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# Isotope effect on the spin dynamics of single-molecule magnets probed by muon spin spectroscopy

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**Muon spin relaxation ( $\mu$ SR) experiments on a single molecule magnet enriched in different Dy isotopes detect unambiguously a slowing down of the zero field spin dynamics for the non-magnetic isotope. This occurs in the low temperature regime dominated by quantum tunnelling, in agreement with previous ac susceptibility investigations. In contrast to the latter, however,  $\mu$ SR is sensitive to all fluctuation modes affecting the lifetime of the spin levels.**

Single Molecule Magnets (SMMs) are transition metal or lanthanide-based systems characterized by a large magnetic moment whose dynamics is governed by the magnetic anisotropy which creates a double well energy potential.<sup>1</sup> Through a rational chemical design, anisotropy barriers exceeding a thousand Kelvin have been obtained with blocking of the magnetization observed at temperature as high as 60 K.<sup>2</sup> The quantum nature of SMMs, however, dominates the low temperature regime revealing itself in many fascinating effects related to under-barrier mechanisms of relaxation.<sup>3</sup> Among them, quantum tunnelling of the electronic magnetization was found to be very sensitive to the environment and in particular to the presence of nuclear spins. The acceleration of the quantum tunnelling in isotopically enriched Fe<sub>8</sub> SMM using <sup>57</sup>Fe (nuclear spin value  $I = 1/2$ ) was for the first time evidenced by measuring the time dependence of the magnetization.<sup>4</sup> Following this, the quantum tunnelling between hyperfine levels was also investigated in detail in lanthanide-based SMMs.<sup>5</sup> More recently the spin dynamics of some SMM comprising either tri-positive <sup>161</sup>Dy ( $I = 5/2$ ) or <sup>164</sup>Dy ( $I = 0$ ) ions has been investigated by using alternate current (ac) susceptometry. Also in this case quantum tunnelling relaxation was slowed down by reducing the hyperfine field.<sup>6, 7</sup> Furthermore, the control of the nuclear magnetic environment is crucial to enhance quantum coherence in spin systems which can be potentially employed as quantum bits in quantum

information technology.<sup>8</sup> The great appeal of molecular spins to store information or to be operated in quantum gates requires addressing individual or arrays of molecules, for instance by creating monolayer deposits on a surface<sup>9</sup> or embedding a molecule inside an electrical junction.<sup>10</sup> In these cases different tools need to be developed to investigate the spin dynamics. Going beyond the use of XMCD and other synchrotron-based characterization tools, often used to study SMMs dynamics at

the nanoscale,<sup>11</sup> Muon Spin Relaxation ( $\mu$ SR) emerges as a powerful and versatile technique. In  $\mu$ SR, fully spin-polarized muons, which are positively charged elementary particles with spin value  $1/2$ , are implanted in the sample. The spin of the implanted muons interacts with the magnetic fields produced by nearby molecules which govern its temporal evolution.<sup>12</sup> The implanted muons decay into positrons (mean lifetime  $\sim 2.2 \mu$ s), which are emitted preferentially along the muon spin direction at the time of decay. Thus, using appropriately positioned detectors it is possible to reconstruct the time dependence profile of the muon spin polarization. This technique has been extensively employed to characterize the magnetic behaviour of SMMs,<sup>13, 14</sup> since it allows a direct investigation of the magnetization dynamics of individual molecules and on a time scale faster than what is currently accessible by magnetic techniques like ac susceptibility. Furthermore, thanks to the possibility of controlling the muon implantation energy,  $\mu$ SR has been also used to investigate depth resolved magnetic properties of thin films of TbPc<sub>2</sub> evidencing the critical role of the packing of the molecules.<sup>15</sup> Another example of Ln-based complex investigated with this technique is [Dy(hfac)<sub>3</sub>(PyNO)]<sub>2</sub> (DyPyNO), where PyNO = pyridine-*N*-oxide and hfac<sup>-</sup> = hexafluoroacetylacetonate. Interestingly, this SMM exhibited the same magnetic behaviour, in the entire temperature range, in bulk and sublimated thin film forms. Moreover, depth resolved experiments provided a homogeneous response from the whole SMM film volume.<sup>16</sup>

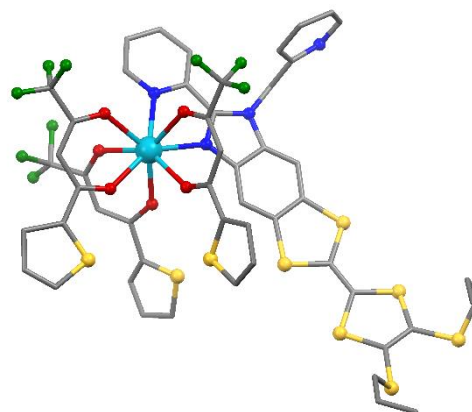


Figure 1 – Molecular structure of **Dytta**. Turquoise Dy, red O, blue N, green F, yellow S and grey C (for clarity H atoms are omitted).

Although several others SMMs were studied by  $\mu$ SR so far, the effect of nuclear moments on the molecular spin dynamics has not yet been investigated using this technique. In this communication, we show that  $\mu$ SR is able to detect effects of isotopic enrichment on the molecular spin dynamics. Here we report on the  $\mu$ SR investigation of the [Dy(tta)<sub>3</sub>(L)]·C<sub>6</sub>H<sub>14</sub> (**Dytta**) system, where tta<sup>-</sup> = 2-

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thenoyltrifluoroacetate and L=4,5-bis(propylthio)-tetrathiafulvalene-2-(2-pyridyl)-benzimidazole methyl-2-pyridine (see Figure 1).<sup>17</sup> In particular we performed these characterizations on two isotopically enriched variants of this mononuclear complex with <sup>161</sup>Dy ( $I = 5/2$ ) and <sup>164</sup>Dy ( $I = 0$ ), and hereafter referred to as <sup>161</sup>Dy<sup>ttta</sup> and <sup>164</sup>Dy<sup>ttta</sup>,<sup>6</sup> respectively. In this system the Dy<sup>III</sup> ion is connected to three tta<sup>-</sup> ions and one bidentate L ligand, as shown in Figure 1, which could promote the grafting on gold surface. In this configuration, the metal is at the centre of a N<sub>2</sub>O<sub>6</sub> square antiprism environment leading to a  $D_{4d}$  local symmetry around the Dy<sup>III</sup> ion. The  $J=15/2$  manifold resulting from the spin-orbit coupling of the  $L=5$  and  $S=5/2$  of the 4f<sup>9</sup> configuration is split by the crystalline field. The anisotropic distribution of the electrostatic potential around the Dy<sup>III</sup> ion stabilizes the Kramers doublet  $M_J = \pm 15/2$ . This corresponds to an easy axis magnetic anisotropy and effective  $g$  values of the ground state  $g_x=g_y=0$  and  $g_z \sim 20$ . *Ab initio* calculations confirmed this picture and estimated the first excited doublet,  $M_J = \pm 13/2$ , at  $\sim 180$  K.<sup>17</sup> Magnetic measurements performed on solid state compounds revealed a SMM behaviour, *i.e.* slow relaxation up to 15 K with and without the application of a static magnetic field.<sup>24</sup> Two relaxation mechanisms were evidenced: *i*) a thermally activated process, though with an estimated energy barrier much smaller than that estimated from the separation between the ground and first excited doublets, as often observed in highly anisotropic systems,<sup>5</sup> and *ii*) a temperature-independent process, attributed to fast quantum tunnelling in zero field.<sup>17</sup> In this latter regime, an increase in the relaxation time of about an order of magnitude was observed when passing from <sup>161</sup>Dy<sup>ttta</sup> to <sup>164</sup>Dy<sup>ttta</sup>.<sup>6</sup> On the contrary, no isotope effect was evidenced in the thermally activated regime.

Microcrystalline powders of <sup>161</sup>Dy<sup>ttta</sup> and <sup>164</sup>Dy<sup>ttta</sup> (see Table S1 for isotope compositions and Figure S1 for PXRD spectra) were investigated at the GPS spectrometer of the Paul Scherrer Institute. Conventional bulk  $\mu$ SR measurements (with implantation energy of  $\sim 4$  MeV corresponding to a few 100  $\mu$ m stopping depth) were performed in zero magnetic field (ZF). The time dependence of the muon spin polarization,  $P_Z(t)$ , was recorded as a function of temperature and selected spectra measured for both samples are presented in Figure S2 and S3, whereas spectra for all measured temperatures are shown in Figure S4 and S5. At high temperature  $P_Z(t)$  decays exponentially from its initial value to zero, as expected when the local magnetic field experienced by each muon is fluctuating. As the temperature is decreased, the damping rate of the polarization increases gradually. However, below  $\sim 30$  K, we find that  $P_Z(t)$  exhibits a shallow dip at short times, and then a recovery to  $\sim 1/3$  followed by a slow relaxation at even longer times. As in the case of other SMMs,  $P_Z(t)$  can be fitted throughout the full temperature range by a phenomenological Kubo-Toyabe model<sup>18</sup> multiplied by a square root exponential relaxation function<sup>15</sup>.

$$P_Z(t) = \left[ \frac{1}{3} + \frac{2}{3}(1 - \Delta t)e^{-\Delta t} \right] e^{-\sqrt{\lambda t}}. \quad (1)$$

This function accounts for depolarization due to a Lorentzian

distribution of local static magnetic fields of width  $\Delta$ , with an additional relaxation,  $\lambda$ , due to fluctuating magnetic field components from the Dy<sup>III</sup> magnetic moments. The square root in the dynamic component originates from averaging many inequivalent sites of the molecule where muons can stop.<sup>19, 20</sup> Best fits of  $P_Z(t)$  (see ESI for details) provide the values of  $\Delta$  and  $\lambda$  as a function of temperature, as shown in Figure 2, and exhibit a similar behaviour to other investigated SMMs.<sup>14-16, 20</sup> These parameters are representative of the magnetic properties and spin dynamics of the single molecule, since each implanted muon is sensitive to the dipolar fields from its nearest neighbour. The temperature dependences of  $\Delta$  and  $\lambda$  reflect the gradual evolution of Dy<sup>III</sup> spin dynamics, from fast fluctuating spins at high temperature to a quasi-static (*i.e.* very slow dynamics) at low temperature. We outline three specific regimes: *i*) at high temperatures fast thermally activated spin fluctuations dominate, with  $\Delta=0$ , *i.e.* no local static magnetic fields probed by muons, and a relatively small  $\lambda$ . The latter increases upon decreasing the temperature due to the slowing down of the fluctuations of the Dy<sup>III</sup> magnetic moments on a time scale comparable with the muon spin Larmor precession frequency. *ii*) Around 30 K,  $\lambda$  exhibits a narrow peak coinciding with an abrupt increase (non-zero value) in  $\Delta$ , which corresponds to the appearance of static magnetic fields. *iii*) Finally, at low temperature, large quasi-static fields (large  $\Delta$ ) are experienced by muons together with a pronounced decrease of  $\lambda$ .

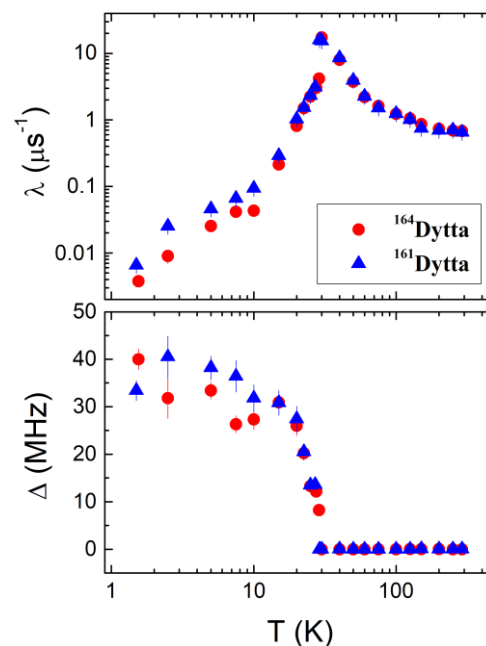


Figure 2 – Temperature dependence of the relaxation rate (top) and width of local static magnetic fields distribution (bottom) for <sup>164</sup>Dy<sup>ttta</sup> and <sup>161</sup>Dy<sup>ttta</sup> measured by  $\mu$ SR in zero field.

Whereas no significant dissimilarities are observed in the high temperature region, below  $\sim 15$  K clear difference emerges, exceeding the experimental uncertainty and revealing a faster dynamic relaxation  $\lambda$  for <sup>161</sup>Dy<sup>ttta</sup>. In a similar way to what is observed in ac susceptibility measurements, the isotope effect is visible in the temperature region where under-barrier

relaxation dominates. However, when comparing  $^{161}\text{Dy}^{\text{II}}$  to  $^{164}\text{Dy}^{\text{II}}$ , only an increase by a factor  $\sim 2$  is observed in  $\lambda$ , to be compared with a factor  $\sim 10$  for the relaxation time of the bulk magnetization detected by ac susceptometry.<sup>6</sup>

The isotope effect is also evident below 15 K when looking at the correlation time,  $\tau$ , of the local magnetic field experienced by muons, as shown in Figure 3 (full temperature range data are reported in Figure S7). This parameter can be extracted from the  $\mu\text{SR}$  spectra assuming two different regimes. At low temperature, where quasi-static magnetic fields dominate, the correlation time depends only on  $\lambda$  as  $\tau = 2/(3\lambda)$ , whereas at high temperature, where thermal fluctuations dominate,  $\tau = \lambda/2\Delta_0^2$ . Here  $\Delta_0$  is the size of the fluctuating field, whose value can be estimated from the saturation value of  $\Delta$  extrapolated at low temperature. This was taken to be  $\sim 35$  MHz for both  $^{164}\text{Dy}^{\text{II}}$  and  $^{161}\text{Dy}^{\text{II}}$ . Note that there is some scatter in  $\Delta$  at low temperature since it is on the limit of what is measurable using  $\mu\text{SR}$ . However, the exact value of  $\Delta_0$  will only affect our estimates of  $\tau$  at high temperature by up to 10-20%. Moreover, the fact that  $\lambda$  and  $\Delta$  are the same at high temperature supports our conclusion regarding the lack of isotope effect at high temperature.

It is interesting to note that the extracted  $\tau$  captures the dynamics of the  $\text{Dy}^{\text{III}}$  magnetic moments but not necessarily in the same way as bulk magnetic measurements do. Indeed, the extracted correlation times are about 1-2 order of magnitude shorter than those extracted from ac susceptibility (Figure 3). We point out that whereas ac susceptibility is sensitive to excitations with wave-vector  $q=0$ ,  $\mu\text{SR}$  (as a local probe) is sensitive to excitations integrated over all  $q$  values of the Brillouin zone.<sup>21</sup> This difference is however not relevant for pure paramagnetic solids, *i.e.* where intermolecular interactions are negligible. In the case of **Dy<sup>II</sup>** it has been observed that dipolar interactions, though weak, play a relevant role in the dynamics at low temperature, where quantum tunnelling is dominating. On the contrary, the  $\tau$  extracted from  $\mu\text{SR}$  data is shorter over the entire investigated temperature range. To reconcile ac susceptibility and  $\mu\text{SR}$  results we should consider that the former is mainly sensitive to relaxation processes that reverse the magnetization, *i.e.* inter-well transitions changing the sign of the spin projection along the anisotropy axis. In fact, in zero field, the equilibrium population of excited spin levels is practically unaffected by the weak oscillating field. On the contrary  $\mu\text{SR}$ , beyond probing faster dynamics, is sensitive to all types of fluctuations which affect the lifetime of the spin states, including intra-well transitions as well as decoherence. It is therefore not surprising to observe a less pronounced isotope effect by  $\mu\text{SR}$ . The hyperfine fields are in fact crucial to establish the resonant condition for the reversal of the magnetization by quantum tunnelling, but they are expected to have less influence on the lifetime (or width) of the states. Indeed, it is well known that nuclei, which are not strongly coupled with the electronic spins, provide the largest contribution to decoherence.<sup>22</sup> Finally, it should be remarked that other nuclei, such as  $^1\text{H}$  and  $^{19}\text{F}$ , may affect the electronic spin dynamics of the  $\text{Dy}^{\text{III}}$  ion, but this would not explain the difference between the two samples or the different  $\tau$  measured by  $\mu\text{SR}$  and ac susceptibility.

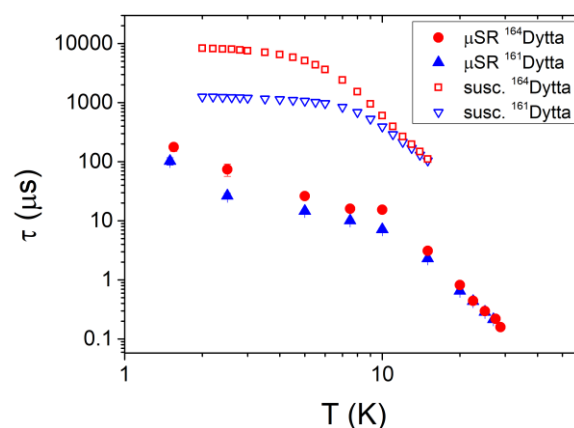


Figure 3 – Correlation time extracted from  $\mu\text{SR}$  and relaxation time of the magnetization extracted from ac susceptibility as a function of temperature for  $^{161}\text{Dy}^{\text{II}}$  and  $^{164}\text{Dy}^{\text{II}}$ . Data are reported in log-log scale.

As evident from Figure 3,  $\tau$  from  $\mu\text{SR}$  shows more pronounced temperature dependence than ac susceptibility data below 10 K. This is also in agreement with the sensitivity of muons for the intra-well transitions. Similar low temperature behaviour has been observed also for the  $\text{DyPyNO}$  SMM.<sup>16</sup> This latter has an energy separation between the ground  $M_J = \pm 15/2$  doublet and the first excited doublet with  $M_J = \pm 13/2$  of  $\sim 170$  K, comparable to that calculated for **Dy<sup>II</sup>** SMMs. Interestingly,  $\mu\text{SR}$  data of  $\text{TbPc}_2$ , which has a much larger separation ( $\sim 800$  K) between the ground and first excited doublets, show that  $\tau$  is fully saturated below 50 K.<sup>15</sup> Moreover,  $\tau$  of  $\text{TbPc}_2$  extracted by  $\mu\text{SR}$  is closer to what measured by ac susceptibility applying a magnetic field of 1 kG.<sup>14</sup>

To summarize, our  $\mu\text{SR}$  investigation confirms the capability of the technique to capture fine details of the spin dynamics of molecular systems, down to isotopic effects in the tunnelling of the magnetization. Moreover, this alternative way to study the spin dynamics provides a different and complementary perspective, compared to traditional magnetometry. This arises from its local probe character and the consequent sensitivity not only to processes which lead to magnetization reversal, but to *all* sources of spin fluctuations. This aspect is of particular interest in light of current trends in using molecular spin systems for quantum information to realize quantum gates.<sup>23</sup> In this respect, the final goal is using single molecules or isolated supramolecular structures to perform quantum operations. This poses the additional challenge of preserving, in isolated molecules on substrates, not only the memory effect but also an acceptable quantum coherence time. Thanks to the possibility of implanting muons at different energies, they can be used to probe the dynamics of molecules close to a surface or an interface.  $\mu\text{SR}$  technique provides therefore an almost unique tool to obtain information on the lifetime of spin states and how this is affected by the proximity to the substrate.

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## Conflicts of interest

There are no conflicts to declare.

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