Torque-detected ESR of a tetrariron(III) single molecule magnet

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1. Introduction

Magnetic anisotropy is an essential ingredient of the behavior of many magnetic materials, including molecules known as Single Molecule Magnets (SMMs). In these materials, an axial Ising-type anisotropy produces an energy barrier to magnetic moment reversal and results in slow magnetic relaxation at low temperatures (T) [1]. Transverse anisotropy components also play a key role in causing tunneling through the barrier in a strongly field- and symmetry-dependent fashion [2]. To date, the most powerful method to investigate magnetic anisotropy in SMMs is electron spin resonance (ESR) operated at high frequencies and in high fields (HFESR) to fully reveal the fine structure of the ground spin state [3–6]. Sensitivity and accessible frequency ranges are crucial parameters for HFESR. Cavity perturbation techniques can be used to detect magnetic resonance transitions on single crystal samples at frequencies up to 700 GHz, but these spectrometers are limited to discrete frequencies or very narrow frequency ranges [7,8]. On the other hand, broad band methods, such as frequency domain magnetic resonance spectroscopy (FDMRS) [9–11] suffer from their low sensitivity. Indeed, measurements performed on single crystals of SMMs using FDMRS are very rare, and only studies on single-crystal mosaics have been published [12,13].

As an alternative, magnetic resonance transitions can be detected by measuring magnetization changes induced by the absorption of radiation [10], a technique introduced more than 40 years ago [14]. To this aim, different magnetic sensors were used to probe the effect of microwave irradiation off and on resonance, including SQUIDs [15], micro-SQUIDs [16], and Hall bars [17,18]. SQUIDs and micro-SQUIDs are highly sensitive but they have a slow response time and, in addition, cannot be operated in very high magnetic field (above 8 T for SQUIDs and much less for micro-SQUIDs). On the contrary, Hall bars are highly sensitive and have a fast response time. In any case, use of these setups was so far limited to either single frequencies or very narrow frequency ranges.

We have now combined our experience in FDMRS and torque magnetometry to develop a novel tool for magnetic characterization which has been named torque-detected ESR (TDES). Technical details have been already presented elsewhere [19]. Torque magnetometry (TM) measures the mechanical couple experienced by a magnetic sample in a homogeneous magnetic field (H) due to the noncollinearity between H and the magnetization (M), i.e. due to the presence of transverse magnetization [20]. When the sample has a permanent magnetic moment, the torque signal allows measuring the magnetization directly. For a paramagnet, the appearance of a transverse magnetization is a consequence of magnetic anisotropy. In a paramagnetic molecule with N thermally accessible spin states, the component of the torque signal along a given axis i is:

$$
\tau_i = \sum_{j=1}^{N} \tau_{ij} \exp\left(-E_j/k_B T\right) / \sum_{j=1}^{N} \exp\left(-E_j/k_B T\right)
$$

(1)
where $E_i$ is the energy of the $i$th spin state (in general, a function of the spin Hamiltonian parameters and of the applied magnetic field), $k_B$ is the Boltzmann constant and:

$$\tau_{ix} = -\left(\frac{\partial E_i}{\partial \mu_0 H}\right)_i$$

is the contribution provided to the torque by the $i$th state. Here, $\theta_x$ is the angle used to describe the rotation of the sample around the $x$-axis. Resonant absorption of microwave (MW) radiation changes the population of the states with respect to Boltzmann distribution in a way which depends on the transition probabilities, on the MW power, and on the spin–lattice relaxation time. It consequently leads to a change in the torque signal, which can be used to detect magnetic resonance transitions. The torque signal was measured here by using a highly sensitive CuBe cantilever, which enables studying very small single crystals. The cantilever response is fast compared with commercial SQUIDs, and the device can be operated up to high magnetic fields and in a broad frequency range. Furthermore, the MW radiation has virtually no effect on the measured torque values off resonance. Finally, conventional torque measurements performed in advance on the crystal of interest “in situ” provide an initial estimate of the magnitude and orientation of the anisotropy tensor. As a disadvantage, the torque signal – and consequently the sensitivity of TDESR – is strongly dependent upon the applied field direction because all torque components vanish whenever the field lies along a principal magnetic direction [20]. Under these special conditions the technique cannot be used. However, by properly adjusting the field orientation, TDESR can be made several orders of magnitude more sensitive than FDMRS.

We herein present a combined study by TM, TDESR and HFESR on a single crystal of $[\text{Fe}_4(\text{Dpm})_2(\text{dpm})_2] \cdot 3\text{H}_2\text{O}$ (1) where Dpm is 2,2,6,6-tetramethyl-3,5-heptanediol (also known as dipivaloylmethane) and H$_2$D is the tripodal ligand ($R,S$)-2-hydroxymethyl-2-(2-methyl-butoxymethyl)propane-1,3-diol [21]. Among SMMs of the Fe$_x$ family, this particular derivative was chosen because it exhibits very narrow lines in the HFESR spectra recorded on a powder sample [21]. Moreover, all molecules in the crystal are magnetically equivalent and iso-oriented, a most favorable situation for single-crystal studies (see below).

The crystal structure of 1, as determined by single-crystal X-ray diffraction at 120(2) K [21], has monoclinic symmetry and belongs to space group $P2_1/n$ with $a = 17.0632(7)$, $b = 15.5838(7)$, $c = 19.5691(8)$ Å and $\beta = 110.600(1)^\circ$. The molecular structure viewed perpendicular to the metal plane and along the $b$ crystal axis is shown in Fig. 1a and b, respectively. The system consists of four Fe$^{3+}$ ions ($S_i = 5/2$) that are antiferromagnetically coupled to give a total ground spin state of $S = 5$. Disregarding the 2-methyl-butoxyethenyl residues on tripodal ligands, the molecule has approximate axial ($D_2$) symmetry along the normal to the metal plane ($n$), which is thus expected to be close to the unique (easy) magnetic axis of the system.

The crystallographic symmetry, however, is $C_2$ and the twofold axis is directed along the line joining Fe1 and Fe2, which is parallel to the $b$ axis of the unit cell. Therefore, Fe1 - Fe2 must represent a principal direction ($y$) for the second-order anisotropy tensor of the $S = 5$ state, the easy axis ($z$) and the third principal direction ($x$) being forced to lie in the $ac$ plane. HFESR spectra recorded on a polycrystalline sample have been previously [21] used to determine the anisotropy parameters appearing in the spin Hamiltonian of Eq. (3) and gathered in Table 1 (entry 1):

$$H = \mu_0 H_0 S \cdot H + D(S_z^2 - S(S + 1)/3) + E(S_x^2 - S_y^2) + B_0^2 \hat{O}_z^2$$

In Eq. (3), $D$ and $E$ are the zero-field rapping parameters that describe second-order rhombic terms of anisotropy (the nonaxial molecular symmetry permits $E \neq 0$). $B_0^2$ is associated with the fourth-order axial operator [1]:

$$\hat{O}_z^2 = 35S_z^2 + [25 - 30S(S + 1)]S_x^2 + 3S_y^2(S + 1)^2 - 6S(S + 1)$$

The negative $D$ value and the small $|E/D|$ ratio (0.067) point to a dominant easy-axis anisotropy, as required for a SMM, while the positive $B_0^2$ value results in a “compressed” parabolic shape for the anisotropy barrier, as detailed in Ref. [22].

We have investigated a single crystal of 1 using TM to accurately determine the orientation of the easy magnetic axis, and subsequently using TDESR. Magnetic resonance transitions detected as a function of field and frequency have been used to extract the anisotropy parameters of the $S = 5$ ground state. In the third part of the work, we have studied a single-crystal sample by HFESR, applying the magnetic field along the easy axis and in the hard plane. The parameter sets obtained by the different techniques are in excellent agreement with each other and provide an accurate characterization of magnetic anisotropy in this SMM.

2. Experimental

Well-formed monoclinic crystals of 1 were prepared as described in Ref. [21]. The crystals grow as rod-like prisms developed along the [101] zone axis, with (010), (101), (010) and (101) as main crystal faces. Technical details of the TDESR setup, which operates in the frequency range 30–1440 GHz (1–48 cm$^{-1}$) in fields up to 8 T and at temperatures down to 1.7 K, can be found elsewhere [19]. For the TM and TDESR measurements, a face-indexed single crystal of approximately 100 $\mu$g
mass was fixed on the cantilever with vacuum grease and visually aligned using an optical microscope. The accuracy of alignment was estimated to be ±1°. The crystal was oriented with its (101) face lying flat on the cantilever and the (010) face perpendicular to the rotation axis of the goniometer. In this way, the rotation was performed around the crystallographic b axis and the magnetic field H was applied orthogonal to the rotation axis, i.e. in the ac plane. The sample orientation is described using the angle \( \theta_b \) being \( \theta_b = 0 \) when the [101] zone axis is parallel to the magnetic field (Fig. 1). In this configuration, the cantilever detects the b-component of the torque vector \( \tau_b \) and positive \( \tau_b \) values indicate a tendency of the sample to rotate clockwise in Fig. 1b.

HFESR measurements on a face-indexed single crystal of 1 were performed with the Quasi-Optical setting of the spectrometer, operating in double pass transmission. The exciting frequency of 230 GHz is propagated in the cryostat with a corrugated guide which ends on a taper. A recently developed one-axis rotating holder [23] is attached to the taper, with a flat mirror placed below the sample for the reflection of the exciting frequency. The main feature of the rotating holder results from the use of a rotating piezoelectric micropositioner. It allows rotating over \( \sim 340° \) with an absolute measurement of the angle by the use of a resistive encoder. The transmitted light is then detected with a hot-electron InSb bolometer. The sample was visually oriented and fixed on the support using vacuum grease. The accuracy of initial alignment was estimated to be ±1°. Fitting of the spectra was carried out using a dedicated software [24,25].

### 3. Results and discussion

Angle resolved measurements by TM and TDESR have been carried out on face-indexed single crystals of 1 by applying the magnetic field in the ac plane and rotating the sample around the b axis. The rotation angle \( \theta_b \) was defined as the angle between the magnetic field and the [101] zone axis (Fig. 1b). In Fig. 2a we report the results obtained at \( \mu_0 H = 0.5 \) T and \( T = 1.65 \) K for a full rotation of the sample. The torque oscillates with a 180° period and vanishes at 90° intervals of \( \theta_b \) when the field lies along the principal magnetic directions in the ac plane. The angles of zero torque are reproduced by the expression \( 33.4(3)^° + n \times 90° \) (\( n \) = integer), the intercept being close to the orientation of a calculated from the crystal structure \( (\theta_b = 30.78°) \). Furthermore, the positive \( \tau_b \) value measured at \( \theta_b = 0 \) indicates that the sample tends to rotate so as to bring n along the applied field. Hence, considering the precision with which the crystal was visually aligned (±1°), the easy axis (z) is very close to n and the x direction consequently lies essentially in the plane of the metals.

Isothermal torque curves were also measured for fields up to 8 T applied close to the hard plane. This arrangement is convenient as it leads to a characteristic peak in the torque signal, which can be used to accurately determine magnetic anisotropy [26]. As a further advantage, when the angle \( \theta \) between the magnetic field and the easy axis approaches 90°, isofield values of \( \tau_b/(90 - \theta) \) for different \( \theta \) settings fall on the same curve.

Hence, changing crystal orientation leads to a simple rescaling of the torque curve. If the cantilever is operated in the linear response regime (e.g. for small flexion), a single scale factor can then be refined to account for instrumental calibration constant, sample mass and inaccuracies in crystal orientation, while information on magnetic anisotropy is extracted only from the field dependence of the torque signal [26]. Fig. 2b presents field dependent torque curves measured at \( T = 1.63 \) K by applying the magnetic field in the ac plane at different angles \( \theta \) from the easy axis. The solid traces are best fit curves obtained with the parameters of Table 1 (entry 3).

### Table 1

Spin Hamiltonian parameters of 1 obtained using different techniques.*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Technique</th>
<th>( g )</th>
<th>( D ) (cm(^{-1}))</th>
<th>( E ) (cm(^{-1}))</th>
<th>( 10^3 g_E ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HFESR (powder)(^b)</td>
<td>2.00</td>
<td>-0.449(1)</td>
<td>0.030(1)(^c)</td>
<td>2.4(5)</td>
</tr>
<tr>
<td>2</td>
<td>TM (( n ) dependence)(^b)</td>
<td>2.00</td>
<td>-0.4059(2)</td>
<td>0</td>
<td>1.00(1)</td>
</tr>
<tr>
<td>3</td>
<td>TM (( n ) dependence)(^b)</td>
<td>2.00</td>
<td>-0.4502(2)</td>
<td>-0.038</td>
<td>0.97(3)</td>
</tr>
<tr>
<td>4</td>
<td>TM (T dependence)(^b)</td>
<td>2.00</td>
<td>-0.4051(4)</td>
<td>0</td>
<td>1.21(6)</td>
</tr>
<tr>
<td>5</td>
<td>TM (T dependence)(^b)</td>
<td>2.00</td>
<td>-0.4490(3)</td>
<td>-0.038</td>
<td>1.42(5)</td>
</tr>
<tr>
<td>6</td>
<td>TDESR(^d)</td>
<td>1.989(2)</td>
<td>-0.4457(7)</td>
<td>0</td>
<td>1.00(1)</td>
</tr>
<tr>
<td>7</td>
<td>HFESR (crystal)(^d)</td>
<td>2.00</td>
<td>-0.447(3)</td>
<td>-0.038(1)</td>
<td>1.6(6)</td>
</tr>
</tbody>
</table>

* Numbers in parentheses are estimated standard deviations (esds) supplied by the least-squares fitting routines (parameters with no esd have been held fixed).

\(^b\) Ref. [21].

\(^c\) Absolute value.

\(^d\) This work.
from Zeeman energy and magnetic anisotropy energy. As explained in detail elsewhere [20], in low fields the magnetic anisotropy dominates over the Zeeman effect and the torque signal is proportional to \( H^2(\chi_{zz} - \chi_{xx}) \), where \( \chi_{zz} \) and \( \chi_{xx} \) are the low-field susceptibilities along \( z \) and \( x \), respectively. By contrast, high \( H \) values cause the magnetic moment to flip along the applied field, affording a strong decrease of the torque signal. The curves were subject to least-squares fitting using spin Hamiltonian in Eq. (3). In the least-squares routine, \( D \) and \( B_0^4 \) were treated as adjustable parameters along with an overall scale factor and with the \( \theta \) value for all crystal orientations except one (89.1°), to avoid correlation with the overall scale factor. The Landé factor \( g \) was held fixed at 2.00, as appropriate for high-spin iron(III). Since both \( D \) and \( E \) contribute to magnetic anisotropy in the \( ac \) plane in a highly correlated fashion, we imposed \( E = 0 \) to obtain a rough estimate of the \( D \) parameter. Differences between nominal and best fit \( \theta \) values did not exceed 0.3°, while the resulting \( D \) and \( B_0^4 \) parameters (Table 1, entry 2) were found comparable, although not identical, with those provided by HFESR on a powder sample (Table 1, entry 1). It is rewarding that torque data clearly point to a positive \( B_0^4 \) consistent with powder HFESR.

Fig. 3a displays the field dependence of the torque signal recorded at six different temperatures for \( \theta = 88.5° \). Here \( H_{br} \) was found to increase with increasing temperature, as plotted in Fig. 3b, and its \( T \) dependence already provided a rough estimate \( D = -0.40(2) \) cm\(^{-1} \) for \( E = B_0^4 = 0 \).

The curves in Fig. 3a were again fitted to Eq. (3), treating \( D \) and \( B_0^4 \) as adjustable parameters with \( g = 2.00 \) and \( E = 0 \). A scale factor was also refined at each temperature to account for small possible changes in the response of the cantilever. The best fit parameters gathered in Table 1 (entry 4) compare well with those extracted from Fig. 2b, though with a slightly larger \( B_0^4 \).

Both entries 2 and 4 in Table 1 feature \( D \) values ca. 10% smaller in absolute value than found by powder HFESR, as a likely consequence of neglecting rhombic anisotropy. In fact, according to Eq. (3) for a positive (negative) \( E \) parameter \( x \) is the hard (intermediate) axis and the magnetic anisotropy in the \( ac \) place is increased (decreased) with respect to a purely axial system with the same \( D \). Therefore, neglecting \( E \) leads to an overestimation (underestimation) of \( |D| \). Based on our data, we then argue that the \( ac \) plane contains the easy and intermediate axes, while \( b \) is the hard axis. The correctness of this conclusion was fully confirmed by single-crystal HFESR (see below), which showed that \( E = -0.038(1) \) cm\(^{-1} \). Indeed, when the \( E \) parameter was set to –0.038 cm\(^{-1} \) in our analysis the best-fit \( D \) parameter was found to agree with the value determined by the other techniques (see Table 1, entries 3 and 5).

We have used the same single crystal to perform the TDESR measurements. The ac magnetic field component of the MW radiation was oriented perpendicular to both the externally applied field and the easy axis. Therefore the selection rules of “perpendicular” ESR apply (\( \Delta M = \pm 1 \)). Fig. 4a gives the TDESR spectra recorded at 20 K at two different magnetic fields (4.0 and 4.5 T) applied in the \( ac \) plane at \( \theta = 5° \), i.e. close to the easy axis. The frequency was swept in the range 110–260 GHz and the signal \( \Delta \sigma \) defined as the difference between the torques measured with and without MW irradiation. Notice that because the spectra were recorded at constant field and temperature, the torque signal without irradiation is also constant. Five sharp peaks, roughly evenly-spaced in frequency, are detected in this frequency range. The lines shift to higher frequencies as the magnetic field is increased from 4.0 to 4.5 T, thus proving that they are of magnetic resonance origin. In fact, when the field was further increased to 4.8 T, a sixth resonance line was observed [19]. The line-to-line separation is ca. 26.3 GHz, to be compared with the frequency spacing of parallel...
transitions that can be calculated using the $D$ parameter reported in Ref. [21], $2|D|/\hbar = 26.9$ GHz.

A closer inspection of Fig. 4a reveals that the line-to-line separation decreases smoothly with increasing frequency, as expected when $B_0^4$ and $D$ have opposite signs. The best-fit parameters obtained by fitting the frequency and field dependence of resonance lines (Fig. 4b) are given in Table 1 (entry 6). Due to the small angle between the magnetic field and the easy axis, the measurements did not provide reliable information on the $E$ term, which was therefore fixed to zero for simplicity. However, $D$ and $B_0^4$ could be precisely determined from the observed resonances. Calculated data included in Fig. 4b clearly show the outstanding quality of the fit. Notice that the broad frequency range which can be accessed allows spanning a wide portion of the energy spectrum for the system.

Magnetic resonances in anisotropic systems are expected to depend on magnetic field direction, as confirmed by Fig. 5a. When the magnetic field is applied in the $ac$ plane at different $\theta$ angles, the intensity of the peaks undergoes pronounced variations which largely reflect the angular dependence of the torque signal itself. More relevant to the present study is the observed shift of resonant peaks, which can be clearly resolved even for a small angular change thanks to the narrow lines. Such an angular dependence is plotted in Fig. 5b for the $-5 \rightarrow -4$ and $-4 \rightarrow -3$ transitions and allows determining the spin Hamiltonian parameters in Eq. (3), like in angle-resolved experiments by conventional ESR. The best-fit parameters so obtained ($D = -0.444(7)$ cm$^{-1}$, $B_0^4 = 1.1(4) \times 10^{-5}$ cm$^{-1}$, $g = 1.99(5)$ and $E = 0.00(3)$ cm$^{-1}$) are in excellent agreement with those provided by constant-angle TDESR (Table 1, entry 6).

To validate the results of TM and TDESR spectroscopy and to obtain a definitive proof of the magnitude and orientation of in-plane anisotropy, HFESR spectra were recorded at 230 GHz and 10 K on a face-indexed crystal of 1 (Fig. 6). The magnetic field was applied along the easy axis and in the hard plane, at different angles from the $b$ axis of the monoclinic unit cell (b). Experimental (bold) and simulated traces have been vertically shifted for a better visualization. A linewidth of 500 G has been used for all simulations with the parameters reported in Table 1 (entry 7).

4. Conclusions

We applied a novel torque-detected (TD) ESR technique along with traditional torque magnetometry to determine the spin Hamiltonian parameters in the ground $S = 5$ state of an Fe$_4$ single
molecule magnet. Torque measurements on a single crystal of the compound were carried out at constant $H$ and $T$ as a function of field orientation, so as to individuate the principal magnetic directions. As expected, the easy magnetic axis was found to lie within a few degrees from the normal to the metal plane. Field-swept torque curves were also collected at different $T$ and field orientations and afforded reasonably accurate estimates of the axial anisotropy parameters $D$ and $B_0^2$. TDESIR studies, carried out in situ on the same single crystal as a function of $H$, field orientation and frequency, revealed well-resolved resonances that allowed a spectroscopic-quality determination of $D$ and $B_0^2$. The results were validated through a parallel investigation of the material by angle-resolved high-frequency ESR. Our work demonstrates that TDESIR may represent an important addition to the pool of experimental techniques available for the characterization of anisotropic, ESR-active materials. It is a versatile and technically simple method which supplies ESR-quality information but offers the sensitivity typical of torque magnetometry. For this reason, it potentially enables the investigation of single crystals with mass in the microgram range. As a further advantage, it can be operated in high magnetic fields and in a broad range of frequencies, thus allowing to explore wide portions of the field-dependent energy spectrum of the system.

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