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# Magneto-optical interactions in single-molecule magnets: Low-temperature photon-induced demagnetization

B. Donnio [a], E. Rivière [b], E. Terazzi [c], E. Voirin [a], C. Aronica [d,1], G. Chastanet [d,2], D. Luneau [d], G. Rogez [a], F. Scheurer [a], L. Joly [a], J.-P. Kappler [a], J.-L. Gallani [a,*]

[a] IPCMS, CNRS, UdS, UMR7504, 23 Rue du Lœss, BP43, 67034 Strasbourg Cedex 2, France
[b] Université Paris Sud, CNRS, ICMMO, UMR8182, Equipe de Chimie Inorganique, Bâtiment 420, 91405 Orsay Cedex, France
[c] Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 Quai E. Ansermet, 1211 Geneva 4, Switzerland
[d] Université Claude Bernard Lyon 1, Laboratoire des Multimatériaux et Interfaces, UMR5615, Campus de la Doua, 69622 Villeurbanne Cedex, France

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ABSTRACT

We show that the irradiation of SMM molecules at optical wavelengths can drive an increase or a decrease of the magnetic moment of a SMM, even though the energy of the photons does not correspond to a precise electronic or spin transition, the light pulse triggering a phonon-assisted spin transition. The process is sensitive to the power of the incident light. This result most probably explains why it has been so far impossible to observe the opening of the hysteresis loop on thin films of SMM with the XMCD technique. The consequences of these observations are manifold: they bring a means of controlling molecular magnets, open prospects in the field of quantum computing, and may enable the realization of coherent microwave sources through stimulated superradiance.



## 1. Introduction

Single-molecule magnets (SMM) are paramagnetic molecules, usually with a large spin $S$, in which magnetization can be saturated in the $+S$ or $-S$ state by applying an external magnetic field. The energy diagram has two wells, corresponding to the two spin states, separated by an energy barrier. Under the proper field and temperature conditions a stable magnetization can be kept for long periods of time (years). The effect is purely intra-molecular, such molecules, therefore, literally behave as nano-magnets, hence their name. Once the system is prepared in a $+S$ or $-S$ state, its magnetization may eventually relax in two ways: the electrons can re-populate the other energy well via a thermally activated process (going "over the barrier") or via quantum tunneling (going "through the barrier") [1]. Below the blocking temperature, *i.e.*, the temperature above which the magnetic moment becomes free to fluctuate, the magnetization curve resembles that of a ferromagnet, it exhibits a significant hysteresis with a remnant magnetization and a coercive field.

In classical ferromagnets the appearance of a magnetic moment and its relaxation are collective phenomena, implying sizeable amounts of matter, the formation of Bloch or Néel walls and Weiss domains, etc. In the case of SMM, at least at the first order, there are no intermolecular interactions and no supramolecular structures formed. The first, and by now well known, SMM is $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$, MnOAc for short, first synthesized in 1980 [2] and identified as SMM in 1991 [3]. MnOAc has one of the highest blocking temperatures $T_B \sim 3.5$ K (considering a relaxation time of 100 s, see below), its spin ground state reaches a rather high value ($S = 10$), and its coercive field also is quite impressive ($H_c \sim 1T$ at 2 K). The interest for SMM is threefold: academic, of course, but many studies are spurred by the hope of using SMM for high-density magnetic information storage [4,5], and SMM are moreover envisioned as building blocks (qubits) for implementing quantum algorithms in computers [6–8].

Our own research aims at organizing SMM on surfaces using mesomorphism and at probing the magnetic properties of such assemblies. During the course of our experiments we synthesized several $Mn_{12}$ derivatives and studied some more compounds. In-house magnetometry on bulk samples has been performed with a commercial SQUID magnetometer while the thin-film studies have been performed at synchrotron sources using the X-ray Magnetic Circular Dichroism (XMCD) [9,10] technique. This choice was driven by the great sensitivity offered by the technique and its chemical sensitivity which allows to specifically probe the

* Corresponding author.
*E-mail address:* gallani@ipcms.u-strasbg.fr (J.-L. Gallani).
[1] Current address: Université de Lyon, CNRS, UMR 5182, Laboratoire de Chimie, Ecole Normale Supérieure, 69007 Lyon, France.
[2] CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Dr. A. Schweitzer, Pessac, 33608, France.

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magnetic behaviour of a given element in a molecule. XMCD is based on the principle that resonant polarized photons are more or less absorbed (dichroism) by a magnetic material depending on the relative orientation of the photons helicity and sample magnetic moment. Still, even though the compounds displayed all the requested characteristics of a SMM when studied in the bulk with a SQUID (coercive field, remnant magnetization, ac relaxation), they failed to do so when studied with XMCD technique. Other groups having experienced the same problems, the consensus was that the SMM could either be beam-damaged or distorted by the strong surfaces forces, resulting in the loss of the SMM behaviour, which was actually true in many cases. Given the peculiar nature of the SMM magnetism we nevertheless wondered whether it could not be that the measurement itself would lead to a demagnetization of the sample, since the electrons that were involved in the light absorption process are the very same at the heart of the SMM behaviour [11]. This prompted photo-SQUID experiments, in which the magnetometry was performed with a SQUID under photon irradiation, which confirmed that it was indeed possible to demagnetize or magnetize a SMM upon shining photons onto it. In this paper we will describe the sequence of experiments which led us to this unexpected conclusion.

After a brief reminder of the fundamentals of SMM magnetism with the canonical example of MnOAc, we shall report XMCD magnetometry results obtained on three different SMM, underlining the differences between SQUID and XMCD results. We shall then describe our photo-SQUID experiments. We will tentatively propose a phenomenological model which supports some of our data.

## 2. Magnetism of SMM

### 2.1. Fundamentals

There are many different sorts of SMM compounds, all of them include 3*d* and/or 4*f* ions which are at the origin of the magnetic properties. Let us first briefly recall some essential features of single-molecule magnets with the arch-example of MnOAc. This compound is made from a polyoxometallate core containing 12 Mn atoms, surrounded by 16 acetate groups. The $S = 10$ spin ground state comes from the eight $Mn^{III}$ ions and the four $Mn^{IV}$ ions which are coupled ferromagnetically, the two subsets being antiferromagnetically coupled. For the stabilization of the magnetization there must be some Ising magnetic anisotropy (an easy axis), that is, a negative zero-field splitting parameter $D$. This creates an energy barrier $U_{eff} = S^2\,|D|$, at the first order, to the thermal relaxation of the magnetization, with $U_{eff}/k_B \sim 62$ K for MnOAc. In MnOAc, most of the magnetic anisotropy of the ground state stems from the magnetic anisotropy of the eight $Mn^{III}$ ions (the outermost Mn ions). The coordination around each $Mn^{III}$ ion is not regular octahedral, but Jahn–Teller distorted, two bonds are longer than the other four (Jahn–Teller elongation). These crystal-field distortions together with a spin–orbit interaction result in a zero-field interaction at each $Mn^{III}$ ion. Hence, the vectorial projection of single-ion anisotropies on to the ground state gives rise to the easy axis type magneto-anisotropy. The $S = 10$ ground state is split into 21 $\pm M_S$ sublevels in zero field, with the $M_S = \pm 10$ levels being the lowest in energy.

When prepared in the $M_S = \pm 10$ state and the magnetic field removed, a SMM can go back to the equilibrium state by going over the energy barrier with a thermally activated process. In the case of MnOAc the parameters used to fit the Arrhenius type dependence of the relaxation time of the magnetization, $\tau$, are: $\tau_0 = 4.7 \times 10^{-9}$ s and $U_{eff}/k_B = 66$ K [12]. This means that the relaxation time of the magnetization of MnOAc is of the order of months at 2 K. The fact that the low-temperature slow relaxation of the magnetization of SMMs occurs at the molecular level and does not result from collective interactions (even though weak intermolecular dipolar interactions eventually induce collective magnetic behaviour below 50 mK) has been experimentally established, in particular with low-temperature calorimetry (no specific heat anomaly) and magnetometry on diluted samples. It is worth underlining here that magnetizing or demagnetizing a SMM always is a dynamical process, meaning that the SMM actually is out of equilibrium most of the time.

In addition to the properties described hereabove, SMM are also peculiar objects in the sense that even though nanometric, they still display easily observable quantum behaviour. In particular, the relaxation of the magnetized molecule to its equilibrium state may occur via quantum tunneling of spin. This phenomenon has been described in details by Gatteschi and Sessoli [13]. Quantum tunneling can be pure, temperature-assisted or phonon-assisted. The relaxation time should be temperature independent if relaxation occurs through quantum tunneling, at least at very low temperatures [14].

The relaxation to equilibrium (*i.e.*, $M = 0$) is not the only relaxation process. In fact the whole magnetic behaviour of SMM should rather be seen as something dynamic, under the influence of several time-dependant processes. In particular, the response of a SMM to an applied field also is time-dependant, as exemplified by the fact that the shape of hysteresis curves varies with the field sweep rate: it takes some time for the molecules to go from the metastable to the stable well, and the magnetization, therefore, always lags behind the applied field [15]. Similarly, when a static magnetic field is applied, the metastable well drains out and the stable one is slowly populated. The rate at which quantum tunneling of the magnetization occurs is set by several factors: temperature, applied external field, angle between applied field and molecule easy axis, dipolar field from adjacent molecules and nuclear spins.

### 2.2. Measuring the magnetic properties of SMM thin films

Many groups have reported attempts at measuring the magnetic properties of SMM deposited as thin films or isolated molecules on surfaces. The first question to address was that of the survival of the molecules to the deposition process and beam damage. These studies have been performed with spectroscopic techniques such as XAS, XES and RPES [16–21]. As of today, it is now possible to say that the stability of the molecules has been improved and that the experimental conditions for measuring them properly are known (in particular beam damage is mastered). The question of the functionality, that is measuring the magnetic properties of the monolayer, is a difficult one. As the sensitivity of commercial SQUID magnetometers is usually insufficient, experimentalists have turned to more exotic techniques such as XMCD [11,22] and depth-resolved β-detected nuclear magnetic resonance (β-NMR) [23]. There have also been attempts at probing the spin state of isolated molecules using a STM [24,25].

In the case of MnOAc and its derivatives, all studies conducted so far have concluded that the SMM behaviour was probably lost since no opening of the magnetization curve could be recorded on monolayers, even though it was spectroscopically assessed that the molecules were intact. Mannini et al. have reported the first observation of an open hysteresis in monolayers of $Fe_4$, using low-temperature XMCD (0.55 K) measurements [26,27]. However, even though the hysteresis loop presents a typical butterfly shape no remnant signal was observed in contrast with the corresponding SQUID measurements. No remnant magnetization could be detected, or only a very weak one [28], an effect that could be due to photon-induced demagnetization, as shall be seen hereafter (Section 3.2).