

## Valence band resonant photoemission of Mn<sub>12</sub> single molecules grafted on Au(111) surface

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### Abstract

In the present work, we address the determination of the electronic structure of a monolayer of Mn<sub>12</sub> clusters, grafted on Au(111) substrate by a suitable functionalization, by means of X-ray absorption and resonant valence band photoemission (RESPES) spectroscopies taken across the Mn 2p–3d absorption edge. The absorption edge of the Mn<sub>12</sub> monolayer is compared with that – reported in literature – of bulk Mn<sub>12</sub>, showing that the deposition procedure does not significantly affect the intimate nature of the Mn<sub>12</sub> cluster. Quantitative comparison between RESPES spectra data allow us to extract the Mn 3d density of states from the Mn<sub>12</sub>-monolayer valence band spectrum, which is dominated by the Au 5d states. The shape of the experimentally obtained valence band DOS is in good agreement with the theoretical DOS, obtained by first-principle LDA + *U* calculations, confirming the importance of correlation effects in the determination of the electronic properties of the Mn<sub>12</sub> cluster.

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### 1. Introduction

Single-molecule magnets (SMMs) represent a new class of magnetic materials, consisting of almost non-interacting, identical point-like nanoscale entities, whose magnetic behaviour, though strongly reminiscent of bulk magnets [1,2], arises from a purely molecular mechanism rather than from bulk magnetic interactions [3,4]. These magnetic properties confined in a single molecule, make SMMs very appealing for applications as molecular-scale units for

information storage or qubits for quantum computation [5–7]. In Mn<sub>12</sub>-acetate (Mn<sub>12</sub>O<sub>12</sub>(OAc)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub> · 4H<sub>2</sub>O · 2AcOH), which is the most studied compound among this new class of materials, eight Mn(III) and four Mn(IV) ions are magnetically coupled via superexchange interactions to give a ground electronic state with *S* = 10. Most of the theoretical treatments of Mn<sub>12</sub> have been based on the rigid-spin model [8,9], while only few studies have addressed the internal magnetic and electronic structure of the Mn<sub>12</sub> molecules and the intramolecular interactions responsible for the formation of the molecule's collective spin. In fact, a comprehensive approach to these systems would derive their internal magnetic properties directly

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from the cluster electronic structure. Recently, Boukhvalov et al. [10,11] have pursued this approach, by applying first-principles LDA +  $U$  calculations to the  $Mn_{12}$  system, thus providing a picture of its electronic structure and exchange interactions, and obtaining a finite energy electronic gap and an integer value of the total spin of the molecule.

Any practical applications of SMMs as molecular-scale units require the possibility to address, probe and eventually manipulate the individual molecules. To this aim, it is crucial to develop deposition strategies able to (i) produce two-dimensional distribution of oriented cluster on suitable substrates and (ii) preserve the magnetic properties of such clusters.

To this end, we recently demonstrated the possibility of firmly grafting  $Mn_{12}$  clusters on the Au(111) surface by a proper cluster derivatization consisting in the full replacement of the acetate ligands in  $Mn_{12}$ -acetate with new carboxylates containing acetyl-protected thiols. The elemental composition of such monolayer was verified by XPS, suggesting the integrity of the adsorbed clusters, while the formation of a 2D distribution on the gold surface of single entities of dimensions corresponding to those of the  $Mn_{12}$  clusters (hereafter referred to as  $Mn_{12}$  monolayer) was shown in STM images [12].

Testing the magnetic properties of the  $Mn_{12}$  clusters grafted on the substrate is clearly a crucial issue to validate any future application of these 2D SMM systems. However, the magnetic properties of fractions of a monolayer are extremely difficult to be measured, due to the insufficient sensitivity of conventional magnetic probes (e.g. SQUID, torque, Hall probe, etc.). On the contrary, X-ray absorption magnetic circular dichroism (XMCD) has demonstrated to be a very powerful technique to investigate the surface magnetism in the sub-monolayer regime [13]. This technique has been recently successfully applied to study the magnetic properties of bulk  $Mn_{12}$  crystals under cryogenic condition [14,15]. We therefore expect it possible to exploit XMCD to investigate magnetic properties of a single layer of  $Mn_{12}$  clusters. Nevertheless, the feasibility of this kind of measurement is not trivial, due to the possible beam damaging caused by the high photon intensity needed to obtain a dichroic signal from a single layer. In the first part of this work, we therefore report some preliminary X-ray absorption spectroscopy (XAS) results on  $Mn_{12}$  clusters deposited on Au(111) surfaces, demonstrating that a proper signal-to-noise ratio is attainable without any significant damage of the  $Mn_{12}$  monolayer. Furthermore, our measurements confirmed that the deposition procedure did not damage the cluster nor alter *significantly* its intimate nature, in agreement with the indications of our previous XPS results [12].

In this work, we mainly address the important issue of determining the valence band electronic properties of the  $Mn_{12}$  monolayer. In fact, in spite of extensive measurements on the magnetic properties of  $Mn_{12}$ , only few results on its electronic structure are available, regarding bulk crystalline samples [16]. We exploit resonant photoemission

spectroscopy to single out the density of states directly associated only to Mn atoms. Our results are directly compared with LDA +  $U$  theoretical calculations, providing an experimental evidence of the importance of correlation in determining the electronic properties of this system.

## 2. Experimental

Samples have been prepared as described in Ref. [12]: the  $Mn_{12}$  clusters were functionalized with an acetyl-protected thiol at the end of an hexadecanoic acid chain ( $HCOO(CH_2)_{15}SAc$ ), yielding a fully substituted derivative  $Mn_{12}O_{12}[O_2C(CH_2)_{15}SAc]_{16}$ , to which we will refer to as  $Mn_{12}$ - $LC_{15}SAc$  or simply  $Mn_{12}$  in the following. The deposition of the nanoclusters on the Au(111) surface was obtained by immersing for 5 h the gold substrates in a diluted (0.3 mM) cluster solution in THF, together with a catalytic amount of aqueous  $NH_4OH$  to facilitate the deprotection of the thiol groups and to promote robust anchoring to the gold surface through Au–thiolate stable bond.

Au films deposited on mica substrate (Molecular Imaging) and flame annealed before immersion in the  $Mn_{12}$  solution were used as substrates.

XAS and RESPEs measurements were carried out at the BACH beam-line of the ELETTRA synchrotron radiation laboratory in Trieste. The radiation source was based on two APPLE-II helical undulators, while the photon dispersion system consisted in three gratings working in the energy ranges 35–200 eV, 200–500 eV, and 500–1600 eV, respectively. The small spot dimensions on the sample (about  $200 \times 310 \mu m^2$ ) allows to select different sampled areas for each measurements, thus minimizing any beam-induced damage. At the manganese  $L_{2,3}$  edges, the energy resolution was about 0.05 eV. The X-ray absorption spectra were obtained by measuring the total electron yield and normalizing it to the monitor current. The RESPEs measurements exploited a VSW 150 mm, 16 channels hemispherical analyser, with a total energy resolution of 0.37 eV.

## 3. Results and discussion

Before discussing the results of resonant photoemission, we briefly recall the nature and advantages of this technique. 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 states can occur: (a) direct photoemission, (b) autoionisation 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 emis-

sion 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 [17]. On the other hand, in the case of the third competing channel, i.e. simple Auger emission, the kinetic energy of the outgoing electron 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 [18].

It is clear that given the element specificity of the absorption edges and the selection rules for the transition from the core state to the empty state, resonant photoemission at a given photon energy can involve only states of that specific element and of a given symmetry. If the competing Auger channel can be proved to be negligible, this technique 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 valence band spectrum taken at resonance photon energy and that taken in out-of-resonance conditions.

In our case, exciting the Mn  $L_{2,3}$  edges we expect to single out the Mn 3d contribution from the whole valence band spectra. However, in our system RESPEC analysis is in principle complicated by the fact that the  $N_2$  ( $4p_{1/2}$ ) absorption edge of gold – which is a particularly suitable substrate for grafting thiol-containing molecules – occurs at about the same energy as the Mn  $L_3$  ( $2p_{3/2}$ ) edge of manganese oxides. We have therefore carefully measured the  $N_2$  ( $4p_{1/2}$ ) absorption edge on a clean gold surface, finding that the intensity of this edge is extremely small compared with the Mn absorption edge (less than 5%) and its contribution to both XAS and RESPEC measurements for the  $Mn_{12}$  monolayer system can be therefore safely neglected. Indeed, while in the case of atomic Au the 5d shell are completely filled, in the solid a slight hybridization occurs between 5d and 6p-s states producing a small fraction of holes in the d band [19,20], which in turn acknowledge the presence of a Au  $N_2$  absorption edge and its extremely small intensity.

In Fig. 1, we report the XAS spectrum of one monolayer of  $Mn_{12}$ - $LC_{15}SAC$  on Au (thin solid line); and compare it with that reported by Moroni et al. for a polycrystalline  $Mn_{12}$ -acetate sample [14] (dotted curve). Being involved the valence band d-states, the XAS technique is very sensitive to small changes in the chemical and structural (perturbing the crystal field) environment of Mn atoms. The similarity between the two absorption spectra indicates that the deposition procedure does not significantly affect the intimate cluster nature and that further investigations on its electronic structure can be carried out.

In Fig. 2 (bottom panel) we report the valence band spectra of the  $Mn_{12}$ - $LC_{15}SAC$  monolayer on gold at different photon energies, spanning across the Mn  $L_{2,3}$  edges. The corresponding absorption spectrum is shown in the top panel. It is easy to see that the valence band features located in the 2–8 eV binding energy region show a typical resonant behaviour, characterized by an increasing inten-

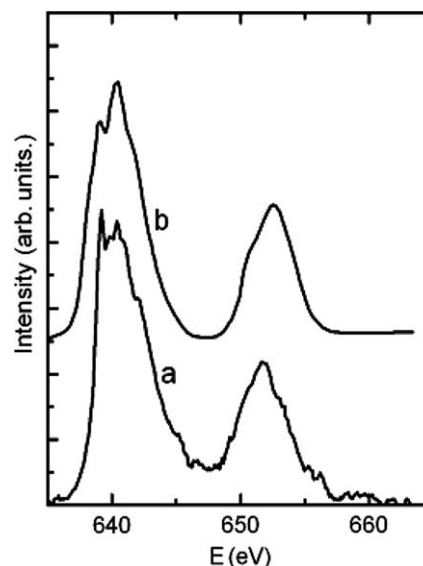


Fig. 1. X-ray absorption spectra of:  $Mn_{12}$ - $LC_{15}SAC$  monolayer on Au(111) (a), compared to  $Mn_{12}$ -Ac bulk (b), taken from Ref. [14] and shifted by  $-2.3$  eV leftwards for a better comparison.

sity at photon energies corresponding to the maxima of the absorption edge. Notably in the spectrum sequence no feature at constant kinetic energy – which in this plot would appear as a peak moving to higher binding energy with increasing photon energy – can be detected. This result rules out any significant contribution from the Auger decay channel. Moreover, the occurrence of resonant Auger emission can be also ruled out, as in this case – at variance with the experimental data – an increase in the valence band width at resonance would be observed [18].

In Fig. 3 lower panel, the valence band spectra of the  $Mn_{12}$ - $LC_{15}SAC$  monolayer on Au are shown for different photon energies. The solid curves are taken at an out-of-resonance photon energy ([a] = 638.1 eV in Fig. 2), the dotted and dashed curves are taken with a photon corresponding to the first ([b] = 639.4 eV in Fig. 2) and second ([c] = 640.9 eV in Fig. 2) maximum of the Mn edge, respectively.

The difference between on-resonance and out-of-resonance curves ([b]–[a]) and ([c]–[a]), which provide the resonance spectra of the system, are shown in the middle panel of Fig. 3. These two spectra actually represent an image of the Mn 3d DOS of the  $Mn_{12}$  monolayer and both show two features: a main peak in the 2–8 eV range and one broad feature at higher binding energies. By comparison with Kim et al. [16], we can attribute these two features to  $e_g$  and  $t_{2g}$  Mn states, respectively. We note here that, while the energy position of Kim's spectra is somewhat arbitrary due to the insulating nature of the bulk compound, in our system the energy of Mn states is unambiguously linked to the substrate Fermi level position and is an intrinsic property of the monolayer system, determined by the possibly complex electrostatic properties of the interface (e.g. formation of an interface dipole [21]). In the upper panel of

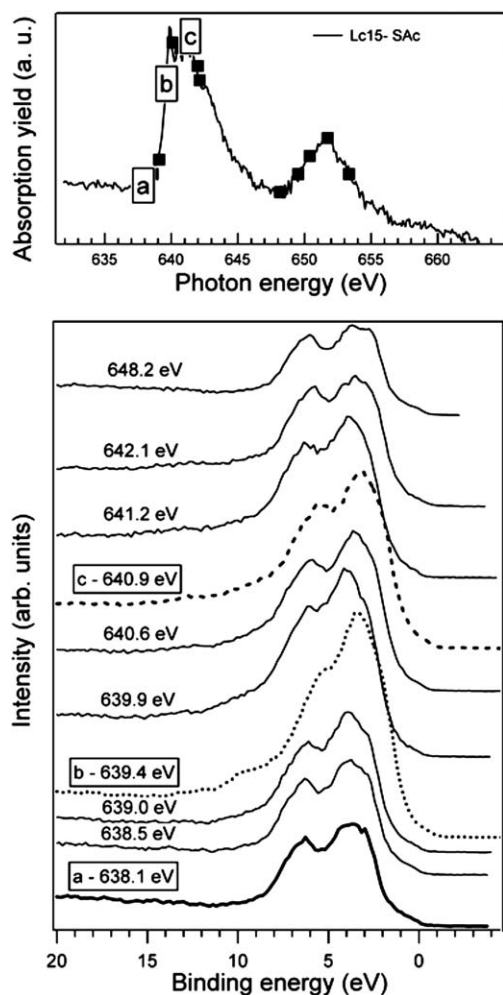


Fig. 2. Lower panel: valence band photoemission spectra of  $\text{Mn}_{12}\text{-LC}_{15}\text{SAC}$  monolayer at different photon energies (indicated in the panel) spanning the Mn  $L_{2,3}$ . The various photoemission spectra have been aligned to the Fermi level. Upper panel: X-ray absorption spectrum of  $\text{Mn}_{12}$  monolayer. Dots and letters indicate the energies of the single curve in the lower panel.

Fig. 3 we report the theoretical DOS calculated with two different approaches: LDA +  $U$  (where the Coulomb correlation effects are taken into account) and simple LDA. In this theoretical model, the complete  $\text{Mn}_{12}$ -acetate cluster (which is the smallest of all known realistic  $\text{Mn}_{12}$  molecules) is considered, while only the presence of water of crystallisation and other solvate complexes is neglected. At first approximation this model is suitable to describe different kinds of  $\text{Mn}_{12}$  clusters, as it neglects the possible influence of different ligands on the cluster electronic properties. The theoretical DOS reported in Fig. 3 have been obtained, following the theoretical method described in Ref. [10], by summing up all the spin-resolved components, and have been shifted by  $-0.5$  eV in order to align the experimental and theoretical (LDA +  $U$ ) valence bands. LDA +  $U$  data refer to a value of Coulomb repulsion of  $U = 4$  eV, as chosen from previous comparison with RIXS and XPS spectra [11]. The agreement of the experimental

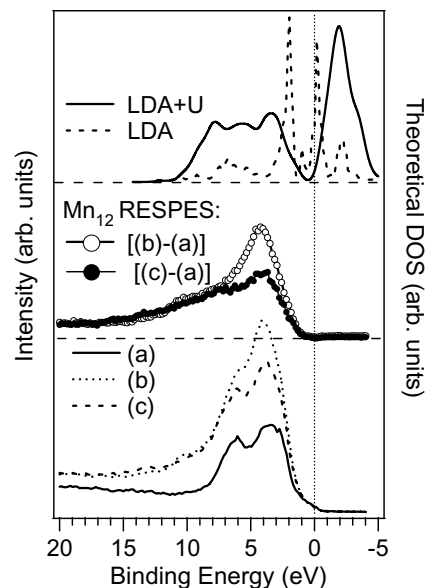


Fig. 3. Valence band spectra of the  $\text{Mn}_{12}\text{-LC}_{15}\text{SAC}$  monolayer (lower panel): for different photon energies: solid line photon [a] (off resonance), dashed and dotted line photon [b] and [c] (resonance). Difference spectra [(b)-a] (empty symbols) and [(c)-a] (filled symbols) are also shown (vertically shifted for convenience) and compared with (upper panel) the DOS calculated by the LDA +  $U$  (solid line) and LDA (dashed line) approaches, respectively (see text for details).

data with LDA +  $U$  calculations is fairly good, while clearly the LDA theoretical data, which predict a metallic nature of  $\text{Mn}_{12}$ , are in substantial disagreement with our data. These results therefore confirm the importance of taking into account the electron correlation for a proper description of the electronic properties of these systems and show that resonance photoemission spectroscopy is a powerful technique to experimentally address this issue.

#### 4. Conclusions

We investigated a monolayer of  $\text{Mn}_{12}\text{-LC}_{15}\text{SAC}$  grafted on a Au(111) substrate using X-ray absorption and resonant photoemission spectroscopies at the Mn  $L_{2,3}$  and Au  $N_2$  edges. The measurement of the valence band at the Mn  $2p\text{-}3d$  resonance allowed us to extract the Mn  $3d$  density of states. Comparison with recent calculations shows the relevance of correlation effects in the electronic structure of the  $\text{Mn}_{12}$  cluster. A more detailed comparison between theoretical and experimental data, which takes into account the possible influence of ligands on the electronic properties, will be object of a future work.

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