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A counterintuitive three-order of magnitude slowing of the spin-lattice relaxation rate is observed in a high spin qubit at high magnetic field via multifrequency pulsed electron paramagnetic resonance measurements.

Quantum information processing (QIP) offers the potential to transform current approaches to computationally difficult problems.[1] A specific approach to QIP employing molecular inorganic clusters was proposed in 2001.[2] Here, high-spin coordination clusters were suggested as nano-sized quantum information processors, inspiring the investigation of a legion of high-spin, multinuclear molecules.[3] A central obstacle to realizing this proposal, however, is decoherence, a mechanism by which encoded information in quantum bits (qubits) decays with time.[4] The timescale of this decay relates to two fundamental parameters of the spin qubit, the spin-lattice and spin-spin relaxation times, T_1 and T_2, respectively. T_2 directly represents the decay owing to decoherence, while the thermal limitation of the maximum time window of information stability is represented by T_1. Both of these parameters are short in high-spin systems, lower than milliseconds for T_1 and microseconds for T_2, values that are well below the generally accepted limits for utility.[5] Thus, increasing T_1 and T_2 is a vital goal in the development of a spin-based quantum computer.

By employing synthetic inorganic chemistry to tune chemical parameters it may be possible to suppress decoherence in high-spin molecules.[6] Enhancing T_1 by electronic structure design is possible by synthetic fine-tuning, while similarly lengthening T_2 requires employment of a separate synthetic paradigm. Nuclear spins are a potent source of decoherence,[7] thus, inspection of the majority of high-spin qubits reveals one reason for typically short T_2 parameters, namely, ligand sets rich in nuclear spins. For example, the well-studied S = 10 qubit $[(tacn)_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]^{7+}$ possesses a multitude of ^{1}H and ^{14}N magnetic nuclei in its triazacyclononane (tacn) ligands.[8] Thus, we and others embrace a nuclear spin-free synthetic paradigm and work primarily with elements of exceptionally high natural abundance of spin-free isotopes.[9-11] These efforts enabled the realization of millisecond T_2 lifetimes in a $S = {}^1/_2$ transition metal complex, a substantial advance for molecular electronic spin qubits.[10] Yet, the realization of comparably long T_2 values in molecules with $S > {}^1/_2$ remains elusive.

Understanding the impact of a spin's intrinsic properties on decoherence creates the foundation for the future design of molecular processors. Indeed, in high-spin qubits zero-field splitting can cause M_S levels to mix and consequently influence dynamic behaviour.[12] Quantifications of the importance of this mixing to T_1 and T_2 in high-spin qubits are exceedingly rare. Yet, understanding the role of mixing on decoherence is vital, especially considering that M_S mixing in specific cases can engender long T_2 parameters.[13] A variable strength magnetic field is a key extrinsic method to study decoherence owing to M_S level mixing induced by a zero-field splitting. Indeed, a magnetic field strength can be scanned through a regime where the Zeeman energy is comparable to the zero-field splitting and therefore enable fine-tuning of M_S level mixing. Thus, investigation of the viability of a qubit across this regime enables probing the magnitude of T_1 and T_2 as a function of M_S mixing. As a test case to study the role of this mixing on T_1 and T_2, we selected a recently published $S = {}^5/_2$ qubit, which has heavily mixed M_S levels at low field owing to a highly rhombic zero-field splitting.[11]

Herein we describe multi-frequency pulsed electron paramagnetic resonance (EPR) spectroscopic measurements[14] of the coordination complex $(Ph_4P)_3[Fe(C_5O_5)_3]$ (**1**). Access to multiple frequencies enables the progression from a high to low degree of M_S mixing in the high-spin qubit. We demonstrate that a large magnetic field enables a counterintuitive three-order-of-magnitude suppression of the main mechanism of information loss for this qubit system. We attribute this result to a weakening of M_S mixing at high field. These data highlight the possibility of long T_1 and T_2

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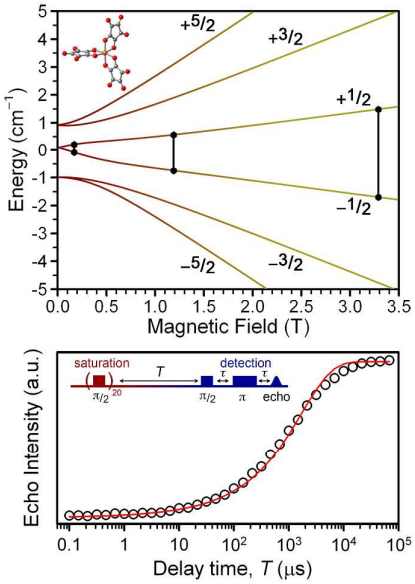

Fig. 1. Top: Magnetic field dependence of the M_S levels of the $S = {}^5/_2$ species $[Fe(C_5O_5)_3]^{3-}$ (structure inset) for a magnetic field aligned perpendicular to the molecular z-axis. From left to right, the black vertical lines indicate the magnetic fields where EPR transitions are observed with X-, K_a-, and W-band microwave radiation. Red to yellow fading in the energy levels emphasizes the transition from the low- to high-field limit. The M_S level labels correspond to the high field limits. **Bottom:** Example saturation recovery curve of **1a** at 7 K and applied field of 3.28 T. The red line is a best-fit exponential recovery function with T_1 = 3.9(2) ms. Inset: The saturation recovery pulse sequence.

parameters in high-spin species through control of M_S level mixing.

Performing T_1 and T_2 measurements to elucidate the effect of field in high spin coordination complexes necessitates an observable EPR transition. For $[Fe(C_5O_5)_3]^{3-}$, pulsed and continuous wave EPR spectra show a strong transition that moves to higher field with increasing microwave frequency, from 1650 G at X-band (≈ 9.5 GHz) to 1.17 T at K_a-band (≈ 35 GHz) and finally 3.28 T at W-band (≈ 95 GHz) (see Figs. 1, S1). This observation is consistent with the enhanced splitting of the probed M_S levels with increasing magnetic field. Importantly, the identity of this transition changes as a function of field owing to the comparable magnitude of the axial zero-field splitting of $[Fe(C_5O_5)_3]^{3-}$ (D = –0.3 cm^{-1}) relative to the X-, K_a- and W-band quanta (≈ 0.32, 1.18, and 3.14 cm^{-1}, respectively). At low field, the EPR transition occurs between M_S levels that possess significant $M_S = \pm{}^1/_2, \pm{}^3/_2$ and $\pm{}^5/_2$ character. At high magnetic field, however, the purity of the M_S levels increases due to diminished mixing (see Figs. 1, S2, and the ESI for more details). Thus, the observed transition at 3.28 T is best described as between nearly pure $M_S = \pm{}^1/_2$ levels. As will be detailed below, this evolution as a function of field has important implications for the qubit.

To control for sample environment, we analysed two separate sample preparations. First, **1** was cocrystallized with a diamagnetic congener, $(Ph_4P)_3[Ga(C_5O_5)_3]$, in a molar ratio of

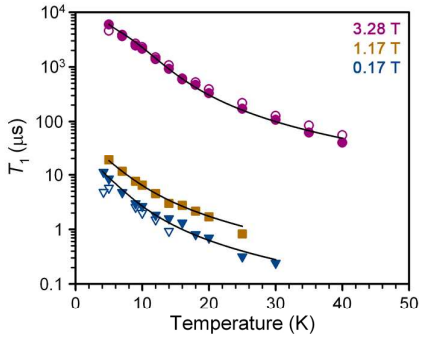

Fig. 2. Temperature dependence of the spin-lattice relaxation time T_1 for **1a** (filled symbols) and **1b** (empty symbols). Black lines represent best fits to the data that account for spin-lattice relaxation *via* direct and Raman processes.

1:1000 Fe to Ga (**1a**). Second, **1** was dissolved at 0.5 mM concentration in SO_2, a nuclear spin-free solvent (**1b**). The isolation of **1** in these two matrices simplifies analysis by minimizing contributions from intermolecular electronic (from other $[Fe(C_5O_5)_3]^{3-}$ molecules) and electronuclear interactions (from the solvent).

The electronic spin-lattice relaxation time (T_1) is an important measure of the sensitivity of a spin qubit to thermal effects. Indeed, the short T_1 at 0.17 T for **1** was previously found to be the dominant limiting factor for T_2. Herein, we probe this behaviour more thoroughly with saturation recovery pulsed EPR experiments (see Figs. 1, 2, S3, and S4) as a function of temperature and magnetic field. In these experiments, the recovery of the intensity of a Hahn echo was monitored following a train of microwave pulses that saturated the EPR transition. The rate of this recovery is $1/T_1$. At 5 K, T_1 dramatically increases by three orders of magnitude with applied field, from 11.2(2) μs at 0.17 T to 19(1) μs at 1.17 T and finally 6.0(5) ms at 3.28 T at 5 K in **1**. The observed T_1 at 5 K and 3.28 T is long for high-spin iron(III) species (with oxygen donor ligands[15] or otherwise[16]) and other high-spin, mono and multinuclear species.[8ab,9a,17,18]

The spin relaxation rate ($1/T_1$) represents an intuitive way to conceive of the inherent limitation that T_1 imposes on T_2. Here, this rate describes how quickly thermal effects induce information loss in an electronic qubit. The temperature and field dependence of $1/T_1$ contain mechanistic information underlying the slow spin-lattice relaxation (Figs. S5-S7). The observed increase in $1/T_1$ with increasing temperature is common, however, the dramatic decrease in $1/T_1$ with applied field is not. Indeed, the most common field-dependent process, the direct process, favours an increasing $1/T_1$ with increasing magnetic field.[12,19] Other common processes, Raman and Orbach processes,[12,14] are typically field independent. When the Raman process is field dependent, an increased magnetic field engenders faster $1/T_1$ rates. The Orbach process is field dependent only if the applied magnetic field significantly shifts the energies of the spin levels relative to the activation energy barrier for spin reversal. In this latter case, the relaxation time increases when the activation barrier increases with field (Fig S8). As depicted in Fig. 2 (and Figs. S5-

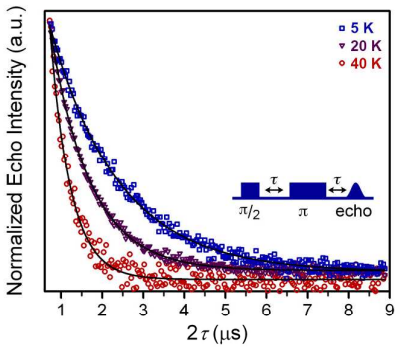

Fig. 3. Pulse sequence and selected 3.28 T echo decay curves at **1a.** The black lines represent best fits of exponential decay functions to the echo intensity data; parameters for these fits are included in Table S2.

S7), the best fits were obtained with a combination of Raman and direct processes (see ESI for additional discussion). The expected field dependences of these processes are at odds with the observed impact of increasing magnetic field on $1/T_1$. It is important to note, however, that the rates here are directly related to the matrix element for the observed EPR transition. With increasing field, this element is expected to decrease owing to lower M_S level mixing, which may be leading to the remarkable slowing of $1/T_1$. We therefore assign the unusual field dependence of $1/T_1$ to modulation of the identity of the M_S levels by the applied field. We note a distinct paucity of multifrequency pulsed EPR investigations in high-spin molecules, especially those spanning the low- to high-field regimes of the Zeeman diagram.[20] Indeed, The rare case of a slowing $1/T_1$ with field determined by pulsed EPR occurs for radicals frozen in a glass, an inapt comparison for **1a**.[21] Separately, ac susceptibility studies reveal slowing relaxation rates at high fields owing to metal nuclear spins or phonon bottlenecks.[22] We note these latter observations are not pulsed EPR, i.e. not on individual transitions. Thus, the foregoing findings motivate future spectroscopic studies to develop a larger body of work on the behaviour.

The impressive suppression of $1/T_1$ *via* magnetic field suggests that the $1/T_1$-limitation for T_2 is lifted, and evokes the possibility of observing long coherence times for the first time in a high-spin qubit. Thus, variable field and temperature Hahn-echo experiments were performed on **1** to study the stability of encoded information when a fast $1/T_1$ is no longer preclusive. Here, the response of **1** to two microwave pulses was monitored as a function of interpulse spacing, yielding the decaying response depicted in Figs 3, 4, S9, and S10. At low field these data show an oscillation superimposed on the decay due to interactions with surrounding nuclear spins, a phenomenon known as electron spin-echo envelope modulation (ESEEM).[23] The timescale of the decay, T_2, is 560(19) and 1630(21) ns at 0.17 and 3.28 T, respectively, for **1a** at 5 K. The parameter drops with increasing temperature, falling to 151(7) and 498(12) ns for **1a** at 0.17 and 3.28 T, respectively. At higher temperatures, the T_2 values for **1a** at 3.28 T eclipse the T_1 parameters for 0.17 T, directly demonstrating that the large field lifts the $1/T_1$-limitation of T_2.

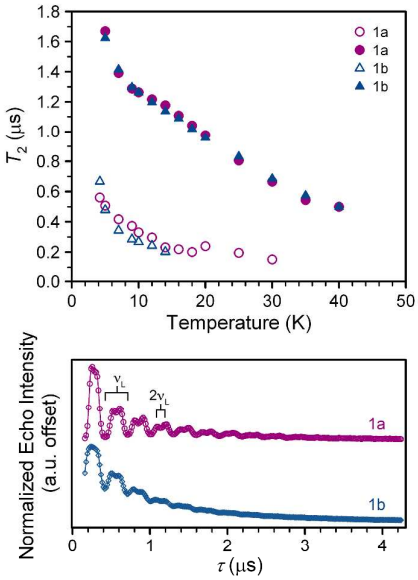

Fig. 4. Top: Temperature dependence of T_2 for **1a** and **1b** at 0.17 and 3.28 T. Empty symbols represent data collected at 0.17 T while filled symbols are at 3.28 T. Errors for the parameters are within the size of the data points. **Bottom:** 0.17 T echo decay curves as a function of interpulse spacing τ at 4.2 K for **1a** and **1b**, demonstrating different ESEEM depths as a function of diamagnetic matrix. Evidence of the Larmor frequency (ν_L) on the modulation is highlighted.

Further, the large magnetic field may also minimize the influence of any intermolecular interactions.[24] Here, an applied field locks electronic spins into alignment with H and subdues intermolecular electronic spin flip-flops from inducing decoherence. However, T_2 is independent of concentration in the range of 1:1000 Fe:Ga (see ESI) which implies that this effect may be minor. Furthermore, one may expect that the $M_S = \pm^1/_2$ levels utilized at higher field would be comparatively less sensitive to dipolar interactions with other magnetic moments than higher M_S levels. Thus, a similar argument employed for rationalizing the trend in T_1 may also apply to the decoherence mechanisms.

The slow $1/T_1$ and enhanced T_2 at 3.28 T suggested the tantalizing possibility that an exceptionally long T_2 could be attained following elimination of environmental nuclear spins. Instead, we observed that T_2 is essentially identical between **1a** and **1b** despite significantly less nuclear spins in the latter. Indeed, the noticeably weaker ESEEM in **1b** relative to **1a** (Fig. 3) at 0.17 T reflects the relatively lower amount of ^{1}H nuclei in the vicinity of the iron(III) ion in **1b**. The strength of ESEEM is influenced by the length of the pulses in the Hahn echo experiment, thus we note that identical measurement pulse sequences were used for the two samples. The observation of ESEEM in **1b** may indicate incomplete solvation by SO_2, such that a $\{(Ph_4P)[Fe(C_5O_5)_3]\}^{2-}$ ion-pair is the effective analyte. In this case, the nuclear spins of a closely-bound Ph_4P^+ counterion may engender decoherence despite dissolution in SO_2. Alternatively, the high-spin of the iron(III) ion may simply possess a larger than anticipated radius of interaction with ^{1}H

nuclei and allow solubilized, relatively distant Ph_4P^+ counterions to remain effective for decoherence.

The foregoing results indicate that larger magnetic fields may enable longer relaxation times by suppression of M_S-level mixing. Importantly, our focus here on a single transition is a fundamental stepping-stone to the entire M_S manifold of large spins. Here, the possibility of exploring multiple transitions is an enticing next step. The implications of these studies extend past application to QIP. Indeed, careful examination of the field dependence of $1/T_1$ and T_2 in high-spin ions is a crucial component in the development of agents for dynamic nuclear polarization[25] or magnetic resonance imaging.[26] Thus, these current results suggest the possibility of using ions that are presently excluded due to relaxation times determined at low field/frequency. Interestingly, the lack of dramatic enhancement of T_2 for **1** in nuclear spin-free solvent underlines the importance of considering cation identity[27] and ion-pairing effects. Indeed, the construction of closed-shell nuclear spin-free cations may enable the elimination of a potentially significant source of decoherence in species even when isolated in nuclear spin-free media. Such molecules are a synthetically challenging prospect, and are a current focus of our laboratory.

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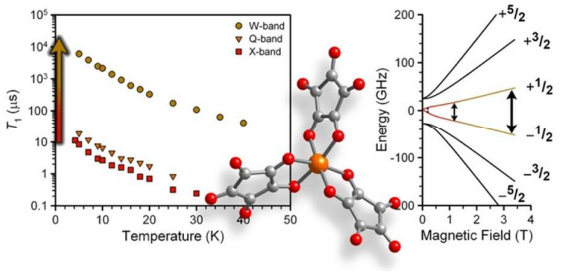
Table of Contents Graphic



Synopsis

The high-spin molecule $[Fe(C_5O_5)_3]^{3-}$ displays a remarkable slowing of spin lattice relaxation upon application of a high magnetic field.