Structural, Electronic and Magnetic Properties of Molecular Nanomagnets on Surfaces

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TESI PER IL CONSEGUIMENTO DEL TITOLO DI DOTTORE DI RICERCA
(In Russia) il problema poteva soltanto essere posto.

Non poteva essere risolto (in Russia).

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Chapter 1

Molecular Nanomagnets

1.1 Introduction

Magnetism is one of the fundamental properties of matter that, at the nano-scale, gives rise to novel and amazing phenomena. The discovery and the study of these phenomena were possible only with the development of Nanotechnology. Its bottom-up approach offered the possibility to build magnetic nano-systems (nanomagnets) by assembling atoms and molecules [1], [2].

This gave birth a new field of physics, referred to as nanomagnetism [3], that has attracted a growing interest not only for the fundamental research but also for the technological applications. In facts, nanomagnets have been envisaged as nano-devices smaller, faster and cheaper than the traditional systems.

Among the several nanomagnets which have been realized so far, a new class of materials, called Molecular Nanomagnets (MNMs) [4],[5], has attracted a wide attention as they could help to fill the gap between the quantum and classical interpretations of magnetism. Actually, MNMs straddle between classical and quantum world and involve fascinating phenomena like quantum tunneling of magnetization [6], quantum phase interference [7], and quantum coherence [8]. Nevertheless, the interest around MNMs is growing since they represent the smallest possible magnetic storage device as they can retain information into a single molecule. More recently, MNMs have been also proposed as qubits in quantum computation and information processing as well as magneto-refrigerants for special applications.
CHAPTER 1. MOLECULAR NANOMAGNETS

MNMs arise within the study of Molecular Magnetism pioneered by Olivier Kahn[4]. This is an interdisciplinary field where physicists and chemists collaborate very closely: chemists provide techniques to design and synthesize the molecules and physicists develop techniques to measure magnetism and interpret it by means of suitable physical models. Molecular nanomagnets are the result of this "alliance".

From a chemical point of view, MNMs are molecules completely identical to each other in size and shape. They have a magnetic core, either of transition metals or rare earths, surrounded by organic ligands which screen each molecule from the other. They behave as independent objects and this is the reason why they are also called Single Molecule Magnets (SMMs). However the main characteristics of MNMs is that the spins of the magnetic core strongly interact by super-exchange coupling to give a high-spin ground state \( S \). Moreover, they exhibit large uniaxial magneto anisotropy resulting in an anisotropy potential barrier \( \Delta \) in which the \( 2S+1 \) components of the total spin are confined. In other words, MNMs combine large spin and magneto anisotropy to give rise to a potential barrier for reversing the direction of the magnetization. As a consequence a slow relaxation of the magnetization at low temperature and in absence of magnetic field can be observed.

This effect is similar to the bulk ferromagnets where the motion of the domain walls is at the origin of the hysteresis loop. In MNMs the hysteresis loop rises from the purely molecular origin given by the anisotropy potential barrier.

Indeed, unlike classical nanomagnets which are prepared by fragmentation of macroscopic multi-domain particles (top-down approach), MNMs are prepared by solution methods and, once purified, have sharply defined sizes. Moreover, MNMs offers several advantages: i) the peripheral ligands can be easily changed with the desired ones; ii) since they are soluble in a wide range of solvents, they facilitate the preparation of thin films; iii) MNMs have different functionalities like, for instance, switchability of magnetic states with light or electric field and large magnetocaloric effect, which can be in principle combined to obtain completely novel devices.

The exploitation of the functionalities, quoted above, opens a completely new field of research with the aim to realize molecular nano-devices. Two alternative strategies are envisaged: either the development of suitable methods that allow the positioning of a single-molecule between two electrodes or the assembling and addressing of MNM
1.1. INTRODUCTION

monolayer on surface. The first strategy is based on electromigration techniques to
catch a single-molecule between two electrodes like in a break-junction device [9].
Then, statistical transport measurements are performed looking for a signature of the
single molecule. Another possibility is to use the scanning tunneling microscopy (STM)
tip as the first electrode and the conducting substrate as the second one. So far, only
few atoms on surfaces have been probed in this way, revealing interesting Kondo effect

The second strategy is known since several years, but in spite of this, a com-
plete electronic and magnetic characterization of MNMs monolayer remains mostly
unknown. Actually, the achievement of spatially isolated and integer MNMs on sur-
face is not trivial as the interaction of the molecules with the surface is expected to
strongly modify their original properties. For instance, all the attempts to deposit the
most studied $Mn_{12}$ on gold surface showed the disappearance of the hysteresis loop
[12], [13] and a complete reduction of the magnetic core [14].

Thus, new deposition methods, in terms of the choice of the surface, peripheral
ligands and kind of deposition (solution, evaporation, electrospray, laser ablation etc.)
should be studied. On the other hand, high sensitive techniques which allow us a
complete characterization of MNM monolayer properties without affecting them must
be explored.

In this work all these issues addressed above are discussed and suitable strategies
for the assembling of three different MNM families on the gold surface is proposed.
Moreover the study of the interplay among the structural, electronic and magnetic
properties in MNMs is also carried out with several techniques on campus (STM and
XPS) \(^1\) as well as at Large Scale Facilities (XAS and XMCD)\(^2\). The ultimate aim will
be the understanding of the effects of the surface on the molecule’s properties. This
will drive the choice of proper strategies for the deposition.

The thesis is organized as follows: in Chapter 1 the $Mn_{12}$, $Mn_6$ and Cr-based
rings families are introduced. In Chapter 2 the methods used for their deposition on
surface are presented along with the description of the specific derivatives belonging
to these families. In Chapters 3, the experimental techniques for the characterization
of MNMs adsorbed on surface and the preparation of the samples are described.
Results and discussion are presented in Chapter 4 followed by concluding remarks and

\(^1\) STM stays for scanning tunnelling microscopy and XPS for X-ray photoemission spectroscopy.
\(^2\) XAS stays for X-ray absorption spectroscopy and XMCD for X-ray magnetic circular dichroism.
perspectives.

1.2 $\text{Mn}_{12} - \text{ac}$

The first and best studied MNM is the mixed-valent $[\text{Mn}_{12}\text{O}_{12}\text{Ac}_{16}(\text{H}_2\text{O})_4] \cdot 2\text{HAc} \cdot 4\text{H}_2\text{O}$ \(^3\) (in short $\text{Mn}_{12}\text{Ac}$) synthesized by Lis in 1980 [16]. The structure of this complex (Fig. 1.1) is made by a $[\text{Mn}_{12}\text{O}_{12}]$ core containing a central cube of four $\text{Mn}^4$ ions and a non-planar ring of eight $\text{Mn}^{3+}$ ions. The $\text{Mn}^4$ ions are placed in the center of an almost perfect octahedra of oxygen atoms while the $\text{Mn}^{3}$ ions are in the center of octahedra susceptible of Jahn Teller distortion with one O-Mn-O axis longer respect to the other two. These axes represent also the molecular axis of the $[\text{Mn}_{12}\text{O}_{12}]$ core. The molecular structure has space group $I\bar{4}$ and tetragonal symmetry. The core is additionally coordinated by sixteen carboxylate groups and four $\text{H}_2\text{O}$ ligands.

The $\text{Mn}_{12}$ possesses a total high-spin ground state $S=10$ resulting from the antiferromagnetically coupled $\text{Mn}^3$ ($S=2$) and $\text{Mn}^4$ ($S=3/2$). In general the height of the barrier $\Delta$ between the up and down spin states is given by $S^2|D|$ or $(S^2-1/4)|D|$ for integer or half-integer spin ground states, respectively. \(^4\) In case of $\text{Mn}_{12}$ with $S=10$ and $D/k_B = -0.65K$, where $k_B$ is the Boltzmann’s constant, $\Delta$ is about $65K$ and corresponds to the energy difference between the lowest lying $m_s = \pm 10$ and the top lying $m_s = 0$. The potential barrier gives rise to the hysteresis loop in the magnetization curve at very low temperature (few Kelvin).

The thermal relaxation of the high-spin magnetic moment is driven by the Arrhenius law: $\tau = \tau_0 \exp(\Delta/k_B T)$. At higher temperature ($k_B T \geq \Delta$) the magnetization flips easily because the thermal energy is large enough to overcome the barrier. On the other hand, decreasing the temperature, the rotation of the high-spin is gradually frozen because $\Delta \sim k_B T$, then the hysteresis loop of the magnetization appears. Moreover, an imaginary component of the AC susceptibility $\chi''$ can be observed. Fitting the $\chi''$ versus T curves to the Arrhenius law, the prefactor $\tau_0 = 2.1 \times 10^{-7}s$ and $\Delta/k_B = 61K$ for the $\text{Mn}_{12}\text{Ac}$ are obtained. On the basis of these parameters, the blocking temperature $T_B$, defined as the point at which $\tau = 100s$, is about 3 K.

$\Delta$ is also roughly proportional to the product of the magnetic anisotropy and the volume of the molecule. This represents a dilemma, because the smaller volume of the

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\(^3\)Where HAc is the acetic acid group $CH_3COOH$.

\(^4\)D is the zero-field splitting.
molecule, the smaller the values of $\Delta$ and hence $T_B$.

![Figure 1.1: Structure, magnetic coupling and spin ground state of the $\text{Mn}_{12}\text{ac}$, $\text{Mn}_6$ and $\text{Cr}_7\text{Ni-piv}$ molecular nanomagnets.](image)

### 1.3 Hexhanuclear $\text{Mn}^3$

In spite of the preparation of many MNMs containing manganese, iron, cobalt, nickel and vanadium, for many years the $\text{Mn}_{12}$ remained the molecule that can work as magnet at the highest temperatures. By the way, its practical application is still hindered by the low blocking temperature, which does not typically exceed a few kelvin in the most fortunate cases.

Therefore, in recent years great research efforts have been devoted to the synthesis of molecular systems with larger magnetic anisotropy. To this end, a very interesting example is provided by a $S=12$ member of the family with general formula $[\text{Mn}_6^3\text{O}_2(R-sao)_6(\text{O}_2\text{C}R)_2(\text{ROH})_x(\text{H}_2\text{O})_y]$ (hereafter $\text{Mn}_6$), which possesses the new $\Delta_{\text{eff}}$ record-value of $86.4K$, leading to a blocking temperature of about $4.5K$. 
CHAPTER 1. MOLECULAR NANOMAGNETS

The representative core (Fig. 1.1) of the \([Mn^3+O_2(sao)_6(O_2CP_{h}2(EtOH)_{4}])\] derivative [17] contains a non-planar triangular subunits linked by two central oximato atoms (Fig. 1.2). This class of compounds shows a ferromagnetic (FM) exchange between the two antiferromagnetically (AF) coupled \(Mn^3\) triangles (Fig. 1.1). Fitting of the magnetization data collected in fields up to 7 T affords \(S = 4\) for the spin ground state [18]. However a number of important structural changes leading to different values of \(S\) and \(U_{eff}\) take place in the related complexes \([Mn^3+O_2(Et−sao)_6(O_2CP_h2(EtOH)_6])\) [19]. The increased steric bulk and non planarity of the \(Etsao^{2−}\) ligands cause a shortening (by \(1\AA\)) of the phenolato oxygen square pyramidal Mn distance and a severe twisting of the Mn-N-O-Mn moieties within each \(Mn_3\) sub-unit (Fig. 1.2, scheme). The structural changes force a switch in the dominant magnetic exchange interactions from AF to FM (Fig. 1.1) and thus the stabilization of a spin \(S = 12\) ground state [19], [15].

These compounds however, are characterized by a weak exchange value \((J < 1cm^{-1})\), which results in the population of low-lying excited states \((S = 11, S = 10, ..)\) and then tunneling involving excited-state multiplets, leading to a dramatic reduction in the energy barrier of magnetization relaxation [19]. This problem has been successfully solved by further replacement of the carboxylates via a simple metathesis type reactions. This produces analogous complexes with identical cores except for the Mn-N-O-Mn torsion angles \(\alpha_v\) that are modified according to the steric bulk of the ligand.

The complexes with the largest torsion angles [15] shows an increase in the magnitude of the pairwise exchange parameter \((J)\) and an increase in the effective \(\Delta_{eff}\) up to 86.4 K, higher than the \(Mn_{12}\)-acetate.

1.4 Cr-based antiferromagnetic wheels

Beyond the application of MNMs as high-density data storage, another intriguing application concerns their use as qubit for the quantum computing and information.

Several systems have been already proposed for this purpose. Quantum dots or arrays of Josephson junctions have been successfully tested but also single ions in
1.4. CR-BASED ANTIferromagnetic Wheels

Figure 1.2: The complexes with $S=4$ (on the left) and with $S=12$. The colors indicate: violet-Mn, red- oxigen and blue-nitrogen. On the bottom the structure of $\text{sao}$ and $\text{Et-sao}$.

crystalline or molecular matrix as well as nuclear spins have shown their potentialities as qubit.

Indeed we can take some advantages in using MNMs with respect to other solid state systems. For instance, MNMs form scalable arrays whose features and the chemical preparation of molecular qubits are cheaper than other top-down approaches. As compared with single ion electron spin systems, because of larger physical size, MNMs need lower spatial resolution for the addressing of the single molecule with experimental techniques. Moreover the read-out process can be easily assisted by local field.

Another important aspect is the presence of well-defined and well separated excited states in MNMs that can be exploited, for instance, as additional resource for computational schemes involving multiple qubits.

A simple and beautiful example of MNMs is represented by a molecular ring containing eight $\text{Cr}^{3+}$ ions disposed in an almost perfect octagonal geometry, with chem-
ical formula \([Cr_5F_6(O_2CtBu)_{16}]\) [20]. Each ion is at the center of an octahedra made by 4 oxygens and 2 fluorine atoms bridged by a single fluoride and two pivalates (Fig. 1.1). The Cr-Cr distances along each edge is in the range of 3.294-3.473 Å.

The wheel is antiferromagnetically coupled leading to an \(S = 0\) ground state but the replacement of one \(Cr^{3+}\) with a \(Ni^{2+}\) produces the \(Cr_7Ni\) ring with spin 1/2 as a ground state (Fig. 1.1). This represents an effective two-level system where the doublet ground state is energetically well-separated from the first one, \(S = 3/2\) excited state (13K at zero magnetic field) without significant leakage. The application of a static magnetic field \(B_0\) along the molecular axis splits the degenerate ground state \(S = 1/2\) in two levels: \(S_2 = -1/2\) (or \(|0\rangle\)) and \(S_2 = +1/2\) (or \(|1\rangle\)). Most importantly it tunes the energy levels structure of the ring decreasing the energy separation between the state \(|1\rangle = |S = 1/2, S_z = +1/2\rangle\) and \(|2\rangle = |S = 3/2, S_z = -3/2\rangle\). Hence for the implementation of the quantum computing game the best compromise between the above quoted conflicting conditions must be found. A reasonable compromise turns out to be \(B_0 = 2T\) if the ring is cooled at \(T = 1K\). Then the quantum algorithm (i.e. rotation of the total spin \(S\) within the basis states) can be obtained by applying sequences of pulsed magnetic fields \(B_1(t)\) orthogonal to the static field \(B_0\).

A further requirement for qubit encoding is that the system must have coherent dynamics of spin much longer than the gating time.

The decoherence is determined by the minimum field pulse needed to perform transitions without population loss to excited states. It was found that in \(Cr_7Ni\) the main source of decoherence is the (super-)hyperfine interaction between the electron spins and the nuclear ones. Recent works estimated an intrinsic decoherence time of 3.8\(\mu s\) for the per-deuterated \(Cr_7Ni\)-analogue. This value is much higher than the gating time, thus allowing quantum transitions to be implemented.
Chapter 2

Molecular nanomagnets on surfaces

2.1 Generality of the deposition methods

The exploitation of MNMs [21] for any practical application requires the deposition of densely packed monolayer of spatially isolated molecules on well-defined surfaces. This should open the way toward the access to the electronic and magnetic properties of individual molecules. That is the reason why recently considerable interest has been devoted to their assembling and addressing on surfaces [22].

One of the main advantages offered by MNMs is the possibility to synthesize many derivatives tailoring the ligands shell according to the needs of specific experiment or application. On the other hand much has been done in the functionalization of surfaces where self-assembled-monolayers (SAMs) of organic molecules can be systematically achieved [23].

In this way, for a given molecule, several combinations of molecule ligands shell and bare or functionalized surfaces exist. Then it is easy to figure out that chemical synthesis offers a huge number of possibilities to reach the desired results. However this task is non trivial because the surface as well as the functionalization of the molecules itself may influence the structural and physical properties of the nanomagnets.

For instance, in $Mn_6$ clusters even small changes in the structure due to the functionalization may corrupt the magnetic response [24]. Moreover the hysteresis has
been reported to disappear in single layers of $Mn_{12}$ grafted on gold surfaces [12], [13]. Hence, a preliminary investigation of the derivatives before their deposition is mandatory in order to discern how and which factors affect the molecules.

Among the several deposition methods used in the past, the deposition from solution has showed to be the most easy and reproducible technique. The molecules can be grafted either directly on bare surfaces, or on previously functionalized surfaces. In the first case a substrate is dipped for a given time in a solution of MNMs. After the absorption process, typically few minutes, the sample is rinsed with proper solvent, dried and quickly introduced in the experimental chamber. The second involves a two step procedure: the functionalization of the surface followed by the deposition of the molecules.

The direct deposition is typically achieved using MNMs functionalized with thiol groups to prompt the covalent bond with gold surface. The indirect deposition, on the other hand, can be driven either by ligand exchange reaction or by electrostatic interaction. In this thesis both methods are addressed.

### 2.2 Au(111) and HOPG surfaces

For the deposition of MNMs on surfaces, a very flat, clean and conductive surface is required. Gold, silicon and graphite surfaces satisfy these requests and are commonly used because homogeneous monolayers of well isolated molecules can be obtained. The choice of the surface is also based on the easiness of preparation. This is the reason why gold and graphite are preferred instead of silicon which requires a quite difficult chemical procedures to avoid the fast oxidation of the surface (SiO$_2$) which compromises the molecule deposition.

Herein gold single crystal Au(111) (or gold films on mica) and highly oriented pyrolitic graphite (HOPG) have been used. These substrate provides atomically flat surfaces specially in the case of HOPG, while Au(111) provides very large monoatomic (typically tens of nanometers) terraces. The HOPG substrate is preferred in case of molecules with carbon based functionalizations while the Au is used for sulphur based functionalizations. In the former the molecules graft on the surface by $\pi-\pi$ interaction, in the latter the strong covalent bond between the sulphur and gold atoms is exploited.
2.2. AU(111) AND HOPG SURFACES

Gold is a face center cubic metal. At the surface, the atoms are packed very tightly with hexagonal alignment, showing the typical $23 \times \sqrt{3}$ herringbone reconstruction (Fig. 2.2 on the left). The resulting compress surface have one extra gold atom every 23 lattice constants of the bulk. The Au(111) single crystal used has a cylindrical shape of about 6mm of diameter and 2mm of height. The surface is prepared by repeated sputtering-annealing cycles. In case of gold on mica, freshly surfaces are prepared by flame annealing procedure.

Graphite is a layered material made of large plates of carbon weakly bonded one each other (Fig. 2.2 on the right). The weak bound makes possible the cleaving of one layer by sticking a piece of adhesive tape to the surface. This pulls up the top layer of graphite leaves a clean and flat surface below.

Figure 2.1: Scheme of the deposition of MNMs on gold surface by solution (on the left) and of the drop-casting procedure for the thick film (on the right).
2.3 Functionalization of the surfaces

Many studies demonstrated that $M_n_{12}ac$ undergoes to a large fragmentation of the molecules and to a reduction \(^1\) of the core because of its interaction with the surface [14]. Nevertheless the magnetic properties were affected and the disappearing of the hysteresis loop has been reported [12], [13]. Thus the idea of looking for a new strategies of deposition in which the molecules are decoupled from the surface arose. The most simple idea is the deposition of the molecules on a previously functionalized surface with self assembled monolayers (SAM) of organic ligands. Thus new $M_n_{12}$ derivatives were synthesized suitable for the interaction with end groups of such ligands either by ligand exchange interaction or by electrostatic interaction.

The $M_n_{12}$-bet is one of those derivatives synthesized to interact electrostatically \(^1\)Herein with reduction is meant the presence of a large component of Mn\(^{2+}\) in Mn X-ray absorption spectra at the L edges.
2.3. FUNCTIONALIZATION OF THE SURFACES

Figure 2.3: The structures of the betaine ligand and the MES and MPA functionalizations for the gold surface. On bottom: scheme of the $Mn_{12}bet$ grafted on a previously functionalized gold surface.
CHAPTER 2. MOLECULAR NANOMAGNETS ON SURFACES

with functionalized surfaces. Herein, two different surface functionalizations of gold were studied: the Mercapto - EthaneSulphonate \([HS(CH_2)_2SO_3Na]=\text{MES}\) and Mercapto - Propionic Acid \([HS(CH_2)_2CO_2H]=\text{MPA}\) reported in Fig.2.3.

Both these ligands have as head-group the mercapto radical -SH that gives the bond with the gold surface. The sulphonate \(SO_3Na\) end-group of the MES compared with the \(CO_2H\) group of the MPA has the advantage to discern the role played by the sulphur (S) on the magnetic core. In fact it is thought that the S alone or together with the gold surface is the responsible of the molecule reduction.

The functionalization of the surfaces is accomplished by dipping the surface in a solution of organic ligands for a given time. The mechanism of reaction among the MES or MPA with molecules is the same. The formation of a SAM is proved by the presence of typical depression of gold surface called vacancy islands (VIs) [27].

The cationic terminations of the molecules loose the anionic \(\text{PF}_6^-\) ligands while the \(SO_3Na\) and \(CO_2H\) end-groups of the MES and MPA free \(H^+\) and \(Na^+\) ions in solution respectively.

Then the \(H^+\) ions react with \(\text{PF}_6^-\) to compensate the charge unbalance and remain in solution while \(COO^-\) and \(SO_3^-\) terminations are finally free to react electrostatically with the cationic molecules.

Finally the surface is washed with a proper solvent in order to remove the excess ligands that may form a second layer and rinsed with nitrogen flux.

Because the cationic ligands are all around the molecule, they cannot react all together with the anionic SAM. Thus some of them remain electrically uncompensate and drive the orientation of the molecules on the surface because of the competition between the repulsive interaction among the molecules and the attractive interaction with the anionic SAM. Importantly the repulsive interaction repels the molecules far away one each other and isolated molecules can be obtained.

\[\text{The STM and XPS analysis of the } Mn_{12}\text{-bet on MES have been already studied in [25] and more extensively in ref. [26]. Herein for sake of completeness these results are reported again and compared with those of the } Mn_{12}\text{-bet on MPA.}\]
2.4 MOLECULAR NANOMAGNET DERIVATIVES

2.4.1 Mn$_{12}$-betaine

The substitution of 16 acetate ligands in Mn$_{12}$ac clusters with 14 betaine ($^{+}N(CH_{3})_{3}-CH_{2}COO^{-}$) hexafluorophosphate (HPF$_{6}$) gives rise to polycationic (COOH-N$^{+}$) Mn$_{12}$bet [28]. This is characterized by a core reduced of two - electrons with respect to Mn$_{12}$ac and by a spin S=11 as a ground state(Fig. 2.4)[29]. The positive charge of z = +16 per cluster is partially compensated by the presence of 14 hexafluorophosphate anions (PF$_{6}^{-}$) in the crystal lattice [23].

The advantage of this derivative with respect, for instance, the tributylammonium salt ZHPF$_{6}$ [29], is the shorter separation between the cations and the Mn$_{12}$O$_{12}$ core which result in a more stable reduced form.

The structure of the Mn$_{12}$O$_{12}$ core is similar to that found in all Mn$_{12}$ derivatives with the difference that only four Mn$^{3+}$ ions exhibit JahnTeller distortion, with the anisotropy axes lying almost perpendicular to the mean plane of the cluster. The four remaining coordination sites do not show axial distortion and exhibit longer Mn-O bonds. This suggests a partial reduction to Mn$^{2+}$ with oxidation state +2.5 [30]. The polycationic nature of this derivative makes it suitable for the indirect deposition technique exploiting the electrostatic interaction with a SAM with anionic end-groups.

2.4.2 Mn$_{6}$-3tpc

Both Mn$_{6}$ with S=4 and S=12 are functionalized in a similar way to achieve the derivatives (Fig. 2.6) with chemical formula: [Mn$_{3}^{3+}$O$_{2}$(sao)$_{6}$(O$_{2}$C - tpc)$_{2}$(EtOH)$_{4}$] (Mn$_{6}$-3tpc S=4) and [Mn$_{3}^{3+}$O$_{2}$(Et - sao)$_{6}$(O$_{2}$Ctpc)$_{2}$(EtOH)$_{4}$(H$_{2}$O)$_{2}$] (Mn$_{6}$-3tpc S=12).

The functionalization is made by two 3-thiophenecarboxylic acid, (3-tpc) for the direct grafting on gold surfaces exploiting the strong S-Au affinity. The 3-tpc ligands present the S-atoms in the outer position (3) of the thiophene (TP) ring and point out in opposite direction roughly perpendicular to the [Mn$_{3}$] planes.

The influence of the 3-tpc ligands on the magnetic properties of the derivatives [31] has been studied by variable-temperature direct-current (DC) and alternating-current (AC) magnetic susceptibility measurements on polycrystalline (PC) compounds.

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Thus the Mn$_{12}$bet can be figure out made by Mn$^{2.5+}$ : Mn$^{3+}$ : Mn$^{4+}$ = 4 : 4 : 4 or alternatively by Mn$^{2+}$ : Mn$^{3+}$ : Mn$^{4+}$ = 2 : 6 : 4.
CHAPTER 2. MOLECULAR NANOMAGNETS ON SURFACES

Figure 2.4: Scheme of the magnetic coupling in $\text{Mn}_{12}\text{ac}$ leading to a $S=11$ starting from the two electron reduction in $\text{Mn}_{12}\text{ac}$ molecule with spin $S=10$. Grey arrows: $\text{Mn}^{3+}$ with spin $2$; Yellow arrows: $\text{Mn}^{2+}$ with spin $5/2$; Green arrows: $\text{Mn}^{4+}$ with spin $3/2$.

The monotonic behavior of the dc-$\chi T$ measured as function of the temperature on the $\text{Mn}_6$ with $S=4$ compound (Fig. 2.5 a) indicates the dominant antiferromagnetic character of the interactions between metal centers. These results support the $S=4$ spin ground-state. In the case of $\text{Mn}_6$ with $S=12$ the dc-$\chi T$ dependence on temperature presents a maximum at $3 \text{ K}$, before decreasing at lower temperatures. This behavior prove the dominant ferromagnetic interactions between the metal centers. The relatively large values of the low-temperature $\chi T$ can be well understood in terms of the ferromagnetic ($S=12$) spin ground-state combined with the magnetic anisotropy responsible for the decrease of $\chi T$ below $3 \text{ K}$. These results are supported by the fitting of the DC-field magnetization data $M(H)$ in the range $0 - 7T$ for temperatures between $2 - 25K$ with axial zero-field splitting plus Zeeman Hamiltonian showed (Fig. 2.5b).

AC-susceptibility measurements were performed in zero-applied field for tempera-
Figure 2.5: a) Temperature-dependence of $\chi_T$ for both complexes in PC form, measured at 0.1 T. b) Field-dependence of the molar magnetization $M$ for $S=4$ (top) and $S=12$ (bottom) in PC form. The solid lines are the fit to the experimental data. c) Temperature-dependencies of the in-phase $\chi'$ (top) and out-of-phase $\chi''$ (bottom) AC-susceptibilities for $S=4$ (left) and $S=12$ (right) in PC form, at the indicated temperature and frequency ranges.
ture from 1.8 to 15 K and frequency range 50 – 9300 Hz (Fig. 2.5 c). The results show the appearance of two peaks in $\chi''$ signal indicating the presence of two Jahn-Teller (JT) isomers magnetically not equivalent for the $S=12$ compound as already seen in the prototype $Mn_{12}$ MNM [32].

The fit of the frequency dependence of the $\chi''$ peak maxima to an Arrhenius law provides $\Delta_{eff} = 28$ K for the $Mn_6$ $S=4$ and $\Delta_{eff} = 55$ K for the $S=12$ compound with fast relaxation and $\Delta_{eff} = 67$ K for $S=12$ with slow relaxation.

All these results prove that the $Mn_6$-3tpc nanomagnets, though slightly affected by the functionalization, retains the main magnetic properties.

2.4.3 $Cr_7Ni$ derivatives

Several $Cr_7Ni$ derivatives of the pivalate template [$Cr_7NiF_8Piv_6$] (HPiv = pivalic acid, $CH_3CCOOH_{10}$) have been studied.

1. $Cr_7Ni$-3tpc [$Cr_7NiF_8C_{90}H_{70}N_3O_{32}S_{16}$] has sixteen 3-thiophenecarboxylates arranged in two groups: eight equatorial carboxylates which lie approximately in the plane of the $Cr_7Ni$ ring and eight axial carboxylates approximately perpendicular to the plane, alternately lying above and below the plane around the octagon. We expect a parallel orientation of the ring to the surface is favored because of the maximization of the S - Au bounds. The molecule has a maximum diameter of approximately 2.2 nm and a height of 1.5 nm.

2. $Cr_7Ni$-thiob [$Cr_7NiF_8C_{86}H_{159}NO_{32}S$] has a single sulfur atom bound at the center of the ring by means of an aminoa (NH$_2$) and a butane groups. This should induce the molecule to bind with gold surface keeping the plane of the ring parallel to the surface. It contains pivalate rather than 3-thiophenecarboxylate and a slightly smaller diameter of 1.8 nm and a height of 1.1 nm.

3. $Cr_7Ni$-4ntpp [$Cr_7NiF_3((CH_3)_3CH_2COO)_{15}(O_2H_23C_14N_1S_1)]$ contains only one protected sulphur atom linked to the $Cr_7Ni$ ring by the $O_2C(CH_3C_3H_2)_2$ chain. This should assure a longer separation from the surface. The nominal size are: height = 1.6 nm and diameter = 2.2 nm. No magnetization measurements with standard magnetometry were carried out.
2.4. MOLECULAR NANOMAGNET DERIVATIVES

Figure 2.6: Molecular nanomagnets derivatives functionalized for the grafting on gold surface by covalent bond with the sulphur atoms (yellow)
Chapter 3

Experimental section

In this Chapter the techniques used in this work are briefly introduced from theoretical and experimental point of view. Scanning Tunneling Microscopy (STM) and X-ray Photoemission Spectroscopy (XPS) were combined to characterize the topography and chemical composition of MNMs on surface. Up to date, these techniques are widely used and they can not be set aside for a preliminary understanding of the structural and electronic properties of MNMs.

For a deeper investigation, we exploited the high brightness and resolution of Synchrotron facilities in Grenoble and in Trieste. X-ray Absorption and X-ray Magnetic Circular Dichroism (XAS and XMCD respectively) were used for the investigation of the electronic and magnetic properties of MNM sub-monolayers.

3.1 Scanning Tunneling Microscopy

The basic idea of the STM is simple and fascinating: it is a electric circuit in which a voltage source, the tunneling bias, is applied between two electrodes separated by a tunable resistance, the gap, determined by the size of the vacuum, gas or liquid. One electrode is a sharp tip and the other one the sample under study. If the gap is small enough, the electrons have a not vanishing probability to tunnel the potential barrier of the gap and a tunneling current can be read. This is a purely quantum mechanical effect due to the wave-like nature of the electron. The Schrödinger equation allows to describe the motion of the electron inside the sample or the tip and in between. In a 1-dimensional case and for a potential barrier $V(z)$, the Schrödinger equation reads:
\(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n(z)}{\partial z^2} + V(z)\psi_n(z) = E\psi_n(z)\)  
(3.1)

where \(\hbar\) is the Planck’s constant, \(z\) is the position and \(m\) is the mass of the electron.

If \(E < V(z)\), the electron is inside the potential barrier, such as between sample and tip, and the solution of the equation 3.1 is the following wavefunction:

\[\psi_n(z) = \psi_n(0)e^{-kz}\]  
(3.2)

where:

\[k = \sqrt{\frac{2m(V - E)}{\hbar}}\]  
(3.3)

quantifies the exponential decay of the wave inside the barrier.

In general \(V(z)\) can be assumed constant \(V \equiv V\) and so we can consider a rectangular barrier. In the simplest case it is just the vacuum level and for states at the Fermi level, \(V - E\) is the work function \(\phi\) (Fig. 3.1). Finally, the transmission probability, or the tunneling current \((I)\), is given by the square of the norm of \(\psi\) which gives:

\[I \propto e^{-2kd}\]  
(3.4)

where \(d\) is the sample-tip distance.

From 3.4 it is clear that \(I\) decreases drastically with \(d\) and a current can be read only if the tip-sample separation is very small (order of magnitude of few Å) and quite stable. ¹

This is the reason why the theoretical understanding of the tunneling mechanism is known from long time while the first experimental observation of the tunneling current did not come until 1982 when Binnig and Rohrer [33] used a piezoelectric driver to control the height of the metal tip above the surface and confirmed the expected exponential behavior of the current of 3.2.

Fig. 3.1(top panel) shows the situation discussed above when the tip and the sample are far each from the other and separated by vacuum. The electrons are confined into the sample and tip (with work function \(\phi_s\) and \(\phi_t\) respectively) which can be considered

¹For typical work function value of 4-5 eV results \(2k \sim \text{Å}^{-1}\) and the tunneling current decrease an order of magnitude for every 1 Å
Figure 3.1: (Top panel) Two not-interacting electrodes separated by vacuum. The electron wavefunctions do not overlap. $\varphi_t$ and $\varphi_s$ are the work function of the tip and sample respectively. (Middle panel) The tip is close to the sample and they are in electrical equilibrium with the same Fermi level. (Bottom panel) A bias voltage is applied across the gap. The electrons have not vanishing probability to tunnel from the states below the Fermi level of the tip into empty states just above the Fermi level of the sample. The electron wavefunction decreases exponentially into the barrier.
well separated states because their wavefunctions do not overlap. The Fermi levels of two materials differ by an amount equal to the work function difference.

In the middle panel of Fig. 3.1, the two electrodes are very close (tens of Å) and in electrical equilibrium. In this condition they have the same Fermi level. An asymmetrical potential barrier arises because $\varphi_t \neq \varphi_s$.

The difference of the work functions gives rise to an electrical field in the vacuum region. In absence of bias voltage the tunneling can not take place yet.

Upon a bias voltage is applied across the gap (Fig. 3.1 bottom panel), only the states within $V$ above or below the Fermi level contribute to the tunneling current and an "evanescent" wavefunction appears. The electrons below the Fermi level in the negative side (tip) tunnel into empty states just above the Fermi level in the positive side (sample)$^2$. At higher energy there are not electrons to tunnel, while at lower energy there are no empty states to tunnel into. In this way the STM tip is able to probe the empty states of the system under study few electronvolts above the Fermi level.

**Operating with STM**

There are mainly two operating modes to acquire STM images: constant current mode and constant height mode. In the former (Fig.3.3), at given bias voltage $V_{\text{bias}}$, the tip is scanned in the two lateral dimensions, while a feedback circuit keeps the current constant generating an electrical signal ($V_z$) which drives the vertical movement of the tip by means a piezo-electrical element (Fig.3.2). In this way, scanning the tip over a whole area, line by line, the $V_z$ is recorded as function of the voltages regulating the horizontal scan ($V_x$ and $V_y$). By converting $V_x$, $V_y$ and $V_z$ into the tip position, a topographic image of the surface can be obtained.

In the constant height mode, the feedback loop is open, so the current is free to change and the tip height remains constant above the surface. Then the surface image is given by the changes of the current as function of $V_x$ and $V_y$, rather than in the tip height. This mode is used only in special cases of extremely flat surfaces because of the small and constant tip-sample height in order to avoid the crashing of the tip.

In order to get a right interpretation of the STM measurements, it is crucial to get

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$^2$Inverting the polarization the electrons tunnel from the filled states below the Fermi level of the sample into the empty states just above the Fermi level of the tip.
3.1. SCANNING TUNNELING MICROSCOPY

Figure 3.2: Schema of a piezoelectric tube working on a sample. The directions of the motion are also indicated.

atomic resolution images (Fig. 3.4). For this purpose the main requests are: highly stable tunneling current, stabilization of the tunneling gap, isolation of the mechanical vibrations and electronic noise, high precision in the displacement of the STM tip, and high lateral resolution connected with highly sharp tip.

Standard STM systems are isolated from the environment by a damping system which suspends the stage of measurements. Fine tip displacements are guaranteed by a piezoelectric tube (Fig. 3.2) made by four piezo elements (quartz) which can be controlled independently. The lateral displacement is get applying a voltage across all four piezos at once. The vertical displacement is obtained increasing a voltage on one side of the piezo and decreasing it on the opposite side. This gives the contraction one side and the extension of the other side.

The lateral resolution of the STM images is limited to the finite tip radius. The most widely methods used for the preparation of sharp STM tip are by electrochemical
etching of tungsten wire or by cutting of Pt-Ir wire. The former is most commonly used in ultra-high-vacuum (UHV) where oxidation does not occur, while the latter might be advantageous for the stability of the tunneling in air.

It is generally believed that the good STM images result from tunneling of a single or at most few atoms on the tip. This suggests that only with sharp tips good images can be achieved. However, even blunt tip can work well and in special cases they are more advantageous than sharp tip. This is the case of the spectroscopic counterpart of STM, the scanning tunneling spectroscopy (STS), where people found that only with blunt STM tip reproducible $I(V)$ curves \[34\] can be obtained. Hence, the simultaneous topographic and spectroscopic measurements are compromised.

**Image analysis**

Usually, the STM images are interpreted as topography of atoms at surface, but at atomic level the meaning of topography should be taken carefully and the nature of the tunneling mechanism must be reminded.

Strictly speaking, the STM image is a contour of constant surface charge density near the Fermi level. That is why the surface corrugation must not be confused with the exact position of atoms and their nuclei. However, the interpretation of the STM images as a surface geometry is adequate only when the current flows through a small portion of the STM tip with the density of the states approximately constant near the Fermi level.

Transition metal tips are generally used because they have this property. However, the structure of the tip is not controlled at atomic level and anomalous tips may occasionally give rise to artefacts \[35\]. The most common artefacts are referred to multiple tip which take place when simultaneous tunneling occurs through multiple atoms on the tip and to distortion of the surface atoms. For example, in ref. \[36\] the authors observe a triple tip that results in faking of a partially ordered monolayer of adsorbate molecules (Fig. 3.4). Thus one must be careful to distinguish these artefacts from actual properties of the surface.

**STM apparatus**

STM apparatus is an independent system placed in the SESAMO-MFE Lab at the Physics Department of the Modena’s University. It is made by three stainless steel
3.1. SCANNING TUNNELING MICROSCOPY

Figure 3.3: Schematic representation of STM operating in constant current mode. The piezodrives \( P_x \) and \( P_y \) scan the metal tip over the surface. The control unit (CU) applies the necessary voltage \( V_{bias} \) to the piezodrive \( P_z \) to maintain the constant tunneling current \( J_T \) at bias voltage \( V_T \). The broken line indicates the line profile tip over a surface step A and a spot C with lower work function constraining the tip to go far from the sample(B). \( \Delta s \) and \( \delta \) represent the vertical and horizontal uncertainty respectively.
Figure 3.4: Top panel: Room temperature STM image with atomic resolution of a Au(111) single crystal surface. Bottom panel: Multiple STM tip on a surface covered by molecules. The tip artefact shows apparent partial ordering of molecules [36].
3.2 X-RAY PHOTOEMISSION SPECTROSCOPY

UHV chambers divided by metal valves which assure the reciprocal independence (Fig. 3.5). The base pressure in the STM chamber is of \(10^{-10}\) mbar.

The first chamber is provided of an fast lock entry where the samples are introduced into and brought from the air exposure to high vacuum conditions. The second and third chamber are equipped of sputtering and annealing set up for the preparation of the Au(111) surface.

All STM measurements were carried out by an Omicron UHV VT-STM system at room temperature and constant-current mode with typical imaging conditions of 0.5 V and 0.3 nA for clean surfaces and 2.0 V and 30 pA for adsorbate molecules.

The image analysis were made from a set of images obtained independently and in identical experimental conditions.

3.2 X-ray Photoemission Spectroscopy

X-ray Photoelectron Spectroscopy is a surface analysis technique based on the well known photoelectric effect explained by A. Einstein in 1905.

When a metallic surface is irradiated with mono-energetic X-rays (Fig. 3.6), the light is absorbed and electrons are photo-emitted from the surface with a kinetic energy given by:

\[
E_K = h\nu - E_B - \varphi_s
\]  

where \(E_B\) is the binding energy of the core level from which the electron originates, \(\varphi_s\) is the spectrometer work function and \(h\nu\) is the photon energy. MgK\(_\alpha\) (1253.6 eV) or AlK\(_\alpha\) (1486.6 eV) X-rays are ordinarily used and have a limited penetrating depth in a solid of the order of 1-10 micrometers. The kinetic energy of the electrons leaving the surface can be detected by an electron spectrometer (energy analyzer) as discrete events. Then a spectrum of the event number per second (counts/sec) as function of the kinetic energy (or alternatively the binding energy) is achieved. Energy peaks occur corresponding to the binding energy of the electrons that are ejected from the core levels into the vacuum and their position gives therefore a direct identification of the atoms. Moreover, because the core electron binding energy varies slightly depending on the chemical environment of the atom, XPS allows to get information also on the chemical bonds. The intensity of the peaks depends on the cross section related to the
photon energy, the element and the specific level excited.

More in detail, the probabilities of interaction of the electrons with matter exceed those of the photons as a consequence the path length of the photons is bigger than those of the electrons (escape depth). Thus, while the ionization process occurs to a depth of a few micrometer only those electrons that originate within tens of Angstroms below the surface leave the surface without energy loss. They are these electrons which produce the peaks in the spectrum. On the other hand, those electrons that emerge from the sample having lost part of their kinetic energy by random and inelastic scatterings inside the solid, form the continuous background.

Summarizing, the main advantages of the XPS technique are:

1. surface sensitivity (10 – 1000Å below the surface) because of the short escape depth of the electrons;

2. element sensitivity due to the characteristic distribution of electronic states of each element of the periodic tables and their ions;

3. chemical sensitivity due to the modification of electronic states upon the bonding between different chemical elements.

XPS apparatus

In this section we describe the XPS apparatus shown in Fig. 3.5b. It is made of a first chamber for the preparation of the surfaces and a main chamber where the XPS measurements are carry out with an Omicron (EA125) hemispherical analyzer.

The samples can be transfer from one chamber to the other by means a manipulator having four degree of freedom and mechanical fine guide in order to put the sample in a well defined position upon the XPS measurements.

The sample mounted on the sample-holder is placed at the end of the manipulator kept by springs and connected to the earth as reference potential. Moreover a heater filament is fixed behind the sample in a way that its face is opposite to the filament.

All the measurements were performed with $MgK_\alpha$ X-ray source (1253.6 eV) and CAE operating mode.
3.2. X-RAY PHOTOEMISSION SPECTROSCOPY

Curve fitting

As already said, XPS allows to analyzes the bonding states of a specific element. In the XPS spectra several components of a given peak can be superimposed and slightly shifted in energy. The reason of the energy shift can be ascribed to different chemical bonding states in which an element can be. For instance, in the case widely discussed later of the molecules adsorbate on surface exploiting the strong sulphur-gold bonding, the $S_{2p}$ peak contains several components related to different bonding states and geometrical configurations. A quantitative evaluation of the contribution of each component can be carried out fitting the data to theoretical curves by minimizing the deviations.

The limited instrumental resolution and the finite core level lifetime are usually fitted by a convolution of Gaussian and Lorentzian curves (Voigt profile). As fitting parameters, the expected area ratio (branching ratio) of the two peaks split by spin-orbit interaction (the so-called spin-orbit doublet), should be fixed to constrains the theoretical curves to reproduce the expected values.

Quantitative Analysis

XPS is a widely used technique in surface science for the chemical composition and bonding states analysis of molecules adsorbate on surface. From an accurate quantitative analysis of the spectra, the relative concentration of each element and the surface coverage can be evaluated. Moreover, by fitting the spectra with proper theoretical curves the chemical bonding states can be inferred. The aim of this section is to show how the element concentrations and the surface coverage can be derived from the integration of the peaks. Finally the curve fitting procedure is discussed.

Let us suppose that the system under study is a unknown surface. Once all the experimental parameters (relative position between X-ray gun and sample, optimization of intensity, slits width, pass energy etc.) are set, a broad scan survey XPS spectra scanning the binding energy from 0 (the Fermi level) to 1000 eV is collected. A set of detectable narrow peaks superimposed to a continuous background indicates the presence of different elements on the surface that can be identified. In order to catch more details of the elements observed, i.e. the chemical composition, we collect separated spectra of them in a short energy range wide enough to encompass the background on

---

3 A pass energy of 25 eV is normally adequate for routine details scan.
both side of the region of interest. Sufficient scanning must be done to obtain good
counting statistics and clear spectra. Then the resulting spectra is an average of many
spectra (sweeps) each of them acquired with a given counting rate (counts per second).
The measurements are untreated data and they are stored. Hereafter, the analysis of
the spectra involves a number of operations on the spectra. At this point, it is worth
saying that the treatment of the original data (integration, spike removal, baseline
subtraction, etc..) should be performed with caution because in most cases there is no
"correct" way for carrying out these operations. First of all we need to subtract the
background. In case of linear background, namely without steps, a line can be easily
subtracted. Now the peak area can be calculated between the two extremes of the
peak.

In case of homogeneous surface, the intensity of a specific peak (or core level) $I_i$ is
given by the following relation:

$$I_i = K \sigma_i \phi T \lambda \left[ 1 - e^{-\frac{8}{\lambda}} \right] n_i$$

(3.6)

where:

- $K$ is a factor of proportionality which depends on the experimental conditions;
- $\sigma_i$ is the photoelectric cross-section for the core level $i$. \(^4\)
- $\phi$ is the angular distribution factor which describe the intensity variation with the
  angle $\theta$ between the photon path and detected electron. In dipole approximation
  and for unpolarized light it is described by the differential cross section $d\sigma/d\Omega$
  [39]:

$$\phi \approx \frac{d\sigma}{d\Omega} = \frac{1}{4\pi} \left[ 1 - \frac{1}{4}(3\cos^2 \theta - 1) \right]$$

(3.7)

where $\beta$ \(^5\) [37] is the ”asymmetry parameter” which depends on the angular
symmetry of the atomic level excited and varies with the atomic number $Z$.

- $T$ is the transmission function of the analyzer depending on the detection effi-
icency of the electrons emitted from the surface and on the kinetic energy. \(^6\)

\(^4\)These values are calculated and tabulated by Yeh and Lindau [37] for all the electrons in the
atomic shells.

\(^5\) $\beta = 2$ for electrons in a closed shell

\(^6\)For Energy Analyzer 125 and in CAE mode $T \propto E_K^{-0.99}$. 

3.2. X-RAY PHOTOEMISSION SPECTROSCOPY

- \( \lambda \) is the mean free path of the photo-electrons (typically 1-10Å) [38];
- \( s \) is the thickness of the surface.
- \( n \) is the number of atoms in the analyzed volume.

From the 3.6 two very important factors can be defined:

1. the **atomic sensitivity factor**:

\[
S = \sigma \phi T
\]  

(3.8)

2. the **effective thickness**:

\[
d(s, \lambda) = \lambda \left[ 1 - \exp \left( -\frac{s}{\lambda} \right) \right]
\]  

(3.9)

A list of sensitivity factors of the elements of our interest for this work are summarized in Table 3.1. The effective thickness quantifies the reduction in overall intensity for electrons arising from the surface by elastic scattering. It can be considered as the thickness of a surface from which the electrons are ejected without inelastic scattering. In this context two limit cases of the 3.6 relation are considered:

- thick film \( s >> \lambda \) then:

\[
d = \lambda \Rightarrow I_i = K\sigma_i \phi T \lambda n_i \quad \text{or} \quad I_i = K S_i \lambda n_i
\]  

(3.10)

- thin film \( s \leq \lambda \) then expanding the exponential term in Taylor series:

\[
d \sim s \Rightarrow I_i = K\sigma_i \phi T d n_i \quad \text{or} \quad I_i = K S_i d n_i
\]  

(3.11)

These relations will be applied later when the XPS analysis on the thick film and monolayer of molecular magnets will be carried out. From equation 3.6 we can find the number of atoms \( n_i \) of a specific element. As the factor of proportionality \( K \) is unknown, the evaluation of the absolute value of \( n_i \) can not be determined so we can calculate only the relative number of atoms. Indeed the relative concentration is more useful than the absolute value because it permits to calculate the stoichiometry ratios. If \( a \) and \( b \) are two elements under study with approximately the same effective thickness, then the relative number of atoms is:
\[
\frac{n_a}{n_b} = \frac{I_a S_b}{I_b S_a} \quad (3.12)
\]

Finally a generalized expression for determination of the atomic concentration \(C_x\) of any \(x\) element detected from XPS can be written as an extension of 3.12:

\[
C_x = \frac{n_x}{\sum_i n_i} = \frac{I_x/S_x}{\sum_i I_i/S_i} \quad (3.13)
\]
Figure 3.5: Scheme of the main component of the STM (a) and XPS (b) apparatus. The triangles indicate the metal valves. The insert in b) shows the scheme of the XPS experimental set up.
Figure 3.6: Principle of the photoelectric effect for an atom inside a solid with work-function $\varphi_s$. A photon with given energy $h\nu$ excites an electron from the 1s core level with binding energy $E_B$ to unbounded state with kinetic energy $E_K$. The energy conservation law holds.
### Table 3.1: Photoelectron cross-section $\sigma$, Asymmetry parameter $\beta$, angular distribution factor $\phi$, binding energy $E_b$, kinetic energy $E_k$ and sensitivity factors for the elements of our interest.

$\phi$ values are calculated keeping a $\theta = 75^\circ$ photon-electron angle for all our measurements. The binding and kinetic energies, $E_b$ and $E_k$ respectively, are given in eV.

<table>
<thead>
<tr>
<th></th>
<th>Au4f</th>
<th>Mn2p</th>
<th>Cr2p</th>
<th>Ni2p</th>
<th>S2p</th>
<th>F1s</th>
<th>N1s</th>
<th>C1s</th>
<th>O1s</th>
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<tbody>
<tr>
<td>$\sigma$</td>
<td>0.4176</td>
<td>0.3011</td>
<td>0.254</td>
<td>0.469</td>
<td>0.038</td>
<td>0.0011</td>
<td>0.039</td>
<td>0.022</td>
<td>0.063</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.006</td>
<td>1.457</td>
<td>1.456</td>
<td>1.396</td>
<td>1.225</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.09554</td>
<td>0.642</td>
<td>0.1027</td>
<td>0.102</td>
<td>0.099</td>
<td>0.111</td>
<td>0.111</td>
<td>0.111</td>
<td>0.111</td>
</tr>
<tr>
<td>$E_b$</td>
<td>84</td>
<td>653.7</td>
<td>577</td>
<td>852</td>
<td>166</td>
<td>686</td>
<td>402</td>
<td>287</td>
<td>531</td>
</tr>
<tr>
<td>$E_k$</td>
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<td>599.9</td>
<td>674</td>
<td>399</td>
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<td>S</td>
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<td>3.27E-5</td>
<td>3.86E-05</td>
<td>1.20E-04</td>
<td>3.56E-06</td>
<td>1.83E-05</td>
<td>5.12E-06</td>
<td>2.53E-06</td>
<td>9.71E-06</td>
</tr>
</tbody>
</table>
Coverage estimation

Let us suppose that we have a gold substrate $A$ with thickness $s$, area $A_T$ and number of atoms $N_a$ in the volume $V$.

The density of gold atoms is:

$$n_a = \frac{N_a}{V} = \frac{N_a}{N_a V_a} = \frac{1}{A_a d_a}$$  \hspace{1cm} (3.14)

where $A_a$ and $V_a$ are the area and volume of the primitive cell respectively and $d_a$ is the lattice parameter orthogonal to the surface.

If $t_{eff}$ is the mean number of effective layers crossed by the electrons, then $\lambda = d_a t_{eff}$ and the relation 3.10 can be written as:

$$I_a = \frac{K S_a \lambda}{A_a d_a} = \frac{K S_a d_a t_{eff}}{A_a d_a} = \frac{K S_a t_{eff}}{A_a}$$  \hspace{1cm} (3.15)

If the substrate $A$ is covered by a thin layer $B$ with $N_b$ number of atoms, then the relation 3.11 can be applied. The $dn_b$ product is called surface density $S_d$ and is related to the surface coverage $f \equiv N_a/N_b$ as the following relation for $n_b$ shows:

$$n_b = \frac{N_b}{V} = \frac{N_b}{A_T d} = \frac{N_b}{N_a A_a d} = \frac{1}{f A_a d} \Rightarrow S_d = dn_b = \frac{1}{f A_a}$$  \hspace{1cm} (3.16)

This relation shows that the surface density can be viewed as the number of B atoms per unit area (atoms/nm$^2$). By replacing $S_d$ in 3.11 we have:

$$I_b = \frac{K S_b}{f A_a}$$  \hspace{1cm} (3.17)

Finally $f$ can be determined from the ratio between $I_b$ and $I_a$:

$$f = \frac{I_a S_b}{I_b S_d t_{eff}}$$  \hspace{1cm} (3.18)

In this simple relation only the knowledge of the sensitivity factors and $\lambda$ is required. The former can be easily calculated and the values for all the elements are tabulated (inserisci tabella) while typically $\lambda$ is between $1 - 10 \text{Å}$. The relation 3.18 neglects the attenuation of the gold signal due to the following deposition of the thin film. This is a good approximation when the gold electrons pass through the film without inelastic scattering. This is can be evaluated using the general formula 3.6 where $\lambda$ and $s$ must be carefully estimated.

\footnote{For $f = 1$ there is one B atom for each cell of gold.}
3.3 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is a synchrotron technique widely used for the characterization of the matter. Its main advantages are: 1) it is an atomic probe and spectra for almost every element on the periodic table can be measured; 2) it is one of the few techniques which allows to probe in solids noncrystalline and highly disordered materials, including solutions; 3) it is a surface-sensitive technique and monolayers as well as sub-monolayers can be studied. Notably, the latter property is crucial for the aim addressed in this thesis because the comparison between monolayers and bulk samples is the strategy adopted in order to study the modifications of the MNMs after their absorption on the surface.

In the X-ray absorption process, the photon energy is varied across a core level and an electron is excited to a state just above the Fermi level. At the excitation energies the absorption increases drastically because of high probability of such transitions and a sudden raise of intensity, called absorption edge, is observed. When the photoelectron leaves the absorbing atom, its wave is backscattered by the neighbor atoms (Figure XAS). The outgoing photoelectron wave and backscattered wave can give rise to a constructive and destructive interference which correspond to maxima and minima points in the spectra respectively. For sake of convenience related to the practical application of XAS and interpretation, the XAS spectra are usually divided in two regions:

1. *X-ray Absorption Near Edge Structure* (XANES), where the energy of the incident X-ray beam arrives $\sim 50$ eV above the absorption edge. XANES spectra are strongly sensitive to the formal oxidation state and the local symmetry (e.g., octahedral, tetrahedral coordination) of the absorbing atom.

2. *Extended X-ray Absorption Fine Structure* (EXAFS), which starts approximately from 50 eV and continues up to 1000 eV above the edge. The photoelectrons have high kinetic energy and single or multiple scattering by the nearest neighboring atoms normally dominates. EXAFS is used to determine the distances, coordination number, and species of the neighbors of the absorbing atom.
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Theory

Starting from the very beginning, the energy of an electron in a potential \( \varphi(r, t) \) and in non-relativistic approach, is simply \( H = \frac{p^2}{2m} + e\varphi(r, t) \) where the first term is the kinetic energy, \( p = -i\hbar \nabla \) is the momentum operator of the electron and \( e \) is the electron charge. If the electron interacts with an electromagnetic field, the momentum operator is replaced by the vector potential \( A : p \rightarrow p - (e/c)A \) and the Hamiltonian reads:

\[
H = \frac{1}{2m} [p - (e/c)A(r, t)]^2 + e\varphi(r, t) \quad (3.19)
\]

Assuming for sake of simplicity that \( p \) and \( A \) commute and working in transverse gauge in which \( \varphi(r, t) = 0 \) and \( \text{div}A = 0 \) then:

\[
H = \frac{p^2}{2m} - \frac{e}{mc} [p \cdot A(r, t)] + \frac{e^2}{2mc^2} A^2(r, t) \quad (3.20)
\]

The Hamiltonian describing the electron-electromagnetic field interaction reduces to the terms containing \( A \). The vector potential solely (the third term) creates and destroys photons and in second quantization it can be written as a linear combination of creation and annihilation operators. The \( p \cdot A \) term, on the other hand, can create or destroy a photon, but not both. The creation of a photon (emission process), and the photon annihilation (absorption process), are accompanied by a change of electronic state of the system from an initial state to a final state. So we have found the origin of the absorption process, which provides the annihilation of a photon driven by the \( p \cdot A \) term. In second quantization, the associated absorption Hamiltonian operator is:

\[
H_{ab} \propto (\hat{e}_q \cdot r)a_q e^{i(kr)} \quad (3.21)
\]

where \( a_q \) is the annihilation operator and \( \hat{e}_q \) is the polarization vector of the light.

Let us calculate the X-ray absorption spectra. The X-ray absorption intensity \( I_{XAS} \) for a electron transition between the initial state \( \Phi_i \) and the final state \( \Phi_f \) is given by a relation due to Dirac but called Fermi Golden rule:

\footnote{\( H = \nabla \times A \)}

\footnote{\( q = 0 \) and \( \pm 1 \) for linear polarization and left and right circular polarization respectively}

\footnote{Fermi called this formula Golden rule because of its practical application.}
3.3 X-RAY ABSORPTION SPECTROSCOPY

\[ I_{\text{XAS}} = |\langle \Phi_f | H_{ab} | \Phi_i \rangle|^2 \quad (3.22) \]

As the wavefunction of a bound electron has a significative amplitude only in a restricted region of space, in 3.21 the exponential term describing the electric field oscillations can be approximated to \( e^{ikr} \sim 1 + ikr + \ldots \). In case of hard and soft X-rays, where the photons interact with internal electrons, the condition \( k \cdot r << 1 \) results satisfied because \( \hbar \omega << \left[ 2/(Z_{\text{eff}} \alpha) \right] E_I \) where \( E_I \) is the ionization energy of the bound electron moving in a potential created by an effective charge \( +Z_{\text{eff}} e \) and \( \alpha \) is fine structure constant. Thus the electric quadrupole term can be neglected and in electric dipole approximation the probability of X-ray absorption reads:

\[ I_{\text{XAS}} \propto |\langle \Phi_f | \hat{e}_q \cdot r | \Phi_i \rangle|^2 \delta_{E_f - E_I - \hbar \omega} \quad (3.23) \]

where the delta function describes the conservation of energy: a transition takes place if the energy of the final state equals the energy of the initial state plus the X-ray energy. This relation holds in case of infinite lifetime of the final states, but the core hole lifetime is finite and the delta function must be replaced by Lorentzian function which introduces an uncertainty in its energy according to Heisenberg’s uncertainty principle. The relation 3.23 is a very general expression and usually the initial state \( \Phi_i \) and final state \( \Phi_f \) wave functions are not exactly known so limiting practical calculations. If we assume that in the transition process only one-electron is involved and all the charge rearrangements due to the presence of the core hole are neglected, then it possible to rewrite \( \Phi_i \) as a core wave function \( (c) \) and \( \Phi_f \) as a free electron wave function \( (e) \):

\[ I_{\text{XAS}} \propto |\langle e | \hat{e}_q \cdot r | c \rangle|^2 \rho = M^2 \rho \quad (3.24) \]

This is the one-electron approximation where the matrix element is written for a single electron matrix element and the series of delta functions represents the density of states \( (\rho) \). The matrix element often is constant or slowly varying in energy and is

\[ ^{11}\alpha = e^2/(4\pi \varepsilon_0 \hbar c) \approx 1/137. \]

\[ ^{12}\text{In case of the K edges from carbon (Z = 6, edge = 284 eV) to zinc (Z = 30, edge = 9659 eV), the value of } k \cdot r \sim 0.04. \text{ Because the transition probability is equal to the matrix element squared, hence the electric quadrupole transition is smaller by } \sim 2 \times 10^{-3} \text{ and can be neglected compared to dipole transitions.} \]

\[ ^{13}\text{The finale state is considered as the initial state with an electron added to the valence band and an electron removed from the core: } \Phi_f = c e \Phi_i \]
abbreviated with \( M \). In dipole approximation, the shape of the absorption spectrum resembles the partial density of the empty states projected on the absorbing site, convoluted with a Lorentzian function. This approximation gives a relatively adequate simulation of the XAS spectra shape for the K edge of the transition metals. In this case the interaction between the electron and hole in the final state is relatively weak, but a more accurate description can be obtained if the unperturbed density of states is replaced by the density of states in presence of the core-hole.

**Dipole Selection rules**

The Wigner-Eckart theorem states that the \( |\langle \Phi(J, m_j) | T^k_q | \Phi(J'm'_j) \rangle| \) matrix elements of spherical tensor operators \( T^k_q \) with rank \( k \) \(^{14} \) on the basis of angular momentum eigenstates can be expressed as the product of the reduced matrix element, independent from the angular momentum orientation (q and M), and the Clebsch-Gordan coefficient:

\[
|\langle \Phi(J, m_j) | T^k_q | \Phi(J'm'_j) \rangle| = C(JkJ'; MqM') < \Phi(J') || T^k || \Phi(J) >
\]

The C coefficients can be simply expressed in terms of 3j-symbol, then:

\[
|\langle \Phi(J, m_j) | T^k_q | \Phi(J'm'_j) \rangle| = (-1)^{J-m_j} \frac{1}{(J-J')} [J' m_j q m'_j] |\langle \Phi(J) || T^k || \Phi(J') \rangle|
\]

The dipole selection rules are, then, directly determined by the triangular relations for \((J1J')\) and unless \( m_j = q + m'_j \) in the 3j-symbol:

\[
\Delta J = 0, \pm 1 \quad \Delta m_j = q \quad J' - J \geq 1 \quad (3.27)
\]

This means that dipole matrix element \( M \) in 3.24 is non-zero and the transition can occur. The magnetic quantum number \( m_j \) is changed according to the polarization \( q \) of the X-ray. The latter rule will be discussed more in detail in the magnetic circular dichroism section.

When a single electron is involved, because the X-ray photon brings an angular momentum \( l = +1 \) and spin zero, the conservation laws give: \( \Delta l = \Delta j = \pm 1 \), (i.e. \( s \rightarrow p, p \rightarrow s \) or \( d \) etc.) and \( \Delta s = 0 \).

\(^{14}\text{This is the general definition, but in our case we are interested in tensor with rank 1 which corresponds to the position vector } \mathbf{r} \text{ and for polarized light } q: T^k_q \equiv \hat{e}_q \cdot \mathbf{r}.\)
The reduced matrix element in the 3.26 basically gives the Fano’s propensity rule [40] which states that the transition in which \( l' = l + 1 \) is strongly favored over transitions \( l' = l - 1 \).

The quadrupole transitions, on the other hand, imply final states that differ by 2 (or 0) from the initial state (\( \Delta L = \pm 2, 0 \); i.e. \( s \to d, p \to f \) and \( s \to s, p \to p \), etc.). They are some hundred times weaker than the dipole transitions and can be neglected in most cases. Anyway they are visible though as pre-edge structures in the K edges of 3d-metals and in the \( L_{2,3} \) edges of the rare earths as well.

**XAS versus XPS**

Among the several spectroscopic techniques used for the chemical and physical characterization of the matter XPS and XAS are surely the most widely and successfully used. The basic principle is the same: they induce the excitation of a core electron from the ground state to some excited state (Fig. 3.7).

In the following the main differences are listed:

- A different finale state is reached from the core electron and as a consequence the resulting spectra provides different information. In XPS monoenergetic X-ray excites an electron from the core level to an energy high above the Fermi level in a way that it can be considered as a free electron. Instead in XAS the core electron is excited into a bound state at energies just above the Fermi level.

- If in XPS one measures the variation in the kinetic energy of the emitted electron at a constant excitation energy, in XAS one measures the photo-current emitted by the sample by scanning the photon-energy across the absorption edge.

- The spectral shape in XPS is determined by the electronic configuration of the ground state and by the reaction of the system on the core hole after the X-ray excitation. Then the core-hole potential and the spin-orbit coupling give rise to a splitting of the core levels. This also holds for XAS, but in case where no reaction with the core-hole takes place its spectra reflects the density of empty states.

- In XPS the dipole selection rules are relaxed and all final state symmetries are allowed. In X-ray absorption the electron is excited to bound states and the electric dipole transition poses strong selection rules to the final states with a
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Figure 3.7: Comparison between XPS (on the left) and XAS (on the right) techniques. Representation of the measurement systems (top panel) and diagram levels with core electron excited by X-ray source (bottom panel).

given symmetries. This makes X-ray absorption sensitive to the symmetry of the ground state with its characteristic multiplets [41].

- From a practical point of view, XPS can be installed on campus and can be widely exploited from the user making a lot of experience, on the other hand XAS requires tunable X-rays with high brightness that only Synchrotron facilities can provide.

- Finally, by exploiting circular and linear polarization of X-rays, XAS becomes a unique tool to characterize the anisotropy charge and moment distributions in magnetic thin films as well as magnetic bulk.
3.4 X-ray Magnetic Circular Dichroism

Dichroism is the polarization dependence of the absorption of light. In general the response of an charge distribution to an electromagnetic field is anisotropic and depends on the local symmetries of the material under study. Magnetic dichroism is a similar effect, but is driven by the symmetries of the magnetization distribution created by unpaired electrons. In ferromagnet or antiferromagnet the absorption can be different with the photon linear polarization parallel or perpendicular to the magnetic easy axis. This is called magnetic linear dichroism. Materials with a net moment like ferro- or ferri- magnets can also exhibit an absorption dependent on the orientation of the photon spin (or helicity) relative to the easy axis. This is called magnetic circular dichroism. The application of linear and circular magnetic dichroism to the X-rays brings to the definition of X-ray Magnetic Linear Dichroism (XMLD) and X-ray Magnetic Circular Dichroism (XMCD).

Most conventional magnetic techniques used for the study of magnetic materials measure the total magnetic response containing contributions from different elements. The use of tunable X-rays allow to select specific elements in the sample through one of their characteristic absorption edges. More, different edges of the same element provide information on the magnetic contributions of different kinds of valence electrons through the dipoles election rules \( 3.24 \). For example the excitation of the \( L_{2,3} \) edges provides the d-empty density of states because of the \( p \rightarrow d \) dipole selection rule. Similarly the K edge is sensitive to p-density of states. The success of these techniques is closely related to the development of the Synchrotron facilities which provide tunable X-rays with high brightness. This makes XMLD and XMCD sensitive to the surface magnetism at monolayer level and to the specific element. Another important advantage of XMCD is the possibility provided by the related Sum Rules, developed by T. Thole et al., to evaluate the spin and orbital moment separately for a given element. The XMCD principle and the Sum Rules will be the subjects of the next section.

The two step model

The basic physical mechanism underlying XMCD can be easily described by the simple model, proposed by Stöhr and Wu in 1994 \([42]\). Let us consider the \( L_{2,3} \) edges of 15Neglecting the \( p \rightarrow d \) transitions.
Figure 3.8: Top panel: energy level scheme of an hypothetical system with six electrons exhibiting magnetic circular dichroism. Circularly polarized photon transfers its angular moment only to the orbital moment of the electron. RCP photon induces the transition $m_l = 0 \rightarrow m'_l = +1$. The transition induced by LCP is forbidden $m_l = 0 \not\rightarrow m'_l = -1$ because the $m'_l = -1$ level if filled. Bottom panel: a picture of the two step model. The spin-dependent excitation of a electron arising from p level split by spin-orbit interaction into d ”spin detector” band.
3.4. X-RAY MAGNETIC CIRCULAR DICHROISM

the 3d TMs. In the first step, a right (left) circularly polarized photon transfers its angular moment $+\hbar$ ($-\hbar$) to the orbital angular moment of the electron in the p shell. This process leads to the excitation above the Fermi level of the electron from the initial state to a final state allowed by the selection rules. In dipole approximation, the spins are not altered by the photons ($\Delta S = 0$ and $\Delta L = \Delta J = 0, \pm 1$) because they do not interact directly with the photon electric field. Hence the excitation is independent from the electron spin unless this is coupled to the orbital angular moment by a strong spin-orbit interaction. Thus the spin-orbit interaction is at the origin of spin-dependent X-ray absorption (Fig. 3.8). The effect of the spin-orbit coupling is twofold. Firstly it splits the p states by opposite spin-orbit coupling ($l+s$ and $l-s$, respectively). Therefore the photoelectrons originate from the $p_{3/2}$ (L$_3$ edge) or $p_{1/2}$ (L$_2$ edge) level and absorbs an angular moment from the photon which can be transferred in part to the spin. In particular right circularly polarized photons (RCP) transfer to the electron a moment opposite that of left polarized photons (LCP). Hence photoelectrons with opposite spins are created in the two cases. This is a statistical process: for the $p_{3/2}$ initial state (L$_3$ edge), RCP excites 62.5% spin-up and 37.5% spin-down electrons and the reverse holds for LCP. For $p_{1/2}$ initial state (L$_2$ edge) RCP excites 25% spin up and 75% spin down electrons, and LCP does the opposite. Spin-up and spin-down are defined relative to the photon spin direction (Fig. 3.9).

The second important effect concerns the radial electron wave-function which becomes slightly expanded or contracted depending on the spin-orbit configuration. This alters the radial integrals which determine the transition rates. In the second step, the spin-polarized electrons are excited by X-ray (photoelectron) into d band which acts as a “spin-detector” consisting of the d final state split by exchange interaction. This is the case of ferromagnetic metals, in which an imbalance in empty spin-up and spin-down states exists and hence transitions involving one spin orientation will be favored. Conversely, for a d band with equal spin-up and spin-down occupancy there is no dichroic effect since the total (spin-up + spin-down) transition intensities for RCP and LCP are identical.

The transition rate depends on the number of available final states with spin-parallel to the photoelectron spin, and so the differences in the spin-polarized density

\footnote{The quantization axis of the “detector” is given by the magnetization direction, which for maximum dichroism must be aligned with the photon spin direction.}
Figure 3.9: a) Coordinate system and conventions for RCP, LCP and photon spin. b) Correspondence between directions of an external magnetic field $\mathbf{H}$, magnetic moment and minority electron spin vectors in an magnetic material completely aligned by the external field.
of states lead to different transition probabilities for spin-up and spin-down photoelectrons. Since the photoelectron spin is governed by the helicity of the absorbed photon, the transition rates become different for RCP and LCP. For instance, in the ferromagnets Fe, Co and Ni the d shell becomes increasingly filled, resulting in a decreasing number of d holes, N. Then, the dichroic effect is proportional to the spin magnetic moment due to the exchange interaction given by the difference between the number of spin-up and spin-down holes:

\[ I_{XMCD} \propto m_s = -2\langle S_z \rangle \mu_B/h = (N^\uparrow - N^\downarrow) \mu_B. \]

The orbital moment \( m_o = -\langle L_z \rangle \mu_B/h \) which arises from the spin-orbit interaction is significantly smaller (50 meV) than the exchange interaction (1 eV). This lead to the quenching of the orbital moment overall when the crystal field is the dominant interaction.\(^{17}\)

In this simple model an important experimental parameter can be obtained. This is the dichroic signal \( I_{XMCD} \) given in terms of the relative weight of the photoelectron polarization \( P_e \) and the densities of unoccupied states \( \varrho \):

\[ I_{XMCD} \propto \frac{\mu^+ - \mu^-}{\mu^+ + \mu^-} \propto \frac{p(\uparrow) - p(\downarrow) \varrho(\uparrow) - \varrho(\downarrow)}{p(\uparrow) + p(\downarrow) \varrho(\uparrow) + \varrho(\downarrow)} \approx 2P_e \frac{\varrho_{sp}}{\varrho_{tot}} \] (3.28)

This equation states that XMCD signal is simply given by the difference between the two polarization normalized by the white line intensity (Fig. 3.10). Moreover it implies that the XMCD signal gives directly the degree of the spin-polarization of the system.

To carry out the 3.28 the following assumption is made: \( p^+ \downarrow = p^- \uparrow \) and \( p^+ \downarrow = p^- \uparrow \), namely in dipole approximation the polarization of the photoelectron is reversed when the helicity is inverted. It should be noted also that a change in the photon spin relative to the fixed magnetization direction is equivalent to a change of the magnetization direction relative to the fixed photon spin [43]. From an experimental point of view this property is extremely important because a change of the light polarization from left to right from a bending-magnet source implies a change in the optical path of the X-rays through the monochromator. Hence, in the XMCD measurements it is convenient to fix the light polarization and change the magnetic field in order to avoid energy shifts and/or resolution changes which reduces critically the normalization between the spectra with opposite polarization. In spite of this, in this thesis the XMCD spectra were obtained changing the photon spin at fixed field

\(^{17}\)For the cobalt it results: \( m_o = 0.14\mu_B \) and \( m_s = 1.64\mu_B \)
Figure 3.10: Example of XAS spectra with RCP and LCP for the Iron ($L_2$ and $L_3$ edges). The difference gives directly the dichroic signal.

direction. This method is surely more rapid and has the advantages of minimizing the field’s inhomogeneity and could be made because the XAS spectra with different helicity did not show any modification of the resolution and/or energy shift.

Sum Rules

Another important advantages of the XMCD technique is the possibility of extracting directly from the dichroic signal the ground state expectation value of the spin and orbital moment separately. This can be done by applying the sum rules developed by T. Thole et al [44] and Carra [45]. The basic idea of the sum rules is that as the spin and the orbital moment of the electron are parallel in the $j = l + s$ level and antiparallel in the $j = l - s$ level, one can argues that the orbital moment could be given by the sum of the dichroic spectra corresponding to the two $j = l \pm s$ absorption edges and the spin moment by the difference.
In the following a simple expression for the spin and orbital moments of TMs normalized to the integrated sum over the RCP, LCP and linearly polarized light ($\mu_0$)\(^{18}\) is given:

\[
\langle L_z \rangle = 2 \left[ \Delta L_3 + \Delta L_2 \right] \times \frac{(10 - n)}{\int_{L_3 + L_2} (\mu_+ + \mu_- + \mu_0)} \tag{3.29}
\]

\[
\langle S_z \rangle = \frac{3}{2} \left[ \Delta L_3 - 2 \Delta L_2 \right] \times \frac{(10 - n)}{\int_{L_3 + L_2} (\mu_+ + \mu_- + \mu_0)} - \frac{7}{2} \langle T_z \rangle \tag{3.30}
\]

where $\Delta L_{3(2)} = \int_{L_{3(2)}} d\omega (\mu_+ - \mu_-)$, $z$ is the photon spin direction, $(10 - n)$ is the number of holes, and $\langle T_z \rangle$ is the expectation value of the magnetic dipole operator due to the anisotropy of the spin moment which can be induced by anisotropic charge distribution around the atom or by spin-orbit interaction. For 3d TMs the spin-orbit coupling is small and if the charge distribution is isotropic (like in a cubic symmetry) it can be neglected. Indeed this is not the case of RE metals in which spin-orbit coupling is dominant but analytical expression for $\langle T_z \rangle$ can be found [45], otherwise it can be determined with angular dependent measurements [46].

A simpler formulation of the sum rules useful for a more straightforward experimental applications can be derived introducing the integrals $p = \Delta L_3$ and $q = \Delta I_{L_3} + \Delta I_{L_2}$ of the XMCD spectra. Neglecting the anisotropic terms they read:

\[
\frac{m_s}{\mu_B} = - \frac{(6p - 4q)}{r} N_{eff} SC \tag{3.31}
\]

\[
\frac{m_o}{\mu_B} = - \frac{(4q)}{5r} N_{eff} \tag{3.32}
\]

where $N_{eff}$ is the isotropic number of 3d holes and $r = I_{L_3} + I_{L_2}$ is the integral of white line intensity at the $L_3$ and $L_2$ edges of the isotropic XAS spectra after the subtraction of a two-steps-like function which removes the jumps between the two edges. The SC factor is introduced in the next section.

**Validity and applicability of the Sum Rules**

Although the validity of the sum rules was confirmed for first time more than 10 years ago [47] they still are a matter of debate from both theoretical and experimental point

\(^{18}\) $\mu_0$ is the X-ray absorption with linearly polarized light and with the polarization vector parallel to quantization axis.
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of view.

The main requirement for their application is that the spin-orbit coupling is much larger than the Coulomb interactions in the final state. This is the case for RE and, at the most, for the heavy elements at the end of the series of 3d TMs where the spin-orbit coupling is the largest. For the light TMs, $L_3$ and $L_2$ edges are closer and closer until they overlap and a transfer of intensity occurs between the two edges (jj-mixing). Then the individual integration of the two edges becomes troublesome. Deviations between the expected values and those measured by XMCD can be quantified by the branching ratio (BR) which gives the relative intensities between the $L_2$ and $L_3$ edges. From the sum rules is evident that the jj-mixing affects only the spin-moment because it is given by the difference between $L_3$ and $L_2$ edges and as a consequence its value is reduced.

Some phenomenological methods have been proposed to quantify the jj-mixing by fitting procedure based on the determination of a Spin Correction factor (SC) [48] defined as:

$$SC = \frac{1}{1 - 2X} \quad (3.33)$$

where $X = \frac{2BR - 1}{BR + 1}$ is the mixing factor defined as the relative transferred area from one edge to the opposite. For example, if $X=0$ no area is transferred and no mixing is present (pure jj coupling). In this case the branching ratio between the $j_{3/2}$ and $j_{1/2}$ excitation is $4:2$. At the opposite end (pure LS coupling [49]) $X=0.5$ and it corresponds to full mixing, namely 50% of the $j_{3/2}$ and 50% of the $j_{1/2}$ intensity is transferred. Then the corrected spin-moment is obtained from 3.30 multiplied by SC.

Another issue concerns the determination of the effective number of 3d holes $N_{eff}$ in the ground state. This is not easy to obtain and it can be calculated by ab initio approach (DFT), but in many cases, the charge distribution is almost isotropic and it is a good approximation to use the nominal values [46] [50].

**ID08 Dragon Beamline**

The ID08 Dragon beamline located at European Synchrotron Radiation Facilities (ESRF) in Grenoble is an intense source of polarized soft X-rays. It is principally used to probe the electronic and magnetic properties in a wide range of systems like nanoclusters, ultrathin films, superconductors and semimetals. As the photon energy
is tunable in the range 0.4-1.6 KeV it is an ideal tool for studying transition metals and rare earths.

The beamline is equipped with:

- two APPLE II undulators providing $\sim 100\%$ circular/linear beam polarization and high flux $10^{13}$ photons/s of polarized light;
- spherical grating monochromator with an energy resolution close to $\Delta E/E = 5 \times 10^{-4}$ at 850 eV;
- optics focussing down to 40 mm (FWHM) vertical beam size;
- low temperature (about 10K) superconducting magnet 7T;
- STM facility.

All the measurements were carried out in total electron yield detection mode. Because of this, the samples were fixed on an molybdenum sample-holder by means of tantalum wires to ensure a proper electrical contact.

After a preliminary topography characterization of the samples by the STM, the samples were transferred to the cold finger of a liquid-helium cryomagnet, which was kept under ultrahigh vacuum ($10^{-10}$ mbar). The measurements were taken in the $10-25$ K temperature range and at different applied magnetic fields in the range 1 – 5 T. The directions of the impinging beam and the magnetic field are both perpendicular to the sample surface (along the z-axis).

### 3.5 Preparation of the samples

**Mn$_{12}$-betaine**

SAM of MES or MPA on Au(111) were obtained by soaking the gold substrate in a diluted solution (1 mM) of ethanol for 10 min. Then the Mn$_{12}$ – bet molecules were deposited by immersion of the MES or MPA functionalized gold substrate in a diluted solution (1 mM) of acenonitrile for 3 and 10 min respectively.

**Mn$_{6}$-3tpc**

Sub-monolayers of Mn$_{6}$ – 3tpc with S=4 (1) and with S=12 (2) have been obtained by dipping for 10 min the Au(111) single crystal in a 1mM $CH_2Cl_2$ solution of 1 and
2. Then the samples were rinsed in CH$_2$Cl$_2$ and rapidly introduced into the UHV experimental chambers.

**Cr$_7$Ni derivatives**

All the Cr$_7$Ni derivatives have been deposited on the Au(111) surface using a 5mM solution, dipping time of 10 min, and DCM or THF as solvents. Different concentrations and deposition times have been also examined. For times below 30s and concentrations lower than 0.5mM, we did not observe any cluster adsorption. The highest cluster coverage, without formation of 3D aggregates, can be reached for concentrations ranging from 5 to 9mM and does not significantly vary with dipping times ranging from 10 min up to 20 h.

The parameters of the deposition process are optimized to get the highest coverage attainable. For comparison, XPS spectra were also taken on the relative thick films of 1 and 2.
Chapter 4

Results and discussion

In this Chapter the experimental results for each MNM family are presented. It is organized as follows: in part 1, the morphology, surface coverage, and grafting strength of the adsorbed investigated by STM are shown. In part 2, the chemical composition and the stoichiometry of the monolayers as well as the bonding nature between the ligands and the gold is studied by XPS. In part 3, by combining the STM and XPS results the suitable derivatives for the study of the electronic and magnetic properties of MNMs are selected.

Finally, in part 4, the electronic and magnetic properties of MNMs sub-monolayers (s-MLs) are addressed by means of XAS and XMCD techniques. The effects of the surface on the molecular properties are studied in comparison with the results obtained on the thick films (TFs) given by drop-casting a saturated solution on freshly cleaved HOPG. Moreover the effects of different functionalizations used for a given MNM are studied in comparison with the not functionalized compounds.

4.1 Mn₁₂-betaine

4.1.1 Topography

First, we studied the topography of MES and MPA on Au(111) in order to verify the formation of a complete SAM. Fig. 4.1 a) and b) show representative STM images of the two functionalizations studied. The black spots, deep 2Å and large few nm, are typical vacancy islands (VIs) of the gold surface. The presence of the VIs proves the
bond between the gold surface and the thiol head-groups of MES and MPA ligands as well as the formation of a complete SAM.¹

Few white spots are also visible on top of the SAM with height lower than 4 Å and diameter smaller than 3 nm (see line profile on top of Fig. 4.1). We ascribe this partial second layer to residual solvents and organic ligands. However, the presence of these molecules do not affect the identification of the Mn₁₂-bet clusters because of their smaller sizes.

The results of the Mn₁₂-bet clusters deposited on top of the MES and MPA -SAM are showed in Fig. 4.1 c) and d). We observe a quite similar scenario for both functionalizations. The larger white spots have random and uniform distribution with diameter of 3.0 ± 0.5 nm and height of 1.4 ± 0.2 nm comparable to those of the Mn₁₂-bet clusters (2.2 and 1.6 nm respectively)² (see line profile of the Fig.4.1 c) and d)).

The surface coverage of the larger white spots, supposed to be the Mn₁₂-bet clusters, is estimated by statistical analysis of the STM images. Taking into account the real diameter of the molecules of 2.2 nm, rather of that measured of 3 nm, we find that the average area occupied by a single molecule is 39 ± 7 nm² for both Mn₁₂-bet on MES and MPA. Hence, the surface coverage is about 8 – 12%. Smaller white spots are still visible and we ascribe them to residual solvents as well as to organic ligands.

### 4.1.2 Chemical composition

XPS measurements of the S-2p core level of the MES and MPA film are shown on top of Fig.4.2. The S-MES spectrum is characterized by two peaks at about 162.2 and 168.0 eV binding energy corresponding to the sulfur atoms bonded to gold and sulfonate sulfur, respectively. The S-MPA spectra has only the peak at 162.2 eV characteristic of the sulfur atoms bonded to gold. Moreover, the quite similar lineshape between the S-MES and S-MPA at 162.2 eV, let us suppose the quite similar sulphur chemical bonding.

The XPS spectra of Mn-2p showed in Fig.4.2, is characterized by 2p₃/2 (641 eV) and 2p₁/2 (654 eV) spin-orbit doublet. The branching ratio (L₃/L₂) is larger than

¹Porier proved that a surface covered by alkanethiol chains of whatever length with 5-9% of VIs reaches a limit where the adsorption of ligands is saturated and the formation of a complete monolayer takes place [27]. In this situation the adatoms are not visible because they migrate to the steps of the surface and do not compromise the identification of the molecules once grafted on the surface.

²We assume that the molecular axis is perpendicular to the surface.
Figure 4.1: Room-temperature image of a of Au(111) surface after a 10 min immersion in MES (a) and MPA (b). Gold terraces are uniformly covered by a first thiolate layer. White spots correspond to sparse second layer of molecules with height smaller than 2Å and diameter smaller than 3nm. (see line profile). The black region are the vacancy islands whose presence prove the formation of a complete SAM of MES and MPA as well. c) and d) show STM images of $Mn_{12}$-bet clusters on MES and MPA respectively. The line-profile of the molecules (white and large spots) shows that their diameter is about 2.4nm while their height is about 1.2nm in MES and MPA as well.
Figure 4.2: XPS core level intensity of S2p (upper panel) and Mn2p (lower panel) for Mn$_{12}$-bet on MES (red lines) and on MPA (black lines). The branching ratio ($L_3/L_2$) of the Mn spectrum is larger than that expected because of the Au$_{1/2}$ component at about 641.5 eV.
that expected because of the Au$p_{1/2}$ component at about 641.5 eV. The quite large intensity measured for both $Mn_{12}$-bet on MES and on MPA proves the presence of the clusters.

A quantitative analysis of the XPS spectra of the $Mn_{12}$-bet on MES, in ref. [25], demonstrated that each $Mn_{12}$ clusters is found every 20 - 36 nm$^2$. Supposing a molecular diameter of about 2.2 nm, a coverage of about 10 – 20% was derived in agreement with the STM analysis. The surface coverage was found change with the deposition time of the MES/Au substrate on a $Mn_{12}$-bet solution. Isolated $Mn_{12}$-bet was found for 3 min of deposition time, while three dimensional aggregates were found after 10 min. Indeed, in the case of $Mn_{12}$-bet on MPA/Au, we do not find considerable variations for different deposition times.

Unfortunately, the energy resolution of XPS is not sufficient to resolve the oxidation state and chemical environment of $Mn_{12}$-bet on MES and on MPA. However, this will be investigated in the following by using XAS technique.

### 4.1.3 Electronic properties

The study of the electronic properties of $Mn_{12}$ is a crucial point because of well known redox instability of its manganese core. As already widely discussed in the Chapter 3, XAS unlike XPS technique has the advantage of providing an unique tool to investigate the oxidation state and chemical environment of a given element with a sub-monolayer resolution.

The measurements carried out on the $Mn_{12}$-bet on MES and MPA are compared in Fig. 4.3. The spectra of the compound $MnO_2$ (with $Mn^{2+}$) and the thick film of $Mn_{12}$-bet are also reported as references. The TF spectra, supposed to give the fingerprint of the intact $Mn_{12}$-bet, shows mix-valent states with the higher peak at about 639.6 eV characteristic of the $Mn^{2+}$. This suggests that deviations from the expected ionic weights ($Mn^{2+}$: $Mn^{3+}$: $Mn^{4+}$ = 2:6:4) occurs in the TF.\(^3\) This is supported by $Mn_{12}$-bet spectrum calculated by the normalization of the XAS spectra of reference compounds ($MnO$ for $Mn^{2+}$, $Mn_2O_3$ for $Mn^{3+}$ and $MnO_2$ for $Mn^{4+}$). Actually, the main peak is at about 641.3 eV relative to the $Mn^{3+}$ while small contributions comes from the $Mn^{2+}$ and $Mn^{4+}$ at 639.6 and 642.5 eV.

However, these deviations, do not invalidate our investigation of the effects of the\(^3\) The cause of this modifications can be ascribed to the specific solvent used (acetonitrile).
gold surface functionalized with MES and MPA, on the Mn$_{12}$-bet properties. The results show that the XAS spectra of the Mn$_{12}$-bet on MES are almost identical to those of MnO$_2$ suggesting that it undergoes towards a full reduction of the core. The s-ML of Mn$_{12}$-bet on MPA preserves all the features and their relative intensities observed in the TF. Indeed, we observe only a slight modification of the contribution due to the Mn$^{4+}$ at about 642.5 eV. However, we can conclude that the Mn$_{12}$-bet on MPA is much more stable, in terms of oxidation state and geometrical environment, than the Mn$_{12}$-bet on MES.

As the main difference between the MES and MPA functionalization consists in the presence of the sulphur atom in the end-group, we suggest that a charge transfer of the electrons, either from the gold surface to the molecules via sulphur or directly from the sulphonate end-groups, occurs. In this way the full reduction of the Mn$_{12}$-bet on MES/Au could be explained.

Finally, we proved that Mn$_{12}$-bet on MPA appears more suited than MES to preserve the electronic properties of the Mn$_{12}$ core. Hence, in the following, we focus on it for the study of the magnetic properties of the Mn$_{12}$-bet core.

### 4.1.4 Magnetic properties

XAS and XMCD spectra for the TF and s-ML of Mn$_{12}$-bet on MPA are reported in Fig. 4.4. In both cases the main dichroism occurs at about 639.6 eV with positive sign. The dichroism at 642.5 eV is negative for the TF and positive for the s-ML. In principle, from the XMCD sign it is possible to disentangle the magnetic coupling between Mn ions with different oxidation states. Indeed, this is not trivial. Hence, we base our investigation on the XMCD results already found in ref.[13] and carried out on the monolayer of Mn$_{12}$ with 4-(methylthio)benzoic terminations on the gold surface. Those authors obtained XAS and XMCD spectra quite similar to those of our Mn$_{12}$-bet as TF. They concluded that the XMCD spectra are the fingerprint of interacting Mn ions (and not of isolated Mn ions) with Mn$^{2+}$ and Mn$^{3+}$ magnetic moments parallel to the magnetic field direction and those of Mn$^{4+}$ antiparallel. Actually, this picture of the relative magnetic couplings agrees with that expected for the Mn$_{12}$-bet (Fig. 2.4).

---

4 The positive sign of the XMCD spectra are related to magnetic moments parallel to the magnetic field direction.

5 Note that the conventions used in ref. [13] for the XMCD sign are opposite to ours.
Figure 4.3: XAS spectra of the calculated $Mn_{12}$-bet (dark cyan), $Mn_{12}$-bet on MPA / Au (blue curve), the TF of $Mn_{12}$-bet (black curve), $Mn_{12}$-bet on MES / Au (red curve), and $MnO_2$ compound taken as reference of $Mn^{2+}$ (green curve). The difference between the dark cyan and black curve suggests a slight modification of the $Mn^{2+}$: $Mn^{3+}:Mn^{4+}$ ratio from the original compound. Nevertheless, the similarity between the blue and black curves suggests the redox stability of the $Mn_{12}$-bet on MPA. Finally, the similarity between the red and green curves show the complete reduction of the $Mn_{12}$-bet core.
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Figure 4.4: XAS and XMCD spectra of $Mn_{12}$-bet as TF (on the left) and as adsorbed on MPA / Au (on the right). In blue the integrated XMCD signal are reported and show an almost complete orbital moment quenching.
Figure 4.5: Top panel: Normalized XMCD signal at 10 K of Mn$_{12}$-bet as TF (black points) and after the deposition on MPA / Au substrate (red points). Bottom: Simulated magnetization curves for Mn$_{12}$-bet with S=11 ground state, anisotropy energy barrier $\Delta = 35K$, and temperature ranging from 5 to 15 K.
By comparing the normalized XMCD intensity of $\text{Mn}_{12}$-bet TF (45 %) with the s-ML (25 %) we find a considerable decrease probably related to the modifications of the super-exchange coupling between the Mn magnetic moments. This is also suggested by the opposite sign already observed at 642.5 eV between TF and s-ML.

In Fig. 4.4 the blue lines are the integral of the XMCD signal proportional to the orbital magnetic moment (eq. 3.4). As it is vanishing, the orbital magnetic moment is almost quenched and so the total magnetic moment is given only by the spin contribution.

The quantification of the spin magnetic moment by means the application of the XMCD sum rules is complicated in case of Mn, due to the very strong j-j mixing effect which makes the $L_2$ and $L_3$ edges difficult to separate. Thus only a qualitative analysis of the XMCD data can be done.

The point is to study the effect of the substrate on the magnetization curves in $\text{Mn}_{12}$-bet. Fig. 4.5 reports the normalized XMCD signal measured for $\text{Mn}_{12}$-bet TF and adsorbed on MPA / Au. A sequence of XMCD spectra is collected for fields up to 5 T and temperature of 10 K.

The XMCD signal of the TF well reproduces, at least qualitatively, the behavior of the magnetization simulated by means of the diagonalization of the $\text{Mn}_{12}$ spin-Hamiltonian for temperatures ranging from 5 to 15 K (on bottom of Fig. 4.5). The saturation of the magnetization appears to be reached for fields higher than 5 T. On the other hand, the XMCD signal of the s-ML of $\text{Mn}_{12}$-bet on MPA as function of the magnetic field, shows a paramagnetic behavior with a dramatic reduction of the normalized XMCD signal.

### 4.2 Mn$_6$-3tpc

#### 4.2.1 Topography

Fig. 4.6 shows the topography of the Au(111) surface after dipping in a solution of the compounds 1 (left panel) and with 2 (right panel). In both cases the surface appears only partially covered by a s-ML distribution of molecules and, notably, no presence of 3D aggregates was observed.

The images of both compounds show larger white spots A with average diameter of 3.5 $\pm$ 0.5 nm in fair agreement with the value expected for a single Mn$_6$-3tpc molecule.
Figure 4.6: Top panel: room temperature STM images (2V and 0.03nA) for the Mn \(_6\) derivatives. The letter A indicates the presence of entities with size comparable with those of the MNMs. The letter B indicates the presence of fragments and the letter C indicates the impurities due to the residual solvent. Bottom panel: line profiles and a 3D view of details.
(1.8 nm) if we take into account the non-negligible curvature radius of the tip. The average height A of \(1.1 \pm 0.2\) nm is slightly smaller than the nominal height of the \(Mn_6-3tpc\) of 1.5 nm). This difference could be ascribed to the lower conductivity of the organic molecule with respect to the gold surface. Hence, we suppose that the A features can be identified with the \(Mn_6-3tpc\) clusters.

The smaller white spots B have average diameter and height lower than 2 and 0.6 nm respectively. They can be ascribed to fragments of molecules partially damaged from the solvent or from the interaction with the gold surface. Finally, the presence of very small entities C with average height lower than 0.2 nm are related to solvent impurities since they are present also when the gold substrate is dipped in the pure solvent (\(CH_2Cl_2\)).

A statistical analysis of the STM images gives that the features A (assigned to \(Mn_6-3tpc\)) cover about 20-35% of the gold surface for the s-ML 1, and only 15-25% for the s-ML 2 (see Table 4.1). The surface coverage including the features B (fragments of \(Mn_6-3tpc\)) can be roughly estimated at around 50% in both compounds.

The strength of molecule grafting on surface is also checked by increasing the tunneling current. Indeed the molecules are not shifted by the scanning tip, even when increasing the tunneling current up to 0.5 nA.

### 4.2.2 Chemical composition

XPS measurements are performed on the s-MLs of 1 and 2 as well as on drop-casted thick films used as reference for the analysis of the core-level lineshapes and stoichiometric ratio.

Fig. 4.7 shows the Mn-2p, N-1s, and O-1s core level spectra. Although the TFs and s-MLs spectra are quite broad they appear very similar and no chemical shift is observed. Therefore this suggests that the grafting process and the interaction with the gold surface do not significantly alter the chemical state of the \(Mn^{3+}\) ions.

Quantitative analysis of the XPS spectra allows to extract the stoichiometry ratios of the elements constituting the derivatives. The results are summarized in Table 4.1.

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6 More information are given in XPS analysis
7 More detail will be derived from XAS spectra in the next section
8 All core level intensities were normalized accounting for the atomic sensitivity factors and for the attenuation of the electronic signal due to the presence of an overlayer.
The N-1s/Mn-2p and O-1s/Mn-2p ratios measured for the s-ML 1 and 2 are in agreement with the corresponding values obtained for the TFs. Moreover they fit well with the nominal values (reported in brackets) suggesting the stability of the $Mn_6$ core in the deposition process. The observed small excess of oxygen is likely due to air exposure.
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Figure 4.7: Core level XPS spectra of the s-MLs and the corresponding TFs. All core-level intensities have been normalized in order to facilitate the comparison. In the case of the s-MLs the Mn-2p3/2 core level line is superimposed on the Au-4p1/2 feature. In order to obtain the isolated Mn-2p core level component, the attenuated gold contribution has been subtracted.
Table 4.1: Stoichiometry ratios of the elements in \( Mn_6 \) derivatives 1 and 2 TF and s-ML. The expected stoichiometric values are reported in brackets. In columns 6 and 7 are reported, respectively, the average area occupied by each S atom bond to gold and the free TP ligand coverage, as estimated considering a molecular density in TP SAMs ranging from \( 1S\ldots at./(22\AA^2) \) to \( 1S\ldots at./(34\AA^2) \) [23]. In the last two columns the Mn6 coverages derived by XPS and STM are compared.

<table>
<thead>
<tr>
<th>( Mn_6 )</th>
<th>N/Mn [1]</th>
<th>O/6Mn</th>
<th>S/6Mn [2]</th>
<th>Area/S ( \AA^2 )</th>
<th>free TP cov.</th>
<th>Au/Mn</th>
<th>XPS cov. %</th>
<th>STM cov. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-ML1 (S=4)</td>
<td>1.1 ± 0.2</td>
<td>30 ± 5 [22]</td>
<td>11 ± 2</td>
<td>90 ± 10</td>
<td>80-100</td>
<td>25-35 %</td>
<td>140 ± 30</td>
<td>26-38 %</td>
</tr>
<tr>
<td>s-ML2 (S=12)</td>
<td>0.9 ± 0.2</td>
<td>33 ± 5 [24]</td>
<td>12 ± 2</td>
<td>100 ± 10</td>
<td>90-110</td>
<td>20-30 %</td>
<td>170 ± 30</td>
<td>20-30 %</td>
</tr>
<tr>
<td>TF1 (S=4)</td>
<td>1.1 ± 0.2</td>
<td>25 ± 5 [24]</td>
<td>3 ± 1</td>
<td>90-100</td>
<td>3 ± 1</td>
<td>25-35 %</td>
<td>140 ± 30</td>
<td>26-38 %</td>
</tr>
<tr>
<td>TF2 (S=12)</td>
<td>1.1 ± 0.2</td>
<td>30 ± 5 [28]</td>
<td>2 ± 1</td>
<td>100 ± 10</td>
<td>25-35 %</td>
<td>140 ± 30</td>
<td>26-38 %</td>
<td>20-35 %</td>
</tr>
</tbody>
</table>
CHAPTER 4. RESULTS AND DISCUSSION

The average surface density for each $Mn_6$ molecule is derived from the Au-4f/Mn-2p ratio obtaining a value of one molecule every $(8 \pm 2$ nm$^2$) and $(10 \pm 2$ nm$^2$) for the s-ML 1 and 2 respectively. As the actual dimension of each cluster is about $2.5$ nm$^2$, the estimated surface density corresponds to a surface coverage of $26 - 38\%$ and $20 - 30\%$ for the s-ML 1 and 2 respectively.

The S-2p/6Mn-3p ratio provides the number of S atoms present for each $Mn_6$ cluster. While in both TFs this value only slightly exceeds the expected stoichiometric value of 2, in the s-MLs it is five or six times higher. This excess of S suggests that a fraction of thiophene (TP) ligands cleaves their bond to the $Mn_6$ molecular core and adsorbs as free molecules on the surface.

**Sulphur core level fitting**

More insight about the adsorption process can be obtained from a detailed analysis of the S core-level lineshape. In Fig. 4.8, the S-2p core levels of both s-MLs are shown along with their best fit curves. The S core-level of TF 1, reported for comparison, is quite broad and located at around 163-164 eV binding energy, which is typical for TFs of thiophene (TP) [51], [52].

The S-2p spectra of the s-MLs 1 and 2 have completely different lineshape, with strong contributions around 161-162 eV. The curve fitting of the S-2p core levels is performed using Voigt functions for the components split by spin-orbit interaction (see Fig. 4.8 caption for detail). For both s-MLs, four components were used at 161.3 (S2), 162.3 (S1), 163.3 (S3), and 164.3 eV (S4), respectively.

The presence of the S1 and S2 components has been reported in several papers and assigned to TP molecules chemisorbed on gold through a sulfur bond. Nevertheless the exact origin of the binding energy difference between S1 and S2 is still a matter of debate. Some authors attribute them to two different adsorption geometries, [51], [53]. Others suggest that S1 is related to free S-atom absorbed on gold and S2 to the presence of alkyl-thiolate species derived from the cleavage of TP rings [54]. The attribution of S1 to chemisorbed atomic sulfur can be excluded due to the well-known stability of sulfur inside the TP molecule. In any case S1 and S2 are assigned to different sulfur molecular species bonded to gold. As the $(S1 + S2)/6Mn$ ratio is $9 \pm 2$ in both derivatives and the S/6Mn ratio is $11$ and $12 \pm 2$ in the s-ML 1 and 2

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9Similar behavior will be reported also in the case of $Cr_7Ni$ derivatives in the next section.
Figure 4.8: S-2p core level fit for the s-ML of \( M_n \) \( S=4 \) and \( S=12 \). Fitting parameters: spin-orbit splitting of 1.2 eV, branching ratio of 0.5, Lorentzian width of 574 meV, and Gaussian width of 780 meV for all components. The S-2p core-level of TF \( M_n \) \( S=4 \) is also reported for comparison. The TF \( M_n \) \( S=12 \) spectrum (not shown) presents a very similar line shape.
respectively, then we conclude that 80-90% of the sulfur in excess is due to chemisorbed thio-ligands not bonded to the $Mn_6$ clusters.

For both s-MLs, the values of the $Au/(S1 + S2)$ ratio corresponds to a very similar surface density: 80-110 Å$^2$ per S atom. Since typical values of molecular density in self-assembled monolayer of TP range from 22 Å$^2$ to 34 Å$^2$ per S-atom [23], we estimate that in our case about a quarter of the surface is covered by a layer of free thio-ligands, forming a largely incomplete monolayer. These findings are fully confirmed by the STM measurements already discussed.

The S3 and S4 components are assigned in literature to TP molecules not directly bound to the gold surface [51],[52]. As for both compounds, the two 3-tpc ligands stem in opposite directions from the cluster core (Fig. 2.6), only one of them can bind to the surface. We tentatively attribute the S4 component to sulfur atoms in 3-tpc ligands which are bound to the cluster, but not to the gold surface $^{10}$. This attribution is supported by the S4/6Mn ratio (0.95 for the s-ML1 and 0.85 for the s-ML2). The S3 component is then tentatively assigned to 3-tpc ligands detached from the core of the cluster and weakly adsorb on top of the first adlayer$^{11}$ [55]. The S3/(S1 + S2) ratio indicates that about 10% in s-ML 1 and 20% in s-ML 2 of the first layer is covered by a second layer of unbound free TP ligands.

In summary, for the 1 and 2 s-ML we got the picture of well-isolated clusters strongly grafted on the gold surface via covalent bond between S and Au atoms. The molecules are surrounded by free TP ligands chemisorbed on the gold, forming a SAM which partially covers the surface. On top of the first layer the presence of a relatively small amount of weakly adsorbed free ligands is also revealed by XPS.

The different values of coverage for the two compounds may be tentatively ascribed to a different strength of the bond between the TP rings and the $Mn_6$ core. In fact, as shown in the Fig. 2.6, the TP rings of complex 1 are linked to the core by two oxygen bridges, whereas in complex 2 there is only one oxygen bridge suggesting a weaker bond. As a consequence complex 2 has a higher probability of loosing its functional groups so compromising its grafting capability.

$^{10}$This attribution is also supported in the case of $Cr_7Ni$ discussed later [55]

$^{11}$It cannot be observed in STM images presumably because weakly bonded species cannot be easily imaged by the STM tip
4.2. MN$_6$-3TPC

4.2.3 Electronic properties

In general, the interpretation of the absorption and dichroic spectra is not trivial, because their lineshapes change drastically with the strength of the crystal field and spin-orbit interaction. However, an help can be obtained from the comparison with similar spectra of well known reference systems and with simulated spectra as well.

XAS spectra taken with right and left circularly polarized light and the relative XMCD spectrum at the Mn $L_3$ and $L_2$ edges for the TF and s-ML of the derivative 1 and 2 are showed in the Fig. 4.9. The multipeaks of the absorption edges are due to a combination of the electron-electron interaction within the Mn ions, the crystal field felt by the Mn ions and the hybridization of Mn3d, O2p and N2p orbitals.

First we observed that the two almost isostructural compounds 1 and 2 show similar XAS and XMCD lineshapes as TF and as adsorbed on surface.\textsuperscript{12}

Second, by comparing the XAS spectra taken on the s-ML and TF, it is quite clear that an important modification, specially in correspondence of the $L_3$ peak, takes place. Notably this modification is identical in compounds 1 and 2 suggesting that well defined and systematic changes occur when the Mn$_6$ - 3tpc interacts with the gold surface.

In order to understand if the origin of these changes is due to modification of the Mn oxidation state, in Fig. 4.10 we compare isotropic XAS spectra with reference spectra of MnO (Mn$^{2+}$), Mn$_2$O$_3$ (Mn$^{3+}$) and MnO$_2$ (Mn$^{4+}$). A, C and D features are typical of the Mn in the oxidation states 2+, 3+ and 4+ respectively. From the comparison we observe that C peak dominates in TF, s-ML and Mn$_2$O$_3$ spectra while E and F at the $L_2$ edge are aligned only with the peaks in Mn$_2$O$_3$. This proves that the magnetic core of the 1 TF is actually made by Mn with oxidation state 3+. More interestingly, this characteristic is preserved in the s-ML.

We stress that no contribution of Mn$^{2+}$ (peak A around 639.6 eV) is visible in the s-ML unlike Mn$_{12}$-ac where it is well known that a systematic reduction of the

\textsuperscript{12}This is quite expected although, as showed in Fig. 2.6, the derivative 2 has all the 6 Mn in the center of an octahedron, whereas the derivative 1 has 4 Mn in the center of the octahedron (D4h symmetry) and 2 in square pyramidal geometry. Indeed, these structural differences do not appear from the comparison of XAS and XMCD lineshapes of 1 and 2. This can be understood if we consider that the XAS spectra gives an average of the absorption signal at the Mn sites. Then the contribution to the XAS signal in 1 is mainly given by the Mn in the octahedron rather than Mn in the square pyramidal position.
Figure 4.9: XMCD and XAS spectra with right (black line) and left (red line) polarization for the TF (upper panel) and s-ML (lower panel) of 1 and 2 compounds. The green line is the two step function subtracted to the XAS spectra. The blue curve is the integral curve of the XMCD spectra. The parameter $q$ is the integration of the XMCD spectra at the $L_2$ and $L_3$ edges. The very small value of $q$ indicates the quenching of the orbital moment.
Figure 4.10: Isotropic XAS spectra of TF and s-ML compared with reference spectra of MnO2, Mn2O3, MnO with Mn in different oxidation states 4+ (D), 3+ (C) and 2+ (A) respectively. The feature B is present in Mn6 compounds and Mn12-biph as well and it appears related either to another crystal symmetry or to deviations in the single crystal quality.

magnetic core occurs after the adsorption on the gold surface [14]. This means that the Mn$^{3+}$ ions in $Mn_6$-3tpc derivatives are much more resistant towards the reduction, so demonstrating the efficiency of the 3tpc functionalization.

The superimposition of XAS and XMCD spectra taken for TF and s-ML reported in Fig.4.11 shows more clearly the differences. First, feature B of the $L_3$ edge is present in either TF and s-ML, and in the reference spectra, is much higher in the TF. Indeed Ghigna[56] as well as Voss [14], observed the peak B in the $Mn_{12}$ - biph spectrum (Fig 4.10 brown curve) and they assigned it to a different crystal symmetry or to a poor single crystal quality. As we do not have crystals but powders with molecules randomly oriented, the attribution of B and its modification still remain an open problem.
Figure 4.11: Direct comparison between the XAS spectra (a) of the TF and s-ML of 1 reported in Fig. 4.10 and the relative XMCD spectra (b).
Second, an apparent transfer of spectral weights from C to A in s-ML with respect to TF occurs. This can be understood looking to the polycrystalline spinel manganite oxides well known for their large tetragonal distortions. These compounds exhibit a Jahn-Teller elongation of the $Mn^{3+}$ ions located in the center of the octahedral environment with five degenerate 3d orbitals split in three $t_{2g}$ and two $e_g$ orbitals.

In Fig.4.12 the Piedmontite and the $ZnMn_2O_4$ spectra are compared with $Mn_6$-3tpc TF while the $Mn^3acac$ and $ZnGa_1Mn_1O_4$ are compared with the relative s-ML. The similarity between the isotropic XAS spectra of $ZnMn_2O_4$, Piedmontite and $Mn_6$-3tpc TF (Fig. 4.12 left side) let us suppose that the Mn ions are surrounded by similar environment. Actually the strong distortion of manganite oxides as large as 18% with a apical/in plane ratio of 1.18 is close to the expected ratio of 1.19 in the $Mn_6$.

Whereas, the XAS spectra of the $Mn^3acac$ and $ZnGa_1Mn_1O_4$, having apical/in plane ratio of 1.06, are similar to the $Mn_6$-3tpc s-ML suggesting an almost perfect octahedra symmetry. Thus, we conclude that $Mn_6$-3tpc clusters adsorbed on gold surface to undergo towards a structural modification which reduces the elongation of the O-Mn-O axes.

**Multiplet simulations**

The origin of these spectral changes has been studied in ref.[57] using the Ligand Field Multiplet simulations. In this case the calculation was performed including the $D_{4h}$ point group symmetry and with 10Dq, the SlaterKoster transfer integral, the on-site Coulomb energy between 3d electrons, and the charge transfer energy from O2p to Mn 3d orbitals set to 1.3, 1.8, 8.0, and 5.0 eV, respectively. The other parameters can be found in the reference [57] and therein.

In order to simulate the experimental spectra, the Ds parameter (which takes into account the tetragonal distortion), was varied from 0 eV to 0.5 eV. Moreover, the core-hole lifetime and the experimental resolution were simulated applying a Lorentzian broadenings of 0.36 eV for the $L_3$ edge and 0.49 eV for the $L_2$ edge and Gaussian broadening of 0.3 eV respectively.

Actually, the simulations well reproduce all the features at the $L_3$ edge of the spinel manganite oxides with larger and larger apical/in plane ratio and prove that the relative intensity between A and C features in Fig.4.11a) is actually due to the
Figure 4.12: Left side: isotropic XAS spectra of 1 TF compared with those of strongly distorted $Mn^3acac$ and $ZnGa_1Mn_1O_4$ (apical/in plane ratio=1.18) compounds in D4h symmetry. Right side: isotropic XAS spectra of 1 ML compared with those of almost isotropic $Mn^3acac$ and $ZnGa_1Mn_1O_4$ (apical/in plane ratio=1.06) compounds in Oh symmetry. Moreover the digitalized XAS spectra (dark green) from the ref. [57] simulated with multiplet calculations are reported.
modifications of the geometrical environment around the Mn ion. Fig. 4.12 shows that the XAS spectra of $Mn_6$ as TF and as s-ML are in reasonably agreement with those simulated for $10Dq = 1.3eV$ and for $Ds = 0.4eV$ and 0.25eV respectively.

**Mn 3d density of states**

The experimental DOS associated with the Mn 3d states of s-ML 1 was also derived using resonant photoemission spectroscopy (RESPES) at the Mn $L_{2,3}$ edge and compared with the corresponding DOS calculated by means of LDA+U [58]. With respect to the standard photoemission techniques, RESPES has the advantage of extracting only the partial DOS corresponding to Mn 3d states avoiding the contribution of oxygen, carbon, and all other atoms forming the organic shell of the molecule. Moreover the not negligible contribution of the gold in the s-ML can be also subtracted.

In more detail resonant photoemission is a particular mechanism occurring when the energy of the photons, used to excite the electron emission, is varied in the narrow range encompassing the absorption edge of a core level (in our case the Mn 2p edges).

At these energies, three different electron emission mechanisms from the valence band (VB) states can occur: (a) direct photoemission, (b) autoionization associated to the decay of the electron initially promoted from the core level into an empty bound state of the atom during the photon absorption (e.g. Mn 2p $\rightarrow$ 3d); (c) Auger emission of a valence electron after the creation of the core-level hole induced by the incoming photon.

The first two emission mechanisms provide an outgoing electron with the same kinetic energy, which can therefore interfere determining a resonance enhancement of photoelectron intensity at proper photon energies [59]. In general the Auger channel can be proved to be negligible. Furthermore, the Auger electron kinetic energy does not depend on the photon energy but is fixed as it derives from the energies of the electron levels involved in the process, and no interference mechanism occurs [60]. RESPES allows therefore to single out from a compound the valence states mainly belonging to the atoms whose edge is excited, by considering the difference between the VB spectrum taken at resonance photon energy and that taken in out-of-resonance conditions.

Fig.4.13 a) shows the photon energies selected on Mn $L_{2,3}$ edges used to carry out the photoemission measurements, while the Mn6-3tpc VB spectra at increasing photon
Figure 4.13: Panel a): Mn6-3tpc/Au(111) VB spectra at increasing photon energies across the Mn $L_{2,3}$ edge. The corresponding energies used for the RESPES measurements are indicated by black dots superimposed on the absorption spectra. Panel b): Mn6-3tpc VB spectra at increasing photon energies from 634 to 656 eV in 1 eV steps. Panel c) VB spectra in panel b) subtracted for the gold contribution at $h\mu=634$ eV to single out the enhancement corresponding to the Mn 3d DOS.
Figure 4.14: Partial DOS for 3d orbitals of Mn obtained by the (a) LSDA and [(b)-(e)] LDA+U method using a U value from 2 to 8 eV. Dashed line on panel (c) corresponds to the experimental spectrum in Fig. 4.13.
energies from 634 to 656 eV in 1 eV steps are reported (Fig. 4.13b)).

As the Mn$_6$ molecules cover only approximately 30% of the substrate, the main contribution to the spectra comes from the Au VB states. Therefore, the enhancement corresponding to the Mn 3d DOS is singled out subtracting (at each VB spectrum) the first one (off-resonance spectrum) measured at $h\nu = 634$ eV (Fig. 4.13c)). The resulting spectra show an enhancement around the $L_3$ edge while a very small, if any, resonance appears at the $L_2$ edge. Moreover no Auger signal is detected in the spectra. These characteristics seem to be common to all the MNM submonolayers we investigated: Mn$_6$, Mn$_{12}$Ac, [61] and Cr$_7$Ni[62].

In Fig. 4.14, we show the results of the LDA+U calculations reporting the 3d derived DOS for different values of the Coulomb repulsion (U) in Mn$_6 - 3tpc$. For U below 4 eV, the system is still metallic and a gap (of about 1.5 eV) opens only for U=4 eV. The experimental Mn DOS has been slightly shifted in energy and normalized in height to be superimposed to the calculations. We found that the comparison with the DOS calculated for U=4eV provides the best agreement in terms of bandwidth, shape, and energy position of the maximum. The experimental and theoretical bandwidths coincide and the overall shapes are quite similar. The two features at approximately -4 and -9 eV of BE are well reproduced. The slight discrepancy between -1 and -3 eV can be due to several reasons, one of them could be that the experimental spectra correspond to a final state with n-1 electrons, whereas the one obtained theoretically is a n-electron state.

4.2.4 Magnetic properties

The differences observed in Fig. 4.11b) between the XMCD spectra of Mn$_6$ derivatives as TF and as s-ML reveal deviations in their magnetic properties that we are going to discuss in the following.

XMCD provides an unique tool to separate the spin and orbital contributions to the total magnetic moment. This can be done applying the XMCD sum rules developed by Carra and Thole et al. [45], [44].

Indeed, the application of the XMCD sum rules for transition metals faces some limitations. These are specially related to the j-j mixing effect due to the 2p-3d electrostatic interaction relatively large compared to the 2p spin-orbit interaction. This

\[\text{By the way, we notice that the Auger signal is perfectly detectable in a Cr}_7\text{Ni thick layer [62].}\]
4.2. MN₆-3TPC

Figure 4.15: XMCD signal for the TF and s-ML of 1 and 2 for field up to 5T and different temperatures (10, 15 and 25K). The s-ML show a strong reduction of the total magnetic moment compare to the TF.

causes the overlapping of the \(2p_{3/2}\) and \(2p_{1/2}\) manifold levels with a transfer of spectral weights, in XAS spectra, from \(L_2\) edge to \(L_3\) or viceversa.

An exception is represented by heavy transition metals, where the spin-orbit coupling is quite strong and the \(L_2,3\) edges can be easily separated. Then the resulting magnetic moments can be reliably estimated from the sum rules. In the case of lighter transition metals the \(J\)-\(J\) mixing is strong with the impossibility to separate the \(L_{2,3}\) edges. As a consequence the application of the sum rules produces a spin magnetic moment reduced up to 50% of the real value compromising their validity.

In the case of Ni, for instance, the validity of the sum rules is well established, while in the case of Cr and Mn is usually inappropriate. In spite of this, a simple phenomenological model which permits to quantify the deviation of the calculated spin magnetic moments from the real values was proposed by Goering[48]. This model is
based on the calculation of a spin correction factor (SC) related to the branching ratio (see Chapter 3). Then, an approximated estimation of the transfer of spectral weights from one edge to the other can be obtained.

We will try to apply very carefully this method in the case of Cr for Cr$_7$Ni rings (see next section). Then, the validity of this model is checked a posteriori by comparing the spin moments so calculated with standard magnetic measurements and spin-Hamiltonian simulations.

In the case of Mn the applicability of the anisotropic sum rules is also complicated by the determination of the magnetic dipole term ($T_z$) and charge anisotropy which cannot be neglected in such strongly anisotropic Mn$_6$ complexes. Thus we will not apply the sum rules for Mn and we will limit the study to the interpretation of the dichroic signal.

As in the sum rules, the orbital moment is proportional to the total XMCD area ($q$ in Fig. 4.9) it is not affected by the j-j mixing and its applicability still holds. Fig. 4.9 shows that $q$ is vanishing for both TF and s-ML as a consequence the total quenching of the orbital moment can be directly observed. Indeed, this result is expected in 3d transition metals because of the large crystal electric field compared with the spin-orbit coupling.

In Fig. 4.15 the integral of the normalized XMCD spectra at the $L_3$ edge relative to the spin part of the total magnetic moment is plotted as function of the magnetic field up to 5T and for different temperatures (10, 15 and 25 K). The results for the s-ML and the TF are reported with error bars assumed to be about 20%. A net decrease of the XMCD signal of the s-ML with respect to the TF occurs and this reduction varies from 30% to 50% by increasing the temperature.

A possible explanation of the spin moments reduction could be the transition from a high-spin to a low-spin state driven by the competition between the exchange coupling (between the 3d electrons) and the crystal field strength. The isolated Mn$^{3+}$ atom has a stable high-spin Hund’s rule ground state, whereas an itinerant low-spin ground state is formed in Mn metal. In ref. [63] these two states have been systematically investigated for Mn atoms, from bulk to thin film, monitoring the XAS lineshape [64].

$^{14}T_z$ can be determined experimentally on highly oriented molecules on surface or on crystals by performing XMCD measurements as function of the angle between the X-ray and the magnetic field direction. In our case the easy axes of the molecules is rather isotropic in the space and as a consequence $T_z$ cannot be determined.
Those authors found a smooth shape of XAS spectra for itinerant systems (low-spin) while localized 3d states (high-spin) have a multipeaks structure. Actually, XAS lineshape for both s-ML and TF of 1 and 2 have multipeaks structure. This suggests that even after the grafting on surface, 1 and 2 derivatives still have localized 3d states with high-spin state. We conclude that the modifications observed between s-ML and TF of both derivatives cannot be ascribed to spin-transition.

A different explanation of the magnetization reduction in the s-ML could be ascribed to the distortion of the local environment of Mn sites, as indicated from XAS spectra, with a modification of the relative distances between the Mn ions. Then, the Mn-Mn exchange coupling could be reduced so considerably affecting the molecular spin ground state.

4.3 Cr\textsubscript{7}Ni derivatives

4.3.1 Topography

Fig. 4.16 shows representative STM images (acquired at 2\textdegree{V} bias voltage and 30pA in constant-current mode) of the Cr\textsubscript{7}Ni − 3tpc, −thio\textsubscript{b}, and −4mtpp derivatives that we call for sake of simplicity 1, 2 and 3 respectively.\textsuperscript{15}

All the images show the presence of a quite homogeneous submonolayer distribution of large and small white spots indicated with A and B respectively. Moreover, only in the STM images acquired for 1 and 2 black spots indicated with C are also visible.

An accurate analysis of the line profiles of these images (Fig. 4.16 in the middle) showed that the average diameter of A for 1, 2 and 3 images are 4.0 ± 0.5 nm, 3.5 ± 0.5 nm and 3.5 ± 0.5 nm respectively. If we take into account the curvature radius of the STM tip and assume that the rings lie flat on the surface, these values agree with those expected for the Cr\textsubscript{7}Ni derivatives (2.2, 1.8 and 1.7 nm respectively). Furthermore, the measured average height of A is 1.0 ± 0.1 nm for 1 and 3 and 0.8 ± 0.1 nm for 2. Indeed these values are much lower those expected for the clusters (1.5, 1.1 and 1.6 nm for 1, 2, and 3 respectively). The reasons of these deviations can be easily explained in 3 by the lower conductivity of the clusters peripheral ligands compare to the gold surface. While in 1 and 2 the measurements of the height is

\textsuperscript{15}Hereafter we will indicate with 1, 2 and 3 the compounds as well as the relative STM images reported in Fig. 4.16.
Figure 4.16: Top panel: room temperature STM images (2V and 0.03nA) for the Cr$_7$Ni derivatives. A indicates the presence of entities with size comparable with those of the MNMs. B indicates the presence of fragments and C are the Vacancy Islands (see text). Bottom panel: line profiles and a 3D view of the entities indicates with the letter A.
complicated by the presence of a self-assembled monolayer (SAM) of organic ligands (about 0.5-0.6 nm height) surrounding the \(Cr_7Ni\) clusters (see scheme 4.17). \(^{16}\)

In facts, in 1 and 2 the black spots C, having a depth of a monatomic Au terrace (2.4 Å) and wide 50-100 Å\(^{27}\), \(^{65}\) are typical depressions of the gold surface called vacancy islands (VI). Their presence indicates the formation of a SAM of organic ligands (thiophene for 1 and of alkanethiol for 2) surrounding the clusters \(^{51}\),\(^{53}\).

Thus, although the 3-tpc ligands in 1 should be strongly attached to the cluster core through Cr-O bonds part of them dissociate in solution. Notably, the dissociation does not depend on the use of a polar solvent (THF) because VI formation has been observed also with a non-polar solvent (toluene). Whereas in 2, the formation of a complete alkanethiol SAM \(^{23}\), \(^{27}\) is accomplished by the breaking of the ammoniumthiol template from the cluster ring. On the other hand, in 3, a lower amount of small entities B and the absence of the VI suggests that a very low number of ligands breaks in solution.

Furthermore, we observed that the kinetics of the VI formation in 1 and 2 is quite different. In 2 the VI appear after 10 min of immersion while in 1, the VI become more evident only for the longest immersion time of 20\(h\). The longer time required for the formation of a densely packed thiophene SAM with respect to the alkanethiol can be explained by a lower mobility of the adsorbed TP molecules bonded to gold \(^{51}\).

At support of the identification of the spots A with \(Cr_7Ni\) clusters, we note that the difference expected among the size of these compounds are well reproduced by the experimental values. Thus the measured diameter for 1 is actually 0.5 nm larger than 2 and 3, and the diameter of 2 and 3 are almost the same. Moreover the experimental height of 1 and 3 are identical while that of 2 is lower just as expected.

Finally, the small white spots (B) have average height and diameter lower than 0.8 Å and 2 nm respectively and can be ascribed to a fragments of clusters either grafted on surface or lying on top a first layer (Fig. 4.17).

From a statistical analysis of the STM images, we estimated a larger surface coverage of A in 3 (25-30%) than for 1 and 2 (16-24% and 5-8% respectively). The corresponding average area occupied by a single cluster were 20 ± 5 nm\(^2\) for 1, 40 ± 10 nm\(^2\) for 2 and 8 – 9 ± 2 nm\(^2\) for 3.

\(^{16}\)At variance of 3, we assume that in 1 and 2 the electronic contribution of the peripheral ligands around the cluster, imaged by the STM tip, is similar to that of the SAM, the STM profile can be directly linked to the sample topography.
CHAPTER 4. RESULTS AND DISCUSSION

Figure 4.17: Scheme showing the identification of the entities A, B and C indicates in Fig. 4.16

At last the low noise-level and the stability of the clusters even at higher tunneling currents (up to 500 pA, they are not shifted by the scanning tip) confirmed the expected strong covalent bond between sulphur functionalized \( \text{Cr}_7\text{Ni} \) rings and the gold surface.

4.3.2 Chemical composition

The STM results are supported by quantitative XPS investigations. Fig. 4.18, reports the core levels of the samples 1 and 2.\(^{17}\) All the core level intensities have been normalized taking into account the atomic sensitivity and the attenuation of the electronic signal.

First we measured the Cr-2p, F-1s, and Ni-2p XPS core levels for the sub-monolayers and thick films (not reported here) of 1, 2, and 3 derivatives. As no energy shift was observed, we conclude that the chemical bonding of these elements is preserved after the deposition on the surface.

Then a quantitative analysis of the core levels spectra was carried out and the resulting stoichiometry ratios are reported in Table 4.2. As the F-1s/Cr-2p and Cr-2p/Ni-2p ratios are close to those expected and reproducible in all runs, this proves the ring stability for 1, 2, and 3 compounds.

The Cr-2p/S-2p ratio provides indications about the stability of the functionaliza-

\(^{17}\)The core levels of the 3 compound are omitted for sake of clearness.
4.3. \textit{Cr}_7\textit{Ni} Derivatives

Figure 4.18: Core level XPS spectra for Au(111) surface dipped for 10 min in a 5 mM solution of \textit{Cr}_7\textit{Ni} − 3tpc (black) and \textit{Cr}_7\textit{Ni} − thiob (red) derivatives in THF. The background contribution has been subtracted. The \textit{Cr}_7\textit{Ni} − 4mtpp is not reported.

For the compounds 1 and 2 the large excess of sulphur supports the presence of a SAM of thiol ligands, just as observed by STM images. Whereas in 3 the excess of sulphur is not sufficient to form a complete SAM as proved by the Au/S ratio which is basically the same for 1 and 2, but almost two times higher in 3.

Taking into account the gold signal attenuation due to the SAM and the clusters, from the Au-4f/Cr-2p ratio we can derive an average area per cluster of 10 ± 3 nm$^2$ for 1, 36 ± 8 nm$^2$ for 2, and 7.8 ± 2 nm$^2$ for 3. Then if we suppose that the nominal area for 1 is 3.8 nm$^2$ and 2.5 nm$^2$ for 2, and 3, the relative values of coverage are 22-30%, 6-9%, and 25-30% respectively. Notably these values fit well with those estimated from STM (see last column of Table 4.2).
<table>
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<tr>
<th>s-ML - Cr&lt;sub&gt;7&lt;/sub&gt;Ni</th>
<th>F/Cr [8/7]</th>
<th>Cr/Ni [7]</th>
<th>Cr/S</th>
<th>Au/S</th>
<th>Au/(Si + S2)</th>
<th>SAM (Å&lt;sup&gt;2&lt;/sup&gt;/S)</th>
<th>Au/Cr</th>
<th>XPS cov. %</th>
<th>STM cov. %</th>
</tr>
</thead>
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<tr>
<td>3tpc</td>
<td>1.09 ± 0.05</td>
<td>6 ± 2</td>
<td>0.16 ± 0.01 [0.44]</td>
<td>21± 2</td>
<td>22± 2</td>
<td>20-26</td>
<td>150 ± 30</td>
<td>22-30</td>
<td>16-24</td>
</tr>
<tr>
<td>thiob</td>
<td>1.13 ± 0.05</td>
<td>5 ± 2</td>
<td>0.04 ± 0.01 [7]</td>
<td>20± 2</td>
<td>27± 2</td>
<td>23-31</td>
<td>500 ± 100</td>
<td>6-9</td>
<td>5-8</td>
</tr>
<tr>
<td>4mtpp</td>
<td>1.08 ± 0.05</td>
<td>6 ± 2</td>
<td>0.47 ± 0.01 [7]</td>
<td>50 ± 2</td>
<td>-</td>
<td>-</td>
<td>110 ± 30</td>
<td>28-35</td>
<td>25-35</td>
</tr>
</tbody>
</table>

Table 4.2: Stoichiometry ratios obtained from the quantitative analysis of the core level intensities for Cr<sub>7</sub>Ni-3tpc (1), -thiobutane (2) and -4mtpp (3) sub-monolayers. In brackets are reported the nominal stoichiometry ratios. The last two columns report the surface coverage estimated by XPS and by STM (corresponding to the spots A in Fig. 4.16) techniques.
For a more accurate investigation of the thiophene and alkanethiol SAM in 1 and 2 respectively, we isolated the different contributions to the S-2p core level (Fig. 4.19). The S-2p fitting procedure has been performed using spin-orbit split doublet components (Voigt functions) with the following parameters: spin-orbit splitting of 1.2 eV, branching ratio of 0.5, Lorentzian width of 574 meV, and Gaussian width of 600 meV for all components.

First of all the main peak of the S-2p spectrum for the TF (not reported here) is found at about 164 eV while for the s-ML of 1 and 2 it is about 162 eV. This energy shift is clearly due to the interaction of the S atoms with the gold surface. The several features appearing in the s-MLs spectra are characteristic of different chemical bonding states of the S. The identification of such features is discussed in the following.

For the s-ML 2, three components are observed at 161.4 eV (S2 peak), 162.2 eV (S1), and 163.3 eV (S3) (see Fig. 4.19 and 4.20). S1 and S2 can be assigned to thiolate S atoms bonded with gold in different configurations. For instance, S1 could be ascribed to thiol ligands still bound to the molecule and to the surface as well, while S2 could be ascribed to thiol ligands detached from the cluster and grafted on the gold surface. S3 can be tentatively assigned to unbound S grafted on top of the SAM [68],[69],[52] (Fig. 4.20).

From the Au/(S1 + S2) ratio, reported in Table 4.3, we can derive a packing level for the first monolayer of 23-31 Å²/S atom, comparable with previous STM studies on alkanethiol SAMs which indicate a packing level ranging from 22 to 34 Å² per molecule [23]. From the S3/(S1 + S2) ratio, we can derive that about 15% of the first SAM is covered by a second layer of unbound free alkanethiol ligands. Once again this value agrees with the STM analysis of the B spots.

For the s-ML 1, four components are observed at 161.5 (S2), 162.3 (S1), 163.3 (S3), and 164.2 eV (S4) (see Fig. 4.19 and 4.20). Like in s-ML 2, S1 and S2 can be ascribed to S atoms of thiophene molecules chemisorbed on gold in two different adsorption configurations [51]: S1 to thiophene rings bounded to the clusters and the gold surface while S2 component is associated with a sulfur species bonded to gold.

\[\text{Indeed, the S2 component is usually assigned to isolated atomic S deriving from the cleavage of the C-S bonding [66], [67]. On the other hand, Ishida et al. give a different assignment, suggesting the presence of a thiol bounded through sulfur, in an sp configuration [52]. In both cases the S2 component is associated with a sulfur species bonded to gold.}\]
Figure 4.19: Comparison between S-2p core level fits for the ML of $Cr_7Ni - 3tpc$ (top panel) and $Cr_7Ni - thiob$ (bottom panel). The fitting parameters are: spin-orbit splitting = 1.2 eV, branching ratio = 0.5, Lorentzian width = 574 meV, and Gaussian width = 600 meV for all components.
Figure 4.20: Scheme of the assignment of the Sulphur components (S1, S2, S3 and S4) in the s-ML 1 (top panel) and 2 (bottom panel)

and S2 to thiophene rings bonded only to the surface.

A different interpretation has been given by Sako et al. [54]. They suggest that the thiophene ring could break in solution due to the cleavage of one C-S bond. In this hypothesis, the grafting of the cluster would be assured by alkyl-thiolate chains instead of thiophene rings. By the way in both cases S1 and S2 are associated with two sulfur species bonded to gold (Scheme 4.20).

From the Au/(S1 + S2) ratio (Table 4.3), we can derive a packing level for the first monolayer of 20-26 Å²/S atom, slightly higher than in the case of the s-ML 2.

S3 and S4 are assigned to unbound thiophene molecules in agreement with previous XPS investigations [52] [68]. In particular we assign again S3 to 3-tpc ligands detached from the clusters and bound to gold surface. Then the S3/(S1 + S2) ratio, gives that only the 8% of the surface is covered by a second layer of thiophene ligands in agreement with STM surface coverage analysis of the B spots.

If we assume that the the compound 1 grafts preferentially flat on surface with only 4 thiophene rings bonded to the surface while the others 12 unbound, then the S4

\[^{19}\text{This can be explained if we consider that in 1, for each cluster, there are probably four 3-tpc ligands bonded with gold and twelve unbound. While in 2 there is only 1 sulphur atom per cluster.}\]
component can be related to those thiophene ligands unbound to the surface but still bound to the clusters. This is supported by the S4/Cr ratio of 1.5 ± 0.2 reasonably in agreement with the expected value of 1.7 (12/7).

4.3.3 Electronic properties

The black curves, reported in Fig. 4.21, are the XAS spectra measured at the $L_{2,3}$ edges of Cr and Ni for the TFs of $Cr_7Ni – piv$ (the compound without functionalization) and of several derivatives: 3tpc, thiobutane, phenoxybenzoic and Co-phtalocyanine (CoPc)\(^{20}\)\(^{21}\).

The spectra lineshape for the Cr is quite similar to those measured in ref. [70], [71],[50] where the Cr has oxidation state 3+, high - spin state and local Oh symmetry. Whereas the spectrum for the Ni exhibits the characteristic lineshape of the divalent Ni. The 2 peaks at the $L_2$ edge are the fingerprint of the high-spin state and local Oh symmetry [50],[71],[72],[73].

The almost identical XAS lineshape in the TFs of the $Cr_7Ni$-piv compound and in all the derivatives shows that the functionalization does not effect the local environment and oxidation state at the Cr and Ni site. This is a quite important result because allow us to change the peripheral ligands with the most suited without altering the structural and electronic properties of the $Cr_7Ni$ core.

The XAS spectra taken for the s-MLs of 1 and 3 are also reported in Fig. 4.21 (red curves). The s-ML 2 is excluded for the study of the electronic and magnetic properties of the $Cr_7Ni$ core on surface because of its very small coverage and the low signal/noise ratio in the XAS spectra.

Once again the XAS spectra of $Cr_7Ni$ derivatives as TF and s-ML are almost identical demonstrating the effectiveness of the 3tpc and 4mtpp functionalization to preserve the local properties at the Cr and Ni sites. Thus we proved that the oxidation states and geometrical environment around the magnetic ions are not altered from the interaction of the molecules with the gold surface.

Notably we monitored the XAS lineshape for long exposition times of the samples to the X-ray beam. No sign of degradation was observed even after some hours. Thus

\(^{20}\)The structures of phenoxybenzoic and Co-Pc are reported in Fig. 4.22. These derivatives are the subject of new studies on the deposition of $Cr_7Ni$ clusters on graphite.

\(^{21}\)In Fig. 4.21 the XAS spectra for the 4mtpp TF derivative is omitted for sake of simplicity, while its s-ML is reported (red curve)
we succeeded the deposition on gold surface of Cr$_7$Ni clusters with high redox and structure stability. This is not trivial result if it is compared with the instability of Mn-based nanomagnets, like the $Mn_{12}$ [14] and the $Mn_6$, grafted on the gold surface.

**Multiplet simulations**

In order to get more information we simulated the XAS and XMCD spectra using a Ligand Field Multiplet model$^{22}$[76],[77],[78],[79]. In this case the crystal field model is sufficient to simulate the Cr and Ni spectra, so the charge transfer contribution was not included. This indicates that the hybridization level between the 3d orbitals of Cr and Ni, and the 2p orbitals of the surrounding atoms (O and F) is negligible.

The calculation takes into account the spin-orbit coupling and treats the environment of the absorbing atom through the crystal field parameters ($10D_q$, $D_s$ and $D_t$). First the energy levels of the initial and final states are calculated in spherical (SO3) symmetry. The parameters used in the calculation are: the Slater integrals and, the 2p and 3d spin - orbit interactions in the initial ($F_{2p}^2$, $F_{3d}^4$, $\zeta_{3d}$) as well as in the final states ($F_{2p}^2$, $F_{3d}^4$, $F_{2p}^2$, $G_{1p}^4$, $G_{3d}^3$, $\zeta_{2p}$, $\zeta_{3d}$). Then the solid is simulated adding a crystal field Hamiltonian as a perturbation of the atomic results and projecting the SO3 symmetry in any desired point group symmetry using the approach exposed by Butler [79]. For instance, in Oh symmetry the 3d orbitals are split into $e_g$ and $t_{2g}$ orbitals with an energy difference of $10D_q$. A further lowering of the symmetry to D4h splits the orbitals by the additional $D_s$ and $D_t$ parameters.

First, the experimental spectra were simulated computing the atomic parameters for the transitions $2p^63d^8 \rightarrow 2p^53d^9$ and $2p^63d^3 \rightarrow 2p^53d^4$ for Ni$^{2+}$ and Cr$^{3+}$ respectively (Tab. 4.3).

Then the Slater integrals and the ligand field parameters were tuned to reproduce the XMCD and isotropic XAS experimental spectra. Thus, the former were reduced to 80% of the original values to include intra-atomic configuration interaction [41]. Whereas, for the latter we found: $10D_q = 1.5$ eV, $D_s = D_t = 0$ for the Ni$^{2+}$ and $10D_q = 2.1$ eV, $D_s = 0.05$ eV, $D_t = 0$ for the Cr$^{3+}$.$^{23}$

An almost perfect local Oh symmetry was found for the Ni$^{2+}$ ($D_s=0$), while the Cr$^{3+}$ is in a slightly tetragonal D4h symmetry ($D_s = 0.05$ eV). Anyway the very small

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$^{22}$The Ligand Field Model (LFM) was first developed by Yamaguchi et al.[74] and was more completely generalized in the works of Thole, van der Laan and co-workers [75], [76].

$^{23}$Dt was set to zero in order to minimize the number of parameters used.
Figure 4.21: Cr and Ni isotropic $L_{2,3}$ XAS spectra taken for the TF of several $Cr_7Ni$ derivatives (black curves) and the s-ML of -4mtpp and -3tpc derivatives (red curves). The identical XAS lineshape suggests that the oxidation states and local environment are not affected by the peripheral ligands and gold surface as well.
Figure 4.22: The $Cr_7Ni$ derivatives synthesized for the anchoring on graphite substrate.
value of Ds allows us to consider an Oh symmetry also for the Cr$^{3+}$ ions.

<table>
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<tr>
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</tr>
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<td>$F_{dd}^4$</td>
<td>6.078</td>
<td>5.404</td>
</tr>
<tr>
<td>$F_{pd}^2$</td>
<td>6.177</td>
<td>5.221</td>
</tr>
<tr>
<td>$G_{pd}^1$</td>
<td>4.630</td>
<td>3.830</td>
</tr>
<tr>
<td>$G_{pd}^3$</td>
<td>2.633</td>
<td>2.178</td>
</tr>
<tr>
<td>$\xi_{2p}$</td>
<td>0.083</td>
<td>0.102</td>
</tr>
</tbody>
</table>

Table 4.3: Crystal field parameters ($10D_q$, $D_s$ and $D_t$), Slater-Condon integrals, and 2p and 3d spin-orbit interactions used in multiplet calculations for Ni$^{2+}$ and Cr$^{3+}$ for the initial and final states. All the values are in eV.

The calculated spectra at the $L_{2,3}$ edges, shown in Fig. 4.23, are broadened with a Lorentzian ($W_{L_2} = 0.2$ eV and $0.4$ eV, $W_{L_3} = 0.6$ eV and $0.4$ eV for Cr$^{3+}$ and Ni$^{2+}$ respectively) and Gaussian ($W_G = 150$ meV) to simulate the core hole lifetime and the experimental resolution.

All the peaks in the experimental spectra are well reproduced confirming that the ligand field multiplets dominate the spectral shape.

The random orientation of the molecules in TF would require to perform angular averages of the absorption cross section for all possible orientations of the magnetic field with respect to the molecular axes.

However, van Elp et al. [80] found that, at least in case of Ni$^{2+}$ and Cr$^{3+}$ in Oh symmetry, the difference between the XAS spectra taken at different orientations was vanishingly small. So the calculations in Fig. 4.23 were simply performed applying a magnetic field of 0.3 meV, which corresponds approximately to that experimental of 5 T, along the [001] crystallographic axes [81].
4.3. \textit{Cr}_7\textit{Ni} DERIVATIVES

Figure 4.23: XAS (top) and XMCD (bottom) spectra for Cr (left) and Ni (right) simulated with crystal field multiplet simulations (red curves). The parameters used in the simulations are: $10D_q=2.1$ eV, $D_s=0.2$ eV for $Cr^{3+}$ and $10D_q=1.5$ eV and $D_s=0$ for the Ni. $D_t$ is set to 0. Gaussian and Lorentzian broadening are applied in order to fit the experimental data (see text). The TF Cr$_7$Ni-3tpc spectra at the $L_{2,3}$ edges are also reported for comparison (black curve).
4.3.4 Magnetic properties

The type of exchange interaction between the Cr and Ni magnetic moments can be deduced from the sign of the XMCD signal. Fig. 4.24a) and b) show the normalized XMCD spectra at the $L_{2,3}$ edges of Cr and Ni at 5T and 10K for the -piv and -3tpc TF respectively. By using the sign of the $L_3$ edge as probe of the magnetic coupling, we find that the relative dichroic signals between the Cr and Ni are opposite. As expected, the Cr and Ni magnetic moments are antiferromagnetically coupled in the ring with the Cr magnetic moment parallel to the field and that of the Ni antiparallel. Moreover, the XMCD intensities of the Cr for the -piv and -3tpc TF are comparable while those of the Ni are quite different. This suggests that the functionalization induces some changes in the Cr-Ni magnetic coupling.

Surprisingly, a completely different behavior is observed for the s-MLs of -3tpc on gold surface (c spectra) where, in the same conditions of field and temperature (5T and 10 K), the $L_3$ signals of Cr and Ni have the same sign. Thus, the Cr and Ni magnetic moments are ferromagnetic. The same effect is observed for -4phen and -4mtpp derivatives where the different functionalizations do not prevent the reversing of the Ni magnetic moment (e and g spectra).

As it will be discussed later, we suggest that the reversal of the Ni spin moment in the s-MLs with respect to the TF can be simply explained in terms of the strong reduction of the $J_{Cr-Ni}$ exchange parameters.

Now we dwell on the causes responsible of the modifications of the Cr and Ni magnetic coupling: the solely clusters-gold surface interaction or the combined effect of the gold surface with the X-ray beam. The former induces a structural modification of the Cr$_7$Ni rings upon the deposition via strong covalent bond, while in the latter X-rays induce emission of secondary electrons from the gold surface which in somehow affects the molecules. \(^{24}\) Unfortunately we cannot distinguish the two causes, anyway it is clear that the gold surface plays a crucial role affecting directly or indirectly (via X-ray beam) the molecules in their magnetic properties.

We tried to deposit the Cr$_7$Ni derivatives (-3tpc, -4mtpp and -4phen) on a different surface, in this case HOPG surface, using the same deposition procedure. The results

\(^{24}\)The solely effect of the X-ray beam is excluded because the XAS lineshape shows any sign of degradation even after long exposition time, and notably the Cr-Ni antiferromagnetic coupling is preserved in the Cr$_7$Ni TFs
Figure 4.24: XMCD spectra at the $L_{2,3}$ edges of Cr (on the left) and Ni (on the right) at 5T and 10K of the samples: a) TF $Cr_7Ni$ - piv, b) TF $Cr_7Ni$ - 3tpc, c) s-ML $Cr_7Ni$ - 3tpc / Au, d) s-ML $Cr_7Ni$ - 3tpc / HOPG e) s-ML $Cr_7Ni$ - 4phenoxybenzoic / Au, f) s-ML $Cr_7Ni$ - 4phenoxybenzoic / HOPG, g) s-ML $Cr_7Ni$ - 4mtpp / Au, h) s-ML $Cr_7Ni$ - 4mtpp / HOPG. The relative sign of the XMCD signal at the $L_3$ edge between the Cr and Ni is related to their magnetic coupling. HOPG surface preserves the Cr-Ni antiferromagnetic coupling as in the TFs at variance of the gold surface where the Cr and Ni are ferromagnetic coupled for all the derivatives studied. The functionalization of the $Cr_7Ni$ ring plays a role in the strength of the magnetic coupling.
show that the XAS spectra (not reported) are still identical to the relative derivatives on gold substrate. Most importantly, the Ni and Cr XMCD signals at the $L_3$ edge have opposite signs. This means that the Ni magnetic moment is antiferromagnetically coupled to that of the Cr just like expected in $Cr_7Ni$ rings. Moreover the XMCD intensity, for both Cr and Ni, are comparable to the relative TF at least in -3tpc derivative.\(^{25}\)

Unfortunately, we did not achieve a s-ML distribution of well isolated $Cr_7Ni$ rings on HOPG maybe due to the not appropriate functionalization. However, this measurements allow us to conclude that the HOPG surface is quite interesting surface as it can be used for the deposition of $Cr_7Ni$ rings without altering their magnetic and electronic properties. We suppose that, probably, this can be extent to others MNM families. Therefore, in the next future, we will address our interest into the study of more appropriate $Cr_7Ni$ derivatives for the grafting on HOPG surface.

**XMCD sum rules for thick films**

Quantitative analysis of XMCD spectra provides the spin and orbital magnetic moments by means of the sum rules (equation 3.4). As already discussed in the Chapter 3, their application faces several drawbacks, which must be carefully considered, namely: (i) the magnetic dipole operator ($T_z$); (ii) the determination of the effective number of 3d holes \(^{26}\) and (iii) the j-j mixing effect due to the quantum mechanical overlap between the $L_2$ and $L_3$ excitations [48], [82].

In our particular case some assumptions can be done and verified *a posteriori*: the anisotropic charge ($N_{ani}$) and spin density ($T_z$) can be neglected because of the almost perfect octahedral symmetry around each metal site[80],[41],[83]. As a consequence the isotropic XMCD sum rules 3.4 can be used including the nominal numbers of 3d holes (7 for $Cr^{3+}$ and 2 for $Ni^{2+}$).

For what concern the j-j mixing effect, it can be safely neglected for Ni because of the large separation between the $L_3$ and $L_2$ edges. Whereas for Cr, $L_3$ and $L_2$ strongly overlap and the quantification of the j-j mixing is necessary. For this purpose we used the simple model proposed by Goering [48] where the j-j mixing is estimated

\(^{25}\)Unfortunately, we do not have the XMCD measurements of -4phenoxybenzoic and -4mtpp derivatives TFs.

\(^{26}\)The effective number of 3d holes can be expressed as sum of isotropic and anisotropic terms: $N_{eff} = N_{iso} + N_{anis}$. 
by means of a spin correction factor (SC) based on the determination of the branching ratio \((L_2/L_3)\) as described in Chapter 3. Thus, the resulting SC factor of 1.75 was multiplied by the spin moment calculated from the XMCD sum rules.

On the other hand the orbital moment is not affected by j-j mixing as it is proportional to the whole XMCD integral indicated with \(q\) in Fig. 4.25. For the Cr\(\gamma\)Ni-3tpc as TF and as s-ML, \(q\) vanishes for the Cr while it is not negligible for the Ni. This means that the orbital moment is quenched Cr while there is a partial contribution for Ni of about 8 – 12% of the spin moment.

Before to apply the XMCD sum rules to the s-ML of Cr\(\gamma\)Ni derivatives, \textsuperscript{27} we tested their validity on the Cr\(\gamma\)Ni-piv as TF in comparison with theoretical calculations based on spin-hamiltonian model. At this aim, XMCD spectra were collected for fields up to 5 T and three different temperatures (10, 15 and 25 K). The magnetic moments derived from the application of the XMCD sum rules for Cr and Ni separately are reported in ref. [50]\textsuperscript{28} along with the simulations based on the following spin-Hamiltonian:

\[
H = \sum_i J_{i,i+1} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \sum_i d_i (s_{iz,i}^2 - s_i (s_i+1)/3) + \sum_{ij} D_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \mu_B \mathbf{H} \cdot \sum_i g_i \mathbf{S}_i \tag{4.1}
\]

where the first term represents isotropic nearest-neighbor exchange, the second and third terms represent anisotropic interactions (crystal-field and anisotropic exchange, classical dipole-dipole coupling) and the last term is the Zeeman coupling to an external field \(H\).

The microscopic parameters (exchange coupling, crystal field and gyromagnetic factors) of the spin-Hamiltonian are obtained by fitting of AC-susceptibility (\(\chi\)) and specific heat curves. The results for the Cr\(\gamma\)Ni-piv are: \(J_{Cr-Cr} = 1.46\) meV \(J_{Cr-Ni} = 1.69\) meV, \(d_{Cr} = -0.03\) meV, \(d_{Ni} = -0.6\) meV, \(g_{Cr} = 1.98\), \(g_{Ni} = 2.2\).\textsuperscript{29}

Finally the total magnetic moment (spin plus orbital moment) associated to each single ion of the ring is numerically determined performing a spherical average to simulate the random orientation of Cr\(\gamma\)Ni-piv powders\textsuperscript{84}.

\textsuperscript{27}We will present only the results for the -3tpc derivative.

\textsuperscript{28}The Cr magnetic moment was multiplied by 7 in order to take into account its total contribution in the single Cr\(\gamma\)Ni ring.

\textsuperscript{29}In agreement with the XMCD analysis, the gyromagnetic factor of Cr ions is very close to the spin-only value of 2, indicating the quenching of the orbital moment and that the Cr magnetic moment is almost entirely due to the spin. Whereas \(g_{Ni} = 2.2\) suggests an orbital contribution of 10% to the spin.
Figure 4.25: XAS with left (red) and right (black) polarization and XMCD spectra of TF and s-ML of Cr7Ni - 3tpc at 5T and 10K. The integral curves are also reported (blue curves) with the p, q and r parameters used in XMCD sum rules.
Figure 4.26: $Cr_7Ni$-3tpc TF (left panel) and s-ML (right panel). Cr and Ni total magnetic moments, experimentally derived by the sum rules, vs applied magnetic field at 10K, 15K and 25K compared with the results of spin Hamiltonian calculations.
The fair agreement between theoretical and experimental magnetization curves, for all the temperatures, confirms the validity of the isotropic XMCD sum rules, at least for the $Cr_7Ni$ ring, and the possibility to calculate reliably the Cr spin moment by renormalizing the sum rule by SC.

In ref. [50] the same analysis is also lead on the $Cr_8$-piv compound precursors of such metallic rings. These results have the advantage that can be compared with conventional magnetization measurements (SUID, Hall probe etc.) which, unlike XMCD technique, are not element sensitivity and a total magnetic moment is measured.

The Hall probe measurements carried out on polycrystalline (PC) samples along with the spin-Hamiltonian simulations[50], are in reasonable agreement with the total magnetization derived by use of XMCD sum rules. This findings provide a further support for the validity of the sum rules for the $Cr_7Ni$-piv nanomagnet as thick film.

Following the same sequence of XMCD measurements for the $Cr_7Ni$-3tpc as TF, we can understand the effect of the functionalization (in this case the 3tpc) on the core magnetic properties. The isotropic XMCD sum rules were applied with the same assumptions done for the $Cr_7Ni$-piv.\textsuperscript{30} The results are reported in Fig. 4.26 (left side) with the spin-Hamiltonian simulations.

Once again, we found a good agreement between theory and experiment for all the magnetization curves at different temperatures. Notably, the switching of the Cr-Ni magnetic coupling from anti- to ferromagnetic observed at 5$T$ and 25$K$, is nicely predicted by the model and can be explained in terms of the interplay between Zeeman and isotropic-exchange contributions [50].

This time the fitting of AC and specific heat measurements ?? gives the same crystal field and gyromagnetic factors of the $Cr_7Ni$-piv but reduced values of $J_{Cr-Cr} = 1.24$ meV and $J_{Cr-Ni} = 1.44$ meV of 15% with the an $J_{Ni}/J_{Cr}(= 1.16)$ ratio unchanged. We ascribe this effect to the presence of the 16 thiophene functionalizations in the $Cr_7Ni$ - 3tpc which induce small structural changes in the ring.

**XMCD sum rules for sub-monolayers**

The results reported so far, allowed us to test the validity of the sum rules and study the effect of the functionalization on the $Cr_7Ni$ magnetic core. Hereafter, we focus on the effects of the gold surface on the magnetic properties of the $Cr_7Ni$-3tpc.\textsuperscript{30}The same SC factor (1.75) was used for the estimation of the Cr spin moment.
4.3. CR\textsubscript{7}NI DERIVATIVES

We already discussed the XMCD signal at 5T and 10K for the 3tpc derivative as s-ML and we found that the Cr and Ni are ferromagnetically coupled (Fig. 4.25 right side). Indeed, as usual, the XMCD measurements were extended to different fields (1, 3, 4 and 5 T) and temperatures (10, 15 and 25 K). Then, by applying the XMCD sum rules, the Cr and Ni magnetic moments were derived separately. The magnetic moments as function of the external magnetic field and at different temperature are reported in Fig. 4.26 (right side).

The results show that in the CR\textsubscript{7}Ni as s-ML, the Cr and Ni magnetic moments are always positive. Moreover, the absolute values of the total Cr magnetic moment (7Cr) in a single ring as well as the Ni magnetic moment increase considerably.

In order to understand the reasons of the different magnetic behavior of the CR\textsubscript{7}Ni-3tpc as thick film and as s-ML on the gold surface, we changed arbitrarily the Cr-Cr and Cr-Ni exchange-constants in the spin-Hamiltonian simulations. The crystal field and gyromagnetic parameters were fixed to those already found for the TF of the CR\textsubscript{7}Ni-3tpc and CR\textsubscript{7}Ni-piv.\footnote{This idea is suggested by the AC and specific heat measurements done on the TF of CR\textsubscript{7}Ni-piv and CR\textsubscript{7}Ni-3tpc. In facts, for these compounds the crystal field and gyromagnetic parameters are the same, but the exchange-constants are slightly different.}

Actually, a further reduction of the Cr-Cr and Cr-Ni exchange-constants to 1.05 meV and 0.5 meV respectively allowed us to get theoretical magnetization curves in reasonably agreement with the experimental ones (Fig. 4.26).

We suggest that the reduction of the exchange-constants is due to the presence of the -3tpc ligands around the CR\textsubscript{7}Ni rings and in particular to the carboxylate groups which in somehow fix the Cr-Cr and Cr-Ni relative distances and the relative super-exchange interaction. We already found that the replacement of pivalate in CR\textsubscript{7}Ni-piv with thiophene-carboxylate in CR\textsubscript{7}Ni-3tpc, reduces the exchange interaction of about 15 %. Probably the strong interaction between the CR\textsubscript{7}Ni-3tpc clusters and the gold surface modify the structure of the carboxylates and as a consequence the super-exchange interaction through the metal ions.

From the diagonalization of the spin-Hamiltonian, the energy levels spectrum was also calculated for the TF of the CR\textsubscript{7}Ni-piv and the s-ML of the CR\textsubscript{7}Ni-3tpc (Fig. 4.27). The comparison shows that even if the ad hoc macroscopic parameters used for the s-ML lead to a compression of the calculated energy levels spectrum with respect to the CR\textsubscript{7}Ni-piv (Fig. 4.27), the low multiplet structure is basically the same.
implies that the main properties of Cr$_7$Ni-3tpc clusters after the adsorption on gold surface are not compromised. 32.

Hence, the energy gap between the S=1/2 and S=3/2 spin states, $\Delta_{1/2-3/2}$, is still large enough to allow efficient *qubit* encoding in the ground doublet [84], and the quartet states can still be used as auxiliary resources for *qubit* manipulation [86].

32For instance should be possible still observe quantum oscillations described in ref.[85]
33E.g. the ground-doublet to first-excited-quartet gap $\Delta_{1/2-3/2}$ is 13 K in the Cr$_7$Ni-piv TF and it is about 8 K (or 0.7meV) in the Cr$_7$Ni-3tpc s-ML
Figure 4.27: Calculated field-dependence of the low-lying energy levels of $Cr_7Ni$-piv TF (on top) and $Cr_7Ni$-3tpc s-ML (on bottom), relative to the ground-state energy. The magnetic field is set parallel to the ring axis. The macroscopic parameters used in calculations are: $J_{Cr-Cr} = 1.46$ meV, $J_{Cr-Ni} = 1.69$ meV, $d_{Cr} = -0.03$ meV, $d_{Ni} = -0.6$ meV, $g_{Cr} = 1.98$, $g_{Ni} = 2.2$ for the $Cr_7Ni$-piv TF and $J_{Cr-Cr} = 1.05$ meV, $J_{Cr-Ni} = 0.5$ meV, $d_{Cr} = -0.03$ meV, $d_{Ni} = -0.6$ meV, $g_{Cr} = 1.98$, $g_{Ni} = 2.2$ for the $Cr_7Ni$-3tpc s-ML.
Chapter 5

Conclusions

In this work we made an important step towards the real application of molecular nanomagnets. So far, electronic and magnetic properties of MNMs were measured only on small crystals, containing a collection of ordered identical molecules. Nevertheless, the realization of MNM-based devices needs the assembling of MNMs on surface.

As shown, we succeeded in the deposition by solution of $Mn_{12}$-bet, $Mn_6$ and $Cr_7Ni$ families of nanomagnets on gold substrate by direct covalent bond or by electrostatic interaction on previously functionalized surfaces. Moreover we implemented a suitable protocol of experimental techniques to observe the main properties of submonolayer of MNMs. The effects of the surfaces on the nanomagnets properties have been reliably measured and the interplay among the structural, electronic and magnetic properties came to light.

STM and XPS were used on campus to characterize the topography and chemical composition of the adsorbed on surface, while XAS and XMCD synchrotron techniques were used to study the oxidation states, geometrical environment and magnetism of MNMs in combination with theoretical models (ligand field multiplet and spin-Hamiltonian simulations).

Among the several derivatives of the most famous $Mn_{12}$-ac nanomagnet, we studied the $Mn_{12}$-bet properly synthesized for the electrostatic interaction with anionic end-groups of functionalized gold surface by MES and MPA ligands. The results proved that both the functionalized surfaces allowed to get a bidimensional distribution of isolated molecules on surfaces. In spite of this, only MPA seams to preserve the
electronic properties of $Mn_{12}$-bet core, while the MES favors a charge transfer directly from their sulphonate end-groups or from the gold substrate mediate by sulphonate.

The investigation of the magnetic properties of $Mn_{12}$-bet on MPA / Au showed a drastic reduction of the dichroic signal with respect to the relative thick film. Remarkably, whereas the dichroic signal measured at $10K$ as function of the magnetic field reached almost the saturation in the thick film of $Mn_{12}$-bet, in the relative submonolayer it increased linearly.

A new family of $Mn_6$ nanomagnets was also investigated. The interest about it, lies in the possibility of playing with the magnetic coupling between the metal ions introducing structural distortions into the molecular core. In this way a MNM with the record of anisotropy energy barrier was synthesized.

In this work, we studied two $Mn_6$ derivatives exhibiting high and low spin. They were properly functionalized with 3tpc ligands for the direct grafting on the gold surface. A similar surface coverage of intact molecules was obtained for both derivatives. The analysis of the structural and electronic properties done comparing the XAS spectra at the $L_{2,3}$ edges with reference compounds and Ligand Field Multiplet simulations, revealed that the molecules - gold interaction induced strong modifications in the geometrical environment around $Mn^{3+}$ ions although their oxidation state is preserved. These structural modifications affect directly the magnetic spin moment which result strongly reduced. The vanishing of the XMCD integral curves proved the quenching of the orbital magnetic moment.

Possible routes towards the implementation of molecular gate for quantum computation was also investigated. We studied several $Cr_7Ni$ derivatives with different sulphur-based ligands for the grafting on gold surface. By XPS and STM analysis we selected those showing higher coverage of isolated and apparently intact molecules. At variance with $Mn_{12}$ and $Mn_6$ nanomagnets, the oxidation states and chemical environment of the Cr and Ni sites are completely preserved after the deposition on the gold surface. The simulation of XAS spectra by Ligand Field Multiplet calculations allowed to get a precise description of the local symmetries and crystal field strengths.

The analysis of XMCD signal sign at the $L_{2,3}$ edges of Cr and Ni showed the expected antiferromagnetic coupling between the Cr and Ni spin moments in the TF, while in the submonolayer they are ferromagnetically coupled. The switching of the spin moment is ascribed to the interaction with the gold surface alone or in combination
with the emission of electrons from the gold surface stimulated by X-ray irradiation.

However, the gold surface plays a crucial role. Indeed, the XMCD measurements performed on the $Cr_7Ni$ derivatives on graphite in the same experimental condition showed that the Cr-Ni antiferromagnetic coupling as well as their electronic properties are preserved.

The validity of the XMCD sum rules was tested on $Cr_7Ni$-piv and $Cr_8$-piv compounds in comparison with the results of Hall probe measurements and spin-Hamiltonian simulations. Hence XMCD measurements were carried out on $Cr_7Ni$-3tpc as thick film and as adsorbed on the gold surface for fields up to 5 T and temperatures of 10, 15 and 25 K. Then we calculated the spin and orbital contribution to the total magnetic moment for both Cr and Ni ions and the magnetization curves were plotted at different temperatures.

The results showed that the main contribution to the magnetization of the Cr is due to the spin part of the total magnetic moment as the orbital moment is quenched. For Ni, the orbital moment is not quenched and it is the 10% of the spin magnetic moment. Most importantly, the measurements proved that the gold surface induces strong modifications in the Cr-Ni exchange coupling ($J_{Cr-Ni}$) accomplished with the reversing of the Cr-Ni magnetic coupling into ferromagnetic.

The effects of the sulphur functionalization was also disentangled comparing the measurements carried out on the thick films of the $Cr_7Ni$-3tpc with the not-functionalized compound ($Cr_7Ni$-piv). Comparing the simulations with the experimental results we found that even though the sulphur functionalization reduces slightly the $J_{Cr-Ni}$, the Cr-Ni antiferromagnetic coupling is still preserved.

The energy levels scheme were calculated for the $Cr_7Ni$-piv and the $Cr_7Ni$-3tpc on the gold surface. The comparison allowed to conclude that even though the magnetic properties of the $Cr_7Ni$ ring are affected by the gold surface, they still satisfy the main requirements for their application as qubit.

In conclusion, we proved that the gold surface surely provides a useful substrate where the MNMs can be strongly grafted. On the other hand it strongly affects their properties. We found that this is true specially for Mn-based nanomagnets where the magnetic properties are always modified. As we proved for the deposition of $Mn_{12}$-bet on functionalized (MPA) surface, the structural and electronic properties of MNMs can be preserved only decoupling the nanomagnets from the surface by indirect
deposition. Nevertheless, the decoupling of the molecules from the surface must be properly addressed. In facts, at variance with MPA, the MES ligands induce a full reduction of the Mn oxidation states.

Indeed, an exception is represented by the Cr$_7$Ni rings where the local properties studied at the Cr and Ni sites appear more robust and less sensitive to the redox instability induced by the gold surface. However, the magnetic properties are affected by the interaction with the surface which modifies the superexchange-coupling through the magnetic ions.

In this panorama, it turns out that the retainment of the original properties of deposited MNMs passes through the systematic investigation either of different surfaces or of suited decoupling from the surface. This purpose opens a completely new route towards the development of new deposition strategies.

Preliminary results presented in this thesis for Cr$_7$Ni on graphite surface suggest the use of different substrates. This is also stimulated by the well known possibility offered by graphite to get ordered monolayer of phthalocyanine by evaporation in ultra high vacuum. We think that proper ligands attached to the nanomagnet core will drive their addressing in well ordered monolayer even for the deposition by solution.

Finally, we are confident that the choice of proper surfaces and new protocols of deposition will provide larger control into the addressing of nanomagnets on surface. Screening the nanomagnets from the surface preserving their properties should be possible as well as exploiting their interactions to improve their properties. In this sense the interaction with surface is not necessarily a negative fact. However, this is a very difficult task that goes beyond the aim of this thesis but we are called to tackle it in the next future.
Chapter 6

Aknowledgement

Desidero innanzitutto ringraziare il Prof. U. del Pennino e il Prof. M. Affronte per il costante supporto. Un ringraziamento particolare va a Valdis Corradini per aver guidato la mia ricerca e per aver avermi introdotto al laboratorio SESAMO-MFE e allo studio delle tecniche di sincrotrone. Inoltre ringrazio Ivan Marri per avermi introdotto alla simulazione degli spettri e per i suoi indispensabili suggerimenti.

Ma la realizzazione di questo lavoro non sarebbe stata possibile senza l’aiuto di tante persone a partire da Alessandro Gambardella, Roberto Biagi e Valentina De Renzi del gruppo SESAMO-MFE; Marco Evangelisti e Alberto Ghirri del gruppo nanomagnetismo di Modena; Julio Cezar del Sincrotrone ESRF di Grenoble; S. Carretta, P. Santini e il Prof. G. Amoretti per le simulazioni teoriche; Lorenzo Pardini e Valerio Bellini per le discussioni teoriche; i chimici: F. Tuna, G. Timco, R.E. Winpenny di Manchester; C. J. Milios, L. F. Jones, E. K. Brechin di Edinburgo e E. Coronado di Valencia per la sintesi dei magneti molecolari.

Infine ringrazio i miei genitori e mio fratello Antonio che mi hanno sempre sostenuto e incoraggiato nelle mie scelte. Un raggiamenti speciale va a Corinna che ha condiviso con me ogni respiro di questi tre anni di dottorato. È a voi che dedico questa tesi.
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