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<b>Beamline:</b> ID12	<b>Date of experiment:</b> from: to:	<b>Date of report:</b> 12/08/2013
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## Report:

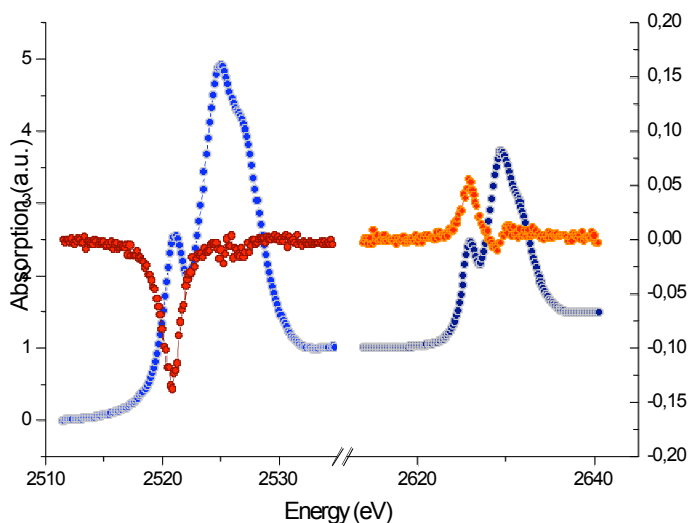
### Scientific background

The present project is devoted to the XMCD studies of photo-switchable high spin molecules arranged on surface. Single molecule magnets, displaying switchable properties, might be of great interest for information storage at the molecular scale. The development of processing techniques to organize these molecules is indeed an important step. In this context, a photo-switchable high spin molecules,  $\text{MoCu}_6$  and  $\text{MoCu}_2$ , have been obtained and fully characterized [1]. The photomagnetic mechanism at low temperature was determined through XMCD measurements [2]. We succeeded in addressing the  $\text{MoCu}_6$  molecular entity on surface following two different approaches allowing soft and non-destructive conditions: Langmuir-Blodgett and Langmuir-Schoefer techniques. The photomagnetic effect with precise magnetic values of the Molybdenum ion has to be measured. XMCD is a method of choice for determining the Mo local electronic and magnetic changes during the photo-magnetic [2].

### Experimental details

In our preceeding work on bulk  $\text{MoCu}_6$  and  $\text{MoCu}_2$ , we demonstrated that the photomagnetic process at low temperature is due to the spin transition of the molybdenum ions:  $\text{Mo(IV)}$  ion is low spin  $S=0$  in the ground state and becomes high spin  $S=1$   $\text{Mo(IV)}$  in the photoexcited state. No charge transfer was found between  $\text{Mo(IV)}$  and  $\text{Cu(II)}$  ions. In order to study the role of  $\text{Cu(II)}$  ions in the photomagnetic properties,  $\text{MoZn}_{2-x}\text{Cu}_x$  photomagnetic compounds were synthesized with varying values of  $x$  ( $0 \leq x \leq 0.4$ ). In these systems, the relaxation temperature increases with the amount of  $\text{Cu(II)}$ . We focussed our experiments on three  $\text{MoZn}_{2-x}\text{Cu}_x$  compounds, with  $x=0$  (no copper),  $x=0.1$  and  $x=0.4$ .

The measurements were made during the 4 bunch mode to take advantage of the low photon flux to avoid radiation damages. Attenuators were also used to reduce the beam flux. For each sample, we measured the XMCD at Mo  $L_{2,3}$  edges with the HU52 Apple II undulator of ID12, at 2 K and  $\pm 17$  T. We also measured the XANES at Cu K edge. For each  $\text{MoZn}_{2-x}\text{Cu}_x$  system, the sample was cooled at 2 K and XMCD measured in 17 T magnetic field (phase (i)). Under these conditions, the system is quasi diamagnetic and no appreciable XMCD was detected. In a second phase (ii), the sample was irradiated with a 4505 nm LED. The XMCD spectra was then measured for the photo-excited magnetic phase. At Mo  $L_{2,3}$  edges, we observed shape modification of the XAS and the apparition of a XMCD signal. At Cu K edge, no modifications were found. The sample was then warm up to room temperature to check of the reversibility: we observed that the laser and the x-rays irradiation induced negligible irreversible damages. During the warm up, we measured the XANES at Mo  $L_{2,3}$  edges as a function of the temperature. Thus we were able to compare the relaxation mechanism in the three  $\text{MoZn}_{2-x}\text{Cu}_x$  systems.



XMCD at Mo  $L_{2,3}$  edges in  $\text{MoZnCu}_{0.05}$  after photo-excitation by a 455 nm LED

## Results

We have obtained a very complete set of data for our three samples. After the application of the sum rules, we will be able to determine the oxydation state and the spin and orbit magnetic moments of the molybdenum ion in the photoexcited state, for each sample. No changes were observed on the copper ion. These results are essential to clarify the role of the copper and molybdenum ions in the photomagnetic process (charge transfer *vs* spin transition, relaxation temperature).

- [1]-(a) A. Bleuzen, V. Marvaud, *et al.* Inorg. Chem., 2009, 48, (8), 3453-3466; (b) J.-M. Herrera, V. Marvaud *et al.* Angew. Chem. Int. Ed. 2004, 43, 5468.
- [2]-(a) M.-A. Arrio *et al.*, J. Phys. Chem. C, 2010, 114, 593-600 ; (b) M.-A. Arrio *et al.* ESRF Highlight 2010, p65. (c) S. Brossard *et al.* J. Amer. Chem. Soc., 2011, 134, 222.