



High-Field Pulsed EPR Studies of the Relaxation Profiles in $(n\text{-Bu}_3\text{NH})_2[\text{V}(\text{C}_6\text{H}_4\text{O}_2)_3]$

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Introduction

Fundamental investigations of paramagnetic transition metal complexes are of significant interest due to potential applications of these species in areas of spintronics and quantum computing. Focus on vanadium(IV) complexes is, of late, quite severe, owing to generally long spin-lattice and spin-spin relaxation times detected from X-band EPR spectroscopic methods. Indeed, these complexes have demonstrated the longest spin-spin relaxation times yet detected for metal-based molecules.^{1,2}

Applications of high magnetic fields induce high polarization in electronic spins and are thus important in potential future magnetic applications. For example, higher polarization induces higher signal to noise for imaging based on magnetic resonance. For applications in quantum computing, higher fields enable better initialization of all spin-based qubits into the same state.

The long observed relaxation times for vanadium-based qubit systems are all from X-band measurements, meaning applied fields of around 3600 G were necessary. The high-field behavior of molecules containing these ions is essentially unknown. Hence, we used the instrumentation of the Maglab to perform the first high-field test of magnetic relaxation times in a proof-of-concept vanadium(IV) molecular qubit system, $(n\text{-Bu}_3\text{NH})_2[\text{V}(\text{C}_6\text{H}_4\text{O}_2)_3]$ (**1**).^{3,4}

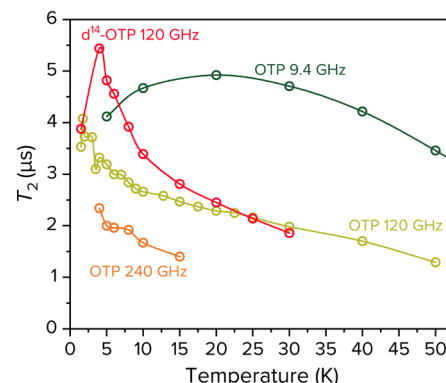


Fig.1 Variable-temperature T_2 data for **1** at variable frequencies and solvents (OTP and d^{14} -OTP). The color traces are guides to the eye.

Experimental

Two frozen glasses of **1** were made at approximately 0.1 mM concentration with protiated *o*-terphenyl (OTP) and deuterated *o*-terphenyl (d^{14} -OTP) as solvent. Inversion recovery and Hahn-echo pulsed experiments were performed as a function of temperature with a custom built heterodyne EPR 120/240/336 GHz spectrometer and its 12.5 T SC magnet.^{5,6}

Results and Discussion

Quantitation of T_1 was performed via inversion recovery measurements at variable temperatures at the maximum-amplitude position in the echo detected field-swept spectra, whereas T_2 was performed by application of two-pulse Hahn-echo sequences at variable temperatures. Under these conditions, the temperature dependence of T_1 and T_2 in **1** was discovered (see **Fig.1**). Interestingly, the T_2 parameters of **1** in OTP at 120 and 240 GHz are much shorter than those at 9.4 GHz. Similarly, T_1 also decreases at the higher frequencies, having a value of 71 ms at X-band frequency relative to 1 ms at 5 K.^{3,4} All parameters are temperature dependent, generally dropping in magnitude with increasing temperature.

Conclusions

The conclusions of the foregoing results are twofold. First, the strong temperature dependence of T_2 and the relatively short magnitude of T_1 indicate that spin-lattice relaxation is an important limiter of spin-spin relaxation times at the studied temperatures. Second, the strong T_1 dependence on magnetic field strength likely highlights the importance of the direct relaxation mechanisms in this temperature regime. Hence, V(IV) qubits comprise a qubit class wherein the traditional advantages of high magnetic field strength cannot be leveraged effectively.

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References

- [1] Zadrozny, J., *et al.*, ACS Cent. Sci., **1**, 488 (2015).
- [2] Yu, C.-J., *et al.*, J. Am. Chem. Soc., **138**, 14678 (2016).
- [3] Atzori, M., *et al.*, Inorg. Chem., **57**, 731 (2018).
- [4] Lin, C.-Y., *et al.*, Chem. Sci., Advance Article (2019).
- [5] van Tol, J., *et al.*, Rev. Sci. Instrum., **76**, 074101 (2005).
- [6] Morley, G., *et al.*, Rev. Sci. Instrum., **79**, 064703 (2008).