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Report:

The aim of our experiment was to study by Synchrotron Mößbauer Spectroscopy (SMS)[1] the magnetization dynamics of nanosized films of tetrairon(III), a molecular complex featuring a Single Molecule Magnet (SMM) behavior[2] in bulk[3] as well as at the nanoscale.[4–7] SMMs are a class of very promising materials that show magnetic bistability at the molecular level due to the existence of a double-well potential hampering the reversal of the magnetization. This makes them ideal candidates for the creation of devices for the quantum storage of information. Among this class of molecules, derivatives of the Fe_4 family were the first ones to show, thanks to the use of synchrotron radiation, the preservation of the magnetic bistability and the quantum tunneling of the magnetization after deposition on a surface.[4,5] Before this experiment based on SMS, it was possible to investigate magnetic bistability of monolayers of SMMs only on the time-scale necessary to record a hysteresis loop by X-ray Magnetic Circular Dichroism: investigations were therefore limited to very low temperatures, where quantum tunneling dominates the magnetic relaxation. Using SMS it has been possible to go beyond these limitations. We produced a derivative of Fe_4 fully enriched in ^{57}Fe and suitable for chemisorption by self-assembling on gold surfaces.[5] A temperature dependent Mößbauer study was performed on a bulk sample of this material (a dropcast sample) and subsequently a similar study has been carried out on a monolayer sample. By means of SMS we explored a wide temperature range, starting from 200 K temperature, where the systems are substantially paramagnetic, down to about 2.2 K temperature (base temperature of the cryostat) at which the magnetic moments are seen as fully frozen and the typical multiplet structure expected[8] for Fe_4 was observed (see Figure 1a). The characterization of the bulk sample and the fit we carried out subsequently during the data analysis revealed the presence of the expected 3 inequivalent iron sites that are present in the structure of the molecule in line with previous reports on standard Mößbauer characterization of unfunctionalized Fe_4

clusters in the bulk phase. More importantly, this initial characterization, allowed us to test the ID18 setup and clarify the capabilities in measuring also a molecular ultrathin film.

Monolayer samples have been prepared exploiting the ESRF chemistry lab facility and assistance of the staff. The spectra obtained with the monolayer sample (see Figure 1b), resulted about two orders of magnitude less intense than those of dropcast sample. Moreover the typical fine structure of the spectra of the Fe_4 monolayer featured a significant alteration, the analysis of which confirmed, on one hand, the intactness of the molecular system and, on the other hand, a significant distortion of the molecular cluster in agreement with theoretical calculations.[9]

From the analysis of the temperature evolution of the spectra it has been possible to extract significant information on the properties of the grafted Fe_4 molecules: on increasing the temperature, the external lines lose intensity faster than in the dropcast sample and this indicates a reduction of the $|D|$ value of the system as confirmed by the fitting of the spectrum at the lowest recorded temperature. Significantly the transition rate between the electronic spin states of the molecule ($M_S = \pm 5$ and $M_S = \pm 4$) extracted from the fit of the spectra results comparable with that found for the dropcast sample, thus, indicating that the deposition on a surface does not significantly modify the spin dynamics, as suggested by previous XMCD evidences.

A careful comparison of the extracted parameters with those deduced from an *ab initio* modelling of the molecular system chemisorbed on the gold surface evidenced several surface-induced structural modifications. Hower, the local distortions at different iron sites resulted in partially compensating effects. Thus this clarifies how the Fe_4 can retain a comparable magnetization dynamics to the bulk phase.

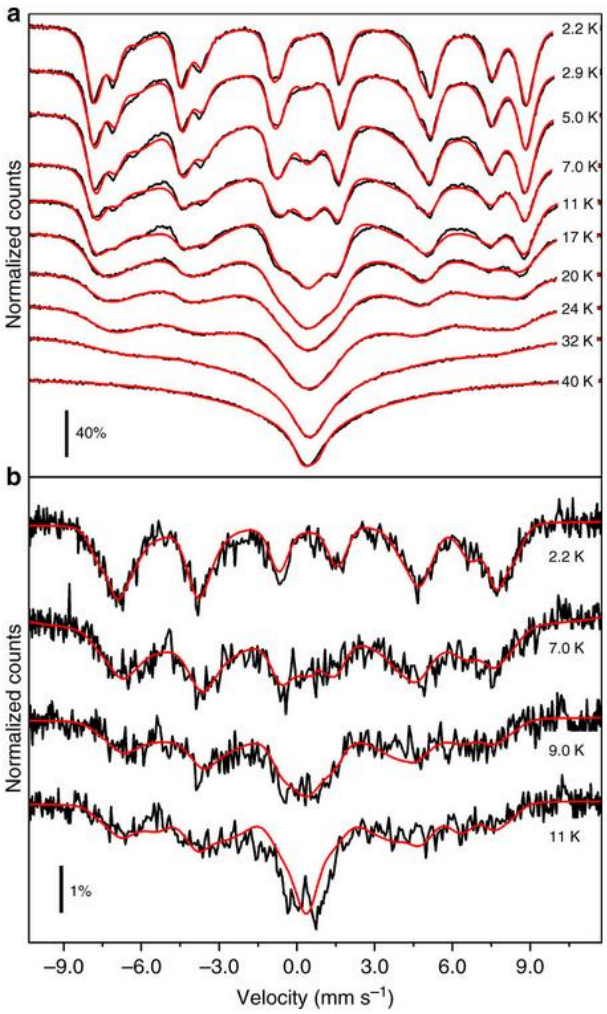

Figure 1. *Mößbauer spectra of the dropcast and monolayer samples for various temperatures.* ***a*** *Experimental spectra (black lines) of the Fe_4 dropcast sample and best fit curves (red lines).* ***b*** *Experimental spectra (black lines) of the Fe_4 monolayer sample and best fit curves (red lines). The velocity axis values are relative to the α-Fe standard. Figure reproduced from ref. 10.*

We strongly believe that these results[10] pave the way for an increase of the interest in the use of SMS by the molecular spintronics community because of the potentialities related to the study of the dynamics of ^{57}Fe-based SMM in different environments (*i.e.* different substrates), that are relevant for instance for the use of this system in innovative devices, being spin-phonon coupling expected to play a crucial role for example in magnetic transport. Moreover, given that iron, in its different oxidation states and coordination environments, alone or combined with other metal ions, is among the most employed elements to build molecular nanomagnets[2] and spin cross-over systems,[11,12] the exploration of the potentialities of synchrotron based Mößbauer spectroscopy will be of great relevance for the whole community of molecular magnetism.

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