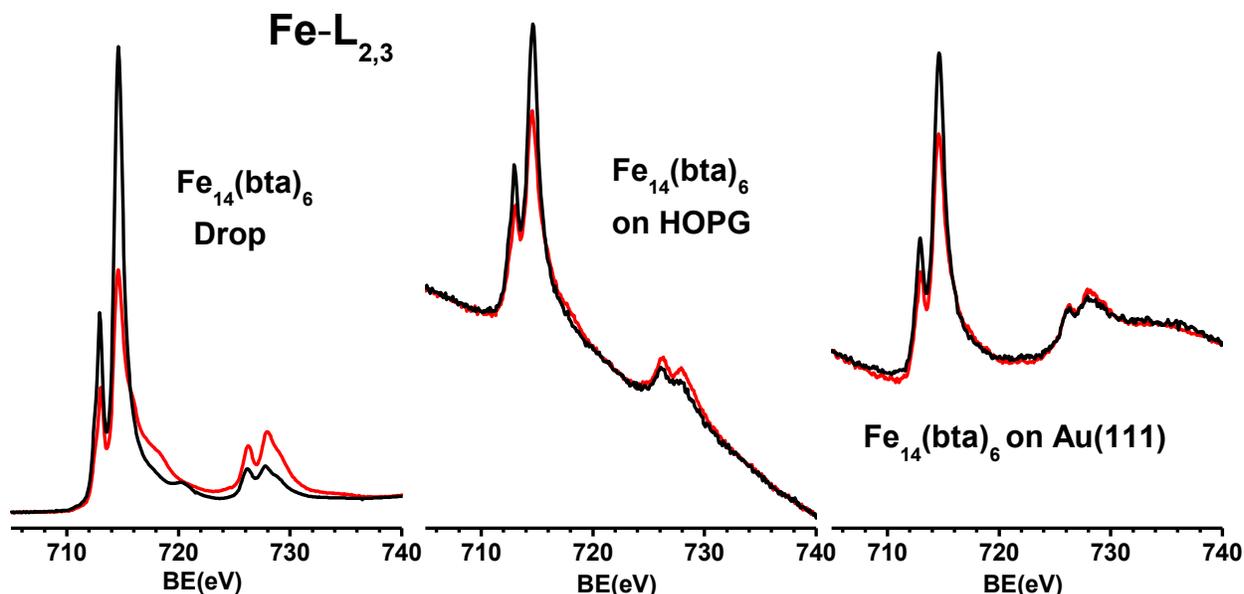


Probing Magnetocaloric Effect at single molecule level in Fe₁₄ cages and molecular dimers deposited on surfaces.

A first result of this beamtime was the experimental prove that the difference in the MCE effect between thick film (TF) and sub-monolayer (sML) of the molecular Fe₁₄(bta)₆ on the surface [see ref. 1] it is not ascribed to the high reactivity of the gold surface since we found the same difference also on HOPG surface. The sub-monolayers (sML) were obtained by immersing the HOPG, Au(111) single crystal or the Au/mica flamed-annealed surface in a 10⁻⁴M solution of Fe₁₄(bta)₆ using dichloromethane (DCM) as solvent. Thick films (TFs) were obtained by drop casting the saturated solution on the same substrates.

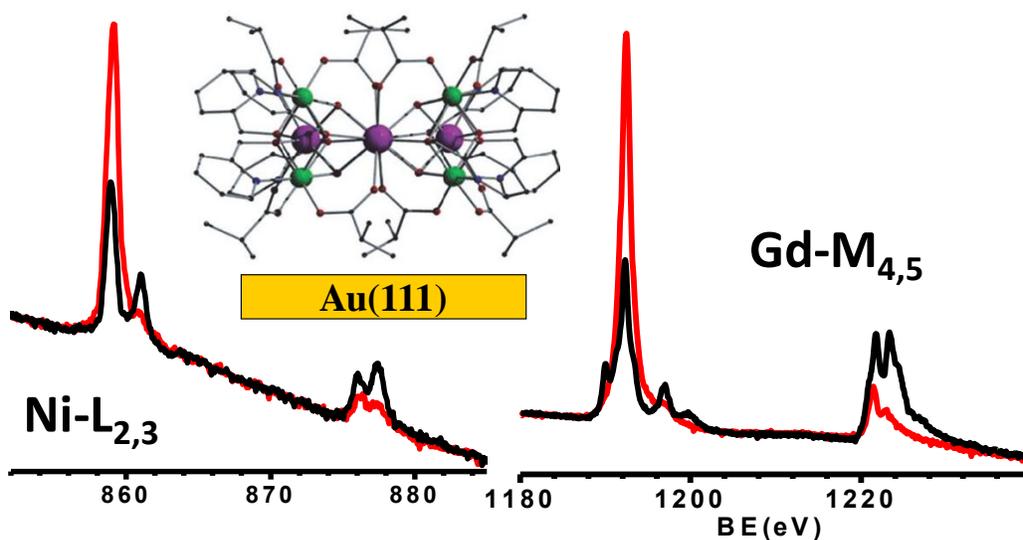
Figure 1 shows the Fe-L_{2,3} absorption spectra taken using both photon helicities for the ML Fe₁₄(bta)₆ on Au(111) and HOPG surfaces and for the TF (on the left). While the shape of both XAS and XMCD spectra are essentially identical for TF and sML, the relative intensities of XMCD signal are different.



This change in the magnetic features of Fe₁₄(bta)₆ is not astonishing since a simple magnetochemical analysis reveals the presence of many states with similar low energy but different spin values as already evidenced by early magnetization measurements on bulk. Assuming a simple spin model with two J constants to account for a different type of Fe...Fe interactions within the Fe₁₄(bta)₆ cage, we have that states with different molecular spin actually co-exist within a small energy range and, by slight changes of the J'/J ratio, the ground state can actually span from 19 to 25. Thus, we ascribe the change in the

magnetization to a small distortion of the Fe cage and/or to the interaction of the isolated $\text{Fe}_{14}(\text{bta})_6$ molecule with the gold surface.

We then decided to test a new molecular system which exhibit giant MCE on bulk measurements. In the structure of the Gd_4M_8 molecule^[2] there are 4Gd^{3+} each of spin $7/2$ and 8M^{2+} . The 4 Gd in a square arrangement which are planar and 8M atoms disposed in 4 couples. With this planar distribution of the we expect to reduce the distortion of the molecule when it is deposited on the surface. Each gadolinium and M atoms are at the center of a slightly distorted octahedron. For what concern the surface deposition, we are already able to obtain sMLs of Gd_4M_8 deposited by liquid phase on Au(111) and HOPG surfaces. STM and AFM (not shown) reveal a sub-ML distribution of isolated Gd_4M_8 on surfaces. The XPS core-levels clearly confirms the chemical integrity of the deposited derivatives. We have then performed preliminary XMCD measurements to verify the stability of the Gd_4M_8 molecules under beam exposure. In Fig. 2 we show the XAS spectra, at the Ni- $L_{2,3}$ and Gd- $M_{4,5}$, of the Gd_4Ni_8 deposited on Au(111) which reveal the stability of the oxidation state (Gd^{3+} and Ni^{2+}) and of the local symmetries at the metallic if compared to the thick film.



References

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