

# Enhancing coherence in molecular spin qubits via atomic clock transitions

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Quantum Computing is an emerging area within the information sciences revolving around the concept of quantum bits (or qubits). A major obstacle is the extreme fragility of these qubits due to interactions with their environment that destroy their "quantumness". This phenomenon, known as decoherence, is of immense fundamental interest.<sup>1,2</sup> There are many competing candidates for qubits, including superconducting circuits,<sup>3</sup> quantum optical cavities,<sup>4</sup> ultracold atoms<sup>5</sup> and spin qubits,<sup>6-8</sup> and each one has its strengths and weaknesses. When dealing with spin qubits, the strongest source of decoherence is the magnetic dipolar interaction.<sup>9</sup> To minimize it, spins are typically diluted in a diamagnetic matrix. For example, this dilution can be taken to the extreme of a single phosphorus atom in silicon,<sup>6</sup> while in molecular matrices a typical ratio is one magnetic molecule per 10,000.<sup>10</sup> However, there is a fundamental contradiction between reducing decoherence by dilution, and allowing quantum operations via the interaction between spin qubits. To solve this apparent paradox, the design and engineering of quantum hardware can benefit from a "bottom-up" approach whereby the electronic structure of magnetic molecules is chemically tailored to give the desired physical behavior. Here we present a very effective way of eliminating decoherence in solid-state molecular spin qubits without resorting to extreme dilution. It is based on the design of molecular structures with crystal field ground states possessing large tunneling gaps that give rise to optimal operating points, or atomic clock transitions, at which the quantum spin dynamics become protected against dipolar decoherence. This approach is illustrated with a holmium molecular nanomagnet in which long coherence times (up to 8.4  $\mu$ s at 5 K) can be obtained at unusually high concentrations. This finding opens new avenues for quantum computing based on molecular spin qubits.

One of the proposed approaches to obtaining spin qubits is that of using magnetic molecules.<sup>8-16</sup> Up to now, coherence has been optimized through dilution and deuteration to minimize dipolar and hyperfine interactions, respectively.<sup>10,16</sup> A class of molecules in which these two sources of decoherence can be minimized by alternative means are the so-called polyoxometalates. In the past, these metal-oxide clusters have been used as model systems in molecular magnetism due to their ability to host magnetic ions in chemically tailored environments of high symmetry and rigidity.<sup>17</sup> Currently, these molecules are seen as potential building blocks in quantum computing architectures.<sup>18-22</sup>

38 In the present study we chose the  $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$  complex (abbreviated  $\text{HoW}_{10}$ ) which has been subject to  
 39 extensive structural, magnetic and spectroscopic characterizations that raised the possibility of observing  
 40 coherent spin dynamics.<sup>23,24</sup>  $\text{HoW}_{10}$  is formed by two molecular tungsten oxide moieties encapsulating a  
 41  $\text{Ho}^{+3}$  ion (Fig. 1). The geometry around  $\text{Ho}^{+3}$  exhibits a slightly distorted square-antiprismatic environment,  
 42 which can be approximated by a  $D_{4d}$  “pseudo-axial” symmetry. This results in a splitting of the  $J = 8$   
 43 ground state spin-orbit manifold according to its  $m_J$  quantum numbers. Quantitatively this splitting can be  
 44 described in terms of a crystal-field (CF) Hamiltonian (double summation in eq. 1) which, for  $D_{4d}$   
 45 symmetry, contains the axial CF terms  $B_2^0\hat{O}_2^0$ ,  $B_4^0\hat{O}_4^0$  and  $B_6^0\hat{O}_6^0$  (see Methods for definition and discussion  
 46 of terms in eq. 1).<sup>24</sup>

$$48 \quad \hat{H} = \sum_{k=2,4,6} \sum_{q=0}^k B_k^q \hat{O}_k^q + \hat{J} \cdot \vec{A} \cdot \hat{I} + \mu_B \vec{B}_0 \cdot \vec{g} \cdot \hat{J} - \mu_N g_N \vec{B}_0 \cdot \hat{I} \quad (1)$$

49  
 50 This results in an isolated  $m_J = \pm 4$  ground doublet, separated from the first excited states ( $m_J = \pm 5$ ) by  
 51  $\sim 20 \text{ cm}^{-1}$ . This picture provides a reasonable description of the magnetic properties of this molecule.<sup>23</sup>  
 52 However, minor deviations from  $D_{4d}$  symmetry that are present in the crystal make operative the  
 53 tetragonal  $B_4^4\hat{O}_4^4$  CF interaction. Interestingly, the match between the ( $\pm$ integer) values of the ground state  
 54 spin projections,  $m_J = \pm 4$ , with the tetragonal (i.e.,  $q = 4$ ) order of the main symmetry axis of the molecule,  
 55 results in the  $B_4^4\hat{O}_4^4$  [ $\hat{O}_4^4 = \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4)$ ] interaction generating an unusually large quantum tunneling gap,  
 56  $\Delta \sim 9.18 \text{ GHz}$  ( $\sim 0.3 \text{ cm}^{-1}$ ).<sup>24</sup> This gap is a crucial factor for the coherence of electron spin dynamics in  
 57 molecular spin qubits, and is the main subject of the present study.

58  
 59 The standard approach for probing coherent spin dynamics involves the use of “electron spin echoes” in  
 60 pulsed Electron Paramagnetic Resonance (EPR). The  $\text{HoW}_{10}$  system is attractive in this regard because  
 61 its predicted tunneling gap ( $\sim 9.18 \text{ GHz}$ , Fig. 1) is close to the X-band frequency associated with the most  
 62 sophisticated EPR spectrometers. While the magnitude of the gap is set by  $B_4^4$ , interesting details of the  
 63 EPR spectra are determined also by the hyperfine interaction between the Ho electron and nuclear spins  
 64 (second term in eq. 1). Holmium occurs naturally in only one stable isotope ( $^{165}\text{Ho}$ ) with a nuclear spin of  
 65  $I = 7/2$ . A strong hyperfine coupling ( $A_{Hf} = 830 \pm 10 \text{ MHz}$ ) results in the observation of eight  $(2I + 1)$  well-  
 66 resolved transitions via continuous-wave (CW) high-frequency EPR measurements.<sup>24</sup> The energy level  
 67 scheme that arises from the combination of CF and hyperfine coupling, together with the Zeeman  
 68 interaction (3<sup>rd</sup> and 4<sup>th</sup> terms in eq. 1), gives rise to a series of avoided level crossings between  $m_J = \pm 4$   
 69 states (with the same  $m_I$ ), resulting in multiple gaps in the energy diagram near zero-field (Fig. 1a).

70  
 71 Single-crystals of  $\text{Na}_9[\text{Ho}_x\text{Y}_{(1-x)}(\text{W}_5\text{O}_{18})_2] \cdot n\text{H}_2\text{O}$  (where Y is non-magnetic) were prepared with Ho  
 72 concentrations ranging from  $x = 0.25$  to  $x = 0.001$ , i.e., up to three orders of magnitude away from the  
 73 usual high-dilution limit,<sup>10</sup> allowing a study of the effects of dilution on electron dipolar spin-spin

74 decoherence. Fig. 2a displays electron-spin-echo- (ESE-) detected EPR spectra recorded at 5 K for a  
 75 dilute ( $x = 0.001$ ) sample at frequencies from 9.1 to 9.8 GHz, with  $\theta = 29^\circ$  ( $\theta$  is the angle between  $B_0$  and  
 76 the z-axis of the crystal); ESE signals were generated using a two-pulse Hahn-echo sequence (see  
 77 Methods).<sup>25</sup> Four broad peaks of equal intensity are observed at the two lowest frequencies (9.11 and  
 78 9.18 GHz), which were selected to be close to the gap minima in Fig. 1b. With increasing frequency,  
 79 these peaks split and move symmetrically apart, as expected on the basis of predictions in Fig. 1b. For  
 80 the most part, the data lie on the simulated curves, with the obvious exception of the two lowest  
 81 frequencies and some lower field ( $< 60$  mT) data points. The simulations are based on previously  
 82 determined Hamiltonian parameters,<sup>24</sup> and the spectra are plotted against the re-scaled longitudinal  
 83 applied field,  $B_{0z}$  ( $= B_0 \cos\theta$ ), to facilitate comparisons between different samples (see Methods).

84  
 85 Two-pulse ESE measurements were separately utilized to determine 5 K transverse relaxation times,  $T_2$ ,  
 86 at selected points within the spectrum for the  $x = 0.001$  concentration. The longest  $T_2$ 's are found in the  
 87 vicinity of the gap minima for the smallest crystals (see Figs. 2b, 3 and Methods), with values ranging  
 88 from 5.2 to 8.4  $\mu$ s, whereas the values are substantially shorter away from the minima. In fact, the  $T_2$   
 89 values exhibit sharp divergences right at  $B_{\min}$  (Fig. 3). The key to understanding this behavior is the  
 90 quadratic field dependence of the EPR transition frequencies close to the gap minima (see Methods),

91

$$f = \Delta + \frac{\gamma_z^2}{2\Delta} (B_{0z} - B_{\min})^2, \quad (2)$$

92

93 such that the derivative  $df/dB_{0z} \propto (B_{0z} - B_{\min}) \rightarrow 0$  as  $B_{0z} \rightarrow B_{\min}$ . Although not explicitly included in eq. 1,  
 94 nearly all sources of dipolar decoherence (due, e.g., to dynamics associated with the nuclear bath and  
 95 collective electron spin excitations, or magnons) can be approximated as a time-dependent magnetic  
 96 noise,  $\delta B_0(t)$ , acting on the central spin qubit (the spin being measured) via the Zeeman interaction, i.e.,  
 97 processes that flip nearby spins cause variations in the local field,  $\delta B_0$ , at the position of the central spin,  
 98 thereby altering its frequency/phase. Many of these processes involve indirect pairwise spin flip-flops  
 99 (spin diffusion) that are extremely hard to mitigate, and persist to very low temperatures. The extreme  
 100 axial anisotropy of  $\text{HoW}_{10}$  results in an insensitivity to the perpendicular applied field component,  $B_{0\perp}$  (see  
 101 Methods). Meanwhile, sensitivity to  $\delta B_{0z}(t)$  vanishes (to first order) as  $B_{0z} \rightarrow B_{\min}$  and  $df/dB_{0z} \rightarrow 0$ ,  
 102 resulting in a vanishing contribution to the dipolar decoherence. This is the concept behind so-called  
 103 'atomic clock transitions'. Named after atomic clocks, these transitions are protected against  
 104 environmental noise sources according to the principle described here (i.e.,  $df/dB_0 = 0$ ), resulting in a  
 105 clock frequency that exhibits exceptional phase stability.<sup>26,27</sup> Indeed, one expects the dephasing time,  $T_2$ ,  
 106 to scale as  $(B_{0z} - B_{\min})^{-n}$  ( $n > 0$ , see Extended Data Fig. 1),<sup>28,29</sup> thus explaining the observed divergences  
 107 at the clock-transitions (CTs). For comparison,  $T_2$  measurements are displayed in the right panel of Fig. 3  
 108 for several 'normal' EPR transitions, i.e.,  $m_J = -4$  to  $+4$  transitions away from the gap minima, where the

109 frequency dependence approaches the linear regime and  $df/dB_{0z} \rightarrow \gamma_z = 139.9$  GHz/T (Fig. 1). Although  
110  $T_2$  is moderately peaked at the centers of these resonances, the sharp divergences seen at the CTs are  
111 clearly absent (see Methods for further discussion).

112  
113 ESE-detected measurements for an  $x = 0.01$  sample reveal essentially identical divergences in  $T_2$  at the  
114 CTs to those seen in Fig. 3, with maximum values ranging from 4 to 8  $\mu\text{s}$  (see Extended Data Figs. 1 and  
115 2). However,  $T_2$  values associated with ‘normal’ EPR transitions well away from the CTs are much shorter  
116 ( $\sim 100$  ns, not shown). Because the collection of ESE spectra requires the detection of an echo, the  
117 observation of these ‘normal’ EPR transitions is challenging for  $x \geq 0.01$ . These findings are consistent  
118 with the idea that dipolar ‘noise’ increases with increasing Ho concentration, resulting in shorter  $T_2$ ’s for  
119 the ‘normal’ EPR transitions, yet an apparent insensitivity to the Ho concentration at the CTs.

120  
121 Fig. 4 displays 5 K ESE-detected spectra for a concentrated  $x = 0.1$  sample which are in stark contrast to  
122 those in Fig. 2: narrow resonances are observed at the CTs that do not shift at all with frequency, i.e., the  
123 data do not follow the simulations even though CW measurements indicate no measurable variation in  
124 the spin Hamiltonian parameters with Ho concentration.<sup>24</sup> The total suppression of ‘normal’ EPR  
125 transitions is attributed to a further reduction of  $T_2$  upon increasing the Ho concentration, to the extent that  
126 an echo can no longer be detected. Nevertheless, the  $T_2$  values at the CTs remain long ( $\sim 0.7$   $\mu\text{s}$ ),  
127 resulting in the narrow ESE-detected resonances. Indeed, because the echo intensity is  $T_2$ -weighted, the  
128 resonance lineshape is a direct manifestation of the field dependence of  $T_2$  at  $B_{\min}$ . Analysis of CW EPR  
129 spectra suggests that the main contribution to the linewidth is a Gaussian distribution in the  $B_4^4$  parameter  
130 ( $\sigma_{B_4^4} = 0.63$  MHz). This causes significant vertical broadening of the tunneling gap,  $\Delta$ , and EPR transition  
131 frequencies, as illustrated in Fig. 1b, which includes contours at the  $\pm\sigma_\Delta$  and  $\pm 2\sigma_\Delta$  levels ( $\sigma_\Delta = 123$  MHz is  
132 the standard deviation in  $\Delta$ —see Methods). These simulations indicate measurable intensity at the CTs  
133 up to at least 9.4 GHz. However, the  $B_4^4$  distribution does not shift the CTs appreciably to lower or higher  
134 fields, i.e., all molecules in the distribution have their CTs at essentially the same  $B_{\min}$  values. This  
135 explains the observation of narrow CT peaks spanning a wide frequency range in the  $x = 0.1$  sample  
136 (Fig. 4); similar behavior is also discernible at other concentrations (see Extended Data Fig. 3).

137  
138 After magnetic ‘noise’, several other sources of decoherence remain. First and foremost, the CTs do not  
139 protect against direct flip-flop processes that involve the central spin qubit.<sup>28,29</sup> These energy-conserving  
140 events involve coupling to other spins via the off-diagonal component of the dipolar interaction ( $\hat{S}_1^+ \hat{S}_2^- +$   
141  $\hat{S}_1^- \hat{S}_2^+$ ). The inhomogeneous broadening will provide some protection against this source of dephasing,  
142 because it requires the central spin to be resonant with other spins. Nevertheless, direct flip-flops likely  
143 explain the shorter  $T_2$ ’s at the CTs in the  $x = 0.1$  sample. However, unlike the aforementioned indirect  
144 spin diffusion processes, direct flip-flops can be controlled at the stage of device design through the  
145 tuning/detuning of individual CT frequencies. Finally, coupling to lattice dynamics (phonons) via the CF is

146 also likely to provide significant decoherence pathways, particularly as the temperature is raised.<sup>16</sup>  
147 Indeed, a significant temperature dependence of  $T_2$  is found at the CTs (more than a factor of 2 decrease  
148 upon heating the sample to 7 K), suggesting that  $T_2$  may become limited by spin-lattice relaxation  
149 ( $T_1 \approx 20 \mu\text{s}$  at 5 K). This is something that will be the subject of future investigations.

150  
151 The critical result from this study is the demonstration that CTs can be employed as a means of  
152 enhancing the coherence of molecular spin qubits in concentrated samples. Therefore, instead of  
153 attempting to suppress magnetic noise, which can be impractical at the stage of device design, we have  
154 shown here that one can fortify the molecular spin qubit itself against this noise through the use of CTs. In  
155 terms of design criteria, the molecule of choice should possess a large tunneling gap within the ground  
156 magnetic doublet matching the working frequency of the EPR cavity. The key to this strategy is the  
157 chemical design of molecular structures with appropriate CF states. In rare earth complexes with integer  
158 spin, this goal translates into matching the  $m_J$  components of the ground doublet with the rotational order  
159 ( $q$ ) of the main symmetry axis of the molecule (see Methods). While this is not trivial to achieve, the case  
160 of  $\text{HoW}_{10}$  is not an isolated example. For example, within rigid polyoxometalate chemistry, the Terbium  
161 derivative of the  $[\text{LnP}_5\text{W}_{30}\text{O}_{110}]^{12-}$  series with pentagonal structure (approximate  $C_{5v}$  symmetry) has been  
162 characterized as having an  $m_J = \pm 5$  ground state with an even larger tunneling gap of  $\sim 21$  GHz that may  
163 be suitable for pulsed Q-band EPR.<sup>30</sup> Tunability across this range (10 – 100 GHz) is desirable and  
164 practical for quantum information applications, given that it sits at the current high end of the electronics  
165 spectrum. Moreover, operation at these CTs requires application of only very moderate magnetic fields  
166 ( $< 0.2$  T in the present example). Of course, this strategy can and should be combined with other known  
167 ideas that are already being applied with great success, such as using rigid lattices with low abundance of  
168 nuclear spins.<sup>16</sup> Nevertheless, it is remarkable that working with CTs offers the unique advantage of  
169 allowing long coherence times with high concentrations of molecular spin qubits. In fact, for other  
170 molecular spin qubit candidates,  $T_2$  values of the order of tens of  $\mu\text{s}$  were only observable in deuterated  
171 and highly diluted samples of  $\text{Cr}_7\text{Ni}$  molecular wheels<sup>10</sup> and  $\text{Cu}(\text{mnt})_2$  complexes.<sup>16</sup>

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174

175 **Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

176

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186 the samples. S.H., M.S. and D.K. designed the experiments, while M.S. and D.K. performed the  
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192

### 193 **Figure Legends**

194

195 **Figure 1: HoW<sub>10</sub> tunneling gap.** (a) Zeeman diagrams for the  $m_J = \pm 4$ ,  $I = 7/2$  ground state, with  $B_0/z$ : the  
196 thin gray lines assume exact  $D_{4d}$  symmetry, while the thick black curves assume an 'axial +  $B_4^4\hat{O}_4^4$ '  
197 parameterization.<sup>24</sup> (Inset) The corresponding 9.64 GHz CW EPR spectrum (from Ref. [24]) is observed  
198 well below the  $D_{4d}$  prediction (gray arrow denotes expected highest field resonance), providing evidence  
199 for the tunneling gap. Indeed, the 'axial +  $B_4^4\hat{O}_4^4$ ' parameterization gives excellent agreement with the data,  
200 both in terms of resonance positions (blue arrows) and intensity (arrow thickness). The red vertical lines,  
201 meanwhile, indicate the locations of CTs. (b) 3D EPR intensity map including inhomogeneous broadening

202 due to a Gaussian distribution in  $B_4^4$  ( $\sigma_{B44} = 2.1 \times 10^{-5} \text{ cm}^{-1}$ ); darker shading represents stronger intensity,  
203 with contours at the  $\pm\sigma_\Delta$  (red) and  $\pm 2\sigma_\Delta$  (blue) levels ( $\sigma_\Delta = 123 \text{ MHz}$ , the s.d. in  $\Delta$ ). Red arrows denote  
204 CTs, dashed lines denote locations of 9.64 GHz resonances, and the inset shows the  $\text{HoW}_{10}$  molecule.  
205

206 **Figure 2: ESE-detected spectra for a dilute sample.** (a) Variable frequency measurements at 5.0 K for  
207 an  $x = 0.001$  crystal, with  $\theta = 29^\circ$ ; the frequencies are indicated in GHz above each trace. (b) Frequency  
208 versus field plot of the resonances in (a). The data are in good agreement with simulations (solid curves)  
209 based on the ‘axial +  $B_4^4 \hat{O}_4^4$ ’ parameterization [24]. Selected  $T_2$  values (in  $\mu\text{s}$ ) determined from the  
210 measurements in Fig. 3 are indicated close to some of the data points in (b). Vertical error bars in (b)  
211 denote pulse excitation bandwidths ( $\pm 1/2\tau_{\pi/2}$ , where  $\tau_{\pi/2}$  is the duration of the  $\pi/2$  pulse), while horizontal  
212 error bars represent standard deviations ( $\pm$ s.d.) deduced from Gaussian fits to the resonances in (a).  
213

214 **Figure 3:  $T_2$  divergence at the CTs.** Field-swept  $T_2$  measurements recorded at 5.0 K for a small  $x =$   
215  $0.001$  crystal at  $\theta = 22^\circ$  and various frequencies indicated in the right panel. The first four panels illustrate  
216 the divergences in  $T_2$  at the CTs, referenced to the left-hand ordinate; the data are plotted in an expanded  
217 view as a function of  $(B_{0z} - B_{\min})$ , with best-fit  $B_{\min}$  values given in each panel. The right-hand panel,  
218 meanwhile, displays  $T_2$  values well away from the CTs (see Fig. 1b), referenced to the right-hand  
219 ordinate. Error bars denote the standard error in  $T_2$ .  
220

221 **Figure 4: ESE-detected spectra for a concentrated sample.** (a) Variable frequency measurements at  
222 5.0 K for an  $x = 0.10$  crystal, with  $\theta = 20^\circ$ ; the frequencies are indicated in GHz above each trace. The  
223 ESE resonances are attributed to CTs. (b) Frequency versus field plot of the CTs in (a). Optimum  $T_2$   
224 values (in  $\mu\text{s}$ ) are indicated next to the 9.11 GHz data. Meanwhile, the curves correspond to predictions  
225 based on the CW EPR parameterization [24]. (c) Field-swept  $T_2$  measurements recorded at 5.0 K for a  
226 separate  $x = 0.10$  crystal at  $\theta = 25^\circ$  and frequencies of 9.12 (blue squares) and 9.20 GHz (red circles).  
227 Vertical error bars in (b) denote pulse excitation bandwidths ( $\pm 1/2\tau_{\pi/2}$ , where  $\tau_{\pi/2}$  is the duration of the  $\pi/2$   
228 pulse), while horizontal error bars represent standard deviations ( $\pm$ s.d.) deduced from Gaussian fits to the  
229 resonances in (a). Error bars in (c) denote the standard error in  $T_2$ .  
230

231 **Extended Data Figure 1:  $T_2$  scaling.** Field-swept  $T_2$  measurements for the  $x = 0.001$  (a) and  $x = 0.01$  (b)  
232 concentrations at 5 K; the data are plotted as a function of  $(B_{0z} - B_{\min})$  on both log-log (main panels) and  
233 linear (insets) scales. The blue lines are power-law fits to the positive  $(B_{0z} - B_{\min})$  data (green points), with  
234 the obtained exponents given in the figures. Error bars denote the standard error in  $T_2$ .  
235

236 **Extended Data Figure 2:  $T_2$  divergence at the  $x = 0.01$  concentration.** Field-swept  $T_2$  measurements  
237 recorded at 5.0 K for two separate crystals at frequencies of 9.12 GHz (blue squares) and 9.20 GHz (red  
238 circles). Error bars denote the standard error in  $T_2$ .



239 **Extended Data Figure 3: ESE-detected spectra for the  $x = 0.01$  concentration.** (a) Variable frequency  
240 measurements at 5.0 K, with  $\theta = 30^\circ$ ; the frequencies are indicated above each trace. Similar to spectra  
241 for the  $x = 0.001$  sample, the broad 9.2 GHz CT peak splits into two upon moving away from the tunneling  
242 gap minimum (see also Fig. 1). However, weak ESE intensity can still be detected at  $B_{0z} = 165$  mT at all  
243 four frequencies. This is due to vertical broadening of the CT, caused by a Gaussian distribution in  $B_4^4$ .

## 245 Methods

### 247 **Experimental Details**

248 Pulsed EPR measurements were performed on a commercial Bruker E680 X-band spectrometer  
249 equipped with a cylindrical  $TE_{011}$  dielectric resonator (model ER 4118 X-MD5) with a center frequency  
250  $f_0 = 9.75$  GHz. Single-crystals of  $Na_9[Ho_xY_{(1-x)}(W_5O_{18})_2] \cdot nH_2O$  ( $x = 0.001$  to 0.25) were prepared according  
251 to the method described in Ref. [23]. Samples were re-crystallized prior to study, then transferred to the  
252 spectrometer directly from the mother liquor and cooled rapidly in order to prevent loss of crystallinity due  
253 to evaporation of lattice solvent. The sample temperature was controlled using an Oxford Instruments  
254 CF935 helium flow cryostat and ITC503 temperature controller. A strong temperature dependence of  $T_2$   
255 at the CTs required operation of the cryostat at a base temperature of 5.0 K in order to ensure good  
256 thermal stability and sample-to-sample reproducibility.

257  
258 For each series of measurements, a single crystal was mounted on a 4 mm diameter quartz rod and  
259 positioned at the center of the cylindrical resonator for perpendicular mode excitation. The tendency for  
260 samples to rapidly lose solvent, and the low symmetry  $P\bar{1}$  space group of the  $HoW_{10}$  compound, made it  
261 impossible to index and align crystals prior to mounting. However, the Bruker E680 and ER 4118X-MD5  
262 dielectric resonator combination allows for *in situ* sample rotation about a single axis. Each crystal was  
263 therefore aligned as best as possible on the basis of angle-dependent CW EPR measurements  
264 performed at 9.75 GHz and 5.0 K. The remaining misalignment,  $\theta$ , between  $B_0$  and  $z$  was determined by  
265 scaling the applied field to match the simulations in Fig. 1 (see below). A  $\theta < 30^\circ$  criterion was then  
266 applied; crystals not meeting this condition were discarded and a new sample selected for study.

267  
268 When overcoupled for ESE measurements, the bandwidth of the resonator,  $\Delta f = f_0/Q \approx 250$  MHz, where  
269 the loaded quality factor  $Q \approx 40$ . This is sufficient to allow variable-frequency measurements with  
270 reasonable microwave  $B_1$  fields down to a lower limit of  $\sim 9.1$  GHz. The  $B_1$  fields were independently  
271 measured under the same conditions via the Rabi oscillation frequency ( $\Omega_R$ ) of a spin- $1/2$  EPR standard  
272 (the organic radical bisdiphenylene-2-phenylallyl dissolved in polystyrene);  $B_1$  values varied from  $\sim 4$  G at  
273 9.1 GHz, to 9 G at 9.75 GHz ( $\Omega_R = 11$ –25 MHz for  $s = 1/2$ ). A two-pulse sequence ( $T/2 - \tau - T - \tau - \text{echo}$ ,  
274 where  $T$  characterizes the pulse durations and  $\tau$  the delay time between pulses) was employed for all  
275 ESE measurements reported in this work. The values of  $T$ ,  $\tau$  and the source power were optimized at

276 each frequency, with the assumption that the optimum conditions correspond approximately to the Hahn-  
 277 echo sequence,  $\pi/2 - \tau - \pi - \tau - \text{echo}$ , where  $\pi$  refers to the tipping angle. For  $T_2$  measurements,  $\tau$  was  
 278 varied and the resultant echo amplitude then fit to a single exponential decay.

279

## 280 **Pulse Sequences**

281 Because the ESE measurements were performed well below the center frequency of the cavity, and due  
 282 to the lack of *a priori* knowledge of the matrix elements associated with the observed transitions, pulse  
 283 sequences were adjusted at each frequency by one of two methods: (1) the  $\pi/2$  pulse length ( $T/2$ ) and  
 284 source attenuation were adjusted to maximize the echo intensity relative to the spectrometer noise for the  
 285 ESE-detected spectra in Figs. 2a and 4a, thereby explaining the variability of the vertical error bars  
 286 denoting excitation bandwidth (defined as  $2/T$ , or  $1/\tau_{\pi/2}$ , where  $\tau_{\pi/2}$  is the duration of the  $\pi/2$  pulse in the  
 287 Hahn-echo sequence); and (2) Rabi oscillation measurements were used to determine the optimum  $\pi/2$   
 288 pulse length for the detailed  $T_2$  measurements displayed in Figs. 3, 4(c), and Extended Data Figs. 1 and 2  
 289 [the Rabi pulse sequence was optimized via method (1)]. On this basis, a Rabi frequency,  
 290  $\Omega_R = 98 \text{ Mrad}\cdot\text{s}^{-1}$  (15.6 MHz), was determined for 0 dB attenuation at the CTs, resulting in a minimum  $\pi/2$   
 291 pulse length of 16 ns for the employed spectrometer. This corresponds to an optimum dephasing factor  
 292  $Q_\varphi = 820$ , defined here as  $Q_\varphi = \Omega_R \cdot T_2$ , a figure of merit for qubit operation. We note, however, that this  
 293 does not preclude shorter pulses using a more powerful microwave source, suggesting the possibility of  
 294  $Q_\varphi$  values up to  $1.5 \times 10^6$  using the modified definition in Ref. [9]. Interestingly, this value is identical to the  
 295 one reported in Ref. [9] for an  $\text{Fe}_8$  nanomagnet, in spite of the vastly different frequencies employed in the  
 296 two measurements, primarily because of the much longer coherence in the  $\text{HoW}_{10}$  system. Based on  
 297 knowledge of the spectrometer used for the  $\text{Fe}_8$  study, we estimate a  $Q_\varphi = \Omega_R \cdot T_2$  of just 50 for  $\text{Fe}_8$ ; of  
 298 course, the same arguments concerning limited source power apply in that case. The  $\text{HoW}_{10}$   $Q_\varphi$  value  
 299 compares favorably with other candidate molecular spin qubits using both definitions, e.g., the optimum  
 300  $Q_\varphi$  ( $= \Omega_R \cdot T_2$ ) varies from  $\approx 2,000$  for the  $\text{Cr}_7\text{Ni}$  wheel [7], up to  $\approx 10,000$  obtained recently for a  $\text{Cu}^{\text{II}}$   
 301 coordination complex [16]. However, one should bear in mind that extreme dilution/deuteration was  
 302 employed in these cases.

303

## 304 **The Spin Hamiltonian**

305 The energy spectrum associated with the Hund's rule spin-orbit coupled ground state of the  $\text{Ho}^{+3}$  ion, with  
 306  $L = 6$ ,  $S = 2$ , and  $J = |L + S| = 8$ , can be described by the following effective Hamiltonian (eq. 3):

307

$$308 \quad \hat{H} = \sum_{k=2,4,6} \sum_{q=0}^k B_k^q \hat{O}_k^q + \hat{J} \cdot \vec{A} \cdot \hat{I} + \mu_B \vec{B}_0 \cdot \vec{g} \cdot \hat{J} - \mu_N g_N \vec{B}_0 \cdot \hat{I} \quad (3)$$

309

310 The double summation describes the CF interaction in terms of extended Stevens Operators  $\hat{O}_k^q$  ( $k = 2, 4,$   
 311  $6$ , and  $|q| \leq k$ ), with associated coefficients  $B_k^q$ ,<sup>31,32</sup> and with  $\hat{O}_k^q$  expressed in terms of the total electronic

312 angular momentum operators  $\hat{j}$  and  $\hat{j}_i$  ( $i = x, y, z$ ). Using this convention, the axial ( $q = 0$ ) coefficients  
 313 determined from magnetic and continuous-wave (CW) EPR measurements are:<sup>23,24</sup>  $B_2^0 = 0.601 \text{ cm}^{-1}$ ,  $B_4^0 =$   
 314  $6.96 \times 10^{-3} \text{ cm}^{-1}$ , and  $B_6^0 = -5.10 \times 10^{-5} \text{ cm}^{-1}$ . This parameterization results in the  $m_J = \pm 4$  CF states lying  
 315 lowest in energy (Fig. 1), separated from the  $m_J = \pm 5$  excited states by  $\sim 20 \text{ cm}^{-1}$ .<sup>23</sup> The 2<sup>nd</sup> term in eq. 3  
 316 describes the hyperfine coupling between the  $\text{Ho}^{+3}$  electron and  $I = 7/2$  nuclear spin, resulting in the  
 317 observation of eight  $(2I + 1)$  well-resolved electro-nuclear transitions via high-field CW EPR  
 318 measurements; here,  $\hat{I}$  denotes the total nuclear angular momentum operator, and  $\vec{A}$  the hyperfine  
 319 coupling tensor, for which the parallel component,  $A_{\parallel} = 830 \pm 10 \text{ MHz}$ , has been determined from the high-  
 320 field CW EPR spectrum.<sup>24</sup> The final two terms in eq. 3 respectively parameterize the electron and nuclear  
 321 Zeeman interactions with the local magnetic induction,  $\vec{B}_0$ , in terms of a Landé  $g$ -tensor ( $\vec{g}$ ) and isotropic  
 322 nuclear  $g$ -factor ( $g_N$ );  $\mu_B$  and  $\mu_N$  represent the Bohr (electron) and nuclear magneton, respectively. The  
 323 parallel component of the Landé  $g$ -tensor,  $g_z = 1.25(1)$ , has been determined from CW EPR studies.<sup>22</sup>

324  
 325 In addition to the axial ( $q = 0$ ) CF parameters, CW EPR measurements at X-band frequencies can only be  
 326 accounted for by including a sizeable tetragonal  $B_4^4 \hat{O}_4^4$  [ $\hat{O}_4^4 = \frac{1}{2}(\hat{j}_+^4 + \hat{j}_-^4)$ ] interaction, with  $B_4^4$   
 327  $= 3.14 \times 10^{-3} \text{ cm}^{-1}$  (see Fig. 1a and Ref. [24] for detailed explanation). It is this term (which is allowed  
 328 because of a small distortion of the  $\text{HoW}_{10}$  molecule away from exact  $D_{4d}$  symmetry) that generates  
 329 avoided level crossings between  $m_J = \pm 4$  states, as seen in Fig. 1a. In principle, the sixth order tetragonal  
 330  $B_6^4 \hat{O}_6^4$  interaction is also symmetry allowed. However,  $\hat{O}_6^4$  contains the commutator  $[\hat{j}_z^2, (\hat{j}_+^4 + \hat{j}_-^4)]$  and is,  
 331 thus, indistinguishable from  $\hat{O}_4^4$  within the truncated  $m_J = \pm 4$  ground doublet. Therefore, we employ only  
 332 the  $B_4^4 \hat{O}_4^4$  term to capture the effects of the distortion away from exact  $D_{4d}$  symmetry. The key point is that  
 333  $\hat{O}_4^4$  connects the  $m_J = \pm 4$  states in 2<sup>nd</sup>-order, resulting in unusually large ( $\sim 9 \text{ GHz}$ ) quantum tunneling  
 334 gaps. For  $B_0 \parallel z$ , the frequencies of the resultant weakly allowed EPR transitions between these states  
 335 then follow a field-dependence of the form (see Fig. 1b),

$$336 \quad f = \sqrt{\Delta^2 + \gamma_z^2 (B_{0z} - B_{\min})^2} \approx \Delta + \frac{\gamma_z^2}{2\Delta} (B_{0z} - B_{\min})^2, \quad (4)$$

337  
 338 where the approximate quadratic expression applies for fields close to the gap minima,  $B_{\min}$ . Indeed,  
 339 because  $\hat{O}_4^4$  represents the only off-diagonal CF interaction in eq. 3, an almost exact mapping of the first  
 340 expression of eq. 4 onto curves generated via exact diagonalization of eq. 3 is possible, yielding the  
 341 following parameters:  $\Delta = 9.18 \text{ GHz}$ ,  $\gamma_z = 139.9 \text{ GHz/T}$  ( $= 1.25 \times 8 \times \mu_B/h$ , i.e.,  $g_z = 1.25$ ), and  $B_{\min} = 23.6,$   
 342  $70.9, 118.1$  &  $165.4 \text{ mT}$ . This analysis assumes  $B_0 \parallel z$ , while the experiments are typically performed with  
 343 a small field misalignment ( $\theta \neq 0$ ), as noted above. However, due to the extreme uniaxial symmetry of the  
 344  $\text{HoW}_{10}$  molecule, the perpendicular component of the effective gyromagnetic tensor associated with the  
 345  $m_J = \pm 4$  doublet,  $\gamma_{\perp, \text{eff}} < 0.1 \text{ GHz/T}$  ( $g_{\perp, \text{eff}} < 0.01$ ), resulting in a virtual insensitivity to the perpendicular  
 346 component of the applied field ( $B_{0\perp}$ ) over the range explored in this investigation; for comparison, note

347 that  $\gamma_{\text{proton}} \approx 0.04$  GHz/T. For this reason, one can approximate the electronic Zeeman term in eq. 3 using  
348 a scalar interaction of the form,  $g_z \mu_B B_{0z} \hat{J}_z$  (where  $B_{0z} = B_0 \cos\theta$ ). Eq. 4 then applies quite generally at the  
349 gap minima, provided the applied field is rescaled to account for any misalignment. For this reason, all  
350 EPR spectra are plotted as a function of the longitudinal applied field component,  $B_{0z}$ . Importantly, the  
351 derivative  $df/dB_{0z} \rightarrow 0$  (i.e.  $\gamma_{z,\text{eff}} \rightarrow 0$ ) as  $B_{0z} \rightarrow B_{\text{min}}$ , resulting in an almost complete insensitivity of the  
352 EPR transition frequencies at the gap minima to magnetic noise associated with the environment, thus  
353 giving rise to the strong  $T_2$  divergences at the CTs. However, the small yet finite  $\gamma_{\perp,\text{eff}}$  ( $< 0.1$  GHz/T) likely  
354 limits  $T_2$  right at the CTs (within  $\pm 0.5$  G of  $B_{\text{min}}$ ) in these studies due to the field misalignment. In fact,  
355  $\gamma_{\perp,\text{eff}} \rightarrow 0$  as  $B_0 \sin\theta \rightarrow 0$ , which may explain the longer  $T_2$  values observed at the lowest field CTs in  
356 Fig. 3, and also suggests that longer  $T_2$ 's may be achievable in precisely aligned samples.

357

### 358 **$T_2$ Scaling**

359 The data displayed in Fig. 3 were obtained for a small crystal of the most dilute sample ( $x = 0.001$ ). It is  
360 the high quality of this crystal that results in the sharp  $T_2$  peaks at all four CTs (all four  $B_{\text{min}}$  locations).  
361 However, it gives weak ESE signals, making it challenging to perform a detailed analysis of the scaling of  
362  $T_2$  with  $B_{0z}$ . Careful  $T_2$  measurements were therefore repeated for larger samples. Unfortunately, the  
363 larger crystals are susceptible to twinning that manifests as a broadening of spectral peaks and  $T_2$   
364 divergences, with the effect being most pronounced at the higher field CTs (see Fig. 2a). However, the  
365 first CT at  $B_{\text{min}} = 23.6$  mT often remains sharp (see below for explanation). Extended Data Fig. 1 displays  
366  $T_2$  measurements for the  $x = 0.001$  and  $0.01$  concentrations, plotted against  $(B_{0z} - B_{\text{min}})$  on both  
367 logarithmic (main panels) and linear (insets) scales. Similar to the data in Fig. 3, the  $T_2$  peaks exhibit  
368 broad tails, with an apparent kink at  $|B_{0z} - B_{\text{min}}| \approx 2$  mT for the more dilute sample. However, when  
369 plotted on a log-log scale, the data follow a power-law (to within the experimental uncertainty) spanning  
370 an order of magnitude in  $(B_{0z} - B_{\text{min}})$  for  $x = 0.001$ , and almost two orders of magnitude for  $x = 0.01$ ,  
371 particularly on the high-field sides of the  $T_2$  peaks. This apparent monotonic behavior of the form  
372  $T_2 \propto (B_{0z} - B_{\text{min}})^{-n}$  supports our assertion that the decoherence is dominated by dipolar field fluctuations  
373 that vanish as  $df/dB_{0z} \rightarrow 0$ . However, the exponent,  $n$ , is both sample-dependent ( $n = 0.33$  and  $0.46$ ,  
374 respectively, for  $x = 0.001$  and  $0.01$ ), and different from previous predictions:<sup>28,29</sup>  $n = 1$  for indirect flip-flop  
375 processes (spin diffusion), and  $n = 2$  for instantaneous diffusion.<sup>25</sup> We believe that sample inhomogeneity  
376 is responsible for these differences in HoW<sub>10</sub>, thus masking the intrinsic  $T_2$  dependence on  $B_{0z}$ , causing  
377 obvious sample-to-sample variability. It is nevertheless interesting that a power-law scaling still holds, as  
378 opposed, e.g., to Gaussian behavior. This clearly merits further theoretical investigation.

379

380 Reduced ESE intensity and faster  $T_2$  decay curves are part of the reason for the increased error bars and  
381 apparent broad tails seen in Fig. 3 and Extended Data Fig. 1. In addition, ESE-Envelope-Modulation  
382 (ESEEM)<sup>25</sup> is detectable in the decay curves recorded in these tails (not shown). However, only one to  
383 two heavily damped periods of oscillation can be seen, thus adding to the error in  $T_2$  (not to mention a

384 potential systematic error that is not taken into account in our analysis). It is these combined factors that  
385 likely explain the apparent kink in some of the data at  $|B_{0z} - B_{\min}| \approx 2$  mT, as well as the weak variation  
386 in  $T_2$  across the 'normal' transitions seen in the right-hand panel of Fig. 3. Interestingly, enough ESEEM  
387 periods can be detected to confirm that it is due to coupling to protons in the sample. Importantly, the  
388 ESEEM vanishes at the CTs, providing further strong evidence that the  $\text{Ho}^{+3}$  spin becomes decoupled  
389 from the surrounding dipolar spin bath as both  $(B_{0z} - B_{\min})$  and  $df/dB_{0z} \rightarrow 0$ .

390

### 391 **Spectral Broadening**

392 The EPR spectra of  $\text{HoW}_{10}$  are inhomogeneously broadened,<sup>24</sup> with the two main contributions originating  
393 from (i) crystal twinning and (ii) strain in the off-diagonal  $B_4^4$  CF parameter.

394

395 (i) Crystals of  $\text{HoW}_{10}$  form as long thin needles that tend to aggregate into aligned bundles. Separating  
396 single crystals from these bundles can be challenging, particularly given that removal of the samples from  
397 their mother liquor for periods of more than a few minutes leads to sample degradation. Even after  
398 separation, our measurements suggest varying degrees of mosaic spread, particularly for the larger  
399 crystals. Indeed, simulations of high-field CW EPR spectra (where the effects of the mosaicity are more  
400 pronounced than at X-band) employed a Gaussian orientational distribution with a full-width-at-half-  
401 maximum (FWHM) of  $1^\circ$ , albeit for a small crystal;<sup>24</sup> the distribution is considerably broader for many of  
402 the samples employed for ESE measurements. Within the context of eq. 2, this mode of disorder  
403 produces a spread in  $\gamma_z$  and the  $B_{\min}$  values, resulting in horizontal smearing of the energy levels in Fig. 1,  
404 as opposed to a vertical smearing produced by a distribution in  $B_4^4$  (see below). The horizontal smearing  
405 becomes more pronounced at higher fields, akin to  $g$ -strain. Consequently, the EPR spectra often  
406 become broader with increasing field, as is clearly evident in Fig. 2, and less so in Fig. 4.

407

408 Although subtle, the effects of sample mosaicity are most pronounced at the CTs. The horizontal spread  
409 in the CTs results in a smearing of the divergence in  $T_2$ . In general, the strongest/narrowest divergences  
410 were obtained for the smallest crystals, which have the smallest mosaic spread. It is for this reason that  
411 the data for the most dilute samples in Figs. 2 and 3 were obtained for two different crystals: the large  
412 crystal employed in Fig. 2a did not produce particularly strong  $T_2$  divergences, with maximum values  
413 reaching only  $\sim 2 \mu\text{s}$ . Meanwhile, a smaller crystal was employed in Fig. 3: this sample gave very good  
414 echoes right at the CTs, in spite of its reduced spin count; however, its ESE spectra vanish into the noise  
415 upon moving appreciably away from the CTs. These trends can be attributed both to a  $T_2$  weighting  
416 effect, which amplifies the otherwise weak ESE signals at the CTs for the more ordered (longer  $T_2$ )  
417 sample, and to the narrower mosaic distribution that further enhances echoes at the CTs. Multiple small  
418 samples were studied, and optimum  $T_2$  values at the CTs in the 6 to 8  $\mu\text{s}$  range were found in nearly all  
419 cases for the  $x = 0.001$  and 0.01 samples (See Fig. 3 and Extended Data Figs. 1 and 2).

420

421 (ii) Other sources of inhomogeneous broadening include: strains in the spin Hamiltonian parameters ( $B_k^q$ ,  
 422  $\vec{A}$ , and  $\vec{g}$ ), caused by microscopic disorder, and inhomogeneities in  $B_0$  due to electron and nuclear dipolar  
 423 fields. The latter may be ruled out as a major source of broadening at X-band (and 5 K) due to weak  
 424 sample magnetization and the lack of any systematic dependence of the EPR linewidth on Ho  
 425 concentration. Meanwhile, the only effect of the diagonal ( $q = 0$ ) CF terms in eq. 3 is to ensure an isolated  
 426  $m_J = \pm 4$  doublet ground state with  $\gamma_z = g_J J \mu_B / h = 139.9$  GHz/T ( $J = 8$  and  $g_J = 1.25$ ). Other than that, the  
 427 low energy spectrum exhibits little or no dependence on  $B_2^0$ ,  $B_4^0$  and  $B_6^0$ ,<sup>24</sup> and should thus be insensitive to  
 428 strains in these parameters. For related reasons, and because of the contracted nature of the 4f shell and  
 429 strong spin-orbit coupling, the  $\vec{g}$  and  $\vec{A}$  tensors are relatively immune to local strains in the crystal  
 430 structure (although the effective interactions will of course be sensitive to sample alignment due to the  
 431 strong axial character of the CF). This leaves  $B_4^4$  which, indeed, has a profound influence on the X-band  
 432 EPR spectrum, as clearly seen in Fig. 1a and discussed in detail in Ref. [24]:  $B_4^4$  directly sets the scale of  
 433 the tunneling gap,  $\Delta$ , which is responsible for the CTs.

434  
 435 The finite  $B_4^4$  parameter arises because of a small deviation of the coordination environment around the  
 436 Ho ion from exact  $D_{4d}$  symmetry.<sup>22</sup> The superposition of disorder onto this weakly distorted structure can  
 437 then give rise to a relatively strong modulation of the local  $B_4^4$  parameter and, hence, to a broad  
 438 distribution for the ensemble. Working under this assumption, we re-simulated CW X-band spectra  
 439 obtained for an  $x = 0.1$  sample at a frequency of 9.64 GHz (Fig. 8 of Ref. [24]), assuming that the main  
 440 source of broadening is a Gaussian distribution in  $B_4^4$ . The best simulation is obtained with a FWHM of  
 441  $5.0 \times 10^{-5} \text{ cm}^{-1}$ , i.e.,  $\sim 1.6\%$  of  $B_4^4$  (or a standard deviation,  $\sigma_{B_{44}} = 2.1 \times 10^{-5} \text{ cm}^{-1}$ ). This, in turn, produces a  
 442 vertical distribution in the corresponding tunneling gap,  $\Delta$ . Because  $\hat{O}_4^4$  connects the  $m_J = \pm 4$  states at the  
 443 2<sup>nd</sup> order of perturbation, the resultant standard deviation of the gap distribution is given approximately by  
 444  $\sigma_\Delta \approx 2\Delta\sigma_{B_{44}}/B_4^4 = 4.1 \times 10^{-3} \text{ cm}^{-1} = 123 \text{ MHz}$  (FWHM of 290 MHz), where  $\Delta = 0.306 \text{ cm}^{-1} = 9.18 \text{ GHz}$  is the  
 445 mean gap value (the factor of '2' emerges because of the quadratic dependence of  $\Delta$  on  $B_4^4$ ).

446  
 447 Fig. 1b depicts the Gaussian broadening of the EPR transition frequencies as a 3D color map, with  
 448 contours shown at the  $\pm\sigma_\Delta$  and  $\pm 2\sigma_\Delta$  levels of the distribution. Because  $B_4^4$  affects only  $\Delta$ , this mode of  
 449 disorder does not shift the magnetic fields ( $B_{\min}$ ) at which the CTs occur for the different molecules in the  
 450 distribution. However, it does distribute them vertically over a relatively wide frequency range (approx.  
 451  $\pm 0.25 \text{ GHz}$  at the  $2\sigma_\Delta$  level). This can explain the observation of ESE intensity exactly at the CTs over a  
 452 wide frequency range for the concentrated ( $x = 0.1$ ) sample seen in Fig. 4. Because the cavity employed  
 453 for these investigations has a center frequency at 9.75 GHz, its sensitivity improves upon increasing the  
 454 frequency from 9.1 to 9.4 GHz. Meanwhile, the number of Ho<sup>+3</sup> spins in the distribution decreases with  
 455 increasing frequency. These two factors approximately offset, explaining the relatively constant ESE  
 456 intensity and signal-to-noise ratio across the studied frequency range. The ESE intensity does peak at

457 9.2 GHz, above which it decays, although not as rapidly as one may expect purely on the basis of the gap  
458 distribution. This is due to the increasing  $B_1$  field of the spectrometer, which enables excitation of more  
459 spins and hence the generation of stronger echoes at higher frequencies.

460  
461 Finally, the question arises as to whether this same behavior is observable at the other concentrations.  
462 Indeed, it is. For example, CTs are very clearly observable in between the 'normal' EPR transitions over a  
463 wide frequency range at  $B_{0z} = 165$  mT for the  $x = 0.01$  sample, as seen in Extended Data Fig. 3. Further  
464 evidence can also be found at some of the higher frequencies, where inspection of Fig. 1a reveals  
465 crossings between nuclear sub-levels ( $\Delta m_l = \pm 1$ ) at fields exactly half way between the  $B_{\min}$  values. If the  
466 applied field is not well aligned to the crystal z-axis, these become avoided crossings (with  $<10$  MHz  
467 gaps), giving rise to new CTs at these higher frequencies. This is a subtlety of the perpendicular field  
468 component,  $B_{0\perp}$ , which will be the subject of a future publication. The avoided nuclear sub-level crossings  
469 *do not* influence any of the conclusions concerning the CTs at the  $B_4^4$  gap minima ( $\Delta$ ). Nevertheless, the  
470 higher frequency CTs are observable, particularly at low fields where the effects of disorder due to  
471 sample mosaicity are less pronounced, and the 'normal' ESE transitions are quenched due to very short  
472  $T_2$ 's.<sup>2,9</sup> This is the explanation for the sharp double peaks seen for the  $x = 0.001$  sample at  $\sim 50$  mT  
473 between 9.4 and 9.7 GHz in Fig. 2a, as well as the sharp zero-field peaks and some of the fine structures  
474 seen between  $B_{\min}$  values at higher fields and frequencies. On the basis of the 50 mT CTs, one can see  
475 that the vertical broadening spans less than 400 MHz in this sample, i.e., less than  $\pm 200$  MHz from the  
476 peak of the distribution. In other words,  $\sigma_{B44}$  clearly varies from sample-to-sample, being smaller for the  
477  $x = 0.001$  concentration. This is the reason why intensity due to the low-frequency CTs (@  $B_{\min}$ ) is not  
478 discernible in between the broad 'normal' transitions in the most dilute sample in Fig. 2a.

479

## 480 **References**

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