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100 **Time-dependent Photo-EPR Applied to Point Defects in Crystals: Limitations and Applications.**

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Optical excitation is commonly used in concert with EPR to create the paramagnetic state of centers in a wide range of materials from complex polymers to highly ordered crystals. However, except for the pioneering studies in the early 80's, there are few reports of time-dependent photo-EPR of point defects in crystalline semiconductors. The scant use is caused, in part, by the limited time response imposed by the commonly used 100 kHz magnetic field modulation and the small number of EPR-active centers inherent to semiconductors. Recently, however, we have analyzed time-dependent data in several types of semiconductors using standard phase-sensitive detection. The results of one such study will be summarized here, emphasizing both the utility and limitations of the technique. The system to be discussed is Be-doped GaN, in which the Be acts a deep acceptor providing electrical compensation as well as yellow luminescence. Charge trapping parameters such as defect level (ionization energy) and capture coefficients are critical to understanding the effectiveness of Be as a dopant. The samples are 0.1 um thick, 0.5 cm^2 GaN platelets doped with 1017 cm-3 Be, and are measured at 3.5 K. The time-dependent photo-EPR data is analyzed using three coupled differential equations based on charge transfer among the Be acceptor, unintentionally added O donors, and the conduction and valence bands. Analysis of the results obtained during illumination with selected photon energies yields an optical threshold of 2.8 eV, which accounts for the effectiveness of the dopant as a compensator, and relaxation energy of 0.5 eV, which accounts for the yellow luminescence seen at 2.2 eV. The significance of these results and complications arising from more heavily Be-doped samples will be reviewed, along with consideration of the limitations imposed by the 100 kHz modulation detection system.

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EPR ORAL SESSION

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101 **Suppressing Spin-spin Relaxation in Silicon Carbide with Natural Isotope Abundance using Dynamic Decoupling.**

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The vacancy-related color centers in the CMOS-compatible material silicon carbide (SiC) are perspective for chip-scale quantum technologies based on ensembles as well as on single centers. Similar to the spin S = 1 nitrogen-vacancy (NV) defect in diamond – which has become a standard solid-state system for quantum applications under ambient conditions – the silicon vacancy (V_{Si}) in SiC possesses selectively addressable spin states through optically detected magnetic resonance (ODMR) [1,2]. In order to achieve long-lived electronic quantum memory in solid state, expensive and non-trivial engineering with spin-free nuclear isotopes, such as silicon-28 or carbon-12, is usually required. We investigate the coherence time properties of the Si-vacancies in a commercial 4H-SiC wafer with natural isotope abundance using the pulsed-ODMR technique [3]. Implementing the common Rabi-, Ramsey-, Spin-Echo- and CPMG-sequences, we can precisely measure spin-lattice (T_1) and spin-spin (T_2) relaxation times. The measurements are not only conducted at ambient conditions, but also at different temperatures and in different magnetic fields. In particular, the coherent spin properties of the V_{Si} defect are investigated in the temperature range from 10K to 300K and at magnetic field strengths of up to 30mT. Remarkably long spin-spin relaxation times in the millisecond range are attained through the suppression of heteronuclear spin cross-talking by applying a magnetic field above ten millitesla in combination with dynamic decoupling (CPMG) from the nearly separated nuclear spin baths. The fundamental limit, given by the spin-lattice relaxation time, tends to ten seconds at cryogenic temperatures.

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EPR ORAL SESSION

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102 Silicon Carbide Magnetoresistive Magnetometer with Electrically Detected Magnetic Resonance Self-calibration Feature for Space Science Application.

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It's commonly known that the wide bandgap nature of the silicon carbide (SiC) semiconductor allows it to be leveraged in electronics exposed to harsh environments. The material therefore has much potential for space missions where very high temperature and high radiation environments are commonly encountered. This work entails the development of a SiC based magnetometer which leverages intrinsic defects to sense near zero magnetic fields in space. The deep level defects give rise to a magneto resistive response referred to as zero-field spin dependent recombination (SDR). The SDR phenomenon allows a change in device current to be measured with changes in external magnetic field. The magnetometer has the ability to self-calibrate either by measuring spacing of the symmetrically spaced zero-field spin interactions (spin-spin and or hyperfine) or by measuring the field/frequency SDR response induced by low-field electrically detected magnetic resonance (EDMR). Leveraging the pn junction of a SiC power MOSFET designed for high power applications, the magnetometer currently exhibits a sensitivity of about 400 nT/sqrt(Hz). However, a future design of the device using custom materials, optimized geometry and fabrication will allow sensitivities to be pushed below the 1nT/sqrt(Hz) threshold, making the technology competitive to heritage designs such as fluxgate and optically pumped He magnetometers flown on most missions in space.

C.J. Cochrane, P.M. Lenahan, JAP, 112, 12, 2012. W.J. Baker, et. al., Nat. Comm., 3, 898, (2012).

EPR ORAL SESSION

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103 Measurement of Paramagnetic Spin Concentration in a Solid-state System using Double Electron-electron Resonance.

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Diamond has been extensively investigated recently due to a wide range of potential applications of nitrogen-vacancy (NV) defect centers existing in a diamond lattice. The applications include magnetometry and quantum information technologies, and long decoherence time (T_2) of NV centers is critical for those applications. Although it has been known that T_2 highly depends on the concentration of paramagnetic impurities in diamond, precise measurement of the impurity concentration remains challenging. Here we demonstrate a method to determine a wide range of the nitrogen concentration (n) in diamond using a wide-band high-frequency electron spin resonance and double electron-electron resonance spectrometer. Moreover, we investigate T_2 of the nitrogen impurities and show the relationship between T_2 and n. The method developed in this work is applicable for various spin systems in solid and implementable in nanoscale magnetic resonance spectroscopy with NV centers to characterize the concentration of the paramagnetic spins within a microscopic volume.[1]

1. V. Stepanov and S. Takahashi, submitted (2016), arXiv:1603.07404

EPR POSTER SESSION

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104 Hyperfine Interactions in Silicon.

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Silicon is a technologically versatile material – ubiquitous in microelectronics and solar cells, a promising platform for spin-based quantum devices and computers, and in nanoparticle form a, viable contrast agent in magnetic resonance imaging. In this talk I will present two examples of recent work from our group studying hyperfine interactions of electron spins in silicon. First I will describe the use of frequency-modulated microwaves in W-band dynamic nuclear polarization experiments to characterize local hyperfine interactions between paramagnetic defects at the surface of silicon microparticles and local nuclear spins. Next, I will discuss the optical hyperpolarization of phosphorus donors in silicon and the optical frequency dependence of EDMR signals in silicon.

EPR ORAL SESSION

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105 Probing Giant Magnetic Anisotropies in Mononuclear Single-molecule Magnets.

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The development and study of molecular nanomagnets has witnessed tremendous progress in recent years, with potential applications on the horizon. Of particular interest are so-called single-molecule magnets (SMMs) that display slow magnetic relaxation below a characteristic blocking temperature, T_B, due to a combination of a large magnetic moment and appreciable spin-orbit (SO) anisotropy. Early efforts aimed at increasing T_B focused on polynuclear clusters and maximization of the molecular spin state, S. However, this becomes challenging for large clusters whilst simultaneously maintaining the molecular anisotropy. Thus, a more direct route to increasing T_B involves optimization of the magnetic anisotropy, albeit for simpler molecules in which one can exert synthetic control over the ligand field (LF). In particular, certain transition metals residing in high-symmetry coordination environments can experience orbital degeneracies and very strong first-order contributions to their SO anisotropy. This talk will highlight recent work involving S = 1 Ni^{II} [1] and V^{III} [2] complexes subjected to rigid trigonal coordination environments in the solid state that are relatively stable against symmetry lowering Jahn-Teller distortions [3]. The resulting giant anisotropies associated with these species have been measured using very high-field (up to 35 T) EPR techniques. In particular, analysis of results for a trigonal bipyramidal (TBP) $[Ni^{II}Cl_3(Me\text{-}dabco)_2]$ complex on the basis of a spin-only Hamiltonian suggest an axial D parameter exceeding $-400\ cm^{-1}$, which is close to the SO coupling parameter, $\lambda = 668\ cm^{-1}$, for Ni^{II}, suggesting an orbitally degenerate ground state. However, the spin-only description cannot work in this limit, therefore necessitating the development of a model that includes the orbital moment. A qualitative theoretical approach will be described that takes into account a full description of crystal field, electron-electron repulsion and spin-orbit coupling effects on the ground state of Ni^{II} in a TBP coordination geometry. The model provides both qualitative and quantitative agreement with the high-field EPR experiments, hence validating its use for spectroscopic studies of orbitally degenerate molecular nanomagnets.

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EPR ORAL SESSION

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Triplet Exciton Generation in Materials for Organic Solar Cells.

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Using time-resolved EPR spectroscopy in conjunction with optical excitation we study charge separation in absorber materials for organic solar cells. When blended with the fullerene-based electron acceptor PCBM, two prominent derivatives of the low-bandgap polymer PCPDTBT differing by the bridging atom (carbon or silicon) exhibit different charge separation yields. While the EPR signatures of photogenerated positive polarons in C- and Si-bridged PCPDTBT are virtually identical, significant differences are observed with respect to the spin-relaxation behaviour. The spin-lattice relaxation time of positive polarons in C-PCPDTBT at low temperature ($T = 80$ K) is found to be more than two orders or magnitude longer than in the Si-bridged polymer derivative. This surprisingly slow relaxation can be rationalized by polarons trapped in defect states that seem to be absent (or are present in a substantially smaller concentration) in blends comprising Si-PCPDTBT. Transient EPR signals attributed to charge transfer (CT) states at the donor/acceptor interface and separated polarons are smaller in the blends with C-PCPDTBT as compared to those with the silicon-bridged polymer. We propose that triplet formation occurs via the CT state, thus diminishing the probability that the CT state forms free charge carriers in blends of C-PCPDTBT with PCBM. This hypothesis is confirmed by direct detection of triplet excitons in C-PCPDTBT:PCBM blends. The shape of the transient EPR spectra reveals that the triplet excitons are, in contrast to those formed in pristine polymer films, not generated by direct intersystem crossing, but result from back electron transfer through CT state recombination. The strong triplet signal is not observed in blends containing the Si-bridged polymer, indicating efficient singlet exciton splitting and subsequent charge carrier separation at the Si-PCPDTBT/PCBM interface.[1]

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EPR ORAL SESSION

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Spin-orbit Coupling in Conjugated Polymers.

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Conjugated polymers consist of only light elements and are generally considered to have negligible spin-orbit coupling (SOC). However, even a small contribution of SOC can have a large impact on charge carrier pair spin statistics and thus on the magneto-opto-electronic properties of materials used for organic light emitting diodes (OLEDs) and other devices. The sole source of SOC is assumed to be inter-site variations of the g-factor due to structural disorder of the polymer and it is observed indirectly as the so-called Δg mechanism in magneto-electroluminescence and magneto-resistance measurements.[1] We observe the effects of SOC in electrically detected magnetic resonance (EDMR) measurements on OLEDs as a magnetic field dependent line broadening mechanism that is already detectable at fields below 700 mT where the line width is still dominated by the unresolved hyperfine couplings to the surrounding hydrogen nuclei.[2,3] At much higher magnetic fields, up to 12 T, EDMR line widths are increasingly governed by the SOC. In this regime, line widths scale with the magnetic field and an increasingly asymmetric line shape emerges due to the rhombic g-tensors of both charge carriers. Preliminary quantum chemistry calculations of open-shell model systems implicitly produce g-tensors that are in excellent agreement with the measurements and suggest that the effects of disorder or g-tensor-strain are negligible in these systems.

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EPR ORAL SESSION

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108 Effect of Spin-orbit Interaction and Topological Gap for ESR Spectra in Low-dimensional Organic Conductors.

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Recently theoretical investigation by Oshikawa proposed that strong spin-orbit interaction causes additional ESR satellite signal and g-shift in 1D metallic system. So, we reexamined detailed X-band ESR spectra (satellite, line-shape, line-width) for low-dimensional metallic systems. Firstly, we focused on a 1D organic conductor $(TMTSF)_2ClO_4$, which shows stable metallic state down to 1K. Since the TMTSF molecule contains heavy selenium elements, there are considerable spin-orbit interactions. When we apply the static magnetic field along 1D conducting direction (H_0//a), a tiny satellite peak was appeared below 12K. In the case of $H_0//c^*$, we cannot observed any satellite peak. We also performed 2D metallic system, BEDT-TTF salts. A series of BEDT-TTF salts with low-symmetry shows anomalous g-shift at low-temperatures. We discuss relationship between the tiny band gap and anomalous ESR behavior observed in low-dimensional metallic systems.

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EPR ORAL SESSION

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109 Spin Dynamics of TAPD-MP$_{Ar}$-C$_{60}$ Spin Correlated Radical Pair.

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Molecular triads which undergo photo-induced electron transfer have a wide range of applications, from understanding and mimicking energy transfer in natural photosystems, to molecular spintronics and the understanding of magnetoreception in migratory birds such as the European robin[1,2]. Our work involves the study of optically generated molecular spin states as a tool to hyperpolarise, entangle and measure nuclear spins in molecules, while leaving the molecule in a diamagnetic ground state in order to minimise the long-term impact on nuclear spin decoherence[3,4]. Current work involves the study of the Donor-Bridge-Acceptor molecules TAPD-MP-C_{60} where M= H_2, Zn, Cd, for the primary purpose of using the charge-separated state (CSS) as source of a long-lived optically-generated electron spin, to interact with nearby nuclear spins and mediate coupling between them. We present studies on these molecules employing time-resolved and pulsed, electron paramagnetic resonance (EPR) and double resonance methods (ENDOR) combined with pulsed laser excitation, to extract the spin Hamiltonian parameters and to quantitatively understand the charge and spin dynamics.

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EPR ORAL SESSION

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110 Structural Information from Hyperfine Couplings in Iron Catalysts.

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Iron(III) has very interesting catalytic properties that can be modulated by its molecular environment. For this reason, one can find in nature or synthesize in the laboratory a myriad of different iron-based catalysts,either monoatomic or forming iron clusters, in low-symmetry sites or coordinated to highly symmetric organic chelators. In all cases, the properties, shape and spin density of the d-orbitals are crucial in determining the catalytic properties of iron. In this contribution we will illustrate how the determination of the spin state and g-values through EPR methods yields useful electronic information using two examples of iron catalysts with very different characteristics. One of the catalysts is an artificial heterocubane with a [Fe_4N_4] core that can reversibly store up to four electrons at very negative potentials. The second system is the protein cytochrome c550, where a single iron ion is coordinated by a four-fold organic ring of porphyrin. This cofactor, called heme group, is ubiquitous in life systems where it performs very different functions (catalytic, transport…) In both cases the study of the hyperfine interactions with magnetic nuclei in close vicinity of the iron yields also useful structural information and allows mapping the electron spin density distribution. The strategy for experimental determination of the hyperfine couplings of nitrogen and/or hydrogen nuclei will be shown for both systems. In the case of the heterocubane, the interpretation of hyperfine data reveals that the unpaired electron is predominantly located at one Fe center with some delocalization to the coordinated olefin moiety ($\rho \approx 18\%$) and to the nitrogen atom in the same chelating ligand ($\rho \approx 0.8\%$). For cytochrome c550 hyperfine couplings reveal electronic details related to the structure that can possibly be discussed in terms of the biological function.

EPR ORAL SESSION

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111 263 GHz Pulse EPR Reports on Proton-coupled Electron Transfer Through the Subunit Interface of *E. Coli* Ribonucleotide Reductase Ia.

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Ribonucleotide reductases (RNR) connect the RNA and DNA world by reducing all four essential ribonucleotides to deoxyribonucleotides. In *E. coli* RNR Ia, the strictly controlled radical chemistry starts in the β subunit at the “stable” tyrosyl radical (Y_{122}•) di-iron cofactor. A long-range radical transfer from subunit β to α generates a putative catalytic active cysteine radical (C_{439}•) in the α subunit that initiates catalysis. Successive studies showed that Y_{356}•(β), Y_{731}•(α) and Y_{730}•(α) are intermediate steps of this inter-subunit (α:β) proton-coupled electron-transfer (PCET). Conformational gating hinders the direct observation of these transient radicals. Therefore, site specific incorporation of the unnatural 3-amino-tyrosine (NH_2Y) and 2,3,5-fluoro-tyrosine (F_3Y) was used to trap all radical intermediates.[1-2] Our 263 GHz pulsed-EPR spectroscopy delivers highly resolved g-values, which are correlated to the individual hydrogen (H) bond network based on ENDOR spectroscopy and DFT models of radical intermediates. Within the α subunit short PCET steps with moderate to strong H bonds perpendicular to the ring were found, consistent with a concerted and collinear PCET.[3-4] At the structurally ill-defined interface EPR spectra of β-Y_{356}• with different mutants of the α subunit (α-Y_{730}F and α-Y_{731}F) reveal that the presence of α-Y_{731} influences the electrostatic environment around β-Y_{356}•. This supports the proposal of an H bond network enabling the proton transfer between the two subunits.[5] Furthermore, it demonstrates an indirect communication between the subunits.

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EPR ORAL SESSION

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112 The Composition and Structure of the Inorganic Core of Intermediate X(WT) and X(Y1212F) of *E. coli* Ribonucleotide Reductase.

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Activation of the diferrous center of the *β2* (R2) subunit of the class 1a *Escherichia coli* ribonucleotide reductases (RNR) by reaction with O_2 followed by one-electron reduction yields a spin-coupled, paramagnetic Fe(III)/Fe(IV) intermediate, denoted X, whose identity has been sought by multiple investigators for over a quarter century. To determine the composition and structure of X, the present study has applied ^{57}Fe, ^{14,15}N, ^{17}O and ^{1}H ENDOR measurements combined with quantitative measurements of ^{17}O and ^{1}H EPR line broadening studies to WT X, which is very short-lived, and to X prepared with the Y122F mutant, which has a lifetime of many seconds. Previous studies have established that over several seconds the as-formed X(Y122F) relaxes to an equilibrium structure. This report focuses on the relaxed structure and the differences between this relaxed structure and the structure of both WT X and X(Y122F) at short quenching times that are revealed by EPR, ENDOR, and ESEEM techniques.

EPR ORAL SESSION

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113 Mechanistic Investigations on Electron Bifurcation by EPR Spectroscopy.

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Electron bifurcation, a process for coupling endergonic and exergonic reactions to overcome thermodynamic barriers, is considered the third mechanism of biological energy conservation and results in the efficient coupling of electrochemical potential to chemical bond formation.[1,2] Overall, the mechanism of bifurcation and how bifurcating enzymes function is poorly understood. We are investigating the mechanism of flavin-based electron bifurcation in the NADH-dependent ferredoxin-NADP+ oxidoreductases, (Nfn), which catalyze the reversible reduction of NADP+ with reduced ferredoxin and NADH. Nfn contains two electron-transfer pathways both of which are comprised of flavins and FeS clusters.[3] EPR spectroscopy in conjunction with x-ray crystallographic and other biophysical techniques, are being used to investigate the oxidation-reduction properties of these centers and how they facilitate gating of electron-transfer to respective pathways. The results reveal that two unique, site-differentiated FeS clusters, Cys_3Asp [2Fe-2S] and Cys_3Glu[4Fe-4S], play key roles in the process through tuning of midpoint potentials and coupling with other redox centers. This presentation will summarize how these features work in concert with key structural properties of the enzyme to achieve bifurcation.

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EPR ORAL SESSION

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Out-of-phase ESEEM: Measuring Distances of Excited Radical-pair States to Identify the Final Electron Donor in Cryptochromes and Photolyases.

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Proteins of the photolyase/cryptochrome family share a conserved tryptophan pathway to transport electrons from the surface to the photo- and redox-active FAD cofactor within the protein.[1] In photolyases the fully reduced FADH-cofactor serves as donor of a catalytically-active electron for repair of light induced DNA lesions, while in cryptochromes the metastable semiquinone FAD radical represents the signaling state for different biological responses to blue light. Recent spectroscopic results presume that the pathway is more diverse in terms of number and amino acid composition than commonly accepted. In detail, certain members of the animal cryptochrome family might use a fourth, more surface exposed amino acid residue as final electron donor for signaling-state generation.[2] The altered environment of this alternative, more distant aromatic residue could reflect the difference between a pure electron transfer pathway in photolyases, and a long-time stabilization of the radical pair for e.g., magnetoreception in avian compasses. Direct characterization of the excited radical pair state can be achieved by transient EPR spectroscopy, which grants access to the g and A tensors of the radical-pair partners, as well as the dipolar and exchange coupling constants D and J. While pulsed electron-electron double resonance spectroscopy lacks the capability to directly measure electron-electron interactions of short-lived radical species, measurements of the out-of-phase electron spin echo envelope modulation (oop-ESEEM) of laser flash induced spin-correlated radical pairs gives direct access to the dipolar and exchange interactions between the radical pair partners.[3,4] Therefore distance measurements, and thereby an identification of the radical partner molecule can be accomplished. Here, we present results of transient EPR and oop-ESEEM measurements of different members of the photolyase and cryptochrome family at x-band and q-band frequencies, which prove that different amino acids at different distances function as final electron donor in animal type cryptochromes.

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EPR ORAL SESSION

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Studying the Structure of Metalloproteins with RIDME Spectroscopy: Application to Nitric Oxide Synthase.

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The most common EPR approach to study the protein structure involves attaching a pair of spin labels (usually, nitroxide radicals) to the protein and then using the double electron-electron resonance (DEER) technique to measure the magnetic dipole interaction between these labels, from which the distance is calculated. A less known and appreciated EPR distance measurement technique, in spite of being around for over a decade, is the relaxation-induced dipolar modulation enhancement (RIDME). It is conceptually similar to DEER; however, where DEER uses a pumping microwave pulse to flip one of the spins (usually designated as spin B) in the spin label pair, RIDME utilizes for the same purpose the natural longitudinal relaxation process. Such an approach makes RIDME uniquely suitable for measuring the distances in pairs where one or both spins represent metal centers characterized by significant g- or *hfi* anisotropy and where using DEER becomes impracticable. The focus of this presentation will be two-fold. First, a general outline of the principles, advantages, and limitations of RIDME spectroscopy will be given. Then, its practical application for measuring distances and conformational equilibria will be demonstrated using the playground provided by the nitric oxide synthase (NOS) enzyme, a modular metalloprotein whose function depends on the conformational mobility.

EPR ORAL SESSION

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116 High-Field EPR Studies on Model Dimeric Mn^{IV} Complexes.

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Mn^{IV} complexes are important in research on natural Photosystem II (PSII) and in design of artificial PSII. Dimeric Mn^{IV} systems have been postulated as intermediates in the catalytic water oxidation relevant to artificial photosynthesis. In this work, weakly antiferromagnetic dimeric tetraazaadamantane Mn^{IV} complexes were studied by high-field EPR, up to 15 T at frequencies up to 640 GHz. In a dialkoxo-bridged complex, EPR spectra coming from the coupled spin states with S=1, 2 and 3 were initially interpreted in terms of the "giant spin" Hamiltonian (Figure 1). The D and E parameters in the S=1 state were -2.3 and -0.75 cm^{-1}, respectively, while in the S=3 state +0.42 and +0.10 cm^{-1} were determined. Contributions to the zero field splitting (zfs) tensor due to the individual ions as well as to the anisotropic metal-metal interactions were extracted from the above experimental results and were subsequently used to simulate spectra using the full spin Hamiltonian expressed in spins of two Mn ions. Diagonalisation of the 16x16 spin Hamiltonian matrices was employed in these simulation procedures. The zero-field splitting in the dimers was found to be dominated by the single-ion zfs contribution. The anisotropic metal-metal interactions appear to be almost exclusively of the magnetic dipolar nature.

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EPR ORAL SESSION

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117 EPR-active Molecular pH Probes at a Protein-Lipid Interface: Turning Electrical Charges On and Off.

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The ionization states of individual amino acid residues of membrane proteins are difficult to decipher or assign directly in the lipid-bilayer membrane environment. The effective pK(a) values of protein groups are determined by a complex interplay between local polarity, Coulomb interactions, and a structural reorganization. The analysis is further complicated by the dearth of information about gradients in polarity, electric potentials, and hydration at the protein-membrane interface. In this work we report on developing pH-sensitive ionizable EPR labels and related methods to 1) profile a heterogeneous dielectric environment along the α-helix of a WALP peptide integrated in a lipid bilayer and 2) asses the effect of anionic lipid surface charge density on effective pK(a) of membrane-burred ionisable sidechains and 3) asses the effect of solid state support on effective pK(a) of membrane-burred ionisable sidechains The change in the protonation state of the pH-sensitive nitroxide was directly observed by EPR. Displacement of the EPR probe upon protonation, similar to that of the "snorkeling" of the charged sidechains of Lys and Arg, was directly observed by DEER and was shown to depend strongly upon the depth of the label with respect to the bilayer surface. Further, it was found that the experimentally observed dielectric constant at the membrane-protein interface is significantly higher than the values expected for the same location in the bulk membrane. The effects of the membrane surface charge density on the dielectric profile at the peptide-membrane interface and on "snorkeling" of the charged nitroxide sidechains was investigated. We have also shown that the effective pK(a) of the probe increases by 2.1 to 2.3 pK(a) units (depending on the depth of the probe) upon replacing zwitterionic PC lipids with anionic PG lipids, with almost 80% of that pK(a) shift is observed upon replacing only half of the PC lipid with PG lipids. Water penetration at the peptide-membrane interface was assessed by HYSCORE.

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EPR ORAL SESSION

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118 **Free Energy Landscape and Protein Configurational Fluctuation Contributions to Radical Rearrangement Catalysis in B_{12} -dependent Ethanolamine Ammonia-Lyase.**

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First-order rate constants (*k*) of the core chemical reaction step of substrate radical rearrangement in the B_{12} -dependent ethanolamine ammonia-lyase (EAL) from *Salmonella typhimurium* are determined by using temperature-step triggered decay of the cryotrapped substrate radical intermediate, and time-resolved, full-spectrum electron paramagnetic resonance (EPR) spectroscopy [1] over the temperature (*T*) range of $197\leq T \leq 230$ K, and from k_{cat} values up to 295 K [2,3]. The piecewise-linear Eyring [ln(kT -1) versus T^{-1}] dependence shows a kinetic bifurcation from native into fast and slow decay components at 220 K, and a kink in the fast decay component at 217 K. The bifurcation and kink are proposed to arise from the effective quenching of native stochastic, collective-atom protein configurational fluctuations that are coupled to the reaction. The reaction at *T* The native and non-native reaction channels represent two distinct dynamical paradigms for radical rearrangement catalysis in EAL, which are described by using a *T*-dependent free energy landscape (FEL) model. This model is cast in a deterministic kinetic model, that is used to simulate the observed decays and reproduce the Erying dependence. Electron spin-echo envelope modulation (ESEEM) spectroscopy of substrate radical- active site group interactions [4,5] are aimed at resolution of two model-predicted sub- states, and microscopic annotation of the kinetic mechanisms. The results reveal unique insights into the interplay of the FEL, activation enthalpy and entropy, and specific configurational fluctuations in the manifestation of enzyme catalysis in B_{12} -dependent EAL, that impact enzyme catalysis, in general.

Supported by NIH R01DK054514.

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EPR ORAL SESSION

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119 **Utilizing Novel 95 GHz 2D-ESR Spectroscopy to Study Nitroxide Partitioning into the Lipid Membranes at Room Temperatures.**

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Small-molecule spin probes like TEMPO have been used to study biological systems by ESR for many years. Their ESR parameters are very sensitive to the local environment and can report on its viscosity, polarity and accessibility for other paramagnetic species. In complex systems high ESR spectral resolution is crucial for obtaining this information by simultaneously observing multiple spectral components which are difficult to interpret when unresolved and overlapped. Using an example of TEMPO partitioning between the phospholipid membrane and aqueous phases we show how combining the benefits of high field (HF) ESR with two dimensional (2D) ESR provides spectral resolution which cannot be achieved by either HF-ESR or 2D-ESR alone. We present results obtained by the 2D-ELDOR (Two-Dimensional Electron-Electron Double Resonance) technique with our ACERT 95 GHz High Field High Power Pulse ESR spectrometer at biological temper! atures. We demonstrate complete separation of ESR signals from different membrane phases and show how our recent method of 2D data analysis is used to separately extract T1 & T2 relaxation times from each phase. We utilize the advantages of the fullSc- code developed at ACERT to obtain the pure absorption spectra from the hypercomplex 2D-ELDOR data recorded. We also study by 2D-ELDOR the interaction of paramagnetic relaxants, such as oxygen and transition metal ions with spin-labeled membrane. We show that much lower concentration of the relaxant can be used to selectively remove one of the components than in CW-ESR. Finally, we discuss some new physico-chemical insights in the behavior of the system obtained by HF 2D-ELDOR such as the anomalous diffusion of oxygen in the membrane phase and the ion-membrane interactions.

EPR ORAL SESSION

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120 Using EPR, ENDOR, and HYSCORE to Elucidate the Structure of Copper and Cobalt Pre-Catalysts.

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Water oxidation can lead to a sustainable source of energy, but for water oxidation catalysts (WOCs) to be economical they must use earth abundant metals. We have reported that 6,6'-dihydroxybipyridine (6,6'-dhbp) based ligands form 2:1 copper complexes that are efficient at electrocatalytic water oxidation in aqueous base (pH = 10-14). The complexes formed were characterized by crystallography and acid dissociation constants were determined. EPR, ENDOR, and HYSCORE experiments also confirmed that the 6,6'-dhbp ligand is bound to copper over a wide pH range, and these experiments show how pH influences pre-catalyst structure. Water oxidation studies with analogous zinc and copper complexes have illustrated that both copper and proximal OH groups are necessary for water oxidation at a low overpotential and moderate rates. Furthermore, our combined work demonstrates the ways in which OH/O- groups on the bipyridine rings can hydrogen bond, support unusual binding modes, and potentially facilitate proton coupled electron transfer. This work has been published in Inorg. Chem. in 2014. We will also describe our recent efforts to make new cobalt and copper complexes as novel catalysts, and again these structures have been characterized by EPR methods.

EPR ORAL SESSION

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125 Nanowire-Based Magnetic Resonance Imaging and Spectroscopy.

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Magnetic resonance imaging (MRI) has had a profound impact on biology and medicine. Key to its success has been the unique ability to combine imaging with nuclear magnetic resonance spectroscopy—a capability that has led to a host of powerful modalities for imaging spins. Although it remains a significant challenge, there is considerable interest to extend these powerful spectroscopic and imaging capabilities to the nanometer scale. In this talk, I will discuss a new platform for force-detected magnetic resonance detection that allows us to bring many of the tools developed for NMR to the nanometer scale. In particular, I will focus on the development of optimal control theory (OCT) pulses, which incorporate average Hamiltonian theory and realize arbitrary unitary operations. I will present initial results demonstrating the use of OCT pulses for dynamical decoupling and chemical shift averaging of nanometer scale ensembles.

EPR ORAL SESSION

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126 EPR Spectroscopy of using Nitrogen-vacancy Centers in Diamond.

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Magnetic resonance (MR), such as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR), can probe the local structure and dynamic properties of various systems, making them among the most powerful and versatile analytical methods. However, their intrinsically low sensitivity precludes MR analyses of samples with very small volumes; e.g., more than 10^{10} electron spins are typically required to observe EPR signals at room temperature. A vast improvement in the current limits of MR will enable the imaging of structures and conformational changes of molecules in solution at the single molecule level. A nitrogen-vacancy (NV) center in diamond is a promising candidate for applications in room temperature magnetic sensing with single spin sensitivity. In this presentation, we will discuss EPR spectroscopy using NV centers in diamond. By employing EPR and double electron-electron resonance (DEER) techniques, we investigate impurities and coherence in diamond. We also demonstrate EPR of several electron spins using NV-based EPR spectroscopy.[1]

This work is supported by NSF and the Searle Scholar program.

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EPR ORAL SESSION

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127 **Nanoliter Biological Electron Paramagnetic Resonance Spectroscopy on a Diamond Chip**.

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Commercial X-band micro-EPR devices have detection thresholds of 1013 spins (40 μL, 0.3 μM) at room temperature[1]. Obtaining greater sensitivity typically requires cryogenics, large magnetic fields, and/or large amounts of analyte. Our lab is developing a new EPR platform based on diamond nanotechnology, capable of detecting ~109 spins which corresponds to minute (1 nL, 1 μM) quantities of biomolecules. The sensor's working principle is analogous to Double-Electron-Electron Resonance (DEER) in traditional EPR, except here we detect an external spin species (the analyte) by Pulsed Optical Detection of another spin species inside the sensor (Nitrogen-Vacancy centers). These techniques rely on detecting statistical magnetization; this was recently demonstrated in landmark experiments using a single-NV sensor[2]. Remaining challenges include long measurement times and laborious sample prep, owing to stochastic placement of NV centers relative to the targets. The EPR detection sensitivity depends on the number of NV centers that are located sufficiently close to the diamond surface to sense external spins. To increase this number, we lithographically structure the diamond surface with high-aspect-ratio nanogratings, which enhances the sensor analyte contact area by more than an order of magnitude. We then dope the sidewalls of the nanostructures with a high density of NV centers. The result is that billions of NV centers come into contact with the analyte, boosting the EPR signal and reducing the signal acquisition time. We recently used a similar platform for detection of NMR and are now extending this work to EPR detection. We will report recent efforts to determine the sensor's detection threshold to nitroxide-labeled proteins, such as MAD2. We will also discuss technical challenges such as analyte diffusion and photodamage, and will outline a path towards detection of label-free biomarkers such as malarial hemozoin nanocrystals.

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EPR POSTER SESSION

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128 **Improving Optical Collection Efficiency for Simultaneous Electrically and Optically Detected Magnetic Resonance on Thin Film Devices**.

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Understanding the magneto-optical-electronic properties of organic semiconductors is essential for improving the efficiency of organic thin film devices such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). A technique capable of simultaneously measuring the electronic, magnetic and optical properties of these materials is required if one hopes to unambiguously establish interrelationships between them. We report here on several ways to simultaneously measure electrically (EDMR) and optically (ODMR) detected magnetic resonance from the same device. First, we present measurements made in a commercial resonator using a home-built sample rod equipped with optical fibers and a small prism to collect light together with electrical access to the thin-film wiring on sample templates described previously.1 The setup allows for simultaneous measurement of EDMR and ODMR experiments within a homogeneous B1 field in spite of the presence of the electrical connections as well as the optical detection setup within the resonator. In this configuration, however, the photon collecting efficiency is strongly limited by the resonator geometry. In order to improve the photon collection efficiency, we integrated a home-built coplanar waveguide resonator into a probe head2 which allows both electrical access and an unobstructed optical pathway to the sample. This eliminates the need to collect light with optical fibers and increases the photoluminescence we are able to collect by a factor greater than 50. The probe head is compatible for use in a Bruker spectrometer and easily accommodates measurements on several sample geometries at a variety of frequencies. This opens the door for extremely versatile experiments.

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award #DE-SC0000909.

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EPR ORAL SESSION

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129 Toward Single Atom Qubits on a Surface: ESR in a Scanning Tunneling Microscope.

William Paul
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Single Fe atoms placed on MgO films have exceptional magnetic properties: Their spin relaxation lifetime can extend to many milliseconds, and their quantum state can be coherently manipulated by RF electric fields. In this talk, we will discuss a scanning tunneling microscopy (STM) investigation of the dynamics of spin-relaxation and the electric-field-driven spin resonance of individual Fe atoms adsorbed to MgO. We show that the T1 lifetime of single Fe atoms on MgO can exceed 10 ms, and can be tuned by adjusting the thickness of insulating MgO film separating it from a silver substrate. Next, we demonstrate electron spin resonance of an individual single Fe atom, driven by a gigahertz-frequency electric field applied across the tip-sample junction, and detected by a spin-polarized tunneling current [1]. The principle parameters of the spin resonance experiment, namely the phase coherence time T_2 and the Rabi rate, are characterized for Fe atoms adsorbed to the monolayer MgO film. We can furthermore use the Fe atom as a sensor of the local magnetic environment (which can be positioned with atomic precision by the STM tip) and we demonstrate its remarkable capabilities in measuring magnetic interactions with nano-electronvolt energy and picometer spatial resolutions. We conclude with an outlook toward quantum devices built atom-by-atom on surfaces.

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EPR ORAL SESSION

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130 Spin Coherence and Spin Relaxation in Monolayer Semiconductors.

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Interest in atomically-thin transition metal dichalcogenide (TMD) semiconductors such as MoS_2 has exploded in the last few years, driven by the new physics of coupled spin/valley degrees of freedom and their potential for new spintronic and 'valleytronic' devices. Although robust spin and valley degrees of freedom have been inferred from polarized photoluminescence (PL) studies of excitons, PL timescales are necessarily constrained by short-lived (3–30 ps) recombination of excitons. Direct probes of spin & valley dynamics of the resident carriers in electron- (or hole-) doped TMDs, which may persist long after recombination ceases, are still at an early stage. In this work, we directly measure the coupled spin-valley dynamics of the resident electrons in n-type monolayer MoS_2 using time-resolved Kerr rotation[1], and reveal very long spin lifetimes exceeding 3 ns at 5K — orders of magnitude longer than typical exciton lifetimes (see Figure). In contrast with conventional III-V or II-VI semiconductors, spin relaxation accelerates rapidly in small transverse magnetic fields B_y. This indicates a novel mechanism of electron spin dephasing in monolayer TMDs that is driven by rapidly-fluctuating internal spin-orbit fields that, in turn, are due to fast electron scattering between the K and K' conduction bands[1]. Additionally, a small but surprisingly long-lived oscillatory signal is also observed (see Figure), indicating the spin coherence of a small population of localized states[2]. These coherence signals are observed in a variety of samples and are studied as a function of applied field and temperature. Related spin coherence and spin relaxation phenomena have also been observed recently in other monolayer TMDs such as $MoSe_2$, WS_2, and WSe_2. These studies provide direct insight into the physics underpinning the spin and valley dynamics of electrons in the new monolayer TMD semiconductors.

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EPR ORAL SESSION

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131 Simultaneous Detection of Transient Electrically Detected and Transient Magnetic Resonance Signals from Organic Solar Cells.

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Techniques based on electron paramagnetic resonance spectroscopy can provide valuable insight into excitation transfer pathways in organic semiconductors used as absorber layers in solar cells.[1,2] However, these measurements are usually performed on “model systems”, and the conclusions drawn from such experiments may not be valid under true solar cell operating conditions. Here we report on the development of a setup that allows for simultaneous detection of transient electron paramagnetic resonance as well as transient electrically detected magnetic resonance (trEDMR) signals from fully-processed and encapsulated solar cells. Combining both techniques provides a direct link between photoinduced triplet excitons, charge transfer states and free charge carriers as well as their influence on the photocurrent generated by organic photovoltaic devices. Our results obtained from solar cells based on poly(3-hexylthiophene) and the fullerene-based electron acceptor PCBM show that the resonant signals observed in low-temperature ($T = 80$ K) trEDMR spectra can be attributed to positive polarons in the polymer as well as negative polarons in the fullerene phase, indicating that both centers are involved in spin-dependent processes that directly influence the photocurrent.[3] Furthermore, we will show how transient EPR measurements on blends comprising low-bandgap polymers and PCBM can help to disentangle complex charge transfer processes and identify loss mechanisms in organic solar cell materials.[2]

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EPR ORAL SESSION

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132 Separation of Hyperfine and Spin-Orbit Interactions in Organic Semiconductors by Multi-Frequency Electrically Detected Magnetic Resonance using Coplanar Waveguide Microresonators.

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Studies of magneto-optoelectronic properties of organic semiconductors, such as organic magnetoresistance and magneto-electroluminescence, have revealed a strong influence of hyperfine fields caused by protons and a weak but non-negligible influence of spin-orbit interactions[1,2]. In order to separate these influences of hyperfine fields and spin-orbit effects on charge carrier states in organic semiconductors we conduct continuous wave electrically detected magnetic resonance (cw-EDMR) spectroscopy over a wide range of frequencies between about 1-20 GHz using both fundamental and higher-harmonic modes of coplanar waveguide resonators[3]. Cw-EDMR spectra of bipolar injection devices (diodes) based on a π-conjugated polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4- phenylenevinylene] (MEH-PPV), reveal that the magnetic resonance spectra conducted at low magnetic fields and frequencies are only weakly dependent on the magnetic field and thus, are predominantly governed by the hyperfine fields. At higher magnetic fields, a significant broadening of the resonance lines is observed consistent with the presence of a spin-orbit induced g-factor distribution. In order to obtain the hyperfine field as well as g-factor distributions, we conduct a global fit of all measured spectra with two inhomogeneously broadened resonance lines, for the paramagnetic resonances lines of electrons and holes, respectively. We use a so-called ‘bootstrap’ procedure in order to obtain confidence limits for the fit results which reveals that for the charge carrier species experiencing higher hyperfine fields, only an upper limit can be placed on the magnitude of their g-factor distributions[4].

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EPR ORAL SESSION
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133 **Estimation of Spin Diffusion Length and Spin-Orbit Coupling Strength in Organic Semiconductors by Means of pulsed Inverse Spin-Hall Effect Measurements**.

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Spin-orbit coupling in condensed matter is crucial for spintronics applications, including generation, manipulation, and detection schemes for spin currents. We have succeeded in employing spin-pumping methods based on ferromagnetic resonance (FMR) to generate pure – meaning charge free – spin currents from a ferromagnetic (FM) substrate into organic semiconductor (OSEC) layers. When the FM is in resonance with pulsed microwave excitation, a strong, pure spin-current is injected into the OSEC, irrespective of the impedance mismatch between the ferromagnetic layer and the organic layer. Because of the weak spin-orbit coupling (SOC) in most OSECs, the inverse spin Hall effect (ISHE) resulting from this spin injection scheme is very subtle, yet with pulsed, high microwave power driving of the FMR, relatively strong ISHE signals can be measured, nevertheless. Here we report the measurement of the ISHE in a variety of OSECs having tunable SOC, ranging from strong SOC (pi-conjugated polymers that contain intrachain Pt atoms) to weak SOC polymers (such as the pi-conjugated polymer DOO-PPV). We find that the ISHE response in these compounds scales with SOC, in spite of the decrease in the spin diffusion length. Remarkably, thin film materials based on Fullerenes exhibit some of the most pronounced ISHE signals, owing to curvature-induced spin-orbit effects1 .

We acknowledge support by the National Science Foundation (DMR-1404634) for sample preparation, execution of the experiments and data processing of the ISHE experiments. We also acknowledge the NSF-Material Science & Engineering Center (DMR-1121252) for supporting Pt-polymer synthesis, execution of the OSV experiments and development of the ISHE device structures, as well as support for the device preparation facilities.

[1] Sun et al., Nat. Mat., DOI:10.1038/NMAT4618 (2016).

EPR ORAL SESSION
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134 **Cu^{2+}-ions as a ESR Probe of Protein Structure**.

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Pulsed -ESR techniques that reliably measure interspin separations in the order of 1.5-10 nm – even in non-crystalline samples – to ultimately provide an “amino-acid-level” picture of structure and structural transitions, have impacted biophysical research. The talk will discuss our efforts in developing Cu^{2+}-ion based pulsed-ESR distance methods and illustrate how they can potentially be used to understand structure function relationships in proteins. The talk will focus on restriction endonuclease EcoRI, which binds to the specific DNA sequence GAATTC with an affinity that is 50,000-90,000-fold greater than that of a miscognate site that differs by only one base pair. In the presence divalent metal ions, such as magnesium, EcoRI the specific sequence of viral DNA with a high specificity. We will describe the insights gained in regard to the high specificity as well as cleavage chemistry from ESR distance measurements. Finally, the talk will describe recent efforts to bind Cu^{2+}-ions site selectively at α-helical and β-sheet sites in protein. The spin probe is assembled in situ from natural amino acid residues and a metal salt, and requires no post-expression synthetic modification. Initial results show that the resultant Cu^{2+}-probe potentially provides distance distributions that are five times narrower than the common protein spin label – the approach, thus, has the potential to significantly overcome the inherent limitation of the current technology which relies on a spin label with a highly flexible side-chain.

EPR ORAL SESSION
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135 **Site-Specific Investigations of the Protein Dynamical Transition via Pulse EPR**.

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The dynamical transition of a solvated protein contains necessary information about the protein solvent coupling and has major implications for water mediated protein-protein and protein-ligand interactions. We investigate the dynamical transition of the Trp-cage protein in a hydrated powder (h~0.2) at select sites along the peptide backbone with spin-label pulse EPR. The electron T_2 serves as a probe for the local magnetic noise induced by the motion of nearby solvent and protein nuclei that is sensitive to noise on the 10^{-6} to 10^{-12} second timescales and thus is capable of probing the wide range of timescales present throughout the protein dynamical transition. In this report we show that measurements of the electron T_2 by Hahn echo as a function of temperature reveal the protein dynamical transition as a strong inflection point at approximately 180 K. In addition we discuss preliminary results of a modified spectral filtering technique to recover local noise correlation time at each temperature of the measurement. We discuss the site-specific protein dynamics revealed by pulse EPR about the protein dynamic transition in context of the chemical properties of the Trp cage protein.

EPR ORAL SESSION

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136 **Bayesian Uncertainty Quantification for DEER Spectroscop.**

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DEER (Double Electron-Electron Resonance) spectroscopy is a solid-state pulse EPR (Electron Paramagnetic Resonance) experiment that measures distances between unpaired electrons, most commonly between protein-bound spin-labels separated by 1.5-8 nm. From the experimental data, a distance distribution P(r) is extracted using Tikhonov regularization. The disadvantage of this method is that it does not directly provide error bars for the resulting P(r), rendering correct interpretation difficult. Further, Tikhonov regularization requires the selection of a regularization parameter, and current methods employ heuristics and introduce bias. Here we introduce a Bayesian statistical approach that quantifies uncertainty in P(r) arising from time-domain signal noise and numerical regularization. This method provides credible intervals (error bars) of P(r) at each r. This allows practitioners to answer whether or not small features are significant, whether or not apparent shoulders are significant, and whether or not two distance distributions are significantly different from each other. In addition, the method quantifies uncertainty arising from the degree of regularization.

EPR ORAL SESSION

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137 **WavPDS: A Wavelet Approach in Denoising Pulsed Dipolar Spectroscopy**.

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Studying biological systems using Pulsed Dipolar Electron Spin Resonance Spectroscopy (PDS) is challenging due to the short relaxation times and low protein concentrations typically used. These frequently result in a low Signal to Noise Ratio (SNR), complicating the analysis. Even if the average distance between spin probes can be estimated, the determination of the distance distribution (DD) is likely to be corrupted by noise. To address the challenge of noise removal in Pulsed Dipolar ESR in order to obtain reliable information, we developed a new wavelet denoising method (WavPDS) to remove/reduce noise. Our method improves the stability and reliability of the DD reconstruction, and reduces the signal acquisition time by an order of magnitude. This enables the study of biomolecular structures at low SNR signals with accuracy. We believe that studies in a wide variety of disciplines will greatly benefit.

EPR ORAL SESSION

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138 Three Homologous TonB-dependent Transporters Utilize Different Mechanisms to Regulate Protein-Protein Interactions.

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Gram negative bacteria utilize a family of specific, high affinity transport proteins to scavenge rare nutrients such as iron, vitamin B12 and certain carbohydrates from their environment. These active transport proteins are localized to the bacterial outer-membrane and obtain energy for transport from cytoplasm membrane proton motive force by coupling to the inner membrane protein TonB. Although a number of high-resolution crystal structures have been obtained for TonB-dependent transport proteins (TBDT), the molecular mechanism by which transport takes place still remains unknown. TonB is stoicheometrically limited with respect to the outer membrane TDBT, and transport is thought to involve cycles of attachment and dissociation of TonB from the outer-membrane transporter. Previous studies have shown that the affinity of TonB for several transporters is enhanced by substrate binding. In both BtuB, the vitamin B12 transporter and FecA, the ferric citrate transporter, binding of substrate induces conformational changes in the energy-coupling segment termed Ton box. Upon substrate binding, Ton box of BtuB and FecA become less ordered and increase their exposure to the periplasm. Here, we studied the structure and dynamics of the FhuA Ton box in the presence or absence of substrate utilizing both CW and pulsed EPR techniques in isolated native outer membrane. Unlike BtuB and FecA, the Ton box of FhuA is disordered with or without substrate. However, substrate binding does change the position of Ton box relative to the barrel axis and appears to extend the Ton box further into the periplasm. The results suggest a mechanism that could enhance TonB affinity for FhuA in the presence of substrate. Remarkably, each of these three homologous transporter, BtuB, FecA and FhuA appears to regulate TonB affinity by a different mechanism.

EPR ORAL SESSION

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138 Measuring Oxidation States in Exchange-Coupled Metal Clusters Using Ligand Hyperfine.

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Some of the most important redox reactions in Nature (e.g., nitrogen fixation, water oxidation, proton reduction) take place at enzyme active sites composed of multiple metal ions. Understanding the electronic structures of these metal clusters has been the target of extensive research efforts. However, obtaining site-specific information on a particular metal ion's oxidation state can be challenging when its electrons are coupled to the unpaired electrons on the other metal centers in the cluster via electron exchange. In this presentation, we provide several examples that illustrate how by measuring the hyperfine interaction with ligand nuclei, the oxidation state of the bonding partner metal ion can be determined. These results help to improve computational models of the enzyme active site and can provide insights into the reaction mechanism.

EPR ORAL SESSION

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Optimization of Pulsed EPR Distance Measurements for Tau Protein Aggregation.

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Tau protein is an intrinsically disordered protein found in neurons where its primary function is to stabilize microtubules. Under certain conditions, tau has a propensity to aggregate into beta-sheet fibrils. The formation of these fibrils has been identified as an important characteristic in neurodegenerative diseases such as Alzheimer's disease. Preliminary double electron-electron resonance (DEER) measurements have led to the discovery of an intermediate state which forms within minutes of initiating tau aggregation. Unfortunately, aggregating systems are particularly difficult to study with DEER due to: 1) dilution of spin labeled protein with analog protein is necessary to prevent interference from inter-protein distances and the total protein concentration is limited by the protein solubility 2) clustering of spins upon aggregation causes a reduction in T1 and T2 relaxation times which reduce the echo amplitude for the same DEER dipolar evolution times. Recent development of new DEER pulse sequences, including 5-pulse DEER [1] and CP-DEER [2], as well as the development of broadband SIFTER [3] have shown promise in improving the performance of pulsed EPR distance measurements; however these techniques have not yet been applied to many realistic biological systems including the study of protein aggregation. In addition to new pulse sequences, the addition of arbitrarily shaped pulses offers a great deal of flexibility in improving the signal to noise and/or reducing the time of DEER measurements which would otherwise be unrealistic. Our study investigates optimizing the performance of distance measurements on tau protein by comparing the performance (i.e. signal to noise) for a variety of pulse sequences and pulse shapes.

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[2] Spindler et al.,*J. Phys. Chem. Lett*, **2015**, 6, 4331.
[3] Schöps et al., *J. Magn. Reson.*, **2015**, 250, 55.

EPR ORAL SESSION

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Conformational Transitions of Maltose Binding Protein in the Native State and as Molten Globule at pH 3 as Monitored by DEER and DQC EPR Spectroscopy.

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Maltose-binding protein (MBP) is a single chain protein composed of two domains that is in a molten globule state at pH 3 as characterized by ANS binding. DEER measurements of seven spin-labeled double mutants in the native state at pH 7 had shown excellent agreement with X-ray data. At pH 3 corresponding DEER measurements of all the mutants yielded a broad distribution of distances. This can be expected if there is no defined tertiary structure and the individual helices point into all possible directions. Depending on maltose binding in a cleft between the domains, MBP exhibits both, an open and a closed conformation with respect to these domains. We have followed this substrate-depending conformational change by means of additional spin-labeled mutants at or near the active site. In these experiments DQC spectroscopy has been particularly helpful as it allows for distance measurements of labels in close proximity. Data show, e.g., that there is a defined structure of the active site of MBP at both pH values even in the absence of substrate.

EPR ORAL SESSION

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141 Selective Membrane Disruption Mechanism of an Antibacterial γ-AApeptide Defined by EPR Spectroscopy.

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Antibiotic resistance is one of the major threats to public health. γ-AApeptides are a new class of antibacterial peptidomimetics that are not prone to antibiotic resistance and are highly resistant to protease degradation. It is not clear how γ-AApeptides interact with bacterial membranes and alter lipid assembly, but such information is essential to understanding their antimicrobial activities and guiding future design of more potent and specific antimicrobial agents. Using EPR techniques at 9 and 95 GHz, we characterized the membrane interaction and destabilizing mechanism of a lipo-cyclic-γ-AApeptide (AA1), which has broad-spectrum antibacterial activities1. The analyses revealed that AA1 binding increases the membrane permeability of POPC/POPG liposomes, which mimic negatively charged bacterial membranes. AA1 binding also inhibits membrane fluidity and reduces solvent accessibility around the lipid head-group region. Moreover, AA1 interacts strongly with POPC/POPG liposomes, inducing significant lipid lateral-ordering and membrane thinning. In contrast, minimal membrane property changes were observed upon AA1 binding for liposomes mimicking mammalian cell membranes, which consist of neutral lipids and cholesterol. Our findings suggest that AA1 interacts and disrupts bacterial membranes through a carpet-like mechanism. The results showed that the intrinsic features of γ-AApeptides are important for their ability to disrupt bacterial membranes selectively, the implications of which extend to developing new antibacterial biomaterials.

1. Kaur, P.; Li, Y.; Cai, J. and Song, L. *Biophysical J*., 2016, 110 (8), 1789-1799.

EPR ORAL SESSION

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142 Distance Measurements Between Paramagnetic Ligands Bound to Parallel Stranded Guanine Quadruplexes.

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Aside from a double helix, deoxyribonucleic acid (DNA) folds into non-canonical structures, one of which is the guanine quadruplex. Cationic porphyrins bind guanine quadruplexes, but the effects of ligand binding on the structure of guanine quadruplexes with more than four contiguous guanine quartets remains to be fully elucidated. Double electron electron resonance (DEER) spectroscopy conducted at 9.5 GHz (X-band) using broadband shaped excitation pulses was used to measure the distances between cationic copper porphyrins bound to model parallel-stranded guanine quadruplexes with increasing numbers of guanine quartets. A monotonic increase in the average Cu^{2+}-Cu^{2+} distance was found as the poly-guanine tract increased within the oligonucleotide sequence, indicative of tetramolecular quadruplexes. A single Gaussian component was found to best model the time domain datasets, characteristic of a 2:1 binding stoichiometry between the porphyrins and each quadruplex, which is consistent with our previous work. Rather unexpectedly, the measured increase in Cu^{2+}-Cu^{2+} distances was not linear with the number of guanine tracts, suggesting a conformational change in the quadruplex secondary structure upon an incremental increase of successive guanine quartets.

EPR ORAL SESSION

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143 Phenylalanine Hydroxylase: Providing Details of a Catalytic Cycle with EPR Spectroscopy.

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Phenylalanine hydroxylase (PheH) is a liver enzyme that catalyzes the hydroxylation of the side-chain of phenylalanine to form tyrosine. This chemistry requires the binding of substrate, L-phe, a cofactor, tetrahydrobiopterin, and molecular oxygen to an Fe(II) active site. In the enzyme's resting state, the metal ion features an octahedral coordination geometry with one coordination face, consisting of the side chains of two histidines and a glutamic acid, provided by the protein and the remaining three coordination sites occupied by water ligands. While the diverse chemistry catalyzed by non-heme iron enzymes is often attributed to the facial arrangement of these open coordination sites, the proposed chemical mechanism for phenylalanine hydroxylation calls for the initial binding of both substrate L-phe and the tetrahydrobiopterin cofactor as second coordination-sphere ligands. In our studies, we have used nitric oxide, NO, as a substitute for O_2 for the purpose of poising the high-spin Fe(II) site in an S=3/2 $\{FeNO\}^7$ form that is amenable to X-band EPR spectroscopy. Using ^{2}H-Electron Spin Echo Envelope Modulation (ESEEM) and ^{1}H – Hyperfine Sublevel Correlation (HYSCORE) methods we have been able to measure weak hyperfine couplings from substrate, cofactor and coordinated water ligands that have provided important details regarding the catalytic mechanism of PheH.

EPR ORAL SESSION

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149 Towards Spin-assisted Long-term Data Storage in Diamond.

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The negatively-charged nitrogen-vacancy (NV-) center in diamond is the focus of widespread attention for applications ranging from quantum information processing to nanoscale metrology. Although most work so far has focused on the NV- optical and spin properties, control of the charge state promises complementary opportunities. One intriguing possibility is the long-term storage of information, a notion we hereby introduce using NV rich, type-1b diamond. As a proof of principle, we use multi-color optical microscopy to read, write, and reset arbitrary data sets with 2-D binary bit density comparable to present digital-video-disk (DVD) technology. Leveraging on the singular dynamics of NV- ionization, we encode information on different planes of the diamond crystal with no cross talk, hence extending the storage capacity to three dimensions. Further, we correlate the center's charge state and nuclear spin polarization of the nitrogen host, and show that the latter is robust to a cycle of NV- ionization and recharge. In combination with super-resolution microscopy techniques, these observations provide a route towards sub-diffraction NV charge control, a regime where the storage capacity could significantly surpass present technology.

EPR/SSNMR ORAL SESSION

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150 Electron Spectral Diffusion Measured via ELDOR for DNP at 7 T.

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Solid-state dynamic nuclear polarization (DNP) is an increasingly popular technique that allows for hundreds fold increases in nuclear magnetic resonance (NMR) signal. The common sample preparation includes a solute of interest mixed with a stable radical at tens of mM concentration frozen into an aqueous glass. Upon on-resonance μw irradiation, the high electron polarization of the radical is transferred to the surrounding solvent nuclei and subsequently to the solute via spin diffusion processes. Recently the indirect cross effect was proposed as a primary mechanism for DNP in static samples at low temperatures, 3-40 K, and high radical concentrations, 20-40 mM, where this mechanism relies on the electron spectral diffusion process. It was demonstrated at 3.35 T that spectral diffusion can be characterized and quantified using electron double resonance (ELDOR) experiments.1,2 We have recently shown that the oversaturation effect, i.e. reduction of DNP enhancement for μw powers above a certain threshold, occurs at 7 T and low < 6 K temperatures.3 Here, we present a DNP / ELDOR study performed on our homebuilt dual DNP / EPR instrument at 7 T, 3 of the electron spectral diffusion dependence on experimental conditions such as μw power, irradiation length, temperature, and radical concentration. These results are discussed in connection with the oversaturation effect and static, low temperature DNP mechanisms and show the necessity of including electron spectral diffusion processes for understanding of the latter.

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EPR/SSNMR ORAL SESSION

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151 Hypersensitivity with Dynamic Nuclear Polarization: Natural Isotopic Abundance and Closed-loop Cryogenic Helium Sample Spinning.

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The ability to record correlation experiments for nuclei at low natural isotopic abundance (^{13}C, ^{15}N) using dynamic nuclear polarization (DNP) [1] shows great promise for the field of NMR crystallography. The low natural abundance statistically simplifies coupled systems to spin pairs, making the measurement of inter-nuclear distances more straightforward. Furthermore, these simplified 2-spin cases permit the measurements of long distances as dipolar truncation effects (seen in multi-spin systems) are not present. It will be shown that dipolar recoupling experiments can be used to obtain not only intra-molecular distance restraints but also inter-molecular distances. Examples will be shown on natural isotopic abundance self-assembled systems, such as certain peptides and guanosine derivatives, where p-stacking interactions and hydrogen-bonding play a large role in the crystal structure – which cannot be easily determined from conventional crystallography methods.[2] In order to further enhance the sensitivity, we will report on a strategy to push the limits of DNP-enhanced solid-state NMR beyond its current state-of-the-art. This leap-forward was made possible thanks to the employment of a closed-loop of cryogenic helium as the gas to power magic angle sample spinning (MAS) for DNP-enhanced NMR experiments. The experimental conditions reported here far exceed what is currently possible and allows reaching sample temperatures down to 30 K while conducting experiments with high spinning frequencies (up to 25 kHz @ 100 K for a 3.2 mm probe). Thanks to the impressive associated gains, which will be presented, sustainable cryogenic helium sample spinning significantly enlarges the realm and possibilities of the MAS-DNP technique and is the route to transform NMR into a versatile and sensitive atomic-level characterization tool.[3] Finally, we will describe our efforts towards understanding the origin of the polarization losses associated with radical doping. Notably, we will investigate NMR signal losses occurring during MAS-DNP experiments and specifically compare the (MAS-dependent) depolarization effect for several "gold-standard" (bi-)radicals currently in use in most MAS-DNP studies (e.g. Totapol/bTbK/Amupol/TEMTriPol/etc.). Using MAS-DNP simulations we will show that these observations can be rationalized and are consistent with the biradicals' structure. Further insight into the depolarization mechanism (multi-parameters phenomenon) can be obtained comparing the result for each crystallite orientation with the result obtained on the powder average.[4]

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EPR/SSNMR ORAL SESSION

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152 Combining Dynamic Nuclear Polarization and Mechanically Detected Magnetic Resonance to Achieve Nanoscale Magnetic Resonance Imaging of Individual Biomolecules and Assemblies.

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A tool for imaging the proton envelope of an individual macromolecule and biological assembly would be a major advance. To realize this opportunity, we are pushing magnetic resonance imaging (MRI) to nanometer resolution using the sensitivity afforded by detecting magnetic resonance mechanically. We have developed attonewton-sensitivity cantilevers with integrated nanomagnet tips capable of detecting nuclear magnetic resonance from a polymer film at cryogenic temperatures with a sensitivity of a few hundred proton magnetic moments.[1] These experiments observe magnetization fluctuations present in small, nanometer-scale volumes of spins. I will describe our efforts to significantly improve the per-spin sensitivity and acquisition time of "nano-MRI" experiments by using dynamic nuclear polarization (DNP) to create a measurable net nuclear spin polarization,[2] pushing the experiment out of the spin-noise limit. Even with a noiseless detector (e.g., a zero-temperature cantilever or a quantum-limited nitrogen-vacancy center), stochastic spin fluctuations in the sample still limit the imaging resolution achievable in a nano-MRI experiment. We have performed numerical simulations of nano-MRI experiments with a number of image-encoding and detection protocols to identify the conditions under which DNP can get us beyond the limits imposed by spin-noise. Taken together, our experiments and simulations suggest that magnetic resonance force microscopy is on its way to becoming a powerful new route for obtaining a three-dimensional image of a single copy of a globular protein, macromolecular complex, and membrane protein.

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EPR/SSNMR ORAL SESSION

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153 Electron Spin Decoupled NMR Driven by Electron Spin Relaxation of Spin Clusters.

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The dramatic benefit of dynamic nuclear polarization (DNP) to amplify nuclear magnetic resonance (NMR) signal is fundamentally countered by line broadening and signal loss due to paramagnetic effects exerted by DNP agents, compromising NMR spectral resolution and sensitivity. Electron spin decoupling would principally eliminate these paramagnetic effects, but has not been experimentally accessible at high magnetic fields. We show that continuous wave microwave excitation of electron spin clusters in a Li ion battery electrolyte system at ~4 K results simultaneously in electron spin decoupling and DNP enhancement, removing paramagnetic effects on 7Li NMR while providing signal enhancements of ~5-20 fold. EPR measurements reveal that favorable electron spin relaxation (long T_{1e}, short T_M) are responsible for a broad excitation of the EPR line, measured directly using electron double resonance (ELDOR) experiments. Additionally, concurrent paramagnetic NMR and DNP analysis concluded that the favorable electron spin relaxation properties originated from coordination of TEMPO-based nitroxides to the Li ion, generating spin clusters. The DNP study here implicates that DNP analysis could be a materials characterization method for detecting clustering in materials systems.

EPR/SSNMR ORAL SESSION

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154 Nanoscale NMR Detection and Imaging Using Nitrogen-vacancy Centers in Diamond.

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We are exploring the use of individual, near-surface nitrogen-vacancy (NV) centers in diamond as atomic-size magnetometers to detect proton NMR in organic material located external to the diamond. Using a combination of electron spin echoes and proton spin manipulation, the NV center senses the nanotesla field fluctuations from the protons, enabling both time-domain and spectroscopic NMR measurements on the nanometer scale. By scanning a small polymer test object past a near-surface NV center, we have recently demonstrated proton magnetic resonance imaging (MRI) with spatial resolution on the order of 10 nm. One key issue in NV-NMR experiments is the loss of spin coherence when the NV center is located near the diamond surface. Although this loss of coherence is frequently attributed to the effect of magnetic noise emanating from unpaired spins on the diamond surface, we will show evidence that electric field noise from fluctuating surface charge can be a significant factor.

EPR/SSNMR ORAL SESSION

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155 Technology for Hyperfine Decoupling and Time Domain DNP in Rotating Solids.

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Hyperfine decoupling and pulsed dynamic nuclear polarization (DNP) are promising techniques to improve DNP experiments.[1-3] We explore experimental and theoretical considerations to implement them with magic angle spinning (MAS). Microwave field simulations using the high frequency structural simulator (HFSS) software suite are performed to characterize the inhomogeneous phase independent microwave field throughout a 198 GHz MAS DNP probe. Adiabatic electron spin inversions of stable organic radicals are simulated with SPINEVOLUTION using the inhomogeneous microwave fields calculated by HFSS. We calculate an electron spin inversion efficiency of 56% at a spinning frequency of 5 kHz. Voltage tunable gyrotron oscillators are proposed as a class of frequency agile microwave sources to generate microwave frequency sweeps required for time domain DNP transfers and hyperfine decoupling in rotating solids. We demonstrate gyrotron acceleration potentials and microwaves sweeps required for the hyperfine decoupling, and the integrated solid effect. In addition to designs and results of a new voltage tunable gyrotron microwave source, we also will describe novel instrumentation for cryogenic MAS including 1) a quadruple resonance transmission line MAS DNP probe capable of producing 320 kHz proton nutation fields within a 3.2 mm diameter solinoid.

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EPR/SSNMR ORAL SESSION

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156 Nuclear Magnetic Resonance Spectroscopy on a Nanostructured Diamond Chip for Chemical Trace Analysis.

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Studying trace quantities of analyte is challenging and timeconsuming using traditional coilbased NMR, owing to poor signaltonoise ratios. This motivates using larger and more expensive magnets and/or cooling samples which restricts general applicability. Noninductive magnetometry detection, when combined with nuclear hyperpolarization methods, promises an alternative lowfield, ambient temperature solution, but typical sensorstandoffs are mm, limiting studies to mm^3 or larger samples. Recently a new technique has emerged based on optically detected magnetic resonance of nitrogenvacancy (NV) centers in diamond which offers a path to highly sensitive NMR at ambient conditions. Rather than detecting the small net thermal magnetization of nuclear spins, these noninductive magnetometers detect the nanoscale variations in their magnetization. This produces an NMR signal which is independent of temperature and magnetic field and is orders of magnitude larger at ambient temperature. Early experiments using singleNV sensors have demonstrated detection of multiple nuclear species in nm 3 volumes of liquids and thin films. A remaining challenge is that measurements typically take several hours and require laborious sample preparation, owing to stochastic placement of analyte relative to the singlespin sensor. In this work we bridge the gap between nm^3 and um^3 . Employing a refined interference lithography method, high aspect ratio diamond nanogratings are fabricated with 400 nm pitch leading to an overall surface enhancement of >10. We then dope the sidewalls of the gratings with a high density of NV centers between 210 nm from the surface. The end result is that billions of NV centers come into nmscale contact with analyte and the ensembleaveraged signal gives a corresponding boost in sensitivity. Using these sensors, we acquired NMR spectra of nL of liquid and powder analytes on minute timescales, orders of magnitude faster than previous diamond techniques. For liquid analytes, the spectral resolution is currently limited by translational diffusion of analyte which prohibits observation of chemical shifts. We are currently investigating whether nanostructures can be fabricated which restrict nuclear translational diffusion without requiring complicated surface tethering strategies.

EPR/SSNMR ORAL SESSION

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157 Gd^{3+} as Polarizing Agent at High Field: Solid Effect vs Cross Effect Dynamic Nuclear Polarization.

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A variety of polarizing agents have been developed for efficient dynamic nuclear polarization (DNP) for high sensitivity gain. In this work we present studies based on a relatively new class of polarizing agents: high spin transition metal ions. Transition metal ions (Gd^{3+}, Mn^{2+}) can act as paramagnetic substitute of intrinsically bound diamagnetic ions in biomolecules. Doping with paramagnetic ions in this case has no (or insignificant) effect on the structure of the biomolecule. This gives an opportunity to obtain site-specific information about the biomolecule and further the research in structural biology. The polarization transfer mechanisms for these polarizing agents are yet to be understood. Here, we demonstrate DNP effects via Gd-DOTA, which invokes solid effect at low concentration owing to its narrow linewidth. Deviation from pure solid effect mechanism at shorter inter-metal distance in the uniform frozen solution matrix is observed. The properties of Gd^{3+} being a high spin 7/2 system featuring a relatively strong zero-field (electron quadrupolar) interaction lead to a non-trivial consequences. In our attempts to shed light on underlying polarization transfer mechanisms, bis-Gd rigid model complexes are investigated. By variation of the molecular tether length between the chelator moieties we are able to investigate the distance dependence of DNP field profiles and enhancements. This study enables us to comment on designing complexes for efficient CE DNP.

EPR/SSNMR ORAL SESSION

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158 Quantum-Enhanced Nuclear Spin Imaging by an Electronic Spin Probe in Diamond.

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Recent developments in materials fabrication and coherent control have brought quantum magnetometers based on electronic spin defects in diamond close to single nuclear spin sensitivity. These quantum sensors have the potential to be a revolutionary tool in proteomics, thus helping drug discovery: They can overcome some of the challenges plaguing other experimental techniques (x-ray and NMR) and allow single protein reconstruction in their natural conditions. While the sensitivity of diamond-based magnetometers approaches the single nuclear spin level, the outstanding challenge is to resolve contributions arising from distinct nuclear spins in a dense sample and use the acquired signal to reconstruct their positions. In this talk I will describe a set of strategies to boost the spatial resolution of NV-based magnetic resonance imaging, that take advantage of a quantum memory intrinsic to the NV system and of quantum interpolation by Hamiltonian engineering. These strategies promise to make diamond-based quantum sensors an invaluable technology for bioimaging, as they could achieve the reconstruction of biomolecules local structure without the need to crystallize them, to synthesize large ensembles or to alter their natural environment.

EPR ORAL SESSION

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159 Broadband Arbitrary Shaped Pulses for Pulsed EPR at 200 GHz.

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Major challenges in high field pulsed EPR are associated with limited available mw power at frequencies above W-band (>100 GHz). This together with the increased g- anisotropy due to the increased magnetic field results in the typical excitation bandwidth of few percent or less of the entire EPR spectrum. Major recent advances in pulsed EPR at X-band and Q-band frequencies are associated with introduction of phase and amplitude modulated pulses that became available with introduction of high frequency (>500MHz) Arbitrary Waveform Generators (AWG). The main advantage of shaped pulses lies in the possibility to excite larger bandwidth than is possible with conventional non-shaped pulses at given mw power. Consequently even larger relative gains associated with implementation of AWG are expected for high field EPR where mw power is scarce and spectra are broad. In this work we introduce our new homebuilt 200 GHz pulsed EPR / DNP spectrometer1 which was recently upgraded to include an AWG with 14bit vertical and 1ns temporal resolution. We demonstrate that high fidelity waveforms produced by AWG allow for efficient correction of many hardware imperfections associated with use of amplifier multiplier chains (AMC) and that phase and amplitude modulated pulses can be efficiently generated at 200 GHz using a ~150mW solid state source (VDI). We illustrate the performance of the AWG shaped pulses by showing that broadband inversion >10MHz was successfully achieved with only ~0.6MHz B1 field exceeding by more than an order of magnitude what is possible with non-shaped rectangular pulses.

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EPR ORAL SESSION

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160 Pushing SIFTER Towards New Application.

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SIFTER (single-frequency technique for refocusing dipolar couplings)[1] is a not often used pulsed EPR (electron paramagnetic resonance) technique to measure distances between spin labels. However, it is possible to achieve a higher signal to noise ratio with SIFTER compared to PELDOR (pulsed electron electron double resonance, also called DEER)[2,3] and DQC (double-quantum coherence)[4]. Drawbacks such as small modulation depths, artifacts resulting from inefficient pulse inversion and an ambiguity in the definition of the background function, have made previous SIFTER experiments ineffective. Here we show that it is possible to overcome the first two drawbacks by utilizing broadband pulses with nitroxide spin labels at X/Q – band frequencies[5] or by using spin labels with narrow spectral width, for example triarylmethyl based radicals (TAM or trityl)[6]. The ambiguity in the definition of the background function is a general problem for single frequency techniques. By applying a three pulse sequence we were able to measure the non-mono exponential part of the SIFTER background and hence obtain a more quantitative description. Furthermore in SIFTER the background can be minimized by using small concentrations and broadband pulses leading to a large modulation depth. The high excitation efficiency achievable with broadband-SIFTER for nitroxides at X-band frequencies, made it also possible to excite multi-spin effects in systems consisting of more than two nitroxide radicals, which might be useful to quantify oligomeric states of proteins.

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EPR ORAL SESSION

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161 Frequency Swept Rapid Scan EDMR.

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We report on rapid scan frequency swept electrically-detected magnetic resonance (EDMR) with ≥ 100 GHz/s sweep rates (equivalent to ~3.6 T/s for a free electron). Our measurements forgo a microwave cavity or other resonator for a very small non-resonant near field microwave probe.[1] This allows us to replace the standard electromagnet with a small permanent magnet and detect EDMR via frequency sweep. The entire apparatus is sufficiently compact that we integrated it into a standard probing station, allowing EDMR measurements to be made conveniently on a wide range of samples of interest. Rapid scan[2] frequency swept EDMR was demonstrated on the recombination current in a biased drain-substrate junction of a SiC MOSFET. “Slow” frequency-swept EDMR utilizing lock-in amplifier detection (amplitude or frequency modulation) on the same device was also performed. Compared to a standard field swept resonator-based EDMR acquisition,[3] while not yet optimized, rapid scan demonstrated a modest level of boost in signal to noise ratio. We expect our sweep rate can increase substantially with a larger bandwidth current amplifier. The elimination of modulation in the rapid scan approach, coupled with the elimination of the resonance cavity and electromagnet, greatly simplifies the EDMR detection scheme and offers promise for more widespread EDMR adoption.

EPR ORAL SESSION

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162 A Rapid Scan Method to Measure T_1 Relaxation Times.

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Electron paramagnetic resonance rapid scan is a method in which the magnetic field is swept through resonance in a time that is short compared to the relaxation times[1]. Spin-spin (T_2) relaxation times can be extracted from simulating the “wiggles” that occur as a result of the fast passage[2]. T_1 relaxation times are traditionally determined from a 3-pulse inversion recovery experiment or from a saturation recovery experiment[3]. Measurements of T_1 are limited by instrumental dead-time and may reflect spectral diffusion. Fast adiabatic passage using frequency sweeps to measure T_1 has previously been described[4]. In our new method, magnetic field is rapidly scanned though resonance to monitor the spin lattice recovery following a saturating period. As an example implementation, a home-built instrument utilizes an arbitrary waveform generator to produce both the excitation radiofrequency at 1.09 GHz and a 75 kHz waveform which is used to drive the rapid scan coils. Irradiated fused quartz and degassed Trityl-CD_3 were selected to demonstrate this method. Relaxation times measured by this method are in good agreement with values obtained by traditional methods.

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EPR ORAL SESSION

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163 EPR Spectroscopy at the Quantum Limit.

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Using the tools offered by circuit Quantum Electrodynamics (QED), namely high quality factor superconducting micro-resonators and Josephson parametric amplifiers that operate at the quantum limit when cooled at 20mK [1], we report an increase of the sensitivity of inductively detected Electron Spin Resonance spectroscopy by 4 orders of magnitude over the state-of-the-art, enabling the detection of 1700 Bismuth donor spins in silicon with a signal-to-noise ratio of 1 in a single echo [2]. We also demonstrate that the energy relaxation time of the spins is limited by spontaneous emission of microwave photons into the measurement line via the resonator [3], which opens the way to on-demand spin initialization via the Purcell effect.

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EPR ORAL SESSION

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Pulsed ENDOR with On-Chip Superconducting Resonators.

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Superconducting coplanar waveguide resonators (CPW) offer many advantages over conventional volume resonators in electron spin resonance applications. In particular they have a high spin number sensitivity and are compatible with dilution refrigerators. Unfortunately, current CPW resonator designs do not allow the application of radio frequency (RF) pulses necessary for electron-nuclear double resonance experiments (ENDOR). To allow the use of broadband RF pulses, we have designed new resonators using one-dimensional coplanar photonic bandgap structures. These resonators require very little power—100 nanoWatts to produce 500 mG microwave magnetic fields—and allow for broadband RF transmission below a lithographically designed bandgap as shown in the accompanying plot. Our photonic bandgap resonators consist of a ½ wavelength, 2-port superconducting CPW device coupled through stepped impedance Bragg reflectors. Both microwave and RF pulses are applied through the same transmission line. We will discuss the resonator design and show results from echo-detected ESR and Davies ENDOR experiments on phosphorus and arsenic donor electron spins in ^{28}Si epitaxial layers. The role of RF and microwave field inhomogeneity will be discussed and we will demonstrate the use of adiabatic RF pulses to achieve uniform spin manipulation. These results demonstrate powerful new devices which can perform spectroscopy on both electronic and nuclear spin transitions at ultra-low temperatures.

EPR ORAL SESSION

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Millikelvin ESR With Superconducting Resonators at Magnetic Fields up to 170 mT.

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Performing ESR at millikelvin temperatures offers several opportunities to enhance both the spin number and concentration sensitivity of the measurement compared to experiments at, e.g., liquid helium temperatures. First, an electron spin polarisation approaching 100% can be achieved while using excitation frequencies in the GHz regime. Second, the use of low-temperatures and quantum-limited amplifiers permits measurements with noise levels limited only by vacuum fluctuations of the microwave field[1]. Finally, high Q-factor superconducting coplanar resonators can be used with small mode volumes[2], further enhancing the ESR signal strength. Aluminum resonators have been used at small magnetic fields for ESR on systems with large zero-field splittings (e.g. bismuth donors in silicon[1]). However, for more general applications in ESR, considering g-factors of about 2 and magnetic fields of several hundreds of millitesla, different superconducting materials are required to maintain high Q-factors. In this context, niobium resonators with Q-factors up to 3200 have been previously used in ESR at 1.7 K and 260 mT to demonstrate adiabatic techniques for high-fidelity spin control[3]. Here we show ESR on an ensemble of phosphorus donors in an isotopically enriched ^{28}Si host lattice, using a superconducting coplanar niobium microwave resonator at 50 mK. At magnetic fields of more than 170 mT, we find the hyperfine split spin transitions of the phosphorus donor spin ensemble, while maintaining a Q-factor of more than 6000. We extract the ESR linewidth by investigating the interaction between resonator and spin ensemble. Furthermore, Hahn echo type experiments indicate that the coherence time of the spin system is larger than expected for the investigated phosphorus doping concentration of 10^{17} cm^{-3}.

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EPR ORAL SESSION

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166 Using CMOS Voltage-controlled Oscillators for Ultra-fast Rapid Scan ESR Experiments.

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Oscillator-based spin detection has recently gained significant attention in the ESR community due to its excellent spin sensitivity in cw-ESR experiments with operating temperatures down to 4 K.[1,2] In the proposed talk we will explain how a voltage-controlled oscillator (VCO), i.e. an oscillator whose oscillation frequency can be controlled by a tuning voltage V_{TUNE}, can be used to perform frequency modulated rapid scan ESR experiments with very high repetition rates significantly beyond 1 MHz. Measured results from a prototype VCO realized in CMOS technology with an operating frequency around 14 GHz and a tuning range of approximately 1.5 GHz demonstrate the excellent performance achievable with the proposed approach.

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EPR ORAL SESSION

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167 Coherent Pump Pulses in Double Electron Electron Resonance Spectroscopy.

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The availability of arbitrary waveform generators (AWGs) with nanosecond resolution has led to significant advancements in the development of improved versions of the Double Electron Electron Resonance (DEER) or Pulsed ELectron DOuble Resonance (PELDOR) experiment.[1-6] So far, these experiments have been performed mainly on spectrometers with two separate microwave sources for observer and pump pulses; however the current trend in EPR instrumentation is towards AWG-based spectrometers with a single microwave source.[7,8] We have investigated the signals generated from coherence transfer pathways involving both observer and pump pulses in DEER experiments on nitroxide-labelled proteins. While these signals are averaged out in the absence of a fixed phase relationship between observer and pump frequencies, they can introduce artefacts in the DEER trace in case of coherent observer and pump pulses. These artefacts can lead to misinterpretation and increased uncertainty in the analysis of the DEER data and therefore strategies for their elimination need to be identified. The different types of echoes generated in experiments with coherent monochromatic or hyperbolic secant pulses at different microwave frequencies were analyzed. The observed echo shapes and relative intensities can be well reproduced by simple Hilbert space density matrix simulations taking the resonator profile and the frequency response of the receiver into account. The position and nature of the artefacts introduced in the DEER trace when these echoes cross the detection window were identified for the four-, five- and seven-pulse experiments and different phase cycling schemes for the elimination of the echo crossing artefacts are proposed, enabling the use of these advanced sequences on coherent AWG-based spectrometers.

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EPR ORAL SESSION

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168 Pulsed Electrically Detected Magnetic Resonance.

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While electrically detected magnetic resonance (EDMR) spectroscopy has been used since the mid-1960s, when Honig [1] conducted first EDMR measurements on phosphorus donor electron states in crystalline silicon, the implementation of pulsed EDMR spectroscopy remained unsuccessful until the early 2000s, mostly due to the dielectric relaxation time related inherent low bandwidths of many materials for which EDMR experiments are most relevant. These problems where eventually overcome by using spin pump-probe schemes [2,3] in which coherent spin excitation sequences are followed by current integration, collecting charge carriers that contribute to the current due to the resonantly manipulated spin ensemble. Following these developments, an increasingly broad range of pulsed spin resonance experiments and their associated pulse sequences were adapted for electrical detection. Examples include transient nutation spectroscopy [3,4], different spin-echo techniques [5,6], or electron nuclear double resonance spectroscopy [7]. Due to the spin-polarization independence of many EDMR signals, an expansion of this technique to a near continuous frequency range has taken place enabling electron spin-resonance spectroscopy from the low MHz range [8] to hundreds of GHz [6,7].

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EPR ORAL SESSION

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175 Precise Delivery of Radiation Treatment to Hypoxic Areas Based on EPR Oxygen Images.

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Precise and localized treatment of tumors is important for elimination of cancer cells and patient post-treatment quality of life. It is well-known that the treatment outcome strongly correlates with tumor oxygenation. Tumor areas with low oxygen, hypoxia, are more radiation resistant. Electron Paramagnetic Resonance oxygen imaging is capable to image oxygen with 1 torr accuracy and 1 mm spatial resolution. For pre-clinical validation of oxygen-guided radiation therapy we use mice models. The radiation treatment with sub-millimeter precision was delivered using XRAD225Cx micro-CT/radiation therapy system. For radiation beam shaping we developed custom tumor hypoxia-shaped blocks 3D-printed using tungsten infused ABS polymer. The calculation of beam geometry and production of blocks was performed at the place of experiment.

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EPR ORAL SESSION

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Interstitial Inorganic Phosphate as an EPR Marker of Tumor Microenvironment and its Role in Tumorigenesis, Tumor Progression and Aggressiveness.

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Recently designed trityl probe with spectral properties that allow for concurrent EPR monitoring of physiologically important chemical parameters such as oxygen, pO_2, extracellular acidosis, pH_e, and interstitial inorganic phosphate, Pi [1], was used in this work *in vivo* in various animal models of cancer. The comparison of the mean values of pO_2 and pH_e in tumor microenvironment (TME) of PyMT transgenic mice which spontaneously develop breast cancer vs. normal mammary glands shows lower values in tumors supporting existence of hypoxic and acidic areas in TME. The dramatic differences, more than 3-fold higher concentrations in tumors vs. normal mammary glands, were observed for interstitial [Pi]. In mouse tumor xenograft models the only parameter which allowed for discrimination between non-metastatic PC14 and highly metastatic PC14HM tumors was interstitial [Pi] (> 2 fold higher for PC14HM). A negative correlation found between [Pi] and pO_2 in normal and tumor tissues is in agreement with association of high [Pi] (and low ATP/Pi ratio) with changes in bioenergetics status upon lower oxygen supply. A positive correlation was found between pO_2 and pH_e in normal mammary gland vs. absence of correlation in tumors supporting tumor reliance on glycolysis independently on oxygen concentration. In all tissues we did not observe correlation between pH_e and Pi. Apparently it means that mechanisms of protons and Pi accumulation in TME can be different. A potential role of interstitial Pi in tumorigenesis, tumor progression and aggressiveness will be discussed including its role as metabolic intermediate, interstitial buffer and proton carrier, and a key factor in "biological carbon:phosphorus stoichiometry" associated with the elevated demand for phosphorus-rich ribosomal RNA, a requirement for rapid growth in the growth rate hypothesis 2.

Supported by NIH grants CA194013 and CA192064.

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EPR ORAL SESSION

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Initial Results of Phase 1 Clinical Trial of OxyChip, an Implantable Probe for EPR Oximetry.

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Clinical interventions to overcome the radiation resistance of hypoxic tumors has been stymied by our inability to gather patient-specific oxygen (pO_2) data, and thus to selectively apply appropriate oxygen-enhancing strategies where they may have an impact on therapeutic potential. Most of the clinical trials aimed to increase tumor oxygen content to mitigate tumor hypoxia and improve tumor response to radiation have not demonstrated clear improvement in patient outcomes. Negative results of these trials may be attributed to a lack of data on the tumor response to hyperoxygenation due to technical inability to measure the oxygen levels in individual patients. The objective of this work was to establish a novel and robust technology, based on electron paramagnetic resonance (EPR) oximetry, as a practical clinical tool for measurement of tumor oxygen to help clinicians make patient-individualized and informed treatment-decisions based on the status of pre-, during, and post-treatment tumor oxygen status. EPR oximetry was performed using an innovative implantable oxygen sensor, called OxyChip, encapsulated in a biocompatible polymer matrix. Preclinical measurements established that the OxyChip is robust and capable of making direct and repeated measurements of pO_2 for 12 months or longer without toxicity or change in oxygen sensitivity. Extensive measurements in animal models of human xenograft tumors of head and neck, pancreas, colon, and breast cancer showed severe hypoxia (The OxyChips, which we designed for human studies, were of 0.6-mm diameter and 5-mm length, such that it can be implanted in the tumor using an 18-G brachytherapy needle. We have designed the first-ever clinical studies to establish the safety and efficacy of the new technology to obtain tumor pO_2 data in cancer patients undergoing surgery, radiation, or chemotherapy treatments. Following implantation into tumor tissue within 20 mm from skin surface, pO_2 measurements were performed noninvasively using an external RF coil working at 1,200 MHz. Repeated measurements of pO_2 were performed after 2 to 31 days of OxyChip implantation. Where possible, measurements were also made on multiple days. In the Phase 1 clinical trial, the OxyChips were removed when the tumors were surgically resected, as is standard of care therapy for these patients. Post-operative assessment of explanted OxyChips and pathology evaluation of the implanted site in the tumor tissue were performed to establish the safety of the procedure. Initial results from the first cohort of surgical cancer patients with SCC and melanoma tumors demonstrated the ability of the chip to measure tumor pO_2 for the first time in humans. The baseline pO_2 values of room-air breathing patients in general were hypoxic (1-5 mmHg). The tumors showed variable responses to 100% O_2 breathing, with the SCC tumor showing no response at all, while some melanoma tumors showed response. Histopathological evaluation of the excised tissues revealed no to minimal inflammation or hemorrhage along the needle tract or at the site of OxyChip. In conclusion, the ongoing EPR oximetry addresses a clinically relevant and timely need to enable reliable and repeated pO_2 measurements in tumors to support the development and optimized application of hypoxia modifiers to improve treatment outcomes.

EPR ORAL SESSION
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178 Feasibility Study of a CW-EPR-based Oxygen-mapping Technique Using a Pair of Isotopic Nitroxyl Radicals.

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A feasibility study of CW-EPR-based visualization of the partial pressure of oxygen (pO_2) and the concentrations of nitroxyl radicals is reported. Since the concentration of a spin probe affects its EPR linewidth (or the relaxation time T2), measurements of pO_2 have traditionally required simultaneous estimation of the probe concentration. Methods for measuring pO_2 using monohydrogenated CTPO (mHCTPO) were developed in the 1990s to overcome this dependence on the concentration of the probe.[1–3] We revisited this problem to visualize pO_2 and the concentrations of spin probes in a three-dimensional subject. To simultaneously measure unknown parameters (pO_2 and the concentrations of the probes), we used a pair of isotopic nitroxyl radicals, such as ^{14}N- and ^{15}N-labeled dicarboxy-PROXYLs (^{14}N-DCP and ^{15}N-DCP) as oxygen-sensitive spin probes.[4] First, we established simultaneous equations to express the effects of the self-broadening of ^{14}N- and ^{15}N-DCPs, cross-broadening between ^{14}N- and ^{15}N-DCPs, and oxygen-broadening on the linewidths of the probes. To estimate the linewidths of the probes, we used a CW-EPR-based single-point imaging (SPI) modality.[5] Linewidth maps could be obtained from T_2^* maps measured from a mixture of 14N- and 15N-DCPs. The concentrations of the probes and pO_2 could then be calculated simultaneously by solving the simultaneous equations. This approach might be useful for oxygen-mapping in biological tissues.

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EPR ORAL SESSION
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179 Molecular Probes for Monitoring Thiol Redox Status *In Vivo.*

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Intracellular thiol–disulfide redox balance is crucial to cell health, and may be a key determinant of a cancer's response to chemotherapy and radiation therapy. The ability to assess intracellular thiol–disulfide balance may thus be useful not only in predicting responsiveness of cancers to therapy, but in assessing predisposition to disease. We and others had developed linear disulfide-dinitroxide probes that are cleaved by free thiols to generate monomeric nitroxides.[1-4] The resulting change in coupling between the nitroxides gives rise to marked changes in EPR spectra, which could provide information on thiol redox status. Linear disulfide probes are flawed because in open systems (e.g., *in vivo*), cleavage by thiols causes the monomers to be at essentially infinite separation and thus they can never recombine to regenerate the disulfide form. Therefore a linear probe can never *equilibrate* with the *in vivo* redox environment. Here we report the design, synthesis, and validation of a cyclic disulfide-dinitroxide that can equilibrate with a thiol-disulfide pool and thus report an effective redox potential for that pool through its EPR spectrum.

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EPR ORAL SESSION

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180 Tracking Field Fluctuations in Pulsed EPR.

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Environmental magnetic field fluctuations are detrimental in electron paramagnetic resonance (EPR) studies of candidate systems for quantum computation applications. First, from a quantum computation perspective, these fluctuations randomize the phase of the spin ensemble with respect to the microwave reference, resulting in loss of quantum control at timescales longer than 1ms.[1] Second, from a spectroscopy perspective, the randomized phase of the spin ensemble during quadrature detection prohibits signal averaging and therefore limits the types of samples that can be studied.

Traditional field-frequency lock schemes have been used in nuclear magnetic resonance (NMR) studies to stabilize slow magnetic field drifts.[2,3,4] In our pulsed EPR studies, the requirement for magnetic field stability is more stringent, requiring fields stable to a part in 10^8 and with rates faster than a kHz. We discuss a dynamic field-frequency lock scheme in which we use phase-locked loops to track the NMR signal of protons in water at room temperature and ^{3}He spins at 2K to generate X-band microwaves which will drive EPR transitions. At the NMR level, we demonstrate that this scheme can maintain field-frequency lock for over 1s in an inhomogeneous magnetic field that limits T_2^* of the nuclei to only a few milliseconds. We discuss current progress in using this approach to follow field fluctuations in our EPR experiments.

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EPR ORAL SESSION

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181 Demagnetization Shifts in Very High Frequency Pulsed Electron Paramagnetic Resonance.

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At high magnetic fields, large spin magnetization effects become important, even at room temperature. We study these effects at 8.6 T and 240 GHz, using as a source the UCSB mm-wave Free Electron Laser (FEL)[1]. The high power afforded by the FEL can invert spin-1/2 electrons in 12-15 ns. We report that the frequency of free induction decays seen in BDPA crystals excited by these short pulses at room temperature is tip angle dependent. We characterize this effect by performing Rabi oscillation experiments on BDPA crystals, and demonstrate that the observed frequency shifts are proportional to sample magnetization. This nonlinear behavior can be explained by coupling between sample magnetization and geometry through the demagnetizing field, an effect we have termed paramagnetic demagnetization. We perform simulations accounting for the demagnetizing field, and reproduce the observed frequency shifts.

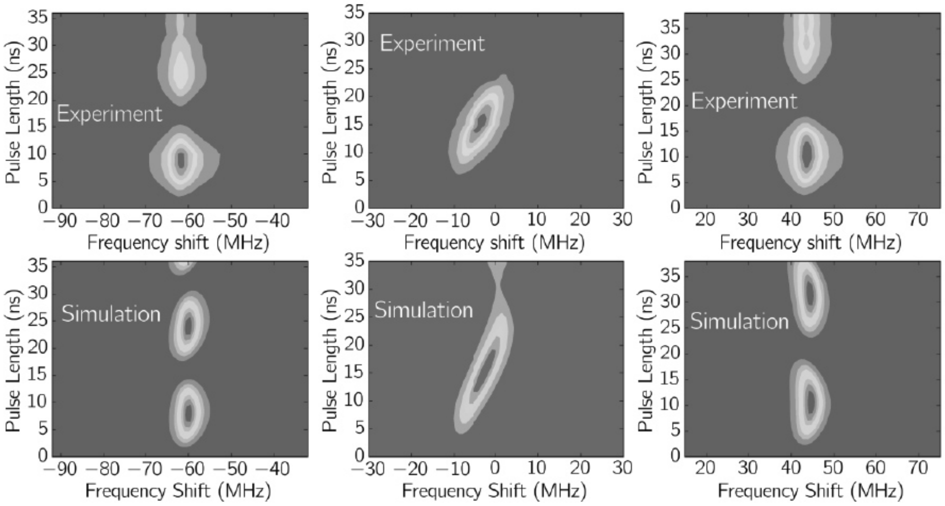

Figure 1. Top: Plots of free induction decay (FID) intensity vs frequency relative to 240 GHz as a function of pulse length. Off resonance and in the small tip-angle regime (upper left and upper right) there is no observed frequency shift, while on resonance (upper middle) we observe a tip-angle dependence in the FID frequency. Bottom: Simulations including the demagnetizing field.

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EPR ORAL SESSION

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182 Frequency-Domain EPR up to Several THz: Direct Observation of Large ZFS in Co^{II} Clusters.

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The Zero-Field Spitting (ZFS) of molecular clusters is of great interest. It is a result of spin-spin and spin-orbit interactions and is therefore a sensitive probe of the electronic structure. Furthermore, the ZFS is considered as key ingredient for slow relaxation of the magnetization in single molecule magnets and single ion magnets. Increasing the ZFS might sustain slow relaxation of the magnetization up to higher temperatures. Therefore ions with inherently large magnetic anisotropy become more prevalent. High-spin Co^{II} ions (d^7, $S = 3/2$) have a large spin-orbit interaction and therefore potentially very large ZFS. The large spin-orbit interaction might invalidate the widely used effective spin approach. Direct spectroscopic observation of ZFS is extremely challenging. Frequency-Domain Fourier-Transform THz-EPR as developed by us allows to measure ZFS in the range from 100 GHz to 5 THz.[1,2] Simulation abilities for frequency-domain EPR were introduced into EasySpin.[3,4] Several Co^{II} molecular clusters were studied and we could directly observe the ZFS and furthermore detect field dependence up to 10 T. The ZFS was found to range from 1.5 to 5.2 THz. Combining these results with CW X-Band EPR, magnetic susceptibility and computational studies allowed us to probe different effective models for the magnetic properties of Co^{II} clusters in great detail. We found that the effective spin model do surprisingly well. However, for the compound with the largest ZFS we found it that it does not reproduce experimental data. This might be due to low-lying excited states. Instead we propose to use a total angular momentum approach.

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EPR ORAL SESSION

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Multi-Extreme THz ESR: Development of Micro-Cantilever ESR up to the THz Region.

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We have been developing the THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature in Kobe. It covers the frequency region between 0.03 and 7 THz,[1] the temperature region between 1.8 and 300 K,[1] the magnetic field region up to 55 T,[1] and the pressure region is extended from 1.5 GPa[2] to 2.7 GPa using the hybrid-type pressure cell.[3] Moreover, our micro-cantilever ESR also enables the measurements of microgram sample using the torque and Faraday methods.[4] Very recently the micro-cantilever ESR measurements of Co-Tutton salt has been extended up to 1.1 THz using the torque method and the super conducting magnet up to 15 T, which is the world record frequency for such mechanical detection of ESR.[5]

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EPR ORAL SESSION

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High Sensitivity Transmission Mode Non-Resonant Stopped-Flow ESR.

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Stopped-flow ESR has been used extensively to monitor reactions involving the formation, decay, or transformation of radicals[1,2]. Typical experiments achieve fast time responses by monitoring the signal decay at a single magnetic field point (usually at the peak)[1,3]. In this approach, any subsequent peak shift or spectral broadening can easily mar the result with artifacts. Here, we demonstrate a microfluidic stopped-flow ESR method using a non-resonant[4] transmission line ESR probe to measure full ESR spectra with high temporal resolution. This technique simultaneously achieves high time resolution and sensitivity. The ESR active volume of the system is 0.3 µl and is defined by the intersection of our transmission line and the fluidic channel. The total volume between the point of mixing to the active region is ~6 µl. This volume can be substantially reduced to 0.8 µl. We demonstrate two different methods to acquire dynamic ESR spectrum. The first is via a $6x10^5$ G/s rapid scan (15 G sweep width) measurement of 20 mM of TEMPO ((2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl) solution with signal to noise ratio of >10 in 25 ms. The second is via “fast” field sweep with field modulation (100 kHz) observations of a 50 µM TEMPO solution quenched by a 50 µM Ascorbic acid solution in 4 min with a resolution of ~6 sec.

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EPR ORAL SESSION

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EPR for a Cu_4S Model for Nitrous Oxide Reductase.

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Nitrous oxide reductase (N_2OR) converts nitrous oxide into dinitrogen and water. Two forms of the active site of N_2OR, model complexes Cu_3S_2 and Cu_4(µ4-S) with phosphorous, and the model complex in this work, Cu_4(µ4-S), are reviewed. Electron paramagnetic resonance (EPR) spectra and simulations are obtained for the one electron reduced complex, the mixed-valence $Cu_4^{1.25+}S$ (alternatively, the sulfur radical). Resolved lines on the high- and low-field sides of the X-band spectrum are attributed to a copper hyperfine splitting of 100 MHz (36 G) (see figure below). The weakest lines from a 1:4:10:20:31:40:44:40:31:20:10:4:1 pattern from four equivalent coppers are best seen on the high- and-low field sides of the expanded spectrum (not shown). The g-values, 2.090 and 2.043, are not readily obtained from the X-band spectrum, but are obtained from the Q-band spectrum. The first harmonic (derivative) spectrum emphasizes the copper hyperfine structure (see figure below). The simulated spectrum fits well to the experimental spectrum. DFT calculations for Cu_4S indicate the spin density is 13% on each of the four coppers and 25% on sulfur. We conclude that the electron is highly distributed over the four coppers and the sulfur, resulting in a hybrid between a copper site and a free radical with EPR parameters intermediate between a mixed-valence complex and a free radical.

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EPR POSTER SESSION

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201 **Chemical Influences on Quantum Coherence in Potential Molecular Qubits**.

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The realization of a quantum computer would change our world by boosting computation periods and cracking nowadays highly save encryption algorithms.[1,2] In contrast to classical bits, a quantum bit (qubit) cannot only be in the states |0> and |1> but also in a coherent superposition of them. Among different proposed systems, electron spin qubits in transition metal complexes are highly attractive. Here the qubit properties can be tuned easily by synthetic means[3] and coherent manipulations can be performed by pulsed electron spin resonance. The critical parameter for quantum computation is the lifetime of the coherent superposition state, characterized by the phase memory time T_M. Apart from a few examples,[4-6] only rather short phase memory times of a few µs were reported for molecular qubits.[7-9] We aim to understand the factors determining $T_M$by systematic investigations on influences of molecular structure, sample matrix and experimental conditions on electron spin relaxation. The compound **Cu_mnt**, $(d_{20}\text{-PPh}_4)_2[\text{Cu(mnt)}_2]$, exhibits extraordinarily slow electron spin dynamics and coherence up to room temperature.[5] The electron spin relaxation properties of **Cu_mnt** in different matrices (frozen solution, doped powder) will be discussed. With an investigation of **Ni(III)_mnt**, $(d_{20}\text{-PPh}_4)[\text{Ni(mnt)}_2]$, we present coherence in Ni(III)-based molecular qubits, identifying novel building blocks for nuclear spin-free molecular qubits. Furthermore, we carefully investigated the impact of ligands, sample matrix and sample preparation on electron spin coherence in a range of transition metal phthalocyanines.[10] The rigid phthalocyanine ligand in combination with a low number of nuclear spins enables long spin-lattice relaxation and coherence times. In addition we discovered that the nature of the SOMO plays a crucial role in dephasing. With this presentation and our systematic EPR investigations we aim to contribute towards rational qubit design.

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EPR POSTER SESSION

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202 **Triplet Exciton Generation in Materials for Organic Solar Cells.**

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Using time-resolved EPR spectroscopy in conjunction with optical excitation we study charge separation in absorber materials for organic solar cells. When blended with the fullerene-based electron acceptor PCBM, two prominent derivatives of the low-bandgap polymer PCPDTBT differing by the bridging atom (carbon or silicon) exhibit different charge separation yields. While the EPR signatures of photogenerated positive polarons in C- and Si-bridged PCPDTBT are virtually identical, significant differences are observed with respect to the spin-relaxation behaviour. The spin-lattice relaxation time of positive polarons in C-PCPDTBT at low temperature (T = 80 K) is found to be more than two orders or magnitude longer than in the Si-bridged polymer derivative. This surprisingly slow relaxation can be rationalized by polarons trapped in defect states that seem to be absent (or are present in a substantially smaller concentration) in blends comprising Si-PCPDTBT. Transient EPR signals attributed to charge transfer (CT) states at the donor/acceptor interface and separated polarons are smaller in the blends with C-PCPDTBT as compared to those with the silicon-bridged polymer. We propose that triplet formation occurs via the CT state, thus diminishing the probability that the CT state forms free charge carriers in blends of C-PCPDTBT with PCBM. This hypothesis is confirmed by direct detection of triplet excitons in C-PCPDTBT:PCBM blends. The shape of the transient EPR spectra reveals that the triplet excitons are, in contrast to those formed in pristine polymer films, not generated by direct intersystem crossing, but result from back electron transfer through CT state recombination. The strong triplet signal is not observed in blends containing the Si-bridged polymer, indicating efficient singlet exciton splitting and subsequent charge carrier separation at the Si-PCPDTBT/PCBM interface.[1]

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EPR POSTER SESSION

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203

A Digital Low-Field Dynamic Nuclear Polarization Spectrometer.

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Since its discovery in 1953[1], dynamic nuclear polarization (DNP) has provided a powerful means for enhancing the proton resonance signal. The majority of recent research effort has focused on high magnetic fields, leading to many transformative experiments[2]. Initial research into solution DNP in low magnetic fields has also been very exciting[3,4]. Models predict the magnitude of DNP enhancement at low magnetic fields could be several times greater than the theoretical limit (γ_e/γ_H = 658x) at high magnetic fields[5,6]. We have constructed a digital DNP spectrometer with commercially available components designed to study the Overhauser (solution) effect at magnet fields from 230 µT – 50 mT (10 kHz-2 MHz/NMR, 6.6 MHz-1.3 GHz/EPR). The system is based on PXI architecture. An embedded controller removes the requirement of a separate PC, reducing the instrument footprint. We developed a magnetic resonance console and software package for single pulse NMR and DNP experiments using commercial instrumentation control programming language. An arbitrary waveform generator (AWG) PXI board is used to generate square pulses for ^{1}H frequencies from 10 kHz to 2 MHz. A RF generator PXI board is used to generate a continuous wave signal from 500 kHz up to 1.3 GHz. The RF signal is cycled on for (5 x T_{1H}), and cycled off before the NMR experiment commences. Single pulse saturation recovery experiments to measure T_{1H} can be carried out in the presence/absence of the radical to assess the DNP leakage factor, *f*. The maximum frequency of operation for ^{1}H with the current AWG card is 12.5 MHz. In the future, operational range of this instrument could be extended to 0.3 T by simply replacing the current RF generator card with one where maximum output is in the 8-9 GHz region.

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EPR POSTER SESSION

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204

Utilizing Novel 95 GHz 2D-ESR Spectroscopy to Study Nitroxide Partitioning into the Lipid Membranes at Room Temperatures.

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Small-molecule spin probes like TEMPO have been used to study biological systems by ESR for many years. Their ESR parameters are very sensitive to the local environment and can report on its viscosity, polarity and accessibility for other paramagnetic species. In complex systems high ESR spectral resolution is crucial for obtaining this information by simultaneously observing multiple spectral components which are difficult to interpret when unresolved and overlapped. Using an example of TEMPO partitioning between the phospholipid membrane and aqueous phases we show how combining the benefits of high field (HF) ESR with two dimensional (2D) ESR provides spectral resolution which cannot be achieved by either HF-ESR or 2D-ESR alone. We present results obtained by the 2D-ELDOR (Two-Dimensional Electron-Electron Double Resonance) technique with our ACERT 95 GHz High Field High Power Pulse ESR spectrometer at biological temper! atures. We demonstrate complete separation of ESR signals from different membrane phases and show how our recent method of 2D data analysis is used to separately extract T1 & T2 relaxation times from each phase. We utilize the advantages of the fullSc-code developed at ACERT to obtain the pure absorption spectra from the hypercomplex 2D-ELDOR data recorded. We also study by 2D-ELDOR the interaction of paramagnetic relaxants, such as oxygen and transition metal ions with spin-labeled membrane. We show that much lower concentration of the relaxant can be used to selectively remove one of the components than in CW-ESR. Finally, we discuss some new physico-chemical insights in the behavior of the system obtained by HF 2D-ELDOR such as the anomalous diffusion of oxygen in the membrane phase and the ion-membrane interactions.

EPR POSTER SESSION

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205 **T-jump and Freeze-quench EPR.**

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Biosynthesis of the macromolecular assemblies in the living cell is a complex process, which ultimately involves activation of the individual macromolecules forming a functional conformation. This is achieved *via* the series of folding and binding events, often employing additional assisting components. The presented setup gives a unique opportunity for studying these processes, combining sudden changing of the reaction temperature with rapid sampling by cryofixation and the subsequent structural analyses by EPR and other spectroscopic techniques. Depending on the volumetric flow rate and the nozzle diameter, the heat up time typically varies between 6 – 90 ms; the temperature rise can reach 50 – 100 ^oC. The reaction solution leaves the T-jump enclosure as a narrow rapid jet with the diameter down to 5 µm and the supersonic velocities up to 350-370 m s^{-1}. The time of flight typically varies between 5 and 15 µs. The sample is freeze-quenched by spraying in the liquid cryomedium at 77 K. Quenched samples contain amorphous glassy water, indicating the cooling rates above 10^7-10^8 K s^{-1}. The EPR data on thermal unfolding of cytochrome *c* from bovine heart is presented.

EPR POSTER SESSION

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206 **Distance Measurements in Gd^{3+}-labeled Proteorhodopsin Oligomers by 240 GHz CW EPR.**

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EPR in combination with site-directed spin-labeling has proven to be a very powerful tool for elucidating the structure and organization of biomolecules in native-like environments. At high fields, S = 7/2 Gd^{3+} spin labels have been shown to be particularly effective in increasing the sensitivity of distance measurements via DEER at Q- and W-band frequencies and above, and are now being developed as distance probes for use with CW EPR lineshapae analysis at very high frequencies. Proof of concept experiments on random solutions of $GdCl_3$ have shown that line broadening measurements of the central |-1/2> to |1/2> transition of Gd^{3+} with CW EPR at 240 GHz are sensitive to inter-spin distances up to ~3.8 nm, and at elevated temperatures. This greatly increased distance sensitivity persists in pairwise distance measurements in a series of model molecular rulers labeled with Gd-PyMTA. Dipolar broadening in these Gd-rulers follows a $1/r^3$ dependence and is resolvable up to inter-spin distances of at least 3.4 nm at 30 K, with similar line broadening trends observed at 215 K and up to room temperature. This extension of maximal resolvable distance from less than 2 nm with CW EPR at X-band with nitroxide labels to more than 3 nm with CW EPR at 240 GHz with Gd^{3+} labels affords much greater flexibility in the study of the structure and oligomerization of green-absorbing proteorhodopsin (G-PR), a seven-alpha helical transmembrane protein. Multiple inter-protein distance measurements made with 4MMDPA-Gd and Maleimide-DOTA-Gd spin labeled G-PR oligomers by W-band DEER reveal a penta- or hexameric organization which agrees with crystal structure of the homologous B-PR. We will present progress made with CW EPR lineshape based distance measurements at 240 GHz towards accessing the extended distances measured by W-band DEER of G-PR oligomers labeled with Maleimide-DOTA-Gd.

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EPR POSTER SESSION

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207 Highly Precise DEER Distance Measurements within Proteins using the Double Histidine Cu^{2+}-Binding Motif.

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ESR is a highly attractive tool in the elucidation of protein structure and dynamics. In order to perform such measurements, stable unpaired electrons must be incorporated into a protein through a process known as spin labeling. The most commonly used label for these purposes is R1, which contains a nitroxide ring attached to the protein backbone via five rotatable bonds. These bonds make R1 highly flexible and due to this flexibility, the location of the nitroxide ring relative to the protein varies greatly. As a result, distance measurements performed with R1 are ambiguous when relating these distances back to protein structure. Here, an alternative labeling procedure is utilized which directly addresses these flexibility concerns. The double histidine (dHis) method uses two strategically placed histidine mutations which subsequently bind a single Cu^{2+} ion. Without any post-expression modifications, the label self assembles through the addition of a small organic chelator (IDA) and a metal salt. The motif was generated in a model system at both α-helical and β-sheet sites. The ESR data indicate similar binding environments for the Cu^{2+} ions in both helix and sheet environments. Additionally, comparable DEER distance measurements were performed using R1 and dHis as a means to assess the reduced flexibility of the motif. The measured width of the dHis distance distribution was starkly reduced as compared to R1, indicating greatly reduced flexibility. In addition, using simple modeling combined with an X-ray crystal structure of the mutant protein, a distance was predicted within 0.5 Å of the experimental most probable dHis distance. Taken together, these data illustrate the exciting potential for the dHis motif for resolving very precise and unambiguous structural and dynamic information for many proteins of interest.

EPR POSTER SESSION

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208 Towards Understanding the Orientation Dependence of NV-Mediated Bulk Nuclear Hyperpolarization in Diamond at High Magnetic Fields.

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Room temperature optical illumination of NV^- doped single crystal diamonds with a 532 nm laser produces ^{13}C polarization enhancements up to 200 times greater than thermal equilibrium at 7.05 T[1]. Surprisingly, both positive and negative nuclear polarizations can be generated by manipulating the orientation of the diamond in the magnetic field. We discuss a possible mechanism for the polarization transfer between the NV centers and nuclear spins, which expands upon a previous model based on an NV dipolar energy reservoir. The model is further informed by EPR experiments through which we determined the orientation dependence of NV^- polarization in the lab frame as well as the true EPR lineshape[1,2]. Through EPR, we also find the NV^- defect polarization varies with the P1 defect concentration, and that the polarization of the ms = 0 state with optical pumping decreases from 46% to 36% in samples as P1 concentrations vary from 20 ppm to 100 ppm, respectively[1].

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EPR POSTER SESSION

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209 Bayesian Uncertainty Quantification For DEER Spectroscopy.

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DEER (Double Electron-Electron Resonance) spectroscopy is a solid-state pulse EPR (Electron Paramagnetic Resonance) experiment that measures distances between unpaired electrons, most commonly between protein-bound spin-labels separated by 1.5-8 nm. From the experimental data, a distance distribution $P(r)$ is extracted using Tikhonov regularization. The disadvantage of this method is that it does not directly provide error bars for the resulting $P(r)$, rendering correct interpretation difficult. Further, Tikhonov regularization requires the selection of a regularization parameter, and current methods employ heuristics and introduce bias. Here we introduce a Bayesian statistical approach that quantifies uncertainty in $P(r)$ arising from time-domain signal noise and numerical regularization. This method provides credible intervals (error bars) of $P(r)$ at each r. This allows practitioners to answer whether or not small features are significant, whether or not apparent shoulders are significant, and whether or not two distance distributions are significantly different from each other. In addition, the method quantifies uncertainty in the regularization parameter.

EPR POSTER SESSION

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210 SpecMan4EPR: The Second Generation of AWG Engine.

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SpecMan4EPR is control software for home-built EPR instruments [1]. One distinctive feature of SpecMan4EPR is its reconfigurable structure, which allows use of the same software for a variety of different instruments – from low frequency EPR imagers to high frequency DNP spectrometers. Widespread use of arbitrary waveform generators (AWGs) applications in EPR has inspired the development of the specialized SpecMan4EPR AWG engine. This engine enhances a pulse engine built around execution of pulse programming language (PPL) scripts that represent microwave pulses, delays and detection triggers. The second generation of AWG engine features a larger pattern library and support for IQ modulators. Although the instrumental part of using AWGs is relatively straightforward, design of the user interface requires consideration of many factors. AWG pulse patterns are multi-parametric and should be generated both inside and outside of the software. We manage to preserve the simplicity of PPL scripts and achieve the desired flexibility of control without compromising Specman4EPR program performance. This poster presents the details of three projects utilizing AWGs: a 700 MHz pulse EPR imager at the University of Chicago, a Q-band EPR spectrometer being developed in NIST, Gaithersburg, and a D-band spectrometer constructed at UCSB. All projects use different AWGs in different configurations, but utilize the same software and user interface.

Epel et al., Conc. Magn. Reson. B, 2005; 26B, 36.

EPR POSTER SESSION

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211 Interaction Between the Prion Protein's Copper-Bound Octarepeat Domain and a Charged C-terminal Pocket Suggests a Mechanism for N-terminal Regulation.

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Copper plays a critical role in prion protein (PrP) physiology. Cu^{2+} binds with high affinity to the PrP N-terminal octarepeat domain (OR), and intracellular copper promotes PrP expression. The molecular details of copper coordination within the OR are now well characterized. Here we examine how Cu^{2+} influences the interaction between the PrP N-terminal domain and the C-terminal globular domain. Using NMR and dipolar-based distance measurements from both continuous wave (CW) and copper-nitroxide double electron-electron resonance (DEER) EPR, we localize the position of Cu^{2+} in its high-affinity OR-bound state. Our results are supported by molecular dynamics simulations and reveal an interdomain *cis* interaction that is stabilized by a conserved, negatively charged pocket of the globular domain. Interestingly, this interaction surface overlaps an epitope recognized by the POM1 antibody, the binding of which drives rapid cerebellar degeneration mediated by the PrP N-terminus. The resulting structure suggests that the globular domain regulates the N-terminal domain by binding the Cu^{2+}-occupied OR within a complementary pocket.

EPR POSTER SESSION

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212 Nanoliter Biological Electron Paramagnetic Resonance Spectroscopy on a Diamond Chip.

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Commercial X-band micro-EPR devices have detection thresholds of 1013 spins (40 μL, 0.3 μM) at room temperature[1]. Obtaining greater sensitivity typically requires cryogenics, large magnetic fields, and/or large amounts of analyte. Our lab is developing a new EPR platform based on diamond nanotechnology, capable of detecting ~109 spins which corresponds to minute (1 nL, 1 μM) quantities of biomolecules. The sensor's working principle is analogous to Double-Electron-Electron Resonance (DEER) in traditional EPR, except here we detect an external spin species (the analyte) by Pulsed Optical Detection of another spin species inside the sensor (Nitrogen-Vacancy centers). These techniques rely on detecting statistical magnetization; this was recently demonstrated in landmark experiments using a single-NV sensor[2]. Remaining challenges include long measurement times and laborious sample prep, owing to stochastic placement of NV centers relative to the targets. The EPR detection sensitivity depends on the number of NV centers that are located sufficiently close to the diamond surface to sense external spins. To increase this number, we lithographically structure the diamond surface with high-aspect-ratio nanogratings, which enhances the sensor analyte contact area by more than an order of magnitude. We then dope the sidewalls of the nanostructures with a high density of NV centers. The result is that billions of NV centers come into contact with the analyte, boosting the EPR signal and reducing the signal acquisition time. We recently used a similar platform for detection of NMR and are now extending this work to EPR detection. We will report recent efforts to determine the sensor's detection threshold to nitroxide-labeled proteins, such as MAD2. We will also discuss technical challenges such as analyte diffusion and photodamage, and will outline a path towards detection of label-free biomarkers such as malarial hemozoin nanocrystals.

1. White et al., *Amer. Lab.*, 2011, 43, 5.
2. Shi et al., Science, 2015, 347(6226), 1135-1138.

EPR POSTER SESSION

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213 The SHARED EPR Network.

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This poster describes recent activities of the NSF-supported Research Coordination Network "Supporting, Highlighting and Advancing Recent Developments in Electron Paramagnetic Resonance" (SHARED EPR). The network is being implemented to promote the development and dissemination of innovative instrumentation and techniques in the area of EPR spectroscopy. The Primary Goals of the network are to: (1) facilitate the advancement of EPR methodology, instrumentation and techniques; (2) foster cross-fertilization and establish new collaborative research opportunities within the U.S. EPR community; and (3) establish international collaborations. During the past year, the network has established a web portal which will provide a centralized location for information regarding EPR research and resources and serve as a gateway to the EPR community for non-specialists. It has provided funds for high school students, graduate students and postdocs for the pursuit of EPR-related research and/or education. The network has sponsored the attendance of U.S. PIs at the annual meeting of the German EPR Priority Program Network titled "New Frontiers in Sensitivity for EPR Spectroscopy" in September of 2015, and it has organized the Grand Challenge Workshop titled "EPR on a Chip: Development and Applications of Micro EPR" at the 2015 Rocky Mountain Conference. SHARED EPR Network plans for the coming year will be discussed.

EPR POSTER SESSION

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214 NV Centers in Silicon Carbide (SiC): Identification, Modeling and Basic Properties.

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Whereas the NV center in diamond has been studied for decades and is still the object of intense research due to its potential applications in quantum computing and nano-sensoring the question of NV-like centers in other, technologically more relevant materials has been put forward recently. In particular Silicon Carbide (SiC) seems to be an excellent candidate for the search of NV centers [1]; here they are predicted to take the form of nitrogen-donor silicon-vacancy pair (N_CV_{Si}). SiC is a mature high-tech material which can be obtained in form of bulk material and epitaxial layers with well-controlled doping and defect properties. Further, SiC exists in many different polytypes giving rise to various NV centers with different optical and symmetry properties.

In this work we present recent results on NV^- spin-triplet centers in the three polytypes 3C (the direct diamond equivalent), 4H and 6H. Our investigation is based on photo-EPR spectroscopy at cryogenic to room temperatures and DFT calculation whereby the full set of EPR parameters, g-tensors, hyperfine splittings as well as zero-field splittings (ZFS) is calculated for the relaxed defect structures. In all three polytypes a resolved ^{14}N related hyperfine splitting of about $|A|=1.2$ MHz provides a clear fingerprint of these centers [2]. In the hexagonal polytypes the ground state ZFS parameters are in the range of 1.3 GHz and crucial to attribute the different spectra to the inequivalent lattice sites involved. We demonstrate that the $N_CV_{Si}^-$ center can be optically manipulated with a preferential population of the $m_s=0$ state. This optical initialization of the groundstate proceeds in particular for the axial symmetric pairs. Selective excitation of axial pairs in 4H/6H SiC suggests, thus, an easy preparation of unidirectional spin ensembles thereby coping one major problem of NV centers in diamond.

The work was funded by DFG (SPP-1601).

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[2] H.J. von Bardeleben et al., "*Identification and magneto-optical properties of the NV center in 4H-SiC*", Phys.Rev.B **92**, 064104 (2015)

EPR POSTER SESSION

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215 EPR Analysis of the Effects of Curcuminoids from Turmeric Spice on Superoxide Free Radicals Formed from a Xanthine-Xanthine Oxidase Reaction.

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Superoxide is a highly reactive oxygen free radical species produced by the human body by processes such as cellular respiration.[1] In a previous Steppingstone MAgnetic Resonance Training Center experiment, it was shown that extracts of juice from fresh cinnamon, turmeric, and ginger reduced the signal of superoxide from a xanthine-xanthine oxidase reaction.[2] However, spices like turmeric contain multiple major active components, such as the curcuminoids curcumin and demethoxycurcumin[3]. As a result, this work seeks to evaluate the efficiency of individual curcuminoids in turmeric. Our experiments measured the signal of the superoxide free radical in two scenarios: when it formed on its own *via* a xanthine-xanthine oxidase system in PBN, and the same system exposed to curcuminoids in an amount proportional to the amount of respective curcuminoids present in commercial turmeric. Kinetic experiments were carried out on a Bruker E-scan EPR spectrometer and both control and non-control sample were tested simultaneously under the same conditions.

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EPR POSTER SESSION

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216 Room Temperature PELDOR Measurements with Rigid Nitroxide Spin Labels on Duplex DNA.

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Although pulsed EPR techniques, such as Pulsed Electron Electron Double Resonance (PELDOR or DEER) provide highly accurate distance information in the nanometer range and enable measurements of conformal changes, these experiments are commonly carried out in frozen solutions at ~50 K. Pushing this to a physiological temperature requires immobilizing the biomolecule to avoid averaging of the dipolar interaction. This has been demonstrated by using trityl spin labels attached to lysozyme immobilized on a bead[1] and to DNA immobilized by a solid support[2]. For the commonly used nitroxide spin labels, the internal rotational motion of the spin label also needs to be suppressed to achieve long transversal relaxation times, required for room temperature PELDOR. This has been demonstrated recently with spirocyclohexyl-nitroxides in a dry glassy trehalose matrix.[3] Here we present room-temperature PELDOR data on double-stranded DNA molecules which are immobilized on nucleosil. The cytosine analog spin label Ç, used in our work, is rigidly attached to the DNA.[4] Because it has no internal degree of motion, long enough relaxations times can be achieved in liquid solution and highly precise distances can be obtained. Moreover, the relative orientation between both spin labels can be achieved from PELDOR experiments with variable probe frequencies, allowing one to obtain detailed information on the structure and conformational dynamics of the DNA.

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217 Radical Intermediates in the Formation and Repair of Spore Photoproduct.

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Spore photoproduct lyase (SPL) is a 4Fe-4S cluster protein that utilizes the cofactor *S*-adenosylmethionine (SAM) to catalyze the repair of a specific photodamage product in DNA known as the spore photoproduct (SP). Both the mechanisms of formation and repair of SP are still actively under investigation and proposed to proceed through radical intermediates.[1,2] The SP is a dimer of thymidine bases. Using a series of isotopically labeled thymidine molecules and electron paramagnetic resonance (EPR) spectroscopy, we show that thymidine exposed to ultra-violet (UV) radiation produces two radical species whose structures support a suggested radical pair intermediate in SP formation.[3] The suggested repair mechanism of SP by SPL involves a series of hydrogen atom transfers through a SAM based radical, a tyrosyl radical, and a cysteinyl radical.[4,5] We made a series of mutations to the relevant amino acid residues in the SPL active site. The changes in binding affinity of SAM due to the various mutations can be monitored through the extent of the spectral changes to the 4Fe-4S clusters' EPR spectra. At 40 K, EPR spectra characteristic of a carbon centered radical appear. The identity of this radical is still under investigation. The unique structure of SP and its efficient repair make bacterial endospores resistant to the deleterious effects of UV light on DNA for extremely long periods of time. Given the utilization of UV light in sterilization processes, it is interesting to fully understand the mechanisms of formation and repair of the spore photoproduct.

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EPR POSTER SESSION

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218 Electronic Structure of a Cu^{II}-Alkoxide Complex Modeling Intermediates in Copper-Catalyzed Alcohol Oxidations.

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In the copper-catalyzed oxidation of alcohols to aldehydes, a Cu^{II}-alkoxide (Cu^{II}-OR) intermediate is believed to modulate the αC-H bond strength of the deprotonated substrate to facilitate the oxidation. As a structural model for these intermediates, we characterized the electronic structure of the stable compound Tpt^{Bu}Cu^{II}(OCH$_2$CF$_3$) (Tpt^{Bu} = (hydro-*tris* (3-*tert*-butyl-pyrazolyl) borate) and investigated the influence of the trifluoroethoxide ligand on the electronic structure of the complex. The compound exhibits an electron paramagnetic resonance (EPR) spectrum with an unusually large gzz value of 2.44 and a small copper hyperfine coupling Azz of 40 10^{-4} cm^{-1} (120 MHz). Single-crystal electron nuclear double resonance (ENDOR) spectra show that the unpaired spin population is highly localized on the copper ion (≈ 68 %), with no more than 15 % on the ethoxide oxygen. Electronic absorption and magnetic circular dichroism (MCD) spectra show weak ligand-field transitions between 5000 and 12000 cm^{-1} and an intense ethoxide-to-copper charge transfer (LMCT) transition at 24000 cm^{-1}, resulting in the red color of this complex. Resonance Raman (rR) spectroscopy reveals a Cu-O stretch mode at 592 cm^{-1}. Quantum chemical calculations support the interpretation and assignment of the experimental data. Compared to known Cu^{II}-thiolate[1] and Cu^{II}-alkylperoxo[2] complexes from the literature, we found an increased σ interaction in the Cu^{II}-OR bond that results in the spectroscopic features. These insights lay the basis for further elucidating the mechanism of copper-catalyzed alcohol oxidations.

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EPR POSTER SESSION

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219 Feasibility Study of a CW-EPR-based Oxygen-mapping Technique Using a Pair of Isotopic Nitroxyl Radicals.

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A feasibility study of CW-EPR-based visualization of the partial pressure of oxygen (pO$_2$) and the concentrations of nitroxyl radicals is reported. Since the concentration of a spin probe affects its EPR linewidth (or the relaxation time T2), measurements of pO$_2$ have traditionally required simultaneous estimation of the probe concentration. Methods for measuring pO$_2$ using monohydrogenated CTPO (mHCTPO) were developed in the 1990s to overcome this dependence on the concentration of the probe.[1–3] We revisited this problem to visualize pO$_2$ and the concentrations of spin probes in a three-dimensional subject. To simultaneously measure unknown parameters (pO$_2$ and the concentrations of the probes), we used a pair of isotopic nitroxyl radicals, such as ^{14}N- and ^{15}N-labeled dicarboxy-PROXYLs (^{14}N-DCP and ^{15}N-DCP) as oxygen-sensitive spin probes.[4] First, we established simultaneous equations to express the effects of the self-broadening of ^{14}N- and ^{15}N-DCPs, cross-broadening between ^{14}N- and ^{15}N-DCPs, and oxygen-broadening on the linewidths of the probes. To estimate the linewidths of the probes, we used a CW-EPR-based single-point imaging (SPI) modality.[5] Linewidth maps could be obtained from T_2^* maps measured from a mixture of 14N- and 15N-DCPs. The concentrations of the probes and pO$_2$ could then be calculated simultaneously by solving the simultaneous equations. This approach might be useful for oxygen-mapping in biological tissues.

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220 Spin Labelled Carbohydrates on Au Nanoparticles.

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Carbohydrates play a vast number of key roles in biological functions, ranging from immune response regulation [1] to cell recognition [2], making them great targets for investigating treatments for cancer (and other diseases), new treatments for bacterial infections, and to gain a greater understanding of the immune response. Model membrane studies have shown that ligand density has a dramatic effect on binding to a surface, with some showing an improvement in binding [3], while others decrease in activity with greater ligand density, e.g. Concanavalin A has an affinity for clustered membrane bound mannose 3-fold weaker than it does in solution [4]. Self-assembled monolayers (SAMs) on nanoparticles provide a convenient model system for controlling the interfacial properties of surfaces, allowing for a flexible and simple model for surface reactions. SAMs can be applied to both flat surfaces and nanoparticles [5], are easily modified and are a useful tool for probing multivalent binding systems. Using bi-functional spin labels, SAMs have been functionalised with sugar moieties and radical spin labels (Figure 1), allowing investigation of enzymatic reactions, controlling and quantifying the degree of clustering on the surface of gold nanoparticles and allowing insight into the effect of substrate density on enzymatic dynamics.

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221 Enhancing Nuclear Polarization for Nanoscale Imaging Using Magnetic Resonance Force Microscopy.

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The ability to image the proton envelope of a near-native, flash-frozen, single copy of a macromolecule or macromolecular complex would be an enabling advance. Studying interesting biomolecules by nanoscale magnetic resonance imaging (nano-MRI) requires near single-spin sensitivity and a depth-of-view of 20 nm or more. Magnetic resonance force microscopy (MRFM) offers the sensitivity and non-invasive 3-dimensional scanning abilities required for nano-MRI by mechanically detecting resonant spins as a force or force-gradient on an attonewton sensitivity microcantilever. Exciting recent advances include the < 10 nm resolution viral imaging experiment of Degen *et al.*[1] and the integrated nanomagnet tipped cantilevers of Longenecker and Marohn[2] that have a demonstrated sensitivity of a few hundred proton magnetic moments. These experiments detected statistical fluctuations in nuclear magnetization. We will describe our efforts to decrease signal averaging time and increase imaging resolution by moving MRFM out of the spin-noise limit. We use dynamic nuclear polarization (DNP) to generate a measurable net nuclear spin polarization. We report the design, fabrication, and implementation of micrometer-scale coplanar waveguides to simultaneously deliver oscillating radiowave and microwave magnetic fields. We use these waveguides to detect electron spin resonance (at 0.6 tesla), observe nuclear magnetic resonance (at 4 to 6 tesla), and acquire the first microwave-enhanced ^{1}H signal in an MRFM experiment (0.6 T, *via* DNP). These experiments observe magnetic resonance signal from a nitroxide-doped polystyrene film, at 4.2 kelvin, and in a large magnetic field gradient from the micrometer-scale magnet tipped-cantilever[3]. We will furthermore discuss our work toward integrating 40 GHz microwave chip-scale sources into our cryogenic apparatus to increase the operating field for electron spin resonance and further enhance nuclear spin polarization through DNP.

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EPR POSTER SESSION

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222 Electrically Detected Magnetic Resonance Spectroscopy of Polymer Layers at B_1 Exceeding B_0 with Copper Microwire on Silicon Nitride/silicon Substrate.

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In contrast to inductively detected magnetic resonance spectroscopy, the sensitivity of electrically detected magnetic resonance spectroscopy (EDMR) of charge carrier states in polymer layers does not depend on ensemble polarization and thus can be carried out on very small sample sizes at room temperature and at very low magnetic field conditions.[1-3] These circumstances allow us to investigate very peculiar parameter domains including a regime where the amplitude of the resonant driving field B_1 is of the same order of magnitude as the static magnetic field, B_0. These are highly non-linear magnetic resonance conditions which for inductively detected magnetic resonance are technically hard to achieve. Theory predicts [4] that under these conditions a collective macroscopic spin phase emerges, which is a magnetic manifestation of what has been known from spectroscopy with electric dipoles as the Dicke effect. The onset of this spin-Dicke effect was recently observed experimentally [5] with $B_1 \approx 1$ mT being approximately 3 times smaller than $B_0 \approx 3$ mT at an excitation frequency of 85MHz. This experiment was achieved by use of conventional RF copper coils for which the excitation strength is limited by sample heating. In order to go beyond this regime, we have fabricated 1 μm thick copper wires to generate large B_1 underneath polymer thin-film devices with bipolar injection contacts with small circular active areas (diameter = 57um). The entire device stack is fabricated on a 1 μm insulation layer that separates the polymer layers from the microwire and the SiN/Si substrate. A microwire, silicon substrate and brass sample holder combination provides a good heat sink and we succeeded to generate an RF field with B_1 exceeding 6.7 mT at $\omega/2\pi \approx$ 85MHz and room temperature.

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EPR POSTER SESSION

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223 Characteristics of ^{14}N- and ^{15}N-labeled Dicarboxy-PROXYLs as Oxygen-sensitive Probes for CW-EPR-based Single-point Imaging (SPI).

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We describe both the oxygen- and concentration-dependence of the relaxation time T_2^* for ^{14}N- and ^{15}N-labeled dicarboxy-PROXYLs, i.e., 3,4-dicarboxy-2,2,5,5-tetra(methyl-d_3)pyrrolidine-3,4-d_2-1-^{15}N-1-oxyl (^{15}N-DCP) and 3,4-dicarboxy-2,2,5,5-tetra(methyl-d_3)pyrrolidine-3,4-d_2-1-oxyl (^{14}N-DCP).[1] We prepared aqueous samples of ^{14}N-DCP and ^{15}N-DCP, and then bubbled nitrogen into the solution to change the oxygen partial pressure. Next, we measured the transverse relaxation time T_2^* of the samples. To visualize the relaxation time T_2^* in three-dimensional space, single-point imaging (SPI) was applied to a mixture of ^{14}N-DCP and ^{15}N-DCP.[2,3] In EPR image scanning, we obtained the spectra of both probes simultaneously and then separated the spectra. We also investigated the cytotoxicity and pharmacokinetics of ^{14}N-DCP and ^{15}N-DCP with murine squamous cell carcinoma (SCC VII) cells and C3H/HeJ mice. No significant cytotoxicity was observed at concentrations below 10 mM, and the EPR signals of ^{14}N-DCP and ^{15}N-DCP persisted long enough after a single intravenous injection to conduct in vivo oxygen measurements. The in vivo half-lives of ^{14}N-DCP and ^{15}N-DCP were approximately 25 min.

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EPR POSTER SESSION

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224 Electron Spectral Diffusion Measured via ELDOR for DNP at 7 T.

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Solid-state dynamic nuclear polarization (DNP) is an increasingly popular technique that allows for hundreds fold increases in nuclear magnetic resonance (NMR) signal. The common sample preparation includes a solute of interest mixed with a stable radical at tens of mM concentration frozen into an aqueous glass. Upon on-resonance μw irradiation, the high electron polarization of the radical is transferred to the surrounding solvent nuclei and subsequently to the solute via spin diffusion processes. Recently the indirect cross effect was proposed as a primary mechanism for DNP in static samples at low temperatures, 3-40 K, and high radical concentrations, 20-40 mM, where this mechanism relies on the electron spectral diffusion process. It was demonstrated at 3.35 T that spectral diffusion can be characterized and quantified using electron double resonance (ELDOR) experiments.1,2 We have recently shown that the oversaturation effect, i.e. reduction of DNP enhancement for μw powers above a certain threshold, occurs at 7 T and low < 6 K temperatures.3 Here, we present a DNP / ELDOR study performed on our homebuilt dual DNP / EPR instrument at 7 T, 3 of the electron spectral diffusion dependence on experimental conditions such as μw power, irradiation length, temperature, and radical concentration. These results are discussed in connection with the oversaturation effect and static, low temperature DNP mechanisms and show the necessity of including electron spectral diffusion processes for understanding of the latter.

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EPR POSTER SESSION

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225 Determination of Zero Field Splitting Distribution and Rotational Correlation Times for Slow-motion Gd(III)-DOTA X-band cw-EPR Spectra Using a General Spin System Stochastic Liouville Equation Solver.

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A general stochastic Liouville equation (SLE) solver has been implemented in EasySpin to simulate slow-motion cw-EPR spectra for general spin systems. This solver can simulate spectra of complex high-spin systems and systems with multiple nuclear spins. We applied the general solver to investigate the high-spin $S = 7/2$ Gd(III)-DOTA system with electron Zeeman and zero field splitting interactions in the spin Hamiltonian. A distribution in the zero field splitting parameter D is determined for Gd(III)-DOTA in frozen 40:60 glycerol:water solution using an iterative model-free minimization procedure[1] to fit frozen X-band cw-EPR spectra. The SLE solver is then used to determine rotational correlation times for Gd(III)-DOTA in the same glycerol:water solution at various temperatures from slow-motion X-band cw-EPR spectra, given the D distribution obtained from the frozen spectra.

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EPR POSTER SESSION

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226 Newly Improved ADANI SPINSCAN EPR/ESR Benchtop Spectrometer.

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Several important features have been upgraded for the ADANI EPR/ESR ergonomic benchtop spectrometer, the SPINSCAN. The detection limit can be as low as 10 nM. Based on CMS-8400, the magnet cooling is improved and the electronic components are completely re-designed, which enables the signal resolution enhancement and reliable data acquisitions.

An electronic unit based on high-speed ADCs allows the 1st and 2nd harmonics measurements of EPR signals. The extended modulation frequency range (10 to 500 kHz) allows the exploration of any EPR line shape for different type of samples. The different signal phase shifting can be informative for resolution enhancement and saturation transfer EPR. The cavity critical coupling is accomplished automatically with higher reliability and reproducibility, especially for liquid samples. There is also the capability to use Ethernet for device control.

A new system software program, e-SPINOZA, has been carefully developed with modern interfaces to provide an environment that is easy to learn, yet powerful enough for experienced users. It has many new features, including (but not limited to) Q-factor measurement, microwave power setting, 2D experiments vs microwave power, vs temperature etc., spectrum fragmentation, spectrum parameter calculations (line-width, g-factor, concentration etc.), data processing (integration, differentiation, smoothing etc.), and control of accessories (temperature control systems, etc.)

The SPINSCAN system, intended for EPR spectra determination in liquid or solid phases to detect paramagnetic species, including free radicals, can be used for a wide range of applications in physics, chemistry, biophysics, geology, medicine, and more. With its high quality and low cost, it is an ideal instrument for routine measurements in any laboratory, especially for education and postgraduate research. Utilizing additional options and scripting programs, it can be a high quality research instrument in commercial applications, such as medicine and pharmacology, dosimetry and food control, controlling petroleum products, and in other disciplines.

EPR POSTER SESSION

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227 Speciation of Vanadyl Porphyrin Complexes Through High Resolution Electron Paramagnetic Resonance.

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Vanadium occurs naturally in the world's crude oil reserves on the order of several hundred ppm. Vanadium poisons the catalysts used in the refining process of crude oil, therefore there is much interest in the separation of vanadium from the crude oil matrix. The exact nature of vanadium in crude oil is as of yet unknown, however most if not all is in the form of vanadyl ions complexed with various porphyrin families (etioporphyrins, benzoporphyrins, etc.). The separation of vanadyl porphyrins from crude oil is non-trivial and speciation of vanadyl porphyrins in crude oil is an ongoing area of research. The goal of this project is to characterize the magnetic properties of the ligand structure of vanadyl porphyrins; ultimately differentiating the various types of vanadyl porphyrins in crude oil. The variation between vanadyl porphyrin ligands is small (on the order of 0.05 MHz) and therefore high resolution experiments will be required. Characterization of the vanadyl porphyrin ligand structure is achieved by combining pulsed Electron Paramagnetic Resonance experimental techniques (Electron Nuclear Double Resonance (ENDOR), Electron Spin Echo Envelope Modulation (ESEEM) and Hyperfine Sub-level Correlation (HYSCORE)) with Density Functional Theory (DFT) and spectral simulations. Thus far we have fully resolved all of the proton couplings in vanadyl tetraphenylporphyrin and can differentiate between the ethyl and methyl protons on the ligands of octaethylporphyrin and etioporphyrin.

EPR POSTER SESSION

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228 Frequency Swept Rapid Scan EDMR.

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We report on rapid scan frequency swept electrically-detected magnetic resonance (EDMR) with ≥ 100 GHz/s sweep rates (equivalent to ~3.6 T/s for a free electron). Our measurements forgo a microwave cavity or other resonator for a very small non-resonant near field microwave probe.[1] This allows us to replace the standard electromagnet with a small permanent magnet and detect EDMR via frequency sweep. The entire apparatus is sufficiently compact that we integrated it into a standard probing station, allowing EDMR measurements to be made conveniently on a wide range of samples of interest. Rapid scan[2] frequency swept EDMR was demonstrated on the recombination current in a biased drain-substrate junction of a SiC MOSFET. “Slow” frequency-swept EDMR utilizing lock-in amplifier detection (amplitude or frequency modulation) on the same device was also performed. Compared to a standard field swept resonator-based EDMR acquisition,[3] while not yet optimized, rapid scan demonstrated a modest level of boost in signal to noise ratio. We expect our sweep rate can increase substantially with a larger bandwidth current amplifier. The elimination of modulation in the rapid scan approach, coupled with the elimination of the resonance cavity and electromagnet, greatly simplifies the EDMR detection scheme and offers promise for more widespread EDMR adoption.

EPR POSTER SESSION

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229 High-field/high-frequency Pulsed/CW EPR with Increased Concentration Sensitivity and High Power.

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High-field high-power pulsed electron paramagnetic resonance (EPR) can offer insight into phenomenon which are inaccessible or obscured in traditional continuous-wave (CW) EPR spectra, particularly when acquired at lower magnetic fields. Despite the significant advantages of high-field pulsed EPR and the ready availability of higher magnetic fields, there are increasing technical challenges in generating high-power microwaves above 10 GHz limiting the availability of such instruments. However, a recently installed pulsed high-power (1 kW) w-band (94 GHz) EPR spectrometer “HiPER”[1] at the National High Magnetic field Laboratory (MagLab) has been made available as part of its user program and has been rapidly applied to investigate a range of problems in the fields of Biology, Chemistry and Physics. In this talk, an overview of the instrumentation and application development program will be presented through a small selection of experiments which highlight the unique capabilities of the spectrometer and significant advantages offered to scientists as part of the MagLab user program. We will illustrate the unique concentration sensitivity of the instrument for biological applications. We have so far shown the high concentration sensitivity of CW EPR measurements of aqueous samples and it has been observed to be 2-20 µM with sample volumes of 50 µL[2], offering significant advantage for characterizing spin-labeled biological systems in solution in a low concentration environment. High sensitivity has also been used for orientation-dependent pulsed electron-electron double resonance (PELDOR) measurements of the bipedal spin label Rx[3] offering a general strategy for the measurement of spin-label orientation in proteins. Applications developed around the large 1 GHz bandwidth and high power of the HiPER spectrometer for dynamic nuclear polarization (DNP), inorganic and organic chemistry, and single crystal studies will also be shown.

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EPR POSTER SESSION

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230 An AWG-based Digital X-band Saturation Recovery Spectrometer for Spin Lattice Relaxation Measurements.

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An arbitrary waveform generator (AWG) forms the basis for an X-band saturation recovery (SR) spectrometer. The outputs of the AWG provide the X-band frequencies for the excitation and observe paths, the reference frequency for detection of the EPR signal in a mixer, trigger the digitizer, and control switches that select amplifier paths. The excitation (saturating) pulse path can be up to 30 dBm (1 W), and the observe paths can be selected from -10 dBm to +15 dBm output after the selecting switch. There is also an attenuator to reduce power in the EPR observe path. In the initial demonstrations, a Bruker ER4118X-MD-5 dielectric resonator was used. Samples were in standard 4 mm o.d. quartz tubes. The observed EPR signal is detected in a quadrature mixer and both channels are amplified to provide signals with appropriate amplitude for digitization. The digitizer can be a digital oscilloscope or a Bruker SpecJet under control of Bruker Xepr software. For convenience, there is a phase shifter in the reference arm path from the AWG to the LO of the mixer. Examples will be shown of T_1 relaxation measurements of sample whose relaxation times are known from previous measurements with the SR spectrometer described previously [1]. By replacing the resonator and a few frequency-sensitive parts, the AWG-based spectrometer could be implemented at any frequency below X-band.

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EPR POSTER SESSION

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231 Spin-dependent Charge Carrier Interaction Processes in Polyfluorene Thin Films.

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Owing to weak spin-orbit coupling, the dynamics of charge carrier interaction processes in conducting polymer films such as charge transport and recombination can be strongly influenced by spin-selection rules, significantly affecting the magneto-opto-electronic properties of these materials.[1] We have studied the role of spin-dependent processes on conductivity in polyfluorene (PFO) thin films by conducting continuous wave (cw) electrically detected magnetic resonance (EDMR) spectroscopy at temperatures between 10 K and 290 K using microwave frequencies between about 100 MHz and 20 GHz and pulsed EDMR at X-band (about 10 GHz). We used PFO for this study in order to allow for the investigation of microscopic order effects since it can exist in two distinct solid state morphologies: an amorphous (glassy) and an ordered (beta) phase.[2] The phases can be controlled in thin films by deposition parameters and are verified by electroluminescence spectroscopy.[3] Under bipolar charge carrier injection conditions, achieved with a Ca electrode for electrons and a poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) electrode for holes (as routinely for organic light emitting diodes), we conducted multi-frequency cw EDMR, electrically detected Rabi spin-beat experiments, Hahn-echo and inversion-recovery measurements, as well as electrically detected electron spin-echo envelope modulation. Our results indicate that, while disorder can influence the observed EDMR signals, including the sign of the observed current changes as well as the magnitudes of local hyperfine fields and charge carrier spin-orbit interaction, they do not qualitatively affect the nature of spin-dependent transitions in this material. In both morphologies, we observe the presence of at least two different spin-dependent recombination processes. At both high and low-temperatures, polaron-pair recombination through weakly spin-spin coupled intermediate charge carrier pair states is dominant, while only at low-temperatures, signatures of spin-dependent charge transport through the interaction of polarons with triplet excitons are clearly seen in the half-field resonance of the triplet spin-1 species.

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EPR POSTER SESSION

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232 Calculation of 2D-SECSY (Spin-Echo Correlation Spectroscopy) and 2D-ELDOR (Electron Double Resonance) Signal Using Stochastic- Liouville Equation (SLE).

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A general technique for numerical calculation of pulsed electron paramagnetic resonance (EPR) by the use of stochastic Liouville equation (SLE) in Liouville space is developed. In this method, the operators in the SLE equation are transformed from the Hilbert space to the corresponding superoperator in Liouville space, including the Hamiltonian operator, the pulse propagator and the relaxation superoperator. The method is quite general, in that it can handle pulses of arbitrary duration and intensity, and can be applied to any pulse sequences. The calculated echo signal is a sum over the signals generated by coherent electronic pathways. For each pathway, the time domain signal is obtained, from which the frequency domain signal is calculated by Fourier transformation. The method can also be used for large electron spins associated with a significant zero-field splitting, as well as for pulse electron-nucleon double (ENDOR) resonance experiments. This method, as coded here in MATLAB, is illustrated numerically to two-dimensional spin echo correlation spectroscopy (2D-SECSY) and two-dimension electron-electron double resonance (2D-ELDOR) signals obtained on a malonic acid crystal.

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233 Mechanistic Investigations on Electron Bifurcation by EPR Spectroscopy.

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Electron bifurcation, a process for coupling endergonic and exergonic reactions to overcome thermodynamic barriers, is considered the third mechanism of biological energy conservation and results in the efficient coupling of electrochemical potential to chemical bond formation.[1,2] Overall, the mechanism of bifurcation and how bifurcating enzymes function is poorly understood. We are investigating the mechanism of flavin-based electron bifurcation in the NADH-dependent ferredoxin-NADP+ oxidoreductases, (Nfn), which catalyze the reversible reduction of NADP+ with reduced ferredoxin and NADH. Nfn contains two electron-transfer pathways both of which are comprised of flavins and FeS clusters.[3] EPR spectroscopy in conjunction with x-ray crystallographic and other biophysical techniques, are being used to investigate the oxidation-reduction properties of these centers and how they facilitate gating of electron-transfer to respective pathways. The results reveal that two unique, site-differentiated FeS clusters, Cys$_3$Asp [2Fe-2S] and Cys$_3$Glu[4Fe-4S], play key roles in the process through tuning of midpoint potentials and coupling with other redox centers. This presentation will summarize how these features work in concert with key structural properties of the enzyme to achieve bifurcation.

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EPR POSTER SESSION

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234 Frequency-Domain EPR up to Several THz: Direct Observation of Large ZFS in Co$^{\text{II}}$ Clusters.

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The Zero-Field Spitting (ZFS) of molecular clusters is of great interest. It is a result of spin-spin and spin-orbit interactions and is therefore a sensitive probe of the electronic structure. Furthermore, the ZFS is considered as key ingredient for slow relaxation of the magnetization in single molecule magnets and single ion magnets. Increasing the ZFS might sustain slow relaxation of the magnetization up to higher temperatures. Therefore ions with inherently large magnetic anisotropy become more prevalent. High-spin Co^{II} ions (d^7, $S = 3/2$) have a large spin-orbit interaction and therefore potentially very large ZFS. The large spin-orbit interaction might invalidate the widely used effective spin approach. Direct spectroscopic observation of ZFS is extremely challenging. Frequency-Domain Fourier-Transform THz-EPR as developed by us allows to measure ZFS in the range from 100 GHz to 5 THz.[1,2] Simulation abilities for frequency-domain EPR were introduced into EasySpin.[3,4] Several Co^{II} molecular clusters were studied and we could directly observe the ZFS and furthermore detect field dependence up to 10 T. The ZFS was found to range from 1.5 to 5.2 THz. Combining these results with CW X-Band EPR, magnetic susceptibility and computational studies allowed us to probe different effective models for the magnetic properties of Co^{II} clusters in great detail. We found that the effective spin model do surprisingly well. However, for the compound with the largest ZFS we found it that it does not reproduce experimental data. This might be due to low-lying excited states. Instead we propose to use a total angular momentum approach.

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EPR POSTER SESSION

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Characterization of Solvent Dynamical Properties Around the B12-dependent Ethanolamine Ammonia-lyase by Using Spin Probe-EPR Spectroscopy.

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The effect of dimethyl sulfoxide (DMSO) on the solvent dynamical properties around the B12- dependent ethanolamine ammonia-lyase (EAL) from Salmonella typhimurium was studied over the temperature (T) range of 190-265 K in frozen aqueous solutions. Spin probe electron paramagnetic resonance (EPR) was used with 4-hydroxy-TEMPO (TEMPOL), and the added DMSO concentration was 0-4 %v/v. The aim is to identify and characterize protein hydration and bulk solvent behavior with the goal of resolving the effects of solvent dynamics on enzyme activity. The rotational dynamics of the TEMPOL as a function of T was revealed by the EPR line shape and was quantified by the rotational correlation time (τc) obtained from EPR simulations. Three motional regions were identified in all samples: (A) low T; τc >10-7.5 s; one rigid component. (B) Intermediate T, τc ≤10-7.5 s, two mobile components (Wf=55±5 %, Ws=45±5 %). (C), Wf begins to rise in proportion to Ws and eventually becomes dominant. The rigid to mobile transition T of the spin probe decreased with increased DMSO concentration. The lowering of the mobility transition T with increased DMSO concentration is consistent with the freezing point depression of aqueous solutions by the DMSO. 1 Arrhenius parameters (Ea, A) from the τc values indicated common, DMSO concentration-independent component phase compositions for Region B, whereas in Region C, the viscosity of the phase corresponding to Ws increased concomitant without significant change in Wf phase viscosity. The results indicate that TEMPOL occupies two phases, and suggest that the Ws and Wf components correspond to the protein hydration layer2 and the "bulk" solvent mesodomain.3 The variation of DMSO concentration and T systematically controls solvent dynamics around EAL, and provides the basis for an approach for investigating the influence of solvent-protein dynamical coupling on catalysis in EAL.

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EPR POSTER SESSION

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236 Out-of-phase ESEEM: Measuring Distances of Excited Radical-pair States to Identify the Final Electron Donor in Cryptochromes and Photolyases.

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Proteins of the photolyase/cryptochrome family share a conserved tryptophan pathway to transport electrons from the surface to the photo- and redox-active FAD cofactor within the protein.[1] In photolyases the fully reduced $FADH^-$ cofactor serves as donor of a catalytically-active electron for repair of light induced DNA lesions, while in cryptochromes the metastable semiquinone FAD radical represents the signaling state for different biological responses to blue light. Recent spectroscopic results presume that the pathway is more diverse in terms of number and amino acid composition than commonly accepted. In detail, certain members of the animal cryptochrome family might use a fourth, more surface exposed amino acid residue as final electron donor for signaling-state generation.[2] The altered environment of this alternative, more distant aromatic residue could reflect the difference between a pure electron transfer pathway in photolyases, and a long-time stabilization of the radical pair for e.g., magnetoreception in avian compasses. Direct characterization of the excited radical pair state can be achieved by transient EPR spectroscopy, which grants access to the **g** and **A** tensors of the radical-pair partners, as well as the dipolar and exchange coupling constants D and J. While pulsed electron-electron double resonance spectroscopy lacks the capability to directly measure electron-electron interactions of short-lived radical species, measurements of the out-of-phase electron spin echo envelope modulation (oop-ESEEM) of laser flash induced spin-correlated radical pairs gives direct access to the dipolar and exchange interactions between the radical pair partners.[3,4] Therefore distance measurements, and thereby an identification of the radical partner molecule can be accomplished. Here, we present results of transient EPR and oop-ESEEM measurements of different members of the photolyase and cryptochrome family at x-band and q-band frequencies, which prove that different amino acids at different distances function as final electron donor in animal type cryptochromes.

The work presented here has been performed in collaboration with:
K. Hitomi and E. D. Getzoff (Scribbs Research Institute La Jolla, CA, USA)
S. Franz and L.-O. Essen (Philipps University Marburg, Germany)

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EPR POSTER SESSION

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237 Development of High-frequency Cantilever-detected ESR Technique and its Application to Metalloporphyrin Complexes.

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High frequency ESR (HFESR) is a powerful method for studying microscopic properties of samples. HFESR allows high g-value resolution and observation of the large zero-field-splitting. However, because of a lack of intense light sources, spin sensitivity of apparatus is very low. Thus it has been difficult to apply HFESR to biological systems with a low spin density such as metalloprotein. To solve this problem, we developed a cantilever-detected high sensitivity HFESR technique. In this technique, a tiny sample (micro-gram order) is mounted on a cantilever end, and a field gradient is applied by a gradient magnet which is located 200 micro-meter under the sample. When a magnetization change associated with ESR absorption is induced, the sample is pulled by the field gradient force, and ESR signals are detected as a cantilever bending. So far, we could detect HFESR signals in terahertz region up to 400 GHz and attained a high spin sensitivity (10^8 spins/gauss).

In this study, we applied our apparatus to protein samples. For example, hemoproteins have a large zero-field-splitting value exceeding 100 GHz. So HFESR measurement is needed for studying more detailed electronic structure of hemoproteins. So far, we used a ferrite magnet to produce a gradient magnet. In this study, we used a dysprosium magnet whose gradient field was two order of magnitude stronger than that for the ferrite magnet. We chose metalloporphyrin (hemin-chloride) as a test sample. Hemin-chloride is one of the model samples of hemoprotein such as hemoglobin or myoglobin and is known to have the large zero-field-splitting. In this study, we succeeded in ESR observations at multiple frequencies up to 160 GHz. However, the signal-noise-ratio is not high, and we need further improvement for observing ESR signals of hemoprotein samples. In this symposium, we will show our apparatus and experimental results on metalloporphyrin.

EPR POSTER SESSION
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Probing the Membrane Binding of Alpha-Synuclein: One Spin Label at a Time.

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Alpha-synuclein (aSyn) is a membrane-binding protein that is intrinsically disordered in solution, but is known to form an α-helical structure upon binding membranes. Due to its implications in Parkinson's disease, aSyn has been a topic of research in order to better understand not only its role in the disease state, but also its physiological role in the cell. Through this work it has been shown that the membrane binding of aSyn is sensitive to both membrane curvature and charge as well as to the N-terminal acetylation of aSyn, a common post- translational modification. We are interested in further probing, in a site-specific manner, how the membrane binding of aSyn is altered by membrane size and charge as well as the effect that N-terminal acetylation of the protein has on membrane binding using electron paramagnetic resonance (EPR). In this work, aSyn was transformed and expressed in E. coli cells in the absence and presence of the fission yeast NatB complex, which enables the N-terminal acetylation of aSyn. Several cysteine mutants throughout the membrane binding region (residues 1-95) were generated and spin labeled. Spin labeled aSyn was then added to POPC/POPG lipid vesicles of varying curvature and charge, by altering the vesicle size and concentration of POPG, respectively. Through the use of continuous wave and power saturation EPR we can site-specifically measure the change in dynamics and membrane accessibility of aSyn as a function of membrane character and N-terminal acetylation to help elucidate the membrane binding behavior of this protein.

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EPR POSTER SESSION
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Trityl Radical Relaxation and S/N at Frequencies Between 0.4-1 GHz.

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Oxygen concentration (pO_2) is among the most important parameters in physiology and pathophysiology of living organisms. Triarylmethyl-based radicals are promising probes to monitor pO_2 in vivo, because of their sharp, single-line electron paramagnetic resonance (EPR) spectra and better stability in vivo compared to the traditional nitroxide-based radicals [1,2]. Changes in relaxation times are more sensitive and accurate measures of pO_2 than are linewidths. Low observation frequency is used to maximize the depth of penetration into tissue. In this work we seek to find the optimum frequency.

Relaxation times and signal-to-noise (S/N) of the OX63 radical at frequencies between 0.4 – 1 GHz were studied. The experiments were carried out on a locally designed and constructed pulse instrument with a cross-loop resonator (CLR) [3] built specifically for these experiments. The spin-lattice relaxation times T_1 and spin-spin relaxation times T_2 were measured at 3 radical concentrations for several frequencies at room temperature. S/N was measured for 2 radical concentrations at room temperature. T_1, T_2 and S/N also were measured for 2 radical concentrations, 3 salt concentrations and 2 temperatures (19 and 37 ^{o}C) at 700 MHz.

In the frequency range 0.4 – 1 GHz, T_1 and T_2 increase as the frequency increases, consistent with motional models. Q-normalized S/N values increase as frequency increases. For the same frequency, relaxation time decreases as the OX63 concentration increases. Addition of NaCl to the solution to mimic in vivo ionic strength decreases T_2 more than T_1. Adding the salt to the radical solution decreases S/N at 700 MHz because salt lowers the resonator Q. When temperature increases, T_1 decreases while T_2 increases. Changing the temperature did not cause much change in S/N at 700 MHz.

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EPR POSTER SESSION

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240 Coplanar Waveguide Microresonators for High-Frequency Optically-Detected Magnetic Resonance.

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It has been shown that planar microresonators are better than conventional resonators in terms of power handling properties and sensitivity for Electron Spin Resonance (ESR) of small samples[1,2]. However, the existing planar microresonator designs are based on the microstrip model that requires metallization on the rear side of the substrate. This back-metallization makes incorporating laser in Optically-Detected Magnetic Resonance (ODMR) experiments difficult. A possible solution to this problem is to build coplanar waveguide microresonators that require metallization only on one side. We discuss several designs of coplanar waveguide microresonator for 29 GHz ODMR. We show that with our design, it is possible to separate the microwave magnetic field from the electric component and concentrate the magnetic field at the sample position.

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EPR POSTER SESSION

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241 Stop-Flow study of Nitroxide Reduction by Human Lymphocytes.

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Here we use a non-resonant transmission mode stopped flow ESR spectrometer with a sensitive RF bridge[1] to observe reduction of nitroxide radicals by human lymphocytes with high sensitivity.

The cavity-less ESR consists of a transmission line for the microwave frequency. The active area for this setup is a channel carved between the signal line and the ground of the transmission line. The ESR-active volume of the system is 0.3 µL. The field was swept at ~400 Gauss/s. Signal-to-noise ratio (S/N) was 10 after 6s averaging. Immediately after mixing, the nitroxide concentration was 200 µM and the cell density was 2×10^8 mL^{-1}. The dead volume and time for the setup were ~12 µL and ~1.4 s, respectively. The time constant obtained from data shown is about 4 min.

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EPR POSTER SESSION

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242 Selective Membrane Disruption Mechanism of an Antibacterial γ-AApeptide Defined by EPR Spectroscopy.

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Antibiotic resistance is one of the major threats to public health. γ-AApeptides are a new class of antibacterial peptidomimetics that are not prone to antibiotic resistance and are highly resistant to protease degradation. It is not clear how γ-AApeptides interact with bacterial membranes and alter lipid assembly, but such information is essential to understanding their antimicrobial activities and guiding future design of more potent and specific antimicrobial agents. Using EPR techniques at 9 and 95 GHz, we characterized the membrane interaction and destabilizing mechanism of a lipo-cyclic-γ-AApeptide (AA1), which has broad-spectrum antibacterial activities1. The analyses revealed that AA1 binding increases the membrane permeability of POPC/POPG liposomes, which mimic negatively charged bacterial membranes. AA1 binding also inhibits membrane fluidity and reduces solvent accessibility around the lipid head-group region. Moreover, AA1 interacts strongly with POPC/POPG liposomes, inducing significant lipid lateral-ordering and membrane thinning. In contrast, minimal membrane property changes were observed upon AA1 binding for liposomes mimicking mammalian cell membranes, which consist of neutral lipids and cholesterol. Our findings suggest that AA1 interacts and disrupts bacterial membranes through a carpet-like mechanism. The results showed that the intrinsic features of γ-AApeptides are important for their ability to disrupt bacterial membranes selectively, the implications of which extend to developing new antibacterial biomaterials.

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EPR POSTER SESSION

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243 Oligomerization of *Anabaena* Sensory Rhodopsin Lipid Bilayers by DEER and Solid State NMR Methods.

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Structure-function studies of membrane proteins in native lipid bilayer environment and, in particular, organization of protein oligomers, are challenging even for the modern spectroscopic and biophysical methods. While DEER in combination with nitroxide labeling is well suited for determination of long-range distance constraints and oligomeric order, high local concentration of electronic spins in oligomers and lipid environment shorten electronic relaxation time and, often give rise to multispin artifacts. Here, we describe optimization of DEER experiments to determine the oligomeric order and obtain intermonomer distance restraints for an integral membrane protein *Anabaena* Sensory Rhodopsin (ASR) reconstituted in the lipid environment, using essentially the same preparation of spin-labeled ASR samples as employed in paramagnetic relaxation enhancement (PRE) NMR experiments. Magnetic dilutions as well as experiments with model lipid vesicles have been carried out to improve deconvolution of the DEER signal arising from defined spin clusters from the one due to random spin-pairs. Further, we show that the oligomeric order can be determined from the direct modeling of the multispin effects. The later approach could be useful when the efficiency of spin-labeling is not known with sufficient accuracy. Such an approach allows for an unambiguous differentiation of the ASR trimers from other types of symmetric oligomers. We then combine long-range DEER data with NMR restraints to refine ASR structure: addition of long-range intermonomer DEER restraints to the previously determined short- and medium-range NMR restraints resulted in a more compact packing of helices and refined positions of side chains at the intermonomer interface compared to the structure determined using the NMR data alone.

DEER experiments were supported by U.S. DOE Contract DE-FG02-02ER15354 to AIS.

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244a **WaDeESR: Wavelet Denoising for Continuous Wave-ESR.**

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Continuous-wave Electron Spin Resonance (cw-ESR) spectroscopy is the most commonly used ESR technique. It is extensively applied to study the dynamics and structure of biomolecules. To obtain the desired spectrum, signal averaging is used. This reduces noise by averaging multiple measurements on the same sample. This is typically time consuming especially for samples with low SNR, and can be limited sample degradation. Also, it is mainly effective in canceling white (random) noise. We developed a novel wavelet denoising method for cw-ESR (WaDeESR) that substantially reduces the signal averaging required by about an order of magnitude (to obtain good SNR). Our extensive studies on model and experimental spectra have shown that our method performs significantly better than other denoising methods. An important feature of our method is its ability to identify and eliminate noise at and near the peaks of the spectrum, and to recover small satellite details.

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244b **WavPDS: A Wavelet Approach in Denoising Pulsed Dipolar Spectroscopy**.

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Studying biological systems using Pulsed Dipolar Electron Spin Resonance Spectroscopy (PDS) is challenging due to the short relaxation times and low protein concentrations typically used. These frequently result in a low Signal to Noise Ratio (SNR), complicating the analysis. Even if the average distance between spin probes can be estimated, the determination of the distance distribution (DD) is likely to be corrupted by noise. To address the challenge of noise removal in Pulsed Dipolar ESR in order to obtain reliable information, we developed a new wavelet denoising method (WavPDS) to remove/reduce noise. Our method improves the stability and reliability of the DD reconstruction, and reduces the signal acquisition time by an order of magnitude. This enables the study of biomolecular structures at low SNR signals with accuracy. We believe that studies in a wide variety of disciplines will greatly benefit.

EPR ORAL SESSION

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245 **Measurement of Paramagnetic Spin Concentration in a Solid-state System using Double Electron-electron Resonance.**

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Diamond has been extensively investigated recently due to a wide range of potential applications of nitrogen-vacancy (NV) defect centers existing in a diamond lattice. The applications include magnetometry and quantum information technologies, and long decoherence time (T_2) of NV centers is critical for those applications. Although it has been known that T_2 highly depends on the concentration of paramagnetic impurities in diamond, precise measurement of the impurity concentration remains challenging. Here we demonstrate a method to determine a wide range of the nitrogen concentration (n) in diamond using a wide-band high-frequency electron spin resonance and double electron-electron resonance spectrometer. Moreover, we investigate T_2 of the nitrogen impurities and show the relationship between T_2 and n. The method developed in this work is applicable for various spin systems in solid and implementable in nanoscale magnetic resonance spectroscopy with NV centers to characterize the concentration of the paramagnetic spins within a microscopic volume.[1]

1. V. Stepanov and S. Takahashi, submitted (2016), arXiv:1603.07404

EPR POSTER SESSION

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246 Mapping the Conformational Landscape of Calmodulin with PELDOR Spectroscopy.

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Calmodulin (CAM) is a promiscuous protein which binds hundreds of proteins, regulating a wide array of functions, in a Ca^{2+} dependent fashion. CaM has two globular domains, each with two EF hands utilized in binding Ca^{2+}, separated by a flexible linker. In the absence of Ca^{2+}CaM adopts a semi-compact structure[1], while binding Ca^{2+} forces a conformational change elongating the protein[2] allowing CaM to bind its target sequence, whereupon CaM adopts a compact conformation. Nitric Oxide Synthase (NOS) is one binding target for CaM. NOS is a multi-domain homo-dimer responsible for the synthesis of NO from arginine and molecular oxygen. Electron transfer from the reductase domain to the oxygenase domain, where catalysis occurs, is regulated by the conformational flexibility of the system. The allowed conformational states of NOS are restricted by CaM binding[3], promoting electron transfer from the reductase domain to the oxidase domain. In order to elucidate the mechanism of binding to NOS, we seek to map the conformational landscape of CaM, both in solution and when bound to neuronal NOS. PELDOR spectroscopy and molecular dynamics (MD) simulations were utilized to explore the conformational states of CaM under a range of conditions. PELDOR studies of doubly spin-labeled CaM T34C-T110C were performed at both Q-band and X-band. PELDOR data shows distances corresponding to the expected distances from the solution and crystal structures of CaM. MD simulations show CaM collapsing into a compact conformation, upon the addition of Ca^{2+}. which is similar to the conformation observed upon binding of a NOS-derived peptide. These data will be discussed in the context of a model where CaM samples a large conformational space, which becomes restricted upon the addition of Ca^{2+} and/or protein binding partner. Possible experimental artefacts including crystal packing constraints and problems with population biasing during rapid freezing are also considered.

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EPR POSTER SESSION
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247 A Surface Resonator Array Based X-band EPR Instrument for Making *In Vivo* Measurements in Finger Nails for Rapid Dosimetry.

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Electron Paramagnetic Resonance (EPR) spectrometry measurement of the radiation-induced signal (RIS) in finger/toe nails is being developed as a method to rapidly and accurately determine individual radiation dose for triage in a radiological/nuclear event. Instrumentation and methodology are being developed for an *in vivo* nail X-band EPR dosimetry method to directly measure RIS in finger/toe nails in the field. Key components under development are resonators with unique geometries that allow for large sampling volumes but limiting the measurements to the nail plate. One resonator under development is a Surface Array Resonator (SRA) consisting of parallel elements which restricts the electric field component of the microwave from penetrating the nail plate and limits the depth sensitivity of the RIS measurements to within the nail plate. Several SRA geometries have been tested in tissue-equivalent nail models and *in vivo* nail measurements of simulated RIS in fingernails of healthy volunteers, where the simulated RIS signals are obtained by applying thin plastic films (containing an EPR active singlet signal) to the surface of nails. The 9-element SRA was found to provide the best detection sensitivity of the nail background and simulated RIS in *in vivo* measurements of the nail plate while minimizing losses due to the lossiness of the soft tissues underlying the nail plate. With the integration of the 9-element SRA within an ergonomic platform for secure positioning of the nail and finger performance testing of the *in vivo* EPR spectrometer in healthy volunteers is underway. Current results show that X-band EPR *in vivo* measurements of the RIS in nails is approaching the detection sensitivities within a clinically relevant range.

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248 Electrically Detected Magnetic Resonance Spectroscopy of Spin-dependent Charge Transitions in the Organic Semiconductor poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) for Different Ethylene Glycol Doping Concentrations at Low Temperature.

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Poly(3, 4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) is a thin-film polymer material that finds wide applications as a transparent thin-film conductor as used for anti-static coatings, as well as electrode material in organic light emitting diodes and display applications. It has been shown in the past that the conductivity of PEDOT:PSS films can be enhanced by adding ethylene glycol (EG) to the PEDOT:PSS aqueous solution before the film is deposited[1]. This study is focused on the microscopic origin of these conductivity enhancements. In particular, we question whether the observed conductivity increase is influenced by changes of the physical nature of the electronic states that conduct electric charge, the so-called polaron states which are typically localized on chromophore size scales.

In order to address this question, we have carried out electrically magnetic resonance (EDMR) experiments on PEDOT:PSS layers with asymmetric electron–hole injection at low temperature (5K) for which PEDOT:PSS is known to show strong spin-dependent recombination currents which produce a single-inhomogenously broadened EDMR signal that is caused by weakly spin-spin coupled recombining charge carrier pairs[2]. For the experiments, EMDR measuurements[3] as well as current voltage functions were measured on Al/PEDOT:PSS/ITO sandwich structures for various EG-doping concentrations (0%, 0.05%, and 0.1% by weight). All devices showed nearly ohmic relationship at room temperature. However, at a temperature of 5K these diodes revealed clearly nonlinear double-diode behavior as well as pronounced EDMR signals which decreased in magnitude with increasing dopant concentration. The EDMR spectra showed that the characteristic resonance features of polaron pair recombination[4], namely the double Gaussian spectral lines display a decreasing line width with increasing EG doping concentration. We conclude that doping with EG causes weaker local hyperfine fields in the material indicative of less localized electronic charge carrier states.

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249 2+1 artifact Suppression in DEER Traces using Gaussian Pulses.

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Double Electron-Electron Resonance (DEER) is a versatile technique for obtaining high precision distance information in proteins. The sensitivity of this technique is strongly dependent on the achievable excitation bandwidth of the microwave pulses with respect to the available spectral width of the spin probes. However, in optimized X-band, as well as in high power Q-band[1] DEER setups, the excitation bandwidths of rectangular pump and observer pulses slightly overlap due to the large side bands of rectangular pulses in Fourier space. This causes an artifact at the end of each time trace since the spins within the overlap are subjected to a single frequency experiment called “2+1” pulse train ESE[2]. For proper data analysis, it is necessary to exclude the last part of the time domain data from background fitting. Otherwise, the artifact causes problems in background correction and leads to artificially narrower widths in distance distributions, especially for long distances. Here, we present an optimized DEER setup for AWG-equipped spectrometers that exclusively uses Gaussian pulses. This allows almost complete suppression of the 2+1 artifact without significant sensitivity losses, which makes the entire length of the DEER time trace accessible for data evaluation.

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250 Low-Frequency Spectroscopy of Nuclear Spin Dressed States via EPR Frequency Shifts.

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The dynamics of resonantly driven spins have been studied intently since the seminal paper by Redfield, which introduced field-modulated NMR, rotary saturation and rotary echoes.[1] Additionally, recent advances in ultrafast atomic spectroscopy and unconventional resonance detection schemes, such as EDMR and ODMR,[2] have renewed interest in resonance dynamics outside of the weak-drive limit (i.e. $B_0 >> B_1$). Spin-exchange optical pumping can enhance noble gas nuclear spin polarization by five orders of magnitude through collisional spin exchange with optically-pumped alkali metal atoms and functions at arbitrarily low quantizing fields, making it a particularly well-suited system for observation of such dynamics. In a sealed glass cell with ^{129}Xe, ^{87}Rb, and buffer gases (He, N_2, etc), optically pumped with a 60-watt, 795 nm diode laser, we drive the Rb spins continuously in the weak-limit, allowing the Rb Larmor frequency $\omega_{0,Rb}$ to be monitored via the Faraday angle of a low-power, near-resonant probe laser, oriented perpendicular to the pump laser. The strong contact-hyperfine interaction present during collisions between Xe and Rb atoms can cause a significant shift in $\omega_{0,Rb}$,[3] allowing us to observe xenon Rabi oscillations in real-time as a modulation of $\omega_{0,Rb}$ at the xenon Rabi frequency, typically on order 100 Hz – 10 kHz. By further implementing a sinusoidal modulation of the xenon driving frequency (which is analogous to implementing a modulation of the quantizing field) we utilize our observation of real-time nuclear Rabi oscillations to perform rotating-frame spectroscopy on these dressed nuclear spin states at almost arbitrarily low frequencies.

Funded by the NSF Materials Research Science and Engineering Center (MRSEC) at the University of Utah (grant #DMR11-21252).

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EPR POSTER SESSION

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251 Conformational Transitions of Maltose Binding Protein in the Native State and as Molten Globule at pH 3 as Monitored by DEER and DQC EPR Spectroscopy.

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Maltose-binding protein (MBP) is a single chain protein composed of two domains that is in a molten globule state at pH 3 as characterized by ANS binding. DEER measurements of seven spin-labeled double mutants in the native state at pH 7 had shown excellent agreement with X-ray data. At pH 3 corresponding DEER measurements of all the mutants yielded a broad distribution of distances. This can be expected if there is no defined tertiary structure and the individual helices point into all possible directions. Depending on maltose binding in a cleft between the domains, MBP exhibits both, an open and a closed conformation with respect to these domains. We have followed this substrate-depending conformational change by means of additional spin-labeled mutants at or near the active site. In these experiments DQC spectroscopy has been particularly helpful as it allows for distance measurements of labels in close proximity. Data show, e.g., that there is a defined structure of the active site of MBP at both pH values even in the absence of substrate.

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252 In vivo EPR System From Scratch, Work-in-Progress.

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A new In Vivo Multifunctional Magnetic Resonance center was established in January 2016 in the Health Sciences Center at West Virginia University. Development of novel i*n vivo* EPR spectroscopy and imaging methodologies will be an integral part of the research at the center. A new EPR system for *in vivo* spectroscopy and imaging is being designed and built that will incorporate all recent developments in continuous-wave (CW) multi-harmonic and rapid-scan EPR, as well as a newly developed field-modulated pulsed EPR methodology. The system is designed to operate in the wide range of frequencies from approximately 150 to 1100 MHz, enabled by utilizing the modern digital electronics (1, 2). A low noise constant frequency source is used as a master clock. It is frequency mixed with waveforms generated by an arbitrary waveform generator to cover the wide range of frequencies for CW and pulsed EPR. Bi-modal and reflection types of resonators are being designed and evaluated that allow positioning the animal along the external magnetic field, mimicking MRI designs (3). The resonator is inserted into a cylindrical RF shield. The rapid scan coils made with Litz wire were winded on a cylinder of a larger diameter coaxial to the shield to achieve approximately 70 G/A efficiency. The coils can safely produce about 100 G peak-to-peak magnetic field scans. This coaxial design permits bringing the coils closer to the sample and provides better isolation from the RF field. Narrow EPR spectra of multifunctional $p\text{O}_2$-, pH-, and Pi-sensitive monophosphonated trityl probes were measured to test the performance of the spectrometer.

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253 Structural Origins of the Temperature-Dependent Free Energy Landscape for Radical Rearrangement in B_{12}-Dependent Ethanolamine Ammonia-Lyase.

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Ethanolamine ammonia-lyase (EAL) isolated from Salmonella typhimurium catalyzes the conversion of ethanolamine to acetaldehyde and ammonia. The kinetics of the chemical step of aminoethanol substrate radical rearrangement, measured by time-resolved continuous-wave electron paramagnetic resonance (CW-EPR) from 295 to 197 K[1,2], reveal a bifurcation from the native pathway into fast and slow decay phases below 220 K. The divergence arises from a temperature-dependent free energy landscape, and is quantified in a 3-state, 2-step kinetic model, in which step 1 represents a reaction-enabling reconfiguration of the substrate radical. Thus, two distinct substrate radical sub-states are predicted at T3,4. Herein, electron spin-echo envelope modulation (ESEEM) spectroscopy is used to identify structural differences in samples, in which the two substrate radical states that lead to the kinetic components are judiciously varied by using controlled decays. The substrate radical state formed with ^{2}H-aminoethanol allows for distinguishing altered substrate C_1-C_2 rotameric states and displacements relative to the in situ hydrogen exchange sites on C5' of the deoxyadenosyl group. Subtle, decay level-dependent alterations in the ^{2}H-ESEEM waveforms evidence a geometric structure change in the substrate radical. This provides support for the kinetic model, and a T-dependent free energy barrier to substrate radical reconfiguration as the origin of the kinetic bifurcation.

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EPR POSTER SESSION

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254 Double-Ring Dielectric Resonators for Frequency-Tunable DEER Experiments.

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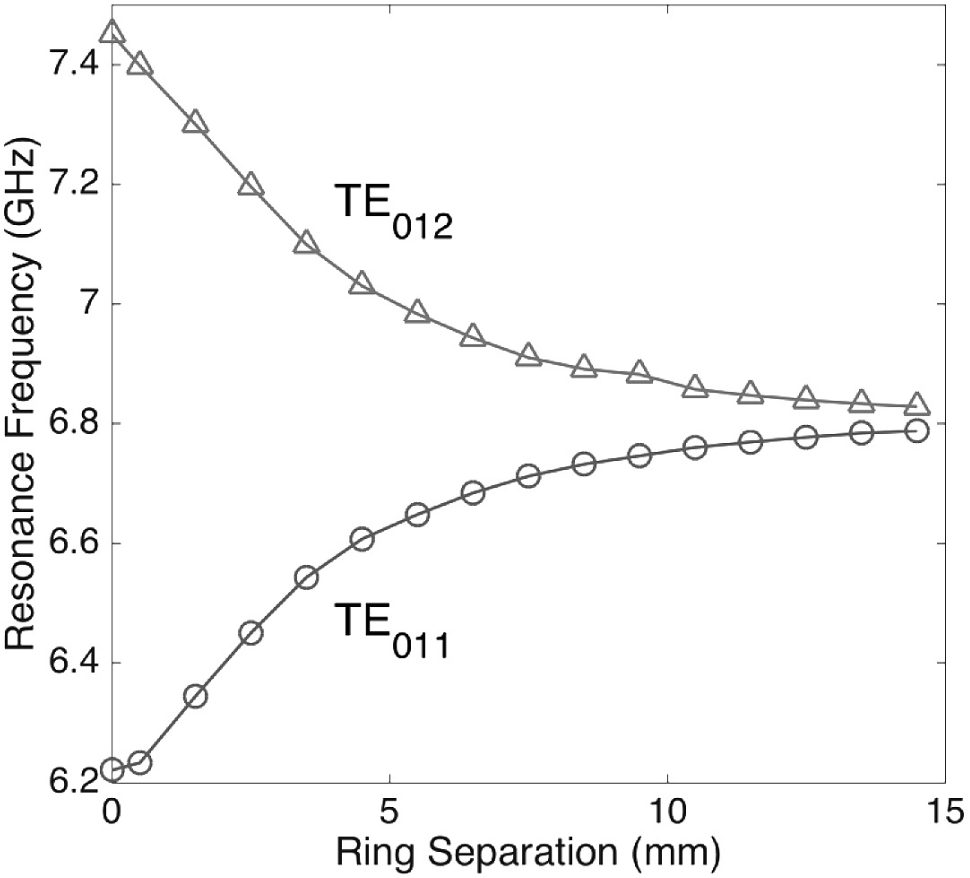
Double electron-electron resonance (DEER) technique uses two distinct microwave frequencies to selectively address two interacting spin species. Thus their dipole-dipole interaction and the distance between the spins can be measured. Single-mode resonators are most commonly used in DEER experiments. The Q-factor of the resonator must be tuned very low (often below 100) to accommodate both spin resonance frequencies. The low Q can lead to a considerable drop in the ESR signal. To address this issue, we have designed a tunable, dual-frequency dielectric resonator for DEER experiments. The resonator consists of two stacked dielectric (sapphire) rings with a tunable gap between the rings. The two resonant frequencies (quasi-TE_{011} and TE_{012}) can be tuned over a broad frequency range by adjusting the vertical separation between the dielectric rings. We demonstrate that the splitting between the two resonant frequencies can be changed from 40 MHz to 1.2 GHz (Figure 1) while maintaining very high quality factors (Q>10,000) at both resonances. Thus, in a DEER experiment one resonant frequency of our resonator can be easily tuned on resonance with one spin species while the other resonant frequency can be tuned to other spin species. By maintaining high Q-factors, the signal-to-noise is greatly improved as compared to using a single broad resonator mode. We will discuss the resonator design and show results from DEER experiments on phosphorus donors in silicon and other systems.



EPR POSTER SESSION

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255 Sterilization by γ-Irradiation: Evaluating the Effects on Pharmaceutical Excipients.

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Sterilization by γ-irradiation is emerging as an alternative technique to classic sterilization methods that are inapplicable to heat- or moisture-sensitive products, as a result of being easy to control, secure, reliable, fast, and having a high penetrating power.[1] However, the radiolytic effect of such ionizing radiation is difficult to predict and can lead to the formation of radical species.[2] The process can so induce degradation of the product, hence affecting the efficacy of sterilized pharmaceuticals. Excipients are substances other than the pharmacologically active drug or prodrug which are included in the manufacturing process or are contained in a finished pharmaceutical product dosage form[3] to improve the properties of the drug, such as enhancing the therapeutic effect of Active Pharmaceutical Ingredients (APIs) or facilitating the manufacturing process.[4] Not only could direct degradation of the APIs diminish the action of the product, but also degradation of pharmaceutical excipients included in the formulation can affect the efficacy of the drug by either altering its chemico-physical properties or reacting with APIs. EPR can provide both qualitative and quantitative information on irradiated pharmaceutical products, allowing the identification and quantification of the radical species formed. In this work we analyse the effect of γ- and X-irradiation on the pharmaceutical excipient histidine by means of EPR techniques, confirming the identity of the main radical species generated and evaluating their reactivity in solution. Our studies represent the first step in the evaluation of γ-sterilization effects on complete pharmaceutical products, providing an increased mechanistic understanding of the sterilization process which will allow radical induced degradation to be avoided.

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EPR POSTER SESSION

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256 Effects of Gadolinium-based Fullerenes on Solid State DNP at Cryogenic Temperatures – EPR and DNP Studies.

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The use of Gd(III) compounds in combination with radicals such as trityl can notably increase nuclear polarization at low temperatures, which has been shown to enhance dissolution-DNP efficiency.[1] Recently theoretical frameworks proposed that the addition of Gd(III) causes a decrease of relaxation times of mixed radicals, which further alters the strength of electron spectral diffusion (eSD). According to this theory, a large part of the DNP enhancement is attributed to the impact of Gd (III) on eSD that is reflected by the narrowing of electron-electron double resonance (ELDOR) spectra.[2] Compared to common Gd-chelates, Gd (III)-based fullerenes are more effective relaxation agents originally designed for MRI with biological compatibility. In this report, we investigated two novel gadofullerenes[3,4] for potential applications in dissolution-DNP. Electron relaxation times, ELDOR and DNP experiments have been done at high fields and cryogenic temperatures. At 95 GHz and 6.5 K, with the addition of $Gd_2@C_{79}N$[3], of one percent of concentration of TEMPO, T_{1e} of TEMPO is shortened from 45 ms to 1.6 ms, and T_{2e} is shortened by 43%. ELDOR spectra of TEMPO under same experimental conditions show significant narrowing by adding $Gd_2@C_{79}N$, which is an indication of electron polarization gradient, according to reference 2, and hence should result in enhanced nuclear polarization. At 200 GHz and 4 K, ^1H DNP enhancement using TEMPO is increased by a factor of 5 by $Gd_2@C_{79}N$. Furthermore, ^1H DNP buildup time is shortened from 1188 s to 9 s with the addition of $Gd_2@C_{79}N$ to TEMPO.

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EPR POSTER SESSION

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257 The Rate at Which Free Radicals Form in Extra Virgin Olive Oil as a Function of Time and Heat.

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Free radicals form in Extra Virgin Olive Oil with the passage of time. These free radicals form at an even faster rate at higher temperatures. Currently, the standard method to measure this rate is spin trapping, where the intensity of the resultant EPR signal is measured as a function of time. Unless the spectrometer is able to maintain a constant temperature in the cavity, the typical method to study a sample held at a higher temperature over time is to heat the sample in a different environment, remove it from that environment, run it in the spectrometer and continue this cycle each time a measurement is needed. However, this method produces variable results, so we attempted to create a more reliable method to get consistent results. In my experiment, seven 5O μL capillary tubes were filled with 2M PBN and oil (5 μL of PBN was diluted with 90 μL of oil) and were placed in a water bath at 90^{0}C. All of the ethanol in the diluted PBN was evaporated to prevent the ethanol from boiling and pushing the solution out of the capillary tubes. Our results show that the rate at which free radicals form increases as the time the capillary tube spent immersed in the water bath increases. The kinetics of this reaction needs to be further studied.

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258 Multiple Frequency Electrically Detected Magnetic Resonance and Near Zero Field Magnetoresistance Study of Transport Mechanisms in Dense a-SiOC:H Thin Films of Varying Thickness.

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Low dielectric constant materials, so called low-k dielectrics, are utilized in state of the art microprocessors for back end of the line interlayer dielectrics to insulate between metal interconnects while reducing capacitive coupling between those interconnects. The most important low-k materials are various compositions of a-SiOC:H, with dielectric constants varying from 3.2 down to approximately 2.0 depending on porosity. Although electronic transport in these films is of great technological importance, little is known about the mechanisms involved. In this study, we utilize near zero field magnetoresistance and electrically detected magnetic resonance (EDMR) at multiple biasing conditions and frequencies to explore point defects in 14-56 nm dense a-SiOC:H thin films grown via plasma enhanced chemical vapor deposition. Multiple frequency measurements (arguably) allow us to identify the breadth of the g tensor components of essentially featureless EDMR spectra.[1] EDMR amplitude versus bias measurements analyzed in terms of energy band diagrams allow us to crudely determine density of states information about the defects involved in transport. In addition, comparisons between EDMR and near zero field magnetoresistance measurements, which generally show close correspondence, provide insight into the physical phenomena involved in the magnetoresistance. Our results indicate that electronic transport in these systems is due to variable range hopping.[2]

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Demagnetization Shifts in Very High Frequency Pulsed Electron Paramagnetic Resonance.

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At high magnetic fields, large spin magnetization effects become important, even at room temperature. We study these effects at 8.6 T and 240 GHz, using as a source the UCSB mm-wave Free Electron Laser (FEL)[1]. The high power afforded by the FEL can invert spin-1/2 electrons in 12-15 ns. We report that the frequency of free induction decays seen in BDPA crystals excited by these short pulses at room temperature is tip angle dependent. We characterize this effect by performing Rabi oscillation experiments on BDPA crystals, and demonstrate that the observed frequency shifts are proportional to sample magnetization. This nonlinear behavior can be explained by coupling between sample magnetization and geometry through the demagnetizing field, an effect we have termed paramagnetic demagnetization. We perform simulations accounting for the demagnetizing field, and reproduce the observed frequency shifts.

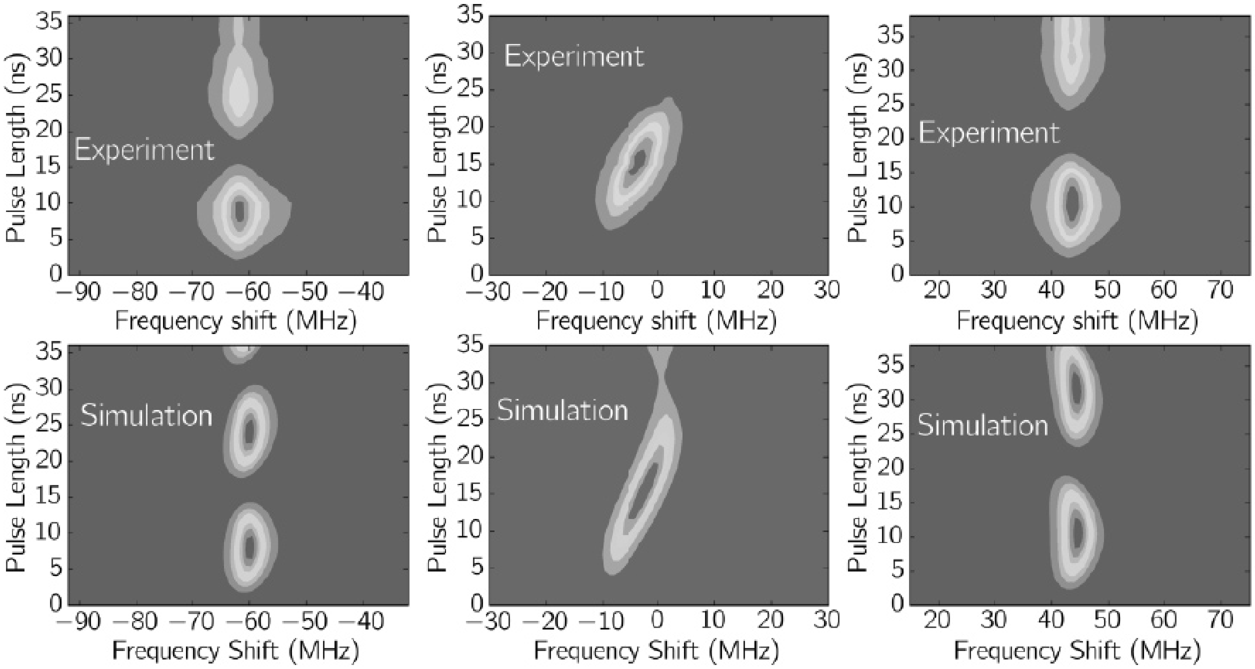

Figure 1. Top: Plots of free induction decay (FID) intensity vs frequency relative to 240 GHz as a function of pulse length. Off resonance and in the small tip-angle regime (upper left and upper right) there is no observed frequency shift, while on resonance (upper middle) we observe a tip-angle dependence in the FID frequency. Bottom: Simulations including the demagnetizing field.

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