The Electronic Structure of Organic Molecular Materials

Theoretical and Spectroscopic Investigations

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In the present thesis the electronic properties of two organic molecules were studied by means of density functional theory (DFT) in connection to their possible applications in organic photovoltaics and molecular spintronics respectively. The first analysed system is the C_{60} derivative PCBM extensively used in polymer solar cells for the charge separation process [1, 2, 3, 4]. Since fullerenes have been shown to undergo modifications as a result of light exposure, investigating their electronic structure is the first step in elucidating the photodegradation process. The electronic excitations from core levels to unoccupied molecular orbitals reveal not only the empty level structure of the molecule, but provide additional information related to the chemical bonds involving a specific atom type. In this way, they represent a means of determining the chemical changes that the molecule might withstand. The electronic transitions from carbon 1s core levels to unoccupied states are explained for the unmodified PCBM by a joint theoretical (DFT) and experimental study using the near edge x-ray absorption fine structure (NEXAFS) spectroscopy.

The second investigated system is the transition metal phthalocyanine with a manganese atom as the metal center. Manganese phthalocyanine (MnPc) is a single molecular magnet in which the spin switch process can be triggered by various methods [5, 6]. It has been shown, for instance, that the adsorption of hydrogen to the Mn center changes the spin state of the molecule from 3/2 to 1. More interestingly, the process is reversible and can be controlled [7], opening up the possibility of using MnPc as a quantum bit in magnetic memory devices. Up to this date, the d orbital occupation in MnPc has been under a long debate, both theoretical and experimental studies revealing different configurations [8, 9, 10, 11, 12, 13, 14, 15]. In this thesis the electronic structure of the phthalocyanine is thoroughly analysed by means of DFT and the calculated results are compared to photoelectron spectroscopy measurements. The combination of theoretical and experimental tools reveals that in gas phase at high temperatures the molecule exhibits a mixed electronic configuration. In this light, the possible control of the specific electronic state of the central metal represents an interesting prospect for molecular spintronics.

A detailed introduction to the studied molecules and their possible applications is given in the first chapter. A discussion of the theoretical methods in direct connection to the experimental spectroscopies is carried out in the second section, while sections three and four contain a thorough description of the obtained results.
List of publications

1. Near-edge X-ray absorption fine structure study of the C$_{60}$-derivative PCBM
   Iulia Emilia Brumboiu, Ana Sofia Anselmo, Barbara Brena, Andrzej Dzwilewski, Krister Svensson and Ellen Moons

2. Elucidating the Exact Metal 3d Electronic Configuration in Manganese Phthalocyanine
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Chapter 1

INTRODUCTION

In view of the increasing need for miniaturization, the conventional building blocks of electronic devices need to be replaced by new materials capable of attaining even smaller sizes, while conserving or ideally increasing functionality. In this sense, organic molecular materials, a class of chemically tunable molecules [16] which display self-recognition and self-assembly properties [17, 18], emerge as an interesting alternative.

The potential applications of this new type of materials are numerous. As single molecule devices, they offer interesting development possibilities for molecular spintronics and electronics [18, 19]. In thin films, they can be employed in fields ranging from photovoltaics to flexible printed electronics [17, 18, 20, 21]. Besides wide applicability, organic molecular materials offer additional advantages such as low cost, low environmental impact and high production efficiency when compared to their conventional counterparts [17, 21]. The class comprises not only organic semiconductors, but also organic metals, including superconductors and ferromagnets [22, 23]. Their different electronic and magnetic properties can be combined and used in increasingly complex electronic devices fabricated through the bottom-up approach [17]. In opposition to conventional photolithography consisting in the progressive removal of material from the bulk until the desired structure is obtained, bottom-up fabrication methods make use of the self-organization properties of organic molecules. In this manner, the device is assembled from fundamental building blocks (atoms or molecules) with increased precision and overcoming the size limitations of the top-down approach [24].

Since the properties of the material as a whole originate essentially at the molecular level, understanding the electronic structure of the individual molecule is crucial and constitutes an important step in explaining how these properties emerge and can be controlled [19]. Experimentally, the occupied states are probed by photoelectron spectroscopy (PES). The different molecular orbitals are excited using soft X-rays or ultraviolet electromagnetic radiation with the appropriate wavelength. The analysis of ejected electrons reveals
information on the photoionized levels and provides a picture of the occupied electronic structure in the molecule. The empty levels on the other hand are probed by X-ray absorption spectroscopy (XAS). The photoinduced excitations of core electrons to unoccupied levels unveil not only the structure of empty bands, but also information on the chemical bonds a specific atom species is involved in.

Theoretical methods such as density functional theory (DFT) provide a fundamental means of explaining and understanding specific experimental results especially for large and complex molecular species. Though there are limitations to the computational tools, since several approximations need to be made, the spectroscopic processes are successfully described for many materials. A detailed discussion of the theoretical approaches to spectroscopy is given in the second chapter.

This work focuses on the electronic structure, investigated primarily by means of DFT, of two organic molecules, both very interesting with respect to their potential applications. The first is the phenyl-[6,6]-C_{60} butyric acid methyl ester (PCBM), extensively used as an electron acceptor in polymer solar cells [1, 2, 3, 4]. PCBM is the standard acceptor material in organic photovoltaic devices, but it has been shown to undergo degradation due to light exposure [25, 26, 27]. Explaining the photoinduced deterioration process is therefore of great importance and one of the goals of the present study is to make the first steps in this direction.

The second investigated system is manganese phthalocyanine (MnPc), a single molecular magnet (SMM) with potential applications in molecular spintronics [5, 6, 7]. The d electronic structure of MnPc has been to this date under intensive debate, with both experimental and theoretical studies reporting different 3d orbital occupations [8, 9, 10, 11, 12, 13, 14, 15]. In this sense, the present work offers a detailed analysis of the manganese 3d levels in MnPc in the attempt to resolve the controversy.
Chapter 1. Introduction

1.1 PCBM and Polymer Solar Cells

Ever since their discovery, fullerenes have attracted much attention in virtue of their interesting properties (high electron affinity, chemical stability, superconductivity when doped) and of the wide variety of potential applications (in solar cells, in drug delivery or molecular electronics) [3, 28, 29, 30, 31].

Fullerenes are spherical pi-electron structures containing 12 carbon pentagonal structures and a variable number of hexagons. The C\textsubscript{60} allotrope is the most famous due to its high $I_h$ symmetry [32]. Fullerenes are n-type semiconductors, with a band gap of approximately 2 eV accompanied by an energetically low lying lowest unoccupied molecular orbital (LUMO) [3]. Since they exhibit high electron affinities, they are excellent electron acceptors in organic solar cells [1, 2, 3, 4]. The photoinduced electron-hole pair created in the light-absorbing material needs to be separated in order for charge transport to take place. The energetically low LUMO of the fullerene provides the driving force for charge separation [1, 3].

The main disadvantage of pure fullerenes is that they are weakly soluble in most of the common solvents [32] posing therefore a challenge to the efficient and inexpensive solution-based processing techniques for polymer solar cell fabrication. On the other hand, soluble fullerene derivatives with similar electronic and charge transport properties have been synthesized. Among these derivatives, phenyl-[6,6]-C\textsubscript{60} butyric acid methyl ester (PCBM, depicted in figure 1.1) is the most successful and has become to this date the most widely used electron acceptor in organic photovoltaic devices [1, 2, 3, 4].

Polymer solar cells consist of an electron-donor - electron-acceptor pair embedded between
two electrodes [3]. The donor is usually an organic polymer, while the acceptor is a high electron affinity material such as C_{60} or PCBM. Depending on the fabrication process, organic photovoltaics (OPVs) have different types of morphology (1.2). The simplest one is the bilayer heterojunction architecture (figure 1.2(a)) consisting of two separate layers deposited on top of each other through vacuum deposition of the molecular components [33]. Though it is the easiest to build, it exhibits the lowest efficiency since the donor-acceptor interface is quite reduced in size. On the other hand, the ordered heterojunction morphology (figure 1.2(c)), consisting of an ordered intermix of donor and acceptor, should provide the highest light-harvesting efficiency but it is the most difficult to construct [34]. The optimal alternative so far from both efficiency and fabrication point of view is the bulk heterojunction architecture (figure 1.2(b)) which consists of a percolated mixture of donor and acceptor materials obtained through a single step solution processing technique [4, 27, 35].

The connection between morphology and device efficiency is intrinsically related to the functioning mechanism of a polymer solar cell. A schematic representation of the general route for light harvesting is depicted in figure 1.3. The first important step, light absorption, takes place in the donor material and results in the promotion of an electron from the highest occupied molecular orbital (HOMO_d), to higher unoccupied levels followed by a relaxation to the lowest unoccupied orbital (LUMO_d). The electron-hole pair represents a localized bound exciton with a typical binding energy of 0.4-0.5 eV, much larger than in the case of inorganic photovoltaic materials, and which can dissociate only given a large enough chemical potential [3]. The necessary energy difference is provided by the lower lying LUMO of the acceptor and dissociation takes place on condition that the exciton reaches the interface before recombination can occur [1]. This poses a limit on the distance from the interface where a photoinduced electron-hole pair can still be harvested and explains why the bilayer heterojunction solar cell morphology has limited efficiency. Having reached the donor-acceptor interface - several transport mechanisms are still un-

Figure 1.2: Schematic representation of different polymer solar cell morphologies: bilayer heterojunction (a), bulk heterojunction (b) and ordered heterojunction (c).
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Figure 1.3: Schematic representation of the general mechanism for photoenergy conversion in polymer solar cells: light absorption (a) and charge separation (b) [3]

Under debate [1, 3] - and given that the LUMO\textsubscript{d}-LUMO\textsubscript{a} energy difference is large enough to overcome the exciton binding energy, charge transfer takes place between the polymer and the acceptor material. The newly formed electron-hole pair with the electron on the LUMO\textsubscript{a} level dissociates further into the two mobile charges via a built-in electric field and can then be transported to the electrodes.

Figure 1.4: (a) The solar spectrum [36] and (b) a typical current-voltage characteristic (IV) of a photovoltaic cell [34].

The main parameters of a photovoltaic device are the quantum efficiency (QE), the open circuit voltage ($V_{oc}$), the short circuit current ($I_{sc}$), the fill factor (FF) and the overall efficiency ($\eta$) [4]. The quantum efficiency is defined as the number of electrons collected at the electrodes divided by the number of incoming photons. In organic solar cells, QE depends on the absorption efficiency of the polymer, the exciton transport to the interface and the donor-acceptor interaction, as well as the charge transport efficiency of electrons and holes through the acceptor respectively donor materials [4].

The other characteristic parameters of a solar cell can be determined by measuring the current-voltage curve for the device. This is done by varying the resistive load connected...
to the OPV while measuring the corresponding current and voltage (figure 1.4). $V_{oc}$ is determined under illumination in open circuit conditions. In the case of polymer solar cells, it is directly related to the energy difference between the acceptor LUMO and the HOMO level of the donor [3]. $I_{sc}$ is measured by setting the value of the resistor to zero and is related to the spectral range absorbed by the photoactive material (a narrower band gap translates into the absorption of a wider range of wavelengths) as well as to the charge carrier mobilities [4]. The fill factor is the ratio between the maximum power and the product of $I_{sc}$ and $V_{oc}$:

$$FF = \frac{I_{MP}V_{MP}}{I_{sc}V_{sc}}$$

(1.1)

where $I_{MP}$ and $V_{MP}$ are the current and voltage corresponding to the maximum power. Since it is directly related to the short circuit current and the open circuit voltage, as well as to the actual device power, the fill factor is an indication of the competition between charge recombination and successful transport to the electrodes [34].

Finally, the overall efficiency of the OPV is defined as the ratio between the maximum achieved power and the input of the electromagnetic radiation ($P_{in}$). In terms of the fill factor, the efficiency, $\eta$ is written as:

$$\eta = \frac{V_{oc}I_{sc} \cdot FF}{P_{in}}$$

(1.2)
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The research-oriented fabrication of organic solar cells has started only recently (figure 1.5), but their efficiencies have been steadily growing, overcoming the 10 % limit in the last years. In order to achieve comparable conversion efficiencies to the conventional silicon photovoltaics, one of the important research directions is the study of the electron acceptor. Since the electronic structure of this material is crucial for the functioning of the cell, understanding it in the context of the light harvesting mechanism would play a very relevant part in the quest for higher efficiencies. Moreover, the analysis of possible photodegradation pathways is crucial to the increase in polymer solar cell stabilities, a necessity when it comes to implementing this type of devices in real-life applications.
1.2 MnPc and Molecular Spintronics

Phthalocyanines are chemically and thermally stable organic semiconductors, structurally resembling porphyrins and able to accommodate different metal atoms in the center of the molecule [38] (figure 1.6). Their electronic and magnetic properties are particularly dependent on the metal and can therefore be tuned by changing the central atom. By virtue of the above mentioned characteristics and of the strong optical absorption in the visible, metal-phthalocyanines (MPc) have been intensively studied to this date in view of their possible application in a diverse number of fields ranging from photovoltaics to quantum computing [7, 39, 40, 41].

A number of transition metal phthalocyanines (TMPc) (figure 1.6) and lanthanide phthalocyanine double-deckers (LPc$_2$) act as molecular magnets and exhibit high temperature Kondo peaks [7, 19] that can be switched on and off in a controlled and reversible manner, making them very interesting candidates for spintronics applications.

Figure 1.6: Optimized geometry of manganese phthalocyanine.

Molecular spintronics is a newly emerging field of research that focuses on the different approaches for electron spin control in organic molecular materials [42] with the purpose of improving information storage and processing [19]. Single molecular magnets are ideal in this sense since they would require little amount of power for performing logical tasks, while their small sizes would give access to quantum phenomena with interesting possible functions in computation [19].
In particular, in the case of MnPc it has been shown that the spin can be manipulated in various ways, ranging from the adsorption of atoms or small molecular groups [6, 7] to quantum size effects [5] and the interplay between superconduction pair formation and Kondo screening [43, 44]. One interesting way of modifying the molecular spin state is by the adsorption of a hydrogen atom [7]. When deposited on a metallic substrate (in this case Au(111)), MnPc exhibits a 3/2 spin which can be detected by scanning tunnelling microscopy (STM) as a Kondo resonance. If a hydrogen atom is adsorbed to the central metal, the spin state of the molecule changes and the Kondo resonance is lost (figure 1.7). The process can be reversed by a voltage pulse or by increasing the temperature [7].

MnPc could be used in a binary memory device with each molecule storing one bit of information. Understanding of the 3d electronic structure of the central metal, which in MnPc is so far under debate, would bring this type of potential application a step closer.
Chapter 2

THEORETICAL SPECTROSCOPY

2.1 Introduction

The macroscopic properties of a material such as conduction, magnetization, and optical properties depend crucially on its electronic structure. Furthermore, it plays a relevant part in different interactions, either with molecules, substrates or electromagnetic radiation. A powerful tool to extract information about the occupied and unoccupied levels in a material is soft X-ray spectroscopy. Photoinduced electron excitations, either from core or valence levels, give rise to the measured signal. The combination of experimental spectroscopic tools with a theoretical description of the electronic structure and transitions provides a means for interpreting measured spectra, especially for large and complex systems. For material science, the study of the electronic structure by theoretical means offers great insight into molecular phenomena. Though extremely useful, the description of the electronic behaviour in a molecule is not an easy problem to solve. The many body wavefunction that solves the Schrödinger equation holds the entire information about the studied system, but an analytical solution does not exist even for the simplest 3-particle molecule \((\text{H}_2^+)\) \[45\]. In order to describe larger systems, such as the two molecules studied in this thesis, approximations need to be extensively used.

Assuming the systems under investigation is composed of \(N\) nuclei and \(n\) electrons. The equation to be solved is:

\[
\mathcal{H}\psi (r_1, \ldots, r_n, R_1, \ldots, R_N) = \partial_t \psi (r_1, \ldots, r_n, R_1, \ldots, R_N) \tag{2.1}
\]

where \(\mathcal{H}\) is the Hamiltonian associated to the specified system and \(\psi\) is the time-dependent wavefunction with \(r_i\) the coordinates for electron \(i\), including the spin, and \(R_i\) the nuclear spatial coordinates. The first approximation to be made is to consider that the time dependence of the wavefunction is trivial, leaving only the time-independent problem to be tackled. Secondly, it can be assumed for the majority of the cases that the behaviour
of electrons adiabatically adjusts to the movement of the nuclei (Born-Oppenheimer approximation) and therefore can be considered separately by replacing the actual positive charges with an external potential as depicted in figure 2.1.

![Figure 2.1: In the Born-Oppenheimer approximation (BOA), the real system is replaced by a system of electrons moving in a nuclear potential. The arrows represent the Coulomb interactions between \( e_i \) and the other electrons.](image)

The problem now is separated into a nuclear problem and an electronic one. The electronic eigenvalue equation can be written as:

\[
\mathcal{H}_e \psi_e (r_1, \ldots, r_n) = E_e \psi_e (r_1, \ldots, r_n)
\]  

(2.2)

where \( \psi_e \) is the electronic wavefunction depending only on the electron coordinates \( (r_i) \), and \( \mathcal{H}_e \) is the electron Hamiltonian:

\[
\mathcal{H}_e = \sum_{i=1}^{n} \left( -\frac{\hbar^2}{2m_e} \nabla_i^2 - v_{ext}^i \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{4\pi\epsilon_0 r_{ij}}
\]

(2.3)

\( -\frac{\hbar^2}{2m_e} \nabla_i^2 \) represents the kinetic energy operator corresponding to electron \( i \), \( v_{ext}^i \) is the external potential which the electron is subjected to and \( \frac{e^2}{4\pi\epsilon_0 r_{ij}} \) represents the repulsive Coulomb interaction of electron \( i \) and electron \( j \) with \( r_{ij} \), the distance between the two. The sum adds up the contributions of each pair of electrons. The elementary charge is denoted \( e \), while \( m_e \) represents the mass of one electron, \( \epsilon_0 \) is the vacuum permittivity and \( \hbar \) is the reduced Planck constant.

There are two major difficulties when it comes to solving this eigenvalue problem. The first one refers to the fact that electron-electron Coulomb repulsion has to be taken into account for \( n \) moving charges. The second difficulty is the fact that \( \psi_e \) is a many-electron function. As it is, the equation is not analytically nor numerically solvable, therefore other approximations need to be made. In the following, the Hartree-Fock (HF) method will be briefly discussed, followed by a more detailed discussion of density functional theory.
Chapter 2. Describing Spectroscopic Properties

2.1.1 Hartree-Fock Theory

In HF theory, the dynamic electron repulsion is removed by considering that each electron is moving in an average potential created by the others, $v_{ee}$. Furthermore, the many-electron wavefunction is replaced by a Slater determinant of one-electron functions $\phi_i(r_j)$ (an exchange antisymmetric linear combination of orbitals):

$$
\psi_e = \frac{1}{\sqrt{n!}} \left| \begin{array}{cccc}
\phi_1(r_1) & \phi_2(r_1) & \ldots & \phi_n(r_1) \\
\phi_1(r_2) & \phi_2(r_2) & \ldots & \phi_n(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_1(r_n) & \phi_2(r_n) & \ldots & \phi_n(r_n)
\end{array} \right|
$$

(2.4)

The electronic total energy in terms of the new one-particle orbitals becomes:

$$
E_e = \langle \psi_e | H_e | \psi_e \rangle
$$

(2.5)

$$
E_e = \sum_{i=1}^{n} H_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} (J_{ij} - K_{ij})
$$

(2.6)

where $H_i = \langle \phi_i(i) | \hat{h}_i | \phi_i(i) \rangle$ (with $\hat{h}_i = -\frac{h^2}{2m_e} \nabla^2 - v_{ext}^i$) is a monoelectron integral representing the sum of the kinetic energy of an electron in orbital $\phi_i$ and its Coulomb interaction with the nuclear potential, $J_{ij} = \langle \phi_i(i) \phi_j(j) | \frac{e^2}{4\pi\varepsilon_0 r_{ij}} | \phi_j(i) \phi_i(j) \rangle$ is the classical electron-electron repulsion and $K_{ij} = \langle \phi_i(i) \phi_j(j) | \frac{e^2}{4\pi\varepsilon_0 r_{ij}} | \phi_j(i) \phi_i(j) \rangle$ represents the exchange interaction.

The many electron problem is replaced with n one-electron equations by considering that the energy is a functional of the Slater determinant, then applying the variational principle and defining a convenient monoelectron operator.

$$
\hat{f}_i \phi_i = \epsilon_i \phi_i
$$

(2.7)

with $\hat{f}_i = \hat{h}_i + \sum_{j=1}^{n} (\hat{J}_j - \hat{K}_j)$

The one-electron equations can be solved self-consistently by starting with trial orbitals and gradually improving them until the value of the energy converges. The main disadvantage of HF theory is the fact that it does not include any correlation effects, since the electron repulsion term is replaced by its average [46].
2.1.2 Density Functional Theory

Another strategy for solving the many-electron problem is to replace the n-variable dependent wavefunction by a 3-variable function, the electron density. This is possible because the electron density \( \rho \) contains the entire relevant information that is included in the wavefunction. As proven by the first Hohenberg-Kohn theorem (HKT1), there is a one to one correspondence between the external potential and \( \rho \) [47]. Furthermore, the charge density uniquely determines the ground state observables [47]. The second Hohenberg-Kohn theorem (HKT2) is an analogue of the variational principle and represents a straightforward way of determining the ground state energy self-consistently [47, 48]. The major differences with respect to HF theory are first the fact that the energy is a functional of \( \rho \) not of \( \psi_e \), while second and very important, in opposition to HF, DFT includes electron correlation as it will be discussed in the following.

Starting from the many-electron Hamiltonian in equation 2.3, all the energy terms are rewritten as functionals of the charge density.

\[
E[\psi_e] \rightarrow E[\rho] = T[\rho] + V_{\text{ext}}[\rho] + V_{e-e}[\rho] \tag{2.8}
\]

\( T[\rho] \) represents the kinetic energy functional, \( V_{\text{ext}} \) is the external potential energy and \( V_{e-e} \) represents the electron-electron interaction. The \( V_{\text{ext}} \) component can be easily written in terms of the electron density as:

\[
\int_\tau \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\tau \tag{2.9}
\]

where \( v_{\text{ext}} \) represents the external potential and the integral runs over the entire volume with \( d\tau \) as the volume element.

In opposition, there is no straightforward way of writing the kinetic energy and electron-electron interaction as functionals of \( \rho \), the challenge lying in the fact that the system is composed of \( n \) moving and interacting charges. In order to overcome this difficulty, in DFT the \( n \)-electron system is replaced with a reference system of the same charge density \( \rho \), but composed of non-interacting particles, each described by an individual Kohn-Sham (KS) orbital [48] (figure 2.1.2) so that the set of orbitals form an orthonormal basis.

In the reference system the classical Coulomb interaction of charge densities can be written as [45]:

\[
V[\rho] = \frac{e^2}{2} \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{4\pi\varepsilon_0 r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{2.10}
\]
where \( \rho (\mathbf{r}) \) is the charge density at position \( \mathbf{r} \) and \( r_{12} \) represents the distance between points \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \).

The kinetic energy of \( n \) independent particles \( (T_s) \), each described by a KS function \( \Phi_i (\mathbf{r}_i) \), is

\[
T_s [\rho] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \langle \phi_i (\mathbf{r}_i) | \nabla^2 | \phi_i (\mathbf{r}_i) \rangle
\]  

(2.11)

All the differences between the real \( n \)-electron system and the reference are contained in the exchange and correlation functional which can be written in terms of the charge density and an exchange-correlation potential:

\[
V_{xc} = \int \rho (\mathbf{r}) v_{xc} (\mathbf{r}) d\tau
\]

(2.12)

The exchange-correlation potential incorporates all the unknown information about the interacting \( n \)-electron system and can be calculated exactly only for simple models [49], for example the uniform electron gas for which \( v_{xc} \) can be computed either by many-body perturbation theory [50] or by quantum Monte Carlo (QMC) simulations [51]. For larger and more complicated systems like molecules or solids, the exchange and correlation cannot be computed directly and therefore approximations must be used. The simplest one is the local density approximation (LDA) in which \( v_{xc} (\mathbf{r}) \) is replaced by the exchange-correlation potential of a uniform electron gas with density \( \rho \) equal to the charge density of the real system as a function of \( \mathbf{r} \). LDA is quite successful for many ground state properties, but it systematically underestimates the band gap in semiconductors and insulators in many cases by more than 50 percent [52, 53]. Furthermore, lattice parameters are underpredicted while phonon frequencies are overestimated [54]. A first improvement to LDA is the generalized gradient approximation (GGA) for which the model is a slowly
varying uniform electron gas and the exchange-correlation is a functional of both the density and its gradient [51]. A major error in both LDA and GGA is the fact that the electron interacts with its own charge density (self-interaction error), leading to the delocalization of charges and the underestimation of the stability of high spin states [55]. On the other hand, GGA brought large improvements in the accuracy of calculated molecular properties relevant for chemistry [51] and therefore the inclusion of higher order derivatives of the charge density seemed to be the natural step for more development. Contrary to these expectations, meta-GGA functionals of both the density and its higher-order derivatives did not bring about the expected advances, their place being instead taken by hybrid functionals (most notably B3LYP) that include a percentage of the exact-exchange from HF theory [49, 51]. The inclusion of exact-exchange is motivated by the adiabatic connection which relates the non-interacting system to the fully-interacting one by a series of partially interacting systems having the same charge density [56]. In B3LYP, the corrections to exchange and correlation are semiempirically included by fitting atomization energies, electron affinities and ionization potentials of a large set of systems, but nonempirical means of including exact exchange are also available, for example in PBE0 [57].

The simple models used and the approximations that accompany them perform strikingly well both from the point of view of computational cost and of the accuracy of calculated results [58]. One major point that should be emphasized is the fact that DFT is essentially exact and the knowledge of the exact exchange-correlation functional would yield the exact ground state charge density, total energy and all the related ground state properties [49]. Another important point is that the Kohn-Sham orbitals are one-particle functions corresponding to the non-interacting system and therefore their nature and relationship to molecular orbitals (MO) in MO theory or Hartree-Fock is largely debated [49]. On the other hand, the KS functions allow a straightforward, even if to a large extent only qualitative, interpretation of calculated results [59]. Finally, in its essence DFT is a ground-state theory, but it can be successfully used to derive a number of spectroscopic properties (related to excitations by electromagnetic radiation) as it will be shown in the following section.
2.2 X-Ray Absorption Spectroscopy

X-Ray absorption spectroscopy (XAS) represents an experimental investigation tool of the structural, electronic and magnetic properties of atoms, molecules and materials [60] and it is grounded on the photon mediated transitions from core occupied states to unoccupied levels or bands. The XAS signal is obtained by systematically increasing the energy of incoming photons, while detecting the peaks in photon absorption. A typical absorption spectrum is depicted in figure 2.2. In order to be absorbed by the atom, a photon should have at least the energy necessary to promote the core electron to the lowest available unoccupied state to which the transition is allowed. The condition is satisfied for distinct photon energies where sharp step-like absorption features called absorption edges appear in the spectrum (K, L\(_1\), L\(_2\) and L\(_3\) in figure 2.2). The K-edge corresponds to the binding energy of the 1s state, while L\(_1\), L\(_2\) and L\(_3\) are related to 2s and 2p levels of a specific atom species.

![XAS Spectrum Diagram](image)

Figure 2.3: An example of a XAS spectrum (redrawn from reference [61]) alongside a schematic representation of the energy levels and transitions that give rise to the different absorption edges.

Zooming in to a specific absorption edge, the spectrum consists of small oscillatory features (figure 2.2) which can be divided into two regions. The near-edge x-ray absorption fine structure (NEXAFS) region spans over the first 30-50 eV above the edge, including in some cases a few pre-edge peaks, and corresponds to excitations of the core electron to unoccupied bound states. All the other oscillatory features are included in the extended x-ray absorption fine structure (EXAFS). They are related to transitions at energies higher than the electron release threshold and involve interference effects with the backscattered electron wavefunction [62].
As mentioned before, the features of the XAS spectrum result from transitions from core levels to unoccupied states as a consequence of photon absorption. The transition probability \( W \) due to the interaction with electromagnetic radiation is described by Fermi’s golden rule:

\[
W = \frac{2\pi}{\hbar} |\langle \Psi_f | T | \Psi_i \rangle|^2 \delta_{E_f - E_i - \hbar \omega}
\]  

(2.13)

where \( \Psi_f \) represents the many-body final state, \( \Psi_i \) the many-body initial wavefunction including the incoming photon, \( T \) is the transition operator and the delta function \( \delta_{E_f - E_i - \hbar \omega} \) accounts for the energy conservation during the process.

So far, equation 2.13 is general and exact. \( T \) contains all possible transitions and can be written as an infinite sum of increasingly complex terms:

\[
T = T_1 + T_2 + \ldots
\]  

(2.14)

where \( T_1 \) accounts for one-photon transitions, \( T_2 \) describes two photon processes, and so on. X-ray absorption is considered to be a one-photon process and therefore only the first term of the expansion will be considered in the following. \( T_1 \) can be further expanded in an infinite sum of operators, the first term being the dipole operator. For the K-edges of light elements such as C, N and O, quadrupole allowed transitions are much lower in magnitude than the dipole allowed [60] and therefore a generally good approximation is to consider \( T_1 = \sum_q \hat{e}_q \cdot r \), where \( \hat{e}_q \) is a unit vector corresponding to a light polarization.
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$q$ and $r$ is the position operator. Quadrupole allowed transitions become more important for the K-edges of transition metal compounds accounting especially for peaks in the pre-edge region [64].

Within the dipole approximation, Fermi’s golden rule becomes [60]:

$$W = \frac{2\pi}{\hbar} \sum_q \langle \Psi_f | \hat{e}_q \cdot r | \Psi_i \rangle^2 \delta_{E_f - E_i - \hbar \omega}$$  \hspace{1cm} (2.15)

With the final goal of determining all transition probabilities for a given system, the question now raised is how to tackle the many-body initial and final wavefunctions. First of all, by considering the transition a one-electron process, the orbitals that are directly involved may be separated from the rest [59, 60]:

$$W = \frac{2\pi}{\hbar} \sum_q \langle \Phi_v | \hat{e}_q \cdot r | \Phi_c \rangle^2 \left| \langle \psi_f | \psi_i \rangle \right|^2 \delta_{E_f - E_i - \hbar \omega}$$  \hspace{1cm} (2.16)

$\Phi_v$ and $\Phi_c$ are the one-electron orbitals corresponding to the vacant and core state respectively, while $\langle \psi_f | \psi_i \rangle$ represents a codeterminant obtained by eliminating these two orbitals from the many-body wavefunctions [59].

By further considering that all the other orbitals remain relatively unperturbed by the transition, the codeterminant can be approximated with one, and the transition probability is determined only by the dipole mediated overlap between the core level and the unoccupied final state.

$$W = \frac{2\pi}{\hbar} \sum_q \langle \Phi_v | \hat{e}_q \cdot r | \Phi_c \rangle^2 \delta_{E_f - E_i - \hbar \omega}$$  \hspace{1cm} (2.17)

The discussion will be continued by specifically referring to the near-edge absorption fine structure (NEXAFS) region.

2.3 Core Level Spectroscopies

In organic molecules, the NEXAFS region of the XAS spectrum is determined by photon-induced transitions of a core electron, typically from the 1s or the 2p level (in the case of organic molecules containing transition metals), to unoccupied molecular orbitals (figure 2.3). It is important to emphasize that NEXAFS, as XAS in general, is an atom specific technique able to reveal information related to the chemical interactions and environment of a particular atom species in a molecule [62]. Furthermore, the polarization of the incoming electromagnetic radiation can be used to obtain information regarding specific
types of molecular orbitals ($\sigma$, $\pi$), revealing at the same time the orientation of the molecule on the substrate and its interactions with the surface layers [59].

The K-edge NEXAFS spectrum of an organic molecule can be calculated using equation 2.17 taking $\phi_c = |1s\rangle$ and considering all possible transitions to unoccupied molecular orbitals described by one-electron functions $\phi_v$.

![Figure 2.5: A schematic representation of a transition responsible for one NEXAFS peak in benzene.](image)

A first approximation is to directly replace the one-electron functions with Kohn-Sham orbitals resulting from ground state DFT calculations. This means that the calculated NEXAFS spectrum will represent the structure of the unoccupied molecular orbitals projected on the $|1s\rangle$ core function. In the strict atomic sense, the dipole selection rule implies that given a 1s initial state, the final states probed can only be p-type orbitals [60]. This is not strictly valid for molecules where a molecular orbital can be represented as an overlap of different atomic-type functions, making a 1s-$\sigma$ transition possible.

The ground state density of unoccupied states is a very good approximation in what concerns X-ray emission (XES) spectra where the many-body final state does not contain any core hole [59], but the description of NEXAFS remains poor [65, 66, 67]. This is due to the fact that the effects of the photoinduced core-hole are completely unaccounted for, although the core level spectroscopy signal reflects a perturbed system [67]. The effects become important especially in the case of aromatic organic molecules [68], since the core hole can modify the molecular orbitals and, as a consequence, the probability of a particular transition. As depicted in figure 2.3, the core hole created on a carbon atom in benzene leads to the change of the lowest unoccupied molecular orbital (LUMO) in the sense that it becomes more localized on the core-excited atom.

The first step in introducing static core hole effects is to replace the specific atom with its nearest heavier neighbour in the the periodic table (Z+1 rule) and perform the calculation.
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Figure 2.6: Comparison between the LUMO of benzene in the ground state and in the presence of a core hole in the 1s state of the indicated carbon atom.

on the positively charged system having one electron removed. The Z+1 approximation is grounded on the fact that the core hole is localized on the particular atom and the reduced screening of the electrons can be accounted for by an extra positive charge on the nucleus [66, 69]. Furthermore, the Z+1 rule can be readily used in any ground state DFT code since the core-excited state is replaced with an equivalent ground state by adding a proton to the nucleus of interest. A variety of systems can be described in the Z+1 approximation [68], but it fails especially in the case of L-edges, where the localization criterion is not met.

A more precise way of representing the electron screening due to the core hole is to consider the particular orbital either as empty (full core hole approach) or having a fractional charge (transition potential method). The transition potential method was first described by Slater [70] and used in a self-consistent DFT-scheme in the Kohn-Sham (KS) formulation for calculating core-electron binding energies by Chong [71].

The method is derived in a multiple scattering theory (MS-Xα) context and consists in expressing the total energy as a power series in the occupation number $\lambda$ [70, 71]

$$E(\lambda) = E_o + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + ... = \sum_{\lambda=0}^{\infty} \lambda^k E_k$$

(2.18)

Here $\lambda$ is a continuous variable, $E$ represents the total energy of the electron system and $E_k = \frac{1}{k!} \left( \frac{\partial^k E}{\partial \lambda^k} \right)_{\lambda \to 0}$. The ionization potential (IP) of an electron from a particular orbital $\Phi_k$ corresponds to the energy difference between the final state having the electron removed and the initial occupied state. If the total energy is represented as a function of the occupation number (figure 2.3), the value $\epsilon_k = \frac{\partial E}{\partial \lambda_k}$ is the slope of the tangent to the energy curve in point $(\lambda_k, E(\lambda_k))$. For the special point $\lambda = \frac{1}{2}$, the slope of the tangent
is equal to the slope of the parabola and $\epsilon_k$ measures the ionization potential of the $k^{th}$ electron [70]. The transition potential method includes relaxation effects due up to the second order [59, 70].

The idea of performing both the ground state and the core-excited calculations in the KS-DFT formalism presents the advantage of keeping a simple molecular orbital picture, while at the same time including electron-hole correlations. It is not straightforward though that KS-DFT which is strictly rigorous for ground state calculations can be directly used for an essentially excited state problem. The argument for applying the formalism anyway is the fact that the variational principle can be derived for any well-defined state bounded from below, the $|1s\rangle$ with fractional charge being such a state [59]. Thus, the KS-SCF procedure consists in variationally determining the lowest core-excited state by imposing the constraint that the core level in question should contain a fractional charge (most common 0 or 1/2) [59]. The IP and excitation energies are then calculated as differences in the total energies of the final states and the initial state respectively [59]. In particular, the ionization potential in KS-SCF formalism ($IP_{KS}$) is calculated using:

$$IP_{KS} = E^{KS}(|1s\rangle_{\lambda=0}) - E^{KS}(|1s\rangle_{\lambda=1})$$  \hspace{1cm} (2.19)

where $E^{KS}(|1s\rangle_{\lambda=0})$ is the calculated total energy of the core-excited state (with a full core hole in the 1s orbital) and $E^{KS}(|1s\rangle_{\lambda=1})$ represents the ground state total energy.

The calculated ionization potential depends on the chemical environment of the specific
atom and it can be used to reveal information related to its interactions with other neighbouring atoms. This information is directly related to the experimental core-level x-ray photoelectron spectroscopy (XPS) which measures the ionization energy by comparing the fixed energy of the ionizing electromagnetic radiation with the kinetic energy of the emitted photoelectrons [72]. The measured core-level XPS spectrum of a particular atomic species can be directly compared to the sum spectrum of all calculated IP values.

The NEXAFS excitation energies calculated in the fractional charge (or full core hole) state must be shifted according to the KS calculated ionization potential, since the ground state binding energy of the 1s orbital differs from $IP_{KS}$ [71, 73]. The agreement to experimental spectra, especially very close to the absorption edge is very good for many organic molecules [65].

Currently, new formalisms of calculating X-ray absorption spectra including core hole effects are under intensive study. Methods based on multiple scattering use the many body perturbation theory formulated in terms of the real space Green’s function and Dyson’s equation in order to include the effect of many body interactions to the desired/possible accuracy level [61, 63]. Other methods are grounded on a two-particle formalism and consist in solving the Bethe-Salpeter equation where states are coupled due to the electron-hole interaction [74].

The advantage of such methods is the fact that multiplet effects are included, but they are less reliable in the case of molecules due to the use of muffin-tin potentials.

### 2.4 Photoelectron Spectroscopy of the Valence Band

Photoelectron spectroscopy (PES), which includes core level XPS, consists in the photoionization of electrons by monochromatic electromagnetic radiation [72, 75] (figure 2.4). Information related to the binding energy for different molecular orbitals can be extracted by analysing the kinetic energy of the photoelectrons, directly revealing the structure of the occupied states in a molecule or solid [75]:

$$E_b^k = E_K^f - \hbar \omega - \Phi$$

(2.20)

where $E_b^k$ represents the binding energy of the kth MO, $\hbar \omega$ is the energy of the ionizing photon, $E_K^f$ represents the kinetic energy of the ejected photoelectron, while $\Phi$, the work function, is a constant of the sample and it equals to 0 for isolated molecules or atoms.

By making use of the highly tunable polarized synchrotron radiation and performing the
measurement at the magic angle ($55^\circ$), it is possible to record the dependence of PES peak intensities on the energy of incoming photons. Excluding diffraction effects, in the simple LCAO-MO picture, where a molecular orbital (MO) is represented as a linear combination of atomic orbitals (LCAO), the change in peak intensity can be directly related to the contribution of a particular atomic orbital (AO) to the MO from which the photoelectron was ejected [75].

As discussed in the previous section, the transition probability in the one-particle dipole approximation is described by equation 2.17. For the particular case of PES of the valence band (VB), the initial state is an occupied one-electron VB orbital ($\Phi_{VB}^k$), while the final state is represented by the wavefunction of a free electron in the continuum ($\Phi_f$).

$$ W = \frac{2\pi}{\hbar} \sum_q \left| \langle \Phi_f | \hat{e}_q \cdot r | \Phi_{VB}^k \rangle \right|^2 \delta_{E_f^k - E_b^k - \hbar \omega} \tag{2.21} $$

where $E_f^k$ represents the kinetic energy of the free electron described by $\Phi_f$ and $E_b^k$ is the binding energy of orbital $k$.

Since the total probability of ejecting an electron from a particular state is an important observable in PES, it is very useful to define the photoionization cross-section as the sum of the transition probabilities from level $\Phi_{VB}^k$ to all available free electron states [76].

$$ \sigma_k = \sum_f W_{k \rightarrow f} \tag{2.22} $$

where $\sigma_k$ is the cross-section of orbital $\Phi_{VB}^k$ and $W_{k \rightarrow f}$ represents the transition probability to the continuum state $\Phi_f$.

In the LCAO-MO formalism, it is simple to assume that the cross-section of a molecular state is directly determined by the cross-sections of its constituent atomic orbitals. In the Gelius model [76], $\sigma_k$ is written as a sum of atomic photoionization cross-sections $\sigma_{\alpha}^k$:
\[ \sigma_k = \sum_{\alpha,A} c_{\alpha A}^2 \cdot \sigma^A_{\alpha} \]  

(2.23)

where the sum runs over all atomic orbitals (\(\alpha\)) and atoms (\(A\)) and \(c_{\alpha A}\) represents the contribution of AO \(\phi_\alpha\) from atom \(A\) to the molecular orbital \(\Phi_k\).

Atomic photoionization cross-sections depend on the energy of the electromagnetic radiation according to the nature of the subshell. In other words, the ionization probability of s states varies with photon energy in a different manner than the one of d levels. In this sense, a major advantage of the Gelius model is that it allows the assignment of PES bands to particular AOs in the molecule. It should be emphasized that besides the Gelius model, a crucial ingredient in peak assignment is the knowledge of \(\sigma^A_{\alpha}\) as a function of photon energy, therefore it is very important to calculate the photoabsorption cross-sections of different atoms in the vacuum ultraviolet and soft x-ray spectral regions (20-1500 eV).

The cross-section \(\sigma_{nl}\) corresponding to an atomic level with principal and angular quantum numbers, \(n\) and \(l\) respectively, can be calculated by applying equation 2.22:

\[ \sigma_{nl} (\hbar \omega) = \frac{2\pi}{\hbar} \sum_f \sum_q |\langle \chi_f | \hat{\mathbf{e}}_q \cdot \mathbf{r} | \chi_{nl} \rangle|^2 \delta_{E_{Kf} - E_{nl} - \hbar \omega} \]  

(2.24)

where the initial state is described by the radial wavefunction of the subshell \(\chi_{nl}\) while the final state is described by the radial function \(\chi_f\).

\(\chi_{nl}\) is obtained by solving the radial one-electron Schrödinger equation using the Hartree-Fock-Slater numerical method [77]:

\[ \left[ -\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} + l (l + 1) \cdot \frac{\hbar^2}{2m_e r^2} + V(r) - E_{nl} \right] \chi_{nl} = 0 \]  

(2.25)

where \(V(r)\) represents the sum of the central Coulomb potential and the free electron exchange potential [77].

\(\chi_f\) is determined by solving a similar equation in the Manson-Cooper algorithm [77], where \(E_{nl}\) is replaced by the kinetic energy \(E_{Kf}'\) of the free electron and \(l\) by \(l' = l \pm 1\), while \(V(r)\) remains the same.

Figure 2.4 depicts the calculated atomic photoionization cross-sections as a function of photon energy of carbon and nitrogen 2s states and of the 3d states of three different transition metals (Mn, Fe and Co). The first remark is that \(\sigma_{2s}\) reaches a maximum value at lower photon energies, very close to the ionization threshold [green05] (26.86 eV for C and 40.0 eV for N), while \(\sigma_{3d}\), larger in value than the 2s cross-section, presents delayed maxima higher above the edge (40.0 eV for Mn, 45.0 eV for Fe and 50.0 eV for Co).
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At energies larger than the maximum point, the cross-section rapidly decays due to the cancellation of the positive and negative components in the dipole matrix element [76]. Furthermore, the C and N cross-sections for all subshells (1s, 2s and 2p) become quickly much smaller than $\sigma_{3d}$. For instance at 100 eV photon energy, the Mn $\sigma_{3d}$ is one order of magnitude larger than the cross-section of the C states [77].

![Figure 2.9: Calculated atomic photoionization cross-sections of (a) carbon and nitrogen 2s subshells and (b) manganese, iron and cobalt 3d levels as a function of photon energy. The values are taken from reference [77, 78].](image)

When combined with an analysis of the contributions of different AOs to molecular orbitals, the knowledge of atomic cross-sections gives valuable insight in the origin of PES peaks. The LCAO-MO formalism is inherently applied in HF and KS-DFT, since it consists of expressing the molecular orbital ($\Psi_k$), i.e. the one-electron HF or KS function, as a linear combination of atomic basis functions ($\psi_\alpha$):

$$\Phi_k = \sum_{\alpha=1}^{NBF} c_{k\alpha} \phi_\alpha$$  \hspace{1cm} (2.26)

where the sum runs over all the basis functions, $NBF$ representing the number of atomic orbitals.

There are several ways of analysing the charge distribution within a particular molecule, the standard being the population analysis algorithm proposed by Mulliken (MPA) [79, 80, 81]. In MPA, the occupation number of a particular orbital $\Phi_k$ is written in terms of the atomic coefficients $c_{k\alpha}$:

$$n_k = n_k \sum_{\alpha=1}^{NBF} c_{k\alpha}^2 + 2n_k \sum_{\alpha=1}^{NBF-1} \sum_{\beta=\alpha+1}^{NBF} c_{k\alpha} c_{k\beta} S_{\alpha\beta}$$  \hspace{1cm} (2.27)
where $S_{\alpha\beta}$ is the overlap integral, defined as $S_{\alpha\beta} = \int \phi_\alpha \phi_\beta d\tau$, with the integral running over the entire volume.

One of the main advantages of MPA is that it gives chemically intuitive results, but as a downside, these results are basis set dependent and become deficient as the basis set is enlarged [81]. In some cases, occupation numbers that are negative or greater than 2 are obtained. These two instabilities are due to the fact that charge is equally distributed between two atoms in the overlap population [81].

In order to overcome the occupation number problem of MPA, Ros and Schuit [81] proposed a different algorithm for charge density partition which considers only the squares of the atomic orbital coefficients ($c_{\kappa\alpha}^2$). The $c^2$ method (SCPA) consists in writing the contribution of a particular basis function $\phi_\alpha$ to the molecular orbital $\Phi_k$ in the following manner [81]:

\[
\frac{c_{k\alpha}^2}{\sum_{\beta=1}^{NBF} c_{k\beta}^2} \tag{2.28}
\]

Where the denominator represents the sum over all atomic orbital contributions to $\Phi_k$.

Equation 2.28 ensures that the occupation number is positive and does not exceed 2. The $c^2$ method does not solve the basis dependence problem of MPA and therefore contributions calculated with different basis sets are not comparable.

By performing a population analysis in the ground state by means of DFT, then multiplying each atomic contribution with the corresponding cross-section at a specific photon energy and finally summing up all contributions it is possible to obtain a theoretical photoelectron spectrum which can be compared to experimental data, giving valuable insight not only in what concerns peak assignments, but also in the electronic structure of the studied material in a simple molecular and atomic orbital picture.

There are several phenomena that can influence PES which have not been discussed here. Among them, the relativistic effects, multiplets in open shell systems, satellite states and vibronic coupling [76] pose challenges to the theoretical description of the spectroscopic process and intensive research is ongoing in the development of effective and straightforward methods for their characterization.
Chapter 3

NEXAFS AND XPS INVESTIGATIONS OF PCBM

With the promise of flexible and light-weight devices that can be produced at low cost on large scales, polymer solar cells have rapidly converged towards real-life applications reaching power conversion efficiencies higher than 10 percent in tandem devices [82]. It becomes therefore more and more important to understand the basic mechanisms which influence on the one hand the light-harvesting process and on the other hand the overall stability of the cell components in order to gain higher control over the relevant device parameters such as life-time, fill factor, open circuit voltage, short-circuit current and efficiency.

A typical organic solar cell consists of a percolated mixture between a polymer used as the photo-active material and an electron acceptor which provides the means for charge separation (figure 3 (a)). The class of photon-absorbers consists of a large variety of organic polymers with different shapes and sizes [3], having the appropriate HOMO-LUMO gap for visible light absorption. In opposition, the class of electron acceptors is far less extended, with one particular fullerene derivative, the phenyl-[6,6]-C$_{60}$ butyric acid methyl ester (PCBM), having become the standard acceptor material. The reason for its wide

![Figure 3.1: (a) A schematic representation of the morphology and functioning mechanism of a bulk heterojunction polymer-PCBM blend solar cell alongside (b) the optimized geometry of the PCBM molecule.](image)
use is the fact that PCBM, in addition to the energetically low lying LUMO typical to fullerenes, is also more soluble in organic solvents than C_{60} [32], and therefore suitable for the low-cost printing fabrication techniques. One of the main problems with using fullerenes, and PCBM in particular, for the charge separation process is the fact that these materials have been shown to undergo photoinduced degradation [25, 26, 27]. With light exposure, the carbon K-edge NEXAFS spectrum of fullerenes deposited on silicon substrates gradually deteriorates showing a strong decrease of the characteristic $\pi^*$ peak as the $\sigma^*$ region becomes increasingly intense [27]. The drastic change in the spectrum reveals changes in electronic levels due to structural alterations of the molecule. Several photodeterioration mechanisms have been recently proposed, such as oxygen intercalation [83], chemisorbtion of radicals [26] or photodimerization [25], but the question remains still open.

Since NEXAFS is a powerful tool in probing the unoccupied states of a molecule, the correct assignment of absorption peaks is the first important step in shedding light on the degradation process. Figure 3 depicts the C K-edge NEXAFS spectra of PCBM reproduced from PAPER I. The spectra are measured using the electron yield technique, which consists in detecting the electrons emitted from the sample as a result of X-ray irradiation [60]. The core-hole created by photon absorption is filled through Auger decay (inset of figure 3) and the primary Auger electron scatters through the sample creating a cascade of free electrons [book]. By analysing all the emitted electrons, in the total electron yield (TEY) technique, it is possible to reconstruct the information related to the soft X-ray absorption process. Since only electrons originating close to the surface have enough energy to escape, sampling is limited to a thin layer. By constricting detection to the primary Auger electrons, as it is the case of the partial electron yield (PEY) technique, the surface layer is analysed exclusively [60]. A comparison between TEY and PEY can therefore be used to reveal information on surface effects.

The characteristic PCBM peaks in the $\pi^*$ region are denoted with the numbers 1 (also referred to as $\pi^*$, at 284.5 eV), 2 (285.8 eV) and 3 (286.2 eV), while the shoulder to peak 1 at 285.0 eV is denoted S. This feature is of particular importance for PCBM photodegradation, since its intensity is gradually growing with light exposure [27]. In a previous study by Bazylewski et al. [ref], its origin was assigned to the breaking of the high C_{60} symmetry by the PCBM tail and it was related to excitations from carbon atoms in the close vicinity of the side chain attachment point [84].

To further analyse the origins of the shoulder, as well as of the other NEXAFS peaks, DFT calculations were performed in order to model the spectroscopic process for this molecule.
In brief, the geometry of PCBM was first optimized and then, for the optimized structure and considering each carbon atom separately, the transition matrix elements from 1s levels to the unoccupied molecular orbitals were determined using the full core hole approach described in chapter 2. To facilitate the comparison with experiment, a gaussian broadening with variable full width at half maximum (fwhm) was added as described in detail in PAPER I.

![Figure 3.2: The experimental PEY- and TEY- Carbon K-edge NEXAFS spectra [85] in the π∗ region. In the left corner, the inset schematically depicts the Auger decay process, while the right corner inset is a schematic representation of the sample consisting of PCBM deposited onto a Si(001) substrate. Only the relevant layers for electron yield NEXAFS are shown. The dimensions of the layers are not at scale and the given numbers represent an approximative size [86].](image)

The single atom spectra were shifted according to each calculated IP and then summed up, either by including all carbons, or only the ones corresponding to a specific molecular moiety. The comparison of the calculated results to the TEY experiment is depicted in figure 3. The energy window was increased so that peaks 4 and 5 and part of the continuum is visible. The trends in the measured NEXAFS signal are well described by the theoretical results, meaning that the one-particle approximation is in this case valid and, in addition, that core-hole effects are important, as previously demonstrated for C60 in a study of [65].

The comparison of the partial contributions to the total spectrum provides a means of assigning the different bands to different molecular components. Thus, the first important observation is that the NEXAFS of PCBM is dominated by the fullerene cage as this component displays all 5 experimental features. Secondly, the π* peak is a result of 1s to LUMO transitions involving only the cage and phenyl carbon atoms. The rest of the side-chain does not contribute to the first peak, alongside C2, C3 and C61 which show large
contributions to peak 5 instead. The latter observation might seem at first surprising, but
the discrepancies can be explained by the difference in atomic orbital hybridization. C2,
C3 and C61 each form four bonds with their neighbours and therefore are sp\(^3\) hybridized.
In opposition, the fullerene carbon atoms are involved in two single bonds and one double,
thus showing a modified sp\(^2\) type of hybridization.
The \((CH_2)_3\) and COOCH\(_3\) groups add to the intensities of peak 4 and its lower energy
shoulder (which does not appear in the experimental spectrum). Peaks 2 and 3 are
exclusively related to the fullerene cage.

![Figure 3.3: Comparison between the experimental TEY spectrum and the calculated results with contribution from selected molecular moieties. The total and the fullerene spectra are multiplied by a factor three for clarity and all spectra were rigidly shifted by 2.0 eV to match the experimental first peak. The dotted lines indicate the experimental bands. The molecular structure inset depicts the different moieties [85].](image)

A very interesting issue to discuss is the unexpectedly high intensity of peak 1 in the phenyl
component. An analysis of the LUMO of PCBM reveals that the orbital is delocalized
over the C\(_{60}\) cage with very little contribution from the side-chain (figure 3). In a simple
ground state picture, this means that the overlap between the 1s state of carbon atoms
in the tail and LUMO is negligible and therefore the transition matrix element should
be zero or very small. This is clearly not the case for the phenyl atoms. The apparent
paradox is in fact an indication that core-hole effects play, in this case, an important
role in the 1s-unoccupied state transitions. The LUMO in the presence of a full core
hole (CH) created on one of the phenyl atoms (C62, figure 3) exhibits strong localization
on the side-chain, thus drastically increasing the probability of the 1s-LUMO transition.
The complete reorganization of the charge around the atom with the CH is naturally
a consequence of the excess positive charge localized on the particular atom and it has
been shown to take place in $C_{60}$ as well [CH effects]. A deeper insight into the process is needed in order to explain the differences between fullerenes which exhibit strong CH effects and other systems, for example phthalocyanines (metal free phthalocyanine and iron phthalocyanine), which are well described using the transition potential method (half core hole) [87].

![Figure 3.4: The lowest unoccupied molecular orbital of PCBM (a) in the ground state and (b) determined in presence of a 1s core hole on the phenyl carbon C62.](image)

Another important aspect that will be discussed in detail in the following is shoulder S. Clearly visible in the experimental spectrum, it appears to be missing from the calculation. A more careful examination, by considering a narrower fwhm of the gaussian broadening and by zooming into the $\pi^*$ region reveals that the shoulder is actually present in the calculated total spectrum and it consists of three distinct features, $S_1$ (284.7), $S_2$ (284.9) and $S_3$ (285.1) represented in figure 3). In order to determine the origins of the three shoulder features, all the single atom spectra were compared to the total. As expected, the side-chain does not give any contribution to S, with the exception of one phenyl atom, C62. As compared to the other phenyl carbons, the slightly different chemical interaction in which C62 is involved, forming a bond with the attachment point carbon C61, gives rise to a small shift in energy (0.2 eV) of the 1s-LUMO transition for this atom, leading to a large contribution to $S_1$.

As opposed to the side-chain, all the atoms in the fullerene cage display low intensity features similar to S. A number of carbons form only one of the peaks, while most of them display two, with a very low number presenting all the three, with slight shifts from atom to atom. In roughly half of the cases, the features are very low in intensity, giving virtually no important contribution to the total shoulder. There are 27 atoms which display stronger peaks and can be divided into two classes. The first consists of atoms in the close vicinity to the cage attachment point shown in orange in figure 3. They have a
more intense S₃ shoulder corresponding to a 1s-LUMO+2 excitation, and essentially lack the other two peaks. The second class (shown in purple in the inset of figure 3) consists of carbons displaying stronger S₁ and S₂ shoulders and completely missing S₃. The peaks are a result of transitions from 1s to LUMO+1 and 1s to LUMO+2 transitions. As can be seen in figure 3, the atoms are located in the left and right hemispheres of the fullerene cage, slightly larger in number on the (CH₂)₃COOCH₃ side.

Figure 3.5: The calculated NEXAFS spectrum of PCBM in the close vicinity of the π✳. The total spectrum and the fullerene component (multiplied by a factor 2) are shown alongside the single atom spectra of C₈, C₂₉ (multiplied by 1.5 for clarity) and C₆₂. The left-side inset shows a comparison to the experiment in a wider spectral window, while the right-side molecular structure shows the groups of atoms to which the selected single atoms belong. The dashed lines mark the positions of the peaks in the total spectrum [85].

As a summary to this chapter, the origins of the peaks in the π✳ NEXAFS region of PCBM were analysed in order to provide a first step for explaining the photodegradation of the molecule. It has been shown that the main features of the spectrum are originating in the fullerene cage, and therefore the photoinduced changes are most likely related to modifications in this part of the molecule. Greater emphasis was laid on shoulder S, since this feature becomes increasingly strong as the π✳ gradually decreases with light exposure. It has been shown that one of the phenyl atoms gives a strong contribution to the lower energy region of peak S, alongside with carbon atoms from the left and right
hemispheres of the fullerene cage. The fullerene atoms in the vicinity of the attachment point, excluding the two atoms that are directly bonded to it, contribute to the higher energy region of S. It is clear that the side chain has an influence on the intensity of this feature, but the correlation is not straightforward since the carbon atoms most affected are not exclusively the ones located close to the attachment point.

The gradual chemisorption of atoms or small molecular groups to the C_{60} cage seems to be a plausible explanation for the photoinduced changes in the NEXAFS and will be further analysed in future projects.
Chapter 4

THE VALENCE BAND ELECTRONIC STRUCTURE OF MnPc

The use of organic molecules in spintronics and electronics applications seems to be the solution for surpassing the miniaturization limit of the conventional silicon devices [88]. In this sense, single molecular magnets (SMMs) are great candidates for the design of new miniature devices that exploit both the semiconducting and the magnetic properties of these materials [89]. One of the most interesting applications is their use as quantum bits in magnetic memory systems, a non-volatile type of memory with high density of stored information and high operation speed [12]. The class of SMMs includes metal phthalocyanines (MPC) and porphyrins (MP). They constitute interesting test molecules due to their high symmetries and due to the fact that the electronic properties of the molecule as a whole are directly correlated to the central metal accommodated by the ring [7, 89].

It has been recently shown that the spin of a single manganese phthalocyanine (MnPc) can be manipulated in a reversible manner, either by the chemical adsorption of atoms or small molecules to the central metal [6, 7], or by the competition between superconducting phenomena and Kondo screening [43, 44] when the molecule is deposited on superconducting substrates. Since the d electrons of the transition metal play the crucial part in the charge and spin-related properties of the phthalocyanine, it is important to elucidate the 3d electronic structure of the MPC. It is especially important in the case of MnPc, for which the configuration of the 3d electrons is under extensive debate, with both theoretical and experimental studies reporting different occupations of the d orbitals [8, 9, 10, 11, 12, 13, 14, 15].

In the isolated transition metal atom, the 3d levels are degenerate, but when the metal is coordinated to different atoms or molecular groups, the field corresponding to the ligands lifts the degeneracy. In ligand field theory, the splitting of the d levels is directly related to the symmetry of the environment that accommodates the metal [90]. Figure 4 shows the structure of MnPc and the ligand field d level splitting in a $D_{4h}$ symmetric environment.
Chapter 4. The Electronic Structure of MnPc

The \( d_{x^2-y^2} \) orbital has the largest amplitude towards the nitrogen atoms and therefore it is the most affected by the repulsive ligand field [90] (figure 4). In opposition, the other \( d \) orbitals have little (\( d_{z^2} \)) or no overlap with the ligand (\( d_{xz}, d_{yz} \) and \( d_{xy} \)) and as a consequence, their energies are affected to a less extent with \( d_{xz} \) and \( d_{yz} \) remaining degenerate.

For a \( D_{4h} \) environment, the \( d \) orbitals are designated according to their symmetries: \( b_{1g} \) (\( d_{x^2-y^2} \)), \( a_{1g} \) (\( d_z \)), \( e_g \) (\( d_{xz} \) and \( d_{yz} \)) and \( b_{2g} \) (\( d_{xy} \)).

The question now raised is to which extent this simple picture can be applied to the real molecule and how are the levels populated in order to obtain the 3/2 spin of the ground state MnPc. There are several electronic configurations that have been reported in the literature both by theoretical as well as experimental studies (a full discussion is given in PAPER II). In the simple ligand-field notation, they are \( b_{1g}^2a_{1g}^1b_{1g}^0 \) (denoted \( S_A \) here), \( b_{2g}^2a_{1g}^1b_{1g}^0 \) (denoted \( S_B \)) and \( b_{2g}^1a_{1g}^2b_{1g}^0 \) (denoted \( S_C \)). The three configurations were analysed by density functional theory in the LCAO-MO formalism as described in more detail in PAPER II. The total and partial densities of states (DOS) were obtained and compared to photoelectron spectroscopy measurements performed at different photon energies, after including the effect of the photoionization cross-sections.

The \( S_A \) configuration has the lowest calculated total energy, while \( S_B \) and \( S_C \) are higher in energy by 0.11 eV and 0.23 eV respectively. From a structural point of view, in the \( S_A \) configuration the \( D_{4h} \) symmetry brakes into \( D_{2h} \) in a Jahn-Teller manner [8]. The higher energy structures are more symmetric and present only small deviations from the \( D_{4h} \) point group (see inset of figure 4).

In agreement with ligand-field theory, the \( d_{x^2-y^2} \) orbital is left unoccupied in both spin channels and corresponds to higher energy eigenvalues than the other \( d \) orbitals (figure 4 (b)). Moreover, the \( d_{xz} \) and \( d_{yz} \) are degenerate. On the other hand, the orbital ordering is
different and more complex than the one predicted by the simple model. Most importantly, in the ligand field theory formalism, the HOMO is always the \(d_{z^2}\) level, while the actual DFT calculation reveal a different HOMO for each of the structures, with only the \(S_C\) structure in direct correspondence to the simple picture. Instead, the \(S_A\) configuration has a degenerate \((d_{xz}, d_{yz})\) HOMO, while in \(S_B\) it is represented by the \(d_{xy}\) level. Since the 3d occupied orbitals have different energy eigenvalues in each of the three electronic structures, and as the phthalocyanine ring contribution is not expected to change much, the differences in d-level occupation should be directly reflected into the total spectrum which, by comparison to experimental data at specific photon energies, should reveal the electronic configuration of the real molecules.

Figure 4.2: The schematic representation of the d orbital occupation in the simple ligand-field theory picture (a) alongside the calculated Mn 3d partial density of states (DOS) (b) of \(S_A\), \(S_B\) and \(S_C\).

Figure 4 shows a comparison between the total calculated density of states (TDOS) and its most important components in the valence band region (the N 2p, C 2p and Mn 3d partial DOS) for \(S_A\), \(S_B\) and \(S_C\), alongside the relevant structural differences. The main regions of the spectra are denoted by letters from A to E, while the individual peaks in each region are denoted by numbers. Focusing only on the first three regions (A, B and C), the general shape is very similar in all three structures, but there are small dissimilarities which will become relevant when comparing to experimental data measured at different photon energies.

The first important difference is the relative position of peaks \(A_1\) and \(A_2\). In all of the
three configurations $A_1$ is the HOMO level and it is mainly due to the Mn 3d states (in $S_A$ this peak contains a small C 2p contribution as well), while $A_2$ has C 2p character. The splitting between these two peaks varies from 0.3 eV in $S_C$ to 0.47 eV in $S_A$ and to 0.65 eV for the $S_B$ structure.

In the B region, for the $S_A$ configuration the Mn 3d contribution to $B_1$ is almost eclipsed by a strong C 2p band. In $S_B$, peak $B_1$ with similar d character is much stronger and further apart the same C 2p contribution, while in $S_C$ the relatively strong $B_1$ band splits into two. Furthermore, in the $S_A$ structure, Mn 3d states contribute to the higher binding energy region of B ($B_4$, $B_5$), while in $S_B$ and $S_C$ the contribution is limited to $B_3$.

The C region of $S_A$ displays a strong Mn 3d peak ($C_1$), while $S_B$ and $S_C$ have only very low intensity d bands in this region.

Figure 4.3: The calculated total density of states (TDOS) in comparison to the partial N2p, C2p and Mn3d densities of states for $S_A$, $S_B$ and $S_C$. The major differences between the optimized geometries of the three configurations are represented on the molecular fragment.

The differences discussed above become very important when comparing the calculated results to measurements performed at different photon energies. Since the atomic photoionization cross-sections vary for the different atomic species and subshells, the differences in the partial Mn 3d DOS translate into a different shape of the spectrum at high photon energies where the probability of exciting d electrons becomes much larger than the probability corresponding to p carbon or nitrogen states.
Figure 4.4: Comparison between the experimental results for the MnPc thin film (a and b) and MnPc in gas phase (c) to the calculated results multiplied by the corresponding cross-sections at 21.2 eV (a), 1486.6 eV (b) and 30 eV -100 eV (c) photon energies.

Figure 4 shows a comparison between the calculated results including the atomic cross-sections with experiments performed on MnPc thin film (figure 4 (a) and (b)) and in gas phase (figure 4 (c)) at different photon energies. For the 21.2 eV case, the C 2p cross-sections are of the same order of magnitude as the Mn 3d, but the large number of carbon atoms in the molecule translates into the fact that the spectra are dominated by the C 2p features. Since the three structures do not differ much in the carbon contribution, for this photon energy, the spectra compare well to each other and to the experiment.

In opposition, at 1486.6 eV, the d states dominate and therefore the slight differences between structures discussed in the previous paragraph become evident. In comparison to the experiment, both $S_B$ and $S_C$ largely overestimate the relative intensity of band A and have completely different B and C regions. In contrast, $S_A$ displays all the experimental features, with only small shifts in the position of several bands, leading to the conclusion that the electronic configuration of MnPc in the thin film is the calculated ground state $S_A$.

For the gas phase experiment, the conclusion does not come as straightforward as for the thin film. With the increase in photon energy, the $A_1$ and $B_1$ peaks show a gradual and simultaneous increase in intensity. Although the intensity increase is observed in all the three structure, none of them describes well the peak positions and relative intensities observed in the measured data. In brief, $S_C$ displays two overestimated $B_1$ peaks alongside
a too intense $A_1$ band. In $S_B$ the $B_1$ band is extremely intense, while both $B_2$ and $B_1$ are shifted towards lower binding energies as compared to the experiment. Finally, the $B_1$ $S_A$ peak is merged into $B_2$ and the $B_2$ feature is shifted in comparison to the measurement. In contrast, a 50% - 50% mixture of the $S_A$ and $S_B$ configurations reproduces much better the trends observed in the experimental spectra, as peaks $A_1$ and $B_1$ gradually and simultaneously grow in intensity, while the position of $B_2$ is closer to the measured binding energy. This suggest that instead of a well defined electronic configuration, the gas phase contains a mixture of the ground state with a higher energy configuration. This could be due to the fact that right before measurement the molecules are heated up to 300$^\circ$C, a temperature corresponding to an energy of the same order of magnitude as the energy difference between $S_A$ and $S_B$.

The fact that two different electronic configurations of the same molecule and corresponding to the same spin state have been experimentally observed opens up the possibility of switching from one two the other. Many new questions arise related to the possibility of separately observing each of the two structures, the existence of useful switching mechanisms and the extent to which they could be reversibly manipulated. Even though yet far from practical applications the possibility of controlling the electronic configuration of a molecule is appealing and worth to explore.
To summarize, the electronic structure of PCBM and MnPc was investigated by density functional theory. The theoretical methods were used to explain the measured spectroscopic properties of the two materials with the final goal of gaining insight into molecular processes.

More specifically, in the case of PCBM, the NEXAFS $\pi^*$ region was analysed in detail since it undergoes dramatic changes as the molecule is exposed to light. An important conclusion is the fact that the photodegradation processes are related to changes of the fullerene cage. Possible deterioration pathways include oxidation, adsorption of small molecular groups and photodimerization. The several alternatives will be investigated in the future by joint DFT, NEXAFS and core level XPS studies.

Secondly, in MnPc, the valence band electronic structure was analysed by DFT and photoelectron spectroscopy in order to elucidate the long-standing debate over the 3d orbital ordering and occupation. It was found that in thin films the configuration of the metal d levels corresponds to the calculated ground state, while the gas phase displays a mixed electronic structure due most likely to the fact that the molecules are heated up right before the measurement. The experimental observation of two distinct possible configurations of the same molecule opens up the prospect of controlling the electronic state of the central metal in view of molecular spintronics and memory applications. Two interesting questions which will be tackled in future projects are related first to the nature of the two “excited” states and second to the existence of useful switching mechanisms from one structure to the other.
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Bibliography


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Chapter 5. Conclusions and Outlook . . .


Near-edge X-ray absorption fine structure study of the C$_{60}$-derivative PCBM

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A B S T R A C T

The fullerene derivative [6,6]-phenyl-C$_{60}$-butyric acid methyl ester (PCBM) are commonly used electron acceptors in active materials for organic photovoltaics (OPV). In small-molecule OPV, the solar cells are built up by vacuum-deposition of thin layers of C$_{60}$ and an electron-donor material. In polymer-based OPV, the active layer is a thin film coated from a blend solution of PCBM and an electron-donating polymer. The electronic structures of these conjugated molecules are important for the dissociation and separation of excitons into mobile charges. For C$_{60}$ and PCBM, the lowest unoccupied molecular orbital (LUMO) is expected to play an important role in the electron transfer and in the transport of electrons from the donor–acceptor interface to the low work function electrode.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is a very useful tool to identify organic molecules at surfaces by probing element-specific excitations of 1s electrons to unoccupied molecular orbitals [1] and has recently been used intensively in the field of OPV materials [2–5] to determine the surface composition of the active layer in bulk-heterojunction solar cells [6–7]. The final states determined from NEXAFS resonances are core-excited and their densities of states differ from the ones of the unoccupied levels in the ground state that are associated with processes such as electron transport in solar cells. NEXAFS at the C K-edge is of particular interest for conjugated polymers and molecules [8–10], as well as for materials that consist solely of carbon, such as fullerenes, fullerene derivatives [11], carbon nanotubes [12] and graphene [13], because it reveals the rich fine structure of their unoccupied orbitals. Already shortly after their discovery, C$_{60}$ and C$_{70}$ were studied by NEXAFS spectroscopy and distinct resonances were found, evidence of their molecular character and weak intermolecular interactions [14]. Besides, these spectra were qualitatively reproduced by Hückel calculations [14]. NEXAFS studies on PCBM have been carried out more recently [2,8,15–17]. While the first studies [2] have an energy resolution that was not high enough to reveal all the different π*-resonances, more recent work [8,15–17] shows a richer π* fine structure. Several strategies have been reported to investigate the origin of the absorption resonances. Bazylewski et al. compared the measured spectra of a PCBM film with Density Functional Theory (DFT) simulations and could distinguish contributions from the PCBM side chain from those of the fullerene and the phenyl [15]. Richter et al. analyzed the resonances in the X-ray absorption spectrum of PCBM in detail [16]. Of particular interest for the present study is the analysis of the shoulder to the first π*-resonance (at 0.5 eV higher photon energy) observed in experimental spectra of PCBM [8,15–17]. Bazylewski et al. attributed this feature, that is absent in C$_{60}$, to the breaking of the symmetry of the strongly delocalized C$_{60}$-LUMO orbital by the presence of the side chain and assigned it to the C atoms around the side chain attachment point [15]. A similar high-energy shoulder has also been found by Patnaik et al. in the absorption spectra of a C$_{60}$-functionalized self-assembled monolayer on gold [18]. There the presence of the shoulder was attributed to the formation of a C$_{60}$ aggregated phase, by analogy with a similar feature observed in graphite. Clearly no consensus has been reached yet regarding the origin of this shoulder and further theoretical investigations are needed.

Here we present a combined experimental and theoretical study of the C K-edge NEXAFS spectra of PCBM. The measurements were performed on spin-coated films of PCBM on silicon, DFT simulations were computed for an isolated PCBM molecule, and the

1. Introduction

The fullerene C$_{60}$ and its derivative [6,6]-phenyl-C$_{60}$-butyric acid methyl ester (PCBM) are commonly used electron acceptors in active materials for organic photovoltaics (OPV). In small-molecule OPV, the solar cells are built up by vacuum-deposition of thin layers of C$_{60}$ and an electron-donor material. In polymer-based OPV, the active layer is a thin film coated from a blend solution of PCBM and an electron-donating conjugated polymer. The electronic structures of these conjugated molecules are important for the dissociation and separation of excitons into mobile charges. For C$_{60}$ and PCBM, the lowest unoccupied molecular orbital (LUMO) is expected to play an important role in the electron transfer and in the transport of electrons from the donor–acceptor interface to the low work function electrode.

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Here we present a combined experimental and theoretical study of the C K-edge NEXAFS spectra of PCBM. The measurements were performed on spin-coated films of PCBM on silicon, DFT simulations were computed for an isolated PCBM molecule, and the

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contributions from various segments of the molecule were considered separately. We have investigated in detail the fine structure of the first $\pi^*$-resonance peak. Our results show that the first $\pi^*$-resonance is composed of contributions of the 1s-LUMO transitions of both fullerene and phenyl carbons, while the next two major resonances only contain contributions from the fullerene. The shoulder towards higher energy in the first $\pi^*$ consists of a set of three small peaks that contain contributions from specific carbon atoms in the phenyl and in the cage.

2. Methods

2.1. Experimental methods

Thin films of PCBM were prepared by spin-coating from a PCBM (99.5%, Solenne BV, The Netherlands) solution in chloroform with a concentration of 12 mg/mL. The spin-coating was performed in air under dark conditions (only illumination from a red dark room photo lamp, from DR Fisher, Germany) with a spin speed of 3000 rpm during 60 s. The substrates were cut from n-type silicon wafers with 001 orientation and a resistivity of 0.001–0.003 $\Omega$cm. They were cleaned according to the standard RCA method, without the final HF-etching step, so that a hydrophilic surface is preserved [19–21]. The films were protected from white light during all stages until measurement. NEXAFS spectra were recorded at beamline D1011 of the MAX-lab National Laboratory for Synchrotron Radiation in Lund, Sweden. Total electron yield spectra (TEY) were obtained from the sample drain current, while partial electron yield spectra (PEY) a multichannel plate detector was used with a retarding voltage of –150 V applied to the entrance grid. Spectra were measured at the magic angle (55° incidence, relative to the sample surface). The spectra were divided by the corresponding spectrum of a gold film on mica that was cleaned by in situ sputtering with argon, and then normalized in the high photon energy region [1,22]. The photon energy scale was calibrated by using the $\pi^*$ peak of highly oriented pyrolytic graphite (HOPG) as a reference [23]. No X-ray damage was observed.

2.2. Computational methods

The geometrical structure of PCBM was optimized with the Gaussian 09 program [24], and a full relaxation of all the atoms was allowed. We used the hybrid B3LYP exchange–correlation functional [25] and the 6-31G(d,p) basis set (valence double $\delta$ plus polarization) for all the centers [26]. The NEXAFS C K-edge spectra were generated for each carbon atom of the PCBM molecule with the gradient-corrected DFT program StoBe [27]. The exchange functional by Becke [28] and the correlation functional by Perdew [29] were employed. The computation of the excitation energies and of the transition moments was performed in StoBe by using an augmented diffused basis set (19s, 19p, 19d) [30]. To describe the core excited C the IGLOO-III triple $\zeta$ basis of Kutzelnigg, Fleischer and Schindler [31] was used and an effective core potential of 4 electrons provided by the StoBe package was chosen for the remaining carbons. The non-carbon atoms were described by a double $\delta$ plus valence polarization basis set also provided by the StoBe package. The excited 1s state was represented as a full core–hole [32]. The ionization potentials [IP] were computed separately for each carbon atom according to the $\Delta$Kohn–Sham method [30] and the values obtained are in the range of 289.8–290.6 eV for the fullerene atoms, 289.6–289.9 eV for the phenyl atoms, and 289.9–293 eV for the rest of the side chain. The energy positions of the single atom NEXAFS curves were approximated according to the computed IP’s ($\Delta$KS-SCF correction). The spectral intensities were generated from the computed dipole transition probabilities and the results were then convoluted by Gaussian curves in order to facilitate comparison with experiment. For each carbon separately, a Gaussian broadening with a fixed full width at half maximum (FWHM) was used in the low energy part of the spectrum, while, starting from a few eV below the IP, the FWHM was linearly increased from the initial value up to 2 eV in order to better reproduce the experimental continuum region. In Figure 1, the 0.4 eV FWHM up to IP-6 eV was linearly increased over the following 9 eV and then kept constant at 2 eV. For Figures 2 and 3 a narrower broadening was employed in order to observe the finer structures slightly above the first peak. More specifically, up to IP-4.8 eV a 0.1 eV FWHM was chosen. It was linearly increased to 2 eV and finally kept constant at this value from IP-3 eV onwards. The total calculated NEXAFS spectrum was obtained by summing up all the single atom 1s theoretical spectra. All calculated spectra were shifted by 2 eV towards higher energies such that the position of the first peak matched the experimental value.

3. Results and discussion

The experimental C K-edge NEXAFS spectrum in TEY-mode and the calculated total spectrum of PCBM are presented in Figure 1. Additionally, the calculated spectra of a selection of different segments of the PCBM molecule are shown in order to investigate the origin of the experimentally observed resonances. The computed spectra are obtained by summing up the single atomic contributions of the carbons that constitute the particular chemical moiety. The general shape of the experimental and the peak positions match earlier reported spectra of PCBM well [8]. Comparison with NEXAFS spectra of C60 also shows that the features of the PCBM spectrum are dominated by the resonances of the fullerene cage [14]. To identify the origin of the resonances, we compared the experimental TEY spectrum with the calculated results. Peak 1 is well reproduced by the calculation, and consists of contributions from the fullerene carbon atoms (denoted as C1–C60 in the inset of Figure 1), and from carbon atoms in the phenyl group (C62-C67). Peaks 2 and 3 contain only contributions from the fullerene cage. The side chain C-atoms contribute to higher energy peaks, starting from peak 4 and its lower energy shoulder centered at around 287.4 eV. This shoulder and a weak contribution between peak 4 and 5 are not observed in the experimental NEXAFS spectrum. Additionally, the intensity ratio of peak 2 to 3 is slightly higher in the calculated total spectrum than in the experimental one. Of particular interest is the origin of the high-energy shoulder of peak 1, S, which is clearly distinguished in the experimental TEY spectrum, but not in the total calculated PCBM spectrum of Figure 1. Actually, an asymmetry in the first $\pi^*$-resonance towards higher photon energies can be observed in the calculated spectrum, as well as the corresponding transitions in the bar graph. Yet, the shoulder S in the experimental TEY-NEXAFS spectrum appears larger than the asymmetry to peak 1 found in the calculated spectrum. We will return to this discrepancy later in the manuscript. To analyze this asymmetry in the calculated spectrum more accurately, we zoomed in into the $\pi^*$-resonance region and used a smaller FWHM for the calculated spectrum in Figure 2, which resolves the resonances contributing to the asymmetry better. The asymmetry of peak 1 found in the calculated spectrum is the result of three individual peaks positioned between 284.6 and 285.2 eV.
To analyze the origins of the three peaks, denoted by $S_1$, $S_2$ and $S_3$ in Figure 3, we have first studied the single carbon 1s spectra in this region to identify the parts of the molecule that provide the main contributions. Then we deduced from the calculated excitation energies which transitions these resonances correspond to.

In Figure 3 the total calculated spectrum and the fullerene contribution are presented, together with single atom spectra of C62 and of two types of carbon atoms from the cage. We found that all carbon atoms in the fullerene cage, except C2 and C3, have contributions to $S_1$ and $S_2$. The atoms that contribute the most to $S_1$ and $S_2$ (atoms 18, 19, 23, 25, 27, 28, 29, 39, 40, 43, 45, 46, 47, 52, 53, 54) are from the right and left molecular hemispheres and are marked in magenta in Figure 3.

The calculated spectrum of C29 is given as an example (the rest being left out for clarity). The atoms that contribute largely to peak $S_3$ (atoms 4, 5, 6, 7, 8, 9, 10, 11, 12, 13) are marked in orange and are close to the PCBM side chain attachment point. The spectrum of C8 is given as an example. The shifts of the main $\pi^*$-resonance in the single atom spectra of the different carbon atoms are caused by energy differences in their 1s ground states, as well as by variations in the core exciton binding energies for the different C sites. The side chain atoms give no contribution at all to the three peaks $S_1$, $S_2$, and $S_3$, with the exception of C62, the carbon of the phenyl group that is bound to C61 (marked in blue in Figure 3), which has a relatively large contribution to peak $S_1$. This peak actually corresponds to the lowest-energy resonance of this atom, i.e. the 1s-LUMO transition of C62. The 1s ground state of C62 is lowered and the resonance is therefore shifted to higher photon energies. For the other phenyl carbon atoms the lowest-energy transition contributes mainly to peak 1 in the total spectrum. The reason...
for this shift lies in the types of bonds the phenyl atoms are involved in. Atom C62 is bound to a third carbon atom, while the other phenyl atoms are bound to hydrogen atoms. However, due to the approximation inherent the energy shift, we cannot completely exclude the contribution of the other phenyl atoms to S3.

Table 1 summarizes the calculated excitation energies and the corresponding assignments for peak 1 and the shoulder peaks, which are all generated by electronic transitions from the 1s state of fullerene and phenyl carbons to LUMO, LUMO+1 or LUMO+2. More specifically, peak 1 is a result solely of 1s-LUMO transitions, while S1 is a superposition of 1s-LUMO+1 transitions for the fullerene type of atoms and of the 1s-LUMO transition of the C62 atom. S2 is mostly due to the fullerene 1s-LUMO+2 electronic transitions and to a number of 1s-LUMO+1 excitations. The third shoulder contribution, S3, is a result of only a few fullerene 1s-LUMO+2 electronic transitions, and, as a consequence, it has lower intensity in the total calculated spectrum.

Our results also show that C61, the atom between the fullerene cage and the PCBM side chain, does not give any contribution to peak 1, S1 or peak 2 (see Figure 1). Indeed, the first 1s electronic transition of C61 to an unoccupied electronic level takes place at higher energies (see Figure 1) and contributes to peak 3 in the total spectrum. The second peak in the single atom spectrum of C61 gives a small contribution to the left shoulder of peak 4 (not observed in the experiment), while the third resonance contributes to peak 4 itself. Contrary to Bazylewski et al., who have associated the shoulder [peak A in Ref. [15]] to the fullerene carbons close to the side chain attachment point [15], we found that the intermediate carbons, C2 and C3, do not contribute to S. It is important to mention that the spectrum of C2 and C3, the two fullerene-carbons covalently bound to C61, (see Figure 1) is very similar to the spectrum of C61, the peaks being just slightly shifted to lower energies (0.3 eV). The differences between the calculated spectra of C61, C2, and C3 in comparison with the rest of the fullerene atoms can be explained by the differences in the orbital hybridization of these atoms. C61, C2 and C3 are all involved in four single covalent bonds and are, thus, sp3 hybridized, while all other carbons in the C60 cage have a sp2-derived hybridization [33].

One interesting feature of both calculated and experimental spectra is the high intensity of the first peak. The high intensity of this transition is due to an excitonic effect that has earlier been observed in compounds like C60 and C70 [32]. The exciton is a quasiparticle, which results from the Coulomb interaction between an electron and a hole. The electron–hole interaction leads to a lowering of the energy of unoccupied levels and a localization of the corresponding molecular orbitals in the region of the atom where the core–hole was created, making the transitions between the 1s orbital and the LUMO far more likely. We observed that the phenyl carbon atoms also contribute strongly to peak 1. Our results show that the phenyl has a similar excitonic effect. The localization of the LUMO over the phenyl moiety, by a core–hole being created in the phenyl 1s states, is even stronger than the localization over

Table 1

<table>
<thead>
<tr>
<th>Peak</th>
<th>Component</th>
<th>Average ( E_{\text{inc}} ) [eV]</th>
<th>Average ( E_{\text{exc}} ) [eV]</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fullerene</td>
<td>289.87</td>
<td>284.46</td>
<td>1s-LUMO</td>
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<tr>
<td></td>
<td>Phenyl (C63–C67)</td>
<td>289.65</td>
<td>284.49</td>
<td>1s-LUMO</td>
</tr>
<tr>
<td>S1</td>
<td>Fullerene</td>
<td>289.87</td>
<td>284.74</td>
<td>1s-LUMO+1</td>
</tr>
<tr>
<td></td>
<td>Phenyl (C62)</td>
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<td>284.70</td>
<td>1s-LUMO</td>
</tr>
<tr>
<td>S2</td>
<td>Fullerene</td>
<td>289.88</td>
<td>284.79</td>
<td>1s-LUMO+1</td>
</tr>
<tr>
<td></td>
<td>Fullerene</td>
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<td>284.90</td>
<td>1s-LUMO+2</td>
</tr>
<tr>
<td>S3</td>
<td>Fullerene</td>
<td>289.91</td>
<td>285.09</td>
<td>1s-LUMO+2</td>
</tr>
</tbody>
</table>

\(^{a}\) C1, C16–C19, C22, C23, C25, C27–C32, C34, C36, C37, C39, C40, C41, C43, C45–C47, C56–C59.

\(^{b}\) C5–C7, C52–C55.

\(^{c}\) C18, C19, C22–C25, C27–C29, C36, C37, C39, C40, C43, C45–C47, C56–C59.

\(^{d}\) C4–C15.
the fullerene (as seen from the higher intensity of C62 in Figure 3). When the core hole is formed on the ester group, a similar effect is also observed in the calculated spectrum (see Figure 1), giving rise to the shoulders to peak 4 (and the slightly increased intensity of peak 4).

As mentioned earlier, the shoulder S in the TEY spectrum is more pronounced than can be accounted for from the asymmetry of peak 1 predicted from the calculated results. Figure 4 shows the \( \pi^- \)-region of the experimental spectra of PCBM collected in PEY and TEY mode. The spectrum of this sample taken in PEY-mode, which is more surface sensitive than TEY, shows an interesting difference. In the \( \pi^- \) region, at 285.0 eV, close to the position of shoulder S the PEY spectrum shows a peak that is considerably larger than the shoulder in TEY. This higher intensity indicates a difference in the molecules at the very surface of the thin film. Contributions originating from a small amount of contamination, or degradation of the molecules, cannot be excluded. Such a surface effect would then also, be it to a smaller extent, affect the TEY spectrum and may explain the discrepancies with the calculations in this energy region. Further studies of this surface effect are needed to better understand its origin.

4. Conclusions

To summarize, we have presented the experimentally obtained high-resolution TEY-NEXAFS spectrum of the PCBM molecule and have been able to match the resonances well with the calculated spectrum, using the full core-hole approach. By analyzing the calculated spectra produced by different components of PCBM, we were able to assign the experimental peaks to specific groups of carbon atoms. Thus, the first experimental peak, the so-called \( \pi^- \)-resonance, corresponds to a 1s-LUMO transition by a core electron from the fullerene or phenyl carbon atoms. Peaks 2 and 3 result from 1s electronic transitions to higher energy unoccupied orbitals in the fullerene cage, while the side chain carbon atoms contribute to peak 4 in the experimental spectrum. The high intensities of the 1s-LUMO transitions responsible for the first experimental band are a direct result of the excitonic effect, which localizes this molecular orbital around the core–hole atom region. A shoulder centered at 285.0 eV, i.e. 0.5 eV above the \( \pi^- \)-resonance peak, is observed in the TEY spectrum. Our simulations demonstrate that only a small contribution to this shoulder originates from the PCBM molecule itself, and the remaining part is due to a modification of the surface of the film. From this study we can conclude that a NEXAFS spectrum of a pure PCBM film should not show a peak at this photon energy of 285.0 eV.

Acknowledgements

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References

Elucidating the 3d Electronic Configuration in
Manganese Phthalocyanine

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Abstract

In order to shed light on the metal 3d electronic structure of manganese phthalocyanine, so far controversial, photoelectron measurements were performed both in the gas phase and as thin film. With the purpose of explaining the experimental results, three different electronic configurations close in energy to one another were studied by means of density functional theory. The comparison between the calculated valence band density of states and the measured spectra revealed that in gas phase the molecules exhibit a mixed electronic configuration, while in thin film, manganese phthalocyanine finds itself in the theoretically computed ground state, namely the $b_{1g}^{1}e_{g}^{3}a_{1g}^{1}b_{1g}^{0}$ electronic configuration.

Introduction

Organic molecules with a 3d transition metal center have become significant owing to the fact that they play a major role in a wide variety of emerging fields such as organic electronics\(^1\) and spintronics.\(^2\) In particular, manganese phthalocyanine (MnPc) is an organic semiconductor and molecular magnet able to act as a spin-filter.\(^3\) Moreover, its spin can be manipulated in a controlled manner\(^4\)\(-\)\(^8\) giving rise to its possible use in molecular spintronics\(^7\) and quantum computing applications.\(^9\)\(-\)\(^11\) In fact, it has been recently shown that the spin polarization of a single MnPc molecule may be controlled either by the chemical coordination of ligands to the central metal,\(^4\)\(^,\)\(^8\) or according to the interplay between Kondo screening and superconducting pair formation.\(^6\)\(-\)\(^12\) In this context, not only would a precise knowledge of the exact metal 3d electronic configuration of MnPc shed light on the above mentioned effects, but it would also prove to be essential in view of spintronics applications by opening the possibility of controlling the orientation of the magnetic anisotropy of the molecule. In fact, it has been recently proven that the addition or removal of ligands could be used to modulate the direction of the spontaneous magnetization.\(^13\) Since the highest occupied 3d orbital and respectively the lowest unoccupied bring, in general, the largest
contribution to the anisotropy, understanding the manner in which the metal states are pop-
ulated may prove essential in both clarifying the origins of the molecular magnetic anisotropy
as well as in reversibly controlling its orientation (from uniaxial, to in plane and vice versa).

As opposed to the majority of transition metal phthalocyanines (TMPCs), for MnPc the
high structural symmetry is broken in a Jahn-Teller (JT) manner. The molecule exhibits
D_{2h} symmetry since an odd number of electrons populate the doubly degenerate e_g molecular
state, making MnPc an interesting model for analysing the correlation between electronic
structure and molecular geometry in view of the JT effect.

According to ligand-field theory, a transition metal placed into a D_{4h} symmetric en-
vironment will exhibit a splitting of its 3d levels as depicted in the inset of figure 1. Con-
troversy exists regarding the manner in which these states are populated in order to give
rise to the intermediate spin (S=3/2) of MnPc. There are three possibilities of metal 3d
orbital occupation that have been discussed which all leave the d_{x^2−y^2} level unoccupied:
the b_1^1 e_g^3 a_{1g}^1 b_{1g}^0 electronic configuration (denoted S_A here), b_2^2 e_g^2 a_{1g}^1 b_{1g}^0 (denoted S_B) and
b_2^1 e_g^2 a_{1g}^1 b_{1g}^0 (denoted S_C). Several experimental studies performed at different temperatures
on either MnPc single crystal, or MnPc deposited on noble metal substrates report not only
different electronic configurations of the metal, but also different symmetries of the highest
occupied molecular orbital (HOMO). More specifically, two studies, one using x-ray absorp-
tion spectroscopy (XAS), the other using both magnetic circular dichroism (MCD) and
absorption spectroscopy, report the S_A (b_2^2 e_g^2 a_{1g}^1 b_{1g}^0 ) electronic configuration as the ground
state, while a third one performed by XAS and x-ray MCD confirms this configuration,
but reveals a different HOMO, namely the a_{1g}. A L-edge XAS study reports two elec-
tronic configurations in competition (S_A and S_B), whereas a different magnetic experiment reveals only S_B (b_2^2 e_g^2 a_{1g} b_{1g}^0 ) as the ground state.

Similar controversy exists in density functional theory (DFT) studies performed using
different exchange and correlation functionals, basis sets and atomic orbital types. A b_2^1 e_g^2 a_{1g}^1
ground state is reported by Liao et al. as well as by Wang et al. On the other hand,
Figure 1: Schematic representation of the MnPc molecular geometry alongside with a simplified and general view of the metal 3d electronic levels according to ligand field theory (top left corner). The molecule is planar and the z axis is perpendicular to the molecular plane.

Marom and Kronik,\textsuperscript{14} by enforcing symmetry, reveal the different character of the Mn highest occupied d level. An $e_g$ HOMO is reported when the symmetry is broken, while by conserving symmetry they obtain either a $b_{2g}$ or an $a_{1g}$ HOMO, the two structures being close in energy and competing. In addition, a joint theoretical (DFT) and experimental (valence band photoemission at 21.2 eV photon energy) study\textsuperscript{15} reports an $e_g$ symmetry for the HOMO level.

In order to clarify the controversy, in the present study the $S_A$, $S_B$ and $S_C$ electronic configurations were analysed by means of DFT with the B3LYP hybrid functional. The computed valence band spectra were compared to photoelectron spectroscopy (PES) measurements performed at different photon energies both in gas phase and thin film. In this
way, exploiting the variation of the atomic orbital cross sections for different photon energies, we could obtain a detailed knowledge of the elemental composition of the electronic states in the valence band.

Experimental

The PES measurements on the gas phase sample were performed at the GAs-PHase (GAPH) beamline of the Elettra synchrotron in Trieste, using a VG analyzer mounted at 54.7° with respect to the electric vector of the light. Manganese(II) phthalocyanine (MnPc) (powder, purity 95%) was purchased from Sigma–Aldrich. The molecules were further purified in situ before the experiment to reduce traces of contaminants. The sample was sublimated using a custom built resistively heated furnace. The MnPc molecules were evaporated at 314±1°C, avoiding dissociation observed at higher temperatures. Calibration of the binding energy of the outer-valence spectra was done by He (vertical ionization energy, VIE = 24.59 eV) and by traces of vaporized water (VIE = 12.62 eV) found in the system. During the whole experiment, the pressure at the ionization region remained constant (ca. 8 × 10⁻⁸ mbar). PE spectra have been normalised to the photon flux and to the analyser transmission function. The thin film experimental measurements were performed for MnPc deposited on Au/mica substrate purchased from George Albert Physikal Vapor Disposition. Before the MnPc deposition, the surface was cleaned by several cleaning cycles (Ar⁺ sputtering, followed by annealing at 450°C) resulting in a reconstructed Au(111) surface. The MnPc molecules, the same used in gas phase measurements, were degassed and thermally evaporated from a quartz crucible in ultra-high vacuum conditions (base pressure approx. 10⁻¹⁰ mbar). The evaporation temperature used did not exceed 315°C in order to avoid the molecule decomposition. A monochromatic x-ray source (Al Kα, 1486.7 eV), a He discharge lamp (21.2 eV) and a hemispherical analyser were used to perform XPS and UPS measurements. The binding energy scale was calibrated with the Fermi level of the gold substrate.
Computational Methods

From the theoretical point of view, single molecule DFT calculations were performed using the Gaussian 09 program. A full relaxation of all the atoms was allowed. The hybrid B3LYP exchange-correlation functional was used along with the 6-31G(d,p) basis set (valence double zeta plus polarization) for carbon, nitrogen and hydrogen atoms, while for Mn, the cc-pVTZ (valence triple zeta plus polarization) was employed. Starting from $D_4h$ symmetry, the system relaxes to $D_{2h}$ symmetry in the case of the $S_A$ electronic configuration. The other two electronic structures are obtained by first depopulating the highest occupied molecular orbital (HOMO) and then occupying a spin-down unoccupied level, followed by a structure optimization. Both of the resulting relaxed geometries are very close to the $D_{4h}$ point group (Fig. 2 (c)). The total and partial density of states (DOS) for the three different electronic configurations was determined using the $c^2$ population analysis (SCPA) method as performed in a previous study. The partial density of states (PDOS) was used to simulate the photoelectron valence band spectra at different photon energies. For this purpose, the PDOS for each atomic orbital was multiplied by its corresponding photoionization cross section at the specific photon energy and a total DOS (TDOS) for this specific energy was determined. In order to facilitate the comparison with experiments, the theoretical bar graphs were broadened using Gaussian functions. For figure 3, the calculated DOS were broadened using a 0.5 eV initial full width at half maximum (fwhm) which was linearly increased to 2.0 eV in the range -5.0 eV to -15.0 eV and then kept constant. The 21.2 eV photon energy simulated spectra were shifted by 3.33 eV and the 1486.7 eV results by 3.8 eV towards lower binding energies in order to align the calculated spectra to the experimental first peak. In figure 4, a gaussian broadening was performed starting with a 0.3 eV initial fwhm which was linearly increased to 2.0 eV in the range -6.5 to -10.0 eV and then kept constant. The spectra were normalized to a C 2p peak centred at -12.1 ev. The mixed spectra were shifted with 1.37 eV to higher binding energies. Similarly, $S_A$ was shifted by 1.37 eV, $S_B$ by 1.31 eV and $S_C$ by 1.6 eV, all of them towards higher binding energies in
order to match the first experimental peak.

Results and discussion

According to the computed total energy, the $S_A$ electronic configuration corresponds to the ground state of the intermediate spin MnPc. $S_B$ and $S_C$ are slightly higher in energy, the first one by 0.11 eV and the second by 0.23 eV. Structurally, the main differences between the three structures concern the Mn-N as well as the C-N bond lengths. The relevant bonds are shown in Fig. 1, where the different types of N atoms are labelled as $N_i$ and $N_m$ and the different C atoms are labelled $C_\alpha$ and $C_\beta$. The largest change in bond length for the different electronic configurations is the Mn-$N_i$ bond length (denoted 'a' in Fig. 1), which varies between 1.957 Å for $S_A$, to 1.971 Å for $S_B$ and 1.967 Å for $S_C$. Other differences, not as remarkable, involve the pyrrole $C_\alpha$ atom ('b', 'c' and 'd' bond lengths in Fig. 1). More precisely, the $C_\alpha$-$N_i$ bond length is 1.384 Å in the case of $S_A$ decreasing to 1.378 Å for the other two electronic configurations. The $C_\alpha$-$N_m$ bond has a length of 1.324 Å in the ground state, changing to 1.328 Å for $S_B$ and to 1.326 Å for $S_C$. Finally, the $C_\alpha$-$C_\beta$ bond length varies between 1.453 Å ($S_A$), to 1.457 Å ($S_B$) and 1.456 Å ($S_C$).

A comparison between the Mn 3d PDOS of the three structures in the HOMO-LUMO region shows that the $d_{x^2-y^2}$ orbital is high in energy and remains unoccupied for both spin channels (Fig. 2 (a)). Differences between $S_A$, $S_B$ and $S_C$ are related to the character of the HOMO, to its position and to the HOMO-LUMO gap (defined as the energy difference between the lowest unoccupied level in the spin down channel and the highest occupied level of the same spin) (Table 1). The $S_A$ HOMO is a partially filled doubly degenerate $e_g$ orbital ($d_{xy}$, $d_{yz}$) with an eigenvalue of -4.46 eV. The calculated HOMO-LUMO gap is 1.35 eV. For the $S_B$ electronic configuration, the HOMO, exhibiting $b_{2g}$ character, is centred at -4.59 eV and the HOMO-LUMO gap becomes 1.65 eV. Finally, the $S_C$ HOMO has $a_{1g}$ symmetry and is higher in energy than the other two (-4.31 eV) with the smallest HOMO-LUMO gap (1.32
Figure 2: (a) The calculated PDOS for the Mn 3d levels of $S_A$, $S_B$ and $S_C$ respectively. The spectra were broadened using gaussian functions of 0.3 eV constant full width at half maximum (fwhm). The dashed lines represent the HOMO position. (b) Comparison between the TDOS, Mn 3d and C 2p PDOS of $S_A$, $S_B$ and $S_C$ respectively. Both bar graphs and broadened spectra (0.3 eV constant fwhm) are shown. The Mn 3d intensities were multiplied by a factor of 4 for clarity. (c) Segment of MnPc with the relevant bond lengths for each structure.

### Table 1: Calculated electronic properties of the $S_A$, $S_B$ and $S_C$ electronic configurations.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Occupation</th>
<th>HOMO symm.</th>
<th>Orbital type</th>
<th>HOMO-LUMO gap</th>
</tr>
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<tr>
<td>$S_A$</td>
<td>$b_{2g}^1 e_{g}^1 a_{1g}^1 b_{1g}^0$</td>
<td>$e_g$</td>
<td>$d_{xz}, d_{yz}$</td>
<td>1.35 eV</td>
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<tr>
<td>$S_B$</td>
<td>$b_{2g}^2 e_{g}^2 a_{1g}^1 b_{1g}^1$</td>
<td>$b_{2g}$</td>
<td>$d_{xy}$</td>
<td>1.65 eV</td>
</tr>
<tr>
<td>$S_C$</td>
<td>$b_{2g}^3 e_{g}^3 a_{1g}^2 b_{1g}^0$</td>
<td>$a_{1g}$</td>
<td>$d_{z^2}$</td>
<td>1.32 eV</td>
</tr>
</tbody>
</table>

Figure 2 (b) shows a comparison between the computed TDOS of the three electronic structures. The origin of the peaks is analysed by comparing the TDOS to the Mn 3d and C 2p partial densities of states. The N 2p PDOS is presented in the supporting information. The main features of the spectra are denoted A-G, while the peaks in each region are designated with numbers. It is very important to note that $S_A$, $S_B$ and $S_C$ differ strongly in the Mn 3d states, fact that generates DOS curves with different profiles for the three electronic configurations.
structures. The main differences between them arise in the low binding energy range of the spectra (features A, B and C). More specifically, feature A, situated in the HOMO region and consisting of two peaks (A_1, of Mn 3d character and A_2, C 2p related), exhibits different A_1-A_2 splitting for each electronic structure. S_C displays the largest splitting (0.65 eV), as the HOMO is shifted to lower binding energies, while the A peaks of S_B are very close together (0.3 eV) since the HOMO is slightly shifted to higher binding energies. The ground state electronic structure (S_A) presents an intermediate splitting of 0.47 eV. Equally important differences arise in the B region. First of all, the B_1 peak, exhibiting Mn 3d character in all three cases, is hardly visible in the TDOS of the ground state structure. Instead, in the S_B spectrum it is easily distinguishable and it becomes a relatively intense double peak in the S_C electronic configuration. Secondly, in the upper binding energy region of feature B, the Mn 3d bands are present at different positions for each of the three electronic configurations. More precisely, in the S_A case, the metal states contribute to peaks B_4 and B_5, while in S_B the slightly less intense Mn bands are shifted to lower binding energies and contribute to peaks B_2 and B_3. In the S_C TDOS, B_3 has Mn 3d character, similarly to peak B_5 which is shifted towards region C. Finally, another important distinction between the three electronic configurations is the fact that the ground state structure exhibits large Mn 3d character in the C feature, while S_B and S_C lack metal 3d states in the same region.

The above mentioned differences are strongly relevant when comparing the computed spectra to PES measurements performed at different photon energies. Figure 3 displays a comparison between the calculated results and the thin film experiments performed at 21.2 eV (UPS) and 1486.7 eV (XPS) respectively. At 21.2 eV photon energy all three calculated spectra compare well to the experiment and they highly resemble one another. In fact, S_A, S_B and S_C have very similar C 2p PDOS and at this photon energy the excitations from the C 2p levels are much more probable than from metal states.

An interesting conclusion comes when comparing the theory with the XPS (1486.7 eV) experiment. In this case, the Mn 3d states become dominant and it is precisely in this feature
Figure 3: Comparison between the thin film experimental results (UPS and XPS) and the computed spectra at (a) 21.2 eV and (b) 1486.7 eV photon energies. The calculated DOS were broadened and shifted as described in the computational methods section.

that the three structures differ, as previously discussed. The shape and intensity ratios of the TDOS peaks of the $S_A$ structure compare well to the experiment, while the other two calculated spectra are noticeably different. Both $S_B$ and $S_C$ configurations overestimate peaks $B_1$ and $A_1$. Moreover, feature C is strongly underestimated in both. This shows that in the thin films investigated here the MnPc displays the $b_{1g}^4e_{1g}^3a_{1g}^1b_{2g}^0$ ($S_A$) electronic configuration, in agreement to previous experimental studies\textsuperscript{17,18}. On the contrary, in the gas phase a mixed electronic structure manifest itself as will be discussed in the following.

The gas phase PES results at different photon energies are compared to calculated spectra obtained by summing the density of states of two electronic configurations ($S_A$ and $S_B$, Fig. 4). The DOS of $S_A$ and $S_B$ configurations enter with equal weight in the total theoretical spectrum. The reason for considering the possible co-presence of more than one electronic configuration in the same measurement is the fact that the features of the experimental results are not present in any of the individual calculated spectra of all configurations, $S_A$, $S_B$ or $S_C$. This is revealed in Fig. 4 (c), displaying a comparison of the 100 eV photon energy computed results to the gas phase experiment performed at the same excitation energy. The $S_A$ spectrum lacks structure in the $B_2$ region and peaks $B_2$ and $B_1$ do not match the position
Figure 4: Comparison between (a) the gas phase experimental results and (b) the simulated mixed electronic configuration spectra for seven different photon-energies (30-100 eV). The dashed lines mark the positions of the calculated bands. (c) Comparison between the 100 eV calculated results and the gas-phase experiment performed at the same photon energy. The dashed lines mark the positions of the experimental peaks. All the calculated spectra were broadened, normalized and shifted as described in the computational methods section.

of the corresponding experimental bands. The $S_B$ reproduces well the $B_2$ region, but the $B_1$ peak is much too intense and $A_2$ completely vanishes. As for the $S_C$ structure, it displays a largely overestimated $A_1$ band and a double $B_1$ peak higher in intensity than the rest of the $B$ region.

As opposed to the pure electronic configurations, the spectra obtained by summing the TDOS of two electronic configurations compare well to the experiment and reproduce the observed trends, namely the intensity growth of the $A_1$ and $B_1$ peaks. A presence of a small percentage of the $S_C$ electronic configuration, as well as of the metal-free phthalocyanine cannot be excluded, but for the current study, this percentage was not quantifiable and therefore the $S_C$ structure and $H_2Pc$ were left out. This shows that in the gas phase experiments the MnPc molecules find themselves in either $S_A$ or $S_B$ electronic configuration. During the gas phase measurements the molecules are heated up to $300^\circ$ C, having a thermal energy approaching our calculated energy difference between the $S_A$ and $S_B$ configurations. Hence Maxwell-Boltzmann statistics at this temperature would provide a mixture of molecules in
configuration $S_A$ and $S_B$. It is not unlikely that the calculations overestimate with a small amount the energy difference between these two configurations and, in this case, the thermal energy could provide a rather equal distribution of the two configurations.

Conclusions

To summarize, DFT calculations of three Mn 3d electronic configurations were performed and the calculated valence band spectra were compared to PES measurements of the MnPc thin film and gas phase at different photon energies. The main result of the present study is that in the thin film, MnPc finds itself in the calculated electronic ground state $b_2^1 e_g^3 a_1^1 b_1^0$, while in the gas phase it exhibits a mixed electronic configuration ($S_A$ and $S_B$). We demonstrate that the ground state of different kinds of samples is determined by factors that one can affect such as temperature, preparation method or intermolecular interactions. In this sense, knowledge of the exact electronic configuration of MnPc and of the fact that it can be modified opens up the possibility for manipulating the direction of the molecular magnetic anisotropy in molecular spintronics applications.

Acknowledgement

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Supporting Information Available:

Comparison between the DOS of $S_A$, $S_B$ and $S_C$. The total densities of states are represented alongside all the components (Mn 3d, C 2p and N 2p).

The gas phase 100 eV photon energy experimental results in comparison to the calculated spectra of $S_A$, $S_B$ and metal-free phthalocyanine multiplied with the corresponding cross-
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Graphical TOC Entry