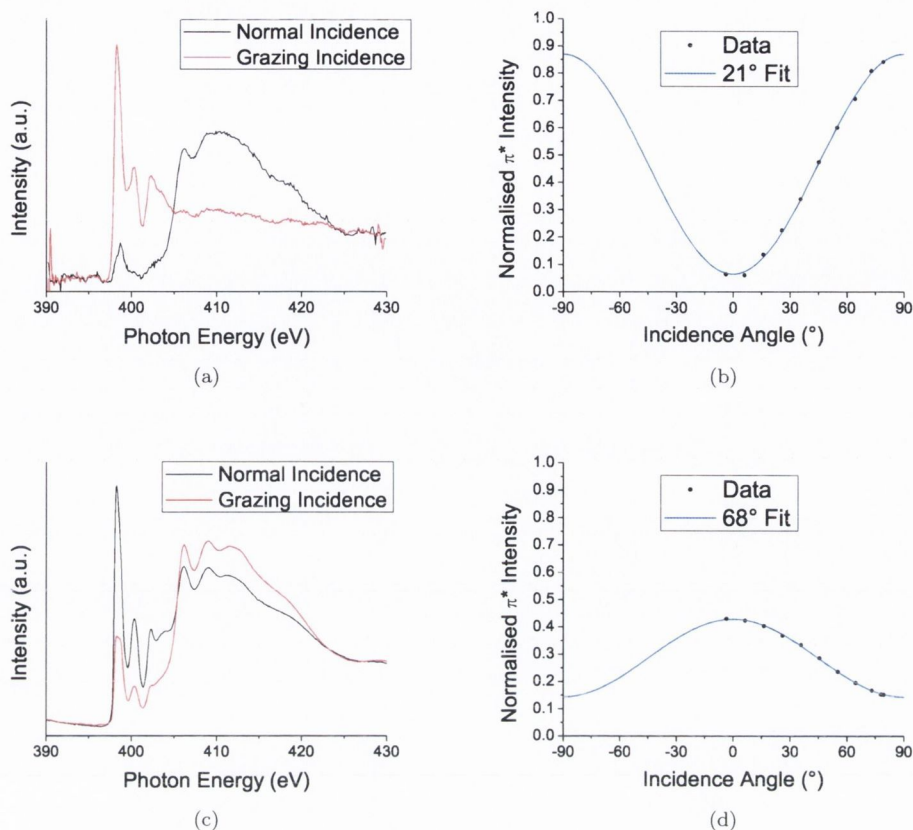


Figure 4.10: Angular dependent NEXAFS of a CuPc on Ge(111). The upper two panels show the results for a monolayer film and the lower two show the results for a 40 Å film. (a) and (c) are example spectra of the most extreme angles measured for and (b) and (d) show the normalised intensity of the leading π^* feature as a function of angle.

as this does not introduce enough “in-plane” intensity in the π^* region to explain the observed NEXAFS. The small in-plane component present is multiplied by 1000 for comparison. The reason for this small intensity is that the separation of the N 1s core electron and the hydrogen is large. This gives only a weak projection of the N 1s electron wavefunction onto the orbitals with in-plane contributions to the π^* intensity, despite the delocalised nature of orbitals in these phthalocyanines.

Fig. 4.12 shows the simulated NEXAFS spectra of MgPc for the second case. Fig. 4.12 (a) shows the results for the geometry optimised planar MgPc and fig. 4.12 (b) shows the results for the same geometry but with two of the wings of the molecule bent at an angle of 15°. Bending the wings of the molecule shows a small in plane intensity in the π^* features not present on the optimised geometry calculation. Working out the molecular tilt from this simulated data as per the process for the experimental data would give a tilt of 9.6°. It is worth noting that there is relatively little change in the spectral *shape* of the data as a result of this bending.

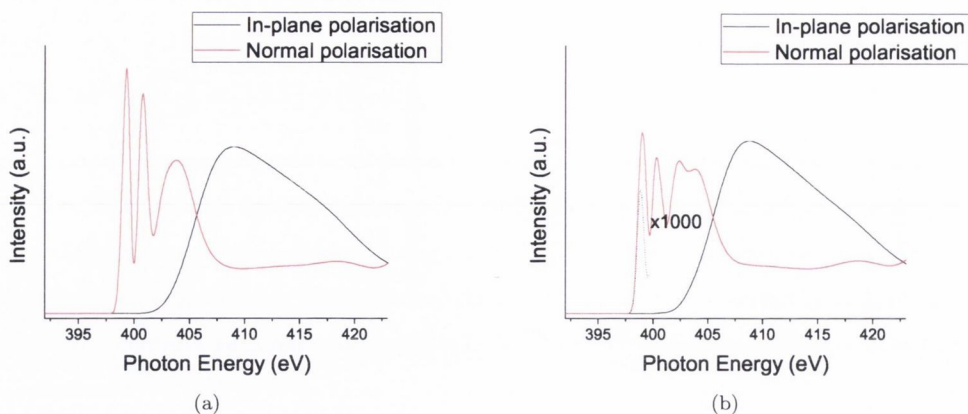


Figure 4.11: DFT based NEXAFS simulation of (a) H_2Pc with the optimised geometry and (b) this same geometry but with the hydrogen atoms bonded to the benzene rings bent up at 45° .

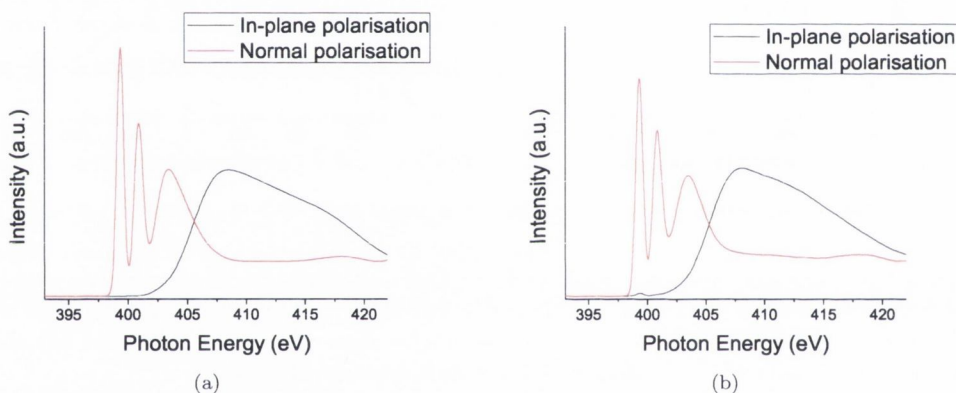


Figure 4.12: DFT based NEXAFS simulation of (a) $MgPc$ for the geometry optimised structure and (b) this structure with two of the wings bent at the joint of the bridging nitrogen at an angle of 15° from the molecular plane.

4.4.4 Summary of extrinsic contributions to the in-plane π^* intensity

This section has demonstrated the possibility of extrinsic contributions to an in-plane intensity in the π^* features. The results show an electronic contribution to this in-plane intensity for some MPc on $Ge(001)$, but it is unclear whether this is the true in all cases. For normal incidence X-rays, the π^* features of $CuPc$ on $Ge(111)$ are less intense than on $Ge(001)$. Under the assumption that this intensity is an extrinsic in-plane feature this is consistent with a weaker interaction observed in STM of MPc on $Ge(111)$ than $Ge(001)$. However, this could equally be due to the higher degree of order often seen in systems where the molecules are mobile across the surface.

It is also demonstrated from DFT that a geometric distortion in the molecule can induce intensity in the π^* peaks in the plane of the molecule. This is unsurprising given that a bend in

the molecular plane will essentially tilt the molecular orbitals. However, it is also shown from these calculations that the distortion must be in the vicinity of the nitrogens through which the tilt is measured.

4.5 Discussion of observed tilts in NEXAFS

The NEXAFS spectra of various metal phthalocyanines on various different substrates have been presented. The results of these experiments are summarised in table 4.1. The effect of polarisation was briefly discussed and shown to have little effect on systems of near flat molecules. A systematic approach was then taken in the analysis of possible origins of this observed tilt. It was first demonstrated that the tilt was not uniform by conducting the experiment on a two-fold symmetric substrate. This sample showed no azimuthal variation in the π^* intensity, a result that would only be expected for a non-uniform, or higher order symmetry tilt. Given the order observed in STM a uniform tilt can reasonably be ruled out.

Secondly the possibility of an *intrinsic* in-plane contribution in the π^* range intrinsic to the molecules was investigated. In the case of weakly bound MPc on HOPG and Ag(111) complete suppression of the leading π^* features was observed. Therefore, as is known to be the case from STM of these systems, the spectroscopy correctly determines the molecular orientation as completely parallel to the substrate. Although shown for both planar and non-planar phthalocyanines, there is significant doubt as to whether flat-lying non-planar phthalocyanines would always show this suppression. These results validate the spectroscopy as a method of determining the tilt in simple cases of planar phthalocyanines where the molecular orbitals are unperturbed.

Thirdly the possibility of an *extrinsic* contribution to the in-plane " π^* " peaks was investigated. In all cases presented in which the molecule is expected to interact more strongly with the substrate, a finite tilt is measured, consistent with the work of Cabailh. However, unlike the work of Cabailh different angles of tilt have been observed at the interface for different phthalocyanines and substrates. Although the range of tilt is fairly small for MPc on Ge(001), between 21° and 28° , it is outside the expected error of the experiments. Moreover, distinct differences are observed for the same phthalocyanine on different substrates. CuPc appears completely flat on the graphite surface, while apparently tilting at 21° on the Ge(111) surface and at 28° on Ge(001) surface. This clearly demonstrates the importance of the substrate-molecule interaction in the tilt observed, but reveals little about its nature.

Two possibilities of an extrinsic contribution to the π^* intensity in flat-lying molecules were considered: A distortion of the molecular plane; and a distortion of molecular orbitals. The conformational changes on adsorption are likely to be either a distortion in the outer hydrogens if the benzene rings of the molecule are involved in bonding [6, 134] or a bending of the entire molecular plane. Computationally it was determined that even a large distortion in the outer hydrogens would not be able to introduce a large enough intensity in the π^* region to explain

Table 4.1: Summary of the NEXAFS results presented within this chapter.

		Substrate				
		Ge(001)	Vicinal Ge(001)	Ge(111)	Ag(111)	HOPG
H ₂ Pc	ML tilt Bulk tilt Notes	21° 70° Extrinsic in-plane π^* peak.				
MgPc	ML tilt Bulk tilt Notes	25° 65°				
SnPc	ML tilt Bulk tilt Notes	25° 25°			0° 20° Flat-lying MPc. Extrinsic π^* suppression?	
PbPc	ML tilt Bulk tilt Notes	21° 45° Extrinsic in-plane π^* peak.				
CuPc	ML tilt Bulk tilt Notes	28° 61°	28° No azimuthal dependence of tilt	21° 68° Apparently better ordered than on Ge(001).		0° Flat-lying. Intrinsic in-plane π^* peak.

the observed tilt. A distortion in the wings of the molecule was shown to potentially produce an apparent tilt. However, the degree of distortion approaching that required has not been observed for any similar system. Bending of planar molecules which has been reported is barely observable; for example, PTCDA on Ag(111) shows no such effect in either carbon or oxygen NEXAFS [135]. Consequently, further work is required to demonstrate whether this is in fact occurring on these substrates.

The second possible extrinsic contribution to the in-plane " π^* " features is a mixing of molecular orbitals with those of the substrate. In the case of SnPc, MgPc and CuPc on the Ge(001) surface only subtle differences between the spectral shape of the interface and bulk can be observed. However, in the case of PbPc and H₂Pc more dramatic changes in the lineshape occur. In these two cases new peaks appear as a result of the interaction with the surface that are not purely of $\sin^2$ intensity dependence. This clearly shows an extrinsic in-plane intensity in the π^* energy range.

As with the *intrinsic* contribution seen in this energy range of CuPc, these peaks can, in theory, be dealt with by an appropriate fitting of the spectra. However, in practice this requires that these new peaks occur at different energy to the leading π^* peak, and even then will significantly reduce the accuracy of the result. Consequently, the possibility of any finite intensity in the leading π^* peak resulting from such interactions cannot be ruled out.

The final potential origin of the observed tilt is also the most obvious, a mixture of flat-lying and disordered molecules. This is difficult to directly determine experimentally as it is not expected to give results necessarily distinct from the other proposed mechanisms. However, two experimental results give some clues in regards to disorder. The NEXAFS results from the thick films and STM presented later, in section 6.1. Both SnPc on Ag(111) and CuPc on Ge(111) tend more toward flat lying at the interface than they do on Ge(001) and in both cases the tilt in the thicker film is more extreme. This is true despite the fact that the CuPc changes from flat lying at the interface to nearly upright in the bulk. Given that any disorder in the films will be observed as a tendency towards 45°, the more extreme angle observed in the bulk is consistent with a more ordered film. This result lends credence to the idea that the observed tilt at the interface includes a significant element of disorder, which is then propagated into the thicker films.

However, this idea too has problems. Under the assumption of a mixture of perfectly flat-lying molecules and randomly oriented molecules, those randomly oriented molecules would have to make up 20-40% of the film. This high proportion of disorder is not seen in STM. Although there is streaking observed in the images, indicative of loosely bound molecules, such a high proportion of disorder seems unlikely, given the high degree of order in the resolvable molecules. There is a reasonable expectation that gently annealing the sample would cause these weakly bound molecules to migrate over the surface, to become well-bound. This provides a possible option for future work.

The summary outlined above leads to the conclusion that there are probably multiple influ-

ences involved which lead to the observed tilt. It seems clear that the observed tilt is neither molecules adsorbing with a uniform tilt nor is it something intrinsic to the molecule. However, there is a significant probability that some intensity in the π^* region results from a distortion of the molecule. As well as that, in some cases the bonding clearly introduces intensity in this region, which may have some influence in all cases given the similarity of the molecules. Finally, the bulk films indicate there is probably some degree of genuine tilt in the form of azimuthally disordered molecules at the interface, further contributing to the finite intensity observed in the π^* region for normal incidence light.

Chapter 5

The origin of metal core-level shift in non-planar MPc

There are two distinct geometric categories of simple metal phthalocyanines. Most MPc are planar, but in cases where the metal has a large ionic radius, steric effects cause a distortion in the plane of the molecule. This results in "shuttlecock" shaped molecules, where the metal protrudes from one side and the D_{4h} symmetry is reduced to C_{4v} . Cabailh observed that the photoelectron spectra of the metal ions in these two cases is dramatically different, with a single state observed in the former, and two states observed in the latter. However, this effect only occurred on Ge(001) and not on GaAs(001). The spectra of MgPc and PbPc on Ge(001) presented in [5] are shown in fig. 5.1 (a) and (b) respectively. The conclusion of Cabailh was that two states are the result of molecules essentially flat on the substrate with metal protruding above or below the molecular plane. This explanation is most likely correct, but does not explain the mechanism by which such a shift in the photoelectron spectra might occur.

There are four main possible mechanisms by which such energy shifts at interfaces can occur. These are:

- (a) Initial state charge transfer between the substrate and metal atom.
- (b) An enhanced molecular dipole.
- (c) Dielectric screening.
- (d) Charge transfer to the molecule in the final state.

Cabailh observed a shift toward higher binding energy in the Ge 3d surface states as shown in fig. 5.1. This is indicative of electron transfer from the surface to the molecule, from which a shift to lower binding energy of the metal ion core level is expected. The molecular dipole for PbPc has been calculated to be positive with respect to the metal [85], with a similar situation expected for SnPc, which again implies a shift to lower binding energy for the species with the metal ion nearer the substrate. Finally, both the final state effects of dielectric screening

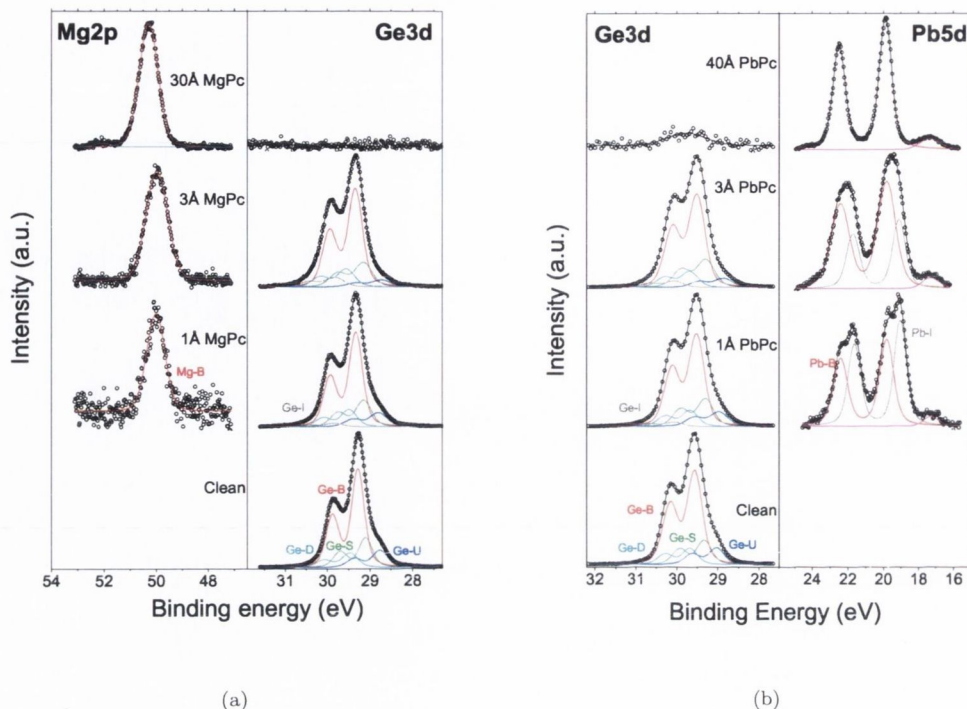


Figure 5.1: (a) Ge 3d and Mg 2p core levels for the Ge(001)-21 surface and three coverages of MgPc. The original data is shown by small circles, the red lines refer to the Ge 3d and Mg 2p bulk components, the green line denotes the Ge second layer component. The blue and light blue lines denote the Ge up and down components from the Ge atoms in the surface dimers. An extra component was required for the thicker layers and is related to Auger peaks. The solid black line gives the total contribution of the components. All spectra are normalised to unity for better comparison (except for the Ge 3d core level for the 30 Å film). Spectra were taken at a photon energy of 100 eV. (b) Ge 3d and Pb 5d core levels for the Ge(001)-21 and three coverages of PbPc. The original data is shown by small circles, the red lines refer to the Ge 3d and Pb 5d bulk components, the green line denotes the Ge second layer component. The blue and light blue lines denote the Ge up and down components from the Ge atoms in the surface dimers, the grey lines represent the interface components for Pb 5d and Ge 3d component and the magenta line is the valence band component. The solid black line gives the total contribution of the components. Spectra were taken at a photon energy of 100 eV. Reprinted from [5]

and charge transfer also cause a shift to lower binding energy. On this basis, regardless of the mechanism by which the shift occurs, it is reasonable to assign the lower binding energy peak of the phthalocyanine to the molecules with the Pb towards the Ge surface. Conversely the higher binding energy peak results from molecules with the Pb protruding away from the Ge surface. Hereafter, these species are labelled “down” and “up” respectively.

This chapter contains an investigation of the mechanisms discussed above. Since these effects are only observable in the first monolayer, and the metal ion is only one of 57 atoms in the molecule, a very strong signal to noise of the metal atom core level is required. Unfortunately there are few phthalocyanines in which the metal ion has core levels of both appropriate energy and large enough cross section. To understand the interaction further experiments based on

the previously investigated phthalocyanines are presented. Firstly, STM is used to demonstrate the validity of the previous explanation, followed by a series of experiments aimed at gaining an understanding of the specific mechanisms. Finally, a discussion of other results related to the above problems is presented.

5.1 STM of PbPc

STM provides a clear and effective technique of demonstrating both the flat-lying nature of the molecules and the presence of both “up” and “down” species. Fig. 5.2 shows STM images for a sub-monolayer coverage of PbPc on Ge(001) in which one PbPc molecule of either species is present. In the filled states image in fig. 5.2 (a) the four benzene lobes of both molecules can be seen, but the one on the left is seen with a bright centre and the other with a dark centre. In the empty states image of fig 5.2 (b) the molecule on the left is simply resolved as a bright lump while for the other two bright spots can be seen in place of only two of the four benzene rings.

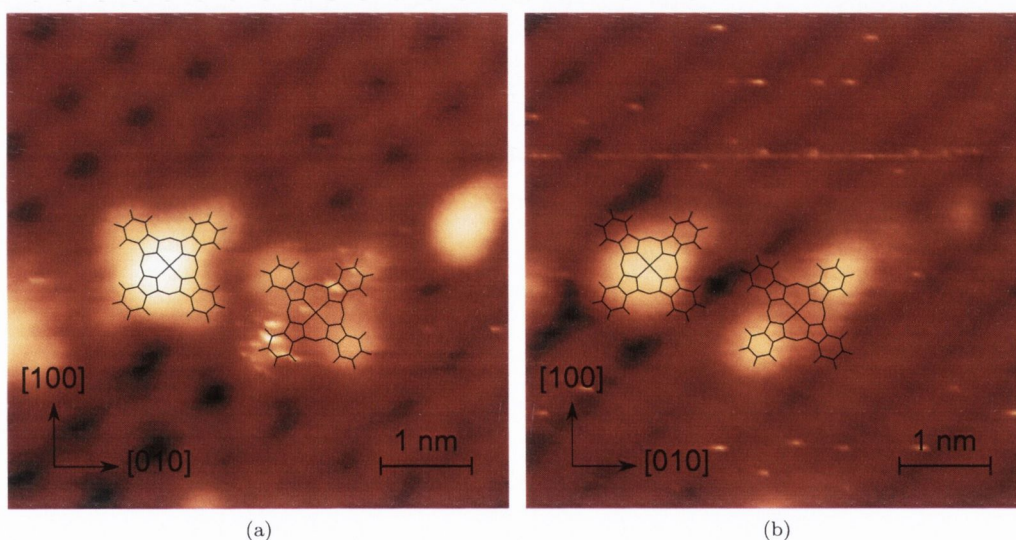


Figure 5.2: STM images of PbPc deposited on Ge (001), for (a) a filled state image at -1.8 V and (b) an empty states image at +1.4 V with 0.1 nA tunnelling current in both cases.

These species almost certainly relate to the “up” and “down” PbPc. However, determination of which is “up” or “down” is less certain. The immediate interpretation would be that the species with the bright spot in the centre in fig. 5.2 (a) is the “up” species and that with the dark centre is the “down”. However, the opposite interpretation is also a possibility, whereby the species with Pb down induces a density of states at this site. Density functional theory calculations of the valence orbitals reveal that the HOMO should have a zero density of states on the metal site, but significant density of states on the four lobes of the molecule. The LUMO should similarly have no density of states on the metal, but in this case, finite density

only on two opposite benzene lobes [136]. In fact, no density of states is expected on the Pb site for the lowest five unoccupied states. These HOMO and LUMO density of states of the free molecule substantially agree with the molecule on the right, whereas the molecule on the left clearly displays density of states on the metal where none is expected for the free molecule. This extra density of states is most likely the result of molecule-tip interaction, or molecule-substrate interaction, the latter being the more likely given the substrate-molecule interaction observed by photoelectron spectroscopy.

This analysis implies that the Pb with a greater degree of interaction with the substrate is that observed on the left of the images. Under the assumption that the molecule for which the lead is closer to the surface is more strongly affected the conclusion would be that the molecule on the left of the images is the “down” PbPc.

These STM results confirm the two conditions necessary for the up-down explanation of the observed shift. These two conditions being that the molecules are flat lying and both “up” and “down” species are present on the surface.

5.2 PbPc on hydrogen passivated Ge(001)

In an attempt to observe the effect of reducing the interaction, and symmetrising the dimers of the Ge(001)- 2×1 surface PbPc was deposited on a monohydride passivated surface. Passivation was confirmed via LEED and PES. LEED showed a pure 2×1 reconstruction (not shown), with no sign of streaks related to the residual 4×2 always present on the unpassivated surface. Fig. 5.3 (a) shows a clear reduction in the surface core level shift in PES. Moreover, a reduction in surface states of the valence band is also seen (see fig. 5.3 (b)), as well as a new peak at 10.4 eV binding energy.

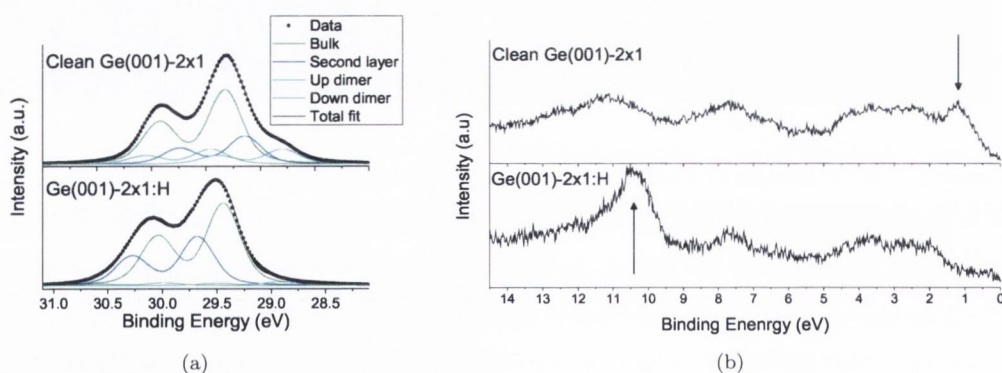


Figure 5.3: PES of (a) Ge 3d and (b) valence band from Ge(001) and the monohydride passivated Ge(001)- 2×1 surface.

Fig. 5.4 shows the Pb 5d core level for a monolayer and bulk-like film of PbPc on Ge(001)- 2×1 :H. In both cases they are fitted with a single doublet. This is clearly enough to provide a good fit to the spectrum. The only difference between the two fits is a slight broadening in

the case of the interface, the width of the Gaussian component for the bulk spectrum being 0.46 eV whereas that for the interface spectrum is 0.55 eV. This difference could be the result of inhomogeneity of states at the interface, the most likely inhomogeneity being a difference between first and second layer molecules, resulting from band bending effects that cause the signal from the second layer to be slightly shifted from that of the first. STM shows that the phthalocyanines follow an island growth mode on this surface (see section 6.2), meaning that for a nominal 1 ML deposition some areas of the surface will be covered by a second layer, providing a probable cause of the observed broadening in the film. However, the shift observed between the up and down states for PbPc on the bare Ge(001)- 2×1 surface is 0.8 eV. Any attempt to fit a second doublet with a shift such as this yields zero intensity for this extra state, clearly indicating that such a shift does not occur on this surface.

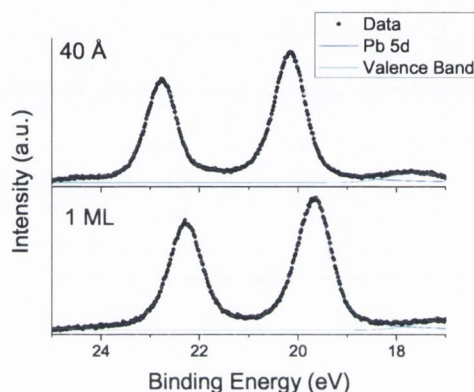


Figure 5.4: PES of the Pb 5d core level of PbPc on the monohydride passivated Ge(001)- 2×1 surface, taken with a photon energy of 100 eV. A single peak is fitted at 17.6 eV to account for the band features.

This test was carried out in the expectation of flat-lying PbPc molecules, with both “up” and “down” species present, as seen on most other substrates. Unfortunately, this assumption was later demonstrated to be incorrect. As shown in section 6.2, the first monolayer of molecules bonds to this substrate with a tilt of approximately 45° in accordance with the bulk monoclinic structure.

5.3 Other systems exhibiting the shift

There are two different situations in which shifts analogous to those of non-planar phthalocyanine on Ge(001) occur. First of all, the observation of two states has been extended to other surfaces, then the results of an interface where an analogous shift occurs for a planar phthalocyanine are presented.

5.3.1 Non-planar MPc on other surfaces

As detailed in section 2.2.2 no cases could be found in the literature where a splitting like that observed by Cabailh occurred at any MPc interface. This included non-planar MPc on a number of different III-V semiconductor surfaces. More interestingly, an investigation of a monolayer of PbPc on (001) and the (111) surfaces of silicon reported no sign of such a shift [55]. This raises the question as to whether it is something unique to the Ge(001) surface.

The non-observation of this core level shift on the Si(001) surface is most surprising as this surface is the most closely related surface to that of Ge(001). Due to the difficult nature of the experiment and the poor signal to noise of the spectra presented by Ottaviano et al. [55] there was value in repeating the experiment. The repeated spectra of a monolayer of PbPc on the Si(001)-2 $\times$ 1 surface, given in fig. 5.5, show a definite second doublet in the Pb 5d core level associated with the phthalocyanine. The low kinetic energy side of the spectrum also shows an asymmetry, perhaps indicative that a third peak is present in the spectrum. However, due to a large background contribution from the substrate, curve fitting is of little value here. This simple test confirms that effect is not unique to the Ge(001) surface.

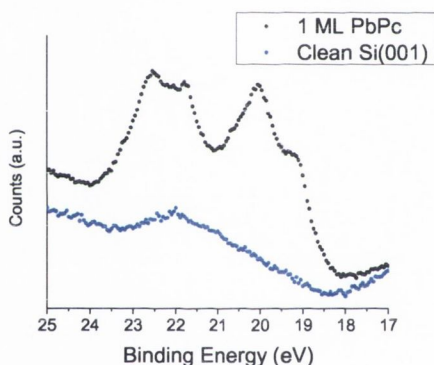


Figure 5.5: PES spectra of Pb 5d core level from 1 ML of PbPc on Si(001) (black dots), overlayed on the background taken from clean Si(001)-2 $\times$ 1 (blue dots). The spectra were taken with a photon energy of 100 eV.

Of further interest is whether the effect occurs as a result of the dimer reconstruction present in both the Ge(001) and Si(001) surfaces. The (111) surface of Ge presents a dramatically different, adatom based, c(2 $\times$ 8) reconstruction as depicted in section 2.1.1.1. The effect of the interactions at this interface were investigated through spectroscopy of core levels of both the substrate and the central lead atom.

Fig. 5.6 shows Pb 5d photoelectron spectra of progressively increasing coverage of PbPc on Ge(111). The raw data show two distinct spin orbit split doublets in all cases, except for the bulk where a single doublet appears. The higher binding energy doublet of the two has a clearly observable shoulder, requiring a minimum of *three* separate doublets for fitting. The doublets will be hereafter defined by binding energy of the 5/2 spin orbit component. The fitting parameters used in fig. 5.6 are summarised in table 5.1.

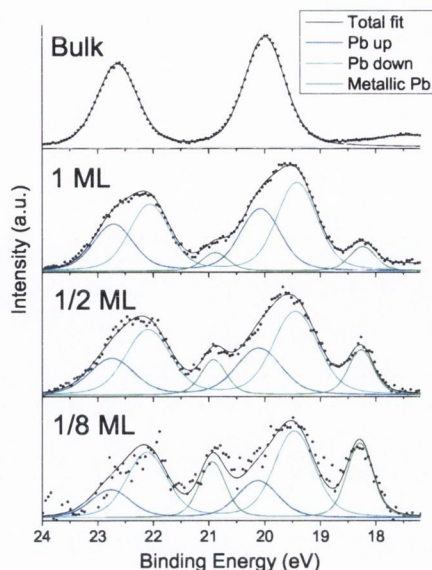


Figure 5.6: Pb 5d photoelectron spectra of PbPc deposited onto the Ge(111)-c(2×8) surface. Three doublets are used in the fitting of the spectrum, two related to Pb in the phthalocyanine (“up” and “down”), and one related to lead stripped from the molecular macrocycle (metallic). The spectra were taken with a photon energy of 50 eV.

Table 5.1: Summary of fitting parameters used in Fig. 5.6. The energy difference between the “up” peak and the “down” and metallic peaks is constant at -0.65 eV and -1.83 eV respectively. GW refers to the Gaussian FWHM, LW the Lorentzian FWHM, SOS the spin orbit split and BR the branching ratio. The intensities are given as a fraction of the total intensity

	1/8 ML	1/2 ML	1 ML		Pb in PbPc	Pb in metal
$I_{\text{“Up”}}$	0.21	0.29	0.37	GW	0.70	0.46
$I_{\text{“down”}}$	0.50	0.53	0.53	LW	0.26	0.17
I_{Metallic}	0.29	0.18	0.10	SOS (eV)	2.64	2.64
				BR	0.75	0.75

Although the core level spectrum in this case appears slightly more complicated, analogous “up” and “down” related features are clearly present. These are the Pb 5d 5/2 peaks occurring at 20.1 eV and 19.5 eV. The lowest binding energy peak occurs at a binding energy of 18.3 eV, which is consistent with Pb atoms in a neutral (metallic) state, as opposed to the +2 state of Pb ions in the molecule. The FWHM of this peak is also significantly smaller than that of the other two peaks (0.55 eV compared to 0.85 eV for the Pb 5d core level of the lead phthalocyanine), again consistent with metallic lead [80]. This shows that Pb is stripped from some molecules upon deposition onto the Ge(111) surface, as was seen for PbPc deposited on Pt(111) [80].

Fig. 5.7 shows the Ge 3d core level spectrum for progressively increasing coverages of PbPc. The clean spectrum is fitted with four components as explained in section 2.1.1.1. The components are: bulk Ge atoms; first layer atoms bonded to the adatoms at -0.25 eV relative to the bulk; adatoms at +0.18 eV; and rest atoms at -0.74 eV. A further two components, at lower binding energy than the bulk peak (Ge_{I1}) and at higher (Ge_{I2}), are included to deal

with interface states generated upon deposition of the PbPc. These extra components should be treated as an indication of where the spectral weight is changing rather than specific, well defined states. However, it is worth noting that no arrangement of the four states employed for the clean surface can account for the adsorbate surface, indicating that new states are induced by the molecule.

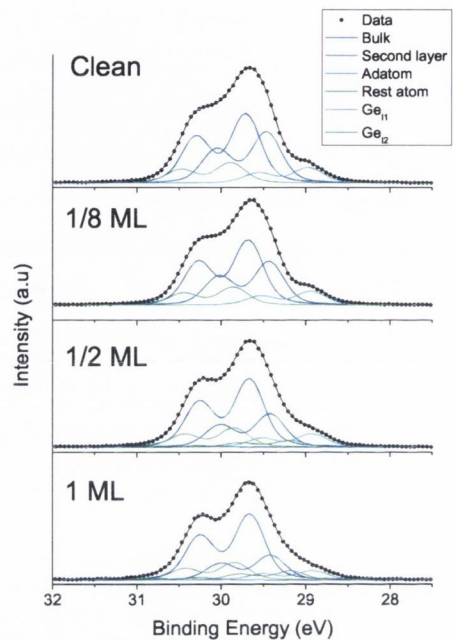


Figure 5.7: Ge 3d photoelectron spectra of PbPc deposited onto the Ge(111)-c(2×8) surface. Four doublets are used in the fitting of the clean germanium spectrum, with a further two included for interface states. The spectra were taken with a photon energy of 100 eV.

Table 5.2: Summary of fitting parameters used in Fig. 5.7. The energy difference between the germanium peaks is kept constant. The intensities are given as a fraction of the total intensity. For all peaks a Gaussian FWHM of 0.33 eV, Lorentzian FWHM of 0.15, spin orbit split of 0.59 eV and a branching ratio of 0.66 were used.

	Clean	1/8 ML	1/2 ML	1 ML
I_{Bulk}	0.44	0.45	0.48	0.51
$I_{Firstlayer}$	0.32	0.31	0.23	0.19
$I_{Restatom}$	0.13	0.13	0.13	0.13
I_{Adatom}	0.10	0.10	0.09	0.07
$I_{Ge_{11}}$	0.00	0.00	0.04	0.07
$I_{Ge_{12}}$	0.00	0.00	0.01	0.02

The dominant change seen in fig. 5.7 (and the summary contained in table 5.2) is in the low binding energy section of the spectrum. The intensity of the adatom contribution is significantly reduced as is the intensity of first layer atoms bonded to the adatoms, while the rest atom contribution remains unchanged. The bulk contribution increases and a significant contribution at 0.48 eV lower binding energy than the bulk (Ge_{I1}) is required for a “good” fit. Finally another component (Ge_{I2}) is included at 0.58 eV higher binding energy than the bulk peak. This feature

is small in comparison to the other peaks. This transfer of spectral weight from low to high binding energy for the Ge 3d core level indicates a transfer of electrons from the surface to the molecule, as is the case for PbPc on the Ge(001) surface.

This shows that the changes in both the core level and the molecule are analogous to those seen for non-planar MPc on the Ge(001) surface. Consequently, the same logic can be applied here as was applied in the designation of the Pb 5d states on the Ge(001) surface.

These results from Si(001) and Ge(111) clearly demonstrate that the up-down shift observed for non-planar phthalocyanines deposited on Ge(001) is not unique. Two related surfaces both display this same effect; the effect is unique neither to Ge nor to the particular reconstruction.

5.3.2 MgPc on Ge(111)-c(2×8)

Following Cabailh, the assumption is that this shift can only occur for non-planar MPc, but this section shall show that it can also occur for planar phthalocyanines. Although PES of MgPc on the Ge(001) surface only shows a single state at the interface a similar experiment conducted on Ge(111) shows two states. Fig. 5.8 shows the PES of the Mg 2p core level for progressive coverages of MgPc on the Ge(111)-c(2×8) surface. Clearly two peaks are required to accurately fit the data for coverages other than the bulk-like spectrum of approximately ten monolayers.

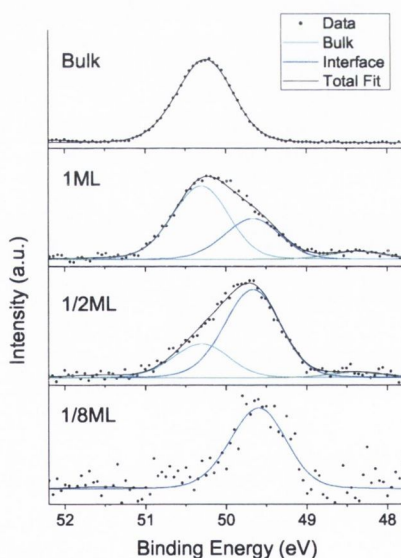


Figure 5.8: Mg 2p PES of MgPc deposited on the Ge(111)-c(2×8) surface. All spectra were taken with a photon energy of 110 eV.

The lowest coverage, approximately an eighth of a monolayer, appears to contain a single peak at 49.6 eV. This contrasts with the results of the non-planar phthalocyanines in which two states are observed even for very small coverages. For slightly greater coverages a second

peak is at 0.6 eV higher binding energy is required for an accurate fit. This second peak then increases in intensity relative to the lower binding energy peak until in the bulk like film it becomes the only peak present.

The PbPc on Ge(111) presented in section 5.3.1 shows a reactive peak resulting from Pb stripped from the molecular macrocycle. This suggests that the peak observed at the interface of MgPc and Ge(111) could be a similar reactive peak. Alternatively, it could be a shift analogous to that of the “up/down” shift seen in non-planar MPc.

If it were a result of Mg removed from the phthalocyanine macrocycle, analogous to PbPc on Ge(111), it would probably be either metallic, or bonded to the Ge substrate. Fig. 5.8 (a) shows the Mg 2p core level of a monolayer of pure Mg deposited on the Ge(111) surface. Although the width is similar to that of the peaks in fig. 5.8 the binding energy is 50.4 eV, 0.8 eV higher than the interface peak of MgPc on Ge(111). This would suggest that the low binding energy structure in fig. 5.8 is not Mg stripped from the molecule and covalently bound to the substrate.

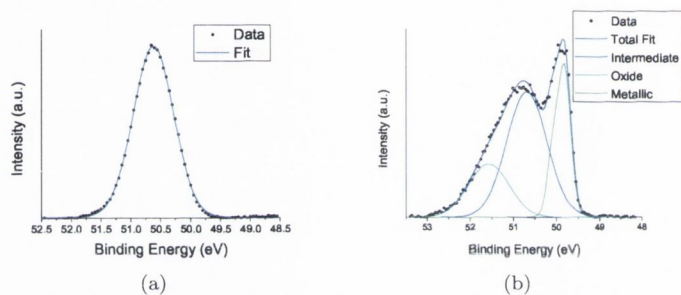


Figure 5.9: Mg 2p PES of (a) a monolayer of Mg metal deposited on the Ge(111)-c(2×8) surface and (b) thick film of Mg metal deposited on the same surface. All spectra were taken with a photon energy of 110 eV.

The other possibility is that the Mg is stripped from the molecule and is weakly bound on the sample, therefore behaving like metallic Mg, with an Mg^0 initial state. The binding energy of this interface peak falls within values published in the literature for Mg metal [137, 138]. However, if this were the case the FWHM should be approximately 0.5 eV [139], rather than the 0.8 eV observed. Furthermore, attempts to deposit thick layers of Mg resulted in an oxidation of the metallic Mg due to ambient water during the period of scanning, on the order of one hour. This resulted in a spectrum consisting of a narrow metallic peak at low binding energy with a broad oxide peak to higher binding energy as shown in fig. 5.9 (b). The fit of this spectrum is done in a similar fashion to the work of Driver et al. [139]. Given that these experiments were all conducted in the same chamber, with similar base pressure, oxidation of the low binding energy Mg 2p peak of fig. 5.8 would be expected if it was Mg stripped from the macrocycle. Since no change was observed even after several hours this is considered unlikely.

The final point which demonstrates that the observed shift of MgPc on Ge(111) is analogous to the “up/down” shift of non-planar phthalocyanines comes from the observed intensities. The

metallic Pb component of PbPc on Ge(111) shown in fig. 5.6 is only a small fraction of the total Pb intensity, whereas for a similar coverage the low binding energy Mg peak of fig. 5.8 is the only peak present. The greater proportion of reacted MPc is unlikely. This single state is never observed for a non-planar phthalocyanine due to the presence of “up” and “down” adsorption sites, but it is consistent with the single orientation of planar MPc.

The observation of a finite intensity in the higher binding energy Mg 2p peak for the half- and one monolayer coverages could be due to tilted molecules. This would be consistent with NEXAFS presented in chapter 4, which indicate a proportion of non-flat lying phthalocyanine for a monolayer coverage. These results show that a shift analogous to that observed for non-planar phthalocyanines on Ge(001) may also occur for planar phthalocyanines.

5.4 Investigation of mechanisms of the observed shift

As outlined at the start of the chapter there are four mechanisms by which a shift such as that observed could occur. This section is an attempt at an investigation of these individual mechanisms.

5.4.1 Study of charge transfer

The most obvious reason for a shift in any photoemission peak is charge transfer. As explained in section 3.3.1.3 neglecting all other effects there is an expected shift of approximately 2 eV to lower binding energy per electron gained. On examination of the substrate core levels for both Ge(001) and Ge(111) a shift to higher binding energy was observed upon deposition of *non-planar* MPc. This would be consistent with electron charge transferred into the metal ion for either substrate as the proposed mechanism of the shift. However, similar shifts are observed in the core levels of the substrate after deposition of *planar* MPc, but not in the metal ion of the molecule. This led Cabailh to conclude that charge transfer is not the cause of the observed shift in the non-planar MPc metal ion core level.

A quick analysis of the numbers reveals the flaw in this conclusion. The “down” component of the metal ion core level contributes approximately a third of the intensity at the monolayer coverage. Each molecule, in a close packed arrangement, covers 6 Ge dimers. Therefore for each “down” metal ion there are 36 surface Ge atoms. The shift of 0.8 eV in the metal ion core level, under the assumption of charge transfer as the only factor, implies slightly less than half an electron transferred from the substrate. For example, if the charge comes from a single Ge atom, 1/18th of the intensity from the upper dimer atom (approximately 8×10^{-3} of the total intensity) could be expected to shift 0.8 eV higher in binding energy.

These changes are less than those seen between different sample preparations due to errors related to film thickness, surface preparation, MPc purity, experimental resolution and geometry, plus any potential other differences in the bonding of different phthalocyanines. And as such it is concluded that the information obtained from the shifts in the substrate core level

can not be extended to an analysis of the shifts in the metal core level.

5.4.2 Study of dielectric screening effects

One possible cause of the two observed states is that of a dielectric screening shift. Where there is a large density of states at the surface there exists the possibility of a shift resulting from the polarisation of charge in the surface upon photexcitation, especially apparent in metals. Semiconductors often display a larger density of states at the surface than in the bulk, in fact it has been shown that Ge(001)- 2×1 reconstruction is temporarily metallic as a result of dimers switching [27, 140]. Two approaches have been employed in an analysis of this: the first is comparison of films of non-planar MPc on a metal surface for which distinctly different regimes of “up” and “down” species are known to be present, namely SnPc on Ag(111); the second is an analysis of expected substrate molecule spacing for the observed shift. The first part of this section outlines the theory, and the second gives the results from the two different approaches.

5.4.2.1 Image charge screening theory

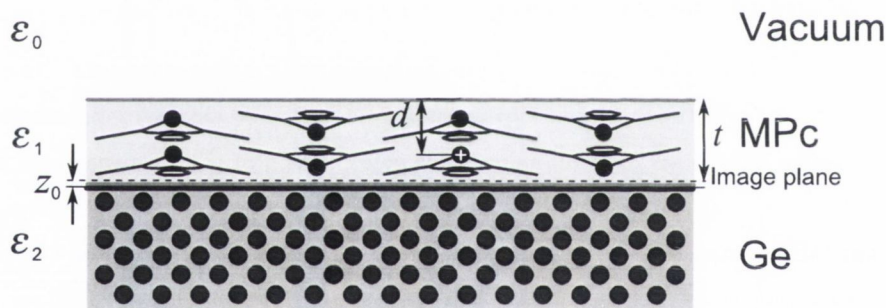


Figure 5.10: Theoretical model of the Ge-MPc-Vacuum system for the purposes of dielectric screening. The dotted line represents the image plane, which lies a distance z_0 above the Ge surface plane. The distance d represents the distance from the surface to the core hole and t represents the film thickness.

A model for the system of dielectric film on dielectric substrate is given in fig. 5.10. Here, there are two dielectric boundaries which screen the charge in the central film. The total screening can be expressed as the influence of an infinite sum of point charges. The first term is the effect of both boundaries, assuming each is independent and satisfying the boundary conditions for the single barrier system. Each subsequent term satisfies the boundary conditions for the influence of the image charges on the *opposite* boundary to that associated with the image charge, similar to the work of Sometani [119]. This gives the total energy shift, using the labels as defined in fig. 5.10, as

$$\Delta E_B(d, t) = \frac{q}{4\pi\epsilon_0} \sum_{n=1}^{\infty} \left[\frac{q_{aan}}{2nt - 2d} + \frac{q_bbn}{2(n-1)t + 2d} + \frac{2q_{abn}}{2nt} \right] \quad (5.1)$$

with

$$q_{aan} = \alpha^n \beta^{n-1} q_0, q_{bbn} = \alpha^{n-1} \beta^n q_0, q_{abn} = \alpha^n \beta^n q_0 \text{ and } q_0 = \frac{1}{\varepsilon_1} \quad (5.2)$$

where

$$\alpha = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1}, \beta = \frac{\varepsilon_0 - \varepsilon_1}{\varepsilon_0 + \varepsilon_1} \quad (5.3)$$

In the simplified case of a dielectric plane this reduces to the formula of Sometani [119], and for a metal substrate, where the dielectric constant is considered to be infinite, reduces to the formula of Chiang et al. [91].

A small correction to the thickness z_0 has to be made for the location of the image plane which is slightly above the surface plane of the substrate, as shown in fig. 5.10. This correction is typically less than 1 Å for metals, depending on the electron density [141]. Although there are no calculations of a similar effect for semiconductors it is assumed to be no greater than for metals due to the lower electron density.

There are three important results from this for determining whether this is the cause of an observed shift. The above formula is independent of electron emitted, therefore all energy levels should exhibit the same shift. This assumption can be invalid for valence levels, due to their less localised nature, but generally holds true for core levels. Furthermore, the observed shift should be approximately three times larger for Auger electrons, in which there are two holes left behind. This is because the shift of eq. 5.1 is dependent on the square of charge and the kinetic energy of Auger electrons depends on the difference in energy between the one and two hole systems (i.e. $2^2 - 1 = 3$). Finally, it gives a relationship for the energy shift as a function of distance from the image plane and film thickness.

5.4.2.2 Dielectric screening results

The SnPc on Ag(111) monolayer films were prepared by two techniques. The first film was prepared by deposition of approximately 3/4 the typical monolayer coverage at room temperature, followed by cooling the sample to below 230 K. This forms a mixed “up” and “down” phase, loosely packed monolayer of SnPc, which is commensurate with the substrate [36, 73]. The second film is prepared by deposition of 10 ML SnPc onto the substrate followed by an anneal at 290°C, forming a close packed ML, which is incommensurate with the substrate, and is of a uniform “down” phase [73].

PES of the Sn 4d core level of both monolayer sample preparations is given in fig. 5.11 along with the Sn 4d core level of the 10 ML film, for which substrate core levels are completely suppressed. The PES of the commensurate monolayer of SnPc given in fig. 5.11 (b) shows a *single* doublet at the interface, in which the fitting parameters required are almost identical to the bulk. There is a slight change in the branching ratio, which is most likely the result of diffraction effects, and a slight reduction in the Gaussian width resulting from a decrease

in thermal broadening in this spectrum. The only other significant difference is a shift of approximately 0.4 eV between this spectrum and that of the 10 ML film, consistent with band bending shifts observed at most organic/inorganic interfaces. Consequently it is clear that image charge screening has no measurable influence over the spectrum.

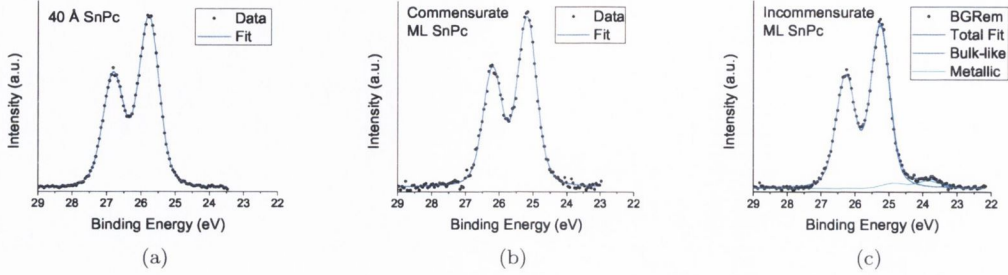


Figure 5.11: Sn 4d PES of SnPc on Ag(111) for: (a) A 40 Å film; (b) a commensurate monolayer structure with mixed “up” and “down” SnPc; and (c) an incommensurate monolayer structure of uniform “down” SnPc. All spectra were taken with a photon energy of 100 eV. The spectra given in (a) and (c) were taken at room temperature, and (b) was taken at 110 K.

Table 5.3: Summary of fitting parameters used in fig. 5.11. The binding energy refers to that of the 5/2 peak, SOS the spin orbit split, BR the branching ratio, GW the Gaussian FWHM and LW the Lorentzian FWHM.

	E_B (eV)	SOS (eV)	BR	GW	LW*
Bulk	25.77	1.0	0.66	0.61	0.20
Commensurate ML	25.39	1.0	0.69	0.57	0.20
Incommensurate ML	25.48	1.0	0.68	0.55	0.20

* LW is fixed to the value determined from the 10 ML spectrum, i.e. 0.20 eV.

In the case of the close packed ML film two doublets can be seen. The position of the lower binding energy doublet is consistent with Sn stripped from the molecule upon annealing as is commonly seen upon heating MPc-metal interfaces [80, 81]. Therefore, the higher binding energy peak is the only peak originating from Sn in the phthalocyanine. The width of this energy peak is again distinctly narrower than that of the bulk; in this case this is most likely due to the high degree of order of the phthalocyanine in this film. Other than this the spectrum is explained in much the same fashion as the commensurate ML structure.

Given that the metallic Ag(111) surface is expected to provide a higher degree of image charge screening compared to that of Ge or Si this explanation is unlikely as a cause of the two states observed for non-planar MPc at other interfaces.

The observation of a single state for SnPc on both Ag(111) can to some extent be understood by the theory of dielectric screening as outlined in section 3.3.1.4. The following analysis uses the Ag(111)-Sn spacing taken from X-ray standing wave (XSW) experiments conducted on both the commensurate monolayer configuration of SnPc on Ag(111) [73]. A dielectric constant of ∞ is assumed for the Ag substrate and the thickness of the film is assumed to be the tin position

plus an atomic radius of 1.4 Å.

MPc are often quoted with different dielectric constants. This is due to the fact that the dielectric constant can vary significantly between gas phase and crystal, for different crystal structures and even in different directions. Theoretical work shows an expected dielectric constant for a single molecule of 3.4 perpendicular to the plane and 15 in the plane [142]. For a crystal this value could be much higher, with calculations for CuPc showing metallic bands leading to an infinite dielectric constant [142].

The value of z_0 which gives the distance of the image plane above the metal surface is difficult to judge precisely. It is determined by the bulk electronic density at the Fermi level [141]. For a Pt(111) surface which is expected to have a significantly higher electronic density than the Ag(111) surface a value of 0.85 Å gave results in close agreement with experiments [91]. The value of z_0 has been calculated theoretically for a few different values of electron density by Lang and Kohn [141] giving an expected range of 0.6-0.85 Å for different metals.

An examination of the effect of different values of the input parameters shows some interesting trends. Given in table 5.4 are the expected energy difference of photoelectrons from the “up” and “down” species for a range of different values of the input parameters. It is clear from this table that the position of the image plane has a significant effect, but more dramatic is the change in shift seen for a larger dielectric constant. The reason for this is that the molecule itself fairly effectively screens the hole if it has a large dielectric constant, the consequence of which is that even perfect screening of the hole has little further influence.

Table 5.4: Expected shifts for different parameters of the screening model outlined in section 3.3.1.4.

	ϵ_1 varied				z_0 varied		
ϵ_1	3.4	7	10	15	7	7	7
z_0	0.69	0.69	0.69	0.69	0.85	0.69	0.64
$E_B(U_p) - E_B(Down)$	0.73	0.42	0.31	0.21	0.50	0.42	0.40

Because the core hole is within the molecule the screening would polarise the molecule both in the plane and perpendicular to this. This means that a value of ϵ_1 much greater than 3.4 could be reasonably expected. This analysis shows that dielectric screening is unlikely to be observable for MPc systems due to effective self-screening. It also applies equally to the surface of germanium where the shifts are expected to be even smaller due to the finite dielectric constant of the substrate.

5.4.3 Study of dipole shifts

If the shift observed in the metal core level was the result of a molecular dipole, analogous to the shifts observed by Yamane et al. [85], it would be expected to be mirrored in other energy levels of the molecule. In the work of Yamane this molecular dipole induced shift was observed in the HOMO of the molecule. Hence an analysis of the HOMO peak is used here to demonstrate

that this is not a possible explanation for the observed shift.

Valence band spectra of progressive thickness films of PbPc on the Ge(001) 2×1 surface are presented in fig. 5.12 (a). The spectra of the HOMO region for the same coverages taken with a longer dwell time and with the background of photoelectrons from the Ge subtracted are shown in fig. 5.12 (b). It is clear that a shift analogous to that seen in the Pb core level is not evident in the HOMO peak. Each of the HOMO spectra presented is fit with a single Voigt peak after removal of the Ge valence band photoelectron background. Regardless of coverage the best fit is purely Gaussian, and has a FWHM of 0.6 eV.

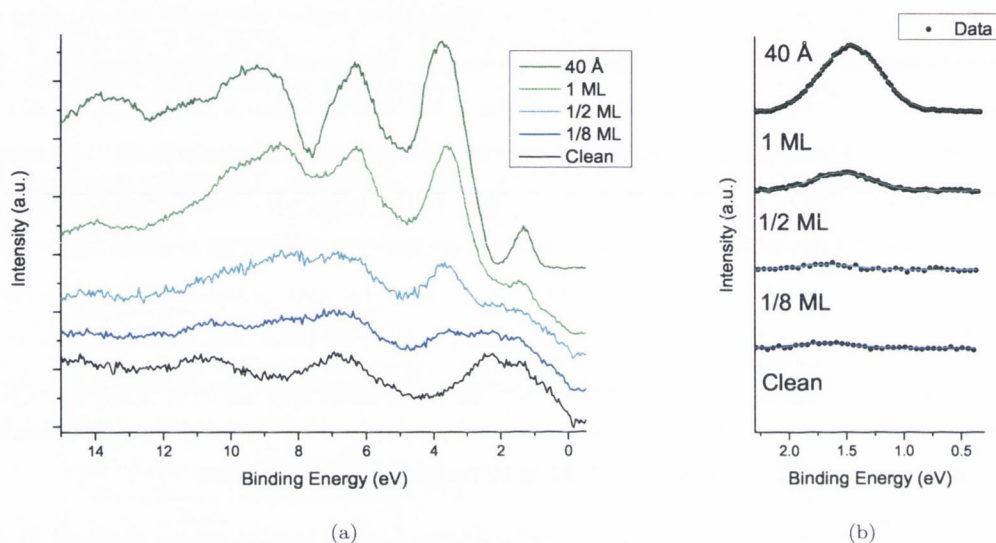


Figure 5.12: (a) Valence band photoelectron spectra of PbPc on Ge(001) for progressive coverages of PbPc and (b) a fitting of the HOMO peak after longer accumulation time and background subtraction. All spectra were taken with a photon energy of 50 eV.

5.4.4 Study of final state charge transfer

This is the most challenging of all effects to determine, either experimentally or computationally. For a large molecule such as this, setting up a system for computational analysis requires in the order of 250 atoms, implying a severe computational load. The most commonly used technique for such systems is DFT. However, it is a ground state theory, which means calculating any excited state spectroscopy has associated problems. There are two commonly used techniques to deal with this: One is a transition state approach in which the system is simulated with half an electron in the core; the other is the use of the $Z + 1$ approximation where the photoexcited atom is replaced with its $Z + 1$ counterpart. In either case the absolute results commonly include significant error, and a similar calculation must be conducted for both the “up” and “down” species.

Moreover, DFT does not take into account any Van der Waals interactions which will likely play a significant role in adsorption. This introduces significant doubt into any calculation

performed. There are semi-empirical techniques that seem promising in relation to these types of systems, but such analysis goes beyond the scope of this current work.

One experimental method which could reveal something about the final state charge transfer is a comparison of PES binding energy with NEXAFS onset energy [88]. Where there is final state charge transfer, the core level can be shifted to lower binding energy than the NEXAFS onset energy. However, this is not necessarily the case. Given that this effect is only observed in the metal core level, the comparison would have to be between the PES and NEXAFS of this atom. Consequently, the experiment would be very difficult due to the small signal available from the absorption of the metal in a single monolayer of MPc.

5.5 HOMO intensity of MPc on Ge(001) and Ge(111)

A comparison of the intensity of the HOMO peak for different MPc shows an interesting trend. In the valence band spectra of fig. 5.12 presented in section 5.4.3 the features of the PbPc molecular valence band grow in prominence with coverage as expected. However, the HOMO region shows a lower intensity in comparison to the other peaks. As a point of reference the intensity of the HOMO is compared to that of the HOMO - 1 peak. A summary of HOMO fit parameters and the relevant intensities is given in table 5.5. The error in the HOMO intensity measured for the eighth ML coverage is large, due to a small signal to background intensity ratio, but the half ML coverage, and more clearly the 1 ML coverage, show that the intensity of the HOMO is less than half that from the bulk signal. Possible angular effects in intensity can be ruled out as the relative intensity of HOMO to HOMO - 1 has almost no angular dependency at either the interface or in the 40 Å film.

Table 5.5: Summary of fitting parameters used in Fig. 5.12 (b) and HOMO - 1 intensities after background subtraction. GW refers to the Gaussian FWHM, LW the Lorentzian FWHM. The intensities are normalised such that the bulk HOMO intensity is 1.

	1/8 ML	1/2 ML	1 ML	40 Å
I_{HOMO}	0.015	0.015	0.050	0.18
I_{HOMO-1}	0.11	0.32	0.7	1
I_{HOMO}/I_{HOMO-1}	0.12	0.05	0.07	0.18
GW_{HOMO}	0.6	0.6	0.6	0.6
LW_{HOMO}	0	0	0	0

In contrast, the planar MgPc on Ge(001) has almost the same intensity ratio between the HOMO and HOMO - 1, as seen in fig. 5.13 with the corresponding fitting and intensity parameters given in table 5.6. This difference between MgPc and PbPc indicates that, although the HOMO peak is not broadened or split as one might expect if the observed shift were the result of a molecular dipole, it is somehow altered by whatever interaction causes the shift. A similar analysis for the planar ZnPc yields I_{HOMO}/I_{HOMO-1} of 0.17 in the bulk compared to 0.13 for the 1 ML coverage and 0.2 for a 1/3 ML coverage. This, like the MgPc indicates no dramatic change in HOMO intensity.

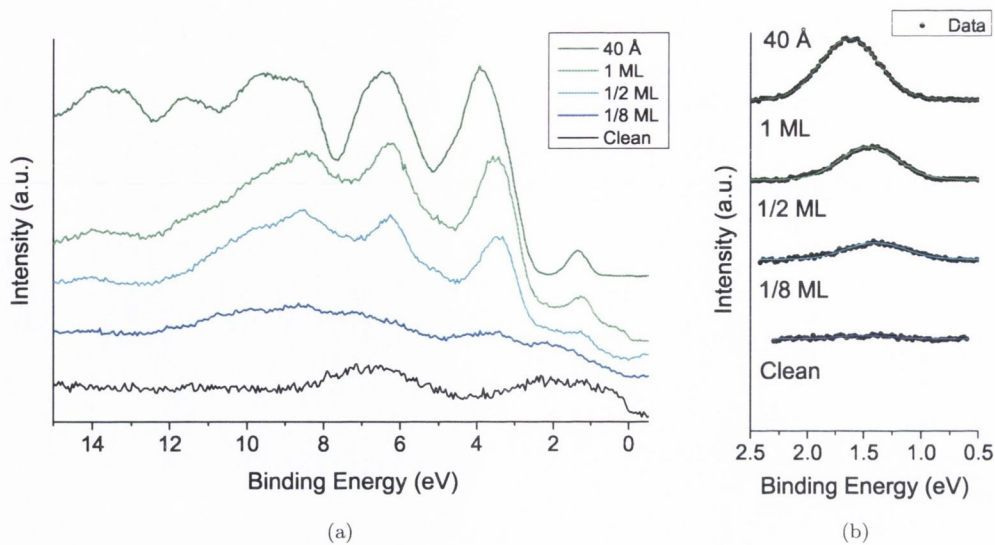


Figure 5.13: (a) Valence band photoelectron spectra of MgPc on Ge(001) for progressive coverages and (b) a fitting of the HOMO peak after longer accumulation time and background subtraction. All spectra were taken with a photon energy of 50-52 eV.

Table 5.6: Summary of fitting parameters used in Fig. 5.13 (b) and HOMO - 1 intensities after background subtraction. GW refers to the Gaussian FWHM, LW the Lorentzian FWHM. The intensities are normalised such that the bulk HOMO intensity is 1.

	1/8 ML	1/2 ML	1 ML	40 Å
I_{HOMO}	0.007	0.033	0.065	0.12
I_{HOMO-1}	0.062	0.31	0.52	1
I_{HOMO}/I_{HOMO-1}	0.11	0.11	0.13	0.12
GW_{HOMO}	0.6	0.6	0.6	0.6
LW_{HOMO}	0	0	0	0

The results for PbPc on Ge(111) are analogous to those of PbPc on Ge(001), i.e. no splitting in the HOMO and a reduction in intensity at the interface, as shown in fig. 5.12. Given in table 5.7 are the fitting parameters used for the HOMO peaks, again with comparison of the intensity relative to the HOMO - 1. In this case the HOMO is suppressed to such a degree that for coverages of less than a complete monolayer it cannot be distinguished from the background signal. For the 1 ML coverage the HOMO is reduced to almost a third of the intensity it has in the bulk. On the assumption that the HOMO suppression is in some way related to the “up/down” effect it is worth noting that the intensity in the core level feature associated with the “down” state is significantly greater for PbPc on Ge(111) compared to Ge(001), in correspondence with the greater degree of HOMO suppression seen on this substrate. This is despite the fact that the interaction seems to be weaker on the terraces which make up the majority of this surface (see section 6.3).

These results all indicate that this HOMO intensity is in some way related to the “up/down” feature observed in the metallic core level. The case for this is further strengthened by an

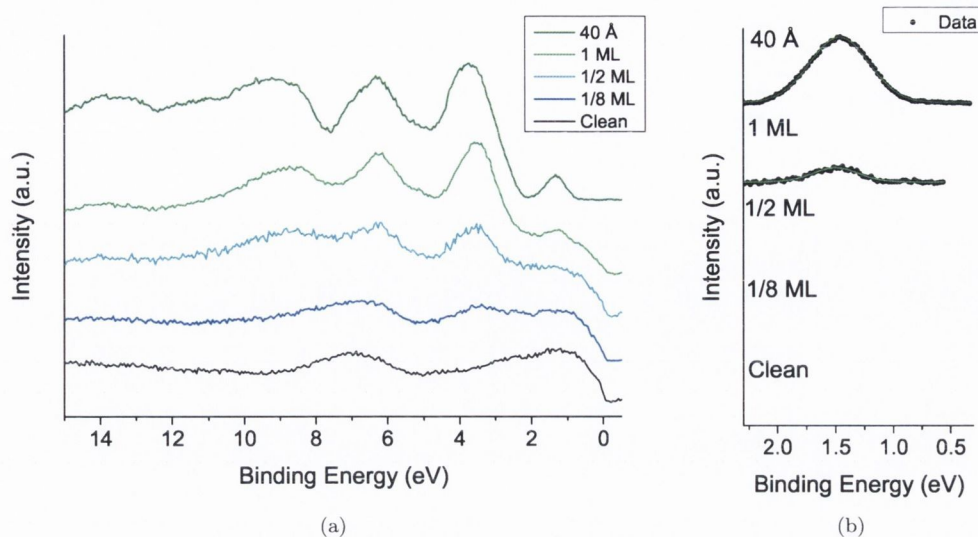


Figure 5.14: (a) Valence band photoelectron spectra of PbPc on Ge(111) for progressive coverages and (b) a fitting of the HOMO peak after longer accumulation time and background subtraction. All spectra were taken with a photon energy of 50 eV. There are no fits for the 1/8 ML and 1/2 ML coverages as no HOMO could be distinguished against the background in these spectra.

Table 5.7: Summary of fitting parameters used in fig. 5.14 (b) and HOMO - 1 intensities after background subtraction. GW refers to the Gaussian FWHM, LW the Lorentzian FWHM. The intensities are normalised such that the bulk HOMO intensity is 1.

	1/8 ML	1/2 ML	1 ML	40 Å
I_{HOMO}			0.004	0.18
I_{HOMO-1}			0.58	1
I_{HOMO}/I_{HOMO-1}			0.067	0.18
GW_{HOMO}			0.45	0.6
LW_{HOMO}			0	0

examination of three slightly different sample preparations: A 1 ML coverage with the sample held at room temperature during deposition (similar to all previous preparations); the same sample annealed for 1 hour at 100°C; a 1 ML coverage of PbPc with the substrate held at 100°C during deposition and cooled immediately afterwards. Fig. 5.15 (a) shows the Pb 5d core level for the three samples with the corresponding HOMO level given in fig. 5.15 (b). A plot of the relation between the relative intensity in the “up” component and the relative intensity in the HOMO is given in fig. 5.16, with the fitting parameters for both sets of spectra are displayed in table 5.8. Again, this link between the “up” intensity and the HOMO intensity is preserved. The decrease in “up” intensity for each respective sample preparation corresponds in each case to an equivalent decrease in the HOMO intensity.

Finally, the same analysis is carried out on the one planar phthalocyanine observed to exhibit a shift in the metal core level at the interface, MgPc on Ge(111). This too shows a similar reduction in relative HOMO intensity at the interface as shown in fig. 5.17, with the

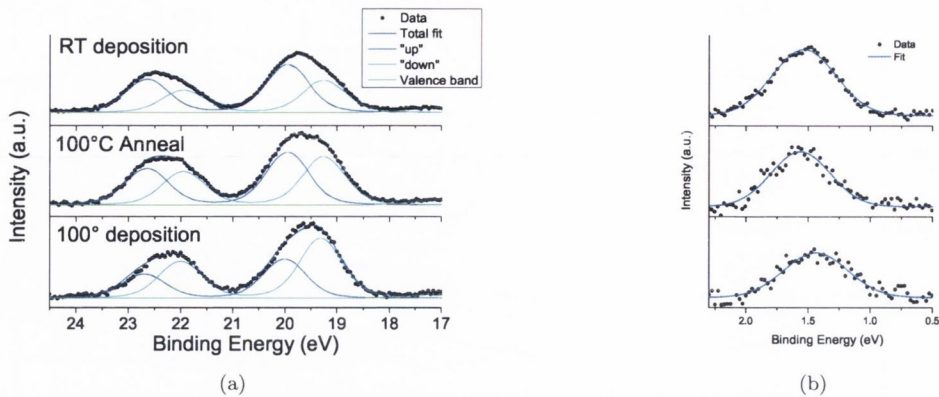


Figure 5.15: PES of (a) Pb 5d and HOMO (b) levels of PbPc on Ge(001). In the top panel are the results of deposition at room temperature, the middle panel the effects of annealing this sample to 100°C and in the bottom panel a separate sample prepared by deposition onto a substrate held at 100°C. All spectra are taken with a photon energy of 50 eV.

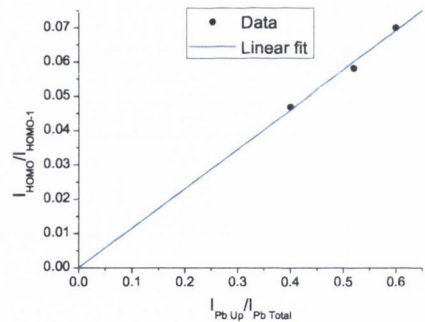


Figure 5.16: Plot of the relative intensity of the HOMO against the intensity in the “Up” component. A linear fit shows the strong correlation between these two features.

Table 5.8: Summary of fitting parameters used in fig. 5.15. Gaussian and Lorentzian components held fixed for each fit, as is the energy shift between the two components.

	Sample preparation		
	RT	100°C Anneal	100°C Deposition
I_{PbUp}	0.60	0.52	0.40
I_{PbDown}	0.40	0.48	0.60
I_{HOMO}/I_{HOMO-1}	0.070	0.058	0.047

summary of fitting parameters given in table 5.9. This result supports the conclusion that the shift is related to a suppression of the HOMO intensity. Moreover, it supports the conclusion that the shift seen in the Mg 2p core level at the interface of MgPc on Ge(111) is of the same origin as those observed for non-planar phthalocyanines.

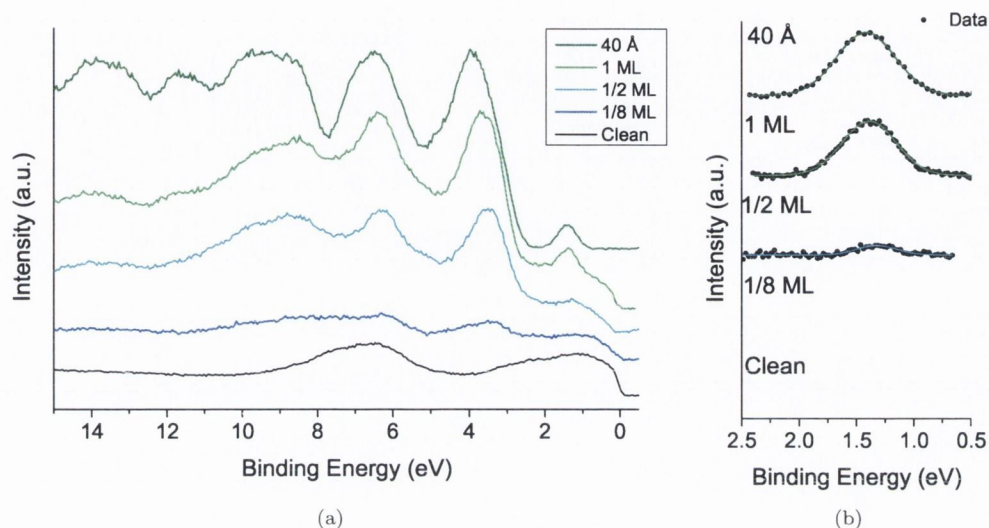


Figure 5.17: (a) Valence band photoelectron spectra of MgPc on Ge(111) for progressive coverages and (b) a fitting of the HOMO peak after longer accumulation time and background subtraction. All spectra were taken with a photon energy of 50 eV. There are no fits for the 1/8 ML ML coverage as no HOMO could be distinguished against the background in this spectrum.

Table 5.9: Summary of fitting parameters used in fig. 5.17 (b) with a comparison to the HOMO - 1 intensities after background subtraction. GW refers to the Gaussian FWHM, LW the Lorentzian FWHM. The intensities are normalised such that the bulk HOMO intensity is 1.

	1/8 ML	1/2 ML	1 ML	40 Å
I_{HOMO}		0.016	0.11	0.13
I_{HOMO-1}		0.48	0.82	1
I_{HOMO}/I_{HOMO-1}		0.040	0.13	0.13
GW_{HOMO}		0.40	0.54	0.59
LW_{HOMO}		0	0	0

The fit width of the HOMO peak in the above analysis is almost identical between bulk and interface spectra for all phthalocyanines on Ge(001), but on Ge(111) it is distinctly narrower at the interface. There are a number of contributors to this linewidth, including inhomogeneity broadening, lifetime broadening, band dispersion and vibrational coupling [143]. The lifetime broadening is expected to be in the order of < 200 meV [87], and can be seen to play a small role in the overall width due to the accuracy of a Gaussian fit. Likewise vibrational coupling effects should be significantly smaller than the observed linewidth [85]. This leaves band dispersion and inhomogeneity broadening as probable causes. Given that this is occurring for less than a single monolayer of material it is unlikely to be the result of band dispersion. In the case of non-

interacting interfaces, where the phthalocyanines form perfectly ordered domains on the order of hundreds of nanometres, HOMO widths as small as 180 meV have been observed for PbPc with similar widths observed for other phthalocyanines [70,85]. Furthermore, the degree of broadening, approximately 0.4-0.6 eV in the bulk, is consistent with studies of inhomogeneity broadening in other organic materials [144,145]. Therefore, this difference in HOMO width is attributed primarily to a greater degree of order in the molecules at the interface of the Ge(111) surface when compared to the Ge(001) surface, consistent with the NEXAFS presented in chapter 4.

5.6 Summary of PES shift in metal core level of MPc

Cabailh, proposed that the two states in the metal core level of non-planar MPc seen at the interface of Ge(001) correspond to molecules where the metal protrudes towards and away from the substrate respectively. However, the mechanism by which this shift occurs was not investigated. The first detail of this chapter was a confirmation of the hypothesis of Cabailh by STM.

Table 5.10: Summary of the shift in metal atom core level observed of the systems presented within this chapter.

		MgPc (Planar)	SnPc (Non-Planar)	PbPc (Non-Planar)
Ge(001)	Shift	No	Yes (0.8 eV)	Yes (0.7 eV)
	HOMO suppression	No	-	Yes
Ge(111)	Shift	Yes (0.6 eV)	-	Yes (0.65 eV)
	HOMO suppression	Yes	-	Yes
Si(001)	Shift	-	-	Yes $\approx$ 0.7
	HOMO suppression	-	-	-
Ag(111)	Shift	-	No	-
	HOMO suppression	-	-	-

After this, it was shown that the observed shift was not such an anomaly as an investigation of the literature would perhaps have suggested. An analogous shift occurred on Si(001) (a different material), Ge(111) (a different reconstruction) and for MgPc on Ge(111) (a planar phthalocyanine). A summary of these results is given in table 5.10. These results, and the fact that such a shift has not been previously observed is a sign of the difficulty of such experiments, which require great care in sample preparation and data collection. Furthermore, the result from MgPc on Ge(111), in which the interface state is at lower binding energy than the bulk like state, strengthens the conclusion that the shift for the non-planar MPc is also to lower binding energy.

The possible causes of the shift are broken down into four categories as explained at the start of this chapter. Each mechanism implies a shift to lower binding energy of the metal atom. The four mechanisms of shift were then investigated in turn. Both polarisation in the initial state and the final state were ruled out as possible mechanisms. The charge transfer mechanisms

are more difficult to distinguish experimentally. The observation of substrate core levels was demonstrated not to be of any benefit for the purposes of an initial state charge transfer. There is the possibility that a NEXAFS experiment of the inner metal atom may provide some clues as to whether a final state screening effect could be involved. However, these are non-trivial experiments that require a beamline expressly designed for NEXAFS. Even then, it is not certain to yield a significant answer.

Finally, a close analysis of the intensity of the HOMO peak was provided. This shows a significantly decreased intensity for those phthalocyanines which exhibit a shifted state in the metal core level. Again, the interpretation of this leads to significant difficulties, but the trend at least was shown to be true in a number of different cases, and without exception for the MPc investigated. Included in table 5.10 is a summary showing for which systems this was observed. Despite the uncertainty as to why such a suppression would occur, it points towards significant initial state differences between the systems where a shift is observed and those where it is not.

If the shift were the result of a purely final state charge transfer then the HOMO should be unaffected. Therefore, it seems likely that the shift under discussion in this chapter is related to initial state charge transfer. However, it is very difficult to rule out the possibility that significant final state charge transfer also occurs.

Chapter 6

Adsorption of Phthalocyanine on Germanium Surfaces

The interaction of large molecules with inorganic semiconductor surfaces ranges from weak Van der Waals bonding to reactive changes in both surface and molecule. Understanding the interactions, and potentially how the molecules are modified upon adsorption is a difficult problem. For Ge, some useful analogies can be made between the chemistry on its surfaces and well established organic chemistry because, like carbon, it is a group IV element [99, 100]. However, care has to be taken with any of these analogies since, although many of the reaction paths have the same trends for the various group IV materials, the bond energies of the final stage and the intermediate stage can vary significantly, making certain reactions either more or less favourable [100].

To investigate adsorption three techniques are used in comparison with each other on three different surfaces of germanium. The three variants of the Ge surface of interest are the Ge(001)- 2×1 surface, the monohydride form of this surface and the Ge(111)-c(2×8) surface. The techniques used are STM, PES and NEXAFS. The STM is used to obtain an idea of the location of the molecules with respect to the substrate, with NEXAFS used as a corollary technique for supporting information about the molecular orientation. This is followed by a discussion of the differences between bulk-like and interface PES, comparing the different substrates, and focusing on the PES from the nitrogen and carbon which make up the macromolecule common to all MPc.

6.1 Adsorption of MPc on Ge(001)

The discussion of the adsorption of MPc on Ge(001) is in two parts. First, data from very low coverages is presented in which isolated molecules are observed on the surface, giving information about the specific adsorption sites. Secondly, there is an analysis of short range ordering which occurs for coverages approaching 1 ML.

6.1.1 Adsorption sites of MPc on Ge(001)

The site at which a molecule bonds to the surface, and even the very presence of specific sites, provides great insight into the bonding which is occurring. By utilising STM, the location of individual molecules relative to the surface reconstruction can be estimated. Moreover, the effect that molecular adsorption has on this reconstruction is also observable. STM of phthalocyanines on the Si(001) surface shows three distinct sites [57]. On the Ge(001) surface a qualitatively similar result is obtained here. Fig. 6.1 (a) shows an area of Ge(001)-2×1 surface after deposition of a fraction of a monolayer of MgPc and fig. 6.1 (b) shows a similar image after deposition of PbPc. In both these images three different repeated patterns occur, which are labelled 1, 2 and 3 in the images. In the case of PbPc shown in fig. 6.1 (b) there are two different possibilities for bonding site 1, labelled 1a and 1b in the image. These relate to two possible orientations of the molecules, as discussed in section 5.1.

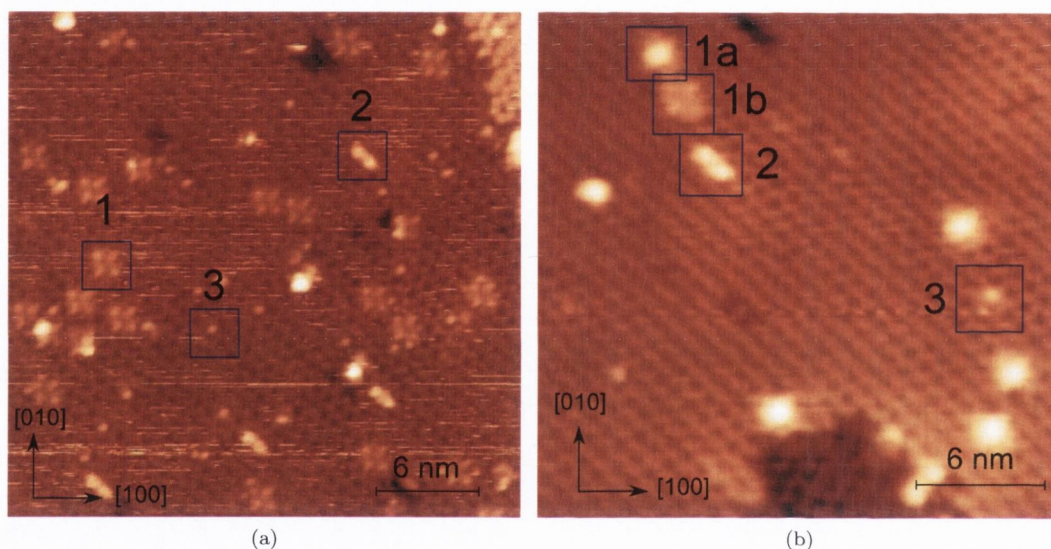


Figure 6.1: STM images of a sub-monolayer coverage of (a) MgPc and (b) PbPc deposited on Ge (001), taken with a sample bias voltage of -1.5 V and current of 0.16 nA.

Those areas marked as 1 are clearly resolved as molecules across two dimer rows, with the four lobes of the benzene rings clearly visible. These make up the vast majority species for both MgPc and PbPc. Those species labelled 2 appear along a dimer row. Finally species 3 appear as a single bright germanium dimer atom, similar to the behaviour observed where a single hydrogen is adsorbed onto the partner Ge atom in the dimer [146]. Also worth noting is the streaking in fig. 6.1, which is indicative of loosely bound molecules. Achieving a stable tip for imaging was a problem for all samples, indicating that there is a significant amount of material on the surface which is able to be picked up by the tip and moved across the surface. This further complicates the image analysis as the changes in tunnelling current for different images is dependent not only on the bias conditions, but also on changes in the tip.

Although species 1 is the majority species, the ratio of species 1 to 2 seems to be preparation

dependent. Three separate sub-monolayer coverages prepared were successfully imaged, two of MgPc and one of PbPc. In the case of PbPc approximately 2% of the molecules clearly imaged were of type 2. For MgPc, one sample yielded a similarly low proportion of species 2, while in the other only species 2 could be clearly imaged, with poorly resolved features of area similar to species 1, presumably arising from the same sites as species 1. The proportion of species 2 in this sample appeared similar to that of the poorly resolved “species 1”, despite the fact that nominally the same preparation was employed. Due to the poor quality of images for this preparation, it is possible these results are not indicative of any genuine difference, but are pointed out as a detail to clarify in future work.

6.1.1.1 Analysis of species 1

For species 1, STM under different bias conditions provides much information as to the bonding location of the molecule on the Ge(001) surface. The only significant distinction in STM between species 1a and 1b is the high intensity of the centre point of species 1a as discussed in section 5.1: In this section species 1b is taken as representative of the molecule as a whole. Likewise, MgPc is equivalent to PbPc for all results obtained under equivalent conditions. On this basis results from PbPc species 1b are presented as representative of both molecules. However, MgPc was never successfully imaged under conditions equivalent to the high bias, empty states image of fig. 6.2 (b). As such, although it is possible that such an image *could* be obtained, discussion related to this cannot be extended to the case of MgPc on Ge(001).

It is clear under all bias conditions that molecules of this bonding type straddle two dimer rows. However, the observed image is dramatically different under different bias conditions, giving an indication of the position of the molecule and the effect on the substrate atoms. The filled states image for a high bias voltage, presented in fig. 6.2 (a) shows four bright spots for each molecule, which relate to the four benzene rings at the outside of the macromolecule. The empty states image, on the other hand, shows only two bright spots, as shown in fig. 6.2 (b). The spacing between these spots is approximately 13 Å, in close agreement with the distance between the outermost carbons of two opposite benzene rings, and poorly matching with any substrate atoms. Therefore these are attributed to the LUMO density of states being located on only two opposite lobes of the molecule, as predicted by DFT for PbPc [136]. By contrast, as fig. 6.2 (c) shows, the low bias image of the filled states of this species has regions of high intensity which correspond well with the up dimers of the $c(4\times 2)$ pattern of the Ge surface, resolved in the region around the molecule. It is reasonable that the density of states of the molecule itself be low for low bias voltages, as this could be in the band gap of the molecule. Therefore, this image is interpreted as primarily imaging a modified density of states of the surface dimers.

The clean Ge(001) surface typically exhibits a mixture of 2×1 and $c(4\times 2)$ reconstructions. However, in all cases the surface exhibited the $c(4\times 2)$ reconstruction in the region around the species 1 molecule. This indicates that the bonding of the molecule to the surface locks the

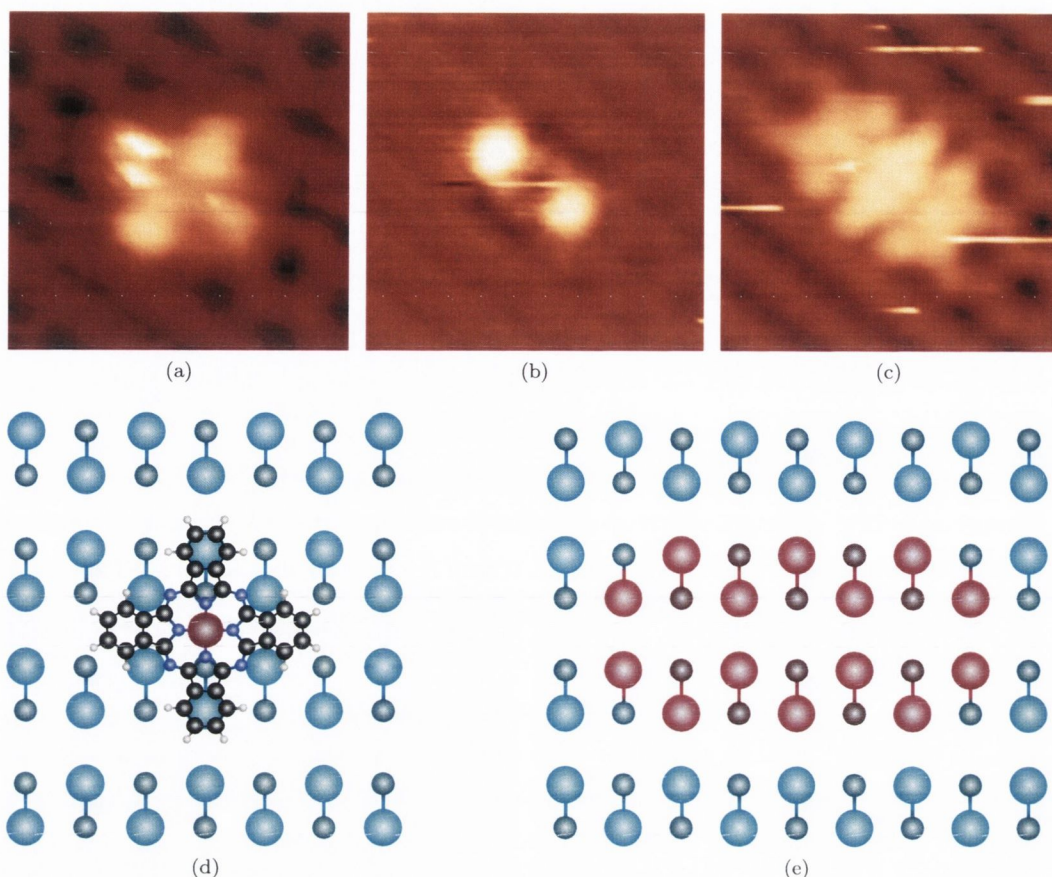


Figure 6.2: STM of species 1 of PbPc on Ge(001). (a) A filled state image, taken with 0.1 nA, -1.8 V bias. (b) An empty state image taken with 0.035 nA, +1.4 V bias. (c) A filled state image taken with 0.035 nA, -1 V bias. (d) A model of the bonding location of species 1 of MPc on Ge(001). (e) A schematic of the Ge surface atoms over which increased intensity is observed in (c).

dimers in a particular tilt direction as is often seen around defect sites [11].

Based on the symmetry and geometry of the molecule and the dimers in the region around the molecule, observed by STM under various bias conditions, a model for the bonding location of species 1 is given in fig. 6.2 (d). A schematic of which substrate atoms correspond to the high intensity areas in the low bias empty states image of fig. 6.2 (c) is given in fig. 6.2 (e). A comparison of the model with the schematic of high intensity Ge dimers seen at low bias conditions given in fig. 6.2 (e) shows that these bright atoms extend well beyond the dimensions of the molecule itself. This indicates that adsorption of the molecule has an influence on dimers beyond the adsorption site. A similar effect is predicted from DFT calculations of NH_3 bonding to the surface of Si(001), where the charge is determined to be delocalised along the dimer rows, but not across adjacent dimer rows [147].

6.1.1.2 Analysis of species 2

Species 2 is imaged identically for both PbPc and MgPc. The images of filled and empty states are distinctly different as shown in fig. 6.3 (a) and (e); these images are always symmetric about one central Ge dimer. A profile along the dimer row for both images is shown in fig. 6.3 (b) and (f) respectively. The two peaks of the empty state image are spaced 8 Å apart, in good agreement with twice the spacing between Ge dimers. Consequently, this is most likely an enhancement of the dimers as opposed to empty states of the molecule itself, as depicted in fig. 6.3 (g). The filled state image again matches in dimension with the Ge dimers, but in this case there is little height variation along the length. Instead, it matches the dimensions of five adjacent dimers, as depicted in fig. 6.3 (c).

Under no bias conditions in which this species was clearly imaged were the expected four lobes of the phthalocyanine visible. This could suggest that these molecules are standing up, with the benzene rings perpendicular to the surface as depicted in fig. 6.3 (d). However, three facts contradict this idea. First of all the height of these is never imaged as greater than 2 Å, less than the height of a flat-lying molecule, although this could potentially be an electronic effect. The second point of contradiction is the NEXAFS presented in section 4.2 which shows no azimuthal dependence, whereas if these were upright molecules they would be expected to generate an azimuthal dependence in that spectroscopy. The alternative explanation, depicted in fig. 6.3 (h), is of a flat lying molecule in which the molecule is not clearly imaged. In this case the observed intensity would likely result from an increased density of states on the substrate dimers.

6.1.1.3 Analysis of species 3

The only change observed under different bias conditions for this species is a change from low to high intensity. It is likely that species 3 relates to contamination adsorbed during evaporation or perhaps hydrogen from the molecule reacting with the surface upon deposition. However, it is also possible that it relates to molecules that for some reason are not able to be imaged. Due to the fact that the STM only ever images this species as a single bright spot, and there is no other available corroborating information, it is not discussed further.

6.1.2 Short range order in a monolayer of MPc on Ge(001)

STM also gives some indication as to the ordering of the molecules as the coverage approaches 1 ML. Attempts to conduct LEED on ML films of MPc show no pattern other than faint 1×1 spots from the substrate, indicating no long range ordering. However, the STM shows that over small distances the molecules are ordered with respect to each other and the surface, as shown in the 30×30 nm area scan given in fig. 6.4 (a). The largest domains observed are approximately ten molecules in length, with typical domains being merely two or five molecules. Although small domains form, these domains are often simply chains of molecules. There are

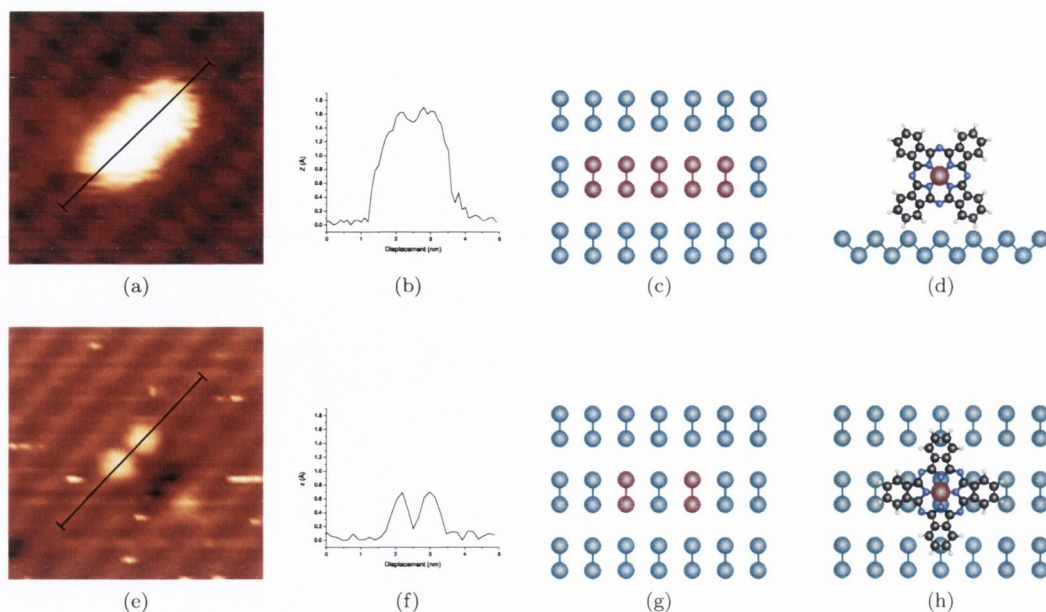


Figure 6.3: (a) Filled state STM image, with 6×6 nm scan size, taken with -1.8 V, 0.05 nA bias conditions, together with (b) the profile from the molecule along the dimer row direction and (c) a schematic of where the high intensity occurs relative to the surface dimers. (e) Shows an empty state STM image, with 6×6 nm scan size, taken with $+1.2$ V, 0.05 nA bias conditions, also with (f) a profile from the molecule along the dimer row direction and (g) a schematic of the dimers in the area of the high intensity. Two possible models are given for the interpretation of these images: (d) an upright phthalocyanine and (h) a flat-lying phthalocyanine.

three inequivalent chain types which form on the surface labelled A, B and C in fig. 6.4 (a). In the case of chain type A and C the two lines marked on the figure represent equivalent chain formations. All the molecules involved in chains seem to be of species 1, that is, they straddle two dimer rows as discussed in the previous section. A minority of molecule type 2 is also present, an example of which is shown in the circle of fig. 6.4 (a).

The presence of only small domains is not surprising given the apparent lack of mobility of molecules over the surface. It is clear from the previous section that isolated molecules remain fixed at specific sites; under of further deposition the sites of these molecules would not be expected to change. Therefore, where the domains generated around individual molecules meet, unless the registry of the original molecules was such that the domains could continue, there will necessarily be a break in the pattern of molecules on the surface.

The measured repeat distances of all the chains can be reproduced by a simple translation of species 1. As demonstrated in section 6.1.1.1, this species has two characteristics: First, it straddles two dimer rows as observed in fig. 6.4 (a) and second, it has a unique registry with the $c(4 \times 2)$ reconstruction of the underlying substrate. Consequently, this suggests that the substrate in general is now $c(4 \times 2)$.

The model for the three chain types can be seen in fig. 6.4 (b). From this model it is clear that chains B and C are both part of a single domain type, but in both cases independent examples of the chain by itself can also be seen. A fourth chain type is observed within the

domains resulting from chain type A, labelled D in fig. 6.4 (b). However, unlike chains B and C this is not observed independently of the domains except as pairs of molecules.

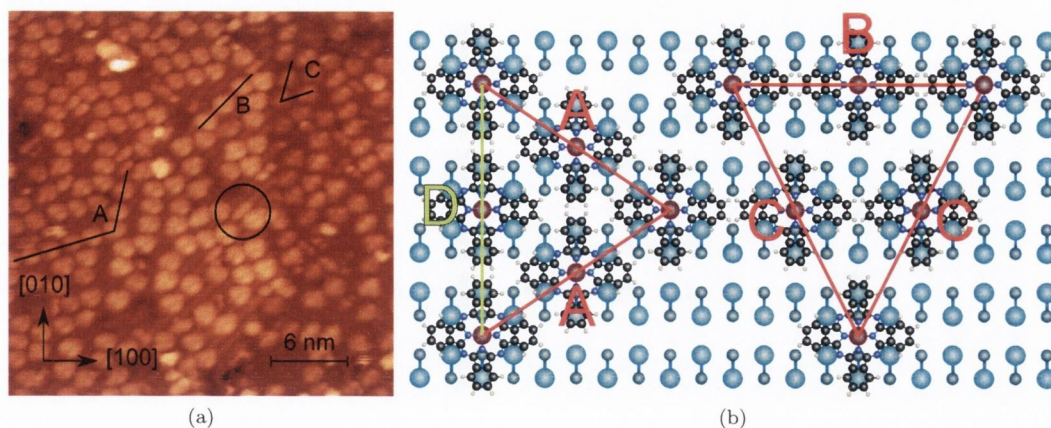


Figure 6.4: STM of approximately 0.8 ML MgPc on Ge(001). (a) A 30×30 nm empty states STM image taken at +1.5 V, 0.1 nA. There are three distinct types of molecular chains formed labelled A, B and C. The two lines for chain types A and C are equivalent. (b) A model of each of these different chain types, together with a proposed type D chain which is not observed independent of chain A.

The observed chain *lengths* follow the general trend $A > B > C$. There are two possible contributing factors to the preference of one chain type over the others. The first is the intermolecular interaction between adjacent molecules. On many weakly interacting substrates where the molecules self-order, similar arrangements to chain type A are observed [48–50]. The second possible contributing factor is the influence of adsorption on nearby substrate atoms. The low bias STM in fig. 6.2 (c) suggests that adsorption affects nearby Ge dimers within the straddled rows. An enhanced adsorption on these sites would favour type B chain formation. Given the prevalence of the close packed chain of type A, the intermolecular interaction seems to be the dominant influence in chain formation.

6.2 Long range ordering of MPc on Ge(001):H

STM was conducted in an attempt to better understand the bonding of MPc to the hydrogen passivated Ge(001) surface. After passivation of the surface the dimers are still intact, but are now symmetric as appears to be the case in fig. 6.5 (a). There is a significant number of defects which show up as bright spots in the STM. Where only one of the Ge atoms in a dimer is bonded to hydrogen the other appears as a bright spot due to an accumulation of charge on the other [146,148]. Some scans under high bias conditions exhibit a large number of these defects in the scan direction as shown in fig. 6.5 (b), indicating they may be generated by the tip, and are most likely the result of depassivated dimers. It is likely that most of the observed defects are the result of incomplete passivation; however, it is also possible they are due to a degree of contamination.

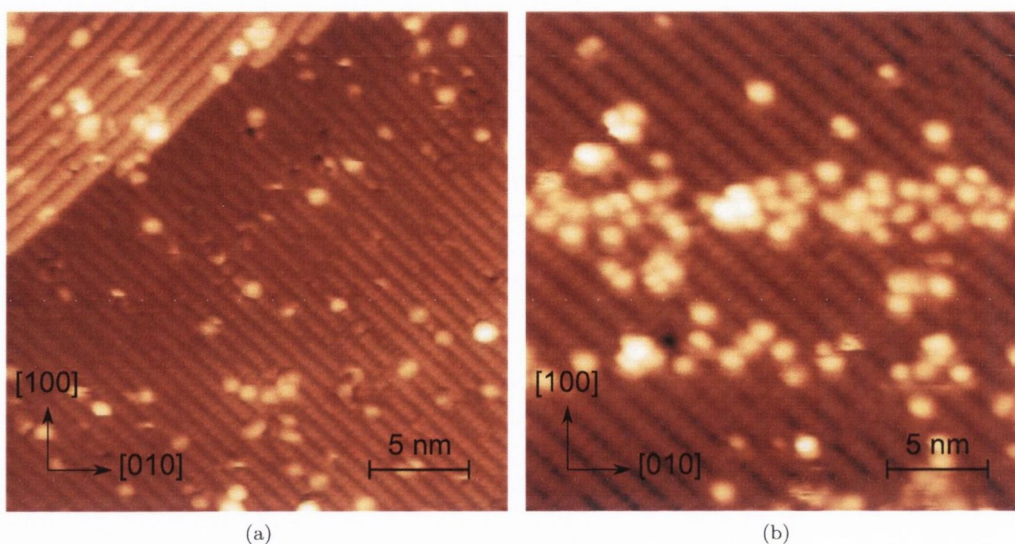


Figure 6.5: STM of the H passivated Ge(001)-2 $\times$ 1 surface. (a) Filled state STM image of surface under bias conditions of -2 V, 1 nA. (b) Two stripes of defects generated by scanning on this same surface under higher bias conditions (-2.5 V, 2 nA).

Progressive amounts of PbPc were deposited onto the passivated surface. For very low coverages imaging of the surface was impossible. This is most likely the result of high mobility of molecules over the surface for these low coverages. With an approximate deposition of the equivalent of a ML islands of phthalocyanine became visible, although in areas where the Ge(001)-2 $\times$ 1:H surface still appeared the resolution was very poor as shown in fig. 6.6, again an indication of mobile molecules remaining on these Ge terraces. The islands have straight sides and very uniform height, resulting from a high degree of order in the phthalocyanine in these islands.

Marked on the image in red are the two edges which make up the primary axes of one domain generated by the molecule. The angle between these two edges is 91°, which on consideration of the error involved as a result of drift gives an approximately square edge for these islands. There are also clearly two different rotational domains of this molecular layer, as indicated by the yellow markers of fig. 6.6 (a). The black circle in this figure highlights a section of the second layer, which clearly has domain boundary edges parallel to those of the first layer. Interestingly, the main island in the centre of the image has a length of over 100 nm with no steps, despite the fact that between the two ends of the island at least four atomic steps in the *substrate* can be detected.

The profile shown in fig. 6.6 (b) shows that the first step of the main island is approximately 16 Å from the Ge substrate, slightly greater than the ≈ 12.5 Å width of the molecules themselves. The second step is half this size, at 8 Å from the first. This seems to indicate that the molecules are not flat to the surface. However, the second step height of 8 Å is significantly less than the expected height for upright molecules indicating they are probably tilted with respect to the substrate.

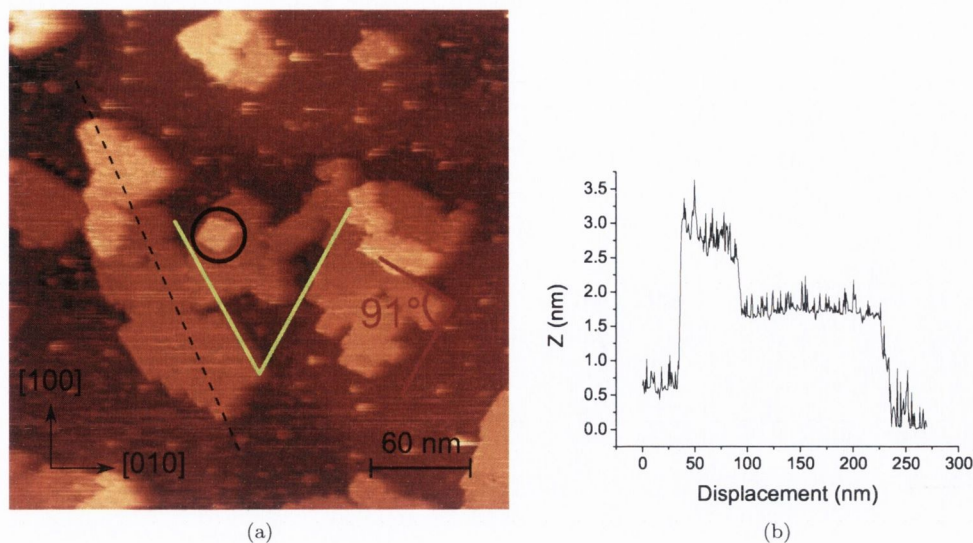


Figure 6.6: (a) A 300×300 nm STM image of PbPc deposited onto the H passivated Ge(001)- 2×1 surface, taken with -2.0 V, 0.1 nA bias conditions. (b) A profile along the dotted line on the left of the image.

To get a further idea of the arrangement of the molecules, a smaller area scan is provided in fig. 6.7. It is clear that there is a high degree of ordering within the islands of PbPc. The surface consists of repeating units of a diamond shaped pattern as marked in the figure. Profiles along the dotted lines are given in fig. 6.7 (b) and (c), showing the length and width respectively of one of these diamond shaped units. The height of each of the four peaks is almost identical. This shows that these units are not single tilted molecules.

Also seen in this figure is the boundary between two domains of the PbPc overlayer. The angle between the different domains is determined from this image to be 50° . However due to the difficult and unstable nature of the imaging of this surface, it was not possible to totally eliminate drift. An image of the same area was taken with the scan direction 90° to this, of the same area (not shown), which gave an angle between the two domains of 54° , indicating the real angle is $52^\circ \pm 2^\circ$. The boundary is quite abrupt with little disturbance of the reconstruction on either side. In the dotted circle a half unit cell of the molecular reconstruction can be seen. This leads to the conclusion that the unit cell relates to pairs of molecules.

This conclusion is supported by an examination of defects. The STM image shown in fig. 6.8 (a) contains a number of defect sites, two vacancy types in circles and misalignment in the square. The solid circle in the centre of the image is of a single missing pair of bright spots, confirming that the observed diamond shape must consist of two molecules. The vacancies in the upper left of the image show a pair of missing molecules. This pair consists of adjacent dimers for which the bright spots are further away, indicating the molecules are more tightly bound in this direction, rather than the four nearest neighbour bright spots which form the diamond shape to which the eye is drawn, as shown in fig. 6.7 (a). As further confirmation of this, it can be seen in fig. 6.8 (b) that the terraces end with a single bright pair. A model

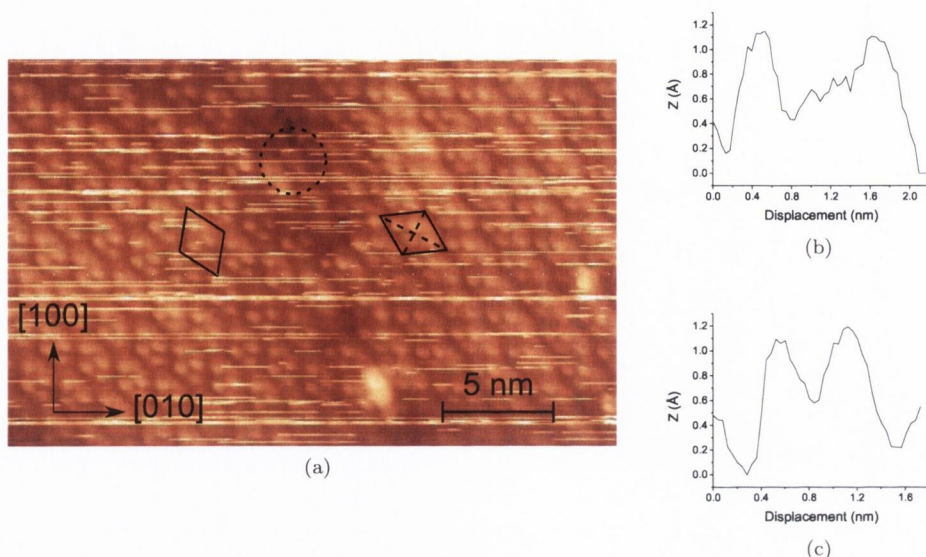


Figure 6.7: (a) A 20×12.7 nm STM image of PbPc deposited onto the H passivated Ge(001)- 2×1 surface, taken with -2.0 V, 0.1 nA bias conditions. The diamond indicates a unit cell of the surface structure and the circle indicates a single pair of bright spots (half a unit cell). Profiles along (b) the length and (c) the width of one unit cell of the surface as indicated by the dotted lines in the image.

of the dimer pairs is given in fig. 6.8 (c), which is consistent with a triclinic crystal structure in which the stacking axis is parallel to the substrate. The defect highlighted in the square is then consistent with one molecule inverted from its correct orientation, essentially taking the monoclinic crystal structure for a single molecule as shown in fig. 6.8 (d).

Finally, for this interface, the growth modes are discussed. Fig. 6.9 (a) shows a series of steps, with a profile across these steps presented in fig. 6.9(b). The lowest terrace in this image is the first layer of molecules clearly imaged, a step of ≈ 16 Å above the Ge surface. The next three proceeding terraces are shown here to have a uniform height of almost 8 Å. This image, similarly observed at other parts of the surface, was taken from a surface in which significant areas of bare Ge(001)- 2×1 :H remains, clearly indicating an island growth mode for this system.

In some images a step, again of just less than 8 Å in height, can be seen leading up to the lowest observable terraces of PbPc. However, if this is a terrace it is always very narrow. An example of this is given in fig. 6.9 (c) with the corresponding profile given in panel (d). This seems to indicate that the 16 Å high islands are in fact bi-layers of phthalocyanine. Due to the ease with which the molecules are picked up by the tip, eliminating double-tip effects, in which a single step is imaged at two points on the tip, is difficult. It is reasonable to assume that double tip effects have been eliminated here for two reasons: the first is the regularity with which the step is observed to be exactly half the height of the island, even for different terrace edge direction and tip preparation; the second is the lack of repeated features from the upper terrace edge in the lower edge. Despite this, a terrace of a single layer of this phthalocyanine

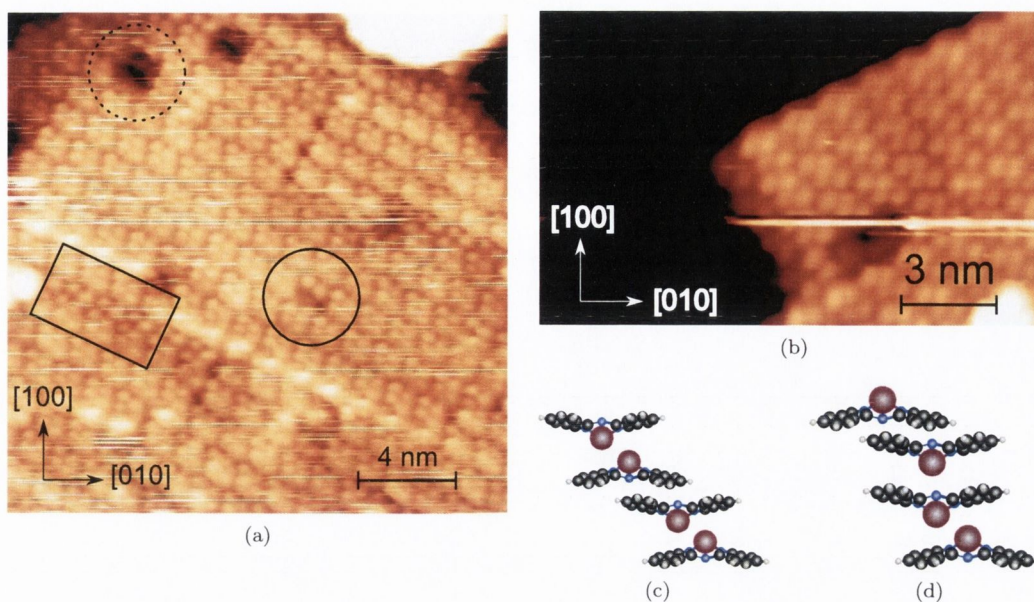


Figure 6.8: (a) A 20×20 nm STM of a terrace of PbPc deposited onto the H passivated Ge(001)- 2×1 surface with three defect types as indicated. The circles indicate a vacancy, and the square denotes a row of monoclinic molecules in the triclinic lattice. The image was taken with bias conditions of -2.0 V, 0.1 nA. (b) An image of a step edge terminated by inward facing PbPc molecule. Models of (c) the terrace construction and (d) the monoclinic defect are given in the bottom right panels.

was never observed.

The conclusion that this first layer comprises a bilayer of the $8 \text{ \AA}$ steps observed individually beyond the first layer is supported by the NEXAFS. The NEXAFS of a deposit of $\approx 1 \times 10^{14}$ molecules/cm², equivalent to 2-3 ML of flat lying phthalocyanine, as shown in fig. 6.10 (a) and (b), yields a tilt angle of 43° . If the first layer was completely upright the tilt would be expected to be closer to 90° . Therefore it is reasonable to conclude that the molecules are tilted at an angle of approximately 45° to the substrate, in agreement with the bulk monoclinic crystal structure.

For a film of approximately $60 \text{ \AA}$ thickness the observed tilt from the NEXAFS changes to approximately 32° as shown in fig. 6.10 (c) and (d). This decrease in angle is inconsistent with the triclinic growth that is observed at the interface and could be the result of a mixed monoclinic/triclinic crystal.

Flat lying molecules on the PbPc terraces as seen in fig. 6.11 could be the seed for such growth. These flat-lying molecules are potentially the precursors to a monoclinic stack in which the c-axis is perpendicular to the substrate.

Finally, no diffraction pattern was observed in LEED from any of these films. This could be a result of the island growth mode which prevented the formation of uniform regions large enough for the diffraction to be clearly observable. Alternatively, it could simply be a result of the high sensitivity of these materials to damage from the electron beam.

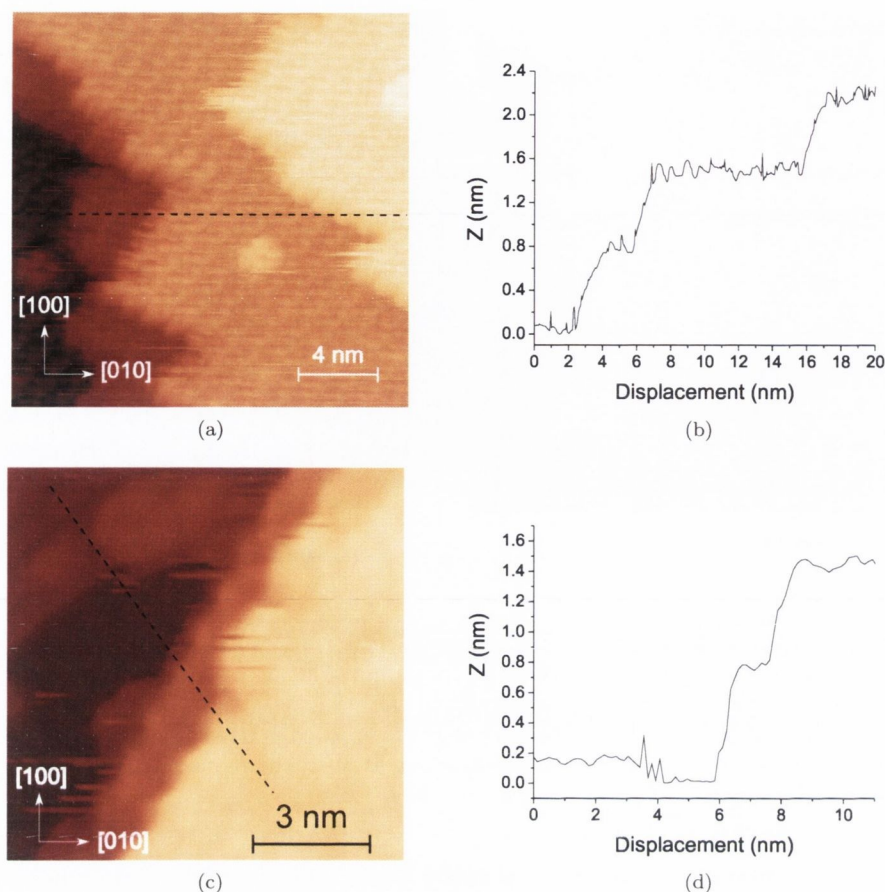


Figure 6.9: (a) A 20 × 20 nm STM image of a series of steps of PbPc deposited onto the Ge(001)-2×1:H surface with (b) a profile along the indicated line. (c) A 10×10 nm STM image with the substrate in the upper left half of the image and the first (16 Å high) terrace in the lower right half, linked by an 8 Å high step. (d) A profile along the dotted line shown in (c).

6.3 Adsorption sites of MPc on Ge(111)

Fig. 6.12 (a) shows a filled state image of steps on the Ge(111) surface with a sub-monolayer coverage of PbPc. The lateral resolution of the molecules is very poor, as was reported for MPc on Si(111) [96]. However, it is still clear that molecules cluster along the step edges, as well as the terrace site marked A. This was not evident on the Si(111) surface. Fig. 6.12 (b) shows a filled state STM image of a terrace containing three different rotational domains of the $c(2\times 8)$ reconstruction (labelled B, C and D). In this case it is at the boundaries between the domains that the molecules are preferentially adsorbed, while the areas where the reconstruction is undisturbed display no adsorbed molecules. It should be noted that the point marked A in fig. 6.12 (a), where a cluster of molecules appears, is the intersection of different rotational domains of the reconstruction, and is not an accumulation of PbPc on a $c(2\times 8)$ terrace. These results provide an interesting contrast with the STM of MPc on Ge(001)-2×1, where the molecules were seen to adsorb at distinct sites across the dimer reconstructed terraces of the surface, as discussed in section 6.1.1.

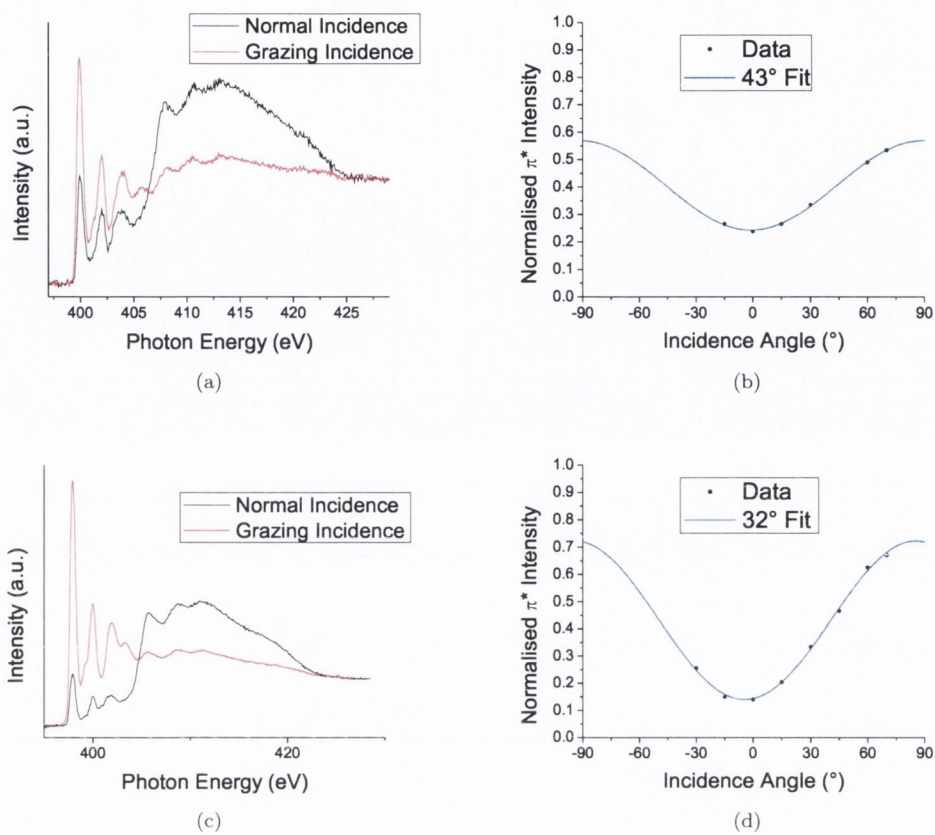


Figure 6.10: Angular dependent NEXAFS of PbPc on Ge(001)-2 $\times$ 1:H. The upper two panels show the results for a nominal 9 Å film and the lower two show the results for a nominal 60 Å film. (a) and (c) are example spectra of the most extreme angles measured for and (b) and (d) show the normalised intensity of the leading π^* feature as a function of angle.

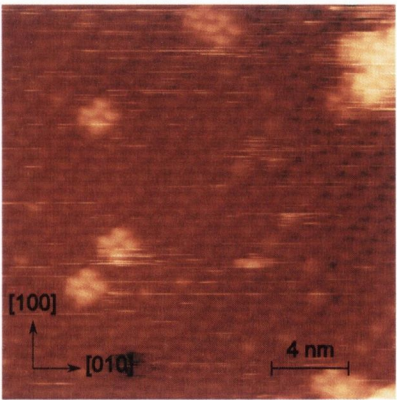


Figure 6.11: A 20 $\times$ 20 nm STM image taken with -2.0 V, 0.1 nA bias conditions of a terrace of PbPc on a Ge(001)-2 $\times$ 1:H surface. Flat-lying phthalocyanine molecules can be seen individually and paired on the terrace.

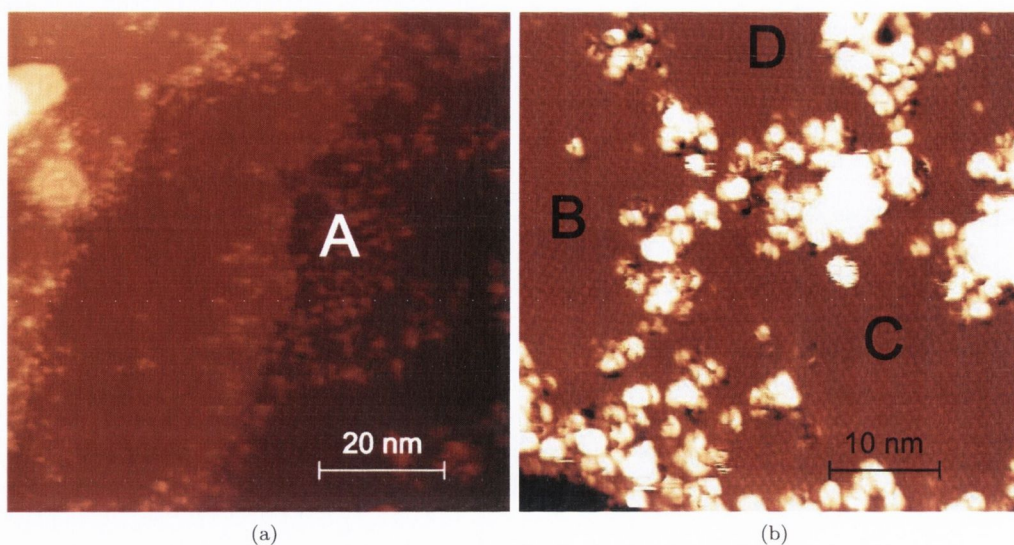


Figure 6.12: Filled state STM images of a sub-monolayer coverage of PbPc on Ge(111): (a) An 80×80 nm image of steps on the surface; (b) a 45×45 nm image of a terrace with three different rotational domains (labelled B, C and D) of the $c(2 \times 8)$ reconstruction.

The possibility that these molecules induce the disruptions in the reconstruction at the sites where they bond, rather than bonding at pre-existing defects should be considered. There are two arguments indicating this is not the case. First, the distribution of molecules as seen in fig. 6.12 is not random, indicating that at least at first the molecules are only weakly bound with significant mobility of the over the $c(2 \times 8)$ domains. Second, an analysis of terrace and domain sizes indicates there is no change between before and after deposition.

These results indicate significant mobility of molecules across the $c(2 \times 8)$ reconstruction, and a marked increase in interaction wherever this reconstruction is disturbed. Moreover, these defects in the reconstruction are reactive enough to strip the metal from non-planar phthalocaynines, as shown in section 5.3.1, while no such reaction is ever observed on Ge(001). Despite this greater reactivity where the adatom reconstruction is broken, the greater mobility of the molecules across the terraces, demonstrates the more passivating effect of the $c(2 \times 8)$ reconstruction when compared with the 2×1 reconstruction of the Ge(001) surface.

Under no bias conditions could a regular arrangement be determined for coverages near to or greater than 1 ML. Furthermore, the individual molecules were never clearly imaged on this surface. This is interesting given the higher degree of order of films of MPc on this surface compared to the Ge(001)- 2×1 surface, as shown by the NEXAFS presented in section 4.4.2. This is probably primarily the result of the weak interaction of the molecules with the substrate, which allows them to be picked up more easily by the STM tip, making any imaging almost impossible at room temperature. However, in most cases where the surface is weakly interacting the inter-molecular interaction allows the molecules to form well ordered islands which are then stable under STM imaging [50, 149]. It may be possible to image molecules on terraces at temperatures well below room temperature, gaining further insight into the adsorption.

However, this facility was not available during the course of this work.

6.4 Photoelectron spectroscopy of the macromolecule on different substrates

The ring structure of the phthalocyanine, also known as the macromolecule, is an ion of -2 charge in which ions of +2 charge can be bonded. PES of this macromolecule can be used to reveal information about the interaction of the molecules with the surface. Each of the surfaces of germanium discussed above displays a significantly different behaviour with respect to adsorption of the molecules. This section now discusses how these differences are reflected in the chemical and electronic changes of the macromolecule.

There are two core levels related to the macromolecule, the N 1s and the C 1s. The lower panels of fig. 6.13 (a), (b) and (c) show the N 1s core level for monolayer coverages of metal phthalocyanines on the surfaces of Ge(001)-2×1:H, Ge(111)-c(2×8) and Ge(001)-2×1 respectively. The N 1s for the bulk films is given in the upper panel of each for comparison. Although for Ge(001)-2×1:H the only available data is for PbPc, it is reckoned to be representative due to the low degree of interaction in this case. The Lorentzian width used in the fitting of the bulk in each spectrum is 0.13 eV. The Gaussian widths of the bulk spectra are similar in all cases, with 0.66 eV for PbPc on Ge(001)-2×1:H in fig. 6.13 (a) and 0.69 eV for the CuPc on both Ge(001)-2×1 and Ge(111)-c(2×8). The monolayer fittings show considerable divergence in shape for the different interfaces.

This shape of the N 1s core level indicates the degree of interaction in the order of Ge(001)-2×1:H < Ge(111)-c(2×8) < Ge(001)-2×1. For PbPc on Ge(001)-2×1:H the N 1s spectrum is almost identical for the interface and bulk. The fit presented here has Lorentzian widths identical to the bulk with a subtly increased Gaussian width of 0.67 eV, demonstrating the weak interaction with this surface. For CuPc on Ge(111) a noticeable broadening occurs, which can be well fit with an increased Gaussian of 0.94 eV. On Ge(001) an even greater degree of broadening occurs, which when fit with purely Gaussian broadening gives a width of 1.05 eV. Although this simple Gaussian broadening no longer fully describes the tails of the core level, as a first approximation it demonstrates the trend. This trend is also consistent with the decreasing degree of mobility of molecules on the respective surfaces as observed by STM.

In all the above phthalocyanines the N 1s core level shows no measurable distinction between the three different nitrogen environments *within* the molecule. However, H₂Pc provides a special case in which nitrogens bonded to hydrogen are clearly distinguishable, shifted by approximately 1.5 eV from all other nitrogens, with the pyrrole nitrogens not bonded to the hydrogen occurring at approximately the same energy as the four bridging nitrogens. This implies an expected intensity ratio of approximately 1:(1+2) between the two distinct nitrogen peaks, as obtained for the bulk in the upper panel of fig. 6.14. In this case there is a dramatic difference between the molecules at the H₂Pc-Ge(001) interface and those in the bulk, as shown

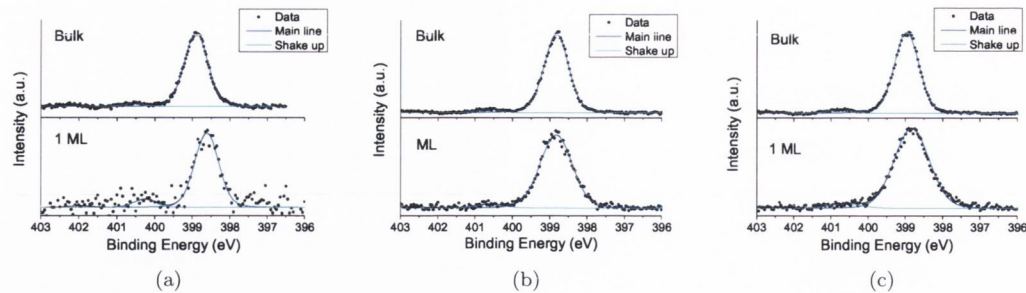


Figure 6.13: PES of the N 1s core level from (a) PbPc on Ge(001)-2×1:H, (b) CuPc on Ge(111)-c(2×8), and (c) CuPc on Ge(001)-2×1. A comparison is given between a bulk-like film and a 1 ML film in each case.

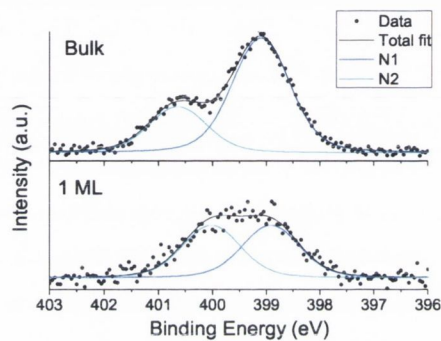


Figure 6.14: PES of a comparison between the N 1s core level of a monolayer film and a 40 Å thick film of H₂Pc on Ge(001)-2×1.

Table 6.1: Summary of alternative fitting parameters for the N 1s spectrum given in fig. 6.14. ΔE refers to the energy difference between the two peaks, I_1 and I_2 refer to the intensity of the two peaks respectively, GW refers to the Gaussian width and LW the Lorentzian width.

	Bulk	Fit 1	Fit 2	Fit 3
ΔE (eV)	1.54	1.09	1.14	1.11
I_1/I_2	0.41	0.41	0.73	1
GW (eV)	1.20	1.71	1.40	1.20
LW (eV)	0.14	0.14	0.14	0.14

by the spectrum of a monolayer of H₂Pc on Ge(001) in the lower panel of fig. 6.14. This change indicates a strong interaction at the interface, such that it can no longer be fit by two components of the same separation as the bulk, nor by a single component. This indicates that the inner nitrogens are in a significantly different environment to the bridging nitrogens, while no longer being bonded simply as in the bulk.

This peak was fitted under various different parameter restriction conditions, a summary of the results of which are give in table 6.1. Achieving a reasonable fitting with two peaks of the same intensity ratio as in the bulk (fit 1) requires an increase in Gaussian width of 0.5 eV. This is significantly greater than seen for any other MPc, even when the worse instrumental resolution for the H₂Pc spectra is neglected. Therefore, it is considered unreasonable. When all parameters bar the Lorentzian width are left free to vary (fit 2), the optimal two peak fit gives the intensity of the smaller peak as 0.7 of the larger peak, with a 1.1 eV separation and a 0.2 eV broadening. However, it can also be well fit with two peaks of equal intensity and the same Gaussian and Lorentzian widths as the bulk (fit 3), requiring a 1.1 eV separation between the two, as shown in fig. 6.14.

Although the fitting cannot precisely indicate what interaction is occurring, from the inten-

sity ratio it is clear that more than just the two nitrogens bonded to hydrogen have a different energy at the interface in comparison to the bulk. These fits would suggest that all four central (pyrrole) nitrogens are in a similar electronic environment at the interface. In reality there are probably three different components, one component relating to each of the different nitrogen sites. But without more substantial basis for the fitting of these three components it adds nothing further to the argument.

Examination of the C 1s level also shows significant changes at the interface, and these changes show the same trend as the N 1s, namely, increasing interaction through the series Ge(001)-2 $\times$ 1:H, Ge(111)-c(2 $\times$ 8) and Ge(001)-2 $\times$ 1 surfaces. However, in this case the distinction is not as great. A comparison of the three different surfaces is given in fig. 6.15, again with the bulk in the upper panel and a monolayer in the lower. For each, a basic fit is given which includes one component for the benzene-like carbons, one for the pyrrole carbons and a shake up feature related to each of these. There is an argument that a further component should be included at slightly higher binding energy than the benzene carbon as a result of a vibrational peak [8], but this adds nothing to the present comparison and is therefore not included. In each case the interface spectrum is fitted with bulk parameters except for the Gaussian width and a uniform shift in the energies of all peaks.

Fig. 6.15 (a) shows the C 1s of PbPc on Ge(001)-2 $\times$ 1:H in which there is almost no difference between the bulk and the interface spectrum, as in the case of N 1s spectrum. Fig. 6.15 (b) and (c) show the CuPc on Ge(111) and Ge(001). The bulk spectra are fit with a Lorentzian width of 0.12 eV and a Gaussian of 0.60 eV. In both cases a small broadening is seen at the interface, which is fit by an increased Gaussian width of 0.76 eV on Ge(111) and 0.78 eV on Ge(001). This is less change than seen for the N 1s. However, in this case there is a redistribution of intensity leading to a reduction of the peak associated with the benzene rings. As with the N 1s core level, this simple Gaussian broadening does not yield a precise fit to the data, for this the Lorentzian must be increased.

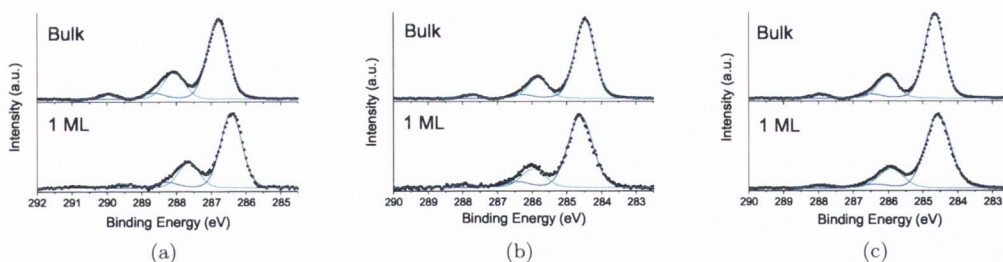
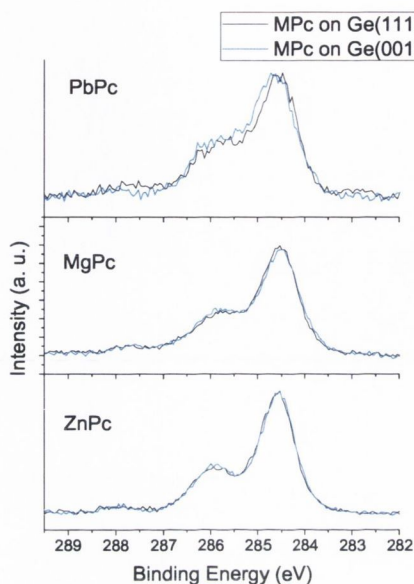


Figure 6.15: PES of the C 1s core level from (a) PbPc on Ge(001)-2 $\times$ 1:H, (b) CuPc on Ge(111)-c(2 $\times$ 8), and (c) CuPc on Ge(001)-2 $\times$ 1. A comparison is given between a bulk-like film and a 1 ML film in each case.

Interestingly, the difference between the C 1s spectra on Ge(001) and Ge(111) is much less significant than that of the N 1s spectra. This fact is further supported by other MPc. As

shown in fig. 6.16 three other MPc tested give an almost identical C 1s spectra for a single monolayer on both the Ge(001) and Ge(111) surfaces. This similarity is surprising given the apparent difference of bonding observed in the STM of MPc on the two surfaces, and the more marked contrast between the N 1s core levels of MPc on the two surfaces. Interestingly, it is also clear that across the Pc range there are significant differences.



(a)

Figure 6.16: A comparison of the PES of the C 1s core level from PbPc, MgPc and ZnPc on Ge(001)- 2×1 and Ge(111)- $c(2\times 8)$.

The redistribution in intensity for the C 1s spectrum is more clearly shown by a direct comparison of the spectra different MPc at the interface of Ge(001) with their respective bulk. Fig. 6.17 (a) shows the C 1s spectra of the same three MPc as fig. 6.16 for a monolayer in comparison to the bulk, scaled such that the area under each curve is the same. The dominant change in all three cases is in the peak associated with the benzene carbons, i.e. the lowest binding energy peak. Furthermore, this peak shows an apparent shift to higher binding energy. There also appears to be significantly greater broadening of the spectrum associated with PbPc when compared with the other two.

Although it is hard to obtain specific shifts from the fitting of such spectra, some important points are worth mentioning. First, no application of peaks with the bulk chemical shifts would fit the spectrum. Furthermore, it cannot be fit with only two peaks, plus their associated shake-up features. Finally, all three spectra can be reasonably fit by shifting of some intensity from the benzene peak to higher binding energy, with a broadening of all peaks. This shows that it is likely that some of the benzene carbons are in a different environment at the interface compared to the bulk. It also shows there is no dramatic distinction between the MPc, with a modified broadening being the only required change in the fitting of each. However, there is a

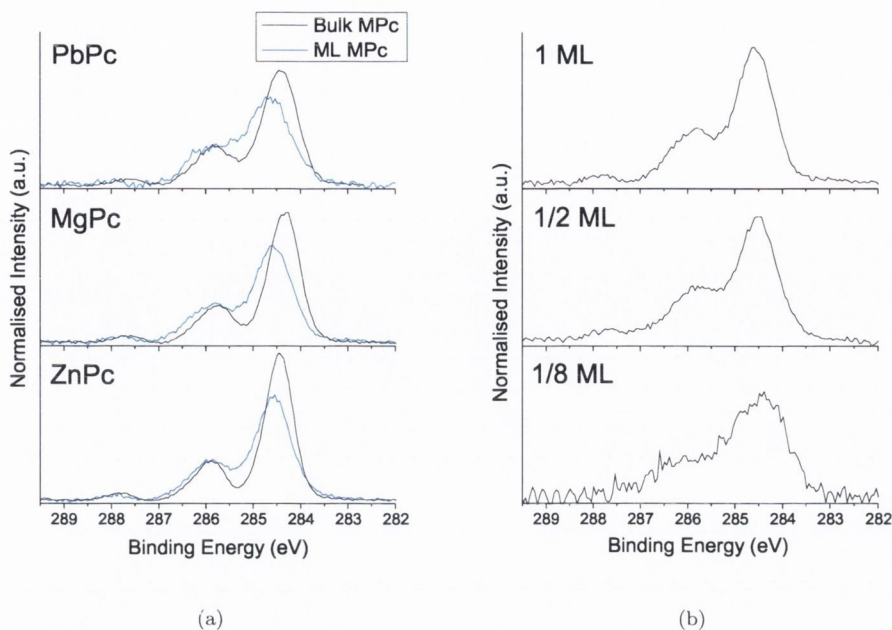


Figure 6.17: (a) A comparison of the C 1s PES from ML and 40 Å coverages of PbPc, MgPc and ZnPc on Ge(001) and (b) a comparison of the C 1s core level of different coverages of MgPc on the Ge(001).

greater broadening of the C 1s for PbPc than the three other planar MPc presented, even in the bulk. This is possibly related to the non-planar structure.

Fig. 6.17 (b) shows the C 1s core level for increasing coverages of MgPc on Ge(001). This also shows differences similar to those observed for the different phthalocyanines, i.e. the degree of broadening decreases for increasing coverage. Likewise, the fitting can be performed as described above for the different phthalocyanines.

These core levels for the macro-molecule are difficult to interpret clearly, but show some important details. First, there is no measurable distinction between the bulk and interface species of MPc on Ge(001)-2×1:H. Secondly, the C 1s shows significant changes which indicate a different environment for some benzene carbons on the other two substrates. This difference is similar for both planar and non-planar phthalocyanines, indicating no dramatic difference in the macromolecule at the interface for these different molecular shapes. Thirdly, to achieve a reasonable fit to both the C 1s and the N 1s requires an increased Lorentzian width. This indicates a shorter core hole lifetime at the interface than in the bulk. Finally, the changes in the N 1s for the same phthalocyanine on Ge(001) and Ge(111) are much more significant than those of the C 1s. This suggests that the substrate specific bonding occurs through the nitrogen. However, there are also significant changes in the C 1s spectrum suggesting the possibility that the benzene carbons are also somehow interacting with the surface.

6.5 Photoelectron Spectroscopy of PbPc on Ge(111) revisited

A review of the data of PbPc on Ge(111) presented in section 5.3 reveals an interesting observation. It was demonstrated there that a reaction occurs at the interface in which the Pb is stripped from the molecule. A comparison of the intensities between the different species shows that the relative intensity of the “down” component is unchanged for the progressive depositions up to 1 ML. This peak yields approximately 50% of the spectral intensity in each case. The sum of the metal and “up” components thereby also summing to approximately 50% of the total spectral area. A summary of these values is reiterated in the first three columns of table 6.2.

Table 6.2: Intensities of the three components fit to the Pb 5d core level of PbPc on Ge(111). The first three columns are the relative areas of the spectra presented in fig. 5.6, with the 1 ML spectrum reprinted in the top panel of fig. 6.18. The values in the last column are the relative area of these components for the spectrum presented in the bottom panel of fig. 6.18.

	1/8 ML	1/2 ML	1 ML	1 ML Annealed at 100°C
$I_{Pb_{Up}}$	0.21	0.29	0.37	0.32
$I_{Pb_{Down}}$	0.50	0.53	0.53	0.52
$I_{Pb_{Metal}}$	0.29	0.18	0.10	0.16
$I_{Pb_{Up}} + I_{Pb_{Metal}}$	0.50	0.47	0.47	0.48

The link between these two species is even more apparent upon gently annealing the sample. Fig. 6.18 shows the Pb 5d core level from a ML of PbPc on Ge(111) before and after annealing for 1 hour at 100°C (the data and fits from the pre-annealed PbPc are reproduced from fig. 5.6 for clarity of comparison. The relative areas of the different components of the fit are given in the last two columns of table 6.2. The annealing enhances the effect of Pb being stripped from the molecule, but this process only reduces the intensity of the “up” doublet, leaving the “down” doublet unchanged.

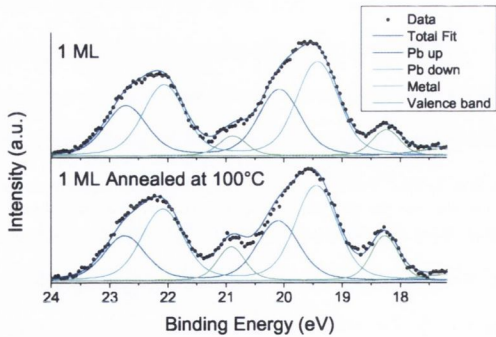


Figure 6.18: Pb 5d of a monolayer of PbPc on Ge(111) before and after annealing at 100°C for 1 hour.

The implication of this result is that it is those molecules which have the metal atom away from the surface in which the reaction occurs, assuming the correct assignment of “up”

and “down”. The two suggested mechanisms by which the metal could be removed from the molecules upon adsorption onto the substrate are substitution and alloying [80,81]. Although highly speculative, these results would seem to imply a substitutional mechanism of the reaction occurring, as an alloying reaction would most likely occur more easily for metal atoms in close proximity to the surface. Assuming this is true, a further consequence of these results is that the metal atom in close proximity to the surface must be inhibiting the substitution reaction of Ge into the macromolecule. Unfortunately due to the complicated nature of the substrate core levels of Ge(111) and the small contribution expected from GePc, if present, no contribution from this species would be likely detectable in the Ge 3d core level. One possible solution would be to evaporate Ge onto a thick film of PbPc, whereby a shift in the Ge core level associated with a substitution reaction could be observed.

6.6 Summary and Discussion

The adsorption of metal phthalocyanine on Ge shows an increasing degree of interaction on the respective surfaces of Ge(001)-2×1:H, Ge(111)-c(2×8) and Ge(001)-2×1. This behaviour is shown to hold for both STM and PES results. The site specific adsorption and monolayer formation have also been observed on all three surfaces.

On the Ge(001)-2×1:H surface the molecules show very little sign of interaction with the surface. For PbPc the first layer is seen to form well ordered islands which take a structure similar to that of bulk triclinic PbPc. A similar effect has recently been observed on NH₃ passivated silicon surfaces for the planar CuPc [150]. From the point of view of use in solar cells such an effect from a simple surface modification is interesting. Where dye molecules such as phthalocyanines lie flat on the surface a much greater degree of charge recombination occurs which limits the effectiveness of devices [47]. Therefore, the influences which cause the molecules to tilt away from the surface at interfaces such as this are of both fundamental and industrial interest.

The interaction of MPc with the surface of Ge(111) shows an interesting anomaly in the general trend of surface interaction described above. Although it generally displays a weaker interaction with the molecules, for very small coverages there is a distinct reaction which occurs on the Ge(111) surface that does not occur on the Ge(001)-2×1 surface. The reaction is a reduction of Pb from PbPc attributed to Pb removed from the macrocycle. This reaction only occurs where the reconstruction breaks down, therefore these seemingly contrasting results are the consequence of the improved passivation of the c(2×8) reconstruction, when compared with the 2×1 reconstruction of the Ge(001)-2×1 surface. The effect can be seen in the tilt determined by NEXAFS as well (see section 4.4.2), where the molecules are observed to lie closer to parallel with the substrate than on Ge(001)-2×1.

The PES of MPc on both Ge(001) and Ge(111) show similar behaviour for a monolayer coverage. In both cases the C 1s and the N 1s core levels from the macromolecule appear

broadened in comparison with the bulk. The broadening of both these core levels on both these substrates was fit as purely Gaussian for comparisons sake. However, in each case the broadening was better fit by introducing an increase in the Lorentzian component as well. This change indicates a shortening in the core hole lifetime of molecules adsorbed on these surfaces.

In the case of the C 1s core level there is relatively little difference between the two surfaces. The N 1s core level on the other hand shows a distinctly greater broadening on Ge(001) than Ge(111). This difference indicates that it is most probable that the surface specific interactions are dominated by nitrogen sites. Apart from the minority molecules adsorbed at defect sites on the Ge(111) surface there is no indication of site specific adsorption on this surface. On the other hand, MPc on the Ge(001) surface shows very specific locations for coverages from a fraction of a monolayer up to a whole monolayer. Consequently, this surface deserves more discussion in relation to the hypothesis of a specific interaction with the nitrogen atoms of the molecule.

This hypothesis is supported by an examination of the models provided in figs. 6.2 and 6.3. None of the reported bonding of aromatic hydrocarbons on Ge(001) or Si(001) occurs across neighbouring dimer rows, as discussed in section 2.2.3. The dominant bond formations of ring hydrocarbons, and exclusively so for the aromatic hydrocarbon benzene, involve a cycloaddition product across a single dimer. In certain cases, cycloaddition products are formed across adjacent dimers in a row, but never across two rows. This is inconsistent with the model of species 1 given in fig. 6.2, but could be an explanation for the minority species 2 presented in fig. 6.3.

A dative bonding argument for the inner pyrrole nitrogen can also be excluded based on geometry. Pyrimidine, pyridine and pyrrole have all been observed to bond on the Ge(001) surface through dative bonding mechanism (although for pyrrole this is not generally the final product) [105, 106, 151]. This dative bonded product for pyrimidine and pyridine both lie almost in the plane of the surface in the *opposite* direction to the pyrrole rings of the MPc. The second argument against this type of dative bonding is the influence on the substrate core level. There is a clear change in the up-dimer of the substrate core level, but these dative bonding mechanisms are all through the down-dimer.

One possible mechanism of bonding, in light of these arguments, is a form of covalent bonding through the bridging nitrogens. The proposed bonding would then be to the four up-dimer atoms adjacent to the bridging nitrogens outside of the porphyrin ring structure of the molecule. However, based purely on a bond length argument, this would require a significant distortion in the molecular and/or substrate geometry for some of the benzene to remain unbonded. Most importantly, the benzene rings sitting on top of the dimers would have to bend up away from the surface. Furthermore, although the STM height profiles are in a large part determined by electronic effects, and therefore don't necessarily reflect the geometry, these too are consistent with the hypothesis. Here the arms of the phthalocyanine above the dimer rows are ~ 0.2 Å higher than those between the dimer rows. These results support

the conclusion of a contribution of molecular distortion to the observed tilt in the NEXAFS discussed in chapter 4.

Chapter 7

Conclusions

The main objective of this work is an improved characterisation of the interface between phthalocyanines and germanium. This has been approached in three parts, each of which is an attempt at understanding and building upon previous results obtained for the MPc-Ge(001) interface. The analyses are also extended to two further surfaces of Ge, the passivated Ge(001)-2×1:H surface and the Ge(111) surface.

First, a systematic analysis of the different contributions to the observed tilt in NEXAFS has shown the complicated nature of interpreting the spectroscopic results. Four different possibilities were considered, namely an ordered tilt, an intrinsic apparent tilt, an extrinsic apparent tilt, and a mixture of flat and tilted molecules. It was shown that the possibilities of an ordered or intrinsic tilt could be excluded for planar phthalocyanines. However, a complication arises for the non-planar phthalocyanines. From DFT calculations of these, there is an expectation that the π^* orbitals will be tilted due to the geometric distortion introduced by the large metal ion. Despite this, it was shown that this is not observed for SnPc on Ag(111), indicating either a failing of the computational results, or more likely, an extrinsic *suppression* of the π^* features.

A study of *extrinsic* effects on the intensity of the π^* features in NEXAFS demonstrates that these can induce an apparent tilt. The increasing tilt observed for CuPc on the HOPG, Ge(111) and Ge(001) surfaces, respectively, matches with an increasing degree of interaction observed in STM of these systems. For both Ge(001) and HOPG the molecules can be imaged with STM and appear flat-lying, suggesting the tilt is not genuine, but rather due to an extrinsic in-plane contribution to the π^* features. This contribution could be either electronic or geometric. An extrinsic electronic contribution to the intensity in the energy range of the π^* features was observed for two different phthalocyanines (PbPc and H₂Pc), but not for the three others measured to date. This demonstrates the possibility of extrinsic electronic effects, but that these alone cannot account for the observed tilt. Two possibilities for geometric distortions of the molecules were considered computationally. It was demonstrated that a distortion of the hydrogens is not a reasonable explanation for the observed tilt, but a bending in the molecular plane could, in theory, account for the tilt. However, this requires a large distortion of the

molecule. Further experiments are required to determine whether this is possible as a sole explanation for the observed tilt.

A study of disorder shows this is also a probable contributor to the observed tilt in NEXAFS. Two results indicate some disorder at the interface. The first is streaking in the STM images, which is indicative of the presence of loosely bound molecules. However, quantifying the disorder from this is not possible, as the loosely bound molecules can not be imaged by STM and are strongly influenced by the process of conducting the experiment. The second is a comparison of the tilt observed in bulk films with that observed in monolayer films. The bulk films appear to have a higher degree of order in cases where the molecules appear closer to flat-lying at the interface. It is expected that disorder at the interface will induce disorder in the film. Therefore, the observed disorder in the bulk agrees with the explanation of disorder as the mechanism for in-plane π^* intensity at the interface. However, again the *degree* of tilt remains a problem. The observed tilt of approximately 25° implies that 20-40% of molecules are disordered, which is considered unlikely given the strong ordering in the molecules that are observable by STM.

From these analyses it is concluded that multiple effects play a role in the observed tilt. Some extrinsic intensity in the energy range of the π^* features is likely for the flat-lying molecules that make up the majority of the first monolayer. This is due to both electronic and geometric effects. In addition to this, it is likely there is some further contribution to this intensity from disordered molecules.

Second, an analysis of an observed shift in the metal core level of non-planar phthalocyanine on Ge(001) provides some insight into the mechanisms by which it occurs. It is shown to occur in MPc where the metal lies close to the surface, as previously assumed. It was also demonstrated that such shifts occur in other similar systems. Therefore, this effect is neither specific to germanium, nor to a specific bonding on the dimerised surface.

In a systematic test of the possible mechanisms for the shift it was shown that polarisation effects of either the initial, or final state can be ruled out as an explanation for the observed results. This indicates the shift is a result of charge transfer in either the initial or the final state. However, distinguishing these effects is difficult. Due to the small proportion of substrate atoms interacting with the central metal of the molecule, initial state charge transfer cannot be determined from the substrate core level. Computational techniques may shed some light on the situation, but these adsorbate systems present a challenge for these techniques due to the size and the complicated interactions involved. One experimental method, involving a comparison of PES and NEXAFS energies, is also proposed for the determination of charge transfer, but this was unable to be performed for the current work.

Despite these difficulties, an analysis of the valence band of these systems indirectly indicates that the observed shift is an initial state effect. A lower intensity is observed in the HOMO of MPc in systems where the metal core levels are shifted than those where no shift occurs. Although its origin is currently unexplained, it does indicate an *initial* state difference in these systems. Therefore, it is concluded that the most likely mechanism of the observed shift is an

initial state electronic charge transfer to the central metal of the molecule.

Third, models for the adsorption of MPc on the three different surfaces of germanium are given. It was demonstrated that the degree of molecule-surface interaction increases over the series: Ge(001)-2×1:H; Ge(111)-c(2×8); Ge(001)-2×1. This is observed in STM and PES of the macromolecule core levels and is also consistent with the NEXAFS results.

The model of adsorption for MPc on Ge(001)-2×1 is similar for both the planar and non-planar molecules tested. It seems likely that this will be the same for all simple MPc. On this surface there are at least two possible adsorption sites, but one makes up the vast majority. A preference for the formation of molecular chains is seen. This indicates that the location of molecules on the surface has an influence on the adsorption site of further molecules. The prevalence of a close packed arrangement suggests that the intermolecular interaction and a fixing of the dimer tilt along the rows, due to molecular adsorption, are the dominant influences in chain formation. It is also possible that modification of the surface charge by the molecule increases the probability of adsorption on adjacent dimers in the same row.

The PES indicates that the nitrogens are involved in the substrate specific bonding, and the STM provides information about the location of the molecule with respect to the substrate. From this a possible mechanism of bonding for the majority species is through all four bridging nitrogens. For this to occur it would require a significant bending in the molecular plane, which could also explain a contribution to the apparent molecular tilt observed by NEXAFS.

A site specific adsorption model could not be determined for the majority of the Ge(111) surface. However, a clear preference for adsorption of molecules at defect sites is demonstrated, with significant mobility of the molecules over the terraces. A reaction occurs for PbPc at these defect sites, in which the Pb is removed from the molecule. The weaker interaction over the c(2×8) reconstructed terraces, combined with the higher reactivity of this surface where the reconstruction is not present, demonstrate the more passivating effect of this reconstruction in comparison to the 2×1 reconstruction of the Ge(001) surface.

On the hydrogen passivated Ge(001) surface there is very little sign of interaction between substrate and molecule. The core levels of the molecule at the interface are nearly identical to those of the bulk. The STM shows islands of MPc, within which the molecules exhibit a high degree of ordering. The molecules tilt at an angle to the surface, and appear to exhibit a bulk-like triclinic crystal structure, even in the first monolayer.

Finally, each of the three aspects of interface characterisation demonstrate the importance of comparison between different systems. The use of different substrates and molecules is critical to a more comprehensive analysis of these experiments. Substrates leading to more ideal and simplified systems, such as where the substrate-molecule interaction is weak, provide one important source of comparison. Also of interest are related, but different substrates. To this end a different crystal face (Ge(111)), a surface modification (Ge(001):H) and a substrate of a related element (Si(001)) have been used here as comparison to the Ge(001) surface.

Furthermore, although the analysis of a given problem is dominated by one technique,

corollary information from other techniques enhances the conclusions that can be drawn. The different aspects of interface characterisation are not independent. An understanding of adsorption (primarily from STM and PES in this thesis) is necessary for an understanding of molecular orientation (measured with NEXAFS here). This is critical for an understanding of electronic effects (observed with PES in this work). This, in turn, reflects back on the understanding of adsorption.

Chapter 8

Future work

This work has significantly furthered the understanding of the MPc-Ge systems investigated and of specific experimental results. All conclusions drawn are consistent with the experimental results of the various techniques employed. However, not all are the only possible conclusion consistent with the results. Further work employing experiments beyond the scope of this work should be considered in confirmation of aspects of this work where doubt remains. At various points in this thesis certain suggestions of the limitations of the conclusions drawn and certain further work has been suggested. This chapter summarises and briefly expands upon these points.

In relation to the NEXAFS presented in chapter 4 two contributors to the observed “tilt” were determined for closed-shell MPc: an extrinsic in-plane intensity in the π^* features and a fraction of tilted molecules. To further understand the relative importance of these two factors, two routes of investigation are suggested. First, a series of experiments measuring the influence of annealing the samples should yield some insight into the importance of tilted molecules. Those molecules which are weakly bound are the likely source of tilted molecules. At elevated temperatures these should either take the more stable flat-lying adsorption sites or sublime off the surface. In either case the contribution of tilted molecules would be reduced. The limit of this reduction in tilt would be the pure extrinsic tilt.

The second suggestion is a geometry relaxed DFT based calculation. A large system is required for calculation, with an expected minimum of 273 atoms for representative results. This calculation should provide quantitative information about the structural distortion of the molecule and any symmetry changes in the molecular orbitals. However, the large system size and the fact that Van der Waals forces are neglected in DFT make the calculation challenging and limit the certainty of the results.

Chapter 5 concludes that electronic charge is transferred to the metal atom of MPc where it lies in close proximity to the substrate atoms. However, the possibility that a final state charge transfer is involved was not eliminated. Two methods are suggested to confirm the given conclusion. The first involves a careful comparison of NEXAFS and PES energies. Due to the

neutral final state of the molecules in NEXAFS, charge transfer after photon absorption should not occur. This means that if the PES shift is the result of final state effects a reduced shift would be observed in the NEXAFS. However, the NEXAFS signal is expected to be weak due to the low proportion of metal atoms at the interface and the small near-edge photoabsorption cross sections of both Sn and Pb. For this experiment, careful calibration of energy and long accumulation times would be required.

The second method of confirmation of the above conclusion is via a calculation using DFT. Again, this calculation would require a minimum of 273 atoms, but in comparison to the calculation described for the NEXAFS a simpler approach could be used. In this case reasonable results are expected without a full geometry optimisation, varying only the spacing of the molecule above the sample. The lateral position should be taken from the model presented in chapter 6. From the Mulliken populations obtained from the DFT, charge transfer to the metal atom could be determined, with a transfer of approximately 0.5 electrons required to account for the observed shift.

The final discussion of future work relates to the adsorption analysis presented in chapter 6. Matching the STM results with a simulation using DFT should reveal detailed information about the precise bonding of MPc on the Ge(001) surface. Again a similar system should be used for the calculation, in this case requiring a full geometry relaxation. On the resultant system the STM must then be simulated. This second step is less computationally demanding, as long as the assumption of a uniform density of states in the tip is valid.

In the case of PbPc on Ge(111) a reaction between the substrate and molecule was observed. To determine whether this is a substitution reaction a submonolayer of Ge should be deposited on a bulk film of PbPc. Any PES shift due to Ge substituting into the Pc macromolecule could then be detected, without the background of non-interacting Ge atoms.

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