

T_1 Anisotropy Elucidates Spin Relaxation Mechanisms in an $S = 1$ Cr(IV) Optically Addressable Molecular Qubit

Nathanael P. Kazmierczak,[†] Kaitlin M. Luedecke,[†] Elisabeth T. Gallmeier, and Ryan G. Hadt*



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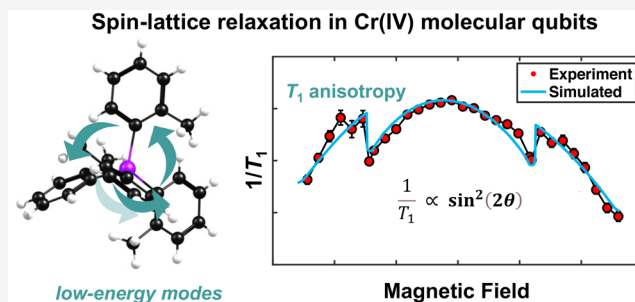


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Supporting Information

ABSTRACT: Paramagnetic molecules offer unique advantages for quantum information science owing to their spatial compactness, synthetic tunability, room-temperature quantum coherence, and potential for optical state initialization and readout. However, current optically addressable molecular qubits are hampered by rapid spin–lattice relaxation (T_1) even at sub-liquid nitrogen temperatures. Here, we use temperature- and orientation-dependent pulsed electron paramagnetic resonance (EPR) to elucidate the negative sign of the ground state zero-field splitting (ZFS) and assign T_1 anisotropy to specific types of motion in an optically addressable $S = 1$ Cr(*o*-tolyl)₄ molecular qubit. The anisotropy displays a distinct $\sin^2(2\theta)$ functional form that is not observed in $S = 1/2$ Cu(acac)₂ or other Cu(II)/V(IV) microwave addressable molecular qubits. The Cr(*o*-tolyl)₄ T_1 anisotropy is ascribed to couplings between electron spins and rotational motion in low-energy acoustic or pseudoacoustic phonons. Our findings suggest that rotational degrees of freedom should be suppressed to maximize the coherence temperature of optically addressable qubits.



The anionic nitrogen vacancy (NV^-) center in diamond constitutes one of the most widely implemented platforms for quantum sensing and imaging.¹ Substitutional replacement of two carbons in the diamond lattice with a nitrogen and a vacancy forms an $S = 1$ paramagnetic defect that exhibits selective photoluminescence behavior depending on the Zeeman sublevel that the spin occupies.^{2,3} Furthermore, optical excitation of the NV^- center accumulates ground state spin polarization through a spin-selective intersystem crossing mechanism. These two features enable optical initialization and detection of quantum states in the Zeeman sublevels of the $S = 1$ defect, permitting a much greater degree of spatial localization than can be achieved with direct resonant microwave readout of the Zeeman sublevels. This functionality has enabled quantum sensing in a variety of applications,¹ including atomic scale magnetic resonance imaging of nuclear spin clusters,⁴ probing intracellular molecular dynamics,⁵ nanometer-scale thermometry with millikelvin accuracy inside a living cell,⁶ imaging magnetic fields in live magnetotactic bacteria,⁷ measuring local ion concentrations,⁸ and strain/pressure sensing.⁸ The main downsides of NV^- centers relate to the large bulk of the diamond lattice, the poor control over where the NV^- defects arise in the lattice, and the fixed nature of the NV^- center coherence properties.⁹

Production of molecules exhibiting the same optical initialization and readout capabilities would overcome these limitations of NV^- centers and open up molecular *in situ* and *in vivo* quantum sensing capabilities on the single nanometer scale. Multiple systems have been investigated on the basis of

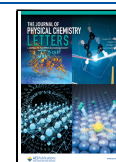
both $S = 1$ and $S > 1$ architectures,^{10–12} but to date, the most successful molecules have been pseudo- T_d $S = 1$ Cr(IV) tetraaryl and tetraalkyl complexes,^{13,14} which display optical addressability and prolonged coherence times when diluted in nonisostructural diamagnetic matrices.¹⁵ However, owing to fast spin relaxation, Cr(IV) molecular qubits do not display spin coherence at temperatures higher than ~ 60 K, at which point T_m becomes spin–lattice relaxation (T_1) limited. This behavior is significantly inferior to that of both NV^- centers and microwave addressable $S = 1/2$ molecular qubits such as VOPc and $[Cu(mnt)_2]^{2-}$, which display coherence up to room temperature.^{16–18} In particular, quantum sensing of biological systems would benefit greatly from the ability to perform room-temperature coherence measurements under ambient biochemical conditions. Therefore, to maximize the full potential of optically addressable molecular qubits, it is essential to identify and remove contributions to fast spin relaxation.

Recently, T_1 anisotropy has emerged as a novel technique for interrogating spin-phonon coupling contributions to spin relaxation and decoherence in $S = 1/2$ systems.¹⁹ This

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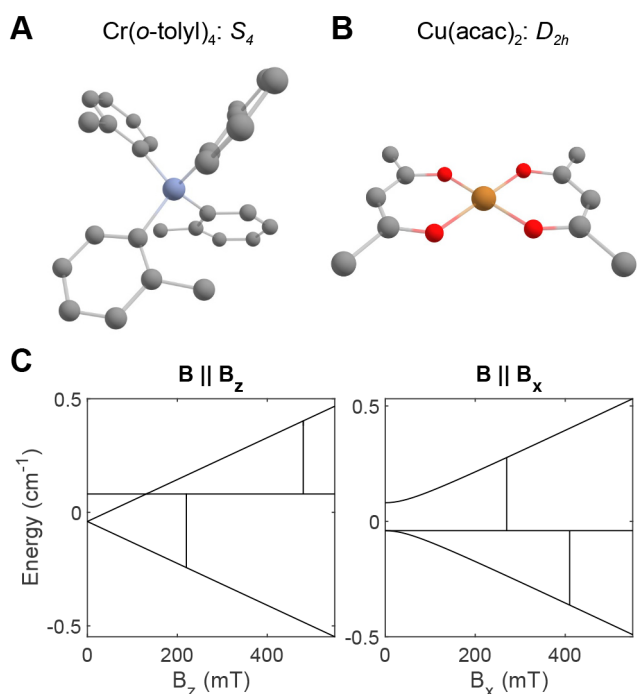
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approach can provide information regarding the vibrational contributions and mechanism of spin relaxation that is not accessible through more common temperature-dependent T_1 measurements. Here, we apply this methodology to $\text{Cr}(\text{o-tolyl})_4$, an $S = 1$ tetraaryl $\text{Cr}(\text{IV})$ optically addressable molecular qubit (Scheme 1A). We find qualitatively different

Scheme 1. Molecular Crystal Structures and Point Groups of (A) $S = 1$ $\text{Cr}(\text{o-tolyl})_4$ and (B) $S = 1/2$ $\text{Cu}(\text{acac})_2$; (C) Simulated Zeeman Levels for $\text{Cr}(\text{o-tolyl})_4$ with $D = -0.117 \text{ cm}^{-1}$, as Determined in This Work^a



^aIn panels A and B, C = gray, Cr = blue, Cu = orange, and O = red. H atoms omitted for clarity. In panel B, slight distortion from planarity. In panel C, vertical lines denote X-band EPR transitions at 9.6 GHz.

T_1 anisotropy patterns relative to $\text{Cu}(\text{acac})_2$ (Scheme 1B) and other copper(II) and vanadium(IV) $S = 1/2$ systems, indicating unique spin-phonon coupling contributions to spin relaxation.

The concept of T_1 anisotropy probes how the spin relaxation rate changes for molecules with different orientations relative to the spectrometer's applied magnetic field (B_0). In general, EPR spectra of powder or frozen solution samples can display resonance positions selective for these different molecular orientations, enabling access to orientation-specific relaxation rates without the need for single crystal experiments.²⁰ $\text{Cr}(\text{IV})$ qubits satisfy this requirement for orientation selectivity, as the microwave absorption spectrum of $\text{Cr}(\text{o-tolyl})_4$ is composed of two transitions between the three M_S sublevels (Scheme 1C), and each spin transition occurs at a different resonance field depending on the molecular orientation (Figure 1A,B). By weighting these orientations with the fraction of molecules absorbing at the given field and averaging over the two spin transitions, we can define an average molecular orientation probed by EPR at any given resonance field (Figure 1C). At X-band, the pure parallel position can be addressed by performing pulsed EPR at 220 and 480 mT (lines atop Figure 1A). While no single position is uniquely selective for the

perpendicular orientation, the Pake pattern horns at 280 and 410 mT display an average orientation around 80° , giving a close approximation to the pure perpendicular position behavior.

The identity of the $M_S = -1 \rightarrow 0$ and $M_S = 0 \rightarrow +1$ transitions depends upon the sign of the axial zero-field splitting (ZFS) parameter D . While a perfectly T_d $S = 1$ molecule cannot exhibit ZFS owing to cubic symmetry and a lack of second-order spin-orbit interactions,²¹ $\text{Cr}(\text{o-tolyl})_4$ crystallizes in the S_4 point group.¹³ The sign of D is sensitive to changes in the electronic structure upon structural distortions from T_d to S_4 , including splitting of ligand field excited state energies and anisotropic orbital covalency.^{21,22} Correct computational modeling of the sign of D is therefore essential for spin-phonon coupling calculations to accurately describe the electronic structure. Although the absolute ZFS parameters for $\text{Cr}(\text{o-tolyl})_4$ have been reported ($|D| = 0.117 \text{ cm}^{-1}$, $E \approx 0 \text{ cm}^{-1}$)¹³, the sign of the ZFS has yet to be determined experimentally. To achieve this, we acquired variable-temperature Q-band echo-detected field sweeps (EDFSs) from 3.8 to 50 K (Figure 1D). Soft microwave pulses were employed to suppress electron spin echo envelope modulation (ESEEM), which can add artifacts to EDFS spectra, and T_m was measured at several field positions and temperatures to ensure anisotropic T_m did not bias the EDFS intensity (Supporting Information Sections 3–4). As the sample temperature increases, the intensity of the spin transition spanning 1100–1290 mT decreases relative to the transition spanning 1160–1370 mT (arrows in Figure 1D). This behavior and corresponding simulation (Figure 1E) indicates that the former is the ground state $M_S = -1 \rightarrow 0$ transition and that the sign of D is negative for $\text{Cr}(\text{o-tolyl})_4$ ($D = -0.121 \text{ cm}^{-1}$), consistent with calculations.^{23,24} Note this sign differs from the pseudo- T_d $\text{Cr}(\text{IV})$ siloxide complex, $\text{Cr}(\text{DTBMS})_4$, which exhibits $D > 0$.²⁵ This indicates that distortions away from T_d can produce categorically distinct electronic structure modifications in $\text{Cr}(\text{IV})$ complexes, which may lead to diverging spin-phonon coupling behavior.

Inversion recovery T_1 measurements at 40 K were conducted on a 1.8% dilution of $\text{Cr}(\text{o-tolyl})_4$ into an isostructural diamagnetic $\text{Sn}(\text{o-tolyl})_4$ matrix (Figure 2A–C). The slowest rates of spin relaxation were recorded at the pure parallel orientations, while the perpendicular orientations also displayed local minima in the spin relaxation rates (Figure 2B). Fastest spin relaxation was observed at the intermediate orientations closest to 45° , which are found both immediately to the outside of the Pake pattern horns and also in the very center of the spectrum (Figure 1C). The T_1 anisotropy pattern can be most nearly described by a $\sin^2(2\theta)$ functional form (Figure 2C), where θ is obtained from the orientation analysis in Figure 1. The $\sin^2(2\theta)$ function accounts for the slower spin relaxation along the canonical (parallel and perpendicular) orientations and faster spin relaxation along the intermediate orientations. Additionally, a $\sin^2(\theta)$ function and a linear function proportional to B (linear in the magnetic field) were considered. Note that the function linear in B does not directly depend upon the molecular angle θ and is therefore more precisely construed as isotropic field-dependent spin relaxation rather than true anisotropy (Supporting Information Section 5). This term may be understood as the slope of the Brons-van Vleck spin lifetime field dependence commonly observed in AC magnetometry, and this slope is indeed negative at X-band fields (0.3 T) for common V(IV) qubits.²⁶ A least-squares fit of

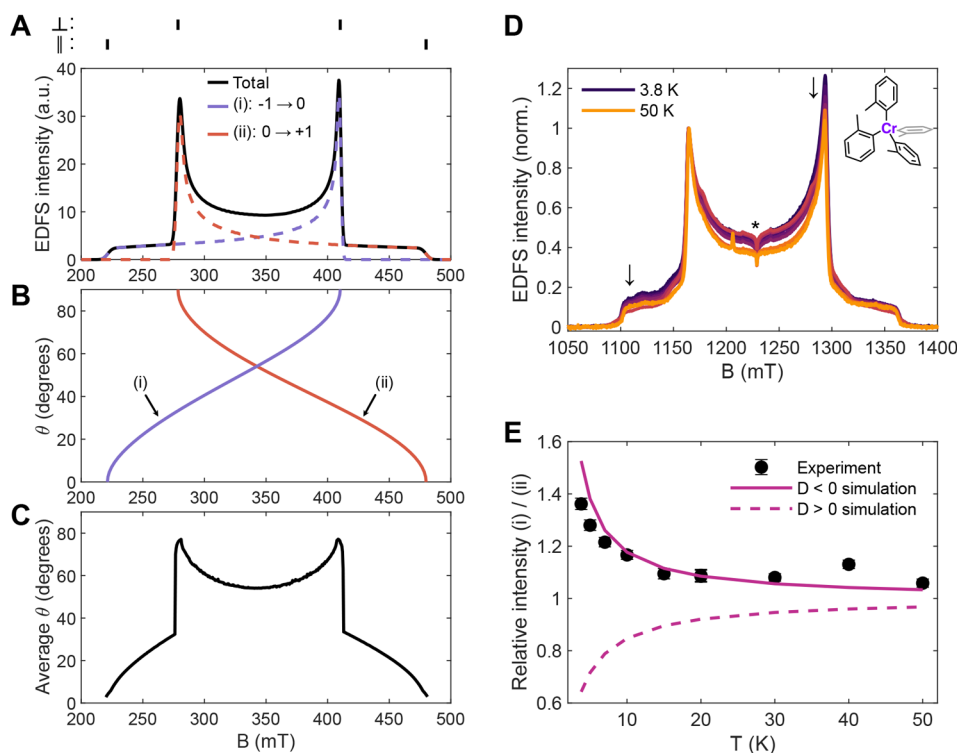


Figure 1. Anisotropy in Cr(IV) pulsed EPR. (A) Simulated X-band EDFS for Cr(o-tolyl)₄ showing the contributions from each spin transition in the case of $D < 0$. (B) Orientation of the molecule with respect to the value of B_0 . $\theta = 0^\circ$ indicates B_0 is parallel to the principal symmetry axis of the axial ZFS tensor. (C) Average orientation of the molecule over all spin transitions. (D) Variable-temperature Q-band EDFs using soft pulses ($\pi = 80$ ns) and normalized to the peak at 1160 mT. * likely indicates an artifact due to cross-relaxation or a double-quantum transition (Supporting Information Section 3). (E) Comparison between experimental powder manifold intensities and simulations for $D < 0$ and $D > 0$.

the inversion recovery data was conducted to quantify the relative contributions of different anisotropy functions (Supporting Information Section 5.1 and 5.3). The 40 K T_1 field dependence of Cr(o-tolyl)₄ can be described by this method as composed of 13% $\sin^2(2\theta)$, 6% $\sin^2(\theta)$, and 5% linear in B contributions, with a 76% constant (isotropic) component. This method of T_1 anisotropy analysis is applicable to any EPR-addressable $S = 1$ complex with an anisotropic powder spectrum.

Crucially, this behavior contrasts with that observed for tetragonal $S = 1/2$ Cu(II), V(IV), and Cr(V) compounds previously investigated by T_1 anisotropy at 100 K, in which the fastest and slowest values of spin relaxation were always found at the canonical orientations.^{19,20,27} To see if this was an effect of the temperature regime studied, we collected T_1 anisotropy at 40 K of 0.1% Cu(acac)₂ diluted in the isostructural diamagnetic matrix Pd(acac)₂ (Figure 2D–F). The 40 K Cu(acac)₂ completely follows the $\sin^2(\theta)$ functional form with no apparent significant contributions from $\sin^2(2\theta)$ (Figure 2F). The spin relaxation rate at the 45° orientation is simply the average of the rates at the canonical positions. These observations point to a qualitatively different origin of T_1 anisotropy in Cr(o-tolyl)₄ vs Cu(acac)₂.

To ascertain the type of vibrations responsible for these distinct patterns, we probed the temperature dependence of the T_1 anisotropy for Cr(o-tolyl)₄ and Cu(acac)₂. We quantify the amount of T_1 anisotropy as a fraction of the largest $1/T_1$ over all field positions (Figure S17). Over the temperature range of 7–60 K, the amount of T_1 anisotropy for Cr(o-tolyl)₄ steadily decreases, with the dominant $\sin^2(2\theta)$ anisotropic contribution decreasing from 23% to 10% of the total T_1

(Figure 3). This decrease with increasing temperature indicates that $\sin^2(2\theta)$ anisotropy arises from very low energy degrees of freedom, likely acoustic or pseudoacoustic phonons²⁸ (*vide infra*). Indeed, the isotropic field-dependent contribution to $1/T_1$ decreases at the same pace over this temperature range, and this contribution is commonly ascribed to the direct process of spin relaxation.²⁶ In contrast, the $\sin^2(\theta)$ T_1 anisotropy contribution increases sharply with temperatures for Cu(acac)₂, constituting only 0.5% of the total T_1 at 20 K but 62% at 100 K (Figure 3). Examination of the field-dependent T_1 for Cu(acac)₂ at 20 K validates that the spin relaxation anisotropy is greatly reduced (Figure S22), while the parallel and perpendicular T_1 at 100 K differ by a factor of 2.4, as observed and analyzed previously by our group.¹⁹ This validates that the $\sin^2(\theta)$ anisotropy for Cu(acac)₂ arises from higher energy molecular vibrational modes (optical phonons) that are not thermally populated at 20 K. Thus, the T_1 anisotropies for Cr(o-tolyl)₄ vs Cu(acac)₂ originate from different types of phonons. Note that both anisotropies are temperature dependent in a manner consistent with the effect of thermal population of vibrational modes.^{29–31} Anisotropic spectral diffusion was ruled out as a principal cause of the observed T_1 patterns for both compounds (Supporting Information Section 5.2).

A major attraction of the T_1 anisotropy methodology lies in the possibility of correlating the observed functional forms (e.g., $\sin^2(\theta)$ and $\sin^2(2\theta)$) to their origins in specific molecular degrees of freedom. Previous work has analyzed $\sin^2(\theta)$ spin relaxation anisotropy for Cu(II) and V(IV) molecular vibrations and shown it to be consistent with totally symmetric modes with metal–ligand stretching charac-

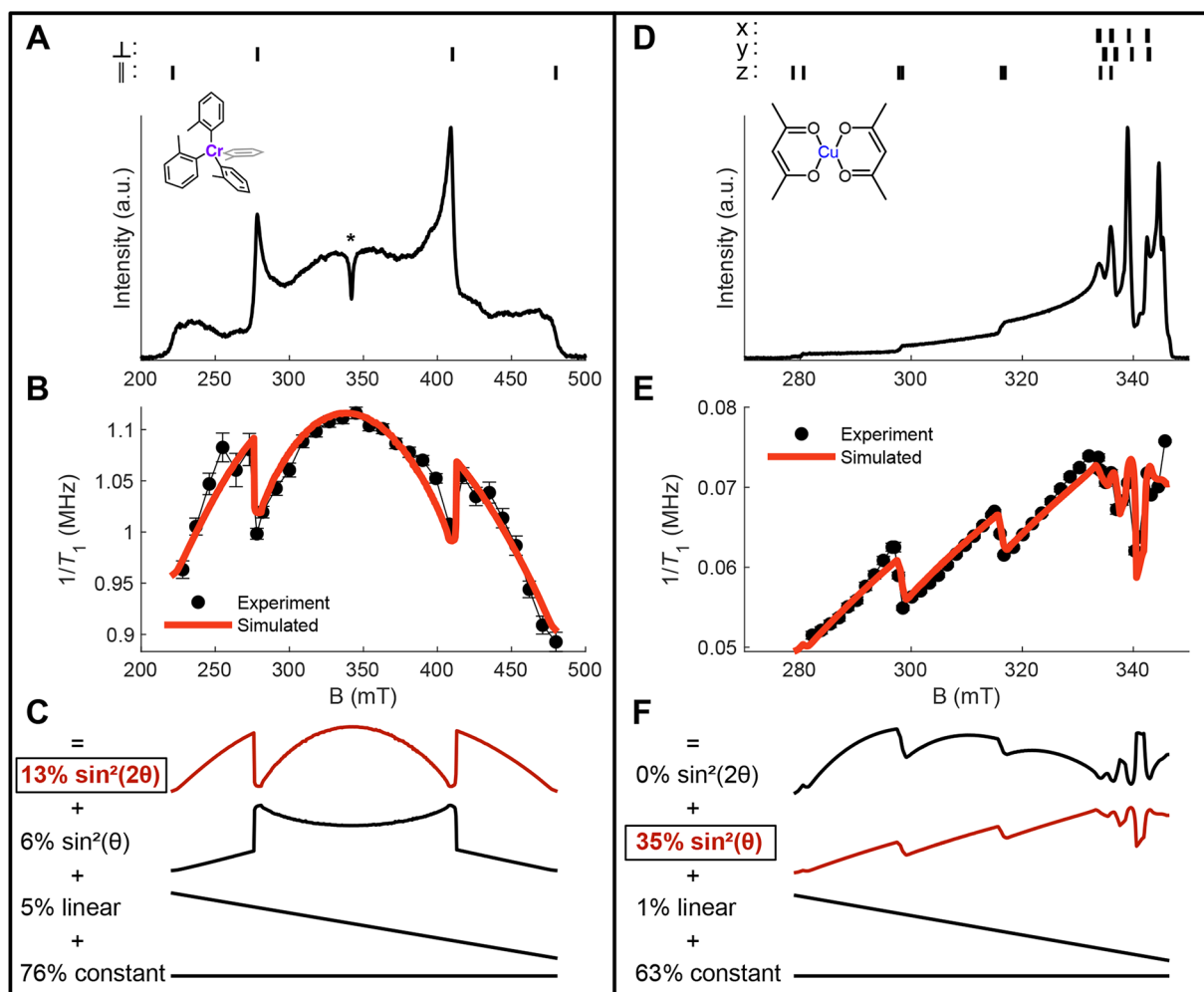


Figure 2. T_1 anisotropy at 40 K of (A–C) $\text{Cr}(\text{o-tolyl})_4$ and (D–F) $\text{Cu}(\text{acac})_2$. (A, D) X-band EDFs. (B, E) T_1 anisotropy by inversion recovery, overlaid with best fit. (C, F) Orientation functions used to construct the T_1 anisotropy fit.

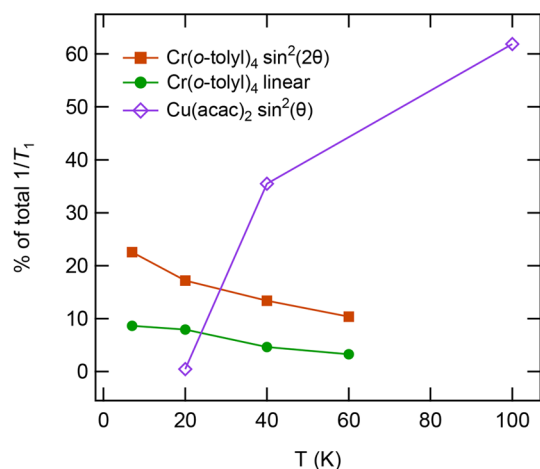


Figure 3. Temperature dependence of T_1 anisotropy contributions for $\text{Cr}(\text{o-tolyl})_4$ and $\text{Cu}(\text{acac})_2$.

ter^{29,32,33} inducing relaxation through a modulation of the minority spin component of the ligand field wave function.¹⁹ However, a new theoretical analysis is required to explain the $\sin^2(2\theta)$ anisotropy in $\text{Cr}(\text{o-tolyl})_4$. While $\sin^2(2\theta)$ T_1 anisotropy has not been previously characterized, T_m

anisotropy with a $\sin^2(2\theta)$ functional dependence has been observed in several $S = 1/2$ systems and has been attributed to rotational motion caused by librations.^{34–36} This induces a change in resonant field position described by $\text{d}B_{\text{res}}/\text{d}\theta$, which is determined by the derivative of the projected g value, $\text{d}g/\text{d}\theta$. The derivative of the g -tensor $\text{d}g/\text{d}Q$ has been successfully used as a simplified model for the spin-phonon coupling coefficient describing spin relaxation, where in this case the vibrational mode Q is equal to a rotation θ , so there may be a connection between $\text{d}B_{\text{res}}/\text{d}\theta$ and spin relaxation in this context as well. Note that here rotational motion refers specifically to any molecular movement that causes rotation of principal tensor axes of the magnetic Hamiltonian. This does not necessarily imply rigid rotor molecular rotations, and possibilities include coupled rotations of different molecules in the solid-state unit cell (pseudoacoustic or acoustic phonons), glassy librations, or molecular vibrations where the first coordination sphere and the extended ligand framework rotate in opposite directions (Supporting Information Section 6.1).

We therefore hypothesized that rotational motion from low-energy pseudoacoustic or acoustic phonons may explain the $\sin^2(2\theta)$ functional form of the $\text{Cr}(\text{o-tolyl})_4$ T_1 anisotropy. As the ZFS ($D = -0.117 \text{ cm}^{-1}$) is smaller than the Zeeman splitting energy at X-band (0.32 cm^{-1} for $g = 2$ at 340 mT), we assume the spins are aligned along the applied magnetic field

and treat the ZFS as a first-order perturbation to the Zeeman splitting of energy levels. Treating $\text{d}B_{\text{res}}/\text{d}\theta$ as a quantity proportional to the spin-flip matrix element for rotational motion, we obtain (Supporting Information Section 6):

$$\frac{1}{T_1} \propto \left| \frac{\partial B_{\text{res}}}{\partial \theta} \right|^2 = \frac{9D^2}{4\beta^2 g^2} \sin^2(2\theta) \quad (1)$$

Thus, the $\sin^2(2\theta)$ form is consistent with the expected T_1 anisotropy due to rotational motion. The decrease in the $\sin^2(2\theta)$ contribution to the T_1 anisotropy with increasing temperature also suggests that the rotational motion arises from low-energy acoustic or pseudoacoustic phonons. The latter may carry significant rotational character when there are multiple molecules per unit cell,²⁸ as is the case here ($Z = 10$).³⁷ Further exploration of structurally diverse $S = 1$ complexes will be required to ascertain the generality of the rotational $\sin^2(2\theta)$ contributions.

The T_1 anisotropy for $\text{Cr}(o\text{-tolyl})_4$ reduces in magnitude at higher temperatures as molecular vibrations begin to dominate spin relaxation through the Raman process. It remains to be asked why the $\text{Cr}(o\text{-tolyl})_4$ higher energy ($>100 \text{ cm}^{-1}$) molecular vibrations do not display T_1 anisotropy, while the $\text{Cu}(\text{acac})_2$ totally symmetric vibrations display strong $\sin^2(\theta)$ anisotropy. This phenomenon is explained by a consideration of the orbital angular momentum matrix elements for a square planar vs pseudo- T_d system. For D_{4h} $\text{Cu}(\text{acac})_2$, the $d(x^2 - y^2)$ ground state has an orbital angular momentum matrix element with the $d(xy)$ excited state of squared modulus 4, while the matrix elements with $d(xz)$ and $d(yz)$ each have a squared modulus of only 1.³³ These orbital angular momentum matrix elements control the amount of minority spin in the ground state wave function. Since the different excited states contribute to the wave function's minority spin along only some magnetic field orientations, the total minority spin for $\text{Cu}(\text{acac})_2$ is greater for the perpendicular orientation than for the parallel orientation, thus giving rise to anisotropic relaxation.¹⁹ However, in the cubic symmetry of the T_d point group, there can be no difference in matrix elements between the equivalent x , y , and z directions, so there can be no difference in the minority spin along different orientations. The small distortion from T_d required to produce nonzero ZFS^{25,38} is evidently too small to yield a significant $\sin^2(\theta)$ T_1 anisotropy in $\text{Cr}(o\text{-tolyl})_4$. Similar arguments were proposed to rationalize the presence of T_1 anisotropy in tetragonal nitridochromium(V) octaethylporphyrin and nitridochromium(V) tetratolylporphyrin, whereas the rhombic $\text{Cr}(\text{V})\text{O}(\text{HEBA})_2^-$ complex did not display appreciable T_1 anisotropy.^{27,39} Therefore, molecular vibrations (optical phonons) are likely to produce isotropic T_1 for $\text{Cr}(o\text{-tolyl})_4$, in contrast to the previously analyzed tetragonal $S = 1/2$ systems.

In summary, our findings provide the first direct evidence for ascribing features of spin relaxation to specific types of motion in an optically addressable molecular qubit. These degrees of freedom are distinct from the totally symmetric optical phonons implicated in $S = 1/2$ microwave addressable molecular systems. As such, these experimental data are critical for defining the nature of spin-phonon couplings and the mechanism of T_1 in theoretical approaches seeking to model spin relaxation lifetimes. We note that the rotational motion contributions analyzed here likely do not dominate spin relaxation rates for $T > 60 \text{ K}$, as the anisotropic component of

the spin relaxation is reduced at higher temperatures due to the increased role of high energy molecular vibrations (Figure 3). Nonetheless, restraining rotational motions for pseudo- T_d $\text{Cr}(\text{IV})$ is likely to prolong spin lifetimes. Such structure–function relationships for spin dynamics will be essential for designing molecular optically addressable qubits displaying room temperature coherence.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.3c01964>.

Experimental methods, temperature-dependent EPR fitting, T_1 anisotropy fitting, and theoretical derivation of T_1 anisotropy functional forms (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Ryan G. Hadt – Division of Chemistry and Chemical Engineering, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, United States; orcid.org/0000-0001-6026-1358; Email: rghadt@caltech.edu

Authors

Nathanael P. Kazmierczak – Division of Chemistry and Chemical Engineering, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, United States; orcid.org/0000-0002-7822-6769

Kaitlin M. Luedecke – Division of Chemistry and Chemical Engineering, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, United States; orcid.org/0000-0002-8163-9417

Elisabeth T. Gallmeier – Division of Chemistry and Chemical Engineering, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpclett.3c01964>

Author Contributions

[†]N.P.K. and K.M.L. are co-first authors.

Notes

The authors declare no competing financial interest.

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