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ABSTRACT BOOKLET

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Making Double Quantum Coherence (DQC) ESR Great Again: An Intrinsically Disordered Protein

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ESR pulsed dipolar spectroscopy (PDS) enables distance measurements in the 10–80 Å range, providing structural insights into doubly spin-labeled proteins. The six-pulse double quantum coherence (DQC) ESR experiment—developed at ACERT Cornell beginning in 1997—has played a central role in structural biology applications, particularly in studies conducted between the early 2000s and 2015 using home-built instrumentation. Over the past decade, significant advances in theoretical modeling and data analysis have facilitated the transition of DQC ESR to commercial spectrometers. These developments have expanded its applicability, enabling improved characterization of conformational heterogeneity in intrinsically disordered proteins.

Flavin Receptors as Biological Qubits for Signal Transduction

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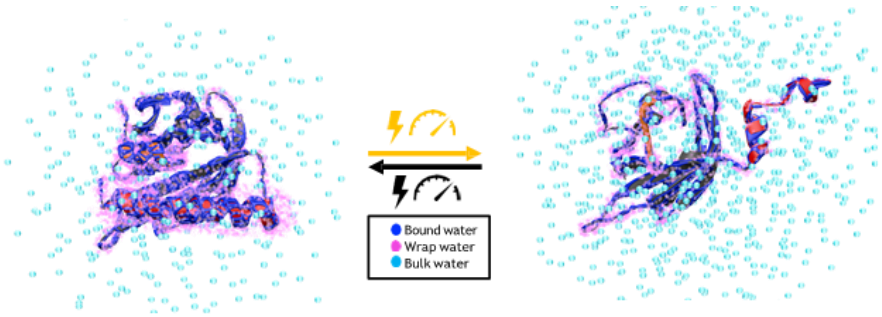
The mechanism by which proteins convert light into mechanical work remains a fundamental question in biology. This study investigates the hypothesis that blue-light activation of the LOV2 domain from Avena sativa phototropin 1 (AsLOV2) triggers concerted water movements that drive protein conformational extension.Using electron and nuclear magnetic resonance spectroscopy combined with high-pressure molecular dynamics simulations, we demonstrate that AsLOV2 activation can be initiated by either blue light or elevated hydrostatic pressure. In both cases, activation is accompanied by the selective and concerted expulsion of low-entropy, tetrahedrally coordinated “wrap” water molecules from the protein's hydration shell — particularly from interfacial regions. These results indicate that hydration water acts as an integral component in reshaping the protein's free energy landscape during activation.

Our findings position interfacial hydration water as an active hydraulic medium capable of powering long- range conformational changes that underlie light-driven protein mechanics. This mechanism provides a novel framework for engineering externally controllable protein-based actuators (e.g., for synthetic biology or smart materials applications).

Furthermore, we observe that blue-light excitation of the FMN chromophore in wild-type AsLOV2 induces spin-state-dependent processes that become evident at higher magnetic fields, demonstrated with a pronounced magnetic field-dependent modulation of fluorescence emission. These magneto-optical effects naturally raise the question: Does hydrostatic pressure elicit analogous spin-dependent processes in AsLOV2? More broadly, can targeted experiments determine whether — and through what mechanisms — quantum spin effects contribute to the control of biological activity in this system?



Magnetoelectric phenomena in EPR: renaissance and perspectives

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Magnetoelectricity is the appearance of changes in electric polarization due to magnetic fields, or of changes in magnetization due to electric fields. Very recently, it has appeared in the panoply of phenomena observed in Molecular Magnetism and has generated significant interest, partly due to the perspective of constructing electrically controllable molecular spin qubits, either based on single spins[1] or on spin-chiral triangles.[2] These latter were predicted to possess long decoherence times by virtue of being mapped onto a protected subspace.[3]

Electron Paramagnetic Resonance (EPR) spectroscopy has proven to be a particularly powerful technique in demonstrating ME phenomena through different variants of the technique: (i) continuous-wave (CW) EPR under static E-fields,[4] (ii) pulse EPR under pulsed E-fields[5] and (iii) Electric-Field Modulated EPR (EFM-EPR), which involves substitution of the modulated magnetic field of CW EPR by a modulated E-field and lock-in detection.[6]

This talk will describe these variants and recent experimental results obtained from spin triangles and paramagnetic species. It will also make connections with techniques such as THz spectroscopy[7] and dielectric/magnetoelectric spectroscopy.[8] As will be argued, such methods will need to gradually become part of standard study protocols for the in-depth understanding of spin-electric phenomena.

Keywords: magnetoelectric coupling – E-field EPR – spin chirality.

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Magnetic Field Induced Berezinskii-Kosterlitz-Thouless Correlations in 3-Dimensional Manganites: An Uncommon Example of TBKT > TN in Multiferroic TbMnO3

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Under an appropriate applied magnetic field, magnetic correlations in nominally *three- dimensional* (3D) materials can effectively become *two-dimensional* (2D) as shown [1] by the temperature dependence of the EPR linewidth ΔH(T) obeying the celebrated Berezinskii-Kosterlitz-Thouless (BKT) theory originally formulated for 2D systems [2]. In this work we provide evidence that this is a more general phenomenon and a large number of materials exhibit this 'magnetic field induced 3D to 2D transformation'. We analyse ΔH(T) of a number of three-dimensional doped rare earth manganites and the multiferroics DyMnO3 and TbMnO3 and find that the BKT model based equation

$$\Delta H_{BKT}(T) = A \exp(3b/(T/T_{BKT} - 1)^{\nu}) + mT + \Delta H_0$$

provides a better fit to ΔH(T) compared to the commonly used critical state model or the spin freezing model [3]. Here A is a proportionality constant, TBKT is the BKT transition temperature, b = π/2 for a square lattice, ν= 0.5 and the last two terms account for the linear temperature dependence, if any, and the residual linewidth at high temperature, respectively. It is commonly expected that TBKT < TN where TN is the 3-D ordering temperature such as an antiferromagnetic transition temperature. Surprisingly, in TbMnO3 [4], we find that the opposite is true with TBKT > TN. We infer, following a recent theoretical work [5], that this result is a consequence of the presence of intermediate range magnetoelastic interactions in the material.

Keywords: Field induced two dimensionality, BKT correlations

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Exploring the limits of pulse dipolar EPR spectroscopy

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Nanometre distance measurements by pulse dipolar EPR spectroscopy (PDS) have been enjoying increasing popularity in integrated structural biology. We serendipitously found that routine RIDME measurements between nitroxide (NO) spin labels and copper(II) centres[1] are feasiblein submicromolar protein concentrations. A systematic study of the concentration limits of PELDOR and RIDME experiments using these spin centres[2] led to combining trityl- based spin labels with copper(II) and variable-time RIDME[3] allowed measuring distances in a 10 nM protein sample.[4]

While the exploration of the sensitivity floor was limited to short distances, we were interested in the long-distance limit of PDS experiments in proteins. Using an antiparallel coiled-coil protein has allowed us to measure PELDOR distances of >10 nm by deuterating all exchangeable proteins and >17 nm by fully deuterating the protein. Sensitivity considerations will be discussed and current data suggests that measurements up to 20 nm are achievable.[5]

Keywords: PELDOR, DEER, RIDME, distance limit, concentration limit

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Non-Uniform Sampling for Pulsed Dipolar Electron Spin Resonance Spectroscopy

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Pulsed Dipolar Electron Spin Resonance Spectroscopy (PDS) is a uniquely powerful technique to measure the unbiased shaped of distance distribution P(r) between two radicals (i.e., those containing unpaired electron spin(s))[1,2]. However, PDS study time takes several hours to obtain a single trace. There are multiple methods to reduce data collection time by increasing the signal-to-noise (SNR) reducing signal averaging time, such as raising the RF power, increasing sample concentration, solvent deuteration[3], protein deuteration[4] or wavelet denoising[5]. Here we introduce another approach to reduce the data collection times by employing non-uniform sampling in PDS experiments. By selectively sampling time-domain points based on their contribution to distance distribution P(r) rather than uniformly, non-uniform sampling significantly reduces data acquisition time without compromising the quality of the reconstructed distance distribution P(r). Our implementation of non-uniform sampling on DEER data successfully reconstructs the distance distribution P(r) within the 95% uncertainty range of the reconstruction obtained from fully sampled data, while requiring 30%-40% of the data. This approach can enhance experimental throughput, approximately reducing data collection time for Q- band by 7-8 hours for a data collection time of 12 hours, and for X-band by 20-28 hours (for standard data collection time: 40 hours). Additionally, this methodology can be used in combination with the aforementioned time reduction techniques to further reduce the data collection time.

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1. Hadamard-Encoded Acquisition for Pulsed EPR Spectroscopy

2.

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8. Frequency-domain pulsed ENDOR is widely used for extracting local structure in paramagnetic systems, but it often suffers from low sensitivity, especially when targeting weak hyperfine couplings corresponding to long electron–nuclear distances or nuclei of low abundance. We present an Hadamard-encoded acquisition strategy that replaces point-by-point frequency stepping with frequency multiplexing: multiple nuclear transition frequencies are excited within a single pulse sequence (either simultaneously or as a short train), and the spectrum is reconstructed by Hadamard decoding. This multiplex advantage reduces baseline noise while preserving spectral resolution (Fig. 1). We implement the method for W-band Mims ^{19}F ENDOR and analyze practical limits imposed by radiofrequency (RF) power, pulse distortions, and relaxation during extended mixing periods. Experiments on fluorine containing radicals and spin-labeled proteins demonstrate consistent sensitivity gains, including up to a two-fold improvement in signal-to-noise ratio, translating to substantially faster acquisitions for long-distance measurements. For fast-relaxing paramagnetic metal complexes, simultaneous multiplexing avoids signal loss and yields robust enhancements.

9. The approach is general and can be transferred to other EPR techniques relying on frequency sweeps, such as ELDOR, ODMR or frequency-domain EPR. We illustrate this generality by applying Hadamard-encoding to ELDOR-detected NMR spectra.

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11. Keywords: ENDOR; pulsed EPR; Hadamard transform; frequency multiplexing; sensitivity enhancement

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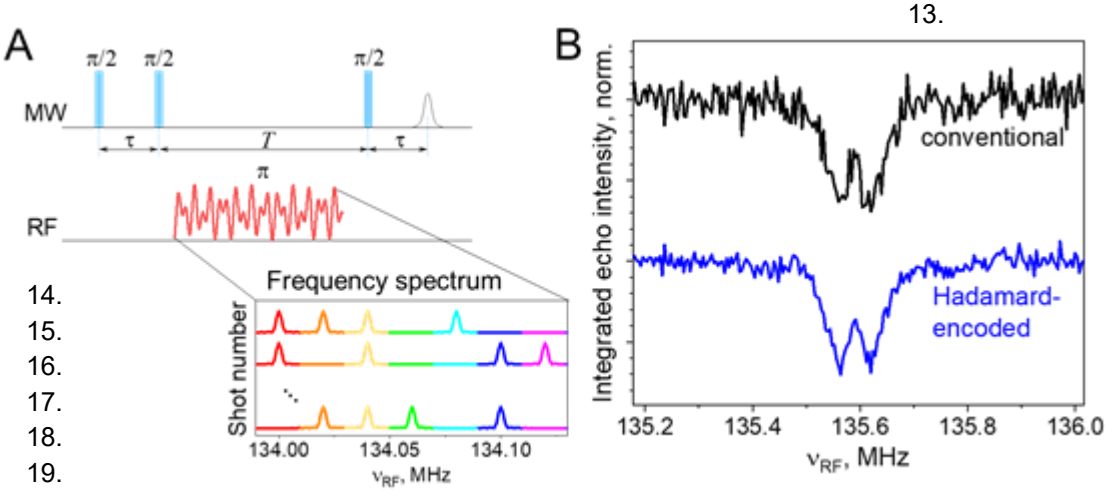

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22. Fig. 1. (A) Illustration of a pulse sequence for Hadamard-encoded Mims ENDOR acquisition. (B) Conventional and Hadamard-encoded ^{19}F ENDOR spectra of a fluorinated trytil radical.

23.

Electron Paramagnetic Resonance: Insights into Spin Dynamics of Switchable Magnetic Materials

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Electron Paramagnetic Resonance (EPR) spectroscopy serves as an essential tool for exploring the spin dynamics, local electronic configurations, and magnetic exchange interactions within switchable molecular magnetic materials exhibiting molecular bistability, such as spin crossover (SCO), single molecule magnet (SMM), and metal-to-metal electron transfer (MMET).[1] Due to the reversible stimuli-induced transitions, these systems experience changes between various magnetic states (such as low-spin/high-spin or diamagnetic/paramagnetic).[2] EPR offers direct, state-sensitive insights into unpaired electrons and their surroundings. This technique facilitates the accurate measurement of anisotropy, zero-field splitting, spin-orbit coupling, relaxation times, and spin–spin interactions, all of which are vital for understanding magnetic bistability and switching mechanisms.

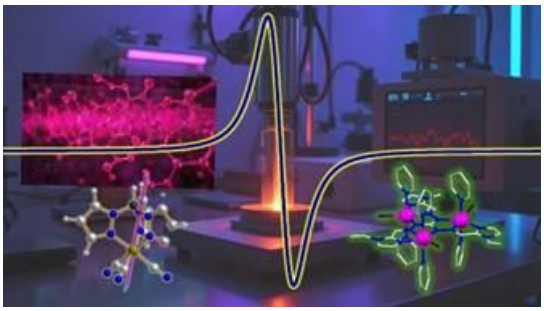

Figure 1: Illustrative representation of the EPR technique as a characterization tool for switchable molecular magnets.

EPR spectroscopy also emerged as an innovative measurement tool for molecular spin-frustrated triangles (M3). Theoretical predictions suggest that the triangles exhibit spin-electric or magnetoelectric coupling, with significant promise for quantum information technology.[3] The possibility of nanoscale manipulation of spin-states by the application of an electric field offers several advantages over the standard magnetic field-based control of spin-states.[4] Experimentally, the M3 systems based on 3d transition metals have been explored to reveal spin electric coupling by utilizing voltage pulses for modulating the phase accumulation within spin-echo sequences in pulsed EPR experiments.[5-7] Despite the rapid experimental progress in this field over the last decade, the role of spin anisotropy, antisymmetric exchange interactions and structural distortions in driving the strength of magnetoelectric coupling effects remains surprisingly missing. We can compare structurally similar spin triangles to reveal the role of the magnetic nuclei of the metal ions in promoting intrinsic decoherence through spin–spin hyperfine interactions using pulsed EPR experiments.

Keywords: Molecular Spin-frustrated Triangles, Spin-Electric coupling, Magnetoelectric coupling

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Toward Ambient-Stable Radical Complexes *via* a Metal-to-Ligand Electron Transfer Strategy

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Open-shell complexes are ubiquitous in chemistry. Nonetheless, the transitory to persistent nature of these radical species often limits their practical applications. Stabilizing π-radical complexes, particularly those containing multiple spin centers, remains a significant challenge for synthetic chemists. In discrete molecular systems, ligand-centered radicals tend to undergo spin pairing, which frequently leads to the formation of singlet diradicals (S = 0) through antiparallel spin exchange interactions, ultimately resulting in overall diamagnetism. Consequently, the development of effective and convenient strategies to stabilize homo-spin π-diradicals under ambient conditions is highly desirable. Herein, we discuss a strategy for generating ambient-stable mono- and diradical complexes through a single-pot metal-to-ligand electron transfer (MLET) during metal–ligand bond formation. The present approach employs a strongly π-accepting ligand framework incorporating azo groups, designed to efficiently handover of electron density from the metal to the coordinated ligand, leading to the formation of ligand-centered radical species during complexation. Notably, the radical complexes are generated *in situ* during the reaction without the need for external oxidants or reductants, simplifying the synthetic pathway and minimizing competing side reactions. Structural, spectroscopic, and electrochemical analyses confirm the formation of ligand radicals, facilitated by the extended π-conjugation and electron-withdrawing nature of the bis-azo chromophore. The resulting π-radical complexes exhibit indefinite ambient stability, highlighting the crucial role of potent π-accepting ligands (pull-down approach of LUMO). This strategy provides an efficient route for stabilising radical complexes and establishes a conceptual framework for designing metal-bound radical architectures through intrinsic electronic communication between metal and redox-active ligands.

Keywords: bis-azo ligands, redox non-innocent ligands, metal-to-ligand electron transfer, p-Radical Complex, ambient stable radical.

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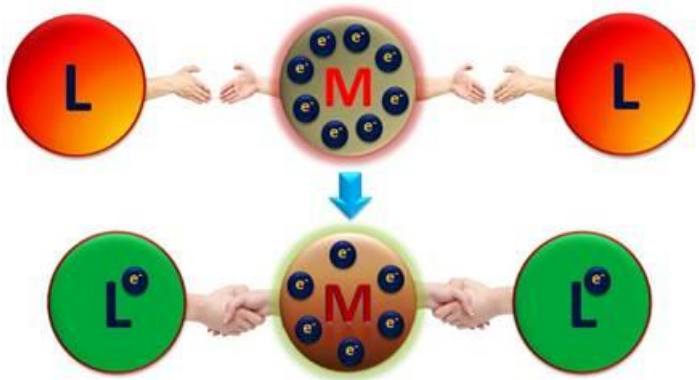

Uncovering a Multispecies Radical Network in UV-Irradiated Pyruvic Acid

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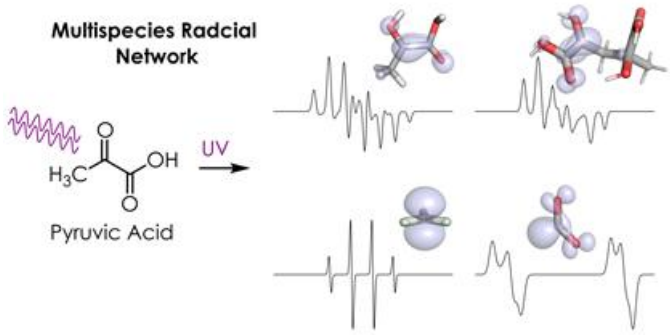

α-Keto acids readily form radicals upon UV irradiation, governing their role in atmospheric photochemistry and enabling their use as endogenous radical precursors in dissolution dynamic nuclear polarization (dDNP). Despite their widespread appearance, the radical chemistry of UV-irradiated pyruvic acid is commonly simplified to a single ketyl species, obscuring the complexity of its photochemical behavior.

Here, we combine isotope labeling with time-resolved and temperature-dependent electron paramagnetic resonance (EPR) spectroscopy to resolve the radical composition formed in UV-irradiated pyruvic acid at cryogenic temperatures. X-band (9.5 GHz) EPR measurements reveal irradiation-time-dependent spectral evolution and distinct thermal decay behaviors that cannot be explained by a single radical species. High-field EPR (94 GHz) and DFT-guided spectral simulations enable deconvolution and assignment of at least four coexisting radicals.

We identify the dominant monomeric ketyl radical, alongside a methyl radical, a carboxylate radical anion, and a thermally persistent covalent dimer ketyl species. These radicals exhibit markedly different formation kinetics and annihilation temperatures, defining a multispecies radical network rather than a single reactive intermediate.

Our findings reconcile solid-state EPR observations with known aqueous photochemical pathways of α-keto acids and provide a mechanistic framework for understanding radical stability and reactivity in UV-irradiated pyruvic acid. This multispecies perspective has direct implications for atmospheric chemistry models and for the optimization and reproducibility of dDNP experiments relying on photo-generated radicals.

Keywords: Radicals; EPR spectroscopy; Photochemistry; Pyruvic acid; Hyperpolarization

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Synthesis and Characterisation of Stable Metal-Radical Complexes by EPR Spectroscopy

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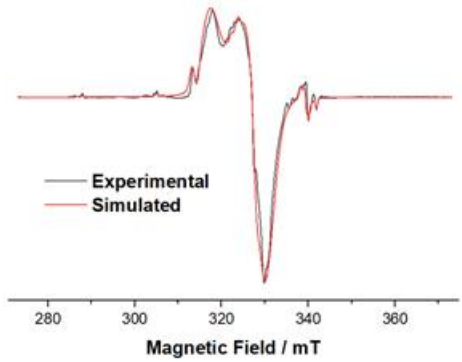
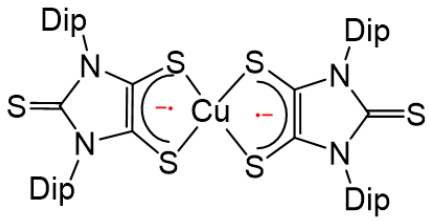
Metal-radical complexes supported by redox-active ligands have emerged as an important class of systems for understanding metal-ligand electronic communication and magnetic behaviour. Electron paramagnetic resonance (EPR) spectroscopy serves as a key technique for probing the distribution of unpaired electron density in such systems. The assistance from signal fitting tools is inevitable regarding the cognizance derived from EPR spectroscopic analysis. This abstract provides an outlook into various stable metal-radical complexes and EPR spectral analysis methodology, focusing on signal fitting through simulation using EasySpin[1] based on MATLAB software.

Our results reveal a clear relationship between the anisotropy of the *g*-tensor and the extent of spin delocalization over the metal center and the NHC ligand framework.

This combined EPR simulation-spin density approach provides a powerful framework for interpreting experimental spectra and offers deeper insight into metal-ligand electronic coupling in metal-radical systems.





$[Cu(II)(SS\text{-}NHC{=}S)_2]$

Figure 1. X-band EPR spectrum (black) of the $[Cu(II)(SS\text{-}NHC{=}S)_2]$ at liquid nitrogen temperature in THF. Red and black lines represent the simulated and the experimental spectra of $[Cu(II)(SS\text{-}NHC{=}S)_2]$ and the simulation is done using the EasySpin program.

Keywords: Metal–radical complexes, Electron paramagnetic resonance (EPR), Redox-active ligands, g-tensor anisotropy, Spin delocalization.

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Photo-Chemical and Thermal Generation of Carbon-Dioxide radical- anion Probed by Spin-trapping EPR Method.

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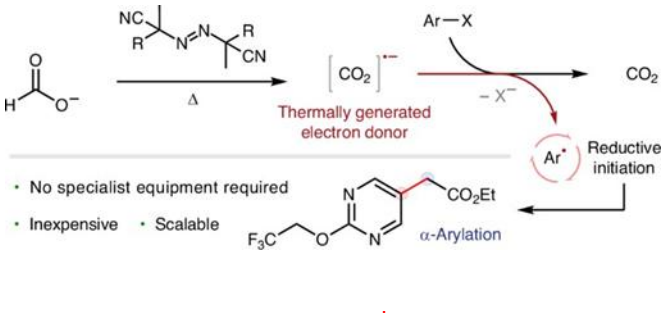
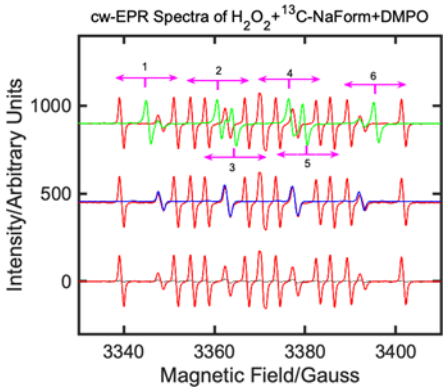
Radical chain initiation approaches play a crucial role in the production of both small-molecule pharmaceuticals and polymeric materials.[1-3] Contemporary initiation techniques based on single-electron reduction are primarily reliant on photochemical and electrochemical processes; Although effective, the practical application of these methods on an industrial scale is often constrained by challenges related to scalability and operational complexity. To address these limitations, we have recently developed a versatile, thermally activated, and industrially scalable approach for reductive radical chain initiation.[4] This methodology has been successfully applied to the α-arylation of aryl(hetero)-halides and is proposed to proceed through the generation of a carbon dioxide radical anion, formed via the reaction of an inexpensive azo-based initiator with a formate salt.



(a) Proposed mechanism for the CO2-anion generation



(b) EPR spectra of DMPO- C-adduct

In this presentation, we report a comprehensive spectroscopic investigation into the formation of the carbon dioxide radical anion using a spin-trapping approach. Thermal and photochemical initiation methods, together with ^{13}C-enriched formate salts, were employed to enable the unambiguous identification of this transient radical species.[5] The effects of solvent environments, including DMSO, water, and mixed-solvent systems, on the detection and stabilization of the short-lived radical intermediate were systematically examined. These findings provide new mechanistic insight into the generation and reactivity of carbon dioxide radical species and elucidate their critical role in the α-arylation of aryl(hetero)-halide substrates.

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SET – driven radical formation in nitroaromatics

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Knowledge of radical electronic structures enables the control of their properties and opens the potential of fine controlling their reactivity. Therefore, EPR is an unmatched technique, needed for the electronic structure characterization of organic radicals. However, the reactive nature of radicals and non-trivial preparational requirements limit the number of usable radical species until now. Enabling the generation of radical species under simple reaction conditions, employing available and inexpensive reactants, is therefore the key component for harnessing the extraordinary properties of organic radicals. In our recent work on nitrobenzene, we uncovered a radical formation process by a thermal single electron transfer (SET) from multiple anionic organo-bases[1]. I will show how the scope of this SET-driven radical formation can be expanded to the wider family of nitroaromatics, employing cw-EPR spectroscopy and DFT calculations. The understanding of the electronic structures of these radical pairs enables the utilization of radical compounds as reacting agents under mild synthetic conditions, laying the foundation for a new class of distinctive reaction mechanisms and thus unexplored opportunities in organic synthesis.

Keywords: single electron transfer (SET), organic radicals, Nitroaromatics

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Frequency and Bandwidth Agile Photonic Band Gap Resonators for Pulse ESR at 35 GHz and Higher Frequencies

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6. Resonant circuits are vital components of magnetic resonance spectrometers, where high-quality factor (Q) probeheads enhance sensitivity through stronger transverse microwave fields (B_1e) and improved noise rejection. Performance of conventional metallic resonators for ESR is limited by frequency-dependent conduction losses, restricting achievable Q-factors to approximately 10,000 at X-band (9.5 GHz) and only 2,000–3,000 at W-band (95 GHz). While using superconducting materials can boost Q, this approach requires cryogenic operation and restricts sample conditions. This work describes a new class of millimeter-wave resonators based on one-dimensional photonic band gap (PBG) crystals, offering a fundamentally different approach to high-Q performance even at room temperature. Unlike our earlier PBG resonators with fixed coupling, the newly developed architecture enables fully tunable external coupling across under-, critical-, and over-coupled regimes, facilitating precise impedance matching and bandwidth control for pulsed EPR experiments. A Q-band (34 GHz) oversized PBG resonator constructed from 2-inch sapphire discs achieved an unloaded quality factor of 27,300 ± 2,300 at room temperature under critical coupling (β = 1.06 ± 0.18) - approximately twenty-fold greater than typical commercial Q-band EPR resonators. Integration into a Bruker E580 Q-band spectrometer produced at least ten-fold improvement in concentration sensitivity for echo-detected nitroxide signals. Additionally, a dual-mode implementation and a PBG configuration with adjustable mode separation were demonstrated, enabling double electron–electron resonance (DEER) experiments. PBG resonators for W-band (95 GHz) pulse EPR are also described. These advances highlight the potential of photonic band gap resonators to significantly extend the sensitivity of pulsed EPR. Supported by NIH R01GM130821.
7.

EPR spectroscopy at the interface to NMR: new experimental designs for biomolecular sciences

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Latest developments in magnetic resonance spectroscopy are aimed at increasing sensitivity and resolution for nuclear spin detection. Paramagnetic centers are natural sources of spin polarization and selective spin probes for structural information, as recognized decades ago in the field of hyperfine spectroscopy. Particularly, electron-nuclear double resonance ENDOR can probe interactions as small as few kHz. The talk will illustrate recent progress in ENDOR polarization transfer experiments. We have recently introduced ^{19}F for distance measurements in biology [1], as well as time-domain pulse dipolar hyperfine spectroscopy (PDHS). PDHS filters hyperfine couplings from other nuclear interactions [2], giving access to hyperfine distance distributions at spectral resolutions down to 1 kHz. Information content in ^{19}F ENDOR can be complemented by broadband chirp pulses, which increase resolution in orientation selection dimension [3]. Finally, paramagnetic centers can be employed to increase NMR signals in liquids via the scalar Overhauser effect [4]. Recent developments in hardware are permitting NMR screening of small molecules with one to two orders of magnitude better sensitivity.

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Progress in pulsed dynamic nuclear polarization

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Magic-angle-spinning NMR in combination with dynamic nuclear polarization (MAS DNP) has traditionally relied on continuous, monochromatic microwave irradiation. We aim to change that by designing DNP pulse sequences. Pulsed MAS DNP is likely to offer increased sensitivity and flexibility.

Pulsed DNP experiments are currently restricted to low magnetic fields. The reason is that suitable microwave sources are not available above 95 GHz (3.4 T, 144 MHz). The design and construction of such sources is, however, an active field of research.

The theoretical description of a one-time magnetization transfer between an unpaired electron coupled to a nearby nuclear spin is under control.[1] Perturbation theory approaches, such as average-Hamiltonian and Floquet theories, have found convenient use in DNP pulse sequence design. This has led to a surge of new DNP sequences, of which X-inverse-X (XiX)[2] and adiabatic solid-effect (ASE)[3] are the most efficient.

In a MAS DNP sample, each polarizing agent serves 100-1000s of nuclear spins. To hyperpolarize these nuclei, a DNP pulse sequence must be applied many times. Thus, analysis of merely the one-time magnetization transfer is an oversimplification. We recently developed the simulation of pulsed DNP in the steady state.[4] This enabled accurate prediction of the optimal repetition time of a DNP sequence.

Intriguingly, magnetization trajectories during a one-time transfer differ from the steady orbits. This suggested to us the use of optimal control of the stroboscopic steady state for the design of DNP pulse sequences, by means of a modified version of the GRAPE algorithm. Optimized waveforms indicate that significant sensitivity improvement is possible beyond XiX and ASE, even at low average microwave power.

Keywords: dynamic nuclear polarization, magic-angle spinning NMR, pulse sequence design, microwave engineering, optimal control

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Electrostatics of lipid interfaces as assessed by EPR of pH- sensitive probes

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Electrostatic interactions are fundamental forces governing the behavior of charged molecules at the lipid membrane interface. These interactions, among other factors, influence ion distribution, membrane protein orientation, and ion channel activity. One of the methods for assessing the surface electrostatic potential is based on the determination of the electrostatic contribution to the pKa shift of the molecular probe placed at the charged bilayer interface. Previously, we successfully employed EPR of phospholipids labeled at the headgroup with a pH-sensitive nitroxide to map bilayer interfacial electrostatics. The goal of our work is to develop spin-labeling EPR methods for assessing lipid membrane surface potential, the local environment at the protein-membrane interface, and water penetration along this interface and their effect on effective pKa of model ionizable groups at membrane-protein surface. I will report on our recent progress in the use of pH-sensitive ionizable EPR labels and related spectroscopic methods to 1) profile a heterogeneous dielectric environment along the α-helix of a peptide inserted into a lipid bilayer and 2) assess the effects of solid support and, specifically, silica nanoparticles on lipid membrane potential and effective pKa of model membrane-burred ionizable sidechains.

This material is based upon work supported by the National Science Foundation under Grant No. 2305172.

Mathematics and computer science of steady state DNP simulations

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Solid state dynamic nuclear polarisation (DNP) experiments pump nuclear spin transitions by transferring magnetisation from unpaired electrons through repeated application of a microwave pulse sequence [1,2]. This is an active research area and a competition; the pulse sequence that produces stronger nuclear magnetisation in shorter time with lower average microwave power is a better one. Theoretical simulations [3,4], including optimal control theories [5], are often used to assist DNP sequence design and optimisation efforts. However, DNP is a difficult simulation target: the nuclear magnetisation pertains to the asymptotic steady state, and sometimes a steady orbit, of driven dissipative dynamics generated in a spin system ensemble by imperfect control hardware, including distributions in distances, orientations, concentrations, confor- mations, microwave amplitudes, and spin relaxation times [6,7].

In this presentation, we report several new methods for efficient simulation and optimal control of asymptotic steady states of heterogeneous dissipative ensembles that we have recently im- plemented in *Spinach* library (https://github.com/IlyaKuprov/Spinach):

(d) a Newton-Raphson steady state solver that efficiently (a few matrix-vector opera- tions) calculates the asymptotic steady state of a dynamical system produced by repeated action by a user-specified propagator on any initial spin state [7].

(d) a modification that allows gradient ascent pulse engineering (GRAPE) method to tar- get stroboscopic steady states and limit cycles that are approached asymptotically as a particular control sequence is repeated infinitely many times.

(d) improvements in sparse matrix logistics of spin dynamics simulations that reflect different additive and multiplicative operation efficiency of compressed sparse col- umn (CSC) and coordinate (COO) sparse matrix storage formats.

(d) improvements in GPU and parallelisation logistics that reflect the balance between communication and computation efficiency of the linear algebra of spin dynamics simulations on different types of computing devices.

Applications to practical DNP experiment simulations and pulse sequence design are covered in the lecture presented at this same conference by Guinevere Mathies.

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Insights into defect evolutions in Nitrogen Incorporated Reduced Graphene Oxide through EPR

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Due to high defect density and good electrical conductance, nitrogen-doped reduced graphene oxides (NrGOs) are highly promising materials for energy storage, energy conversion, and electrochemical applications. However, a systematic investigation into the structural evolution of NrGO with varying degrees of nitrogen incorporation has not yet been reported. To this aim, a series of NrGO samples were prepared via solvothermal route, with melamine playing the combined role of nitrogen precursor and reducing agent. Alongside improved reduction, Raman spectroscopy probes increased disorder in the NrGO matrix with nitrogen incorporation, in accordance with a growing sp^3 fraction and diminishing average separation between defects. Temperature dependent Electron paramagnetic resonance studies of NrGO samples, also correlate with the combined effects of doping and disorder, rather than N- incorporation alone. Low temperature pulsed-EPR study of the highest nitrogen incorporated sample revealed an uncharacteristically fast relaxation of the dangling bonds signal that indicates to a strong coupling of the unpaired electron with the conduction electron reservoir. These results provide valuable insights into the underlying charge transport mechanism of nitrogen incorporated reduced graphene oxides.

From Electron Spins to Nuclear Detection: Bullet-DNP Enabled Observation of Ligand-Protein Interactions at Low Concentration

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The detection of weak ligand-protein interactions is often limited by sensitivity, particularly when only nuclear spins are used as reporters. In thermal equilibrium, the low polarization of nuclear spins severely restricts the achievable signal intensity, making experiments at low concentration challenging. In contrast, electron spins exhibit much higher thermal polarization, providing a powerful resource for sensitivity enhancement using dissolution dynamic nuclear polarization ("bullet-DNP")[1].

This approach provides large signal enhancements, enabling direct NMR detection of a hyperpolarized ligand at 250 nanomolar concentration with minimal mass[2]. Critically, we extend this sensitivity gain to interaction studies by exploiting spin-relaxation contrast at low magnetic field. Maintaining the hyperpolarized ligand-protein solution at low field allows protein-induced relaxation effects to be observable at protein concentrations as low as 2 µM. This achieves a 10-fold reduction in protein sample consumption compared to conventional assays. While detection is performed by NMR, the sensitivity breakthrough relies on high electron spin polarization and the precise manipulation of spin dynamics. This work establishes a methodology in which ESR principles directly empower and extend NMR's capabilities for detecting biomolecular interactions at previously inaccessible sensitivity.

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Lipid-induced tau aggregation investigated by EPR spectroscopy

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Aggregation of the intrinsically disordered protein tau is a hallmark of several diseases, called tauopathies, including Alzheimer's disease. Amyloid aggregates are solid-like protein assemblies that are highly ordered and stable. Strikingly, different aggregate structures are involved in distinct tauopathies, revealing a structure-pathology relationship. Yet, the basic mechanisms and factors that drive tau aggregation and structural differentiation remain unknown.

This study investigates how biological membranes modulate of tau aggregation, utilizing a combination of biophysical techniques, including Electron Paramagnetic Resonance (EPR) spectroscopy. EPR is used to characterize and quantify the interactions between tau and lipid bilayers. We explore how the organization of the lipid membrane, such as lipid composition and local charge density influences tau binding and conformation. Then, we link these properties with the capacity to promote tau amyloid formation. By building a global model of lipid-induced tau aggregation, this work sheds light on how biological membranes can promote amyloidogenesis, contributing to the broader understanding of tauopathies.

EPR spectroscopy to study the structure and dynamics of biopolymers and pH in cells

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The report will present an overview of our results concerning application of pH sensitive trytil and nitroxyl radicals to measurements of pH in cells ; measurement of electrostatic potential in bacterial DNA glycosylase (FPG), using pH sensitive nitroxides and PELDOR study of structure of DNA repair enzyme complexes with DNA and organic molecules [1-3].

Real-time monitoring of critical tumor microenvironment parameters, such as intracellular pH, remains challenging but is crucial for understanding cancer progression and therapeutic resistance. A novel approach using EPR and EPR tomography to study oximetry and pH in cells using triarylmethyl radicals was proposed recently [1]. Integration of 13C1-TAM-OH with cell- penetrating peptides (CPPs) opens new possibilities for assessing pH in aggressive biological systems such as cancer cells. Redox transformations in the TAM→QM→TAM−OH cascade are shown to occur directly in living cancer cells. The conversion of 13C1-QM to 13C1-TAM-OH reaches 46%, confirming the potential of QM as a precursor for generating pH-sensitive radicals. The EPR spectrum of 13C1-OX063-OH is observed for at least 15 hours, demonstrating the suitability of the proposed method for long-term monitoring of metabolic processes in the cellular environment. The study's results also highlight the importance of optimizing the delivery of TAM−OH radicals to cells and improving spectroscopic data analysis to increase the accuracy of pH, oxygen, and redox status assessments. Using QM instead of TAM in experimental designs can overcome TAM stability issues while exploiting the unique properties of 13C1-TAM-OH for modern biomedical applications. The presented data hold promise for improving the accuracy of hypoxia and oxidative stress assessments, which are important for understanding tumor resistance to therapy.

Enzymes use electrostatic interactions to recognize their substrates, pre-organize active sites, and stabilize reaction transition states. Bacterial formamidopyrimidine DNA glycosylase (Fpg) is an enzyme that repairs the promutagenic DNA lesion 8-oxoguanine; its human homologs are important for cancer prevention. General acid-base catalysis in the Fpg active site requires finely tuned proton transfer between residues Pro1 and Glu2. To experimentally assess the protonation state of the Fpg active site, we used EPR spectroscopy with a novel imidazolidine nitroxyl spin label that reacts in the physiological pH range. The label demonstrated high sensitivity in detecting DNA duplex formation and Fpg binding, allowing us to measure changes in the local electrostatic potential. We constructed DNA duplexes in which the spin label was located near the active site (Fig. 1), which was determined using EPR and molecular dynamics. By comparing the EPR spectra of the pH label bound to wild-type Fpg and the catalytically inactive Fpg E2Q mutant, we observed a noticeable deviation at pH 7.00 and above, which can be attributed to the protonation/deprotonation of Pro1.

The work was supported by the Russian Science Foundation grant 25-13-00327.

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Mechanism of CRISPR Target Discrimination Revealed by Site-Directed Spin Labeling

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CRISPR (Clustered-Regularly-Interspaced-Short-Palindromic-Repeats) systems have been adapted into programmable agents for genome-wide manipulation of nucleic acids in many organisms, unleashing a revolution in genome editing and manipulation that is still rapidly advancing. Fundamental understanding on mechanisms of CRISPR target discrimination provides the foundation for CRISPR revolution, and is critical for overcoming remaining obstacles, such as the “off-target effects” that result in undersigned aberrant actions. Our group has been studying nucleic acids and protein-nucleic acid complexes using a unique biophysical technique, site-directed spin labeling, which monitors site- specifically attached stable radicals (e.g., nitroxide spin labels) using electron paramagnetic resonance (EPR) spectroscopy to gain structural (e.g., distance constraints) and dynamic (e.g., motions at the labeling site) information on the parent molecule under physiological conditions. Our current work centers on using site-directed spin-labeling in conjunction with other techniques to understand mechanisms of target discrimination by CRISPR-Cas9 and Cas12a that target double-stranded DNA. In this presentation, I will present work on applying the spin-labeling/EPR approach to reveal connections between effector conformational dynamics and DNA target discrimination by Cas9 and Cas12a.

High-sensitivity magnetometry using optically addressable spin defects in diamond

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Over the past two decades, diamond has emerged as a promising material for the implementation of quantum technologies. Diamond serves as an ideal crystalline host for the defect qubit states due to its qualities such as wide band gap, small spin-orbit coupling and its availability in high quality, isotopically purified single crystals. Among the possible defects in diamond, the nitrogen-vacancy (NV) spin defect has emerged as a leading qubit candidate as its spin state can be optically initialized and measured at room temperature, and can be manipulated via electron spin resonance by microwave radiation. The NV center in diamond has been used to measure a number of physical quantities such as magnetic field, electric field, temperature and stress/strain at ambient conditions [1,2]. Consequently, the NV quantum sensors have not only enabled the measurement of magnetic resonance from a single electron spin and a few nuclear spins [1], but also emerged as a spectroscopic tool for imaging the charge and strain environments intrinsic to the diamond lattice [3,4]. In particular, they have demonstrated high magnetic sensitivities in different NV magnetic sensing platforms due to their excellent susceptibility to magnetic fields. My talk will focus on various magnetic sensing and imaging applications using NV centers [5,6]. I shall also briefly discuss our efforts towards achieving sub-nanotesla sensitivity with a diamond magnetometer setup. The compact design of the magnetometer setup can enable potential applications in geodesy, non-destructive testing of magnetic materials, and electric vehicle battery monitoring.

Keywords: quantum sensor, magnetometry, spin resonance, nitrogen-vacancy center, microscopy

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Peptide-RNA Coacervates for the Evolution of Folded Domains

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Peptide-RNA coacervates can concentrate and compartmentalize simple biopolymers and are thought to have played a key role in early protein evolution given their primordial relevance. To explore how complex protein architectures may have emerged from simple polypeptides, we studied the helix-hairpin-helix (HhH) motif, an ancient and ubiquitous nucleic acid-binding element predicted to form a rotationally symmetric structure called the $(HhH)_2$ motif upon duplication and fusion.[1] Using continuous-wave (CW) and double electron-electron resonance (DEER) EPR distance measurements on site-specifically spin-labeled HhH peptides, we demonstrate that a single HhH motif can dimerize to form the $(HhH)_2$ fold even in the absence of RNA. Importantly, this dimerization is retained within peptide-RNA coacervates and is further promoted by association with RNA. These findings suggest that phase-separating peptides could have facilitated the emergence of complex protein folds through common evolutionary processes such as duplication and fusion.[2]

Given that primitive peptides likely contained mixed L- and D- amino acids, we further examined whether coacervates could buffer the emergence of chiral control. Comparing isotactic (homochiral) and syndiotactic (alternating chirality) variants of an HhH-derived peptide revealed a striking preservation of structure and function, including dimerization, RNA binding, and coacervation. The EPR data were supported by MD simulations. We propose that peptide-RNA coacervates may have supported early protein evolution by stabilizing both structural complexity and functional robustness across diverse chirality patterns.[3]

Keywords: Protein evolution, Peptide-RNA phase separation, Chirality, CW EPR, Double electron-electron resonance (DEER).

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High-field Magic Angle Spinning EPR of P1 Centres in Diamond

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Dynamic Nuclear Polarization (DNP) enhances the sensitivity of Nuclear Magnetic Resonance by transferring polarization from an unpaired electron spin to neighbouring nuclear spins. The development and optimization of DNP require a thorough understanding of electron spin dynamics, obtainable only through pulsed-EPR. Since DNP performance is condition-dependent, typical low-field static EPR experiments are of limited relevance for contemporary high-field Magic Angle Spinning (MAS) DNP, necessitating high-field pulsed MAS-EPR instrumentation and methodology, currently undeveloped [1]. Recently, we reported the first high-field two-pulse MAS-EPR experiments with up to 3 kHz spinning rate [2], enabling observation of electron spin dynamics on a few microsecond timescales. However, electron-nuclear polarization transfer in DNP typically occurs over a longer period.

Here, we demonstrate rotor-synchronized three-pulse stimulated echo detected MAS-EPR experiments with up to a 37 kHz spinning rate at 6.9 T, allowing to observe electron spin dynamics on the hundreds of microsecond timescale (Figure 1). Our results revealed the unique capability of MAS-EPR to separate EPR spectra of diamond P1 defects based on their anisotropy, achieved via the strong dependence of MAS-induced spin dephasing on the anisotropic line width. In addition, by measuring stimulated echoes over multiple rotor periods, we can now estimate how MAS affects the electron spins apparent T1, which is directly relevant to predicting MAS-DNP efficiency. The experiments are accompanied by time-domain simulations confirming the interpretation of the observed changes in the EPR lineshapes.

This work is a step towards a deeper understanding of MAS-DNP mechanisms, aiming to achieve stronger bulk hyperpolarization.

Keywords: P1 defects, Rotor synchronized stimulated echo, High-field MAS-EPR.

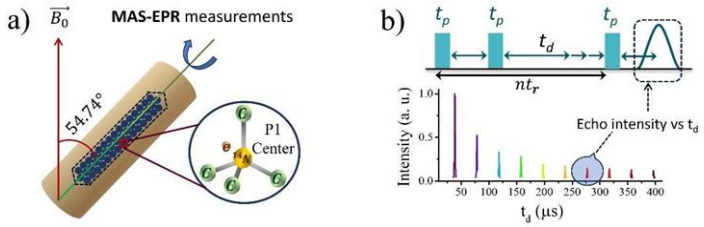

Figure 1: (a) MAS-EPR schematic. (b) 3-p rotor synchronized stimulated echo vs. delay time td.

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Nitroxide radicals for structural investigations on proteins with in-cell EPR spectroscopy

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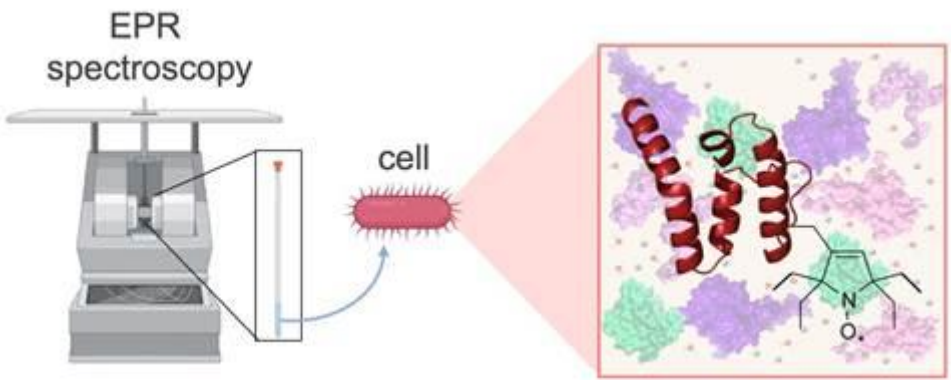
Site Directed Spin Labelling (SDSL) reactions coupled to Electron Paramagnetic Resonance Spectroscopy (EPR) are powerful biophysical methods for protein characterization. Indeed, the incorporation of paramagnetic tags (spin labels) into these biological systems allows the investigation of their structural dynamics and conformational changes at the local level using both continuous wave and pulse EPR experiments[1]. Over the last decade, SDSL-EPR spectroscopy has also emerged as an optimal approach to probe these features directly inside cells (*in-cell* EPR). In this way, proteins can be investigated in their physiological environments without perturbing their native states[2-3].
Here, the application of nitroxide-based spin labels to investigate the structure of cytosolic proteins in various cellular milieus through *in-cell* EPR spectroscopy will be presented. In parallel, optimized methodologies for protein internalization in both prokaryotic and eukaryotic cells will be described to carry out *in-cell* EPR measurements with various nitroxide-labelled proteins. Overall, these results highlight the potential of EPR experiments to provide structural information on proteins under true cellular conditions, while further advancing the state of the art of this magnetic resonance technique in structural biology.



Keywords: nitroxide spin labels, SDSL reactions, *in-cell* EPR, structural biology

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Smartphone enabled electron spin-enhanced nanodiamond diagnostics

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Lateral flow assays leveraging the electron spin mediated fluorescence modulation of nitrogen- vacancy (NV) centres in nanodiamonds have been demonstrated to show significant clinical sensitivity enhancements over traditional gold nanoparticle-based systems [1], in addition to a 96,000 fold improvement in fundamental limits of detection [2] - achieved through a combination of high fluorescence count rates and the ability to reject background auto- fluorescence. This technique has the potential to provide high diagnostic sensitivities for a broad range of biochemical targets at the point-of-care and in resource limited settings, where access to centralised laboratories is limited and introduces significant delays in the time-to- result. Enabling that goal, this work demonstrates a portable system for the optical excitation, detection and spin modulation of NV centres in nanodiamonds at a 20-fold reduction in cost compared with the laboratory-based system used in the original demonstration. In a direct bind assay, the fundamental limit of detection (LOD) for the portable reader system (36 aM [95% CI: 26-49]) was found to be a factor of 15 higher than the microscope system, representing a significant improvement over the LOD for gold nanoparticles. Additionally, due to non-specific interactions, real world assays with highly sensitive nanoparticles are generally not limited by the fundamental LOD of the combined nanoparticle-readout system. In order to demonstrate this, a novel isothermal assay targeting OXA-48, a key antimicrobial resistance gene, was developed in-house - with the LOD taken on the reader showing a minimal reduction in sensitivity compared with the microscope system.
Keywords: Nitrogen-vacancy Centre, Diagnostics

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Oxygen is one of the most important molecules in life. Cells survive and thrive in a precise oxygen environment, and low oxygen or hypoxia is a hallmark of many pathologies. While there are a few technologies that can provide point oxygen measurements, they are less useful compared to three- dimensional oxygen maps due to the inherent tissue heterogeneity. Pulse-mode electron paramagnetic resonance oxygen imaging (EPROI) is the only method that can provide accurate partial pressure of oxygen (pO2) maps in tissues, both *in vitro* and *in vivo*. EPROI is similar to MRI in principle, as it uses a static magnetic field, magnetic field gradients, and radio-frequency energy pulses to generate spatial images of electron spins. In contrast to MRI, EPROI uses much smaller magnetic fields and always needs an exogenous contrast agent due to the absence of EPR-sensitive radicals with high concentration and long relaxation times in the body. What sets EPROI apart is its ability to offer a direct, quantitative, and real- time measurement of oxygen concentration without relying on indirect metabolic markers. For reporting oxygen concentration, soluble trityl radicals such as OXO71[1, 2] or insoluble particulate probes, such as lithium phthalocyanine (LiPC)[3], are used. We have developed a 25 mT EPROI instrument, JIVA-25â, and a human-size 9 mT instrument, CAELI-9. For a long time, EPROI had a single focus area, to address tumor hypoxia and ameliorate it for better therapy outcomes [4-6]. Recent years have seen a surge of new applications, from biomaterial and cell viability assessment to the assessment of cell transplantation devices, blood-brain barrier integrity, blood transfusion, organ preservation technologies, etc. [7-11] So far, EPROI has been limited to small animals, primarily rodents. Recently, we performed a pilot study to assess trityl OXO71 distribution and pharmacokinetics after an IV injection in three rhesus macaques to demonstrate systemic exposures necessary for pO2 imaging in non-human primates [12]. The talk will outline recent work in our group and highlight the current and emerging applications of EPROI.

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Water soluble spin probes with oxygen-sensitive relaxation enable in vivo Electron Paramagnetic Resonance Oxygen Imaging (EPROI). This imaging technique utilizes magnetic field gradients for spatial encoding, creates three-dimensional relaxation maps and offers a real- time snapshot of in vivo oxygen levels of live tissues. EPROI is particularly valuable in investigating tumor hypoxia, optimizing cancer treatment, and evaluating therapeutic responses. Novel applications in organ preservation and bioengineering are expanding the scope of EPROI.

This presentation will cover the state of the art of EPROI and recent improvements in instrumentation and methodology. It will also address challenges associated with spin probe kinetics, and describe the ongoing efforts to extend the technology to clinical settings.

Keywords: Oxygen imaging, In vivo imaging, Animal physiology, Imaging methodology

Coherent dynamics of spins in coupled silicon quantum dots

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Spins in semiconductor quantum dots offer highly tunable coupled spin systems which can be produced at scale using modern integrated circuit manufacturing processes, making them ideal for the development and exploration of scalable spin-based quantum processors. The exchange coupling strength between spins in double quantum dots can be electrostatically tuned using gate electrodes, the initial states created tuned through the speed with which the electron pair is separated, and the spin-dependent charge dynamics (for of example through through Pauli spin blockade) can be used to map combined spin states such as single/triplet onto different charge configurations.

In this presentation I will discuss the parallels between the dynamics of optically generated spin correlated radical pairs [1] and such electrostatically defined double quantum dots [2]. I will show how a charge sensor close to a silicon MOS double quantum dot can be used to measure the parity of a spin pair, or distinguish between the singlet and triplet states, with high fidelity [3]. I will show how exchange oscillations can be observed by preparing different initial states and tuning the interaction time and/or exchange strength [4]. Finally, I will present how such exchange coupling can be used to realise two qubit gates within a scalable quantum dot array.

Keywords: Spin qubits, quantum dots, Pauli spin blockade, exchange coupling

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RF-FT EPR Imaging – from FID to Tumor imaging & oximetry

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MRI is a well-known and fully mature radiological imaging technique invaluable in diagnostic radiology and no modern hospital or clinic can effectively function without MRI scanners, similar to an X-ray or ultrasound imagers. When it comes to examining the details of soft tissue structures, tumors and bone injury nothing can surpass the ability of MRI in providing vivid anatomical details of, not to mention functional and diagnostic capability of relaxation- weighted MR images. FT- EPR imaging, a closely and fundamentally similar modality, however, could not compete with MRI due to the relatively delayed developments due to the non-availability of data acquisition systems that could cope with ns and ms range relaxation times and fast switches and electronic gates with resolution in ns range. Besides, living systems do not have any free radicals distributed in their anatomy with sufficient lifetime or concentrations to permit imaging, mandating the infusions (by i.v or i,p) of stable, biocompatible free radical probes. The author and his coworkers working at the National Cancer Institute, National Institutes of Health a variety approaches to perform *in vivo* have developed USA by bringing the frequency to the radiofrequency regime (~300 MHz), at 10-12 mT fields and using pulsed Fourier transform techniques (ns pulses and Ms/s digitizers and employing water-soluble non-toxic and bio-compatible free radical spin probes based on triaryl methyl radical derivatives (now available from GE Healthcare, USA). could generate high resolution (<mm) images of implanted tumors in small animals. Using the broadening of linewidth of these spin probes by dissolved oxygen, being linearly dependent on the in vivo oxygen partial pressure (pO2), as a handle it was possible to generate quantitative spatial mapping of oxygen in tumors. Tumor hypoxia is the main cause of nearlyfour-fold increase in resistance to radiation as well as chemotherapeutic treatment of cancer. To make EPR imaging and oximetry a viable technic in a clinical setting to treat human subjects it is important that we scale up the resonator. This is not straightforward because of the RF power requirements and the consequent enormous increase in SAR. However, we have shown that using patch antenna and saddle coil resonators it is possible to scale up EPR imaging and tumor oximetry with reduced SAR enabling practical applications in cancer research. These developments will presented and discussed.

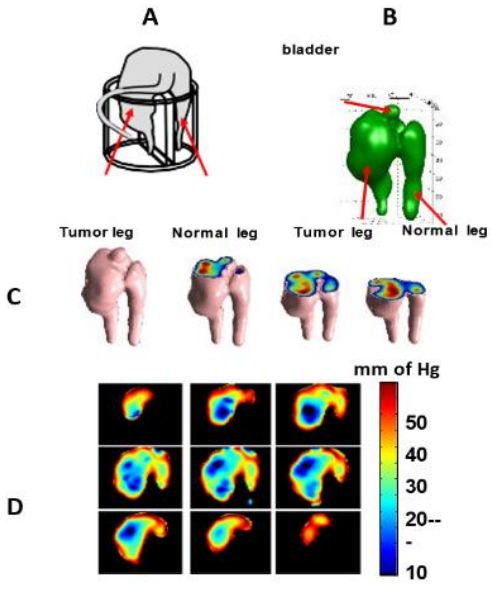

Fig. (A) anaesthetized C3H mouse in resonator (B) surface-rendered 3D image showing clearly the tumor leg, normal leg and the bladder. (C) A few tranverse cut-away views of spin image (D) Sagittal slices of T_2 -weighted oximetric images showing the hypoxic core in the tumor- bearing leg and the heterogeneous distribution of hypoxic zones

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Quantum coherence of non-Kramers electron spins as ultrasensitive quantum sensors of angular vibrations

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Rare-earth ion (REI) electron spins embedded in low-nuclear-spin crystals such as $CaWO_4$ are promising qubit candidates for quantum technologies, owing to their long coherence times at cryogenic temperatures. Coherent manipulation of non-Kramers rare-earth ions remains a largely unexplored frontier in quantum technologies: their strong magnetic anisotropy and vanishing perpendicular g-factors render them inaccessible to conventional EPR techniques.

Here, we report the first pulsed EPR observation of spin coherence in Tb^{3+} (J = 6, non- Kramers) embedded in a $CaWO_4$ crystal. Using a custom X-band probe operating in parallel mode, we overcome the restrictive selection rules that have historically prevented coherent control of such systems. Remarkably, we observe spin coherence times that exceed those of some Kramers rare-earth ions in the same host matrix. By operating at millikelvin temperatures and at parts-per-billion dopant concentrations, conventional decoherence channels such as phonon-mediated relaxation and spin diffusions are strongly suppressed.

Under these conditions, time-domain relaxation measurements uncover a previously overlooked decoherence pathway: angular vibrations of the crystal within the static magnetic field. The extreme magnetic anisotropy of Tb^{3+} ($g_\parallel$ = 17.7, $g_\perp$ = 0) amplifies micro-degree orientational fluctuations into substantial effective field noise, causing rapid dephasing even when conventional magnetic and phononic channels are suppressed at millikelvin temperatures and parts-per-billion dopant concentrations.

This exceptional orientation sensitivity positions Tb^{3+} spins as ultrasensitive quantum sensors of mechanical angular motion, with a field-tuneable sensitivity, while showing the critical importance of mechanical stability in precision quantum experiments.

An Octameric b-Barrel Amyloid Oligomer Stabilized and Detected by Site-Directed Spin Labeling ESR

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Amyloid oligomers represent a toxic intermediate species in the aggregation of proteins in neurodegenerative disease. Their structural characterization has been elusive due to their transient and heterogeneous nature. One amyloid oligomer that has been solved by X-ray crystallography is of a small model peptide called K11V.[1] So far, ESR measurements have characterized the aggregation of the oligomer by size,[2] but distance measurements have been difficult due to the propensity of spin labels to inhibit oligomerization, and the potential for multi-spin and overlapping distance distributions. Using a bifunctional spin label, we were able to spin label K11V in a manner that allows the oligomerization of the peptide and labels the peptide in-range for distance measurements. After stabilization of the known 'cylindrin' peptide hexamer, we were able to convert the hexamer into a new, higher order species, that suggests the formation of an octamer. Simulations using Alphafold were consistent our data, suggesting that the peptides arrange in an octameric beta barrel with a pore large enough to allow ions to flow through a neuronal membrane, supporting a general mechanism of amyloid oligomer toxicity in neurodegenerative disease.

Keywords: Spin Labeling, DEER, Amyloid Oligomer, Alphafold

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Biophysical EPR Using Superconducting Resonators

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Recent advances in device fabrication techniques and quantum control methodology have enabled demonstrations of unprecedented sensitivity in induction EPR measurements using superconducting resonators, including the recent observation of single electron spin dynamics on a spin sample embedded directly in the device substrate at mK temperatures [1]. Applications in biophysical EPR, however, have a unique set of requirements that are not commonly associated with superconducting resonators: operation at temperatures in the range of 10 – 70 K, good drive field homogeneity on relatively large µL sample volumes to enable the measurement of µM concentration samples, a device bandwidth exceeding 100 MHz to enable double resonance experiments, and Rabi drive frequencies of tens of MHz to enable excitation and detection of broad spectra associated with the most commonly used nitroxide spin labels.

We present a new class of superconducting resonators, based on a novel phased array of 16 coupled YBCO microstrip resonators patterned on a sapphire substrate [2], that enable high sensitivity EPR measurements on 3.5 µL vitrified samples with Rabi drive strength up to 50 MHz, sufficient homogeneity to perform complex multiple pulse experiments, control and detection bandwidths greater than 100 MHz, and operation temperatures up to 89 K. The design principles of the devices will be discussed, including adaptable broadband coupling methods and engineering of the spatial microwave field profile. A variety of validation experiments on biradical ruler molecules and spin-labeled biomolecules demonstrate the performance of the devices and their viability for performing general biophysical EPR measurements.

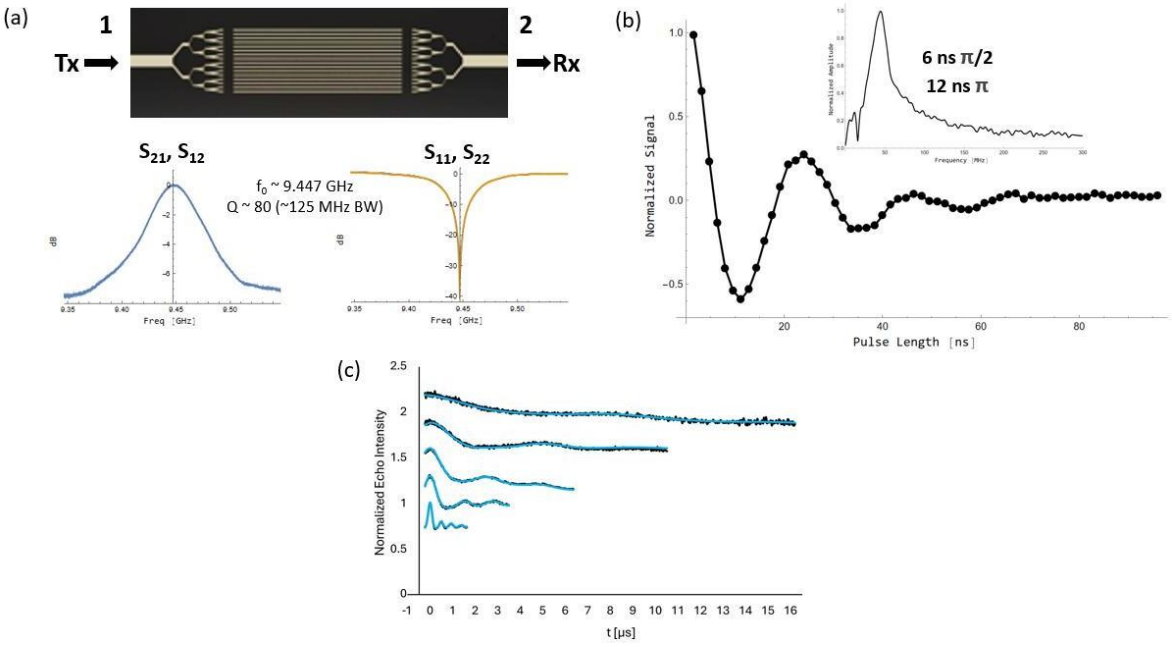

Figure 1. (a) YBCO microstrip superconducting resonator with VNA S-parameter data demonstrating device bandwidth exceeding 100 MHz. (b) Nutation data demonstrates Rabi drive frequency up to 50 MHz with less than 10 W of amplifier power. (c) DEER distance measurement data for 5 biradical ruler samples of 3.5 µL volume each and less than 100 µM concentration.

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Time domain simulation and optimal control of ESR systems

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Modern electron spin resonance experiments increasingly require time-domain simulation and optimisation: with more than two microwave pulses, it is usually impossible to derive analytical energy level / transition moment models for realistic spin systems. Setting up a basic time-do- main simulation for a two-spin system is a five-minute vibe coding job, but bigger simulations can turn into a serious nightmare: relaxation theories, high-spin systems, orbital degrees of freedom, *etc.* can require years of expert coding and debugging.

At the same time, numerical simulation and fitting can save time by answering basic questions about an ESR experiment: *"Is this realistic?"*, *"What are the optimal parameters?"*, *"Would the data answer my question?"*, *"What the hell just happened?"*, *etc.* Particularly the latter. A signifi- cant fraction of collaborative work in any theory group is assisting chemists who run into the weirdest ESR spectrum they have ever seen, google it up, find a PDF with twenty pages of equa- tions, and think *"oookaay... let's see if those nerds on the seventh ffoor are as useful as they claim to be."* Well, we try. This tutorial will provide an overview of modern ESR simulation capabilities and explain how to run simulations, what can be simulated, what cannot, and why.

In particular, we will look at the following topics of current interest:

1. **Quantum optimal control**: *Spinach* contains a sophisticated implementation of the Gradient Ascent Pulse Engineering (GRAPE) method that supports real-life fac- tors like parameter ensembles and instrumental filter function cascades.

2. **Neural network training database generation**: there is never enough experimental data and AI models must therefore be trained on simulations. However, it is in prac- tice also necessary to model every artefact that real data could have and even to inject correctly coloured noise – otherwise the resulting AI is useless.

3. **Parallelisation, sparse array handling, and GPUs**: a single Nvidia H200 card pulls about 60 TFLOP FP64, but serious software engineering needs to happen before it can operate at its full power. Even if you plan to use existing software, understanding factors that make simulations faster and slower is practically useful.

Examples will all be using *Spinach* (https://github.com/IlyaKuprov/Spinach).

Compact pulsed ESR systems – status and applications

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ESR spectroscopy is a powerful tool used across a wide range of scientific, technological, and medical applications. While most ESR instruments rely on continuous-wave (CW) detection, offering relative simplicity in both design and operation, pulsed ESR systems remain significantly more complex. These systems are typically bulky, expensive, and often require specialized expertise to operate, which limits their broader adoption.

In contrast to the long-standing availability and growing popularity of compact CW ESR systems, compact **pulsed** ESR instruments are still rare. Our research group has been actively working to overcome this limitation by developing a new generation of compact, cost-effective, and user-friendly pulsed ESR platforms. This effort encompasses all critical subsystems of pulsed ESR, including the core spectrometer for pulse generation and signal detection, the microwave bridge, high-power amplifiers, modular control software, compact magnet designs, and integrated cryogenic cooling solutions.

In this talk, I will present our recent progress in miniaturizing and streamlining these components, and demonstrate how they can be combined into a complete high-performance system that maintains the capabilities of full-scale laboratory instruments. I will also highlight several applications of these compact pulsed ESR systems, including:

- Structural biology, with systems tailored for distance measurements using DEER spectroscopy,
- Chemistry, for in-line reaction monitoring and transient radical detection, and
- Medical diagnostics, particularly for non-invasive quantification of tissue oxygenation via in vivo oximetry.

Finally, I will offer perspectives on the future of compact pulsed ESR technology and its potential to expand the accessibility and utility of ESR in both research and applied domains.

Keywords: ESR Instrumentation; DEER; Pulsed ESR

Precise Control of Spin States at Q-Band Frequencies

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Arbitrary waveform–generated (AWG) shaped pulses are transforming pulsed EPR spectroscopy by providing levels of control, bandwidth, and selectivity that address key challenges in structural biology and quantum information science (QIS). In structural biology, quantitative distance measurements using pulsed dipolar spectroscopy (PDS) – including PELDOR/DEER, DQC, and RIDME - require excitation bandwidths and pulse profiles beyond the capabilities of conventional hardware. AWG-driven pulses enable tailored inversion and excitation conditions that enhance sensitivity, suppress artifacts, and expand the accessible distance range for biomolecular systems.

Within PELDOR/DEER experiments, WURST pulses adapted from NMR, combined with a broadband Q-band loop-gap resonator, substantially improve modulation-to-noise ratios and overall experimental sensitivity. WURST excitation allows clean separation of pump and probe frequencies and reduces spectral distortions. Beyond PDS, WURST pulses also enable selective excitation, as demonstrated through broadband inversion of electron spins in diamond powders, where nitrogen nuclear-spin sublevels can be distinguished with high precision. Complementary broadband echo experiments provide efficient means to probe electron-spin coherence and relaxation across wide spectral ranges—capabilities essential for both biological spectroscopy and quantum-state control.

To meet these demands, we present an advanced Q-band (35 GHz) EPR platform integrating high-uniformity, high-bandwidth microwave resonators with an AWG-based intermediate-frequency (IF) microwave architecture. This combination provides large resonator bandwidth and arbitrarily shaped pulses, delivering the high fidelity required for resolving long-distance spin labels and for precise qubit manipulation in quantum materials.

Together, these results demonstrate how AWG-based pulsed EPR spectroscopy enables a unified, high-precision experimental framework for structural biology, QIS, and emerging spin-based quantum technologies.

Keywords: Arbitrary Waveform Generation, WURST Pulses, Pulsed EPR Spectroscopy

Applications of Pulsed EPR Spectroscopy to Understand Membrane Protein Structure and Dynamics

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Electron Paramagnetic Resonance (EPR) spectroscopy has emerged as a powerful tool over the last decade for assessing protein conformation, folding, oligomerisation, and dynamics. EPR distance measurements provide high-resolution quantitative information on protein equilibria, dovetailing well with techniques such as X-ray crystallography, HDX mass spectrometry, cryoEM, and computational approaches such as molecular dynamics simulations, as a key part of integrative structural biology. An inherent limitation in membrane protein studies is the need to remove the protein from its natural membrane environment. However, recent developments have provided lipid scaffolds that mimic this environment and offer flexibility in lipid composition, while EPR measurements on membrane proteins can also be performed in cells. Here, I will focus on the application of pulsed EPR spectroscopy (PELDOR/DEER) to the study of integral membrane proteins, highlighting recent case studies from my lab. I will explore folding in human potassium K2P channels (1), an allosteric mechanism that regulates mechanosensitive ion channels (2,3), inhibition asymmetry in membrane pyrophosphatases (4), pH dependence in secondary transporters (5), and the effect of antibiotics on the conformation of the BAM complex, with measurements performed in intact cells (6).

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Transient EPR and Photophysics of Pentacene-Radical Dyads

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The development of new molecular systems for quantum sensing, enhancing magnetic resonance signals and high photoluminescence benefits from a two prong approach that combines both experiment and theory. Chromophore-radicals (ChR) are one class of materials that exhibit tunable photophysics and in some cases can exhibit optically induced spin polarized ground states. Structural modifications of organic chromophores can perturb their optical properties and lead to significant changes in their photophysics. While significant experimental work has been done on ChR systems, both tethered and untethered since the late-1900's, recent computational methods and available computational power have facilitated calculation of their electronic and spin properties. In this presentation I will discuss chromophore-radical (C-R) dyads that have been investigated in my group using both transient EPR and computational methods. Using a combination of computational tools, magnetic resonance and optical spectroscopy, we identify several important design principles controlling the optical pathway as well as the magnetic interactions present in these materials. These results inform our future approaches for approaching the optimization of chromophore-radical tethered systems for different applications.

Biomolecular Condensates as a Common Player in Protein Secretion and Golgi Organization: Insights from GRASP Proteins"

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The role of biomolecular condensates formed via phase separation in cellular organization is gaining recognition as a key mechanism in stress adaptation, gene regulation, and cellular signalling, among others. This study investigates phase separation in conditions relevant for two critical cellular processes: unconventional protein secretion (UPS) and the structural organization of the Golgi apparatus. In the first part, we demonstrated that under starvation-mimicking conditions, the yeast GRASP homologue, Grh1, underwent liquid-liquid phase separation (LLPS) to form condensates, which we propose as being the Compartment for Unconventional Protein Secretion (CUPS) or its precursor. These Grh1 condensates could recruit UPS cargo and exhibited dynamic liquid-to-solid transitions, thereby supporting cellular adaptation to stress. The second part of our study focused on the human Golgi matrix proteins GRASP55 and GRASP65 and their capacity to form condensates. GRASP55, in particular, demonstrated a strong tendency toward LLPS, modulated by pH and by weak hydrophobic interactions, which could contribute to the dynamic self-organization and functional integrity of the Golgi apparatus and the UPS. On the other hand, GRASP65 did not form condensate in functionally relevant scenarios. Together, these findings suggest that GRASP phase separation is a conserved mechanism across eukaryotic cells and may play roles in stress-responsive protein secretion and organelle architecture.

Controlling Spin Dynamics in Intramolecular Singlet Fission via Torsional Modulation

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Intramolecular singlet fission (iSF) enables the generation of correlated spin states and enhanced triplet yields in organic molecules, with potential applications in photovoltaics and quantum technologies. A key challenge in iSF is the rapid recombination of the initially formed correlated triplet pair, which limits access to long-lived and spin-decoupled triplet excitons. Our group demonstrates a molecular design strategy to control both electronic coupling and spin dynamics in the correlated triplet pair in iSF by systematically tuning linker torsion and interchromophore geometry in a series of 6,6′-linked TIPS-pentacene dimers.

By employing planar and twisted linkers, we modulate the balance between through-bond and through-space interpentacene interactions, thereby controlling the exchange interaction (J) that governs multiexciton formation and recombination. Ultrafast transient absorption spectroscopy reveals that increased linker planarity and conjugation significantly accelerate singlet fission but also enhance rapid recombination from the singlet-coupled triplet pair, ^{1}(TT). In contrast, twisted linkers suppress through-bond coupling, slowing iSF while enabling the formation of longer-lived multiexciton states.

Time-resolved electron paramagnetic resonance (tr-EPR) spectroscopy directly resolves the spin evolution following iSF and provides clear evidence for the formation of quintet (S = 2) triplet-pair states. The observed spin polarization patterns indicate exchange-coupled triplet pairs undergoing dynamical exchange fluctuations driven by linker conformational motion. These fluctuations promote spin mixing and population transfer into long-lived quintet and free triplet states, increasing the probability of the system to be used as quantum qubit. Overall, our results establish torsional control as a powerful design principle for engineering organic systems with tunable spin dynamics and long-lived triplet excitons.

Keywords: Intramolecular Singlet Fission, Spin Dynamics Control, Exchange-coupled triplet Pair, Correlated Spin States, Torsional Control.

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EPR Application in Antibody Based Drug Development and Therapeutics

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Monoclonal antibodies (mAbs) have become an important class of medicine, primarily due to their target specificity, prolonged serum half-life, and diverse mechanisms of action. Antibodies are emerging tools in structural biology, drug delivery, and bioimaging. Recently, we have demonstrated the capability of the electron paramagnetic resonance (EPR) spectroscopy using ^{13}C-labeled trityl spin probe (^{13}C-dFT) to report the viscosity of antibody formulations, insulin analogs, and biofluids in vitro, but also tissue viscosity in various organs in anesthetized mice.

Moreover, natural abundance ^{12}C-OX063 and ^{12}C-OX071 probes have been extensively used as molecular oxygen sensors using EPR imaging and Overhauser-enhanced MRI in various animal models. In the present work, we demonstrate the utility of EPR spectroscopy to elucidate the interactions between biologics and ^{13}C-dFT/^{13}C-OX071 probes. EPR spectroscopic results show that ^{13}C-dFT probe binds to human serum albumin and immunoglobulin G (IgG), but not the ^{13}C-OX071 probe. Importantly, both ^{13}C-dFT and ^{13}C-OX071 probes bind to the antibody adalimumab (HUMIRA). The EPR linewidth of ^{12}C-OX071 probe increased by approximately 50 mG, in the presence of adalimumab, which shows that the antibody binding has a very small effect on the linewidth. These results suggest careful design and engineering of antibodies to bind ^{12}C-OX071 and increase the lifetime of the probe and be delivered into targeted cells/organs. These results pave the way for intracellular and organ imaging using magnetic resonance imaging techniques.

Key Words: EPR, trityl probe, antibody, imaging, adalimumab

Unraveling Multielectron CO2 Reduction Mechanisms through Direct Observation of Reactive Intermediates by EPR Spectroscopy

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Electrochemical and photochemical CO_2 reduction provides a sustainable route for converting CO_2 into value-added fuels using renewable energy; however, selectivity remains limited by complex multielectron/proton-coupled electron transfer (PCET) pathways, competing hydrogen evolution, and the transient nature of key intermediates.[1]

Electron paramagnetic resonance (EPR) spectroscopy is a definitive mechanistic tool for CO_2 reduction reaction studies, as it directly probes paramagnetic metal- and ligand-centred species formed during redox processes. Analysis of g-tensors and hyperfine couplings enables precise assignment of oxidation states, electronic structures, and spin-density distributions, thereby distinguishing metal- versus ligand-centred redox events, particularly in systems with non-innocent ligands. In situ and freeze-quench EPR further allow real-time interrogation of electron-transfer sequences, providing direct validation of multielectron PCET mechanisms under catalytic conditions.

In our previous copper-based[2] CO_2 to CO system supported by a redox-active azo ligand, EPR demonstrated that the EPR-silent Cu(I) (d^{10}) precursor undergoes CO_2-induced oxidation to Cu(II), characterized by an axial signal ($g_\parallel > g_\perp > 2.0023$). Subsequent reduction produced a ligand-centred radical ($g \approx 2.00$), establishing cooperative metal–ligand redox participation in the two-electron conversion. However, in our recent nickel-based[3] CO_2/CO to CH_4 system, EPR distinguished a metal-centred $Ni^{II} \rightarrow Ni^{I}$ ($\langle g \rangle = 2.1$, $\Delta g = 0.58$) reduction from a subsequent ligand-centred process yielding the active Ni^{I}–$L^{\bullet-}$ species ($\langle g \rangle = 2.076$, $\Delta g = 0.58$), consistent with computed spin densities. Detection of a Ni–CO adduct confirmed CO as an on-pathway intermediate, while identification of a high-valent Ni^{III}–CH_3 species under electrocatalytic conditions provided direct evidence that methane formation proceeds via a metal–methyl intermediate prior to C–H bond formation.

These results establish EPR as a decisive tool for resolving oxidation states, mapping electron-transfer pathways, and identifying substrate-bound intermediates in CO_2RR. Direct detection of transient paramagnetic species provides a mechanistic basis for the rational design of efficient and selective catalysts.

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Frequency and Bandwidth Agile Photonic Band Gap Resonators for Pulse ESR at 35 GHz and Higher Frequencies

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Resonant circuits are vital components of magnetic resonance spectrometers, where high-quality factor (*Q*) probeheads enhance sensitivity through stronger transverse microwave fields (B_1e) and improved noise rejection. Performance of conventional metallic resonators for ESR is limited by frequency-dependent conduction losses, restricting achievable *Q*-factors to approximately 10,000 at X-band (9.5 GHz) and only 2,000–3,000 at W-band (95 GHz). While using superconducting materials can boost *Q*, this approach requires cryogenic operation and restricts sample conditions. This work describes a new class of millimeter-wave resonators based on one-dimensional photonic band gap (PBG) crystals, offering a fundamentally different approach to high-*Q* performance even at room temperature. Unlike our earlier PBG resonators with fixed coupling, the newly developed architecture enables fully tunable external coupling across under-, critical-, and over-coupled regimes, facilitating precise impedance matching and bandwidth control for pulsed EPR experiments. A Q-band (34 GHz) oversized PBG resonator constructed from 2-inch sapphire discs achieved an unloaded quality factor of 27,300 ± 2,300 at room temperature under critical coupling (β = 1.06 ± 0.18) - approximately twenty-fold greater than typical commercial Q-band EPR resonators. Integration into a Bruker E580 Q-band spectrometer produced at least ten-fold improvement in concentration sensitivity for echo-detected nitroxide signals. Additionally, a dual-mode implementation and a PBG configuration with adjustable mode separation were demonstrated, enabling double electron–electron resonance (DEER) experiments. PBG resonators for W-band (95 GHz) pulse EPR are also described. These advances highlight the potential of photonic band gap resonators to significantly extend the sensitivity of pulsed EPR. Supported by NIH R01GM130821.

Unlocking Nitroaromatic Radicals: Formation and Reactivity

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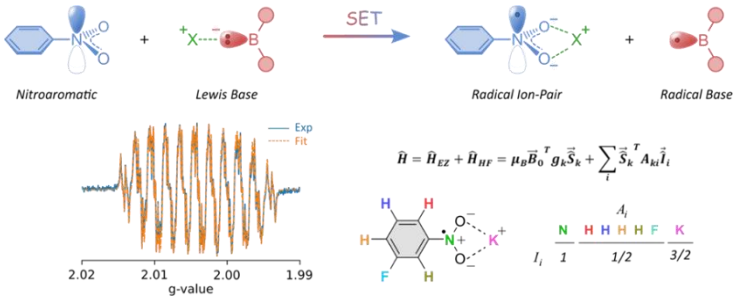
Organic radicals—metal-free molecules with unpaired electrons—exhibit unique magnetic and reactivity properties, enabling applications ranging from qubit implementations[1] to valuable chemical transformations.[2] However, their reactive nature and the synthetic challenges associated with their preparation impose strict structural and electronic constraints, limiting broader exploitation. Developing general strategies for radical formation under mild conditions, using readily available and inexpensive reagents, and applicable to a broad range of molecule, remains a key challenge.

Here, we present our efforts to establish nitroaromatic compounds as a versatile platform for radical formation, enabled by a single-electron transfer (SET) process from a wide range of anionic organo bases. Building on proof-of-concept studies of nitrobenzene,[3] and combining continuous wave X-band EPR spectroscopy, quantum chemical calculations, and synthetic approaches, we demonstrate that this SET-induced mechanism operates across a broad set of commonly used nitroaromatic compounds, including FDA-approved drugs – these findings suggest a previously overlooked prevalence of nitroaromatic radical species. We further show how this framework resolves contested reaction mechanisms[4] and enables the rational exploitation of SET-derived radical pairs to access valuable chemical transformations more efficiently.

Overall, our work highlights the untapped potential of SET-driven radical formation in nitroaromatic compounds and opens the door to extending radical properties to other Lewis acids.



Keywords: Organic Radicals, Single Electron Transfer, Lewis pairs, Nitroaromatics, Regioselectivity.

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A new set of distance rulers for Pulse Dipolar Spectroscopy

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We introduce a new ACERT set of rigid biradicals (“distance rulers”) with well-defined interspin distances spanning 1.5–3.9 nm. In this presentation, we demonstrate how these compounds can be used to optimize experimental conditions for pulse dipolar spectroscopy (PDS), including both DEER and DQC, and how they serve as benchmark systems for the development and validation of new data-processing methods.

We present insights into the behavior of these radicals in various solvents and polymer matrices, obtained using continuous-wave and pulsed ESR. Data analysis and spectral simulations were performed with newly developed ACERT software.

In addition, we highlight special features of selected radicals, such as trans/cis isomerization induced by UV irradiation.

A core mission of ACERT is to support ESR users worldwide. Based on these biradicals, we have developed a set of PDS calibration standards, *ACERT Rulers for ESR Distance Measurements*, which we offer free of charge to the global ESR community. These standards are stable for years and can be used at room temperature.

Characterization of Isolated Metal-Dithiolene-Radical Complexes by ESR Spectroscopy

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Dithiolene is a class of two sulfur-donor ligands. They are redox non-innocent in nature and investigated from 1960s. Air and moisture sensitive redox non-innocent N-heterocyclic carbene (NHC) functionalized tri-sulfur/selenium radical anions were isolated and employed as ligands [$(^{SS}L_{NHC=E})^{0}$ + e^{-} ® $(^{SS}L_{NHC=E})^{\cdot-}$ + e^{-} ® $(^{SS}L_{NHC=E})^{2-}$] isolated by characterized [E = S, Se] only after 2017.[1-2] Most of the metallo-proteins contain metal-complexes, called cofactor, each of which has chemical roles to play via elementary chemical or electrochemical processes in a specific coordination environment. Dithiolene unit is also part of Mo-containing protein (pyranopterin cofactor), Moco enzyme. Herein, I will present synthesis, isolation, and characterization by UV-vis-NIR, XPS, CV, Raman spectroscopy of metal-$^{SS}L_{NHC=E}^{\cdot-}$ complexes of 3d, 4d metal ions. They were structurally characterized by x-ray single crystal diffraction. Spin ground state and the nature of metal-radical interaction were studied by magnetic susceptibility measurements. The metal-radical interactions and distribution of electron densities of all the isolated metal-radical complexes were studied by electron spin resonance spectroscopy (ESR). In addition, some of these complexes are found to act as photo-catalyst for organic transformation, as supercapacitor electrode material and as catalyst for radical polymerization. ESR spectroscopy has been further employed to study the catalytic cycles or to shade lights on the mechanism of how a supercapacitor works.

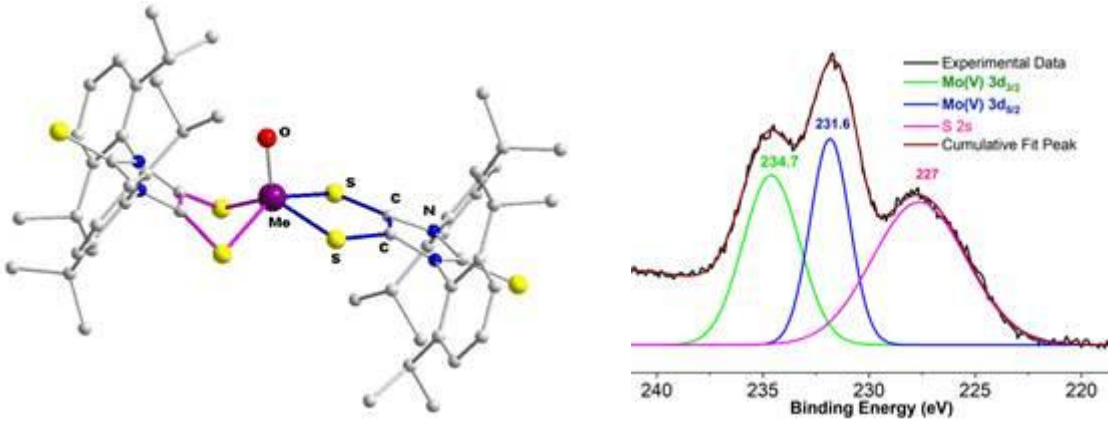

Figure 1. Molecular structure of complex [Mo(V)O($^{SS}L_{NHC=E}^{\bullet-}$)($^{SS}L_{NHC=E}^{2-}$)] (**1**).

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In-Silico and Liposomal Strategies for Developing Novel Antimicrobial Resistance Therapeutics

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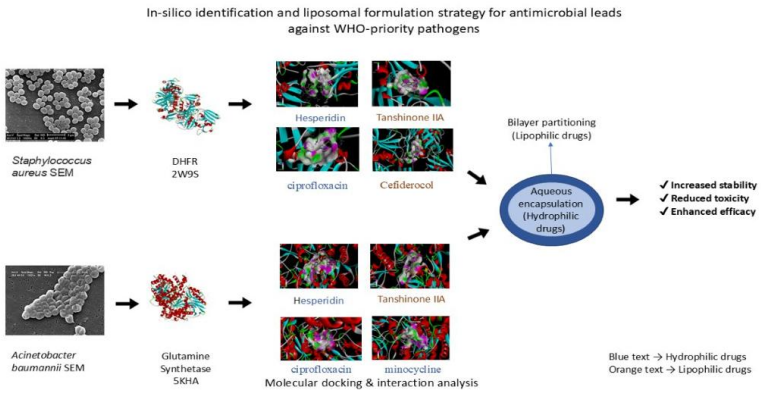
Antimicrobial resistance (AMR) is emerging as a major public health concern worldwide, and recent studies indicate that nearly 83% of patients in India are affected by antibiotic-resistant bacteria. This crisis is particularly severe for WHO-priority pathogens such as *Staphylococcus aureus* and *Acinetobacter baumannii* which exhibit multidrug resistance and biofilm-associated infections that significantly compromise current therapeutic strategies.

This study aims to identify potential antimicrobial lead compounds through systematic in-silico approaches and enhance their therapeutic potential using liposomal drug delivery systems. Essential bacterial proteins involved in metabolism, virulence and biofilm regulation - namely dihydrofolate reductase (2W9S), clumping factor A (1N67), dehydrosqualene synthase (2ZCO), shikimate kinase (4Y0A), glutamine synthetase (5KHA) and BfmR(6BR7) were selected as molecular targets. A curated library of FDA approved, and bioactive phytochemical drug molecules are developed based on the therapeutic relevance and ADMET considerations.

Based on docking outcomes and formulation feasibility, Tanshinone IIA and Hesperidin were selected as representative phytochemicals. From FDA-approved drugs, ciprofloxacin and cefiderocol were shortlisted for *S. aureus,* while ciprofloxacin and minocycline were selected for *A. baumannii.* These potent candidates were prioritized for further validation through molecular dynamics simulations and formulation studies. Limitations of conventional medications such as poor bioavailability, toxicity and non-targeted drug distribution can be resolved by liposomal encapsulation techniques. Furthermore, Electron Spin Resonance (ESR) studies will help explore drug mobility, membrane behaviour, and drug-liposome interactions at the molecular level, offering valuable insight into structural changes and membrane penetration.

Overall, this work demonstrates a translational framework for the creation of next generation antimicrobial treatment therapeutics that combines nanostructured delivery methods with *in-silico* screening



Keywords: Antimicrobial resistance (AMR), WHO-priority pathogens, In-silico drug discovery, Liposomal drug delivery systems, Electron Spin Resonance (ESR)

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Water structuring on poly (vinyl alcohol) surfaces underlies ice recrystallization inhibition activity

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Polyvinyl alcohol (PVA) is the most widely studied synthetic polymer that exhibits ice recrystallization inhibition (IRI), a key mechanism for preventing ice crystal growth during the thawing process of cryopreservation. However, the molecular mechanism by which PVA exerts IRI activity remains unclear, with proposed explanations ranging from direct binding to ice surfaces to structural modifications in liquid water at the ice-water interface. Our findings showed that the IRI activity of PVA is dramatically enhanced in combination with sucrose or trehalose. Electron paramagnetic resonance (EPR) lineshape analysis shows that PVA does not persistently bind to ice nor cause thermal hysteresis, while ice boule growth corroborates that PVA remains unbound to ice. 17O NMR chemical shift analysis and computational studies show that the population of liquid water with tetrahedral water triplet angles is enhanced in the presence of PVA near the ice-water interface. These liquid-water structuring effects are further enhanced by the presence of cosolutes, such as trehalose or sucrose. Exclusion of both PVA and sugar from the growing ice front further concentrates them in the non-frozen liquid phase that interfaces with the ice surface, thereby impeding ice crystal growth. This insight offers a hitherto unrecognized role of PVA in ice recrystallization inhibition of stabilizing non-freezing liquid water enriched with tetrahedral water triplet angles at the ice-water interface. This finding highlights new opportunities for the rational design of synthetic cryoprotectants for cryopreservation, biomaterials, and food science applications.

Investigating the Structural Dynamics of the XRCC4-SUMO Protein System Using Electron Paramagnetic Resonance (EPR) Pulsed Dipolar Spectroscopy (PDS)

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DNA double-stranded breaks (DSBs) are critical forms of DNA damage that, if unrepaired, can lead to cell death, mutations, and cancer [1]. XRCC4 plays a key role in DSB repair via non-homologous end joining (NHEJ) as a homodimeric protein, regulated by small ubiquitin-like modifier (SUMO) chains. These can bind non-covalently or be covalently attached to XRCC4, both potentially enhancing the efficiency of the repair process. Understanding how SUMO modulates XRCC4's structure is key to uncovering regulatory mechanisms in DNA repair. In this study, we utilize Electron Paramagnetic Resonance (EPR) Pulsed Dipolar Spectroscopy (PDS), specifically Double Electron–Electron Resonance (DEER), to investigate structural changes within the XRCC4 dimer upon SUMO binding. Distance measurements were performed within the XRCC4 dimer in the absence and presence of SUMO to establish a structural baseline and assess conformational changes. DEER measurements before and after SUMO binding were carried out using site-directed spin labels at different XRCC4 domains to detect domain-specific structural changes, while strategic spin labelling of SUMO enabled direct determination of its spatial orientation relative to XRCC4 and validation of NMR-derived interaction models. This project aims to enhance our understanding of the structural dynamics of the XRCC4-SUMO protein system, contributing to the broader knowledge of DNA repair mechanisms. Our findings highlight how SUMO binding selectively alters specific domains of XRCC4, revealing regulatory mechanisms.

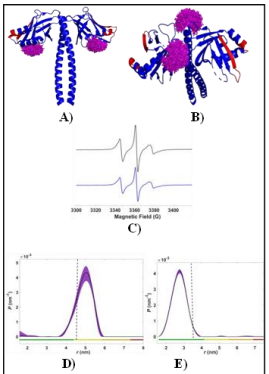

Figure 1: Spin labelling and DEER measurements of XRCC4 variants. A) K72C labelled with MTSSL; B) N118C labelled with MTSSL; C) cw-EPR spectra; D) DEER data for K72C; E) DEER data for N118C.

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Magnetic-Field-Driven Decoherence Suppression in Solid-State Spin Defects

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Spin defects in solid-state materials have emerged as versatile platform for quantum technologies due to their optical addressability and long-lived spin coherence [1]. However, interactions with surrounding nuclear spin environments remain a fundamental source of decoherence, limiting achievable performance across a wide range of defect systems. While this challenge is particularly prominent for the negatively charged boron vacancy (V^-) in hexagonal boron nitride [2, 3], it is equally relevant for other leading platforms such as nitrogen-vacancy centers in silicon carbide and rare-earth-related spin defects.

In this work, we present a general and transferable framework for decoherence suppression based on systematic control of static magnetic field strength and orientation. Using a combination of analytical modeling and detailed numerical simulations, we show that appropriately engineered magnetic-field configurations can access specific subspaces of the spin Hamiltonian in which sensitivity to nuclear-spin-induced magnetic-field fluctuations is strongly reduced. This results in a substantial enhancement of spin coherence without requiring dynamical decoupling or complex control sequences.

Keywords: Spin defects; Decoherence suppression; Magnetic-field engineering; Quantum sensing; Solid-state qubits

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Inverse Electron Spin Resonance Spectroscopy via Variational Quantum Optimization

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Electron Spin Resonance (ESR) spectroscopy is an inherently quantum technique used to probe spin-dependent interactions in paramagnetic systems, with applications spanning materials science, chemistry, and biomedicine. In conventional ESR analysis, spectral interpretation is typically performed using forward modeling approaches, where spin Hamiltonian parameters are iteratively optimized through classical fitting routines. These methods often become computationally expensive and increasingly unreliable for complex spin systems or noisy experimental data, motivating the exploration of quantum-assisted alternatives.

In this work, we present a quantum-based inverse ESR framework that employs variational quantum optimization to directly reconstruct spin Hamiltonian parameters from ESR spectra. The problem is formulated as an inverse quantum task, in which physically meaningful parameters—such as the g-factor and hyperfine coupling constants—are encoded into a parameterized quantum circuit representing spin dynamics. A hybrid quantum–classical optimization loop is then used to minimize a cost function that quantifies the discrepancy between simulated and target ESR spectra.

Unlike traditional forward-fitting techniques and purely data-driven machine learning methods, the proposed approach preserves physical interpretability by explicitly learning quantum Hamiltonian parameters through quantum state evolution. Simulation-based results demonstrate that the framework is feasible and robust under realistic noise conditions. To the best of our knowledge, this work constitutes the first software-based quantum-assisted inverse reconstruction approach specifically developed for ESR spectroscopy. The proposed methodology opens new possibilities for quantum-enhanced spectral analysis, automated ESR interpretation, and the calibration of spin-based quantum sensors.

Keywords: Electron Spin Resonance (ESR), Variational Quantum Optimization, Inverse Quantum Problem, Spin Hamiltonian Reconstruction, Quantum–Classical Hybrid Algorithms.

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Cavity Enhanced detection of weak perturbative fields using coupled spin-cavity system

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We propose a cavity-enhanced quantum sensing protocol for detecting weak external perturbative fields using the noise spectrum of a high *Q* cavity, dispersively coupled to an ensemble of spins. In this scheme, external fields modify the collective spin susceptibility, which is coher-ently transduced into measurable frequency shifts and spectral deformations in the cavity output noise spectrum. By operating in the dispersive regime, the sensing mechanism remains noninva-sive, preserving spin coherence while enabling high sensitivity to small environmental perturba-tions [1, 2]. The cavity noise spectrum acts as a narrowband spectral filter, selectively amplifying signals within targeted frequency windows while suppressing broadband spin bath induced deco-herence and technical noise. This intrinsic noise-engineering capability enhances signal-to-noise ratios and enables frequency-resolved detection of multiple perturbative parameters. The approach is inherently scalable, allowing simultaneous sensing of distinct field components encoded in dif-ferent spectral features of the cavity response.

Our protocol provides a versatile framework for precision quantum metrology in noisy envi-ronments and is directly compatible with existing experimental platforms, including solid-state spin ensembles coupled to microwave or optical cavities. These features establish cavity noise spectroscopy as a powerful tool for robust, high-resolution quantum sensing beyond the standard limits imposed by spin decoherence.

Keywords**:** Cavity; Spin defects; Quantum sensing; Noise spectrum

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Floquet Hamiltonian Engineering of PulsePol: From Ideal to Finite-Pulse Quantum Control

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PulsePol is an elegantly designed pulse-sequence-based quantum control scheme that enables polarization transfer between electron and nuclear spins, for example, in nitrogen-vacancy (NV) centers. However, previous analyses of PulsePol "assume" ideal, instantaneous microwave pulses, which is rarely achievable in experimental conditions due to limited microwave power, especially as we go to higher magnetic fields. In this work, we revisit the PulsePol scheme under finite-pulse constraints and show that its performance significantly degrades because of finite-pulse effects. We use Floquet-based Hamiltonian engineering to identify the source of this deteriorating fidelity and propose the use of Phase-Corrected PulsePol which compensates for finite-pulse errors through a simple phase-adjustment which reestablishes the proper symmetry of the interaction-frame Hamiltonian. Our results demonstrate improved robustness to finite-pulse effects and enhanced polarization transfer efficiency, establishing Phase-Corrected PulsePol as a more practical and reliable scheme for solid-state hyperpolarization of bulk nuclear spins at 0.35 T conditions. Overall, this work bridges idealized quantum control with realistic pulse engineering, establishing design rules for spin-based based quantum control protocols.

Investigation of nuclear spin–induced envelope modulation in magnetometry with a single nitrogen–vacancy center

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Nitrogen–vacancy (NV) electron spin and its proximal nuclear spins is a versatile platform for solid-state quantum sensing and information processing. In techniques such as Electron Spin Echo Envelope Modulation (ESEEM) and Electron Ramsey Envelope Modulation (EREEM), the coherent evolution of proximal nuclear spins becomes imprinted onto the electron spin coherence.

Previous studies have shown that transverse magnetic-field components induce mixing of electronic spin eigenstates, activating forbidden hyperfine transitions that give rise to envelope modulations in the electron spin signal. EREEM has been extensively investigated in the low- field regime (up to 20 mT), where the hyperfine and nuclear Zeeman interactions are comparable in magnitude, leading to pronounced envelope modulation.

In this work, we combine theoretical analysis with experimental measurements to investigate ESEEM of the ^{15}N nuclear spin over an extended magnetic-field range, and we further ex- tend EREEM studies of the ^{15}N nuclear spin to higher fields (~ 40 mT). From the envelope modulation spectra, we can extract the effective nuclear Larmor frequency and the parallel and transverse hyperfine coupling components of the ^{15}N nuclear spin. Understanding this transverse-field mixing is essential for precise control and characterisation of the electron spin environment in solid-state quantum systems.

Keywords: Nitrogen–vacancy center, electron–nuclear hyperfine interaction, ESEEM, Electron Ramsey Envelope Modulation (EREEM), transverse-field induced mixing.

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Towards the Microscopic of Decoherence in SAM Qubits

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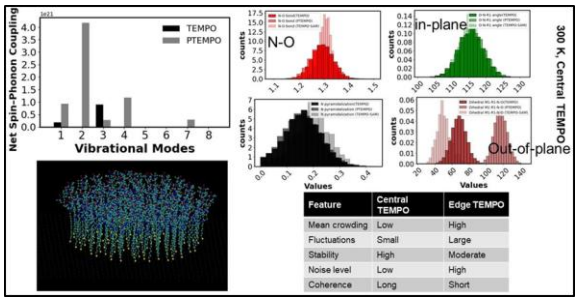
Quantum computing relies fundamentally on the ability to realize robust, coherent qubits that can be precisely controlled and integrated into scalable architectures. Molecular spin qubits are particularly attractive in this context, as they combine long coherence times with chemical tunability and the potential for bottom-up assembly. Among these, nitroxide radicals such as TEMPO have emerged as promising candidates. Recent work [1] has demonstrated that self- assembled monolayers (SAMs) of TEMPO radicals on Au(111) surfaces preserve quantum coherence for times as long as 13 μs, highlighting their potential for solid-state quantum information processing. Despite this advance, the microscopic spin dynamics governing qubit behavior within these monolayers remain poorly understood. In this work, we present a comprehensive theoretical investigation aimed at uncovering the molecular origins of coherence and relaxation in TEMPO-based qubits. Using density functional theory (DFT) and ab initio molecular dynamics (AIMD), we first characterize the electronic structure, low- temperature vibrational modes, spin–phonon coupling, and longitudinal relaxation time (T_1) of an isolated propargyl TEMPO radical. We then extend our study to self-assembled monolayers by employing novel simulation strategies to evaluate spin–spin interactions, Zeeman and hyperfine tensors, and their resulting spin dynamics. Finally, we examine the interfacial behavior of TEMPO SAMs on Au(111), elucidating how molecular motion and structural organization at the surface govern spin-relaxation pathways and ultimately impact qubit performance.

Keywords: Quantum Computing, Qubits, Self-Assembled Monolayer, TEMPO, T1 relaxation.



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Electron Spin Resonance–Based Characterization of Free Radical Activity in Environmental Pollutants

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Environmental pollution from industrial processes, vehicular emissions, and agricultural runoff generates a variety of reactive free radicals that significantly influence ecosystem stability and public health. Electron Spin Resonance (ESR) spectroscopy offers a direct, non-destructive method for detecting and quantifying these radicals, yet systematic evaluations of its applicability across diverse environmental pollutants remain limited. To address this gap, this work investigates ESR-based analysis of free radical activity in particulate matter (PM), heavy- metal–contaminated water samples, and pesticide residues. Key ESR parameters—including signal intensity, g-factor values, and linewidth broadening—are used to assess radical concentration and oxidative reactivity. Results indicate that PM samples exhibit the highest radical densities due to transition metal interactions, while pesticide residues show distinct spectral signatures associated with organic radical formation. Heavy-metal samples demonstrate moderate but stable radical generation linked to redox cycling processes. These findings demonstrate the capability of ESR spectroscopy to differentiate between pollutant classes and provide quantitative insight into their reactive behaviour. The study highlights ESR as a valuable analytical tool for environmental monitoring frameworks, supporting early detection of harmful pollutant-induced radical activity and enabling data-driven approaches for pollution mitigation and risk assessment.

Keywords: Electron Spin Resonance (ESR), Free Radicals Environmental Pollutants Particulate Matter Environmental Monitoring

Photochemical Dehydrogenation *via* Intermolecular Hydrogen Atom Transfer Reaction

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Photochemical transformation of organic frameworks has experienced substantial advancement in recent decades, with photoredox catalysis emerging as a powerful strategy for sustainable organic synthesis. However, applications of precious metal-based photocatalytic transformations are limited due to high cost, limited recyclability, and scarcity of transition metals in nature.[1] Herein, we report a metal-free, visible-light-driven dehydrogenation of 6,5- bicyclic heterocycles via an intermolecular hydrogen atom transfer reaction without requiring transition metals, external oxidants, or harsh reaction conditions. The newly developed dehydrogenation process afforded a,b-unsaturated arylketones from sulfur and oxygen- containing bicyclic heterocycles with excellent functional group tolerance toward both electron-withdrawing and electron-donating groups (EWGs/EDGs).

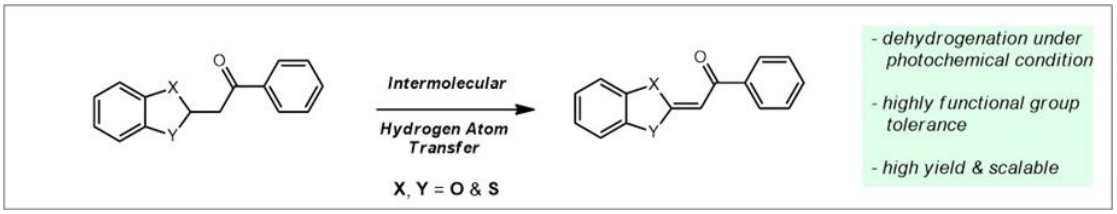

Figure: Synthesis of a,b-unsaturated arylketones via photoinduced HAT.

A detailed mechanistic study established the radical nature of this dehydrogenation process, and an EPR study confirmed the involvement of an oxygen-centred radical intermediate in the intramolecular hydrogen atom transfer process. These findings establish the photochemical dehydrogenation process as a viable alternative to transition metal catalysed protocols systems for selective dehydrogenation reactions under environmentally benign conditions.

Keywords: Hydrogen Atom Transfer (HAT), Dehydrogenation, Visible light photoredox catalysis,

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A Unified ESR–AI Framework for Quantifying Free Radical– Mediated Environmental Stress Across Air, Water, and Soil

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Electron Spin Resonance (ESR) spectroscopy is a quantum sensing technique capable of directly probing unpaired electron spins associated with free radicals, which play a central role in mediating chemical and oxidative stress in environmental systems. Environmental monitoring is traditionally performed separately for air, water, and soil using concentration- based metrics, which often fail to capture the underlying reactive stress mechanisms that propagate across interconnected environmental compartments. As a result, comparative assessment of cumulative environmental stress remains fundamentally limited.

In this work, we propose a **unified ESR–AI framework** for quantifying free radical–mediated environmental stress across air, water, and soil. ESR measurements are treated as quantum spin signatures of environmental stress, while physics-guided artificial intelligence is employed to extract normalized, physically meaningful stress indicators from heterogeneous ESR spectra. The framework integrates ESR data from gaseous, liquid, and solid media and accounts for medium-dependent spectral features, measurement variability, and noise, while preserving radical-specific spin information relevant to environmental impact.

By enabling cross-media normalization and comparison of free radical activity, the proposed approach advances ESR from a medium-specific analytical technique to a system-level environmental diagnostic framework. The results demonstrate robust extraction of stress-related spin signatures and consistent comparison of environmental stress across different compartments. This work establishes a scalable, software-enabled pathway for early-warning assessment of cumulative environmental stress and highlights the potential of ESR-based quantum sensing combined with AI-driven analysis for next-generation environmental diagnostics and ecosystem health evaluation.

Keywords: Electron Spin Resonance (ESR); Free Radicals; Environmental Stress; Quantum Sensing; Cross-Media Environmental Monitoring

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Exploring Environmental Pollutants through Electron Spin Resonance Spectroscopy

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Environmental pollution resulting from rapid industrial growth, urbanization, and agricultural activities has led to increased generation of reactive free radicals, posing serious risks to ecosystems and human health. The primary aim of this study is to highlight the relevance of Electron Spin Resonance (ESR) spectroscopy as a direct and non-destructive technique for identifying and characterizing paramagnetic species in environmental samples. By focusing on commonly encountered pollutants such as airborne particulate matter, contaminated water sources, and pesticide residues, the study emphasizes how ESR can be employed to understand pollution-driven oxidative processes and their potential environmental impact.

The second objective of this work is to examine how ESR spectral features—including signal intensity, g-factor variations, and linewidth changes—can be used to evaluate the oxidative reactivity and chemical behavior of different pollutant classes. The analysis indicates that particulate matter exhibits pronounced free radical activity, while waterborne contaminants and pesticide residues display distinct ESR signatures linked to metal-induced and organic radical formation. These findings demonstrate the effectiveness of ESR in differentiating pollution sources and assessing their associated risks. Overall, the study presents ESR as a valuable analytical tool for environmental monitoring, early risk detection, and the development of informed pollution-mitigation strategies.

Keywords: Electron Spin Resonance (ESR), Environmental Contaminant Analysis, Radical Generation Mechanisms, Air and Water Quality Assessment, Oxidative Stress Indicators, Pollution Impact Evaluation.

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Carbon with Stone-Wales defect as quantum emitter in h-BN

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Paramagnetic color centers in hexagonal boron nitride (h-BN) are promising candidates for quantum technologies due to their potential for stable single-photon emission. However, identifying the precise atomic configurations responsible for such emission remains a challenge. Using hybrid density functional theory, we show that a defect complex formed by carbon substitution at the nitrogen site combined with a Stone-Wales defect (CN + SW) in h-BN gives rise to a single-photon emitter near the 4 eV photoluminescence line. The calculated Huang-Rhys factor of ~1.9 indicates moderate electron phonon coupling, while the strong transition dipole moment (0.94 eÅ) and short radiative lifetime (1.92 ns) suggest efficient optical transitions. To compute and analyze these optical properties, we employed the DEFECTPL Python package, which implements the generating function approach for modeling defect-related luminescence. DEFECTPL enables the calculation of key photophysical parameters such as the Huang-Rhys factor, Debye-Waller factor, photoluminescence spectra, and electron-phonon spectral functions, and includes the effects of isotopic substitution. The excellent agreement between our theoretical predictions and experimental observations of carbon-related emitters in h-BN highlights both the viability of the CN + SW defect and the utility of DEFECTPL as a tool for defect-based quantum emitter discovery.

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ESR Study to Understand the Mechanism of Pollutant Degradation using Novel Hypergolic Activated Porous Carbon

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Porous carbons are indispensable materials across catalysis, energy storage, and carbon capture. Traditionally, these are synthesized from simple sources like biomass through controlled carbonization and subsequent activation. This work presents a novel approach utilizing hypergolic synthesis— leveraging high-energy rocket-fuel reactions—combined with KOH activation to produce highly porous activated carbon (HPAC). This method achieves an optimal balance of high porosity and uniform pore distribution, resulting in a record-high specific surface area (SSA) of 4800 m^2/g.

To investigate the structural origins of this porosity, a quantitative Electron Spin Resonance (ESR) study was conducted. We hypothesize that the ultra-high surface area arises from a unique synergy between pentagonal carbon rings and carbon radicals generated during the initial hypergolic treatment and templating phase. Beyond structural characterization, the HPAC was evaluated for carbon capture, electrochemical applications, and the degradation of toxic pollutants, specifically dyes and antibiotics that contribute to environmental degradation and antibiotic resistance. Efficiency was tested through peroxymonosulfate (PMS) activation, where the catalyst facilitates the breakdown of PMS anions into reactive hydroxyl and superoxide radicals. Our results demonstrate a 90% removal efficiency for Rhodamine B (RhB) within 50 minutes at concentrations of 20 mg/L, maintaining performance over four cycles. Similar efficiencies were observed for various other dyes and antibiotics. ESR and quenching studies (using potassium iodide) identified that surface radicals play the primary role in the degradation process. Furthermore, Liquid Chromatography-Mass Spectrometry was utilized to identify degradation products, confirming the breakdown of complex pollutants into simple alcohols and carboxylic acids. This research establishes hypergolic-derived HPAC as an eco-friendly, high- performance catalyst capable of mineralizing complex organic pollutants through PMS activation.

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Matrix Induced Modification of Spin Crossover in $Fe(phen)_2(NCS)_2$ Complex

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Spin-crossover (SCO) materials exhibiting reversible switching between high-spin (HS, S=2) and low-spin (LS, S=0) states are of considerable interest for spin-based electronic applications. In this work, spin-state biostability and spin-transition behavior of the SCO complex $Fe(phen)_2(NCS)_2$ embedded in an ethylene glycol matrix were investigated. The composite was synthesized using the wet chemical method. The X-ray diffraction pattern (Fig. 1a) matches well with the reported bulk structure with slight shifts in peak positions that may arise from lattice strain induced by matrix confinement. Spin transitions were probed through electrical and magnetic measurements. Current–voltage (I–V) characteristics measured at 300 K and 90 K reveal thermally driven HS ↔ LS switching accompanied by a pronounced hysteresis loop (Fig. 1b–c). At 90 K, the complex stabilizes in the LS state and exhibits higher electrical conductivity, whereas at 300 K it remains in the HS state with reduced conductivity. Time-dependent current (I–t) measurements under dark and illuminated conditions at both temperatures (Fig. 1d–e) show an enhanced photoinduced response at lower temperature. Electron paramagnetic resonance (EPR) measurements performed between 110 and 280 K further confirm the spin transition. At 280 K, a broad resonance near 3000 G ($g \approx 2.1$) along with an additional feature at 2300 G (g~2.9) is observed (Fig. 1f). The latter signal diminishes below 170 K, indicating an HS to LS transition. The transition temperature is slightly lower than that of the bulk compound (~176 K), suggesting modified spin interactions due to matrix embedding.

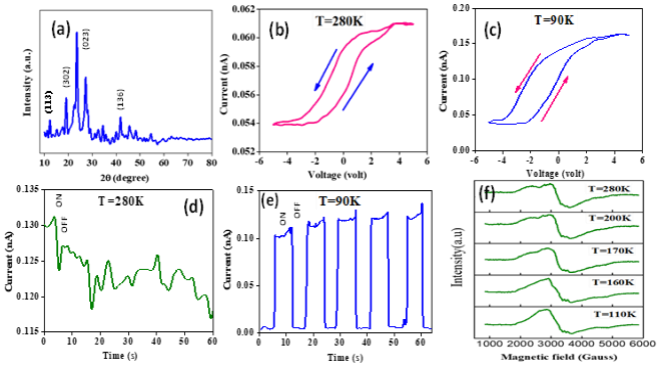

Fig. 1. (a) Room temperature XRD pattern of SCO sample in ethylene glycol matrix (b) I-V characteristics of the sample at 280K and that of (c) at 90K, (d) I-t data obtained at 280K and that of at (e) 90K and (f) EPR spectra of the sample recorded at different temperatures.

Keywords: Spin crossover, electron paramagnetic resonance, switching.

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Mechanistic Investigation of Metalloradical Catalysed Radical Hydrogenation of Olefins

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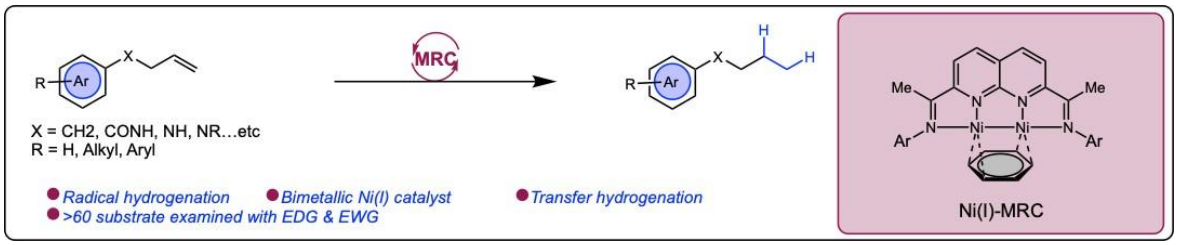
Radical hydrogenation via Hydrogen Atom Transfer (HAT)/ Transfer Hydrogenation to alkenes is an increasingly important transformation for the formation of thermodynamically more stable alkane isomers. Current single-catalyst-based hydrogenation methods require a stoichiometric oxidant in addition to a hydride (H^-) source.[1] Hydrogenation based on radical, metal-catalyzed hydrogen atom transfer (mHAT), transfer hydrogenation mechanisms offers an outstanding opportunity to overcome these difficulties, enabling the mild reduction of these challenging olefins with selectivity that is complementary to traditional hydrogenations with H_2.



Scheme: Metalloradical (MRC) catalyzed radical hydrogenation of olefines

Furthermore, it provides an opportunity for asymmetric induction through transfer hydrogenation using two different hydrogen sources.[2,3] Herein, we disclose the first report on metalloradical (MRC) catalyzed radical hydrogenation of olefins using two distinct hydrogen sources ($NaBH_4$ & $Et_3N.3HF$). Control reaction confirms the generation of the H_2 molecule, which is further activated and subsequently donated to olefins via MRC-catalyzed HAT. The bimetallic nature of MRC makes it even more oxidant-free. Classical radical clock and radical-quenching experiments suggest a radical hydrogenation pathway. A mechanistic investigation utilizing both EPR and paramagnetic proton NMR unambiguously confirmed the involvement of the metal-centre radical. Simulation of EPR spectra perfectly aligns with experimentally observed data. Together, this catalytic system enables hydrogenation of different classes of molecules and introduces a new approach to radical hydrogenation.

Keywords: Metalloradicals, Binuclear metal catalyst, Transfer hydrogenation, Radical Hydrogenation.

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Efficient Access of Cyclohexadienes via Transition-Metal Free Csp^2-Csp^2(CO) Bond Formation

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Cyclohexadiene is an important core structure in numerous natural products, including alkaloids and terpenoids, and exhibits biological activities ranging from anti- bacterial to Anti-cancer.[1] Its derivatives also act as biosynthetic precursors for aromatic amino acids, vitamin K, and folate. Moreover, it serves as a highly reactive intermediate in the synthesis of analgesic drugs such as morphine and codeine,[2] as well as in the well-known Diels- Alder reaction. Herein, we report an efficient synthetic protocol to access a new class of cyclohexadienes from N-benzoyl bromoalkene under transition-metal-free conditions. This strategy begins with the preparation of N-benzoyl bromoalkene from 1,2-dibromocyclohexene *via* C-N bond formation through nucleophilic substitution reaction.[3]

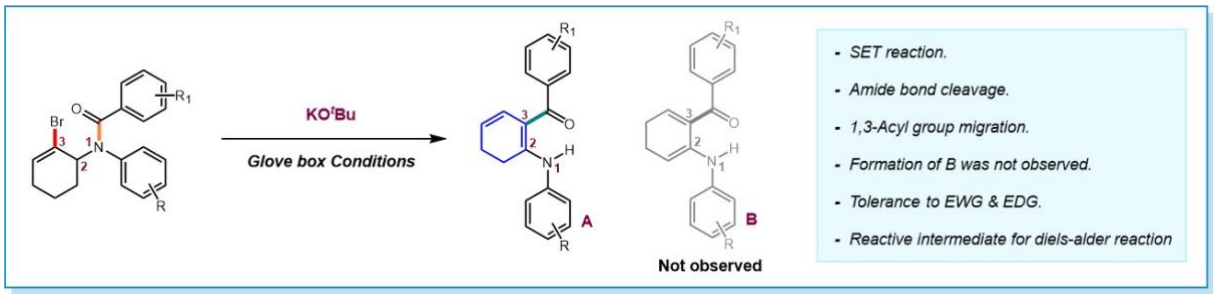

Figure: Synthesis of 1-amino, 2-acyl, 1,3-cyclohexadiene.

Next, KO^{t}Bu mediated SET (Single Electron Transfer) promotes Intramolecular 1,3-acyl migration through amide bond cleavage, leading to Csp^2-Csp^2(CO) bond formation and selectively affords the 1-amino, 2-acyl, 1,3-cyclohexadiene product.[4] The reaction shows broad tolerance towards both electron-withdrawing and electron-donating substituents. *Our mechanistic studies confirmed the generation of a radical species via in situ EPR (Electron Paramagnetic Resonance) studies and radical trapping experiments. Controlled experiments highlighted the crucial role of the carbonyl group in driving the transformation.*

Keywords: Cyclohexadiene, Amide bond cleavage, Acyl migration, SET (Single Electron Transfer).

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A novel Doniac-Sunjic like line shape function to describe asymmetric EPR signals in nanoparticles of $Sm_{0.48}Ca_{0.52}MnO_3$

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EPR spectra of doped rare earth manganites (of the form $RE_{1-x}A_xMn^{3+}{}_{1-x}Mn^{4+}{}_xO_3$ where RE is a trivalent rare earth ion and A is a divalent alkaline earth ion) consist of a single broad signal originating in the stoichiometrically present Mn^{+3} and Mn^{+4} ions. The signals can be asymmetric if the samples are significantly conducting due to the 'skin depth effect' and are described using the modified Dysonian equation proposed by Joshi and Bhat [1]

$$\frac{dP}{dH} = A\left[\left(\frac{\Delta H + \alpha(H - H_0)}{4(H - H_0))^2 + (\Delta H)^2}\right) + \left(\frac{\Delta H - \alpha(H + H_0)}{4(H + H_0))^2 + (\Delta H)^2}\right)\right] - - - (1)$$

where P is the microwave power absorbed, H and Ho are the magnetic field and the resonance field respectively, α is the asymmetry parameter and A is a constant proportional to the intensity. However, recently our EPR studies on nanoparticles (size 8 nm, smaller than the skin depth) of $Sm_{0.48}Ca_{0.52}MnO_3$ showed unexpected asymmetric behavior of EPR signals. We found that the so-called Doniac-Sunjic (DS) like equation

$$\frac{dP}{dH} = A \cdot \frac{d}{dH}\left[\begin{array}{l} S \cdot \frac{2}{\pi}\left(\frac{W_L}{(4(H + H_o)^2 + W_L^2)^f}\right) + S \cdot \frac{2}{\pi}\left(\frac{W_L}{(4(H - H_o)^2 + W_L^2)^f}\right) \\ +(1 - S)\left(\frac{\sqrt{4\ln 2}}{W_G\sqrt{\pi}} e^{-\frac{4\ln 2}{W_G^2}(H+H_o)^2}\right) + (1 - S)\left(\frac{\sqrt{4\ln 2}}{W_G\sqrt{\pi}} e^{-\frac{4\ln 2}{W_G^2}(H-H_o)^2}\right) \end{array}\right] - - - (2)$$

fits the signals satisfactorily [2] (R^2~0.997). Here S is the fraction of Lorentzian signal, W_L and W_G are the Lorentzian and Gaussian linewidths respectively, f is the fitting parameter and A is a constant. In the present work, we further refine the model to account for the fact that the nanoparticles are characterized by two regions, a core and a surrounding surface shell [3]. The disordered shell is understood to give rise to the surface ferromagnetism, and the core is more like the bulk sample, being either paramagnetic or antiferromagnetic. It follows that the shell and the core have different resonance fields. To account for this fact, we modify Eq. (2) to include two different resonance fields and obtain

$$\frac{dP}{dH} = A \cdot \frac{d}{dH}\left[\begin{array}{l} S \cdot \frac{2}{\pi}\left(\frac{W_L}{(4(H + H_{OC})^2 + W_L^2)^f}\right) + S \cdot \frac{2}{\pi}\left(\frac{W_L}{(4(H - H_{OC})^2 + W_L^2)^f}\right) \\ +(1 - S)\left(\frac{\sqrt{4\ln 2}}{W_G\sqrt{\pi}} e^{-\frac{4\ln 2}{W_G^2}(H+H_{OS})^2}\right) + (1 - S)\left(\frac{\sqrt{4\ln 2}}{W_G\sqrt{\pi}} e^{-\frac{4\ln 2}{W_G^2}(H-H_{OS})^2}\right) \end{array}\right] - - - (3)$$

where H_{OC} is the resonance field for the spins in the core, H_{OS} is the resonance field for the spins in the shell. We find that Eq. (3) fits the line shapes much better with $R^2 = 0.9999$. It is believed that this equation would be the appropriate one to describe EPR signals from other nanomanganites as well.

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Deep Learning Assisted Quantum ESR Deconvolution for Resolving Overlapping Radical Spectra

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Electron Spin Resonance (ESR) is a cutting-edge quantum-technique that investigates the dynamics of unpaired electron spins, which are, in essence, two-level quantum systems. In realistic quantum materials and molecular systems, several spin types are often present together, resulting in overlapping ESR signals that constitute a collective quantum measurement. It is this combination of spin-state signals that renders the application of standard spectral fitting and Fourier-based techniques absolutely tough to isolate individual radical contributions amidst experimental noise and significant spin interactions.

In this work we propose a framework combining deep learning with quantum ESR deconvolution for the resolution of overlapping radical spectra. The dataset which was guided by physics was created by simulating thousands of ESR measurements that were composed of superposed Lorentzian-derivative spin responses with randomized resonance fields, linewidths, amplitudes, and stochastic noise. This closely mimicked the quantum spin ensembles observed in real ESR experiments. A one-dimensional convolutional neural network was then trained to perform the inverse quantum measurement mapping from the composite ESR spectrum to its underlying spin-resolved components.

The trained model demonstrates robust recovery of quantum spin information beyond the capabilities of classical deconvolution techniques by accurately reconstructing individual radical ESR signals even in regimes of strong spectral overlap. Reliable separation of quantum spin signatures is made possible by this data-driven method, which also facilitates high-fidelity ESR-based quantum sensing, defect spectroscopy, and radical analysis.
The suggested framework offers a scalable software route toward intelligent ESR instrumentation and next-generation quantum technologies by fusing quantum spin physics with deep learning-based signal inversion.

Keywords: Electron Spin Resonance, Quantum Spin, Deep Learning, Spectral Deconvolution, Quantum Technologies.

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Millikelvin EPR/FMR using 3D loop gap resonators

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A strong and even coupling regime between collective spins and microwave photons is crucial for hybrid quantum systems. Performing electron paramagnetic resonance (EPR) and ferromagnetic resonance (FMR) measurements at cryogenic temperatures offers significant advantages: thermally excited magnons are strongly suppressed, thermal noise is minimized, and intrinsic magnetic dynamics can be studied in an exceptionally clean environment. The three-dimensional (3D) cavity resonators offer several advantages, such as larger mode volume, reduced electric field participation ratio at lossy surfaces, and low internal losses. The EPR/ FMR spectroscopy methods require a uniform, concentrated microwave magnetic field to analyze the magnetic properties of samples. However, the physical dimensions of traditional rectangular cavities (RC) can become impractical at lower microwave frequencies. A compact loop-gap resonator (LGR) is introduced for FMR/EPR studies [1]. The LGR operates as a lumped-element circuit, which provides smaller physical dimensions, a high-quality factor, and a homogeneous magnetic field for small-sized samples. LGR is a compact resonant structure that achieves high microwave resonance frequencies in a much smaller physical volume than RC with better sample accessibility. We have designed a three-loop, two-gap LGR of resonant frequency 7.5 GHz. All individual loops are connected in series and separated by a thin gap of 1 mm. The capacitive and inductive elements are separated with the fair approximation that the RF magnetic field exists inside the loop and the RF electric field inside the gaps.

Keywords: microwave photons, cavity resonators, lumped-element circuit

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Electron Spin Resonance and Magnetic Signatures of Charge Order Melting in $Sm_{0.42}Ca_{0.58}MnO_3$ Nano-manganites

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Rare-earth manganites of the form $RE_{1-x}A_xMnO_3$ where RE is a trivalent rare earth ion and A is a divalent alkaline earth ion, undergo a "charge ordering" (CO) transition on cooling, leading to an increase in the resistivity and antiferromagnetic ordering. Reducing the particle size to nanoscale is an intrinsic way to destabilize the CO state [1] and achieve technologically relevant properties such as magnetoresistance. However, it remains an open question whether this size-induced melting of charge order is complete or whether remnants of short-range CO persist.

In this work, we present a comparative study of bulk and nanosized $Sm_{0.42}Ca_{0.58}MnO_3$ using magnetization and electron paramagnetic resonance (EPR) measurements [2]. The nanoparticles were synthesized by a microwave-assisted reverse micelle method, with optimized surfactant choice and water-to-surfactant ratio to obtain small, nearly monodisperse particles. Structural and microstructural properties were characterized by X-ray diffraction and transmission electron microscopy.

The nanosized samples show a near-complete suppression of charge ordering, evidenced by the absence of characteristic CO signatures in magnetization, peaks in EPR intensity, and the linewidth minimum at the CO temperature TCO [3]. Furthermore, deviations from Curie-Weiss behavior well above the magnetic ordering temperature reveal the emergence of a Griffiths- like phase, indicating short-range ferromagnetic correlations induced by size reduction and disorder. These results demonstrate that nano scaling leads to the melting of long-range charge order while stabilizing a 'Griffiths-like phase' [4] in $Sm_{0.42}Ca_{0.58}MnO_3$ nanoparticles.

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Simulation of pulsed DNP in the steady state

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In pulsed dynamic nuclear polarization (DNP), polarization is transferred from an electron to a nearby proton through precisely timed sequences of microwave pulses. A DNP pulse sequence is repeatedly applied hundreds to thousands of times for a spin system to reach the steady state. Spin system dynamics under a DNP pulse sequence is dissipative, linear, and periodically driven. Modelling explicit propagation is computationally expensive. We recently developed a solution to compute the stroboscopic steady state directly with Newton-Raphson's algorithm [1], based on the kernel of Spinach [2].

We explored DNP pulse sequences: nuclear spin orientation via electron spin locking (NOVEL), time-optimized pulsed (TOP), X-inverse-X (XiX), and two-pulse phase modulation (TPPM) [1,3]. Steady-state simulations at 0.34 (X), 1.2 (Q), and 3.4 T (W band) accurately reproduce the experimental field profiles, optimization of repetition times (Fig. 1), and electron nutation frequency dependence, even with a simple spin system of one electron and one proton. Ensemble averaging over electron-proton distances and microwave B_1 fields further improves agreement with experiments.

The steady-state simulations also accurately predict the experimental behavior with DNP sequences that induce polarization transfer via adiabatic passage and constitute a powerful tool for designing even better DNP sequences. Using our simulation method, we found that supercycling significantly improves the efficiency of TPPM DNP.

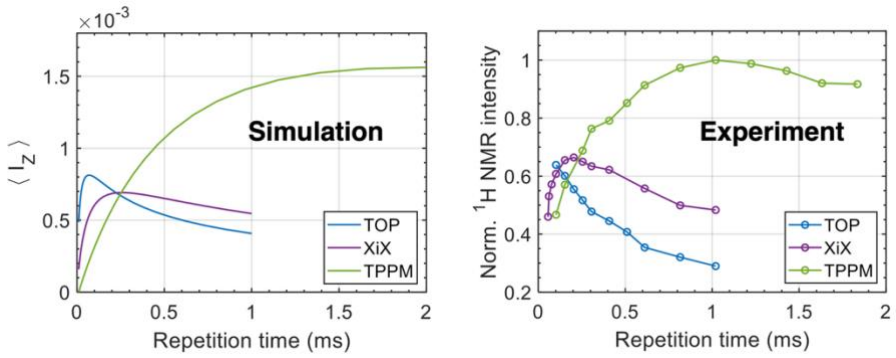

Fig.1. Optimization of the repetition time for TOP, XiX, and TPPM DNP at Q band.

Keywords: Dynamic nuclear polarization, spin dynamics, quantum dissipation, super cycling, microwave pulse sequences

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Automating SF-SVD for Pulse Dipolar Spectroscopy Data Analysis

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Electron Spin Resonance (ESR) Pulsed Dipolar spectroscopy (PDS), which determines distance distributions P (r) between a pair of spin-labeled residues in a protein, is used to probe dynamic structure of proteins. Determination of P(r) from PDS signals is a challenging task. The Srivastava-Freed Singular Value Decomposition (SF-SVD) method allows P(r) determination with higher resolution and yields robust results compared to non-linear least square fitting that relies on arbitrary regularization parameters. However, in its current implementation, SF-SVD PDS data analysis is nontrivial and can require up to 40 minutes to process a complex PDS signal. This is because analyzing one signal is a multi-step process, involving finding a convergence region of the truncated sum of the values of probability distribution (satisfying the Picard condition) and hence computing P(r). Therefore, for rapid data analysis, we aim to automate the process. This automation divides the distance domain in the signal into multiple regions (perhaps even 100) and finds the convergence region of the truncated sum of probability distribution values and P(r) for every region. The automated version of SF-SVD has been applied successfully to simulated PDS signals, achieving an average runtime of 1 min. The method of SF-SVD can be used to solve ill-posed inverse problems in other contexts, such as analyzing the Double Electron-Electron Resonance spectroscopy.

Keywords: SF-SVD, Pulsed Dipolar Spectroscopy, Automation, Picard condition

Deep Learning-Assisted Inversion of Quantum Spin Measurements in Electron Spin Resonance

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Electron Spin Resonance (ESR) spectroscopy probes the response of unpaired electron spins to external magnetic fields and microwave excitation, providing access to quantum spin systems that can be effectively described as basic two-level quantum systems. In practical investigations of quantum materials and spin-based platforms, ESR measurements rarely correspond to isolated spin responses. Instead, experimentally acquired spectra reflect the combined influence of instrumental noise, overlapping resonance features, and spin–spin interactions, which together obscure the underlying spin parameters and limit the reliability of conventional spectral fitting and heuristic analysis techniques.

This work investigates a data-driven strategy for interpreting ESR measurements by combining deep learning with an explicit inversion of the quantum measurement process. Realistic ESR spectra are generated using physics-informed simulations that span a range of spin configurations and experimental conditions. A deep neural network is trained to learn the inverse mapping from the measured ESR signal to physically meaningful spin parameters, thereby treating ESR explicitly as a quantum measurement process rather than a purely spectral analysis problem.

Across varied noise levels and measurement regimes where standard ESR analysis becomes unreliable, the proposed approach enables consistent recovery of spin-related information from measured spectra. This inversion-based perspective improves access to underlying quantum spin properties and is relevant for applications such as spin-based quantum sensing and the analysis of complex spin systems. More broadly, the framework offers a scalable, software- based route for advancing ESR data interpretation and supports ongoing efforts to develop more intelligent methodologies for quantum measurement in emerging quantum technologies.

Keywords: Electron Spin Resonance (ESR), Quantum Spin Systems, Deep Learning–Assisted Inference, Quantum Measurement Inversion, Spin-Based Quantum Technologies.

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New strategies with superconducting tunable resonators in low temperature ESR.

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Superconducting circuits form the backbone of modern quantum computing hardware architecture. Recent efforts have shown that various types of qubits (transmon, flux, etc.) as well as high quality factor resonators, which can function as a bus can be fabricated out of superconducting materials. These resonators in particular, have become popular not only because of their relative ease of fabrication using standard techniques, but also because, due to their high quality factors (~10^5) they can be used for high sensitivity measurements in ESR spectroscopy. The superconducting aspect can be exploited to make the resonant frequency tunable. Since the resonant frequency depends on the total inductance, the kinetic inductance can be varied simply by applying a DC current. Various avenues have been explored with such tunable resonators such as echo silencing [1] which can be useful in the retrieval of photonic states from quantum memories [2]; ENDOR/ELDOR [3], where the sequence to invert the second spins species is achieved by detuning to the required frequency and then applying the pulse. In addition, our group has used the tunability aspect for improving other aspects in low temperature (~10mK) ESR. Superconducting tunable resonators can be used for parametric amplification, where a pump tone at twice the resonant frequency can lead to phase sensitive quantum limited amplification which is important for high sensitivity measurements [4]. We try to achieve wideband excitation, where a combination of wideband chirp pulses and fast tunability can be used to overcome the low excitation bandwidth in ESR thereby further increasing signal to noise ratio. Another interesting phenomenon due to the high quality factor is the very long ringdown times which are usually of the order of 100us. This high unwanted signal can easily drown out echo signals. The tunability aspect can again be of use here, whereby momentarily increasing biasing current above critical current, we can reduce the ringdown time. The results of such experiments will be demonstrated.

Keywords: Resonators, Quantum, superconductors, spin echoes

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Active Learning–Guided Adaptive ESR Acquisition for Rapid Quantum Spin Characterisation

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Electron Spin Resonance (ESR) is a quantum spectroscopy technique for investigating unpaired electron spins, which form the basis of two-level quantum systems. In practical studies of quantum materials and spin-based platforms, acquiring high-quality ESR spectra can be time-consuming because dense field sweeps and repeated signal averaging are often required, especially in low signal-to-noise regimes. This reduces experimental throughput and slows rapid spin characterisation.

Conventional ESR workflows rely on fixed, uniform scanning followed by spectral fitting and post-processing. While widely used, these approaches often spend substantial time sampling low-information regions and may become unreliable when spectra are weak or noisy. In this work, we propose an active learning–guided adaptive ESR acquisition framework that treats ESR as an information-driven measurement process and selects the next most informative measurements instead of scanning the full spectrum uniformly.

Physics-informed ESR simulations are used to generate realistic spectra across varying spin parameters and conditions, and a deep neural network is trained to infer spin signatures from partial measurements. An acquisition policy iteratively chooses field regions or sampling points that maximize information gain, enabling a closed-loop measure–infer–select strategy. The proposed approach reduces the required scans while preserving key spin features such as resonance position and linewidth across different noise regimes. By shifting ESR from fixed acquisition to adaptive measurement planning, this method supports rapid ESR-based quantum sensing and provides a scalable software pathway toward intelligent, measurement-aware ESR experimentation.

Keywords: Electron Spin Resonance, Active Learning-Based Acquisition, Adaptive Spectral Sampling, Quantum Spin Characterisation, Intelligent ESR Instrumentation

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Blind Recovery of DEER Spectral Signatures from Chemical Mixtures

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Blind recovery of overlapping spectroscopic signals is a persistent challenge in chemical analysis, particularly when mixtures deviate from idealized linear behavior. In this work, we investigate whether underlying Double Electron–Electron Resonance (DEER) spectral signatures can be recovered directly from experimental chemical mixtures, without requiring access to pure component spectra during the separation stage. Experimental DEER spectra were collected for two molecular systems, stilbestrol and estriol, along with four controlled mixtures spanning compositions of 90/10, 80/20, 50/50, and 10/90.

A data analysis pipeline combining physically informed preprocessing with blind source separation, implemented using Independent Component Analysis (ICA), was applied to the mixture spectra. The recovered latent components were evaluated against independently measured pure spectra using correlation analysis and peak-position fidelity, emphasizing preservation of the magnetic-field positions that encode distance information in DEER experiments. The dominant spectral features of both molecular species were successfully recovered, with correlations up to 0.91 and preservation of primary peak positions within experimental resolution.

Beyond qualitative recovery, the separated components were further used to estimate the relative contributions of each molecular species within the mixtures. The inferred mixture compositions closely matched the known experimental ratios, particularly for balanced and moderately imbalanced mixtures.

These results demonstrate that ICA-based blind separation can recover physically meaningful DEER spectral signatures from experimental mixtures while also enabling quantitative estimation of component contributions, providing a foundation for future physics-informed unmixing approaches in complex spin systems.

Keywords: DEER, Blind Source Separation, ICA, ESR, Spectral Mixing

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Grain Size Induced ESR and Magnetization Behavior of Hole Doped Bulk and Nano $Nd_{0.65}Ca_{0.35}Mn_{0.94}Cr_{0.06}O_3$ Manganite

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Bulk $Nd_{0.65}Ca_{0.35}MnO_3$ (NCMO) is a charge ordering (CO) manganite exhibiting a charge ordering transition temperature, Tco at 240K followed by an antiferromagnetic(AFM) transition at the Neel temperature (T_N = 150K). In this paper, we report the size dependent magnetic properties of $Nd_{0.65}Ca_{0.35}Mn_{0.94}Cr_{0.06}O_3$ manganite. Bulk and nano particles (~27nm) of hole-doped $Nd_{0.65}Ca_{0.35}Mn_{0.94}Cr_{0.06}O_3$ were prepared through sol gel route. These particles were characterized by XRD, TEM, EDAX and SEM techniques. To investigate the effects of grain size on magnetic ordering, extremely sensitive electron spin resonance (ESR) along with dc magnetization experiments were performed in temperature range $10K \leq T \leq 300K$. Confirmatory field dependent hysteresis measurements were performed on the samples. Reitveld refinement indexed with Pnma space group using orthorhombic unit cell directs that size reduction results in decrease in volume of the unit cell. While dc magnetization result displays vanishing of charge order in both the samples, ESR measurements show charge order fluctuations in the samples as it can detect minor magnetic phases and short-range interactions. From the magnetization measurements, it is observed that the reduction in particle size lowers the ferromagnetic transition temperature (Tc) and there is a distinct variation of $1/\chi$ vs T plots between the bulk and nanoparticles of $Nd_{0.65}Ca_{0.35}Mn_{0.94}Cr_{0.06}O_3$ manganite. EMR signals in the ferromagnetic phase of the bulk sample displays a double line feature which may be attributed to the magneto crystalline anisotropy.