

Ligand Field Effects on Electron Spin Relaxation on Molecular Qubits

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Quantum information science is a quickly growing field that aims to increase the power and speed of communication, computation, and sensing.^{1,2,3} A fundamental component of these technologies is the memory unit known as the quantum bit, or ‘qubit’.^{3,4} In the most simple definition, qubits are two-state quantum systems where are able to maintain spin orientation over extended periods of time.⁴ As such, $S = 1/2$ molecular systems, , are being explored due to their potential as simple two-state systems and their ease of tunability using coordination chemistry.¹ However, a major challenge facing the development of molecular qubits is decoherence – where the orientations of electron spins are perturbed due to interactions with the molecular environment.⁴ These decoherence pathways include coupling with lattice vibrations and magnetic noise. Typically, decoherence is quantified by the phase memory time T_m , which reflects the conservation of the relative orientation of spin phase angles.^{1,4,5} Recent studies have also used the spin relaxation time (T_1) of the electrons as another method of studying this effect.^{5,6} However, the interpretation of these parameters have often been phenomenological in nature.^{5,6} In the past few years, attention has been focused on elucidating the mechanisms of spin relaxation in molecular qubits with an aim towards the rational design of these molecules. Three research articles in particular provide important design principles which can be used to chemically tune qubits with improved coherence.

Recently, Kundu et al. reported on a Lu(II) complex with a high frequency clock transition, making the compound a promising qubit candidate.¹ Clock transitions are based on a two-level system where the energy gap separating Zeeman sublevels are insensitive to changes in the magnetic field (**Fig 1A**). These transitions arise from hyperfine interactions between unpaired electrons and the nucleus. The authors simulated the magnetic hyperfine splitting manifold of several lanthanide qubits through correlation with experimental electron spin echo EPR data. Further experiments elucidate a large clock transition resulting in very long phase memory times of up to $12 \pm 1 \mu\text{s}$ at 5 K and 410 mT, an improvement over previously reported times of $1.0 \pm 0.4 \mu\text{s}$. Interpretation of these data showed a significant nuclear quadrupole interaction, contributing to the hyperfine transition as well as the avoided-level crossing giving rise to the clock transition. Computational calculations demonstrate that the quadrupole interaction arises from the axial three-fold symmetry axis (**Fig. 1B**) of the molecule, implicating the role of the ligand field in engineering clock transitions. Further computational studies show that a large degree of *s*-orbital mixing into the lanthanide *d*-orbitals lead to enhancement of the transition. These results indicate that the tuning of electron-nuclear interaction and *s*-orbital mixing through molecular symmetry may serve as a design principle for engineering qubits with high frequency clock transitions and magnetic insensitivity.

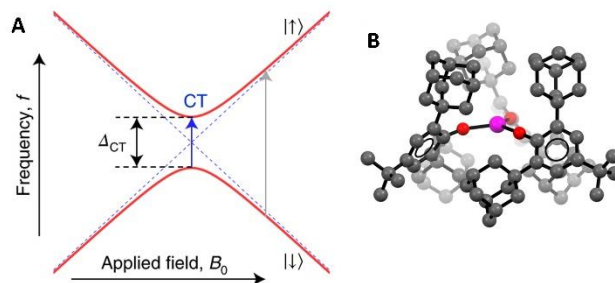


Figure 1. A) Schematic representation of clock transition and B) structure of lutetium (II) tris(aryloxide) adapted from Kundu et al.¹ Hydrogens atoms are omitted for clarity.

In a 2021 paper, Kazmierczak et al. used the principles of group theory to predict spin-phonon coupling pathways in qubits using molecular symmetry.⁶ When considering the first order spin-phonon coupling coefficient $\partial g_i / \partial Q_j$ (the rate of change of the g -value with respect to a vibrational mode), they determine that a ligand field excited state distortion along the vibrational normal mode is necessary for spin-phonon coupling to exist.^{6,7} The authors show that for such a distortion to occur, the symmetry of the excited state must meet certain requirements to be active in coupling. For nondegenerate states, only totally symmetric modes are allowed to participate in spin-phonon couple and provide a electron spin relaxation pathway. The authors apply this theory to computational calculations of two molecular qubits of different symmetries – copper (II) phthalocyanine (CuPc) with D_{4h} symmetry and vanadyl (IV) phthalocyanine (VOPc) with C_{4v} symmetry (**Fig. 2**). The data show that CuPc has a single spin-phonon active vibrational mode below 400 cm^{-1} while VOPc has five active modes, a finding consistent with the proposed theory. These low energy modes are those that dominate vibronic coupling at the low experimental temperatures. It is also shown that the orientation of the vibration, particularly in an axial system, may introduce additional coupling modes and that the existence of degenerate orbitals allows for non-totally symmetric modes to be spin phonon active. A thermally weighted model was then used to consistently correlate with experimental T_1 relaxation trends including features, such as crossover points, which could not previously be interpreted outside of phenomenological grounds. The authors also describe how descent in symmetry can be used to predict spin-phonon active modes and allow for selective ligand design in hindering active vibrations, introducing global symmetry as a design principle for decreasing electron relaxation pathways.

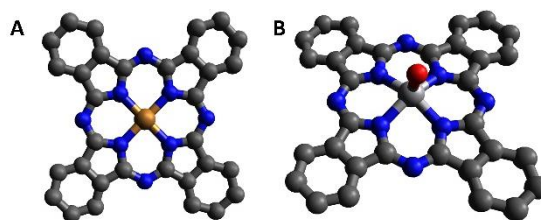


Figure 2. A) copper (II) phthalocyanine and B) vanadyl (IV) phthalocyanine adapted from Kazmierczak et al.⁶ Hydrogen atoms are omitted for clarity.

In a paper related to their previous work, Kazmierczak et al. demonstrate that similar ligand field approaches can be used to predict T_1 anisotropy – changes in spin relaxation time depending on the angle between an applied magnetic field and the molecular axis – thus providing a spectroscopic approach of understanding the mechanism of spin relaxation.⁵ Here, the authors perform a series of pulsed EPR studies of known qubit candidates over a range of molecular orientations. The spectroscopic technique is particularly powerful in this context as it provides anisotropic data, negating the need for single crystal samples. From the data, it is observed that T_1 is maximized and minimized at the parallel and perpendicular orientations respectively, indicating that vibrational modes principally affect spin relaxation as opposed to rotational motions. Furthermore, the EPR data demonstrate that T_1 anisotropy has no correlation with spin Hamiltonian parameters (e.g. g -values), necessitating the development of a new model to interpret the experimental trends. To address this challenge, the authors derive an expression for T_1 anisotropy on the basis of the spin-orbit coupled wavefunction of a model Cu(II) system. The resulting equation relates the T_1 anisotropy ratio with the vibronic coupling term of each orbital modulated by the energy of each state. From the expression, the authors observed that the spin relaxation along each orientation is affected by the extent of orbital mixing in response to a particular vibrational mode. By assuming equal excited state energy and a single dominant vibration, it is possible to simplify this expression of the T_1 anisotropy ratio to 2.5, consistent with the experimental results. Deviations from this average anisotropy value were determined to result from breakdowns in the above assumptions. In one qubit candidate, significant π contribution from the ligand implicated a low-lying excited state, resulting in a low T_1 anisotropy. In another molecular qubit, low lying vibronic modes contributed to spin relaxation, causing a large anisotropy. These deviations were well modeled by the original analytic expression as well as a proposed computational model. The findings from this paper provide a framework for leveraging ligand field effects and electronic structure in engineering qubits with anisotropic spin relaxation.

In summary, these recent studies demonstrate the importance of understanding the ligand field of molecular qubits to engineer species with low electron spin relaxation times. These works show that electron-nuclear and spin-orbit interactions can be tuned to decrease electronic and magnetic noise, thus decreasing the speed of qubit decoherence. Additionally, it is demonstrated that molecular symmetry can be used to predict the density of spin relaxation pathways and T_1 anisotropy. The design principles presented in these papers will allow the engineering of molecular qubits with greater precision and can aid in the development of other techniques for direct experimental insight into the mechanisms of decoherence.

References

1. Kundu, K.; White, J.R.K.; Moehring, S.A.; Yu, J.M.; Ziller, J.W.; Furche, F.; Evans, W.J.; Hill, S. A 9.2-GHz clock transition in a Lu(II) molecular spin qubit arising from a 3,467-MHz hyperfine interaction. *Nat. Chem.* **2022**, *14*, 392-397.
2. Wasielewski, M.R.; Forbes, M.D.E.; Frank, N.L.; et al. Exploiting chemistry and molecular systems for quantum information science. *Nat. Rev. Chem.* **2020**, *4*, 490–504.
3. Atzori, M.; Sessoli, R. The Second Quantum Revolution: Role and Challenges of Molecular Chemistry. *J. Am. Chem. Soc.* **2019**, *141* (29), 11339-11352.
4. Gaita-Ariño, A.; Luis, F.; Hill, S.; Coronado, E. Molecular Spins for Quantum Computation. *Nat. Chem.* **2019**, *11*, 301-309.
5. Kazmierczak, N.P.; Hadt, R.G. *J. Am. Chem. Soc.* **2022**, *144*, 20804-208114.
6. Kazmierczak, N.P.; Mirzoyan, R.; Hadt, R.G. *J. Am. Chem. Soc.* **2021**, *143*, 17305-17315.
7. Lunghi, A.; Sanvito, S. *Sci. Adv.* **2019**, *5* (9), aax7163.