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Polyhedron 24 (2005) 2284-2292



# A comparison between high-symmetry Mn<sub>12</sub> single-molecule magnets in different ligand/solvent environments

S. Hill <sup>a,\*</sup>, N. Anderson <sup>a</sup>, A. Wilson <sup>a</sup>, S. Takahashi <sup>a</sup>, K. Petukhov <sup>a</sup>, N.E. Chakov <sup>b</sup>, M. Murugesu <sup>b</sup>, J.M. North <sup>c</sup>, E. del Barco <sup>d</sup>, A.D. Kent <sup>d</sup>, N.S. Dalal <sup>c</sup>, G. Christou <sup>b</sup>

<sup>a</sup> Department of Physics, University of Florida, PO Box 118440, Gainesville, FL 32611, USA

<sup>b</sup> Department of Chemistry, University of Florida, Gainesville, FL 32611, USA

<sup>c</sup> Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32310, USA <sup>d</sup> Department of Physics, New York University, New York, NY 10003, USA

> Received 5 October 2004; accepted 8 December 2004 Available online 3 June 2005

### Abstract

We present angle-resolved high-frequency electron paramagnetic resonance (HFEPR) data collected for single-crystal samples of deuterated and undeuterated  $Mn_{12}$ -acetate. The spectra reveal fine structures associated with the various  $Mn_{12}$  species corresponding to the different local solvent environments proposed by Cornia et al. [A. Cornia, R. Sessoli, L. Sorace, D. Gatteschi, A.L. Barra, C. Daiguebonne, Phys. Rev. Lett. 89 (2002) 257201], and recently confirmed by Hill et al. [S. Hill, R.S. Edwards, S.I. Jones, J.M. North, N.S. Dalal, Phys. Rev. Lett. 90 (2003) 217204] and del Barco et al. [E. del Barco, A.D. Kent, E.M. Rumberger, D.N. Hendrickson, G. Christou, Phys. Rev. Lett. 91 (2003) 047203]. Each of the fine structures exhibits a distinct dependence on the applied field orientation, thereby highlighting the discrete nature of the disorder. We then compare these data with spectra obtained for two recently discovered high-symmetry ( $S_4$ ) analogs of  $Mn_{12}$ -Ac, differing only in their ligand and solvent structures. None of the highly reproducible fine-structures seen in the  $Mn_{12}$ -Ac samples are found for the new  $Mn_{12}$  complexes, thus confirming the idea that the solvent structure significantly influences the QMT dynamics in  $Mn_{12}$ -Ac. Indeed, the HFEPR spectra for  $Mn_{12}$ -BrAc and  $Mn_{12}$ -*t*BuAc provide spectacular resolution, allowing for unique spectroscopic insights into high-symmetry giant spin SMMs.

Keywords: Single molecule magnets; Nanomagnet; Electron paramagnetic resonance; Quantum tunneling; Manganese

#### 1. Introduction

Research into molecule-based-magnets has made immense strides in recent years, with the discoveries of all organic molecular magnets, room temperature 3D ordered permanent magnets, and single-molecule magnets (SMMs), the latter exhibiting a host of spectacular quantum phenomena; for a review, see [1,2]. SMMs represent a molecular or 'bottom-up' approach to nano-magnetism. They offer all of the advantages of molecular chemistry, while displaying the properties of much larger magnetic particles prepared by conventional 'top-down' (or miniaturization) approaches [1,2]. They also straddle the interface between the classical and quantum realms; for example, they exhibit quantum magnetization tunneling (QMT) [3,4].

 $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4] \cdot 2CH_3COOH \cdot 4H_2O$ , or  $Mn_{12}$ -Ac [1–5], has become the most widely studied SMM, due to its large spin (S = 10) and high symmetry ( $S_4$ ). These factors contribute to the largest blocking temperature ( $T_B \sim 3$  K) against magnetization relaxation of any known SMM. Only recently has a detailed understanding emerged concerning the symmetry

<sup>\*</sup> Corresponding author. Tel.: +1 352 392 5711; fax: +1 352 392 3591. *E-mail address:* hill@phys.ufl.edu (S. Hill).

<sup>0277-5387/</sup>\$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2005.03.079

breaking responsible for the QMT in Mn<sub>12</sub>-Ac [6–10]. Disorder associated with the acetic acid solvent leads to discrete local environments, resulting in a significant fraction of the molecules (>50%) possessing twofold symmetry with a rhombic crystal-field parameter  $E \sim 0.01 \text{ cm}^{-1}$  (or  $ED \sim 0.02$ , where D is the uniaxial crystal-field parameter [7]).

Here, we present accurate angle-resolved high-frequency electron paramagnetic resonance (HFEPR) data collected for single-crystal samples of deuterated and undeuterated Mn<sub>12</sub>-Ac. The spectra reveal multiple fine structures associated with the various Mn<sub>12</sub> species in different local environments. Each of the fine structures exhibits a distinct dependence on the applied field orientation, thereby highlighting the discrete nature of the disorder, as well as suggesting that some of the  $Mn_{12}$ -Ac variants have their easy axes significantly tilted with respect to the global symmetry direction in the crystal [9]. We then compare these data with spectra obtained for two recently discovered high-symmetry  $(S_4)$  analogs of Mn<sub>12</sub>-Ac, differing only in their ligand and solvent structures. The new complexes are [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CCH<sub>2</sub>-Br)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]·4CH<sub>2</sub>Cl<sub>2</sub> [11–13] and [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CCH<sub>2</sub>- $Bu^{t})_{16}(CH_{3}OH)_{4}]$ ·CH<sub>3</sub>OH, abbreviated  $Mn_{12}$ -BrAc and Mn<sub>12</sub>-tBuAc, respectively. None of the highly reproducible fine-structures seen in the  $Mn_{12}$ -Ac samples are found for the new Mn<sub>12</sub> complexes, thus confirming the idea that the solvent structure significantly influences the QMT dynamics in  $Mn_{12}$ -Ac. Indeed, the HFEPR spectra for Mn<sub>12</sub>-BrAc and Mn<sub>12</sub>-tBuAc provide spectacular resolution, allowing for unique spectroscopic insights into high-symmetry giant spin SMMs.

# 2. Experimental

Single-crystal HFEPR measurements were carried out using a millimeter-wave vector network analyzer (MVNA) in combination with a cavity perturbation technique which we have described elsewhere [14]. In order to enable in situ two-axis rotation of the sample relative to the applied magnetic field, we employed a split-pair magnet with a 7 T horizontal field and a vertical access, together with a unique cylindrical cavity in which the sample may be rotated about a second orthogonal axis (this cavity is described in [15]). Single-axis rotation measurements were also performed in a 17 T axial superconducting magnet using the rotating cavity [15]. In both setups, the sample temperature was controlled using helium flow cryostats and calibrated Cernox<sup>™</sup> resistance sensors. Mn<sub>12</sub>-Ac samples were prepared separately by two groups according to the usual methods [5]: deuterated d- $Mn_{12}$ -Ac samples were prepared at Florida State University and removed from their mother liquor prior to transportation to the University of Florida; h-Mn<sub>12</sub>-Ac samples were prepared at the University of Florida and stored in their mother liquor right up until the time of the experiments.  $Mn_{12}$ -BrAc crystals were prepared by a ligand substitution procedure involving the treatment of  $Mn_{12}$ -Ac with an excess of BrCH<sub>2</sub>CO<sub>2</sub>H [11–13].  $Mn_{12}$ -tBuAc crystals were prepared via a method similar to the one in [16], albeit that CH<sub>3</sub>OH solvent was used in the present case, thereby yielding the high symmetry complex (full details will be presented elsewhere [17]). With the exception of the d-Mn<sub>12</sub>-Ac samples, all other crystals were handled identically with a view to avoiding solvent loss from the structure; the needle shaped single-crystals (~1.5 × 0.4 × 0.4 mm<sup>3</sup>) were removed directly from their mother liquor and protected with grease before cooling under 1 atm of helium gas.

## 3. Results and discussion

## 3.1. Mn<sub>12</sub>-Ac: in-plane field rotations

Fig. 1 displays experimental microwave absorption obtained for different field orientations within the hard (*xy*-) plane of a deuterated sample of  $Mn_{12}$ -Ac (i.e., d-Mn<sub>12</sub>-Ac); the temperature is 15 K and the frequency is 51.3 GHz in every case. The peaks correspond to EPR. The data were obtained at 7.5° intervals, and the azimuthal angle  $\phi$  represents the field orientation relative to one of the flat edges of the square cross-section



Fig. 1. Microwave absorption obtained for different field orientations within the hard (*xy*-) plane of a deuterated d-Mn<sub>12</sub>-Ac sample; the temperature was 15 K and the frequency was 51.3 GHz in every case. The peaks in absorption correspond to EPR. The data were obtained at 7.5° intervals, where the angle  $\phi$  refers to the field orientation relative to one of the flat edges of the square cross-section of the sample. The resonances have been labeled according to the scheme described in [9]. The bold traces correspond to field orientations approximately parallel to the hard axes of the  $\hat{O}_2^2$  (3 peaks) and  $\hat{O}_4^4$  (single peak) tensors.

of the sample. The resonances have been labeled according to the scheme described in [9]. For fields applied approximately parallel to the hard plane, only  $\alpha$ -resonances are observed ( $\beta$ -resonances appear for field rotation away from the hard plane – see Figs. 3 and 4 below). The highest field peak,  $\alpha 8$ , corresponds to an excitation between levels which evolve from the  $m_z = \pm 9$  zero-field doublet. The transition from the ground state ( $\alpha 10$ ) is not observed within the available field range for these experiments; at 51 GHz, its expected position is at ~9 T. For a discussion of the resonance labeling scheme, as well as detailed explanations of the temperature, frequency, field and field orientation dependence of the EPR spectra for Mn<sub>12</sub>-Ac, refer to [9].

Immediately apparent from the Fig. 1 is a fourfold variation in the positions of each band of resonances ( $\alpha 8$ ,  $\alpha 6$ , etc.). Note that each peak exhibits fine structures (high- and low-field shoulders), which also depend on the field orientation  $\phi$ ; these fine structures are related to the disorder in the crystal, as discussed further below. The fourfold shifts are caused by the intrinsic fourth-order operator,  $\hat{O}_4^4$ , in the spin Hamiltonian [6–10], as has previously been established for h-Mn<sub>12</sub>-Ac [7]. Fig. 2 shows a grayscale contour plot of the data in Fig. 1, i.e., absorption intensity versus magnetic field strength and the azimuthal angle  $\phi$ . This figure can be compared directly with Fig. 1 of [7], which displays the same data for h-Mn<sub>12</sub>-Ac. Superimposed on the absorption maxima are two kinds of fit to the  $\phi$ -dependent.



Fig. 2. Grayscale contour plot of the absorption intensity for d-Mn<sub>12</sub>-Ac (see Fig. 1), vs. magnetic field strength and the azimuthal angle  $\phi$ ; the darker shades correspond to stronger absorption. Superimposed on the absorption maxima are fits to the  $\phi$ -dependence of the central positions of each peak deduced from Fig. 1 (solid gray and black curves). The horizontal bars represent best fits to the peak positions based on exact diagonalization of the Hamiltonian matrix; the obtained Hamiltonian parameters are given in the main text. The open circles represent peak positions obtained for h-Mn<sub>12</sub>-Ac at the same frequency and temperature (see Figs. 3 and 4). The approximate orientations of the hard axes corresponding to the  $\hat{O}_2^2$  (*HE*, dashed lines) and  $\hat{O}_4^4$  (*HB*\_4^4, dotted line) tensors are indicated at the top of the figure.

dence of each peak. The solid lines were obtained simply by fitting the positions of the peaks obtained from Fig. 1: the central peaks were fit to pure sine functions having fourfold periodicity; meanwhile, the high- and low-field shoulders were fit with superpositions of phase-shifted sine functions having fourfold and twofold periodicities. The fits represented by horizontal bars were obtained by exact diagonalization of the Hamiltonian matrix and are described further below.

We now briefly discuss the origin of the twofold contribution to the positions of the shoulders, which are very apparent in the ranges  $\phi = 300-330^{\circ}$  and  $\phi = 30 60^{\circ}$  in Fig. 1; a more in-depth discussion can be found in [7-10]. The high- and low-field shoulders are due to the n = 1 and n = 3 Mn<sub>12</sub>-Ac hydrogen-bonding variants in Cornia's solvent disorder model [6]. These variants, which comprise 50% of the total molecules, are thought to possess a significant rhombic anisotropy due to the reduced symmetry of the surrounding hydrogen bonded acetic acid solvent molecules. The second-order operator,  $\tilde{O}_{2}$ , associated with the rhombic distortion gives rise to the two-fold behavior, as was clearly demonstrated by del Barco et al. [8]. It is important to recognize that the disorder is discrete, since the acetic acid can only bond at four positions on the Mn<sub>12</sub> molecule. Thus, one expects only two hard directions (HEA and HEB [9]) associated with the n = 1 and n = 3 low symmetry variants, which are separated by 90°. In HFEPR, the  $\hat{O}_2^2$  operator causes shifts in the peak positions. When the applied field is parallel to one of the hard axes, it is obviously perpendicular to the other, which causes shifts in the HFEPR intensity to both the low- and high-field sides of the central peaks, i.e., the shoulders. When the field is applied in between these two directions, the EPR intensity due to the low-symmetry variants collapses into the central portion of the peak, hence the disappearance of the shoulders every 90° (see Figs. 1 and 2). In actual fact, this apparent fourfold behavior reflects the twofold nature of the rhombic distortion caused by the hydrogen bonding acetic acid molecules, with the EPR intensity for a given variant shifting from the low (high) to the high (low) field side of the main peak every 90°, i.e., the periodicity is actually 180°. This twofold behavior is then superimposed on the intrinsic fourfold periodicity, as can be seen from the curves in Fig. 2.

As we have previously reported, there is an offset (phase shift) between the fourfold modulation of the central peak positions, and the twofold pattern associated with the shoulders; the hard directions associated with the  $\hat{O}_2^2$  and  $\hat{O}_4^4$  operators are indicated, respectively, by dashed and dotted lines in Fig. 2. In fact, this is was one of the more important points discussed originally in [7], which has recently been backed up by theoretical calculations [18]. From the fits in Fig. 2, this offset is found to be  $27 \pm 2^\circ$ , which is in good agreement with earlier studies of

h-Mn<sub>12</sub>-Ac [7]. From the maxima and minima in the peak position shifts induced by the  $\hat{O}_4^4$  operator, we estimate that the hard and medium directions associated with this intrinsic zero-field-splitting interaction are oriented at  $-4.5^\circ \pm 5^\circ [+(i \times 90^\circ)]$ , where i = integer] and  $40.5^\circ \pm 5^\circ$  $[+(i \times 90^\circ)]$ , respectively, relative to the square edges of a typical single-crystal sample. Once again, this agrees with previous studies of h-Mn<sub>12</sub>-Ac.

In order to make quantitative comparisons between the disorder-induced effects in h-Mn<sub>12</sub>-Ac and d-Mn<sub>12</sub>-Ac, we performed a single fit to the data in Fig. 2 via exact diagonalization of the Hamiltonian matrix [6–10]. This fit is represented by the horizontal bars in Fig. 2. Our procedure obviously takes into account the misalignments of the  $\hat{O}_2^2$  and  $\hat{O}_4^4$  tensors, as described in [10]. Thus, the employed Hamiltonian is subtly different from the standard form used by most spectroscopists [19–21], which may explain slight differences in the obtained Hamiltonian parameters. We start out by assuming accepted values for the zero-field parameters D and  $B_4^0$  (D = -0.455 cm<sup>-1</sup> and  $B_4^0 = -2 \times 10^{-5}$  cm<sup>-1</sup>), which were verified independently from easy axis measurements. The only free parameters in the fit were then the *E* and  $B_4^4$  coefficients (corresponding to the  $\hat{O}_2^2$  and  $\hat{O}_4^4$  tensors), for which we obtained the values  $\pm 0.014(2)$  and  $\pm 3.2(5) \times 10^{-5} \text{ cm}^{-1}$ , respectively. The  $B_4^4$  value is in precise agreement with that found for h-Mn<sub>12</sub>-Ac [7]. However, the E value is significantly larger than the one obtained in earlier experiments (40%)larger than the upper bound quoted in [7]). We attribute some of this difference to the modified Hamiltonian used in our more recent fits, which takes into account the misalignments of the  $\hat{O}_2^2$  and  $\hat{O}_4^4$  tensors. However, much of the difference appears to be real.

The larger *E*-value found from the present study is somewhat surprising. However, as will be seen below, more recent measurements on a fresh h-Mn<sub>12</sub>-Ac sample are in excellent agreement with the value of 0.014(2) cm<sup>-1</sup>. Thus, the difference is likely related to sample quality and/or solvent loss. A tell-tale sign of the higher sample quality is the observation of both high- and low-field shoulders on the main EPR peaks. In contrast, only high-field shoulders were seen in the earlier experiments on h-Mn<sub>12</sub>-Ac. In fact, the absence of a low-field shoulder is discussed at some length in [9], where it is shown that this peak is unresolved from the broad low-field tail associated with the central portion of the peak. The reason for the asymmetry between the high and low-field shoulder is related to easy axis tilting caused by the solvent disorder (see below). Although both shoulders are seen in the present study, a clear asymmetry can be seen from the data in Fig. 1.

We suspect that the samples used in the earlier experiments may have suffered significant solvent loss, either upon cooling from room temperature under high vacuum, or simply as a result of being stored in air for more than 1 year prior to the measurements. Indeed, variations in the D-strain measured in different Mn<sub>12</sub>-Ac samples has previously been reported by us [22]. Increased *D*-strain leads to broader EPR linewidths, thus probably explaining why the shoulders are clearly resolved in the present investigation, but not in [7]. Without two well resolved shoulders, it is likely that the E-strain was under-estimated in [7]. Based on experience working with SMMs containing considerably more volatile solvents, we have recently developed sample handling procedures which minimize solvent loss, e.g., encapsulating samples in oil prior to cooling under atmospheric helium gas. The differences between the present measurements and those reported in [7,9] highlight the importance of sample handling. Indeed, it is likely that Mn<sub>12</sub>-Ac samples prepared by different groups, and studied by different techniques, exhibit significant differences in their solvent content, resulting in subtly different conclusions concerning the quantum dynamics. For this reason, it is advantageous to prepare Mn<sub>12</sub> SMMs which do not exhibit such a dramatic dependence on solvent content, as is the case for two newer complexes discussed at the end of this article.

# 3.2. Mn<sub>12</sub>-Ac: out-of-plane field rotations

We now consider the angle-dependence of the HFEPR spectra for out-of-plane field rotations. The experimental spectra in Fig. 3 were obtained for a fresh sample of h-Mn<sub>12</sub>-Ac at a frequency of 51.7 GHz and a temperature of 15 K. Data were taken at 0.3° intervals in the polar angle  $\theta$ , i.e., the field orientation is measured relative to the global easy axis of the crystal. The thick curve corresponds to field alignment within the hard



Fig. 3. Microwave absorption spectra obtained for out-of-plane ( $\theta$ ) rotations for a single crystal of h-Mn<sub>12</sub>-Ac. The plane of rotation corresponds to the azimuthal angle  $\phi \approx -15^{\circ}$ . In every case, the temperature is 15 K, the frequency is 51.7 GHz, and the traces are offset for clarity. The resonances are labeled according to the scheme developed in [9].

plane (to within 0.15°). The resonances have again been labeled according to the scheme developed in [9]. Using the two-axis rotation capability, this experiment was repeated for seven different planes of rotation, separated by  $\Delta \phi = 15^{\circ}$  ( $\phi$  is the azimuthal angle). The grayscale contour plots in Fig. 4 display these data for five of the seven rotation planes. The peaks centered at  $\theta = 90^{\circ}$  correspond to  $\alpha 8$  (at  $\sim 6$  T) and  $\alpha 6$  (at  $\sim 4.5$  T);  $\beta$ 7 is seen between about  $\theta = 93^{\circ}$  and  $98^{\circ}$ ;  $\beta$ 7 is then followed in order of increasing angle by  $\alpha 8'$ ,  $\alpha 6'$  and  $\beta 7'$ . The data in Fig. 3 correspond to the  $\phi = -15^{\circ}$  orientation (middle trace in Fig. 4), which is approximately in between the hard axis of  $\hat{O}_4$  and one of the hard  $\hat{O}_2^2$ directions. The positions of the peaks and shoulders corresponding to the  $\alpha 8$  resonances in Fig. 4 have been added to Fig. 2 for comparison with the measurements on the deuterated  $Mn_{12}$ -Ac crystal. As can be seen, the data for the dueterated and undeuterated complexes are in excellent agreement. Indeed, we estimate precisely the same *E* and  $B_4^4$  values for the two complexes (±0.014(2) and ±3.2(5) × 10<sup>-5</sup> cm<sup>-1</sup>, respectively).

Fig. 5(a) displays a simulation of the out-of-plane angle-dependence of the EPR spectra for  $Mn_{12}$ -Ac,



Fig. 4. Grayscale contour maps corresponding to out-of-plane ( $\theta$ ) HFEPR field rotation measurements for five different planes of rotation (indicated in the figures). The darker regions represent stronger EPR absorption. The data are plotted in this manner for direct comparison with subsequent simulations, and data obtained for other Mn<sub>12</sub> complexes. The  $\phi = -15^{\circ}$  plot (middle panel) corresponds to the data in Fig. 3. The 66% and 33% of maximum absorption (corresponding to the peak of  $\alpha$ 8) contour lines are emphasized by light gray and black lines, respectively. The  $\phi$ -dependent overlap of the  $\alpha$  and  $\beta$  resonances suggests discrete easy-axis tilting; this behavior has been emphasized by the vertical dashed curves and the arrows in the  $\phi = -30^{\circ}$  panel. See main text, Fig. 5(b) and [9] for explanation.



Fig. 5. (a) A simulation of the out-of-plane ( $\theta$ ) angle-dependence of the EPR spectra for d- and h-Mn<sub>12</sub>-Ac, without disorder (E = 0). The simulation was generated using the software package SIM [23], and with the Hamiltonian parameters quoted in the main text; the frequency is 51.5 GHz and the temperature is 15 K. In contrast to the experimental spectra in Fig. 4, there is no angle overlap in intensity between neighboring  $\alpha$  and  $\beta$  transitions. (b) A simulation of the  $\phi$  $= -30^{\circ}$  data in Fig. 4. This simulation was generated by adding spectra corresponding to the 3 main species in Cornia's solvent disorder model [6]. The 66% and 33% of maximum absorption (corresponding to the peak of  $\alpha 8$ ) contour lines are emphasized by light gray and black lines, respectively. The low-symmetry n = 1 and 3 variants contribute to the high- and low-field shoulders (see main text and Fig. 4). The flattening of the absorption bands (relative to Fig. 5(a)), and the angular overlap of the  $\alpha$  and  $\beta$  resonances, is reproduced by convoluting the individual contributions to the spectrum with a Gaussian function with a half width of 1.3°. The arrows illustrate the different widths of the high- and low-field shoulders (see also 2nd panel of Figs. 4 and 6).

without disorder, i.e., no E-strain. The simulation was generated using the software package SIM [23], and with the Hamiltonian parameters quoted in the previous section (with E = 0); the frequency is 51.5 GHz and the temperature is 15 K. As can be seen from this simulation, there should be no angle overlap in intensity between neighboring  $\alpha$  and  $\beta$  transitions; we note that adding a realistic E term does not affect the widths of the gaps between the  $\alpha$  and  $\beta$  absorption bands in Fig. 5(a). In contrast, the data in Figs. 3 and 4 exhibit significant overlap of the  $\alpha$  and  $\beta$  resonances. More importantly, the degree of overlap depends on the plane of rotation, i.e., the azimuthal angle  $\phi$ . Note that the black contours represent 33% of the maximum absorption, while the white contours correspond to 66%. The reason for the overlapping of the  $\alpha$  and  $\beta$  intensity has been discussed at great length in [9], and is attributed to a tilting of the easy axes of the low-symmetry Cornia variants away from the global crystallographic *c*-direction. The resulting distribution of easy axis directions leads to a smearing of the  $\theta$ -dependence of the spectra, thereby accounting not only for the  $\alpha$  and  $\beta$  overlap, but also for the lack of any curvature to the bands of absorption (compare, e.g., the simulations in Fig. 5(a) with the data in Fig. 4).

It was argued in [9] that the tilting directions associated with the n = 1 and n = 3 Cornia variants [6] are confined to orthogonal planes defined by the symmetry of the associated rhombic distortion (the  $\hat{O}_2^2$  operator). The present study confirms this assertion. The profile of the absorption intensity, as a function of the angle  $\theta$  (for a fixed field), can be fit reasonably well with a Gaussian function, as shown in Fig. 6 for the  $\alpha$ 8 peaks and shoulders corresponding to the data in Fig. 3. The full-width-at-half-maximum (FWHM) of the high-field shoulder ( $\Delta \theta_{\rm H} = 2.1^{\circ}$ ) is almost 1° less than that of the low-field shoulder ( $\Delta \theta_{\rm L} = 3.0^{\circ}$ ), in agreement with previously published results [9]. The reason for this asymmetry is connected with the fact that the molecules contributing to the high-field shoulder are tilted in a plane perpendicular to the field rotation plane, whereas those contributing to the low-field shoulder are tilted in a plane parallel to the rotation plane (see Fig. 6 of [9]). Thus, the full tilt distribution projects onto the field rotation plane for the low-field shoulder, but not for the high-field shoulder. Unfortunately, one cannot independently measure the widths of the shoulders ( $\Delta_{\rm H}$  and  $\Delta \theta_{\rm L}$ ) as one rotates far away from the azimuthal ( $\phi$ ) directions of maximum splitting (i.e., the hard  $\hat{O}_2^2$  directions, HE), because the shoulders merge into the central peak. However, there is a tendency for the width of the high-field shoulder to increase as one rotates away from *HE* (the FWHM is 2.4° for  $\phi = -45^{\circ}$ ).

The vertical dashed lines in Fig. 4 illustrate the behavior of the 33% width of the central part of the  $\alpha 8$  peak ( $\Delta \theta_{\rm C}$ ). Interestingly,  $\Delta \theta_{\rm C}$  exhibits a clear dependence on  $\phi$ , suggesting that even the Cornia variants which do not possess a significant *E* term (n = 0, 2 and 4 [6]) are tilted. What is more, the maximum  $\Delta \theta_{\rm C}$  occurs fairly close to  $\phi = 0^{\circ}$ , corresponding to the hard  $\hat{O}_4^4$  direction. This suggests that the magnetic axes of these molecules may be tilted along or near to these orientations. We note that the n = 2 cis variants in Cornia's model, which



Fig. 6. Gaussian fits (solid curves) to the out-of-plane ( $\theta$ ) angle dependence of the HFEPR absorption intensity corresponding to the central peak ( $\bigcirc$ ), and the high ( $\square$ ) and low field ( $\triangle$ ) shoulders on the  $\alpha$ 8 resonance in Fig. 3. The FWHM of the three portions of the  $\alpha$ 8 resonance are indicated in brackets in the figure.

comprise 25% of the molecules, are expected to exhibit significant tilting ( $\sim 0.4^{\circ}$  [6]), but no appreciable *E*-term.

Based on the information in Fig. 6, one can deduce that FWHM of the tilt distribution for the n = 1 and n = 3 Cornia variants is *at least* 1°, i.e., that the halfwidth of the distribution is *at least* 0.5°. This is consistent with our previous studies, where it was shown that one could detect molecules in the tails of the distribution which were tilted by as much as  $1.7^{\circ}$ . In fact, the  $0.5^{\circ}$  value deduced above represents the magnitude of the solvent-disorder-induced tilting over and above any random tilting (the latter would not exhibit  $\phi$ -dependence). Thus, the true half-width of the tilt distribution associated with the n = 1 and n = 3 Cornia variants should be larger than this value and, therefore, significantly larger than the value predicted by Cornia et al. (~0.3°) [6].

In order to estimate the actual amount of tilting, we have simulated the out-of-plane angle dependence for the  $\phi = -30^{\circ}$  plane of rotation (Fig. 5(b)), which corresponds approximately to the hard direction of the  $\hat{O}_2$ tensor. The simulation was generated by adding spectra corresponding to the 3 main species in Cornia's solvent disorder model. We assume that 50% of the molecules possess no E term (the n = 0, 2 and 4 variants [6]), so that they contribute to the central portions of the EPR absorption bands. Of the remaining 50% (the n = 1and 3 variants [6]), half possess an E value of +0.014(2) cm<sup>-1</sup>, and the other half an E value of -0.014(2) cm<sup>-1</sup> (a change in the sign of E is equivalent to a 90° rotation of the hard and medium directions). These molecules contribute to the high- and low-field shoulders (see Fig. 3). The flattening of the absorption bands (relative to Fig. 5(a)), and the angular overlap of the and  $\beta$  resonances, is then reproduced by convoluting the individual contributions to the spectrum with a Gaussian function,  $\exp[-(\theta - 90^{\circ})^2/2\sigma^2]$ . The FWHM  $(w \sim 2.35\sigma)$  of the distribution used in Fig. 5(b) is 2.6°, i.e., a half width of 1.3°. Overall agreement with the experimental spectrum in Fig. 4(b) is very good, particularly concerning the widths of the high- and low-field shoulders (as indicated by arrows). We note also that, contrary to recent claims, this value is consistent with magnetic studies [24], as discussed at length in [9].

# 3.3. Mn<sub>12</sub>-BrAc and Mn<sub>12</sub>-tBuAc

We conclude this article by presenting data for the two recently discovered analogs of  $Mn_{12}$ -Ac:  $Mn_{12}$ -BrAc and  $Mn_{12}$ -*t*BuAc. The motivation for comparing these compounds is to investigate the influence of the solvent structure on the properties of the  $Mn_{12}$  core, which is virtually identical for the three complexes. Fig. 7 displays experimental spectra obtained for outof-plane ( $\theta$ -) rotations for  $Mn_{12}$ -BrAc, while Fig. 8 presents the same data in grayscale. Figs. 9 and 10 display



Fig. 7. Microwave absorption spectra obtained for out-of-plane ( $\theta$ ) rotations for a single crystal of Mn<sub>12</sub>-BrAc. The angle step is 0.36°. In every case, the temperature is 15 K, the frequency is 51.5 GHz, and the traces are offset for clarity. The resonances are labeled according to the scheme developed in [9].



Fig. 8. Grayscale contour maps corresponding to the data in Fig. 7. The darker regions represent stronger EPR absorption. In order to aid comparisons with Fig. 4, (a) depicts an expanded region of the full angle dependence in (b). Contour lines corresponding to 66% (light gray), 33% (thick black) and 15% (thin black) of the maximum absorption (of the  $\alpha$ 8 peak) are superimposed on the absorption bands to aid the discussion in the main text.

the same measurements for the  $Mn_{12}$ -*t*BuAc complex. The frequency was 51.5 GHz and the temperature was 15 K for both sets of measurements. It is immediately apparent that the EPR peaks for the BrAc and *t*BuAc complexes are considerably sharper than those obtained for  $Mn_{12}$ -Ac. Furthermore, the fine structures (highand low-field shoulders) are not seen for either of the newer complexes, irrespective of the choice of rotation plane (i.e., the  $\phi$  angle). This strongly suggests that the



Fig. 9. Microwave absorption spectra obtained for out-of-plane ( $\theta$ ) rotations for a single crystal of Mn<sub>12</sub>-*t*BuAc. The angle step is 0.36°. In every case, the temperature is 15 K, the frequency is 51.5 GHz, and the traces are offset for clarity. The resonances are labeled according to the scheme developed in [9].



Fig. 10. Grayscale contour maps corresponding to the data in Fig. 9. The darker regions represent stronger EPR absorption. In order to aid comparisons with Fig. 4, (a) depicts an expanded region of the full angle dependence in (b). Contour lines corresponding to 66% (light gray), 33% (thick black) and 15% (thin black) of the maximum absorption (of the  $\alpha$ 8 peak) are superimposed on the absorption bands to aid the discussion in the main text.

complexities of the EPR spectra for  $Mn_{12}$ -Ac are strongly influenced by the hydrogen bonding acetic acid solvent. Given the corresponding *E*-strain associated with the low-symmetry species in Cornia's model [6], one can thus assume that the QMT dynamics in  $Mn_{12}$ -Ac are significantly affected by extrinsic factors related to the disorder. In contrast, the solvents in the BrAc and *t*BuAc structures do not hydrogen bond to the  $Mn_{12}$  core. Furthermore, the possibility for positional and/or orientational solvent disorder does not exist in the way that it does for  $Mn_{12}$ -Ac (Cornia model [6]). In particular, the BrAc complex contains a full compliment of four symmetric CH<sub>2</sub>Cl<sub>2</sub> solvents per formula unit. Meanwhile, the lone MeOH solvent associated with the  $Mn_{12}$ -*t*BuAc complex resides far from the  $Mn_{12}$ core, and is shared equally among four unit cells. Furthermore, crystals of the *t*BuAc complex do not contain any faster relaxing  $Mn_{12}$  species, as is known to be the case for  $Mn_{12}$ -Ac and even  $Mn_{12}$ -BrAc. The absence of complexity in the HFEPR spectra of  $Mn_{12}$ -BrAc and  $Mn_{12}$ -*t*BuAc suggests that detailed investigations of these compounds may reveal even more information concerning the quantum dynamics of large spins, e.g., a Berry phase associated with the  $\hat{O}_4$  operator [25].

The linewidths are considerably narrower for the two newer complexes, as compared to the  $Mn_{12}$ -Ac. In fact, the  $\theta = 90^{\circ}$  line shape for the Mn<sub>12</sub>-*t*BuAc complex fits somewhat better to a Lorentzian function than to a Gaussian, suggesting that the linewidth may be close to the intrinsic lifetime broadened limit (width  $\approx 0.1 \text{ T}$ , implying  $\tau \approx 0.4$  ns). Furthermore, the linewidths are almost  $m_{\rm s}$  independent. However, there are vestiges of evidence for inhomogeneous broadening mechanisms (g, D, and E strain), such as the asymmetric lineshapes for the Mn<sub>12</sub>-BrAc complex, and a small, but measurable  $m_{\rm s}$  dependence of the linewidths for both complexes. Determining the source of any inhomogeneous broadening will require extensive easy-axis measurements as a function of frequency, field  $(m_s)$  and temperature. Such an undertaking will represent the subject of a future paper.

Further comparison between the grayscale plots for the three complexes leads one to believe that there are essentially no measurable tilts for the BrAc and tBuAc complexes. Not only are there well defined gaps between the and  $\beta$  series' of resonances, in overall agreement with Fig. 5(a), there are also clear evidences for curvature at the edges of each absorption band. This has been emphasized by the 15% contour lines in Figs. 8 and 10. Simulations show that even a modest amount of easy axis tilting dramatically suppresses the curvature seen in the grayscale plots. This curvature is associated with level repulsion, or level mixing. In the high-field limit, the 21 states associated with S = 10 may be described in a basis in which the spin projection quantum number  $m_{\rm s}$ refers to the projection of S onto the applied magnetic field axis. Furthermore, each  $m_s$  state is essentially pure in this high-field limit. Consequently, rotating the field should not produce dramatic shifts in the EPR peak positions, because the Zeeman term  $(g\mu_{\rm B}\boldsymbol{B}\cdot\boldsymbol{S})$  represents the dominant interaction in the Hamiltonian, i.e., the magnitude of the Zeeman interaction does not change upon rotating the field if the spin is free to rotate with the field. However, in the intermediate regime (Zeeman interaction comparable to crystal field), tilting the magnetic field results in a complex interplay between

the axial and transverse terms in the spin Hamiltonian, i.e., the transverse Zeeman interaction  $(g\mu_B B\hat{S}_x)$  may dominate when the field is exactly in the hard plane, whereas tilting of the field results in an out-of-plane magnetic field component which rapidly  $(\alpha \sin \theta)$  amplifies the axial  $(\hat{S}_z \text{ containing})$  terms. This interplay results in strong level mixing of states (described in either an  $\hat{S}_x$ or and  $\hat{S}_z$  basis), and to a non-linear dependence of the resonance positions on the magnetic field strength, leading to the curvature seen in the edges of the absorption bands in Figs. 8 and 10. Therefore, these measurements constitute evidence for coherent superposition states, albeit involving fairly complex admixtures of the simple zero-field S = 10 basis states.

The spin Hamiltonian parameters for  $Mn_{12}$ -BrAc are very similar to those of  $Mn_{12}$ -Ac, and have been published previously by us [13]. Fig. 11 displays fits to single-crystal HFEPR data obtained with the magnetic field applied both parallel [Fig. 11(a)] and perpendicular [Fig. 11(b) and (c)] to the easy axis of the  $Mn_{12}$ -*t*BuAc complex. The frequencies used in these experiments span from 50 to 350 GHz. The fits in Fig. 11(a) and (b), together with hard-plane rotation experiments in Fig. 11(c), provide three separate constraints on the spin Hamiltonian



Fig. 11. (a) Fits to the frequency dependence of HFEPR peak positions obtained with the field applied precisely along the easy axis (to within  $\pm 0.5^{\circ}$ ) of a Mn<sub>12</sub>-*t*BuAc single crystal; the temperature was 15 K for these measurements. Fits for this orientation constrain parameters corresponding to operators in the spin Hamiltonian that commute with  $\hat{S}_z$ , i.e., D,  $B_4^0$  and  $g_z$ . (b) Fits to the frequency dependence of HFEPR peak positions obtained with the field applied precisely within the hard plane (to within  $\pm 0.18^{\circ}$ ); the temperature was also 15 K for these measurements. Fits for this orientation constrain the transverse Landé factors,  $g_x$  and  $g_y$ . (c) Fits (white squares) to the fourfold peak-position shifts (dark shaded regions) for field rotations approximately within the hard plane of the sample. Fits for this orientation constrain the transverse term  $B_4^4$ , with no dependence on any of the other parameters in the spin Hamiltonian. All fits involved exact diagonalization of the Hamiltonian matrix, and ignored terms with twofold symmetry.

parameters, for which we obtain the following values:  $D = -0.462(2) \text{ cm}^{-1}, B_4^0 = -2.5(2) \times 10^{-5} \text{ cm}^{-1}, B_4^4 =$  $\pm 4.3(2) \times 10^{-5}$  cm<sup>-1</sup>,  $g_z = 2$ , and  $g_x = g_y = 1.94$ . In contrast to the data for  $Mn_{12}$ -Ac, the data in Fig. 11(c) are restricted to lower fields. The reason has to do with the fact that the molecules are so well aligned that it is virtually impossible to rotate precisely in the hard plane. Thus, the high-field peaks exhibit a strong twofold distortion associated with the mis-alignment between the field rotation plane and the hard plane. Even for a 0.5° mis-alignment, the effect is dramatic for  $\alpha 10$ ,  $\alpha 8$  and  $\alpha 6$ . Because of the easy axis tilts in  $Mn_{12}$ -Ac, the data in Fig. 2 are relatively insensitive to minor mis-alignments of the rotation plane. However, the tBuAc complex is less forgiving. Nevertheless, the fits in Fig. 11 are sufficient for determining  $B_{4}^{4}$ .

## 4. Summary and conclusions

We use angle-resolved HFEPR spectroscopy to asses the influence of the solvent structure on the quantum properties of several high-symmetry Mn<sub>12</sub> single-molecule magnets, including the most widely studied Mn<sub>12</sub>-Ac. In spite of over 10 years of research, a clear picture has only recently emerged concerning the symmetry breaking responsible for the QMT in  $Mn_{12}$ -Ac [6–10]. Disorder associated with the acetic acid solvent leads to discrete local environments, resulting in a significant fraction of the molecules (>50%) possessing twofold symmetry with a rhombic zero-field-splitting term E = $\pm 0.014(2)$  cm<sup>-1</sup>. Differences in the *E* values deduced from the present measurements and those reported in [7,9] highlight the importance of sample handling. Indeed, it is likely that Mn<sub>12</sub>-Ac samples prepared by different groups, and studied by different techniques, exhibit significant differences in their solvent content (particularly powder samples), resulting in subtly different conclusions concerning the quantum dynamics. For this reason, it is advantageous to prepare Mn<sub>12</sub> SMMs which do not exhibit such a dramatic dependence on solvent content. Indeed, we go on to show that all of the unusual solvent-induced anomalies reported for Mn<sub>12</sub>-Ac are absent in the HFEPR spectra for two related high-symmetry  $Mn_{12}$  complexes,  $Mn_{12}$ -BrAc and  $Mn_{12}$ -tBuAc. The absence of complexity in the HFEPR spectra of the BrAc and  $tBuAc Mn_{12}$  complexes suggests that detailed investigations of these compounds may reveal even more information concerning the quantum dynamics of large spins, e.g., a Berry phase associated with the  $\hat{O}_4^{\dagger}$  operator [25].

# Acknowledgments

We thank David Hendrickson and Wolfgang Wernsdorfer for stimulating discussion. Funding is provided by the National Science Foundation (DMR0103290, DMR0239481 and CHE0414155) and by Research Corporation.

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