Electron Paramagnetic Resonance Spectroscopy: Continuous-Wave EPR for Spin-Counting and Pulsed EPR for Spin-Electric Coupling Measurements

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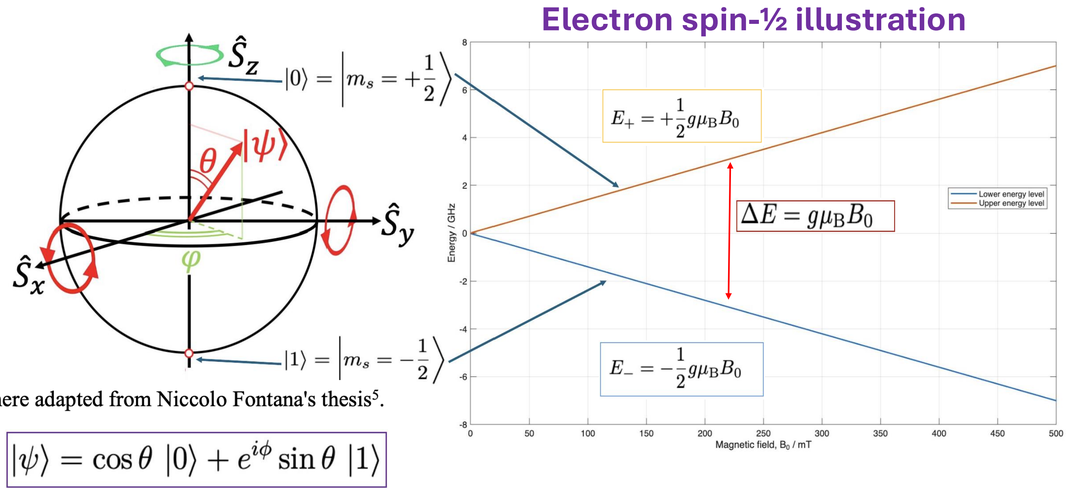
Introduction

Electron Paramagnetic Resonance (EPR) spectroscopy exploits the interaction of the magnetic moment of an unpaired electron with an external magnetic field. This interaction causes the electron's degenerate energy levels to split into discrete quantum states, an effect known as Zeeman splitting[1]. Spin-electric coupling (SEC) looks at moving away from magnetically driven transitions due to the potential advantages that using electric fields may offer. For example, electric fields can be confined to smaller spaces than magnetic fields, increasing the scalability of potential future quantum devices. Although electric-field effects in spin resonance have been studied since the 1960s, the modern molecular-magnet framework for SEC itself was advanced by Trif et al. in 2008. They proposed that in triangular molecular magnets, electric fields can couple to spin states though exchange interactions, spin-orbit coupling, and spin chirality[2]. Recent work has moved on from detecting SEC and towards chemically engineering it[3]. Three such examples of this are the chemically engineered ytterbium (trensal), ytterbium (trenpvan) and ytterbium (trenovan) detailed in this study[4].

Electron Paramagnetic Resonance Spectroscopy

Electron spin-½ illustration



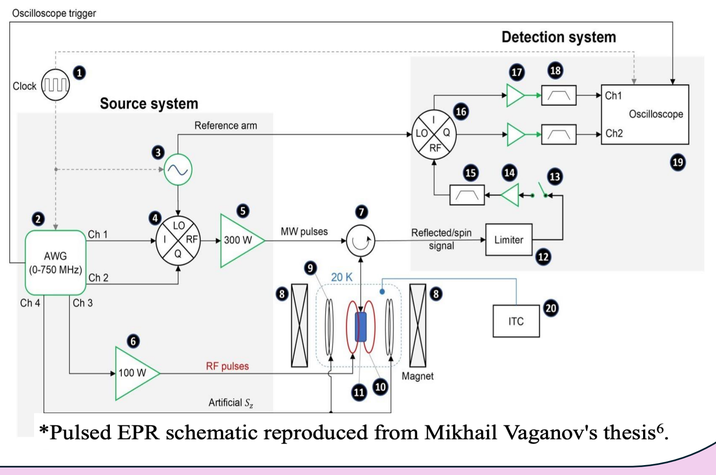
*Bloch sphere adapted from Niccolo Fontana's thesis[5].

$$|\psi\rangle = \cos\theta\ |0\rangle + e^{i\phi}\sin\theta\ |1\rangle$$

Pulsed EPR

Up-conversion:

- The resulting signal at port RF
$$u_{RF} = u_I \cdot u_{LO} + u_Q \cdot u_{LO}^{90°}.$$
- The I/Q phase selects the RF sideband, generating either the sum or difference frequency
$$\omega_{RF} = \omega_{LO} \pm \omega_{1F}.$$



*Pulsed EPR schematic reproduced from Mikhail Vaganov's thesis[6].

Continuous-Wave EPR example: Spin-Counting experiment

The Structure and Reaction

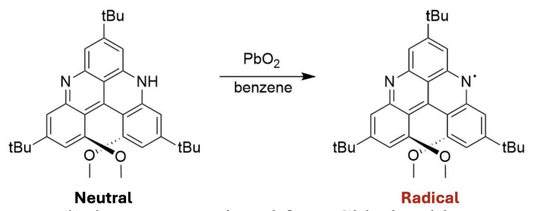
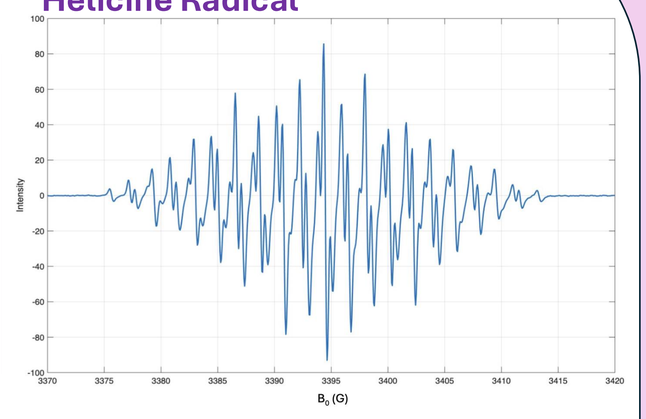
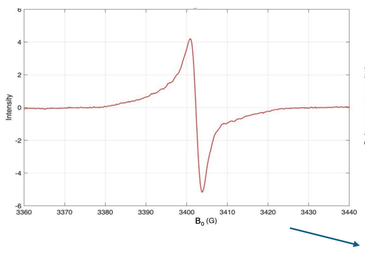


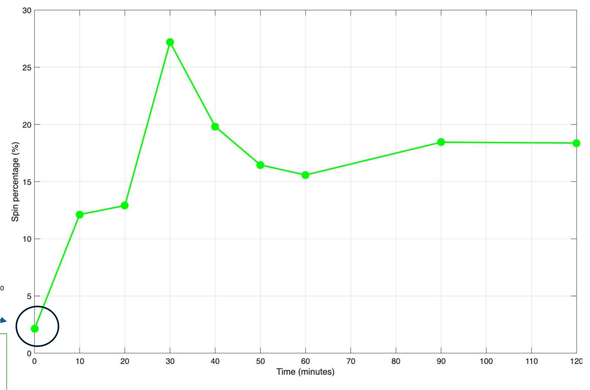
*Diagram reproduced from Chiral stable phenalenyl radical study[7].

Helicine Radical



KL104 Closed Shell molecule

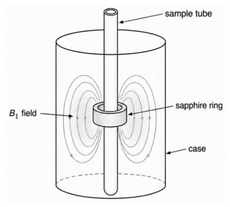




Methodology

- Lead Dioxide filtered out, stopping the reaction.
- EPR sample tube filled to 5mm in height.
- Intensity spectrum with double integral and two linear background subtractions.
- Background fraction 20%.

Inside Cavity:



$$S \propto \int_{V_S} B_1^2(\mathbf{r})n(\mathbf{r})dV$$

Pulsed EPR: Spin-electric Coupling

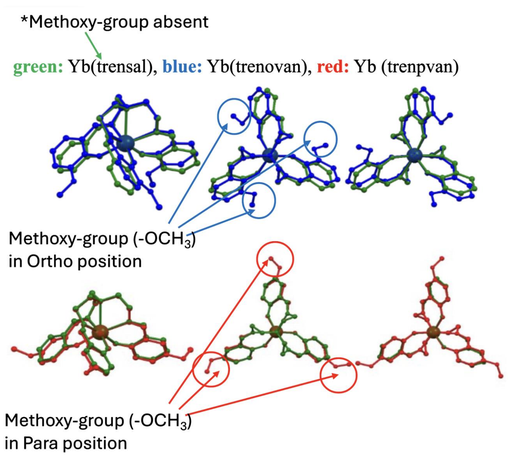


*Diagram adapted from Structural isomerism-tuned magnetisation study[4].

- The spin system is defined by a static spin Hamiltonian containing Zeeman, hyperfine and crystal-field terms
$$\hat{H} = \mu_B g_J \mathbf{B}_0^T \hat{\mathbf{J}} + A_J \hat{\mathbf{J}}^T \hat{\mathbf{I}} + \sum_{k=2,4,6}\sum_{q=-k}^{k} B_k^q \hat{\mathbf{O}}_k(\hat{\mathbf{J}}). \quad (1)$$
- At cryogenic temperatures, the lowest Kramers doublet can be represented as an effective spin-½ system
$$\hat{H}_{eff}^{S=1/2} = \mu_B \mathbf{B}_0^T \mathbf{g}\hat{\mathbf{S}} + \hat{\mathbf{S}}^T \mathbf{A}\hat{\mathbf{I}}. \quad (2)$$
- An applied electric-field perturbs the spin Hamiltonian
$$\hat{H}(\mathbf{E}) = \hat{H}(0) + \delta\hat{H}_{SEC}(\mathbf{E}). \quad (3)$$
- For Yb(trensal) this perturbation can be described as an electric-field-induced modulation of Stevens coefficients
$$\delta\hat{H}_{SEC}(\mathbf{E}) = \sum_{k,q} \delta B_k^q(\mathbf{E})\hat{O}_k^q(\hat{\mathbf{J}}). \quad (4)$$
- The spin-electric coupling for the transition from state i to state j is defined as
$$SEC_{ij} = \frac{\delta\nu_{ij}}{E} = \frac{\nu_{ij}(\mathbf{E}) - \nu_{ij}(0)}{E}. \quad (5)$$
- During the electric-field pulse, this frequency shift produces an accumulated phase
$$\phi_E = 2\pi t_E \delta\nu_{ij}. \quad (6)$$

*Equations adapted from the collection of references.

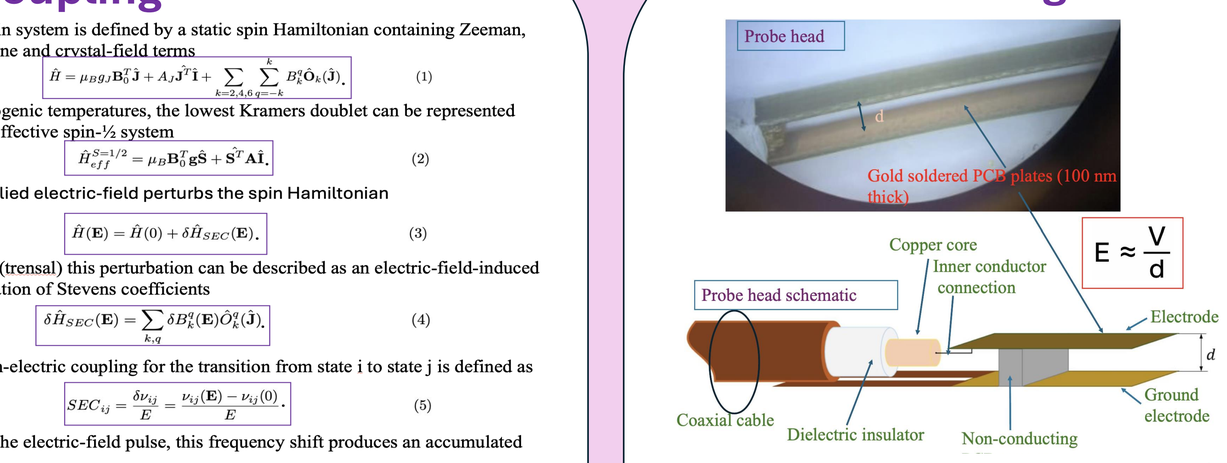
Previous Workings on Ytterbium(trensal)

Experimental details

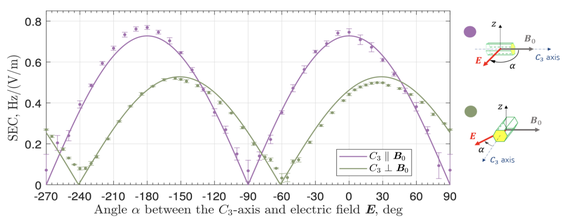
- T = 4.5 K
- 0.01 % Yb(trensal) diluted in Lu(trensal)
- Resonator operated under over coupled conditions

Methodology

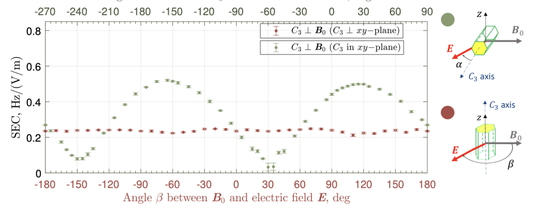
- DC E-field delivered using an inserted E-field probe
- **MD5 Resonator:** dielectric ring, therefore spatial separation
- E-field probe inserted from the top port; crystal inserted from the bottom port
- Static magnetic field B_0 applied horizontally, defining the laboratory z-axis
- Measurements performed using **pulsed X-band ESR**
- 0º-360º sample rotation
- Six different orientations measured



*Probe head schematic adapted from Mikhail Vaganov's thesis[6].



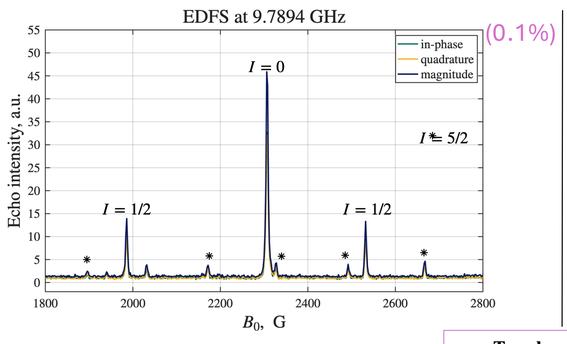
*SEC results reproduced from Mikhail Vaganov's thesis[6].

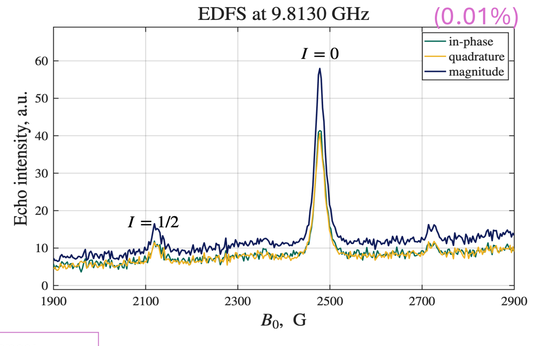


Discussion

- Green and purple orientations are well described by a simple angular SEC model
- SEC remains non-zero across the full angular range
- Red orientation nearly angle-independent, varying between 0.23 and 0.25 Hz/(V/m)
- A full Stevens-parameter fit requires an additional DC offset term

Ytterbium (trenpvan) and Ytterbium (trenovan)





T_1 pulse sequence:

$$\pi - T - \frac{\pi}{2} - \tau - \pi - \tau$$

T_2 pulse sequence:

$$\frac{\pi}{2} - \tau - \pi - \tau$$

Table 1: T_2 relaxation times for Yb(trensal) and Yb(trenpvan).

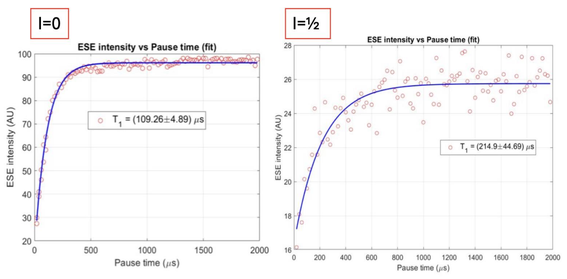
I_{Yb}	Yb(trensal), 0.01% $T_2/\mu s$	Yb(trenpvan), 0.1% T_2/ns
0	1.45 ± 0.01	151
1/2	2.41 ± 0.02	259
5/2	2.85 ± 0.06	368

Values ~10x smaller

Table 2: T_1 relaxation times for Yb(trensal) and Yb(trenpvan).

I_{Yb}	Yb(trensal), 0.01% $T_1/\mu s$	Yb(trenpvan), 0.1% $T_1/\mu s$
0	241 ± 19	353 ± 4
1/2	440 ± 20	369 ± 8
5/2	500 ± 40	420 ± 31

Values consistent



Further Workings

- Performing cryogenic continuous-wave thin-film EPR measurements.
- Assembling the Queen Mary University of London pulsed spectrometer, including programming the microwave bridge and connecting the detection system.
- Evaluating the E-field dependence of Yb(trenpvan) and Yb(trenovan). This should hopefully explain the strange perpendicular-orientation SEC behaviour.

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