FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 22–27, 2018

Snowbird Resort & Conference Center
Snowbird, Utah

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EPR SYMPOSIUM
ORAL SESSIONS AGENDA

SUNDAY, JULY 22, 2018

Pre-Conference Activities	
6:30–10:00 PM	**Bruker EPR Users' Meeting** *Meeting followed by Mixer*

MONDAY, JULY 23, 2018

8:10 AM	***Welcoming Remarks.*** Stefan Stoll, EPR Symposium Chair	
SESSION I: Biomacromolecules I. John McCracken, Chair		
8:15 AM	100	**EPR Spectroscopy Reveals Protein Allostery and Signaling in a Bacterial Outer-membrane Transport Family.** David S. Cafiso, University of Virginia
8:45 AM	101	**PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution.** Gregor Hagelueken, University of Bonn
9:00 AM	102	**ESR Identification of Microtubule-binding Domain in Tau Protein.** Timothée Chauviré, Cornell University
9:15 AM	103	**EPR Distance Restraints as Core for Integrative Structure Modelling of 85 kDa PBTP1/EMCV-IRES Complex.** Christoph Gmeiner, ETH Zürich
9:30 AM	104	**A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements.** Anokhi Shah, University of St Andrews
9:45 AM	*Break*	
SESSION II: Biomacromolecules II. Gail Fanucci, Chair		
10:25 AM	105	**Structural Dynamics of Desensitization in a Pentameric Ligand Gated Ion Channel.** Sudha Chakrapani, Case Western Reserve University
10:55 AM	106	**Light-induced Conformational Changes in Nitroxide-labeled Proteorhodopsin Detected by Time-resolved 240 GHz EPR at Room Temperature.** C. Blake Wilson, University of California Santa Barbara
11:10 AM	107	**Transporter Conformational Dynamics from Spin Labeling EPR Spectroscopy.** Hassane S. Mchaourab, Vanderbilt University
11:40 AM	108	**Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy.** Thomas Schmidt, National Institutes of Health
12:00 PM	*Lunch (included with registration)*	
SESSION III: Spin Centers in Chemistry and Biology I. John McCracken, Chair		
1:30 PM	110	**Histidine Handoff in the Prion Protein: New Cu^{2+}Coordination Features for Protecting Against Neurodegeneration?** Glenn Millhauser, University of California Santa Cruz
2:00 PM	111	**Effect of Silica Support on Electrostatics of Lipid Interfaces in Nano-Bio Hybrid Systems.** Tatyana I. Smirnova, North Carolina State University
2:15 PM	112	**Lipoxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure.** Ajay Sharma, Northwestern University
2:30 PM	113	**2D-Correlated Hyperfine Spectroscopy on a Tetracycline-binding RNA Aptamer.** Thilo Hetzke, Goethe University Frankfurt
2:45 PM	114	**EPR Spectroscopy of Spin Probe, Label, and Time-Resolved, Reaction-Intrinsic Radicals Reveals Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in Ethanolamine Ammonia-Lyase Catalysis.** Kurt Warncke, Emory University
3:00 PM	*Break*	

SESSION IV: Spin Centers in Chemistry and Biology II. Stephen Hill, Chair		
3:40 PM	115	**Vanadyl Complexes: From Qubit Design to Quantum Simulation.** Roberta Sessoli, University of Florence
4:10 PM	116	**Endohedral Fullerenes as Molecular Qubits.** ShangDa Jiang, Peking University
4:25 PM	117	**Quantum Coherence Studies in Actinide and Lanthanide Organometallic Complexes.** Floriana Tuna, University of Manchester
4:55 PM	118	**Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis.** Sonia Chabbra, University of St Andrews
5:30–7:00 PM	*Conference Reception (included with registration)*	
SESSION V: Posters		
7:30–9:00 PM	***Authors Present for Posters Labeled A***	

TUESDAY, JULY 24, 2018

SESSION VI: Spin Devices I. Ania Bleszynski-Jayich, Chair		
8:15 AM	125	**Spin and Orbital Resonance Driven by a Mechanical Resonator.** Gregory D. Fuchs, Cornell University
8:45 AM	126	**Picoliter Diamond NMR.** Victor M. Acosta, University of New Mexico
9:00 AM	127	**Locking and Tracking Magnetic Resonance Spectra of NV^- Center for Real-time Magnetometry.** Kapildeb Ambal, National Institute of Standards and Technology
9:15 AM	128	**Precise Determination of Spin Concentration using Double Electron-electron Resonance.** Susumu Takahashi, University of Southern California
9:30 AM	129	**Electrical Detection of Charge Carrier Magnetic Resonance in the Strong Driving Field Limit When $B_1 \sim B_0$.** Shirin Jamali, University of Utah
9:45 AM	*Break*	
SESSION VII: Spin Devices II. Susumu Takahashi, Chair		
10:25 AM	130	**EPR-on-a-chip – Current Trends and Future Research Directions.** Jens Anders, University of Stuttgart
10:55 AM	131	**Nanoscale EPR of Nitroxide Radicals using a NV Center in Diamond.** Laura Mugica, University of Southern California
11:10 AM	132	**Nanoscale NMR Enabled by Diamond Colour Centres.** Fedor Jelezko, Ulm University
11:40 AM	133	**Electron Spin Resonance of Individual Magnetic Atoms on Surfaces.** Taeyoung Choi, Ewha Womans University
12:00 PM	*Lunch (included with registration)*	
SESSION VIII: Materials. Christoph Boehme, Chair		
1:30 PM	134	**Charge Carrier Separation and Spin-Coupling in Photoactive Materials.** Uwe Gerstmann, University of Paderborn
1:45 PM	135	**Highly Efficient Optical Pumping of Spin Defects in Silicon Carbide for Stimulated Microwave Emission.** Andreas Sperlich, University of Würzburg
2:00 PM	136	**Spin-orbit Coupling Effects on Charge Carriers in Conjugated Polymers.** Hans Malissa, University of Utah
2:15 PM	137	**Light-induced Charge Separation in Polymer-Fullerene Organic Photovoltaics Studied by Multifrequency EPR and DFT.** Jens Niklas, Argonne National Laboratory
2:30 PM	138	**Electronic Structure Investigation of Self-doped type Organic Conductors by Magnetic Resonance Spectroscopy.** Toshikazu Nakamura, Institute for Molecular Science
2:45 PM	139	**Tuning Effective Charge Carrier Hyperfine Field Strengths in PEDOT:PSS Thin Films by Doping.** Mandefro Teferi, University of Utah
3:00 PM	*Break*	

SESSION IX: Other Topics. Stefan Stoll, Chair		
3:40 PM	140	**A Bird's Eye View of the Chemical Compass – Magnetic Field Effects on the Photocycles of Cryptochrome.** Christiane R. Timmel, University of Oxford
4:10 PM	141	**Radiolysis Products at the Interface of Aluminum Oxyhydroxides and Strongly Basic Solutions.** Eric Walter, Pacific Northwest National Laboratory
4:25 PM	142	**Low Symmetry Orienting Potentials and Efficient Computation of ESR Line Shapes.** Keith A. Earle, University at Albany
4:40 PM	143	**Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation.** Jerryman A. Gyamfi, Scuola Normale Superiore di Pisa
SESSION X: Posters		
7:30–9:00 PM	***Authors Present for Posters Labeled B***	

WEDNESDAY, JULY 25, 2018

SESSION XI: Integrated Magnetic Resonance I. (Joint SESSION – EPR & SSNMR) Sophia Hayes & Gail Fanucci, Chairs		
8:05 AM	144	**Time Domain Dynamic Nuclear Polarization (and Some CW Experiments on Proteins).** Robert G. Griffin, Massachusetts Institute of Technology
8:35 AM	145	**Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.** Anne M. Carroll, Yale University
8:55 AM	146	**Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments.** Jean-Philippe Ansermet, Ecole Polytechnique Fédérale de Lausanne
9:25 AM	147	**Magic Angle Spinning Spheres, Electron Decoupling with CPMAS below 6 K, and DNP within Human Cells Using Fluorescent Polarizing Agents.** Alexander B. Barnes, Washington University in St. Louis
9:45 AM	*Break*	
SESSION XII: Integrated Magnetic Resonance II. (Joint SESSION – EPR & SSNMR) Sophia Hayes & Gail Fanucci, Chairs		
10:15 AM	148	**Novel Aspects of Polarization Propagation and Biomolecular Applications of MAS DNP.** Björn Corzilius, Goethe University Frankfurt
10:45 AM	149	**Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger.** Asif Equbal, University of California Santa Barbara
11:05 AM	150	**Breaking Concentration Sensitivity Barrier by Larger Volumes: Photonic Band-Gap Resonators for mm-Wave EPR and DNP of Microliter-Volume Samples.** Alex I. Smirnov, North Carolina State University
11:35 AM	151	**Optical Room Temperature ^{13}C Hyperpolarization in Powdered Diamond.** Ashok Ajoy, University of California Berkeley
12:00 PM	*Lunch (included with registration)*	
SESSION XIII: Methods I. Dane McCamey, Chair		
1:30 PM	152	**Pulsed Magnetic Resonance with a Free-Electron Laser.** Mark Sherwin, University of California Santa Barbara
2:00 PM	153	**Pulsed and 'in-situ' EPR at 395 GHz.** Johan van Tol, National High Magnetic Field Laboratory
2:15 PM	154	**Development of a High Field Nanoscale EPR System using NV Centers in Diamond.** Benjamin Fortman, University of Southern California
2:30 PM	155	**Automated DEER Data Processing using Bayesian Inference.** Thomas H. Edwards, University of Washington
2:45 PM	156	**Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition.** Madhur Srivastava, Cornell University
3:00 PM	*Break*	
SESSION XIV: Methods II. Susumu Takahashi, Chair		
3:40 PM	157	**Electron Spin Resonance with Quantum Microwaves.** Audrey Bienfait, Institute of Molecular Engineering

4:10 PM	158	**Signal Enhancement by Constructive Combination of Transmission and Reflection ESR signals using Non-Resonant Transmission Line Probe Detection.** Pragya R. Shrestha, National Institute of Standards and Technology
4:25 PM	159	**Multi-Frequency Pulsed EPR and DEER Using Rapidly Tunable Superconducting Microresonators.** Abraham T. Asfaw, Princeton University
4:40 PM	160	**Effect of Multiphoton Transitions on Detection of Long Electron Spin Relaxation Times by Double Modulation ESR Spectroscopy.** Boris Rakvin, Rudjer Boskovic Institute
4:55 PM	161	**Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region.** Hitoshi Ohta, Kobe University
General Business Meeting / Shared EPR Presentation		
5:15 PM	***Stefan Stoll, Chair***	
7:00–9:00 PM	***Conference Banquet & Awards Ceremony*** *(Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.)*	
8:00 PM	***Welcoming Remarks.*** Kurt Zilm, Conference Chair	
8:05 PM	***A Half Century of RF, μw's and the Magic Angle.*** Robert G. Griffin, Massachusetts Institute of Technology	
8:35 PM	***EPR Awards***	
8:45 PM	***SSNMR Awards***	

THURSDAY, JULY 26, 2018

SESSION XV: EPR Imaging / In-Vivo. Boris Epel, Chair		
8:15 AM	165	**Redox, Oximetric and Vascular Imaging Provide Insight into the Tumor Microenvironment.** Martyna Elas, Jagiellonian University
8:45 AM	166	**Pre-clinical EPR Imaging System at 800 MHz.** Mark Tseytlin, West Virginia University
9:15 AM	167	**Molecular Oxygen: Extent of Variability in Time and Location in Preclinical Tumors.** Howard J. Halpern, University of Chicago
9:30 AM	170	**Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.** Benoit Driesschaert, West Virginia University
9:45 AM	*Break*	
SESSION XVI: Methods III. Stefan Stoll, Chair		
10:25 AM	171	**The CHEESY Renaissance of Fourier-transform Detected Hole Burning in EPR.** Gunnar Jeschke, ETH Zürich
10:55 AM	172	**Development of ELDOR-detected NMR Spectroscopy at 115/230 GHz.** Zaili Peng, University of Southern California
11:10 AM	173	**^{2}H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates.** Isabel Bejenke, Max Planck Institute for Biophysical Chemistry
11:25 AM	174	**Exploring Frequency-swept Excitation for Distance Measurements of Spin S = ½ Systems.** Frauke Breitgoff, ETH Zürich
11:40 AM	175	**DEER Updates are Available: Upgraded Sensitivity after RELOAD and Unmodulated Background Suppressed with the ROOPh.** Sergey Milikisiyants, North Carolina State University
11:55 AM	***Closing Remarks.*** Stefan Stoll, EPR Symposium Chair	
Post-Conference Activities		
1:30 PM	***SharedEPR Workshop: Software Tools for EPR Spectroscopy – Capabilities and Demonstrations***	

FRIDAY, JULY 27, 2018

Post-Conference Activities	
8:30 AM	***SharedEPR Workshop: Software Tools for EPR Spectroscopy – Capabilities and Demonstrations***

41ST INTERNATIONAL EPR SYMPOSIUM
POSTER SESSIONS AGENDA

MONDAY, JULY 23 • 7:30–9:00 p.m. *(Authors Present for Posters Labeled A)*

TUESDAY, JULY 24 • 7:30–9:00 p.m. *(Authors Present for Posters Labeled B)*

A	200	**A High-Q Anapole Microresonator for Inductive-Detection Electron Paramagnetic Resonance Spectroscopy.** Nandita Abhyankar, University of Maryland
B	201	**Picoliter Diamond NMR.** Victor M. Acosta, University of New Mexico
A	202	**Locking and Tracking Magnetic Resonance Spectra of NV^- Center for Real-time Magnetometry.** Kapildeb Ambal, National Institute of Standards and Technology
B	203	**Better Resolution of High Spin Co Hyperfine at Low Frequency, L-band: Co-bovine Serum Albumin, A Model for Obtaining Co Hyperfine in High Spin Complexes of Biological Interest.** William E. Antholine, Medical College of Wisconsin
A	204	**Insights into the Catalytic Mechanism of [FeFe]-hydrogenase II from *Clostridium Pasteurianum*.** Jacob H. Artz, National Renewable Energy Laboratory
B	205	**Spin Dependent Charge Pumping and Spin Dependent Recombination Study of SiC/SiO_2 Interface Passivation.** James P. Ashton, Pennsylvania State University
A	206	**Electric-Field Quenching of Magnetic Resonance in the Photoluminescence of p-Conjugated Polymer Films.** Douglas L. Baird, University of Utah
B	207	**^{2}H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates.** Isabel Bejenke, Max Planck Institute for Biophysical Chemistry
A	208	**DFT Calculation of Zero-field Splitting in Extended Periodic Systems.** Timur Biktagirov, University of Paderborn
B	209	**Exploring Frequency-swept Excitation for Distance Measurements Between Nitroxide Spin Labels.** Frauke Breitgoff, ETH Zürich
A	210	**Heisenberg Spin Exchange for Anomalous Diffusion in a Percolation Network.** David E. Budil, Northeastern University
B	211	**Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.** Anne M. Carroll, Yale University
A	212	**Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis.** Sonia Chabbra, University of St Andrews
B	213	**Wireless Implantable Coil with Parametric Amplification for In Vivo Electron Paramagnetic Resonance Oximetric Applications.** Nallathamby Devasahayam, National Institues of Health
A	214	**An Ultra-high Vacuum Electron Spin Resonance Spectrometer for the Investigation of Magnetic Atoms and Molecules at Surfaces.** Fabio Donati, Ewha Womans University
B	215	**Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.** Benoit Driesschaert, West Virginia University
A	216	**Automated DEER Data Processing using Bayesian Inference.** Thomas H. Edwards, University of Washington
B	217	**Redistribution of EC-SOD Due to the R213G Variant Influences the Local Redox Environment in Bleomycin-induced Lung Injury.** Hanan Elajaili, University of Colorado
A	218	**Allosteric Conformational Rearrangements of a Prokaryotic Cyclic Nucleotide-gated Ion Channel Probed with Pulsed Dipolar Spectroscopy.** Eric G.B. Evans, University of Washington
B	219	**Effect of Freezing Rate on the Spin Dynamics of Finland Trityl.** Benjamin R. Fowler, University of Alabama
A	220	**Spin-labeled Nanobodies: A New Tool Towards EPR Studies in Cellular Environments.** Laura Galazzo, Ruhr-Universität Bochum

B	221	**Update on the SharedEPR Network.** Gary J. Gerfen, Albert Einstein College of Medicine
A	222	**Magnetic Resonance, Index Compression Maps and the Holstein-Primakoff Bosons: Polynomially Scaling Exact diagonalization of Isotropic Multispin Hamiltonians.** Jerryman A. Gyamfi, Scuola Normale Superiore di Pisa
B	223	**Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation.** Jerryman A. Gyamfi, Scuola Normale Superiore di Pisa
A	224	**PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution.** Gregor Hagelueken, University of Bonn
B	225	**Development of GaAs Switches for Advanced Pulse Sequences for EPR powered by a Free-Electron Laser.** Marzieh Kavand, University of California Santa Barbara
A	226	**Powder and Single Crystal EPR Study of Metal-organic Framework $Cu_{2.931}Zn_{0.069}(btc)_2$.** Anastasia Kultaeva, Leipzig University
B	227	**Pulsed EPR Studies of Spin-Spin Interactions in Trityl Radicals.** Molly M. Lockart, University of Alabama
A	228	**FD-FT THz-EPR as a Tool to Study Magneto-Structural Correlations in Single-Molecule Magnets: (Pseudo)-Tetrahedral Co^{II}Complexes with $[N_2O_2]$ Coordination Environment.** Thomas Lohmiller, Helmholtz-Zentrum Berlin für Materialien und Energie
B	229	**Vanadyl Ligand Speciation Through High-Resolution ^{1}H ENDOR.** Donald Mannikko, University of Washington
A	230	**Trajectory-based Simulations of Electron Paramagnetic Resonance Spectra.** Peter D. Martin, University of Minnesota
B	231	**An EPR Examination of 3D Printing Materials.** Robert M McCarrick, Miami University
A	232	**^{1}H-HYSCORE Reveals Details of the Coordination Chemistry at the Fe(II) Site of Taurine/2-Ketoglutarate Dioxygenase.** John McCracken, Michigan State University
B	233	**Field-Stepped-Direct-Detection Electron Paramagnetic Resonance (FSDD-EPR) at Low Temperatures using a Metal Free Cryostat.** Joseph E. McPeak, University of Denver
A	234	**An Algorithm to Calculate Polycrystalline Pulsed EPR Signals with Relaxation Rigorously in Liouville Space using Stochastic Liouville Equation.** Sushil K. Misra, Concordia University
B	235	**Excitonic Transport in Amorphous Silicon Studied by Pulsed Electrically Detected Magnetic Resonance.** Jannik Möser, Helmholtz-Zentrum Berlin für Materialien und Energie
A	236	**Low Magnetic Field Electrically Detected Magnetic Resonance Spectroscopy with Circularly Polarized RF Excitation.** Adnan Nahlawi, University of Utah
B	237	**Linear Prediction to Supplement FT-EPR of Transient Spin-Correlated Radical Pairs.** Jordan Nelson, Northwestern University
A	238	**Electron Spin Relaxation Times of Spin Labels Without Gem-dimethyl Groups.** Thacien Ngendahimana, University of Denver
B	239	***In Situ* Electron Paramagnetic Resonance Spectroscopy – Understanding Mechanisms in Lithium-Oxygen Batteries.** Thuc Anh Nguyen, University of California Berkeley
A	240	**Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region.** Hitoshi Ohta, Kobe University
B	241	**Combining PELDOR and SAXS to Study the Solution Structure and Function of Type-III-effector Protein YopO from *Yersinia Pestis*.** Martin F. Peter, University of Bonn
A	242	**Dextran-grafted Triarylmethyl Radicals.** Martin Poncelet, West Virginia University
B	243	**Fringe Field Measurements of Ferromagnetic NiFe Films using Electrically Detected Magnetic Resonance.** Henna Popli, University of Utah
A	244	**Simulating Experiments with Shaped Pulses using EasySpin.** Stephan Pribitzer, ETH Zürich

B	245	**Two-Dimensional Distance Correlation Maps from Pulsed Triple Electron Resonance (TRIER) on Model Compounds and Proteins.** Stephan Pribitzer, ETH Zürich
A	246	**Software for Advanced and Global Analysis of EPR data: GloPel and SpecProFi.** Stephan Rein, University of Freiburg
B	247	**Orienting the Dimerization of Retinal Guanylyl Cyclase Activating Protein 1 using DEER Derived Distances and Molecular Modeling.** Graham Roseman, University of California Santa Cruz
A	248	**Imaging of Enzyme Activity by Electron Paramagnetic Resonance (EPR). Synthesis and Characterization of an Alkaline Phosphatase-sensitive Nitroxide Spin Probe.** Urikhan Sanzhaeva, West Virginia University
B	249	**An Equatorial Histidine Swap in the Prion Protein Copper Center is Essential for its Neuroprotective Self-Regulation.** Kevin Schilling, University of California Santa Cruz
A	250	**Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy.** Thomas Schmidt, National Institutes of Health
B	251	**Automation of a Terahertz Frequency Rapid Scan ESR Spectrometer.** Matúš Šedivý, Central European Institute of Technology, Brno
A	252	**Collaborative Research on Molecular Spins for Quantum Information Technologies in the Frame of the European COST Action "Molecular Spintronics".** Roberta Sessoli, University of Florence
B	253	**A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements.** Anokhi Shah, University of St Andrews
A	254	**Lipoxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure.** Ajay Sharma, Northwestern University
B	255	**EPR Imaging at VHF with Field Reversal Background Correction.** Yilin Shi, University of Denver
A	256	**Air Stable Triplet Ground State Diradical Dication and Radical Cation of Conjoined Double Helicene.** Chan Shu, University of Nebraska Lincoln
B	257	**Intermediate Excited States for Optical Excitation and Electrical Generation in Donor: Acceptor based OLEDs.** Andreas Sperlich, University of Würzburg
A	258	**Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition.** Madhur Srivastava, ACERT and Cornell University
B	259	**Characterization of the Distribution of Spin-lattice Relaxation Rates of Lipid Spin Labels in Fiber Cell Plasma Membranes of Eye Lenses with a Stretched-exponential Function.** Natalia Stein, Medical College of Wisconsin
A	260	**Characterization of the Mechanism of Solvent-Protein Coupling to the Radical Rearrangement Reaction in B_{12}-Dependent Ethanolamine Ammonia-Lyase.** Andrew M. Stewart, Emory University
B	261	**Structure and Mechanism of Assembly of the Ethanolamine Utilization (Eut) Bacterial Microcompartment (BMC) Shell Components.** Katie L. Stewart, Emory University
A	262	**Precise Determination of Spin Concentration using Double Electron-electron Resonance.** Susumu Takahashi, University of Southern California
B	263	**Computational Modeling of the Cytotoxic PLA2, ExoU, using SDSL EPR.** Maxx H. Tessmer, Medical College of Wisconsin
A	264	**4-pulse Nitroxide-nitroxide Q-band DEER Revisited.** Markus Teucher, Ruhr-Universität Bochum
B	265	**Anesthesia Free Pre-Clinical Rapid Scan Oximetry.** Oxana Tseytlin, West Virginia University
A	266	**Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in B_{12}-dependent Ethanolamine Ammonia-Lyase Catalysis Revealed by Multiple EPR Techniques.** Kurt Warncke, Emory University
B	267	**Field-reversal Method for Rapid Scan Background Correction.** Lukas B. Woodcock, University of Denver
A	268	**Trityl Radicals for EPR Spectroscopic Measurements on Oligonucleotides.** Christine Wuebben, University of Bonn

100 EPR Spectroscopy Reveals Protein Allostery and Signaling in a Bacterial Outer-membrane Transport Family.

David S. Cafiso

Department of Chemistry and Center for Membrane Biology, University of Virginia, McCormick Road, Charlottesville, Virginia, 22904-4319.

A change in the equilibrium distribution of conformational substates is thought to underlie protein allostery, and to play a role in mediating protein-protein recognition. Site-directed spin labeling when combined with EPR spectroscopy is a powerful approach to examine conformational exchange and structural heterogeneity in globular, membrane proteins and protein complexes. In TonB-dependent transporters, such as the Escherichia coli vitamin B_{12} transporter BtuB, the energy for transport is obtained by a reversible binding of the transporter to the inner membrane protein TonB. This coupling is mediated by an N-terminal periplasmic segment termed the Ton box, which is allosterically regulated by the binding of substrate to the extracellular facing site. Modifying the Ton box, also modifies the binding site for substrate on the opposite side of the protein, indicating that there is a two-way allosteric communication across the transporter.[1] In this transport system, it is possible to label and perform EPR spectroscopy on the transporter in live bacteria.[2] This allows us to determine the effect of the outer-membrane environment on membrane protein structure and to measure structural changes that occur during transport. Recently, we have obtained evidence for the supramolecular organization of outer-membrane proteins (OMPs) into domains or islands. The interactions that drive the formation of these domains underlies the segregation of OMPs and the turnover of OMPS in the bacterial envelope *(supported by NIGMS, GM035215)*.

1. Sikora et al. (2016) *Biophys. J.* 111, 1908.
2. Joseph et al. (2015) *Angew Chem Int Ed Engl.* 54:6196-9

EPR ORAL SESSION

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101 PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution.

Janin Glaenzer[1], Martin F. Peter[1], Gavin H. Thomas[2], Gregor Hagelueken[1]

[1] Institute for Physical & Theoretical Chemistry, University of Bonn, Bonn, Germany
[2] Department of Biology, University of York, York, UK

The tripartite ATP-independent periplasmic (TRAP) transporters are a widespread class of membrane transporters in bacteria and archaea. Typical substrates for TRAP transporters are organic acids including the sialic acid N-acetyl-neuraminic acid. The substrate binding proteins (SBP) of TRAP transporters are the best studied component and are responsible for initial high-affinity substrate binding. To better understand the dynamics of the ligand binding process, pulsed electron-electron double resonance (PELDOR, also known as DEER) spectroscopy was applied to study the conformational changes in the N-acetylneuraminic acid-specific SBP VcSiaP. The protein is the SBP of VcSiaPQM, a sialic acid TRAP transporter from *Vibrio cholerae*. Spin-labeled double-cysteine mutants of VcSiaP were analyzed in the substrate-bound and -free state and the measured distances were compared to available crystal structures. The data were compatible with two clear states only, which are consistent with the open and closed forms seen in TRAP SBP crystal structures. Substrate titration experiments demonstrated the transition of the population from one state to the other with no other observed forms. Mutants of key residues involved in ligand binding and/or proposed to be involved in domain closure were produced and the corresponding PELDOR experiments reveal important insights into the open-closed transition.

EPR ORAL SESSION

Gregor Hagelueken, Wegelerstr. 12, Bonn, NRW, 53115, DE
E-mail: hagelueken@pc.uni-bonn.de

102 ESR Identification of Microtubule-binding Domain in Tau Protein.

Timothée Chauviré[1], Trudy F. Ramlall[2], David Eliezer[2], Jack H. Freed[1]

[1]ACERT (National Biomedical Center for Advanced ESR Technology), Dept. of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, 14853, USA.
[2] Dept. of Biochemistry, VIVO, Weill-Cornell Medical College, 1300 York Avenue, New York, NY 10065, USA

Tau is a microtubule-associated protein that is involved in neurodegenerative taupathies and dementia, especially Parkinson's and Alzheimer's disease[1]. In Alzheimer's disease, the process of formation and aggregation of microtubules (bundles of tubulin) is a crucial step in the malfunction of the brain. However, the mechanism of aggregation in which tau is involved remains unclear. A better knowledge of the conformational structure of tau with or without binding agent is important to understand and may help to generate novel treatment of Alzheimer's disease. Unfortunately, the study of the tau structure in the presence of microtubule is still challenging to achieve by regular characterization techniques due to the low stability, high molecular weight, and intrinsic heterogeneity of the system. In this work, we employed Electron Spin Resonance (ESR) to detect changes in the structure of tau upon binding to microtubules.

In 2014, a first study was initiated by Georgieva et al.[2] which focused on the interaction of tau with lipid membranes. A helical structure in the R3 domain (see fig. 1) was observed by cw-ESR and pulse dipolar spectroscopy (DEER), and identified as a fragment associated with the micelles. In this new study, we employed directly pre-formed microtubules instead of membranes to achieve a more realistic in-vitro tau-microtubule association study. A site-directed spin labeling (SDSL) method was employed and a series of different cysteine mutants was expressed and purified around the hexapeptide pair helical filament area (PHF6) (see fig. 1). A conjugation of 3-maleimido proxyl spin label with tau was achieved with high efficiency. The labeled proteins were then mixed with the microtubule and a change in the conformation of tau was deduced by lineshape analysis and power saturation measurements using cw-ESR.
This work is supported by a NIH grant R01GM123779.

EPR ORAL SESSION

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103 EPR Distance Restraints as Core for Integrative Structure Modelling of 85 kDa PBTP1/EMCV-IRES Complex.

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For many systems of current interest in structural biology, information from high-resolution structure determination techniques, like nuclear magnetic resonance (NMR) or X-ray crystallography (XRD), needs to be complemented by structural information derived from other techniques, such as small angle scattering (SAS) or crosslinking experiments. Electron paramagnetic resonance (EPR), especially double electron-electron resonance (DEER) aka pulsed electron-electron double resonance (PELDOR), combined with site-directed spin labelling (SDSL), represents another powerful tool and has emerged as important method for structural biology during the last decades.[1-3]

In this project, we aim to solve the 3D structure of a 85 kDa large protein/RNA complex following an integrative structure modelling approach, using protein-protein, protein-RNA and RNA-RNA distance restraints, derived from DEER, in combination with data from SAS, NMR and crosslinking. The alternative splicing regulator Polypyrimidine Tract Binding Protein1 (PTBP1) consists of four RNA Recognition Motifs (RRMs) connected by long peptide linkers showing CU/UC base-specific recognition. Further, PTBP1 initiates the 5'cap-independent translation of several *Picornoviridae* RNAs by binding an Internal Ribosomal Entry Site (IRES), in this case of EncephaloMyoCarditis Virus (EMCV), and enables ribosome recruitment.[4] The individual RRMs and RRM/RNA subcomplexes were recently studied in great detail[5-7] and are treated here as rigid-building blocks to determine the PBTP1/EMCV-IRES structure following a modelling approach, mainly based on long-range EPR distance restraints together with information from SAS and protein-protein crosslinking experiments. Combining rigid-body arrangements with flexible peptide or RNA linker models using additional EPR restraints allowed us to elucidate a 3D model of the PTBP1/EMCV-IRES complex. Further biological and structural relevance of a single RRM bound to a flexible RNA linker was monitored by combining *in-vivo* experiments and DEER measurements. The determined complex structure gives insights on the organization of the translation initiation complex and represents successfully how EPR restraints can be used as core for integrative structure modelling.

EPR ORAL SESSION

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104 **A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements.** Anokhi Shah,[1] Amandine Roux,[2] Matthieu Starck,[2] Jackie A. Mosely,[2] Michael Stevens,[3] David G. Norman,[3] David Parker,[2] Janet E. Lovett[1]

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We report a novel gadolinium(III)-spin label complex [Gd.sTPATCN]-SL, developed from the previously published complex [Gd.TPATCN].[1] [Gd.TPATCN] has the narrowest reported CW EPR line in solution, with a peak-to-peak width of 13 G at X-band. [Gd.sTPATCN]-SL exhibits a small zero-field splitting, with the ability to tether to the natural amino acid cysteine via a single, stable thioether bond using a 4-nitropyridine functionality. Here, we demonstrate its potential as a protein spin label for EPR by cysteine selective labeling of both a test peptide and protein, TRIM25cc. [Gd.sTPATCN]-SL is water soluble and offers high labeling efficiency under mild conditions, and is therefore highly desirable for protein systems. Importantly, we show the application of this new gadolinium(III) spin label to double electron electron resonance (DEER) by measuring the distance between a pair of [Gd.sTPATCN]-SL (5.85 nm, σ_r=0.55 nm) in addition to the distance between the gadolinium label and R1 on TRIM25cc. The label provides promising relaxation times at Q-band, allowing for long DEER measurement time windows. The narrow zero-field splitting, which has been shown to suit longer interspin distances,[2] also allows for increased sensitivity and greater modulation depths, expected only to improve when moving to higher fields.

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EPR ORAL SESSION
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105 **Structural Dynamics of Desensitization in a Pentameric Ligand Gated Ion Channel.**
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Desensitization in pentameric ligand-gated ion channels plays an important role in regulating neuronal excitability. Here, we show that docosahexaenoic acid (DHA), a key ω−3 polyunsaturated fatty acid in synaptic membranes, enhances the agonist-induced transition to the desensitized state in the prokaryotic channel GLIC. We determined a 3.25 Å crystal structure of the GLIC-DHA complex in a potentially desensitized conformation. The DHA molecule is bound at the channel-periphery near the M4 helix and exerts a long-range allosteric effect on the pore across domain-interfaces. In this previously unobserved conformation, the extracellular-half of the pore-lining M2 is splayed open, reminiscent of the open conformation, while the intracellular-half is constricted, leading to a loss of both water and permeant ions. However, an unexpected finding was that the peripheral M4 helix, refered to as the "lipid-sensor" showed no conformation difference between the closed, open, and the desensitized states. We carried out spin-labeling/EPR spectroscopic measurements in reconstituted-membranes by CW and DEER methods. Our findings show a highly dynamic M4, whose movement may change the volume and polarity of the internal, drug-binding vestibules. Taken together, this information provides novel mechanistic details of desensitization in pentameric channels.

EPR ORAL SESSION
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106 **Light-induced Conformational Changes in Nitroxide-labeled Proteorhodopsin Detected by Time-resolved 240 GHz EPR at Room Temperature.**
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Proteorhodopsin (PR), a seven alpha helical trans-membrane (7TM) protein, functions as a light-activated proton pump for marine bacterioplankton. The photocycle of green PR is initiated by the absorption of a 520 nm photon at the retinal chromophore, and results in the transport of a proton across the cellular membrane. The PR photocycle has

been characterized by time-resolved UV-vis absorption[1] which reports on the state of the retinal. While it is known that proton transport is accompanied by large-scale conformation changes in PR[2] and other retinal-containing membrane proteins, temporal correlations between conformational changes and the internal state of the retinal remain an area of active research. Time-resolved electron paramagnetic resonance (EPR) in solution state, which has been widely used at X-band frequencies, can be used together with site-directed spin-labeling (SDSL) to study protein conformational changes.[3,4] Time-resolved solution-state EPR at higher frequencies offers greatly enhanced spectral resolution, allowing for better modeling and understanding of the spin label dynamics. We report 240 GHz EPR lineshape analysis of nitroxide-labeled PR, which revealed distinct changes upon light-activation corresponding to changes in protein side-chain mobility due to conformational changes occurring during the photocycle. We show time-resolved EPR data reported at several static magnetic field positions across the EPR lineshape. The conformational change kinetics are temperature dependent. Our results represent a promising step towards detecting time-resolved pair-wise distance changes at room temperature using EPR lineshape analysis of pairs of gadolinium spin labels, which would provide additional conformational information beyond sidechain mobility measurements. *This work is supported by NSF MCB grant 1617025.*

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EPR ORAL SESSION

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107 Transporter Conformational Dynamics from Spin Labeling EPR Spectroscopy.

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My laboratory utilizes the tools of EPR spectroscopy to define the conformational cycle of active transporters. Recent advances in Double Electron-Electron Resonance (DEER) spectroscopy, along with computational methods to generate restrained models of proteins, have enabled unprecedented insight into the substrate- and ATP-coupled alternating access of ABC transporters. Systematic DEER and accessibility analyses of representative subtypes of ABC exporters over more than a decade culminated in transport models for the homodimer MsbA, the heterodimer BmrCD and the mammalian "pseudodimer" P-glycoprotein (Pgp). We exposed commonalities and differences in their cycles including elaborate tuning of the energy input step, and the extent of coupling between various domains and within domains. Recently, we demonstrated that the conformational cycle of Pgp proceeds through sequential ATP hydrolysis in catalytically and structurally inequivalent nucleotide binding sites coupled to formation of a doubly-occluded conformation. I will discuss the advantages and disadvantages of DEER spectroscopy particularly in light of the emergence of high resolution cryoEM microscopy.

EPR ORAL SESSION

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108 Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy.

Thomas Schmidt

National Institutes of Health

With 25.3 million deaths and 38.1 million additional infections worldwide since 2000, the HIV/AIDS pandemic presents itself as a grave health crisis. Although, extraordinary progress has been made in understanding HIV, complete eradication remains elusive. HIV type I reverse transcriptase [L SEP] (HIV-1 RT) catalyzes the conversion of single-stranded, virally encoded RNA into double-stranded proviral DNA, which is the first step towards the integration of viral DNA into the host genome, a prerequisite for the HIV replication cycle.[L SEP] Active HIV-1 RT accommodates DNA as well as RNA through remarkable intrinsic dynamics in the finger and thumb subdomains as identified by variable intermolecular distances in crystallographically determined protein structures. Current drugs suppress such binding events but their inhibitory mechanisms are still under investigation. The configurational space sampled by the finger and thumb subdomains of free, DNA- or drug-liganded HIV-1 RT was investigated

by Q-band double electron–electron resonance pulsed electron paramagnetic resonance spectroscopy, a method for determining long-range distances between pairs of surface-engineered nitroxide spin-labels in the finger and thumb subdomains. In the unliganded state, open and closed configurations for the finger and thumb subdomains are observed, which is in contrasts with the crystallographic data in which the unliganded state only adopts the closed conformation. Upon addition of double-stranded DNA, all constructs adopt open conformations consistent with previous crystallographic data in which the position of the thumb and finger subdomains is determined by contacts with the bound oligonucleotide duplex (DNA or DNA/RNA). Likewise, binary complexes with five different non-nucleoside RT inhibitors populate the open or partially open conformations, indicating that binding of the inhibitor to the palm subdomain indirectly restricts the conformational space sampled by the finger and thumb subdomains. The presented method and results describe the inhibitory restraints placed onto the finger and thumb domain of HIV-1 RT by non-nucleoside RT inhibitors, which render its polymerase function inactive, and hence arrests the HIV-1 replication cycle. Future studies will exploit this inhibitory mechanism to screen previously approved drugs of other treatments and improve known small molecular drugs.

EPR ORAL SESSION

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110 Histidine Handoff in the Prion Protein: New Cu^{2+} Coordination Features for Protecting Against Neurodegeneration?

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A *prion* is a misfolded form of the cellular prion protein, PrP^C. Although the role of PrP in neurodegeneration was established over 30 years ago, there is little understanding of the protein's normal function, and how misfolding leads to profound disease. Recent work shows that PrP^Ccoordinates the cofactors $Cu^{2+}$and Zn^{2+}, and regulates the distribution of these essential metal ions in the brain. Moreover, these metals stabilize a previously unseen fold in PrP^C, the observation of which provides new insight into the mechanism of prion disease.[1, 2] To date, Cu^{2+}coordination was thought to be limited to residues within the protein's N-terminal domain. However, new NMR and EPR experiments suggest that histidine residues in the C-terminal domain assist in stabilizing the Cu^{2+}-promoted PrP^C fold. This talk will describe combined NMR, EPR, mutagenesis and physiological studies that provide new insight into the PrP^C fold and function. *Supported by NIH grants R01GM065790 and S10OD018455 (GLM) and NSF grant CHE-1665455 (RDB).*

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EPR ORAL SESSION

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111 Effect of Silica Support on Electrostatics of Lipid Interfaces in Nano-Bio Hybrid Systems.

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Design of new bio-nano hybrid systems calls for understanding and accounting for the influence of a nanostructured support and nanoconfinement on structure and properties of the membrane-protein interface. In this work we report on spin-labeling EPR studies to assess effects of solid inorganic interface, specifically, silica support, on 1) the phospholipid membrane surface electrostatic potential and 2) effective pK_a of the membrane-burred peptide ionisable sidechains. Novel EPR active pH-sensitive lipids IMTSL-PE and IKMTSL-PE were employed to measure the phospholipid membrane surface potential. The change in the protonation state of the label was directly observed by CW EPR allowing for determination of the effective pK_a of the probe. We have shown that by forming POPC or POPC/POPG mixed bilayers on the surfaces of silica nanoparticles the absolute value of the negative electric potential at the membrane surface could be increased significantly. The potential of the mixed bilayer was observed to be more sensitive to the silica support, suggesting a different mechanism of the bilayer response to the nanostructured surface. Only

single protonation transition was observed for EPR pH-sensitive probe, thus, suggesting that both leaflets of the silica-supported phospholipid bilayers have the same electrostatic surface potential. Addition of cholesterol to phospholipid bilayers did not diminish the bilayer response to silica. Effects of the silica support on transmembrane peptides have been also investigated. Specifically, a model transmembrane α-helical WALP peptide was covalently-modified with cysteine-specific pH-sensitive nitroxides and incorporated into bilayers of various compositions. Placing the bilayer with the integrated transmembrane α-helical WALP peptide on the surface of silica nanoparticles shifts the effective pK_a of the probe in a way consistent with the negative charge on the silica surface but induced a peptide transition upon the probe protonation not observed in liposomes. *Supported by NSF 1508607 to TIS.*

EPR ORAL SESSION

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112 Lipoxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure.

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Abstract: Hydrogen tunneling in enzymatic C-H activation requires a reactive ground-state enzyme-substrate conformation that can achieve a transient tunneling-ready state (TRS) through dynamical sampling.[1,2] It was recently shown that ^{13}C electron-nuclear double-resonance spectroscopy (ENDOR) provides high-precision information on substrate conformation in the H-tunneling enzyme, soybean lipoxygenase (SLO).[3] ENDOR here provides an exquisitely sensitive probe of enzyme control of substrate conformation, demonstrating the influence of subtle enzyme modifications either at a hydrophobic sidechain in contact with bound substrate or at a remote residue within a solvated

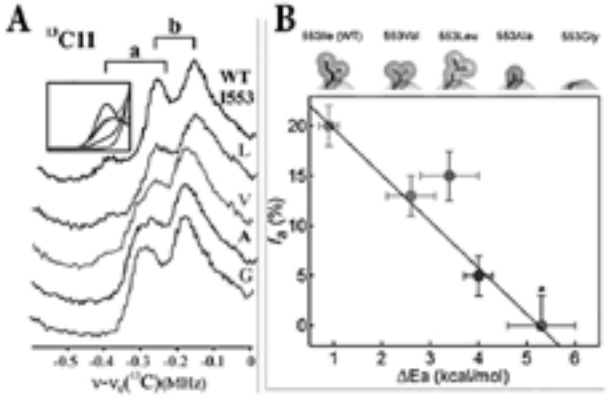

Figure (A) ^{13}C ENDOR spectra for I553X variants. *Inset:* overlay of simulations **(B)** Percentage of a conformer (f_a) versus ΔEa; I553X sidechains shown for reference; 553Leu removed from fitting (black line).

network linked to H-transfer. The differential enthalpic barrier for deuterium and hydrogen transfer, ΔEa, serves as a selective ruler for effective wavefunction overlap at the TRS, and we report a remarkable correlation between the population of the reactive ground-state conformer as obtained from ENDOR spectroscopy and the magnitude of ΔEa, among seven SLO variants **(figure)**. This correlation shows the critical role of ground-state structural precision in achieving a TRS correspondingly optimized for quantum H-atom tunneling, and shows how very modest changes in a single amino acid alter and compromise tunneling. *Supported by National Institutes of Health (NIH): GM111097 to BMH; and GM025765 to JPK. ARO was supported by NIH GM11343 (F32) and startup funds from ECU.*

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EPR ORAL SESSION

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113 2D-Correlated Hyperfine Spectroscopy on a Tetracycline-binding RNA Aptamer.

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In recent years, ELDOR-detected NMR (EDNMR)[1] has gained popularity as a robust and easy method to measure hyperfine couplings of low-γ nuclei in disordered systems. Although initially used at high frequencies (≥ 95 GHz) to prevent an overlap of the central blindspot with signals of low-γ nuclei, it was recently shown, that EDNMR is also an efficient method at smaller microwave frequencies (Q-band, 34 GHz).[2] Weakly coupled ^{14}N resonances, which are separated from the central blindspot by only 2.8 MHz, were readily detected. 2D-hyperfine techniques, such as 2D-EDNMR[3] and THYCOS[4], allow correlating different nuclear spins (e.g. ^{13}C and ^{31}P) to the same paramagnetic spin centre (e.g. Mn^{2+}). In the present study, we use 2D-EDNMR and THYCOS at Q-band frequencies to investigate the interaction of a Tetracycline-binding RNA aptamer to its ligand (tetracycline), which is known to occur via a paramagnetic Mn^{2+} ion.[5] Clear correlation signals between one out of two ^{31}Pcouplings (RNA) and a ^{13}C-signal (tetracycline) are observed. Whereas 2DEDNMR is superior in terms of sensitivity over THYCOS, a necessary background correction introduces uncertainties in an unambiguous peak assignment of the correlation signals. THYCOS, on the other hand, comes with the advantage of a more straightforward data analysis, as no background-correction is required. This study highlights the potential of 2D-EDNMR and THYCOS as useful techniques to assign and distinguish different hyperfine couplings of one nuclear species in rather complex and large biomolecules.

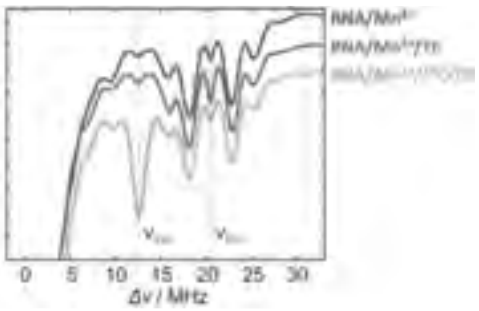

Figure: Q-band 1D-EDNMR on the TC-aptamer.

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EPR ORAL SESSION

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114 EPR Spectroscopy of Spin Probe, Label, and Time-Resolved, Reaction-Intrinsic Radicals Reveals Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in Ethanolamine Ammonia-Lyase Catalysis.

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Progress in bio- and materials-catalyst design and dynamics-based molecular therapeutic approaches in medicine requires a comprehensive understanding of the contributions of configurations and fluctuations in the system and surroundings. We are addressing fundamental aspects of this challenge by identifying and characterizing the choreography of specific protein configurational fluctuations involved in the core chemical step in the ethanolamine ammonia-lyase enzyme from *Salmonella typhimurium*, and the role of solvent as a stochastic, bi-directional dynamical modulator, by using multiple electron paramagnetic resonance (EPR) techniques that probe the successive "spheres of influence," which are, from bulk solvent to protein interior: (*1*) nitroxide spin-probe EPR to resolve temperature (*T*) -dependent dynamics of mesodomain (bulk) and protein-associated domain (PAD, hydration layer) solvent phases,[1,2] with *T*-dependence of the solvent dynamics tuned by using cosolvents, (*2*) nitroxide spin-label EPR to resolve protein surface dynamics at specific sites,[3] and (*3*) time-resolved, full-spectrum EPR spectroscopy to measure first-order kinetics of the substrate radical rearrangment reaction.[4,5] Cryo-*T* conditions (173-250 K) render protein configurational transitions rate-determining, and transform collective atom displacements into localized, incremental displacements, thus revealing the contributions of native collective protein configurations and fluctuations to reaction chemistry.[6] The *T*-dependences of spin probe and spin label motional parameters are compared to the *T*-dependence of the rearrangement reaction kinetics under the different solvent conditions, to identify and characterize the molecular mechanisms of solvent-protein-reaction coupling. *Supported by NIH R01DK054514.*

EPR ORAL SESSION

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115 Vanadyl Complexes: From Qubit Design to Quantum Simulation.

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Magnetic molecules have redesigned the scenario of nanoscale magnetism representing the ideal platform for the investigation of quantum effects in magnetization dynamics. More recently magnetic molecules have been investigated as potential qubit, as chemical tunability can be exploited to realize multi-qubit molecular units acting as quantum gates. Under this respect magnetic molecules represent an alternative platform to more established systems in Quantum Information Processing (QIP).[1] We have recently employed a multi-technique approach based on the combination of ac susceptometry, pulsed EPR techniques and terahertz spectroscopy to investigate *T1* and *T2* of *S*=1/2 molecular systems and to establish magneto-structural correlations, thus identifying in the vanadyl unit a promising spin center. The current challenge we are facing is the realization of molecular quantum gates based on two or more interacting qubits with long coherence time and that can be efficiently manipulated by electromagnetic radiation pulses. An alternative possibility to the use of electronic spins as qubits is the use of nuclear spins to encode qubits that are more weakly coupled to the environment, and hence substantially protected from decoherence.[2] Here we report on a novel scheme for electron-mediated nuclear QIP.[3] The interaction between nuclear qubits is effectively and rapidly switched on and off by exciting the coupled electronic spins via simple microwave (EPR-like) pulses, while single-qubit rotations between effectively decoupled nuclear spins, are obtained by means of radio-frequency (NMR-like) pulses. A prototypical realization of this idea is a molecular architecture composed of two paramagnetic metal ions with magnetic nuclei and sizeable hyperfine couplings. The small interaction between the two electronic spins can be used to effectively couple nuclear qubits and controllably generate entangled two-qubit states. In this approach, long electronic spin coherence times are a key ingredient to ensure the robustness of such a system during the implementation of electron-mediated two-qubit gates. Some neutral vanadyl complexes can be also deposited on metallic surfaces in an oriented manner retaining the unpaired electron in the d_{xy} orbital that weakly interacts with the surface.[4] This open the perspective of addressing individual qubits and gates by exploiting the capabilities of Scanning Tunnel Spectroscopy.[5]

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EPR ORAL SESSION

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116 Endohedral Fullerenes as Molecular Qubits.

ShangDa Jiang

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Quantum computation could outperform classical approaches in cryptography and database searching. Among various quantum bits (qubits) candidates, molecular nanomagnets are found to be prominent since their collective spins are tunable as required. However, the nuclear spins from the ligand can act as a source of Overhauser field to decoher the electron spins. Here we demonstrate that by encapsulating the electron spins in fullerenes, it is possible to elongate the quantum coherence time largely even for the anisotropic high spin systems with many nuclear spins. The rotation of the inner group of the endohedral fullerene ($Sc_3C_2@C_{80}$) can lead to a crossover of the quantum coherence behavior[1]. The anisotropic high spin system ($Gd_2@C_{79}N$) affords diverse Rabi cycles, allowing arbitrary superposition state manipulation between each adjacent level[2]. Our research suggests that this molecular magnetic material of anisotropic high spin fulfills the requirement for implementing Grover's algorithm.

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EPR ORAL SESSION

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117 Quantum Coherence Studies in Actinide and Lanthanide Organometallic Complexes.

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Long-lived quantum coherence is a fundamental property that magnetic molecules functioning as qubits need to posses.[1] Strategies aiming to enhance quantum coherence are centered on the removal of nearby nuclear spins, believed to cause nuclear spin diffusion, and implicitly quantum decoherence. However, this approach is very challenging. Here we demonstrate that memory times long enough to enable coherent spin manipulations even at ambient temperatures are possible in nuclear-spin rich organometallic systems based on f-elements. We take advantage of these properties to measure actinide covalency in cyclopentadinyl complexes, $AnCp^{tt}_3$ (An = Th or U),[2] using advanced pulsed EPR methods, such as: HYSCORE, ENDOR. Transient nutation studies have revealed coherent Rabi oscillations in nuclear-spin rich $LnCp'_3K$ (Ln = Y or Lu) and related complexes,[3] including at 300 K in a single crystal.[4] Ac magnetic susceptibility data confirmed slow magnetic relaxation at low temperatures, associated with very long spin lattice relaxation times.

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EPR ORAL SESSION

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118 Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis.

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Ethylene oligomerization is an industrially important route for linear α-olefins (LAO), especially 1-hexene and 1-octene, co-monomers for polyethylene.[1] Increasing demand for these LAO has propelled research into selective trimerization and tetramerization. The active catalyst is formed by adding an activator to the Cr^{I} or Cr^{III} metal complex in the presence of a PNP ligand ($PNP = Ph_2PN(R)PPh_2$) and a weakly coordinating anion such as $(Al(OC(CF_3)_3)_4)^-$ prior to the reaction. The complex can undergo ligand redistributions, reduction and disproportionation, resulting in the formation of various species with different oxidation states and as a result altered total electron spin. However, the precise nature and action of the active catalyst are still subject to debate.[1-2] In this project, 1-hexene was used as a substrate instead of ethylene due to instrumental limitations. Paramagnetic species from discrete catalyst precursors to in-situ catalysis were examined by continuous wave electron paramagnetic resonance spectroscopy (cw-EPR). One major challenge is identifying the structure of these intermediate species, which will be approached by advanced pulse EPR experiments in combination with a quantum chemistry approach.

During activation and the following catalysis, we intend to identify the structure of intermediate species and this is hampered due to overlapping spectra. Thus, we aim to separate the arising spectra and assign their oxidation states and thus monitor the fate of the chromium species. We have tested a model system consisting of a mixture of discrete Cr^{I} and Cr^{III} precursors and recovered their individual spectra using an inversion recovery filter and assigned their spin and consequently oxidation states from transient nutation experiments. The use of this method on an activated Cr precatalyst will be illustrated for monitoring the various species.

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EPR ORAL SESSION

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125 Spin and Orbital Resonance Driven by a Mechanical Resonator.

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Creating and studying coherent interactions between disparate solid-state quantum systems is a challenge at the intersection of atomic physics, condensed matter physics, and engineering. In general, different physical realizations of a quantum bit (qubit) operate at different frequencies, on different size scales, and couple to different fields. Nonetheless, efforts to create "hybrid quantum systems" are appealing because they could enable a quantum concert – were parts are played by different physical qubits that each offer the best performance in a particular area. There is a growing interest in mechanical motion as a "plastic" degree of freedom for coupling solid-state qubits, with the potential to form a coherent interface between them, and with light. This has motivated intense research into the coherent interactions between mechanical resonators and qubits formed from photons, trapped atoms, superconducting circuits, quantum dots, and nitrogen-vacancy (NV) centers in diamond, to name a few. I will describe our experiments to drive coherent resonance of NV center spins using gigahertz-frequency mechanical resonators through dynamic crystal lattice strain. In high-quality diamond mechanical resonators, we demonstrate coherent Rabi oscillations of NV center spins driven by mechanical motion instead of an oscillating magnetic field.[1,2] We show that the mechanical resonator is a resource to prolog the NV center's spin coherence.[3] We also examine how strain can be used to control NV centers through their excited-state, both the room temperature spin-strain coupling[4] and the extremely strong low temperature orbital-strain coupling.[5]

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EPR ORAL SESSION

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126 Picoliter Diamond NMR.

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NMR is a powerful technique for determining the composition, structure, and function of a variety of molecules, but the sensitivity is presently limited for for sub-nanoliter volumes. An emerging alternative approach is to replace inductive coils with non-inductive magnetometers based on Nitrogen Vacancy (NV) centers in diamond. In a first step, we used few-nm thick layers of NV centers doped into high-surface area nanostructured diamond to perform diamond NMR spectroscopy on ~1 pL of analyte[1]. I will present our recent work to improve the sensitivity and spectral resolution of diamond NMR by separating the polarization and detection steps. Analyte is prepolarized in a larger magnetic field (1.5 T) and then adiabatically flowed to a microfluidic diamond NMR detector at 14 mT. Separating the polarization and detection in this way provides nearly nuclear-T1-limited spectral resolution.

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EPR ORAL SESSION

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127 Locking and Tracking Magnetic Resonance Spectra of NV^- Center for Real-time Magnetometry.

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We describe new measurement methods for real-time magnetometry by locking and tracking magnetic resonance spectra of Nitrogen Vacancy (NV^-) centers in diamond. Real-time magnetometry has many uses from biology to nano-scale electronics. We focus on characterizing static magnetic fields and detecting ferromagnetic resonance from nanoscale magnetic devices, where the small device volume makes it difficult to use conventional techniques. The special intrinsic properties of diamond NV^- centers offer a path forward, but usability of NV^- center methods is limited by the requirement for sophisticated measurement techniques and post processing of measurement data.

This talk focuses on real time data processing and frequency control to lock & track the CW optically detected magnetic resonance (cw-ODMR) peak of NV^- centers. We use a custom-built differential rate detector and active feedback control (PID). The required circuitry is relatively inexpensive and easy to implement, and because we use digital frequency control as opposed to a voltage-controlled oscillator and microwave mixer, our scheme covers wider magnetic field ranges, limited by the signal generator. This method requires no post-processing of the data and it provides sensitivity (6 $\mu T/\sqrt{Hz}$) comparable to more traditional methods. This sensitivity is sufficient to measure the small change in stray magnetic field during ferromagnetic resonance of a nanoscale magnetic device.

EPR ORAL SESSION

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128 Precise Determination of Spin Concentration using Double Electron-electron Resonance.

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Precise determination of spin concentration is critical in many fields from quantum physics and condensed matter physics to biochemistry. Unfortunately, currently available techniques have limitations. For example, lineshape analysis of EPR spectroscopy has been applied to determine the concentration of paramagnetic impurities, however the method remains challenging for wide applications as it highly depends on the choice of the reference sample, position of the samples in the cavity, spin relaxations and so on. Here we discuss a method to determine a wide range of spin concentrations using a wide-band high-frequency electron spin resonance and double electron-electron resonance spectrometer[1]. We also shows the study of spin decoherence time T_2 of the nitrogen impurities in diamond as a function of the spin concentration. The method developed in this work is applicable for various spin systems and can be implemented in other EPR related techniques. Possible applications will also be discussed.

This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).

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EPR ORAL SESSION

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129 Electrical Detection of Charge Carrier Magnetic Resonance in the Strong Driving Field Limit When $B_1 \sim B_0$.

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Spin-dependent recombination currents in π-conjugated polymers allow for the detection of magnetic resonance of charge carrier spin-ensembles with no polarization, and thus, at very weak applied static Zeeman fields B_0 and at room temperature.[1] We have used this in order to study electron paramagnetic resonance under strong driving conditions when the amplitude of the magnetic resonant driving field B_1 is approximately as strong as B_0. Technologically, these room temperature measurements were carried out by using monolithic thin-film device structures in which a polymer bipolar injection device [essentially an organic light emitting diode (OLED)] was fabricated directly on top of an RF microwire.[2] We used the commercial polymer SY-PPV as an active device layer. Once the strong-drive magnetic resonance regime was

achieved ultrastrong light-to-matter coupling evolved and as a result, spin collectivity set in [1,2] which caused a variety on characteristic effects on spin-dependent recombination rate which can be observed with electric current measurements.

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EPR ORAL SESSION

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130 EPR-on-a-chip – Current Trends and Future Research Directions.

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Recently, oscillator-based spin detection has gained significant attention in the EPR community due to its excellent spin sensitivity in continuous wave EPR experiments with operating temperatures down to 4 K[1,2]. The approach has then been extended by our group to the use of voltage-controlled oscillator- (VCO-) based detection that allows for an operation inside a fixed B_0-field permanent magnet by sweeping the VCO's oscillation frequency[3].

In this invited talk, we will start with a brief overview of the most salient features of the VCO-based approach, covering its unique features for all continuous wave, rapid scan and pulsed EPR experiments. Next, we will discuss the current state-of-the-art and the future potential of monolithic realizations of the VCO-based approach (EPR-on-a-chip). Here, we will focus on the possibility of realizing portable, low-cost, yet high-performance EPR spectrometers that can target upcoming EPR markets such as personal medicine. In this context, we will discuss some recent results from our group on arrays of injection locked VCOs that allow increasing the sensitive volume for an improved concentration sensitivity in the lower micromolar range[4]. We will also explain how the VCO-based detectors can be incorporated into phase-locked loops (PLLs) to enable a precise definition of the oscillation frequency, which is essential for quantitative EPR. Finally, we will show that the VCO-based concept also allows for rapid scan and pulsed EPR experiments with very interesting features. This includes remarkable scan rates in excess of 1 GG/s for rapid scan detection as well as dead-time free detection and even the possibility to detect the Rabi oscillations during the pulse in pulsed EPR.

In the last part of the talk, we will discuss the possibilities arising from using the EPR-on-a-chip detectors as B_1-field source for DNP experiments. Here, we will also discuss the possibility of combining the EPR-on-a-chip approach with monolithic realizations of NMR spectrometers (NMR-on-a-chip)[5] that will eventually allow for the realization of portable, low-cost DNP-enhanced NMR spectrometers, which can open up entirely new markets for NMR spectroscopy.

The work is supported by the DFG through the priority program SPP1601 (Stuttgart and Berlin) and Research Grant AN 984/5-1 (Stuttgart).

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EPR ORAL SESSION

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131 Nanoscale EPR of Nitroxide Radicals using a NV Center in Diamond.

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A nitrogen-vacancy (NV) center is a promising candidate for a high-sensitive magnetic sensor at room temperature. Although nanoscale electron paramagnetic resonance (EPR) spectroscopy using single NV centers has been demonstrated [1], NV-based EPR of spins located outside the diamond crystal remains challenging because the NV-based EPR technique often requires a sophisticated sample preparation including stable positioning between target

spins and NV and fabrication of stable NV with a long coherence time. Here we present experimental demonstration of nanoscale NV-based EPR spectroscopy of nitroxide radicals. First, the fabrication of NV centers near the diamond surface employing a low energy ion implantation and subsequent annealing process [2]. Then, a surface chemistry technique is employed to covalently attach nitroxide radicals to the diamond surface [3, 4]. Finally, we discuss double electron-electron resonance (DEER) experiment to measure nanoscale NV-based EPR spectroscopy of nitroxide radicals and analysis of the observed EPR spectrum [5]. *This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).*

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EPR ORAL SESSION

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132 Nanoscale NMR Enabled by Diamond Colour Centres.

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Colour centers in diamond are promising candidates for nanoscale quantum sensing . In this talk, we will highlight new techniques enabling high spectral resolution in nanoscale NMR using diamond magnetometers. We will also show experiments aiming to develop hyperpolarization enhanced NMR and MRI based on polarization transfer form optically pumped electron spins in diamond to nuclear spins.

EPR ORAL SESSION

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133 Electron Spin Resonance of Individual Magnetic Atoms on Surfaces.

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Magnetometry having both high magnetic field sensitivity (energy resolution) and nanoscale spatial resolution has been of great interest and an important goal for applications in diverse fields covering physics, chemistry, material science, and biomedical science. The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Here, we successfully combine electron spin resonance (ESR) and STM, driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)). A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10 μeV) while the ESR linewidth is in the range of only a few MHz (~10 neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions. When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show r^{-3} distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision.

Our ESR-STM may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

EPR ORAL SESSION

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134 Charge Carrier Separation and Spin-Coupling in Photoactive Materials.

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To develop novel materials for photovoltaic or photocatalytic application a detailed atomistic understanding of charge carrier separation and the corresponding recombination processes is crucial. In this work, we show how microscopic modeling of the involved defect states helps to analyze the data obtained from magnetic resonance experiments. This is shown using hydrogenated amorphous silicon (*a*-Si:H) as well as its interface to crystalline silicon (*a*-Si:H/*c*-Si) in heterojunction solar cells [1] as prototype examples. Combining different kinds of electrically detected magnetic resonance (EDMR) and density functional theory (DFT) we analyze the spin-coupling and the spin-dependent recombination in the samples. By this we find that (*i*) the localized interface defects mimic the famous Pb-centers at the Si/SiO_2 interface, (*ii*) we identify the microscopic origin of the more delocalized conduction and valence band tail states, and (*iii*) we discuss how charge carrier separation can be supported by conduction band tail states. (*iv*) Special emphasis is also given to triplet-excitons. Their *S*=1 character is unambiguosly shown via transient EPR revealing a basically axial dipolar spin-spin coupling of about 570 MHz. Direct coupling to *a*-Si:H tail states is shown via PELDOR. From the half-field resonance a mean triplet radius of 5 A can be derived, suggesting that besides tail states more localized electrons are involved. Possible models for the triplet exciton are discussed by calculating the *g* tensor as well as the Zero-Field Splitting (ZFS) from fist principles [2] for reasonable defect models.

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EPR ORAL SESSION

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135 Highly Efficient Optical Pumping of Spin Defects in Silicon Carbide for Stimulated Microwave Emission.

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We investigate the pump efficiency of silicon-vacancy-related spins in silicon carbide. For a crystal inserted into a microwave cavity with a resonance frequency of 9.4 GHz, the spin population inversion factor of 75 with the saturation optical pump power of about 350 mW is achieved at room temperature. At cryogenic temperature, the pump efficiency drastically increases, owing to an exceptionally long spin- lattice relaxation time exceeding one minute. Based on the experimental results, we find and discuss realistic conditions under which a future silicon carbide MASER can operate in continuous-wave mode and serve as a quantum microwave amplifier.

M. Fischer, A. Sperlich, H. Kraus, T. Ohshima, G. V. Astakhov, and V. Dyakonov
Phys. Rev. Applied, 9, 054006, **2018**, doi: 10.1103/PhysRevApplied.9.054006

EPR ORAL SESSION

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136 Spin-orbit Coupling Effects on Charge Carriers in Conjugated Polymers.

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Charge carrier pairs in organic semiconductors that consist of predominantly light elements usually experience weak spin-orbit coupling (SOC).[1,2] Nevertheless, this weak, but non-zero SOC does affect some magneto-opto-electronic properties such as magnetoresistance or -luminescence. We investigate charge carrier SOC effects in electrically detected magnetic resonance (EDMR) thin-film organic diodes made of a range of conjugated polymers, such as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), poly-phenylenevinylene (SY-PPV), polyfluorene

(PFO) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) over a broad range of microwave excitation frequencies.[1,2,3] We find that the EDMR line, which is inhomogeneously broadened with a line width that is mostly field-independent at low frequencies, becomes strongly broadened due to the effects of an anisotropic *g*-tensor (in the case of MEH-PPV, SY-PPV, and PFO) and isotropic *g*-strain broadening (in the case of PEDOT:PSS) at microwave frequencies above 100 GHz.

Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0000909. Part of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-1157490 and the State of Florida. The theoretical work was supported by the DFG in the framework of the Gottfried-Wilhelm-Leibniz Award to S.G.

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EPR ORAL SESSION

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137 Light-induced Charge Separation in Polymer-Fullerene Organic Photovoltaics Studied by Multifrequency EPR and DFT.

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Organic Photovoltaic (OPV) cells are promising devices for solar energy utilization, offering low-cost fabrication and the ability to tune electronic properties. Understanding the charge separation and electronic structure at the molecular level is crucial for improving the efficiency of OPV cells. Illumination of the OPV blends leads to the formation of two paramagnetic species due to photo-induced electron transfer between the conjugated polymer and the fullerene. They are the positive and negative polarons on the polymer and fullerene, respectively, and correspond to radical cations and radical anions. EPR spectroscopy is an ideal method to study the electronic structure of charge separated states, since both of these radical species can be selectively probed. Using the combination of multifrequency EPR and pulsed ENDOR spectroscopy on various OPV blends allowed the determination of g-tensors and ^{1}H hyperfine tensors. The analysis of the tensors revealed that the positive polaron is delocalized on the polymer chain, which seems to be an important reason for the efficient charge separation in these systems as it minimizes the wasteful process of charge recombination. In contrast, the negative polaron is typically localized on a single fullerene molecule. Extensive DFT modeling was performed for polymer cation and fullerene anion radicals. The comparison of experimentally determined and calculated magnetic resonance parameters allowed validation of the calculations and provided additional information. The combination of pulsed light excitation with time-resolved EPR techniques enabled us to study the charge transfer (CT) dynamics in OPV blends. Strong spin-polarization patterns are found, confirming predominant generation of singlet CT states and partial orientation ordering near the donor-acceptor interface. These observations allow a comparison with charge separation processes in molecular donor-acceptor systems and photosynthetic assemblies, and therefore the elucidation of the initial steps of sequential CT in OPV.

EPR ORAL SESSION

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138 Electronic Structure Investigation of Self-doped type Organic Conductors by Magnetic Resonance Spectroscopy.

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So far, we investigated the electronic structure of novel type of organic conductors, ammonium tetrathiafulvalene carboxylate (TTFCOO) and its and tetrathiapentalene derivative (TTPCOO) by high-field ESR and NMR measurements.[1-3] The pristine TTFCOOH and TTPCOOH molecules are closed-shell. Kobayashi and coworkers

(NIMS, Japan) found that self-doped type carrier was generated by substitution of the end group of (NH_3^0) with (NH_4^{+1}), which is regarded as a charge-reservoir. Because of sample limitation (powder), the detailed electronic state (anisotropic g-tenor and linewidth) was not clarified within the framework of conventional X-band ESR spectroscopy. By using W-band, however, a clear powder pattern structure could be found. We can evaluate the principal values of the *g*-tensor for theses salts, assuming anisotropic *g*-values. We found that TTFCOO system shows 1D column structure. On the other hand, the TTPCOO derivative system seems to be isotropic structure within 2D layer. As a result, TTFCOO system is a narrow-gap semiconductor because of 1D instability, while TTPCOO shows a stable metallic state down to 2K. We also perfumed Detailed discussion ^{1}H-NMR measurements down to 2K and clarified electronic states of these systems.

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EPR ORAL SESSION

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139 Tuning Effective Charge Carrier Hyperfine Field Strengths in PEDOT:PSS Thin Films by Doping.

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The omnipresent hydrogen in organic semiconductor and organic conductor thin film materials plays a crucial role in a variety of electronic, optoelectronic, and magneto-electronic properties. Engineering the hyperfine (HF) fields in these materials can straightforwardly be done by hydrogen isotope substitution[1, 2]. This approach requires an expensive organic synthesis method and the range of achievable HF field distributions is always limited due to availability of only one stable hydrogen isotope next to protium, namely deuterium. Here, we report on an alternative approach to the control of charge carrier HF field strengths by doping the organic conductor, poly(3,4-ethylenedioxythiophene):poly styrene-sulfonate (PEDOT:PSS) with ethylene glycol (EG). The idea behind this approach is to change charge carrier mobilities though doping, which, in turn changes motional narrowing in PEDOT:PSS. In order to verify this approach, we fabricated PEDOT:PSS based bipolar injection devices (diodes) with various EG doping concentrations ranging from 0% to 0.15%. We then carried out electrical characterization on all devices in order to determine charge carrier mobilities in the PEDOT:PSS. We then conducted continuous wave multifrequency electrically detected magnetic resonance (EDMR) spectroscopy[3] in order to verify whether narrowing of the effective hyperfine field strengths occurred with increasing mobilities. Finally, we carried out electrically detected Hahn-spin echo measurements[1,4] in order to determine whether the hyperfine field narrowing correlated with increasing spin coherence times (T_2), an unambiguous hallmark of motional narrowing. The results of these experiments indeed confirmed a reduction of the HF field distributions with increasing EG content and an increase of the polaron spin coherence times, with increased charge carrier mobility[5]. Thus, we demonstrate that EG doping of PEDOT:PSS allows for the control of effective local charge carrier hyperfine fields. Doping organic semiconductors therefore likely also enables tuning of macroscopic material properties which depend on hyperfine fields such as magnetoresistance, the magneto-optoelectronic behavior of materials as well as spin-diffusion.

This work was supported by the National Science Foundation through the Utah MRSEC center, grant #1121252. G. Joshi, H. Malissa, and S. Jamali were supported by the Department of Energy, project #DE-SC0000909.

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EPR ORAL SESSION

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140 **A Bird's Eye View of the Chemical Compass – Magnetic Field Effects on the Photocycles of Cryptochrome.**

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Although it has been known for half a century that night-migratory songbirds can detect the strength and direction of the Earth's magnetic field for the purposes of orientation and navigation, the primary sensory mechanisms responsible for this fascinating feat are still obscure. Schulten's suggestion in 1978[1] that this capability might be driven by a quantum mechanical process involving a pair of photoinduced radicals was long considered to be an exotic and highly unlikely hypothesis. However, with the discovery of cryptochromes[2], a family of blue light photoreceptor proteins, this radical pair hypothesis has taken centre stage in the discussion of animal magnetosensitivity and is now, arguably, the most likely mechanism to drive this fascinating process. Here we report our comparative studies of magnetic field effects on the photo-induced electron transfer reactions in a series of proteins from the cryptochromes/photolyase family, including cryptochromes from Arabidopsis thaliana (a flowering plant), Drosophila melanogaster (the fruit fly), a cry-dash protein from Xenopus laevis (the African clawed frog) and E. coli photolyase. The magnetic sensitivity of these reactions is characterized by a combination of optical spectroscopy methods. These range from sub-nanosecond transient and optical cavity based absorption spectroscopies (including both cavity ringdown and broad band cavity enhanced absorption spectroscopies) to fluorescence methodologies. Together, these techniques provide time-, field- and wavelength-resolved spectral data from which detailed insights into the photo- and radical pair chemistry of blue-light photoreceptor proteins are obtained.

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EPR ORAL SESSION

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141 **Radiolysis Products at the Interface of Aluminum Oxyhydroxides and Strongly Basic Solutions.**

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Radiation-induced chemical reactions have broad significance in many scientific fields from water radiolysis in nuclear reactors and nuclear fuel design to spent nuclear fuel storage and high-level nuclear waste reprocessing. Multiple lines of evidence have suggested that interfacial chemistry and energy transfer processes at the interfaces play important roles in radiation induced chemical transformations in heterogeneous systems. Here we present data on a system relevant to Hanford Tank Waste: strongly basic, high in nitrate/nitrite and containing aluminum oxyhydroxide species (Gibbsite, Boehmite, etc.). Traditional spin trapping methods do not yield useful results in these conditions, but previous investigators have shown that nitromethane is an effective spin trap above pH 11 where it exists in the "aci" form. In situ radiolysis and spin trapping with nitromethane detected by Electron Paramagnetic Resonance (EPR) spectroscopy can track many relevant radical species in the aqueous phase, including hydroxyl radicals, nitrite radicals and nitric oxide. Laser-induced fluorescence spectroscopy was used to directly measure hydroxyl radicals at shorter time scales. Together, these spectroscopy techniques along with deterministic simulations can identify and quantify the radiolytic transient species and their temporal evolution profiles. This reveals the interfacial hydration and hydroxylation structure and energetic behavior, and unravels their roles in aluminum oxyhydroxide transformation processes under irradiated conditions.

EPR ORAL SESSION

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142 Low Symmetry Orienting Potentials and Efficient Computation of ESR Line Shapes.

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ESR line shape simulation is an important tool to elucidate details of structure and dynamics, particularly when performed in the context of model parameter fitting. In systems where an ESR active spin label is covalently attached to a macromolecule, one can model probe ordering effects by a suitably chosen orienting potential. Conventional line shape analysis is restricted to orienting potentials of fairly high symmetry, typically possessing a center of inversion, e.g., D_{2h}, which may not be a faithful representation of the environment in which the spin label is diffusing. Regardless of the symmetry of the orienting potential, a key ingredient for generating a line shape simulation is the starting vector, which is typically computed from projections of diffusion operator eigenfunctions onto the equilibrium distribution modeled by the orienting potential.[1] This is often the most time-consuming part of line shape calculations, as it relies on numerical integration of highly oscillatory integrands. In order to improve the efficiency of the starting vector calculation, we have developed a vector recurrence relation with no restrictions on the form of the potential. As it is a homogeneous recurrence relation, the starting vector may be evaluated by standard methods, e.g., singular value decomposition. The vector recurrence relation can also be extended to the Slowly Relaxing Local Structure model,[2] and this is work in progress. We will present illustrative simulations demonstrating the effects of low symmetry orienting potentials on the ESR line shape and discuss what modifications are necessary to line shape simulation software to accommodate orienting potentials of low symmetry. *This work was partially supported by a Faculty Research Award Program grant from the University at Albany.*

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EPR ORAL SESSION

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143 Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation.

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The Stochastic Liouville Equation (SLE) as first proposed by Kubo has seen extensive applications in magnetic resonance (EPR and NMR) due to the pioneering efforts by Jack Freed and collaborators. It is of common knowledge, though, that the SLE in its original formulation does not allow the spin system to approach thermal equilibrium with its environment. This is no inconsequential theoretical problem[1,2]. Indeed, in most magnetic resonance line shape calculations, ad hoc amendments to the SLE are required aimed none other but to allow an approach to equilibrium[2]. Moreover, the evolution of the density matrix describing a physical system must necessarily be of a completely positive, trace preserving (CPT) map nature[3]. At present, it is not clear whether the SLE or its subsequent modified versions are always CPT. In this talk, we present an alternative to the SLE, i.e. the Quantum Markovian Master Equation approach. We show that this method 1) naturally guarantees an approach to equilibrium on a time scale which can actually be computed, and 2) ensures that the dynamical map for the evolution of the effective spin density matrix is CPT. Without loss of generality, we shall focus in this talk on isotropic spin Hamiltonians with fluctuations due to interaction with the environment and discuss some interesting features of the renormalized master equation one obtains with our approach and what we can infer from them. *We gratefully acknowledge funding from the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. [320951].*

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EPR ORAL SESSION

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144 Time Domain Dynamic Nuclear Polarization (and Some CW Experiments on Proteins).

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This presentation will selectively cover closely related sets of experiments that employ time domain and continuous wave (CW) dynamic nuclear polarization (DNP) experiments, magic angle spinning (MAS) NMR, and the application of these techniques to structural determination of amyloid fibrils from Aband membrane proteins.

High field dynamic nuclear polarization (DNP) experiments utilizing subterahertz microwaves (~150-600 GHz) are now well established as a routine means to enhance nuclear spin polarization and the sensitivity in MAS NMR experiments. Specifically, irradiation of electron-nuclear transitions transfers the large electron polarization from the polarization agent to nuclear spins via the Overhauser effect (OE), the cross effect (CE) and/or the solid effect (SE). However, the field/frequency dependence of the CE and SE enhancements scale as , where n=1-2, leading to attenuated enhancements in experiments at 14.1 and 18.8 T. Accordingly, we have initiated time domain DNP in order to circumvent the field dependence of CW DNP. We show that spin locking the electrons and matching the NOVEL condition serves as an effective approach to time domain DNP, and that the spin lock can be modulated to increase the efficiency of the polarization transfer. In addition, a significant reduction in the power required to perform pulsed DNP is achieved by using the integrated solid effect and sweeping the microwave frequency. Finally, we report a new low power approach – Time Optimized Pulsed DNP (TOP DNP) – that utilizes pulses at synchronized with, the nuclear Larmor frequency. Time permitting applications to $Ab_{1-42}$and bR will be presented.

EPR/SSNMR ORAL SESSION

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145 Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.

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Optimizing microwave transmission is important in the development of our low-powered DNP instrument for small sample volumes. Toward this end, we have been using frequency swept EPR and DNP in the same probe to characterize the delivery of microwaves into the sample. The intensities of single EPR scans are affected by many factors besides the microwave power density at the sample, making signal intensities alone an unreliable means for comparing different experimental arrangements. Instead, we have turned to using saturation experiments common in CW EPR as measures of microwave field strength. Calibrating these curves can be challenging since microwave field inhomogeneity effects can be large in DNP probes. To understand this, we have carefully characterized the EPR saturation of P1 centers in thin single crystal high pressure high temperature diamond samples. Simultaneous measurement of EPR saturation for these P1 centers and BDPA-benzene at X-band was used to validate the P1 saturation curve as a measure of microwave field intensity. We find the shape of the P1 center saturation curve is dominated by a distribution in relaxation times more strongly than our estimated microwave field inhomogeneity. Since this shape persists at both low and high static magnetic field, the peak in the curve provides a reliable measure of average microwave field strength at the sample. We can then use saturation of a standard P1 center sample as a basis for quantitative comparison of different probe configurations. This will help us compare different dielectric waveguides, coil geometries and MAS rotor configurations with respect to microwave field efficiency.

EPR/SSNMR ORAL SESSION

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146 Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments.

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We report on the successful construction and operation of an EPR spectrometer running at 260 GHz that was designed with the intent to work on large surface area samples, typically 5 mm in diameter.[1] The loss of sensitivity associated with the absence of a cavity is compensated by the gain of working at high frequency. A compact Martin-Puplett interferometer offering quasi-optical isolation was designed so as to tolerate the high power of our gyrotron. EPR measurements have so far been carried out using a solid state source. Transmission of millimeter wave which maintains

amplitude and polarization was possible thanks to corrugated waveguides made by the stacked-ring technology.[2] This EPR setup is mounted on top of a magnet routinely used for NMR. Thus, we can measure the EPR of the radicals we use in our gyrotron-based Dynamic Nuclear Polarization experiments. Check experiments were conducted using BDPA in toluene at 300K, TEMPOL in glassy frozen solutions at 20K, nano-diamond, TiO2 and polyaniline.

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EPR/SSNMR ORAL SESSION

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147 Magic Angle Spinning Spheres, Electron Decoupling with CPMAS below 6 K, and DNP within Human Cells Using Fluorescent Polarizing Agents.

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We demonstrate that spheres, rather than cylinders, can be employed as rotors in magic angle spinning experiments. Spheres spinning at the magic angle have significant advantages over cylinders, including simplicity and favorable scaling to sub-millimeter scales. We show initial experiments employing spheres for MAS experiments and observe rotational echoes from KBr, demonstrating stable spinning at the magic angle. We also describe the first MAS DNP experiments performed colder than 6 Kelvin, yielding DNP enhancements from biradicals of 242 and longitudinal magnetization recovery times < 2 s.[1,2] Furthermore, we show that microwave driven electron decoupling effectively attenuates detrimental interactions between electron and nuclear spins to increase the resolution and signal intensity in cross polarization (CP) MAS experiments.[2,3] Frequency chirped microwave pulses from custom-developed frequency agile gyrotrons are employed for electron decoupling.[4] Electron spin control is further improved using teflon lenses to focus microwave intensity and increase the electron spin Rabi frequency. Experiments on model systems are extended to intact human cells in the first demonstration of in-cell DNP, using both fluorescent trimodal DNP polarizing agents, and also abbreviated biradicals and sterically protected monoradicals.[5] We show DNP NMR signal enhancements within HEK293 cells of >50, and together with cryogenic MAS 2500 within cryoprotected human cells. Time constants to replenish the DNP enhanced NMR signal within cells are

EPR/SSNMR ORAL SESSION

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148 Novel Aspects of Polarization Propagation and Biomolecular Applications of MAS DNP.

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The active or passive propagation or spreading of enhanced nuclear polarization is of utmost importance in MAS DNP. In a typical experiment, a diamagnetic sample is doped with a paramagnetic polarizing agent which will transfer the large electron polarization to surrounding (core) nuclei. This polarization will then propagate due to spin-diffusion before it is actively transferred from ^{1}H to a low-γ nucleus in an indirect DNP experiment, or is directly read out on the low-γ nucleus in a direct DNP experiment. At the same time, the core nuclei are subject to enhanced paramagnetic relaxation and hyperfine shifts. This results in the appearance of a spin-diffusion barrier, limiting the efficiency of accumulation and spreading of enhanced nuclear polarization.

In this talk, several aspects of DNP with regards to mechanisms and applications are discussed. First, the propagation of magnetization through the spin-diffusion barrier can be actively supported by MAS via electron-driven spin diffusion. We present theoretical as well as experimental data which shows that the same hyperfine interaction which decouples core nuclei from the bulk in static samples can actively enhance homonuclear spin-diffusion rates under sample rotation. Second, localized DNP effects can be evoked by directly attaching a metal-ion binding chelate tag to biomolecules. We will show the effect of protons, particularly within side-chain methyl groups, on the effective

propagation as well as relaxation of enhanced polarization within a protein and demonstrate how protein deuteration can lead to significantly improved DNP enhancement. Finally, we have utilized DNP-enhanced NMR in order to enlighten the catalytic mechanism of a ribozyme. By a combination of nucleotide- as well as strand-selective isotope labeling and heteronuclear correlation-spectroscopy we have selectively probed interstrand contacts which allow us to elucidate the role of a divalent metal-ion co-factor in triggering functional conformational changes within the RNA molecule in frozen solution.

EPR/SSNMR ORAL SESSION

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149 Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger.

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The discovery of a truncated cross-effect in dynamic nuclear polarization (DNP) NMR that has the features of an Overhauser-effect DNP (OE-DNP) will be discussed. The apparent OE-DNP, where minimal μw-power achieved optimum enhancement, was observed when doping Trityl-OX063 with a pyrroline nitroxide radical that possesses electron withdrawing, tetracarboxylate substituents (tetracarboxylate-ester-pyrroline or TCP) in vitrified water/glycerol at 6.9 T and at 3.3 to 85 K, in apparent contradiction to expectations. While the observations are fully consistent with OE-DNP, similar to the OE DNP observed in insulating BDPA sample recently, we discover that a truncated cross-effect (tCE) is the underlying mechanism, owing to TCP's shortened T_{1e}. We take this observation as a guideline, and demonstrate that a crossover from CE to tCE can be replicated by simulating CE of a narrow-line (Trityl-OX063) and a broad-line (TCP) radical pair, with a significantly shortened T_{1e} of the broad-line radical.

EPR/SSNMR ORAL SESSION

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150 Breaking Concentration Sensitivity Barrier by Larger Volumes: Photonic Band-Gap Resonators for mm-Wave EPR and DNP of Microliter-Volume Samples.

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High field/high frequency (HF) EPR of liquid aqueous biological samples remains to be very challenging. The main obstacle steams from high dielectric losses associated with non-resonant absorption of millimeter waves (mmW) by water and other polar molecules. Dimensions of single mode resonators also scale down with mmW wavelength. For these reasons, the optimal volume of aqueous samples for single mode mmW resonators rarely exceeds ca. 100 nl at 95 GHz. The technical problems encountered by DNP NMR of liquid aqueous samples are even greater because the optimal sample volume for static NMR is about 1,000-fold greater (i.e., 100-200 μl). Here we describe a radically new line of high Q-factor mmW resonators that are based on one-dimensional photonic band-gap (PBG) structures, which alleviate some of the abovementioned problems. The resonant structure is based on creating a defect in all-dielectric 1D photonic crystal split by a metal mirror in the middle. A sample (either liquid or solid) up to ca. 5 μl in volume is located on the top of the metallic mirror, corresponding to the E=0 node, and the position of the metal mirror is adjusted for the frequency tuning. The dielectric layers are composed of λ/4 ceramic discs with alternating dielectric constants. A resonator prototype with Q≈520 was built from an 8-layer dielectric structure consisting of alternating λ/4 discs of YTZP and alumina and tested at 94.3 GHz. Nanoporous ceramic disc of 50 μm in thickness was employed as an aqueous sample holder with tunable dielectric constant. Experimental single-scan room temperature 94.3 GHz EPR spectra of 1 μM of aqueous solution of nitroxide Tempone demonstrated signal-to-noise ration of ca. 100. The PBG resonator design is readily scalable to 200 GHz as demonstrated by initial DNP experiments at 300 MHz ^{1}H frequency.
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EPR/SSNMR ORAL SESSION

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151 Optical Room Temperature ^{13}C Hyperpolarization in Powdered Diamond.

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Nitrogen Vacancy (NV) centers in diamond are an attractive platform for dynamic nuclear polarization (DNP) of nuclear spins, particular because they are electronic spins can be optically polarized at room temperature with modest laser powers. In the quest towards NV driven DNP, nanodiamond powder is particularly attractive: they have huge surface areas (>6700 mm^2/mg for 100nm particles), and one could arrange for a close physical contact between the polarized NVs and external nuclear spins.

Indeed the goal of optically "*hyperpolarized nanodiamonds*" has been a long-standing one; yet the strong orientational dependence of the spin-1 NV centers has remained challenging to surmount.

In this work, we overcome these challenges to optically hyperpolarize diamond powder, obtaining high bulk ^{13}C polarization (>0.3%) comparable to the best results in single crystals [1]. We have developed a new, remarkably simple, low-field optical DNP technique that proves to be fully orientation independent. Unlike conventional DNP, our regime exploits the fact the NV electrons can be polarized independent of field, and low-field can be used advantageously to reduce the broadening of the electronic linewidth. Our technique also allows simple control of the hyperpolarization direction, which only depends on the direction of microwave sweeps across the electron spectrum [2].

Based on this technique, we have constructed a low-cost, pencil-sized micro-diamond "hyperpolarizer" that is capable of hyperpolarizing 5um diamond particles. The device is ultraportable and can retrofit any exisiting NMR magnet and deliver hyperpolarized diamond particles with high throughput. The device also opens up several avenues for harnessing the biocompatible surface-functionalized nanodiamonds as MRI tracers.

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EPR/SSNMR ORAL SESSION

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152 Pulsed Magnetic Resonance with a Free-Electron Laser.

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The most powerful magnetic resonance methodologies require sequences of powerful electromagnetic pulses in which the duration, spacing, power, and relative phase are independently controllable. For NMR, and for pulsed EPR at frequencies below 100 GHz, the desired pulse sequences can be generated electronically and then amplified to kW levels using commercially-available amplifiers. However, in the highest-field NMR magnet that is commercially-available now (23.5 T, 1 GHz proton NMR frequency), the Larmor precession frequency for spin-1/2 electrons is 660 GHz; and the recently-demonstrated 32 T superconducting magnet at the NHMFL pushes the Larmor frequency to nearly 900 GHz. At the current time, it is difficult to generate a programmable sequence of phase-coherent pulses with the kW peak powers and nanosecond durations needed to realize the potential of high-power pulsed electron magnetic resonance at magnetic fields above 3.5 T. The UC Santa Barbara Free-Electron Lasers (FELs), which generate high-power quasi-continuous-wave (cw) pulses between 0.24 and 4.5 THz, are now being used to drive a pulsed EPR spectrometer at 8.5 T (240 GHz). This talk will include a discussion of methods we have developed for converting the FEL output into a sequence of one or two pulses with durations as short as a few ns, resonator-free $\pi/2$ times below 10 ns, and, recently, multi-step phase-cycling. These pulse sequences, together with a home-built EPR spectrometer, have enable measurements including Rabi oscillations, longitudinal and transverse relaxation times, and "instantaneous spectral diffusion" in systems including Nitrogen impurities (P1 centers) in diamond, and stable free radicals in both solid and solution phases. The outlooks for generating more complex pulse sequences, for moving to higher frequencies and fields,

and for FEL-powered pulsed dynamic nuclear polarization (DNP) and electron-nuclear double resonance (ENDOR) will also be discussed. *This work is supported by the NSF under grants DMR-1626681 and MCB-1617025.*

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153 Pulsed and 'in-situ' EPR at 395 GHz.

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We describe a 395 GHz Electron Paramagnetic Resonance (EPR) spectrometer operating in both cw and pulsed mode. The frequency matches the frequency of the gyrotron-based 600 MHz Dynamic Nuclear Polarization (DNP) setup and can be used for in-situ EPR in liquid and solid state DNP. The spectrometer source is a solid state multiplication chain delivering 20 mW over a 390-400 GHz band, with the detection system primary element a 2nd harmonic mixer with its 195 GHz local oscillator (LO) generated by a similar multiplication chain (both Virginia Diodes Inc.). A quasi-optical (QO) bridge provides for attenuation, isolation, and polarization control. The linearly polarized millimeter-wave pulses excite the electron spins in the sample, currently without resonator. The signal is detected in the perpendicular polarization. We show results of the relaxation times of impurities in MgO measured by 395 GHz pulsed EPR at 14 Tesla, and of various radicals used in Dynamic Nuclear Polarization (DNP). The set-up allows to measure the EPR spectrum of the electron spins in solutions used in 'in-situ' in the DNP setup, and also allows to directly determine the amplitude of the microwave B_1 field at the sample. *This work was supported by the User Collaboration Grant Program of the National High Magnetic Field Laboratory. The National High Magnetic Field Laboratory is funded by the NSF Division of Materials Research (DMR 1157490 and DMR 1644779), and by the State of Florida.*

EPR ORAL SESSION

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154 Development of a High Field Nanoscale EPR System using NV Centers in Diamond.

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The nitrogen vacancy (NV) center, an atomic defect within diamond, has a unique electronic structure that allows for initialization of the spin state through optical excitation and subsequent spin state detection through the measurement of fluorescence intensity. A combination of spatial fluorescence imaging and anti-bunching measurements allow for the identification and measurement of a single NV center at room temperature. These properties enable optically detected magnetic resonance (ODMR) of single NV centers. The long coherence time of a single NV center makes it a promising quantum sensor for the nanoscale magnetic environment; extending the capabilities of electron paramagnetic resonance (EPR) to single spin levels.[1]NV-based EPR has been well studied at low magnetic fields, but has yet to be extensively studied at high magnetic fields, where an increase in spectral resolution allows for the clear identification of spectral features. Instrument design requires careful considerations to allow for optical access in conjunction with sufficient coupling for microwave excitation at the sample stage. NV centers must also be fabricated such that they are correctly oriented along B_0, possess long coherence times, and are in close proximity to target spins. We have built a high-field ODMR system consisting of high-frequency microwave components, a 12.1 T superconducting magnet, ODMR detection system, microscope system, and sample stage.[2] In this presentation, I will discuss our recent advancements in a high-field NV-based ESR experiment based on the high-field ODMR system. In particular, the implementation of pulse shaping to expand the spectral overlap of microwave excitation and double electron-electron resonance measurements of substitutional nitrogen centers in diamond are discussed. *This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).*

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EPR ORAL SESSION

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155 Automated DEER Data Processing using Bayesian Inference.

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Tikhonov regularization remains the most popular method for inferring distance distributions, $P(r)$, from DEER data. Its main advantage over other methods is its non-parametric nature, which allows it to recover $P(r)$s with nearly arbitrary shape. However, it is not without drawbacks vs parametric model-based approaches. We present the recent integration of robust, reliable, and automated regularization level selection and a Bayesian hierarchical model to infer distance distributions from DEER data. Together, these methods can overcome challenges to non-parametric analysis of DEER data, including nuisance parameter determination and uncertainty quantification.

EPR ORAL SESSION

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156 Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition.

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Pulsed Dipolar Spectroscopy (PDS) methods, such as Double Electron Electron Resonance and Double Quantum Coherence, are powerful methods for studying the structure and function of biological systems. In PDS, a dipolar signal is acquired from the interaction between a pair of spin labels, from which the distance distribution between them, P(r) may be obtained between the distance ranges of 1 to 10 nm. However, due to the ill-posed nature of the inversion of the dipolar signal to yield the P(r), one must resort to regularization or model fitting methods to obtain reasonable results. The method of Tikhonov regularization (TIKR) is commonly used, but it relies heavily on the choice of regularization parameter that yields a compromise between good resolution and stability of the P(r). Model fitting methods, on the other hand, require a priori model functions to estimate P(r), which may not accurately represent the actual distance distributions. This is especially true if the P(r) is multimodal. We developed a new and objective approach based on singular value decomposition (SVD) that yields an optimum approximate solution, obviating the need for regularization.[1] Instead of solving for the complete distance distribution all at once, the method finds the optimal distribution value at each distance or distance range by determining each of their different singular value cut-offs. The new method ensures optimal convergence at all distance ranges, while preventing a premature or unstable solution at some or all distance ranges. We tested the new SVD method on several model and experimental dipolar signals with unimodal and multimodal distributions. The method yields high resolution P(r) without any spurious peaks or negative P(r)'s and consistently performs better than TIKR. The new method can successfully reconstruct multimodal distributions, both overlapping and independent, with varying distribution widths.

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EPR ORAL SESSION

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157 Electron Spin Resonance with Quantum Microwaves.

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In electron-spin resonance (ESR) experiments, the quantum nature of the microwave fields emitted by the spins during their Larmor precession is usually neglected. Using a Josephson parametric microwave amplifier and a small mode volume super-conducting microwave ESR resonator, we first demonstrate the operation of an ESR spectrometer where the detection sensitivity is limited by quantum fluctuations of the microwave field instead of thermal or technical noise[1]. Applied to the detection of an ensemble of bismuth donors in silicon, the spectrometer reaches a sensitivity of 65 spins/$Hz^{1/2}$ [2]. Another path to increase the sensitivity is by generating squeezed vacuum in the detection waveguide, reducing the amount of noise beyond the quantum limit[3].

Finally, the use of a high-quality-factor small-mode-volume ESR resonator also enhances the likelihood of spin relaxation by spontaneous emission of a microwave photon. This effect, predicted by E. Purcell, is large enough in our experiment to become the dominant spin relaxation mechanism. Sub-second relaxation times are achieved, a three-orders of magnitude enhancement compared to the non-radiative relaxation time[2,4]. This provides a novel and general way to initialize spin systems on-demand.

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EPR ORAL SESSION

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158 Signal Enhancement by Constructive Combination of Transmission and Reflection ESR signals using Non-Resonant Transmission Line Probe Detection.

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New spin resonance experimental arrangements often prioritize sensitivity over 'ease of use' considerations[1]. Here we present an experimental arrangement using a non-resonant transmission line(TL) probe that is both simple and sensitive. The non-resonant probe is paired with a highly-sensitive custom microwave bridge[2] which recuperates sensitivity lost due to the probe's low Q. Most TL ESR measurements involve resonant structures with samples placed above the strip lines[1]. Invariably, this arrangement introduces non-uniform B_1. In absence a stationary wave (non-resonance), B_1 is uniform between the signal line and the ground plane as well as along the length of a microstrip TL[7].Therefore, this greatly relaxes sample placement restrictions. The non-resonant 50 Ω TL used in this study has a 0.76 mm between the signal line and the bottom ground plane for sample placement. The ESR signal (absorption and dispersion) is detected from the transmission and the reflection components of the microwave. Combining both components in theory should enhance the signal-to-noise ratio(SNR) by approximately a factor of √2 for the same acquisition time. Verification of the non-resonant TL detection scheme's performance with a 50 μmol L^{-1} TEMPO/ethylene glycol solution indicated enhanced SNR (20 % improvement, after normalizing for sample volume and microwave power) compared to a commercial ESR system equipped with a high-Q resonator. This result was achieved in a format with enhanced ease of use. Further enhancement was demonstrated by pairing a custom magnet with smaller coils with the non-resonant TL probe to decrease sweep time. This modification further enhanced the SNR >100-fold compared to an equivalent time measurement in the commercial ESR system.

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EPR ORAL SESSION

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159 Multi-Frequency Pulsed EPR and DEER Using Rapidly Tunable Superconducting Microresonators.

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Superconducting microresonators have dramatically enhanced the detection sensitivity of conventional electron paramagnetic resonance (EPR) with commercially available volume resonators. Recently, single-shot detection of 10^7 spins has been demonstrated at 2 K using coplanar waveguide (CPW) resonators[1,2] and further improvements in the readout at milliKelvin temperatures have enabled detection of ~1000 spins[3,4] using lumped element resonators. In order to extend the applicability of superconducting resonators to pulsed EPR experiments where multiple resonance frequencies are required, such as double electron-electron resonance (DEER), a method of tuning the resonance frequency post-fabrication is desirable. Conventional methods of tuning the resonance frequency using superconducting quantum interference devices are incompatible with the high magnetic fields that are typically necessary for X-band EPR. In this talk, we discuss frequency-tunable superconducting coplanar photonic bandgap resonators fabricated from thin films of superconducting NbTiN.[5] The resonance frequencies of these resonators can be continuously tuned by applying small DC currents that modulate the kinetic inductance of the superconductor. This method of tuning the resonance frequency is compatible with high magnetic fields. In this way, we demonstrate resonance frequency shifts as much as 100 MHz at 7.6 GHz and 275 mT in no more than ~270 ns without change in the quality factor. Using our frequency-tunable resonators, we demonstrate three-pulse DEER with ^{31}P and ^{75}As donors in a ^{28}Si sample. The EPR frequencies of the two donors are 33 MHz apart at 275 mT. We are able to address both donors by rapidly shifting the resonance frequency during the pulse sequence. Due to our ability to maintain a high quality factor of 3000 at both donor frequencies, we estimate that the detection sensitivity of our measurement is an order of magnitude better than conventional DEER with low-Q single-mode resonators.
Supported by NSF DMR-01420541 and ARO W911NF-13-1-0179 (Princeton) and DOE DE-AC02-05CH11231 (LBNL).

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EPR ORAL SESSION

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160 Effect of Multiphoton Transitions on Detection of Long Electron Spin Relaxation Times by Double Modulation ESR Spectroscopy.

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In recent years' studies of spin system (spin qubit) containing very long relaxation times (transverse, T_2 and longitudinal, T_1) are of interest due to their potential application in quantum information technologies. The ability of Pulsed ESR to extract narrow homogeneous (spin packet) line, has been used to deduced T_1 and T_2 of the monitored spin system. Several decades ago it was suggested that the CW-ESR method based on modulation sidebands known as Double Modulation ESR, DMESR, can be also used as complementary method of Pulsed ESR in detection very narrow "spin packet-like" line from an inhomogeneous line[1]. Early theoretical studies of modulation sidebands and DMESR spectral lines were mostly based of semi-classical approach by applying modified Bloch equations[2] or nonlinear radio-frequency absorption formalism[3]. However, modulation effects in CW-ESR spectroscopy recently was revised and explained by introducing multi-photon transitions[4,5]. In the present consideration description of DMESR spectrum will be discussed by employing newly suggested multiple photon description of CW-ESR spectra. It is shown that lineshaps and saturation effects of the DMESR spectra detected for well-defined standard system with long relaxation times, E' defect in irradiated vitreous SiO_2, can be more accurately described by applying later description.

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EPR ORAL SESSION

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161 Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region.

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THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, has been developed 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]Wewill mainly focus on the recent developments of the torque magnetometry[5]and mechanically detected ESR[6]measurements using a commercially available membrane-type surface stress sensor, and its application to the metal protein systems.

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EPR ORAL SESSION

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165 Redox, Oximetric and Vascular Imaging Provide Insight into the Tumor Microenvironment.

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Tumor microenvironment may determine tumor cell evolution, tumor phenotype and its aggressiveness. We have used non-invasive imaging in preclinical models to characterize tumor oxygen level, redox state and vascular structure.

Metastatic and non-metastatic tumors E0771 tumors show significant differences in their vascular system, tumor oxygenation and tumor redox state. Results from EPR oximetry, EPR redox imaging and Doppler ultrasonography were in agreement with immunohistochemistry and Western blot data showing enhanced oxidative stress, microvascularization and EMT markers in more invasive tumors. These changes were accompanied by a slower growth rate, higher vascularization, and indications of oxidative stress in more aggressive tumors. In a different model of orthotopic breast cancer, 4T1 we demonstrated that ultrasound-sensitive oxygen microbubbles are an effective way to increase tumor oxygenation for several minutes. EPR redox mapping and oximetry, especially in combination with other non-invasive imaging methods provides a powerful window into tumor microenvironment.

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EPR ORAL SESSION

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166 Pre-clinical EPR Imaging System at 800 MHz.

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An electron paramagnetic resonance (EPR) imaging system has been designed and built at West Virginia University. The imaging system will be used for pre-clinical and clinical studies. A semi-digital approach was implemented in the design using an arbitrary waveform generator (AWG) with the bandwidth of 120 MHz. The AWG output is mixed with a constant frequency source to achieve the frequency of interest. A novel approach to resonator tuning, discrete auto-frequency control (DACF), was developed. The DACF periodically produces short (10-100 ms) and wide (1-2 MHz) frequency scans that briefly interrupt 'normal' data acquisition. The EPR system continually switches between the tuning and operating modes. DACF facilitates implementation of the rapid scan (RS) methodology, especially when used in vivo. In addition, a digital feedback system was used to automatically adjust the amplitude and phase of the scans. RS EPR imaging results at 800 MHz will be presented that include real-time co-imaging with positron emission tomography (PET). Second generation RS deconvolution algorithm will be described[1].

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EPR ORAL SESSION

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167 Molecular Oxygen: Extent of Variability in Time and Location in Preclinical Tumors.

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Tumor hypoxia correlates with radiation treatment failure in preclinical and clinical subjects. Recently, we showed that increased cure treating murine FSa fibrosarcomas with radiation boosts defined by EPR pO2 images each tumor hypoxic region compared with radiation boosts to well-oxygenated tumor. This is the first data in mammalian tumors demonstrating increased treatment efficacy from local therapy. Pulsed electron paramagnetic resonance (EPR) spin-lattice relaxation (SLR) pO_2 was used to generate images of absolute molecular oxygen in ~1 mm voxels in leg tumors of mice with ~ 1 torr pO_2. SLR avoids sensitivity of pO2 measurement to the concentration of the soluble spin probe. MRI defined the FSa Fibrosarcoma boundaries in a C3H mouse leg. MRI was registered with EPR pO_2 image. This identified all hypoxic tumor voxels defined as pO_2 less than or equal to 10 torr. Separate experiments defined a whole tumor dose found to cure 15% of tumors. A boost dose was delivered to 100% of hypoxic voxels. This was compared in a randomized experiment to a similar volume boost to well-oxygenated voxels. Rapidly printed conformal 3D printed tungsten loaded plastic blocks defined the radiation boosts. A group of 53 mice demonstrated increased tumor control (60%) using a boost to hypoxic tumor relative to a boost to well-oxygenated tumor (28%) (p=0.04). In the above, three sequential ten minute images in the immediate sequence were obtained. Higher apparent pO2 was seen throughout the first image. In the first image high bolus concentration of the spin probe appears to have overwhelmed the spin-lattice relaxation's immunity to trityl concentration relaxation shortening. In the second pair of images smaller overall variations in pO2 values were seen. This above data ignored, for the FSa tumors the third image. The hypoxic boost provided only 60% control, less than the 95% control expected from separate tumor control dose-finding experiments. The second kind of mouse tumors, MCa4 mammary carcinomas have also been investigated. These cancers were also grown in the gastrocnemius muscle of the legs of C3H mice. The third image compared with the second image, also showed some temporal variability of the 10 torr hypoxic volumes. Similar to the FSa, the radiation blocks based on the second image treated the fraction of the tumor not treated in the third image by all but a few percents of the hypoxia in the hypoxic boosts. MCa4 tumors, however, are not as compact as the FSa tumors. However, oxygen concentrations for the tumors show slightly different volumes with pO2 below 10 torr between the 2nd and 3rd images. These indicate either spin probe distribution changes, noise, or real transient oxygenation changes.

EPR ORAL SESSION

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170 Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.

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Water soluble triarylmethyl (TAM) radicals represent a unique family of stable paramagnetic probes which have found numerous in vivo biomedical magnetic resonance applications. Their use as hyperpolarizing agents of ^{13}C labeled metabolites (such as [^{13}C]-pyruvate) allows to monitor in real time the biochemistry of living organisms, including humans, by MRI/MRS. They possess long relaxation times (narrow linewidths), high stability in biological media and depending on their particular structure, show sensitivities to important physiological parameters such as oxygen, pH, inorganic phosphate (Pi), enzymatic activities, etc. In this talk, we will describe the recent synthetic developments of TAM paramagnetic probes carried out at the In Vivo Multifunctional Magnetic Resonance center at West Virginia University such as the grafting on dextran polymer, the PEGylation in other to increase biocompatibility, the synthesis of a TAM spin label or a highly hydrophilic sulfonated TAM. Finally, we will present the development of alkaline phosphatase (ALP) sensitive paramagnetic probes to enable imaging of ALP activities using EPR a concept that can be extended to other enzymes.

EPR ORAL SESSION

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171 The CHEESY Renaissance of Fourier-transform Detected Hole Burning in EPR.

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The concept of hole burning was introduced to pulsed EPR in the 1990s based on inspiration from optical spectroscopy.[1] For single-crystalline samples, the narrow hole pattern permitted detection of a free induction decay (FID) and application of concepts from Fourier-transform NMR. For glassy frozen solutions that are much more common in application work, the Fourier-transform approach fails, as the FID of the anisotropically broadened holes decays within dead time. Therefore, the multiplex advantage of FID detection was given up and the holes were instead observed by electron-electron double resonance.[2] Echo-detection was not attempted for lack of bandwidth.

New generation pulsed EPR spectrometers based on fast arbitrary waveform generators allow for chirp echo detected EPR spectroscopy (CHEESY) up to 800 MHz detection bandwidth with excitation up to 2.5 GHz bandwidth.[3] Furthermore, the pulse shaping capability of such spectrometers allows for hole burning at the best sensitivity/resolution compromise for a given problem. These developments make hole burning with Fourier-transform detection of echoes attractive, as we have recently demonstrated for the CHEESY equivalent of ELDOR-detected NMR.[4]

This talk explains the general principles of detecting intermediate-strength interactions via hole burning and of performing 2D correlation experiments in such a context. Three types of systems are discussed where the approach can be useful. The concepts are illustrated on the examples of CHEESY-detected NMR and of a HYSCORE-type spectral hole burning experiment.

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EPR ORAL SESSION

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172 Development of ELDOR-detected NMR Spectroscopy at 115/230 GHz.

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Electron-electron double resonance (ELDOR)-detected NMR (EDNMR) spectroscopy is an EPR-based hyperfine spectroscopy developed in the last two decades. The application of this method becomes more popular in recent years due to the availability of high magnetic field, which is employed to conquer the overlapping between central blind spot and NMR signals, especially for low gyromagnetic ratio nuclear spins. Compared with other commonly used hyperfine spectroscopy, for instance, ESEEM (electron spin echo envelop modulation) and ENDOR (electron nuclear double resonance), HF EDNMR has advantages of higher sensitivity and finer spectral resolution enabling high-resolution hyperfine spectroscopy at room temperature. On the other hand, EDNMR usually requires precise control of the pulse intensity which is often challenging for HF EPR systems. In this presentation, we present the principle and implementation of EDNMR in our 115/230 GHz EPR spectrometer at USC. In addition, we discuss room temperature applications of HF EDNMR on solid-state spin systems.

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EPR ORAL SESSION

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173 ^{2}H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates.

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Electron-nuclear double resonance (ENDOR) permits to detect nuclei strongly coupled to paramagnetic centers. In protein studies, ^{2}H-ENDOR is a powerful tool to investigate hydrogen bond networks involved in fundamental processes such as proton-coupled electron transfer. Beside its benefits, ENDOR suffers from low sensitivity and line shape artefacts for small hyperfine couplings. Recently, cross-polarization edited ENDOR (CP-ENDOR) with improved sensitivity for large proton couplings was proposed as an alternative to the well-established Davies ENDOR.[1-3]

Here, we present that CP-ENDOR works also on ^{2}H, an $I = 1$ nucleus, with improved performance for detection of small couplings. We demonstrate this on a single crystal of deuterated malonic acid and a powder sample of perdeuterated BDPA. Furthermore, we employed ^{2}H CP-ENDOR to investigate the structure of an amino tyrosyl radical intermediate ($NH_2Y^\bullet$) trapped during the long-range radical transfer in *E.coli* ribonucleotide reductase. We were able to determine the detailed conformation of the amino group in this intermediate and establish a relationship between the conformation and the enzymatic activity.[4] Of particular importance for this ENDOR analysis were the absence of spectral blind spots and the improved orientation selectivity in CP-ENDOR as compared to Mims ENDOR. While Mims ENDOR is commonly affected by spectral blind spots and requires non-selective mw pulses, which reduce the orientation selectivity, we were able to recover the full, detailed hyperfine tensor line shape from 2D CP-ENDOR experiments.

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EPR ORAL SESSION

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174 Exploring Frequency-swept Excitation for Distance Measurements of Spin *S* = ½ Systems.

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Technological advances in the last years enabled by Arbitrary Waveform Generators (AWGs) provide access to frequency-swept pulses for EPR. Shaped pulses can provide inversion over a wide frequency range and selective excitation.[1] The former promises higher sensitivity for systems with broad spectra, e.g. metalloproteins; the latter can enable more complex pulse sequences which were previously not possible due to pulse imperfections. At Q-band frequencies, broadband pulses were so far mainly exploited to enhance the sensitivity of distance measurements of high-spin systems.[1] Here, we explore the potential gain and current limitations for measurements with shaped pulses of spin S = ½ centers, in particular Cu(II) and the more commonly used nitroxide. Complications in the extraction of distance distributions due to high-spin effects are absent. Using a recently developed Q-band broadband resonator,[2] we explore ultra-wideband (UWB) Double Electron Electron Resonance (DEER) measurements of a bis-Cu(II) model compound. Comparison to X-band measurements performed with the widely used MS3 split-ring resonator (Bruker) shows that the Q-band experiments benefit from an order of magnitude higher signal intensity while nearly a similar fraction of the spectrum can be excited within one measurement. Orientation selectivity in Cu(II) UWB DEER is found to be similar as in Relaxation-induced Dipolar Modulation Enhancement (RIDME) experiments for this system. Cu(II) UWB DEER sensitivity with shaped pump and/or shaped observer pulses is assessed. Selective excitation provided by frequency-swept pulses is exploited for dynamically decoupled distance measurements between nitroxide spin labels. In these experiments, multiple refocusing increases the coherence decay time.[3] Yet to refocus the dipolar interaction, an increased number of pump pulses is needed for multi-pulse DEER. Improved artefact suppression by shaped pump pulses has been shown for 5- and 7-pulse DEER.[4,5,6] Optimization of frequency-swept excitation of the observer as well as the pump pulses is explored.

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EPR ORAL SESSION

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175 DEER Updates are Available: Upgraded Sensitivity after RELOAD and Unmodulated Background Suppressed with the ROOPh.

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Over the past two decades, pulsed electron-electron double resonance (PELDOR), also known as double electron-electron resonance (DEER), has emerged as one of the major tools in structural biology and materials science to measure distances in non-crystalline systems in the nanometer range. However, for some of the most important classes of biological systems, such as membrane proteins, applicability of DEER is often restricted by short electronic phase memory time, which determines the signal-to-noise ratio (SNR) and the range of the longest accessible distances. Signal losses exceeding two orders of magnitude due to spin-spin relaxation are rather common in DEER experiments. Another serious problem is the presence of unmodulated background in the DEER traces, hindering the extraction of structural information. At present, the problem is resolved by acquiring a DEER trace significantly longer than the time scale of intramolecular dipolar modulations resulting in an additional, sometimes dramatic, signal loss. Here, we address the DEER sensitivity issue with a novel, albeit simple, Relaxation Optimized Acquisition (Length) Distribution (RELOAD) detection scheme. Specifically, by using 4-pulse DEER-RELOAD and two membrane protein complexes as examples, we demonstrate that dividing the acquisition of the DEER trace into just two dipolar evolution segments improves SNR by a factor of ~3. We also demonstrate how the unmodulated background can be suppressed in an

acquired DEER signal by Refocusing its Out-Of-Phase (ROOPh) components, however, at unavoidable cost of a decreased SNR due to imperfections of the three additional pulses. Fundamental differences between the in-phase and the refocused out-of-phase DEER signals are also discussed. *Supported by U.S. DOE Contract DE-FG02-02ER15354.*

EPR ORAL SESSION

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200 A High-Q Anapole Microresonator for Inductive-Detection Electron Paramagnetic Resonance Spectroscopy.

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We report the design and fabrication of a planar anapole microresonator with a high fill factor as well a high quality factor (Q-factor).[1] Planar microresonators offer increased sensitivity for EPR spectroscopy of small-volume samples. In these structures, the B_1 field is concentrated over a small volume, which results in an active volume that is much smaller than that of cavity resonators.[2-4] Thus, planar microresonators provide fill factors that are several orders of magnitude higher than those of cavity resonators. In practice, however, miniaturization of the resonant structure typically results in deterioration of the Q-factor, which can offset the gain in sensitivity realized by fill-factor increases. In the current design, we take advantage of recent developments in anapole metamaterials. By reducing radiation losses, this design can potentially provide a gain of at least two orders of magnitude compared to presently reported structures, decreasing the absolute number of detectable spins from approximately 10^8 to approximately 10^6.

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EPR POSTER SESSION

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201 Picoliter Diamond NMR.

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NMR is a powerful technique for determining the composition, structure, and function of a variety of molecules, but the sensitivity is presently limited for for sub-nanoliter volumes. An emerging alternative approach is to replace inductive coils with non-inductive magnetometers based on Nitrogen Vacancy (NV) centers in diamond. In a first step, we used few-nm thick layers of NV centers doped into high-surface area nanostructured diamond to perform diamond NMR spectroscopy on ~1 pL of analyte[1]. I will present our recent work to improve the sensitivity and spectral resolution of diamond NMR by separating the polarization and detection steps. Analyte is prepolarized in a larger magnetic field (1.5 T) and then adiabatically flowed to a microfluidic diamond NMR detector at 14 mT. Separating the polarization and detection in this way provides nearly nuclear-T1-limited spectral resolution.

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EPR POSTER SESSION

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202 Locking and Tracking Magnetic Resonance Spectra of NV^- Center for Real-time Magnetometry.

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We describe new measurement methods for real-time magnetometry by locking and tracking magnetic resonance spectra of Nitrogen Vacancy (NV^-) centers in diamond. Real-time magnetometry has many uses from biology to nano-scale electronics. We focus on characterizing static magnetic fields and detecting ferromagnetic resonance from nanoscale magnetic devices, where the small device volume makes it difficult to use conventional techniques. The special intrinsic properties of diamond NV^- centers offer a path forward, but usability of NV^- center methods is limited by the requirement for sophisticated measurement techniques and post processing of measurement data.

This talk focuses on real time data processing and frequency control to lock & track the CW optically detected magnetic resonance (cw-ODMR) peak of NV^- centers. We use a custom-built differential rate detector and active feedback control (PID). The required circuitry is relatively inexpensive and easy to implement, and because we use digital frequency control as opposed to a voltage-controlled oscillator and microwave mixer, our scheme covers wider magnetic field ranges, limited by the signal generator. This method requires no post-processing of the data and it provides sensitivity (6 $\mu T/\sqrt{Hz}$) comparable to more traditional methods. This sensitivity is sufficient to measure the small change in stray magnetic field during ferromagnetic resonance of a nanoscale magnetic device.

EPR POSTER SESSION

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203 Better Resolution of High Spin Co Hyperfine at Low Frequency, L-band: Co-bovine Serum Albumin, A Model for Obtaining Co Hyperfine in High Spin Complexes of Biological Interest.

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X-band, 9.63 GHz, EPR spectrum for Co-bovine serum albumin (CoBSA) is much like the EPR spectrum for CoEDTA, but no Co hyperfine lines are resolved. In comparison, the L-band spectrum for CoBSA is much simpler in that four lines are clearly resolved. The lines are not evenly spaced, so an S-shape is assumed, and the linewidths vary. It is difficult to decide whether the first four resolved lines are hill- or S-shaped. The four resolved low field lines in the second derivative spectrum are S-shaped, suggesting that they can be assigned to $g_{eff\text{-}max}$. It is not clear whether the lines are for the [+/-3/2> state or for the [+/-1/2> state, but the [+/-1/2> state is assumed. The L-band spectrum has better resolution of Co hyperfine, a second confirmation (CoEDTA and CoBSA) that low-frequency spectra are better resolved for high spin Co. Taking the splitting of the low field lines in the second harmonic L-band spectrum, A_{max}=73 G and $g_{eff\text{-}max}$=7.2 (see figure). A simulation (Easyspin) of the spectrum for CoBSA is shown in the figure. EPR parameters from the simulation are $g_{eff\text{-}max}$=8.0 and $g_{eff\text{-}mid}$=4.22, and A_{max}=656 MHz (58.5 G) and A_{mid}=275 MHz (46.5 G). Although it is tempting to use the parameters from the simulation, the simulations are only consistent with broadened lines and the parameters may not be unique. Nevertheless, the simulation accounts for how spacing for the high field lines could be different than spacing for the low field lines. Thank you to T. Thelaner and T. Camenisch. *Supported by NIH P41 EB001980 (National Biomedical EPR Center) and UW-Milwaukee Research Growth Initiative.*

EPR POSTER SESSION

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204 Insights into the Catalytic Mechanism of [FeFe]-hydrogenase II from *Clostridium Pasteurianum*.

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Hydrogenases, which reversibly catalyze the reduction of protons to hydrogen gas, are broadly distributed as either [NiFe]- or [FeFe]-hydrogenases depending on the metal composition of the active site, and function with high turnover at low overpotentials. The [FeFe]-hydrogenases feature a unique active site, the H-cluster, which consists of a [4Fe4S] cubane with a cysteine thiolate linkage to a diiron site, the $[2Fe]_H$, which is further coordinated by CO and CN ligands and a dithiomethylamine bridge. A variety of investigations have focused on the mechanism of hydrogen

activation at the H-cluster, however, these studies have primarily been limited to a few model hydrogenases. Here, we focus on the [FeFe]-hydrogenase II from *Clostridium Pasteurianum* (CpII), which has unique biochemical properties compared to the well-characterized [FeFe]-hydrogenase I from *C. pasteurianum* (CpI). In this work, CW X-band EPR in combination with FTIR spectroscopy and potentiometric titrations are used to report on mechanistic states at defined oxidation-reduction potentials of catalytic transitions in CpII. The results demonstrate an altered population of catalytic intermediates and a shift in the midpoint potentials of the transitions compared to CpI under similar steady-state conditions. Collectively, this shows that small changes in the outer coordination sphere of the protein structure play an important role in tuning the specific redox properties, and in controlling the catalytic mechanism.

EPR POSTER SESSION

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205 Spin Dependent Charge Pumping and Spin Dependent Recombination Study of SiC/SiO_2 Interface Passivation.

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SiC/SiO_2 based metal/oxide/semiconductor field-effect transistors have enormous promise in high power and high temperature applications. However, this promise is limited by the quality of the SiC/SiO_2 interface. Post-oxidation NO anneals substantially improve the interface, increasing the effective channel mobility by about an order of magnitude. Quite recently, Lichtenwalner et al.[1] showed that the addition of barium results in a substantial further increase in mobility[1]. We have utlized two electrically detected magnetic resonance (EDMR) techniques to investigate the effects of barium on trapping centers near the SiC/SiO_2 boundary: spin dependent recombination (SDR) and spin dependent charge pumping (SDCP). These techniques probe different regions of the SiC bandgap at the SiC/SiO_2 boundary and slightly different physical loctions within the device. The SDR measurement is only sensitive to defects with energy levels near the middle of the SiC bandgap; SDCP is sensitive to levels throughout nearly the entire bandgap. SDCP measurements are exclusively sensitive to to defects very close to the SiC/SiO_2 boundary. The SDR measurements are senstitive to defects which extend slightly into SiC. Our study involves recently manufactured devices with Ba as well as NO passivation. We compared these two newer device types with older devices that were also subjected to NO passivation. The dominating interface spectrum for the newly manufactured NO passivated devices is a silicon vacancy (Vsi) in SDCP measurements. However, with SDR, we found that for the newly manufactured Ba passivated and NO passivated devices, significant contribution from a different defect is clearly present. The most suprising result of our study is the absence of a response from hydrogen-complexed E‘ centers in both new devices. In the older NO passivated devices, the E‘ centers are consistently present. This result may be of substantial technological importance. E‘ centers have been linked to the technologically important negative bias temperature instability[2].

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EPR POSTER SESSION

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206 Electric-Field Quenching of Magnetic Resonance in the Photoluminescence of p-Conjugated Polymer Films.

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Electric fields are central to the operation of optoelectronic devices based on conjugated polymers since they drive the recombination of electrons and holes to excitons in organic light-emitting diodes but are also responsible for the dissociation of excitons in solar cells. One way to track the microscopic effect of electric fields on charge carriers formed under illumination of a polymer film is to exploit the fluorescence arising from delayed recombination of carrier pairs, a process which is fundamentally spin dependent. Such spin-dependent recombination can be probed directly in fluorescence, by optically detected magnetic resonance (ODMR). Depending on the relative orientation, an electric field may either dissociate or stabilize an electron-hole carrier pair. Indeed, we find that the ODMR signal is quenched under

an electric field, but that, even at fields exceeding 1 MV/cm, this quenching saturates. This finding is in contrast to recent reports on complete ODMR suppression in polymeric photodiodes[1], demonstrating that Auger-type trionic interactions constitute the dominant carrier-pair dissociation process in organic electronics.

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 POSTER SESSION

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207 **^{2}H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates.**

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Electron-nuclear double resonance (ENDOR) permits to detect nuclei strongly coupled to paramagnetic centers. In protein studies, ^{2}H-ENDOR is a powerful tool to investigate hydrogen bond networks involved in fundamental processes such as proton-coupled electron transfer. Beside its benefits, ENDOR suffers from low sensitivity and line shape artefacts for small hyperfine couplings. Recently, cross-polarization edited ENDOR (CP-ENDOR) with improved sensitivity for large proton couplings was proposed as an alternative to the well-established Davies ENDOR.[1-3]

Here, we present that CP-ENDOR works also on ^{2}H, an I = 1 nucleus, with improved performance for detection of small couplings. We demonstrate this on a single crystal of deuterated malonic acid and a powder sample of perdeuterated BDPA. Furthermore, we employed ^{2}H CP-ENDOR to investigate the structure of an amino tyrosyl radical intermediate ($NH_2Y^{\bullet}$) trapped during the long-range radical transfer in E.coli ribonucleotide reductase. We were able to determine the detailed conformation of the amino group in this intermediate and establish a relationship between the conformation and the enzymatic activity.[4] Of particular importance for this ENDOR analysis were the absence of spectral blind spots and the improved orientation selectivity in CP-ENDOR as compared to Mims ENDOR. While Mims ENDOR is commonly affected by spectral blind spots and requires non-selective mw pulses, which reduce the orientation selectivity, we were able to recover the full, detailed hyperfine tensor line shape from 2D CP-ENDOR experiments.

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EPR POSTER SESSION

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208 **DFT Calculation of Zero-field Splitting in Extended Periodic Systems.**

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The zero-field splitting (ZFS, also known as magnetic anisotropy) is among the key EPR fingerprints that characterize the electronic structure and microscopic configuration of high-spin paramagnetic centers. Due to its complex nature, interpretation of the ZFS often relies on a combination of the experiment and the first-principles theory. In case of finite-size molecular systems, well-established framework for density functional theory (DFT) based calculation of both the spin-spin [1] and spin-orbit [2,3] ZFS contributions is available. However, to accurately predict the ZFS of high-spin centers in extended periodic systems (e.g. in crystals or at solid surfaces), it is desirable to diminish the finite-size effects. Thus, periodic DFT calculations based on the supercell approach have to be adopted.

Here, we present our recent progress in developing a framework for DFT calculation of the ZFS in extended periodic

systems: First, we demonstrate the accuracy of a recently reported method [4] to predict the spin-spin contribution to ZFS within the supercell approach. As justified by benchmarking tests, this implementation combines chemical accuracy with the efficiency of the pseudopotential method. Furthermore, we present for the first time a pseudopotential based implementation of the perturbative approach [2], which allows to assess the spin-orbit contribution to ZFS. Finally, remaining challenges and limitations of DFT based ZFS calculations are discussed.

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EPR POSTER SESSION

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209 Exploring Frequency-swept Excitation for Distance Measurements Between Nitroxide Spin Labels.

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Technological advances in the last years enabled by Arbitrary Waveform Generators (AWGs) provide access to frequency-swept pulses for EPR. Shaped pulses can provide inversion over a wide frequency range and selective excitation.[1] The former promises higher sensitivity for systems with broad spectra, e.g. metalloproteins; the latter can enable more complex pulse sequences which were previously not possible due to pulse imperfections. At Q-band frequencies, broadband pulses were so far mainly exploited to enhance the sensitivity of distance measurements of high-spin systems.[1] Here, we explore the potential gain and current limitations for measurements with shaped pulses of spin S = ½ centers. For such systems, complications in the extraction of distance distributions due to high-spin effects are absent. While the talk will focus on ultra-wideband (UWB) excitation of Cu(II),[2] the poster will explore the use of frequency-swept pulses for distance measurements between the more commonly used nitroxide spin labels. To excite well separated bands within the narrower nitroxide spectrum for Double Electron Electron Resonance (DEER) experiments, selective frequency-swept pulses are exploited. Dynamically decoupled DEER experiments make use of multiple refocusing to increase the coherence decay time.[3] Yet to refocus the dipolar interaction, an increased number of pump pulses is employed. Artefacts can result due to non-ideal action of the pump pulses[3-5] as well as overlap of the observer and pump bands.[6]Additionally, crossing echoes can introduce artefacts if coherent observer and pump channels are used which can be alleviated by phase cycling.[7] Improved artefact suppression by shaped pump pulses has been shown for 5- and 7-pulse DEER.[4-6] Optimization of frequency-swept excitation of the observer as well as the pump pulses is investigated.

[1] A. Doll, G. Jeschke, *J. Magn. Res.*, **2017**, 280, 64-62.
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EPR POSTER SESSION

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210 Heisenberg Spin Exchange for Anomalous Diffusion in a Percolation Network.

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Heisenberg exchange (HE) between nitroxide spin probes has been measured as a function of spin probe concentration in the aqueous phase of the ion exchange membrane Nafion. The observed fast-motional ESR spectra were analyzed in terms of the first-order perturbation expressions given by Molin, Bales, and Peric, as well as the full slow-motional lineshape calculation of Freed and coworkers. In contrast to three-dimensional isotropic spin probe solutions, the HE dependence on concentration in the membrane is not linear. The results are interpreted in terms of anomalous diffusion within the percolation network of aqueous regions in the membrane. Differences between the various methods for determining HE from the spectrum are discussed.

EPR POSTER SESSION

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211 Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.

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Optimizing microwave transmission is important in the development of our low-powered DNP instrument for small sample volumes. Toward this end, we have been using frequency swept EPR and DNP in the same probe to characterize the delivery of microwaves into the sample. The intensities of single EPR scans are affected by many factors besides the microwave power density at the sample, making signal intensities alone an unreliable means for comparing different experimental arrangements. Instead, we have turned to using saturation experiments common in CW EPR as measures of microwave field strength. Calibrating these curves can be challenging since microwave field inhomogeneity effects can be large in DNP probes. To understand this, we have carefully characterized the EPR saturation of P1 centers in thin single crystal high pressure high temperature diamond samples. Simultaneous measurement of EPR saturation for these P1 centers and BDPA-benzene at X-band was used to validate the P1 saturation curve as a measure of microwave field intensity. We find the shape of the P1 center saturation curve is dominated by a distribution in relaxation times more strongly than our estimated microwave field inhomogeneity. Since this shape persists at both low and high static magnetic field, the peak in the curve provides a reliable measure of average microwave field strength at the sample. We can then use saturation of a standard P1 center sample as a basis for quantitative comparison of different probe configurations. This will help us compare different dielectric waveguides, coil geometries and MAS rotor configurations with respect to microwave field efficiency.

EPR POSTER SESSION

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212 Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis.

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Ethylene oligomerization is an industrially important route for linear α-olefins (LAO), especially 1-hexene and 1-octene, co-monomers for polyethylene.[1] Increasing demand for these LAO has propelled research into selective trimerization and tetramerization. The active catalyst is formed by adding an activator to the Cr^{I} or Cr^{III} metal complex in the presence of a PNP ligand (PNP = $Ph_2PN(R)PPh_2$) and a weakly coordinating anion such as $(Al(OC(CF_3)_3)_4)^-$ prior to the reaction. The complex can undergo ligand redistributions, reduction and disproportionation, resulting in the formation of various species with different oxidation states and as a result altered total electron spin. However, the precise nature and action of the active catalyst are still subject to debate.[1-2] In this project, 1-hexene was used as a substrate instead of ethylene due to instrumental limitations. Paramagnetic species from discrete catalyst precursors to in-situ catalysis were examined by continuous wave electron paramagnetic resonance spectroscopy (cw-EPR). One

major challenge is identifying the structure of these intermediate species, which will be approached by advanced pulse EPR experiments in combination with a quantum chemistry approach.

During activation and the following catalysis, we intend to identify the structure of intermediate species and this is hampered due to overlapping spectra. Thus, we aim to separate the arising spectra and assign their oxidation states and thus monitor the fate of the chromium species. We have tested a model system consisting of a mixture of discrete Cr^{I} and Cr^{III} precursors and recovered their individual spectra using an inversion recovery filter and assigned their spin and consequently oxidation states from transient nutation experiments. The use of this method on an activated Cr precatalyst will be illustrated for monitoring the various species.

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EPR POSTER SESSION

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213 Wireless Implantable Coil with Parametric Amplification for In Vivo Electron Paramagnetic Resonance Oximetric Applications.

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An implantable wireless coil with parametric amplification capabilities for time-domain electron paramagnetic resonance (EPR) spectroscopy operating at 300 MHz.is being developed. The wireless coil and lithium phthalocyanine (LiPc), a solid paramagnetic probe, were each embedded individually in a biocompatible polymer polydimethoxysiloxane (PDMS). EPR signals from the LiPc embedded in PDMS (LiPc/PDMS) were generated by a transmit-receive surface coil tuned to 300 MHz. Parametric amplification was made possible with an external pumping coil tuned to 600 MHz and placed between the surface coil resonator and the wireless coil.

Phantom studies showed significant enhancement in signal to noise using the pumping coil. However, no influence of the pumping coil on the oxygen-dependent EPR spectral line width of LiPc/PDMS was observed, suggesting the validity of parametric amplification of EPR signals for oximetry by implantation of the encapsulated wireless coil and LiPc/PDMS in deep regions of live objects. In vivo studies demonstrate the feasibility of this approach to longitudinally monitor tissue pO_2 in vivo and monitor acute changes in response to pharmacologic challenges. The encapsulated wireless coil and LiPc/PDMS engendered no host immune response when implanted for ~3 weeks and were found to be well tolerated. This approach may find applications for monitoring tissue oxygenation to better understand the pathophysiology associated with wound healing, organ transplantation, and ischemic diseases.

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EPR POSTER SESSION

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214 An Ultra-high Vacuum Electron Spin Resonance Spectrometer for the Investigation of Magnetic Atoms and Molecules at Surfaces.

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Magnetic atoms and molecules adsorbed on single crystal surfaces are model systems to investigate the quantum properties of matter at the smallest length scale. When deposited on suitable surfaces such as MgO/Ag(100), they show relaxation times of thousands of seconds at 2.5 K[1,2]. The localization of spins at the surface, however, limits the number of techniques that can be used to access their magnetic and coherence properties. Combining electron spin resonance with scanning tunneling microscopy allows the individual access of surface spins[3], but so far proved to effectively work only below 4 K. Here we propose a novel spectrometer operating in ultra-high vacuum that can perform ensemble-averaged electron spin resonance measurements on surface spins in a wide range of temperature (4-300 K). Using a coplanar waveguide scheme, it is possible to integrate surface preparation and in situ sample transfer to the measurement setup. Preliminary finite elements simulations indicate a sensitivity down to 10^{10}spins/Hz$^{1/2}$ at 4 K over a surface of 1 mm^2, thus confirming the potential of this design for the investigation of diluted magnetic centers at the surface.

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EPR POSTER SESSION

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215 Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.

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Water soluble triarylmethyl (TAM) radicals represent a unique family of stable paramagnetic probes which have found numerous in vivo biomedical magnetic resonance applications. Their use as hyperpolarizing agents of ^{13}C labeled metabolites (such as [^{13}C]-pyruvate) allows to monitor in real time the biochemistry of living organisms, including humans, by MRI/MRS. They possess long relaxation times (narrow linewidths), high stability in biological media and depending on their particular structure, show sensitivities to important physiological parameters such as oxygen, pH, inorganic phosphate (Pi), enzymatic activities, etc. In this talk, we will describe the recent synthetic developments of TAM paramagnetic probes carried out at the In Vivo Multifunctional Magnetic Resonance center at West Virginia University such as the grafting on dextran polymer, the PEGylation in other to increase biocompatibility, the synthesis of a TAM spin label or a highly hydrophilic sulfonated TAM. Finally, we will present the development of alkaline phosphatase (ALP) sensitive paramagnetic probes to enable imaging of ALP activities using EPR a concept that can be extended to other enzymes.

EPR POSTER SESSION

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216 Automated DEER Data Processing using Bayesian Inference.

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Tikhonov regularization remains the most popular method for inferring distance distributions, $P(r)$, from DEER data. Its main advantage over other methods is its non-parametric nature, which allows it to recover $P(r)$s with nearly arbitrary shape. However, it is not without drawbacks vs parametric model-based approaches. We present the recent integration of robust, reliable, and automated regularization level selection and a Bayesian hierarchical model to infer distance distributions from DEER data. Together, these methods can overcome challenges to non-parametric analysis of DEER data, including nuisance parameter determination and uncertainty quantification.

EPR POSTER SESSION

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217 Redistribution of EC-SOD Due to the R213G Variant Influences the Local Redox Environment in Bleomycin-induced Lung Injury.

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A naturally occurring human single nucleotide polymorphism (SNP) (R213G) in EC-SOD lowers its binding affinity to the matrix, increasing active EC-SOD in plasma and epithelial lining fluid. Mice engineered to express knock-in of the human SNP (R213G mice) are protected against intratracheal bleomycin-induced lung injury. We hypothesized that the redistribution of EC-SOD due to the R213G SNP will have site-specific effects on the redox environment.

Methods Wild type (WT) and R213G mice were treated with a single intratracheal dose of bleomycin (0.1 U/mouse). Blood, Bronchoalveolar fluid (BALF), and lungs were processed 7 days post treatment. $O_2^{\bullet-}$ was measured in blood, lung and BALF by Electron Paramagnetic Resonance (EPR) using CMH or CPH spin probes. H_2O_2 was measured in BALF by Amplex Red. GSH, GSSG, CyS, and CySS concentrations were measured by high-performance liquid chromatography (HPLC), and the redox potential (Eh) was calculated using the Nernst equation. The redox state of two isoforms of the thiol regulatory protein, peroxiredoxin (Prx), cytosolic Prx1 and mitochondrial Prx3 in lung homogenates were tested by redox western blots.

Results $O_2^{\bullet-}$ increased in all three compartments in bleomycin-treated WT mice. $O_2^{\bullet-}$ levels post-bleomycin was less in blood and BALF in R213G mice compared to WT. In contrast, H_2O_2 was higher in the BALF in bleomycin-treated R213G vs WT mice. Though EhCySS did not significantly change with either genotype or treatment in the three compartments, plasma CySS concentration significantly decreased in bleomycin-treated R213G mice. Lung EhGSSG decreased in both strains following bleomycin and was significantly more oxidized in WT compared to R213G mice. Oxidation of lung Prx1 increased similarly after bleomycin in both strains, though Prx3 was not impacted by genotype or treatment. (n=5-6)

Conclusion The redistribution of EC-SOD due to the R213G SNP imparted distinct site specific changes in the redox environment in mice exposed to bleomycin. Future study is needed to fully define the changes in the redox environment over time and how these changes impact redox sensitive signaling pathways responsible for the protective effects observed in the bleomycin-treated R213G mice.

EPR POSTER SESSION

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218 Allosteric Conformational Rearrangements of a Prokaryotic Cyclic Nucleotide-gated Ion Channel Probed with Pulsed Dipolar Spectroscopy.

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Cyclic nucleotide-gated (CNG) ion channels are tetrameric membrane proteins of the 'Kv' superfamily of voltage-gated potassium channels. CNG channels, along with the related hyperpolarization-activated cyclic nucleotide-gated (HCN) channels, are key components in several physiological processes of mammals including visual and olfactory signal transduction, cardiac pacemaking, and neuronal rhythmicity. CNG/HCN channels are activated by the direct binding of cyclic nucleotides (cAMP/cGMP) to a cytoplasmic cyclic nucleotide-binding domain (CNBD). Ligand-dependent conformational changes in the CNBD are allosterically coupled to pore opening by the so-called "C-linker" – an alpha helical domain situated between the pore and CNBD – but the mechanism by which these rearrangements are transduced to the pore is currently unknown[1,2]. To gain mechanistic insight into CNG/HCN channel gating, we have turned to a recently-discovered family of prokaryotic CNG orthologs[3]. Extensive screening yielded a channel from *Spirochaeta thermophila*, termed SthK, with favorable properties for biophysical characterization. We generated a cysteine-free construct of SthK and introduced nitroxide spin labels into the C-linker domain for double electron-electron resonance (DEER) spectroscopy. Intersubunit distance distributions obtained by DEER reveal a previously

unrecognized conformational rearrangement of the C-linker in the presence of activating cyclic nucleotide. In combination with patch-clamp electrophysiological recordings and mutational analysis, the DEER distributions identify structural conformations of the C-linker that underlie key functional states of the channel. Our results provide preliminary evidence of an agonist-dependent rearrangement of the C-linker domain of a CNG channel and may provide new insight into the complex gating mechanism in this important class of ion channels.

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EPR POSTER SESSION

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219 Effect of Freezing Rate on the Spin Dynamics of Finland Trityl.

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Triarylmethyl radicals, commonly referred to as trityls, are employed in biological applications due to their favorable stability and narrow spectral widths. One such application is the use of trityls as polarizing agents for dynamic nuclear polarization (DNP). It is important to understand the spin dynamics of these polarizing agents in order to tune radicals for optimal DNP enhancement. Pulsed electron paramagnetic resonance (EPR) techniques provide insight on the complex interactions in the spin system and reveal how variations in sample preparation affect the spin system. We show that the rate at which samples are frozen during preparation affects the distribution of trityls and their interactions in the frozen state. In particular, spin-lattice relaxation (T_{1e}) and double electron-electron resonance (DEER) measurements are correlated to the DNP efficiency of trityl solutions frozen at different rates. The results show large deviations in spin dynamics as a result of different freezing rates, emphasizing the importance of establishing reproducible methods of sample preparation.

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EPR POSTER SESSION

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220 Spin-labeled Nanobodies: A New Tool Towards EPR Studies in Cellular Environments.

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ATP-binding cassette (ABC) transporters pump substrates across the membrane by coupling ATP-driven movements of nucleotide-binding domains to the transmembrane domains, triggering the switch between inward- and outward-facing (IF and OF) conformations. DEER (Double Electron Electron Resonance) is a powerful technique to monitor the large-scale conformational transition of this class of membrane proteins, as shown for example by our study on the conformational cycle of the heterodimeric exporter TM287/288[1]. By combining molecular dynamics simulations and DEER we could also recently unveil the atomistic mechanism of the IF to OF transition of this protein in membrane bilayers[2]. Here we show how to characterize by EPR nanobodies targeting TM287/288 and the homodimeric exporter MsbA to unravel, respectively, further details of ABC transporters and to explore their use towards applications in cellular environments. In the first case, the nanobody aided the crystallization of the OF state of TM287/288, by binding to the extracellular region of this state. We confirmed by DEER that the Gd-labeled nanobody was specifically targeting the OF state of the nitroxide-labeled exporter in detergent solution, inducing a shift in the IF/OF equilibrium, responsible for the observed decreased ATPase activity. In the second case, a nanobody with high affinity towards the nucleotide binding domain of MsbA was investigated, which did not impair its ATPase activity. Effects induced by nanobody binding on the conformational transition of nitroxide- and Gd- labeled MsbA were monitored in detergent solution and nanodiscs. The presence of two Gd-labeled nanobodies bound to the nucleotide binding domains of MsbA during the nucleotide cycle allowed to follow the conformational cycle of the wild type unlabeled transporter

through detection of inter-nanobody distances. This paves the way for the use of Gd-nanobodies as reporters of the conformational transition of MsbA in cellular environments.

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EPR POSTER SESSION

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221 Update on the SharedEPR Network.

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This poster will describe the recent activities and progress made by the NSF-supported Research Coordination Network named "Supporting, Highlighting and Advancing Recent Developments in Electron Paramagnetic Resonance" (SharedEPR). The network has been established 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: facilitate the advancement of EPR methodology, instrumentation and techniques; foster cross-fertilization and establish new collaborative research opportunities within the U.S. EPR community; and establish international collaborations. The activities and support provided by the network will be summarized in this poster. In October 2017 the network sponsored a joint meeting between the SharedEPR network and the German EPR Priority Program Network SPP1601. The meeting was held at the Mohonk House, New Paltz, NY and was titled "EPR Present and Future." The results of this joint conference will be presented. The SharedEPR is also sponsoring a workshop following this RMC2018 conference titled "Software Tools for EPR Spectroscopy – Capabilities and Demonstrations." Details of this workshop will be presented.

EPR POSTER SESSION

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222 Magnetic Resonance, Index Compression Maps and the Holstein-Primakoff Bosons: Polynomially Scaling Exact diagonalization of Isotropic Multispin Hamiltonians.

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Eigenspectrum determination has long been a setback in the numerical simulation of the magnetic resonance spectra of multispin systems since the dimension of the Hilbert space of such systems grows exponentially with the number of spins -- a problem commonly referred to as the "curse of dimensionality". With the present poster, we illustrate two mathematical instruments which, when harmoniously combined, could greatly help surmount to a fair degree and in a systematic manner the curse of dimensionality. These are: 1) the Holstein-Primakoff bosons and 2) what we have termed the "index compression maps". These two allow a bijective mapping of (multi)spin states to integers. Their combination leads to the block diagonalization of the multispin Hamiltonian, thus a computationally exact way of diagonalizing the latter but which also scales polynomially with the number of spins. We also show that the eigenvectors and eigenvalues of the Liouvillian operator can be easily determined once those of the related multispin Hamiltonian are known. Interestingly, the method also enables an analytical characterization of the multispin Hilbert space -- a feat hardly attainable with other approaches. We illustrate the method here by showing how a general isotropic multispin Hamiltonian could be exactly diagonalized with very less computational cost. Nonetheless, we emphasize that the method could be applied to study numerous quantum systems defined on finite Hilbert spaces and embodied with at most pairwise interactions. *Funding for this research was provided by the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. [320951].*

EPR POSTER SESSION

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223 Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation.

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The Stochastic Liouville Equation (SLE) as first proposed by Kubo has seen extensive applications in magnetic resonance (EPR and NMR) due to the pioneering efforts by Jack Freed and collaborators. It is of common knowledge, though, that the SLE in its original formulation does not allow the spin system to approach thermal equilibrium with its environment. This is no inconsequential theoretical problem[1,2]. Indeed, in most magnetic resonance line shape calculations, ad hoc amendments to the SLE are required aimed none other but to allow an approach to equilibrium[2]. Moreover, the evolution of the density matrix describing a physical system must necessarily be of a completely positive, trace preserving (CPT) map nature[3]. At present, it is not clear whether the SLE or its subsequent modified versions are always CPT. In this talk, we present an alternative to the SLE, i.e. the Quantum Markovian Master Equation approach. We show that this method 1) naturally guarantees an approach to equilibrium on a time scale which can actually be computed, and 2) ensures that the dynamical map for the evolution of the effective spin density matrix is CPT. Without loss of generality, we shall focus in this talk on isotropic spin Hamiltonians with fluctuations due to interaction with the environment and discuss some interesting features of the renormalized master equation one obtains with our approach and what we can infer from them. *We gratefully acknowledge funding from the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. [320951].*

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EPR POSTER SESSION

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224 PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution.

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The tripartite ATP-independent periplasmic (TRAP) transporters are a widespread class of membrane transporters in bacteria and archaea. Typical substrates for TRAP transporters are organic acids including the sialic acid N-acetyl-neuraminic acid. The substrate binding proteins (SBP) of TRAP transporters are the best studied component and are responsible for initial high-affinity substrate binding. To better understand the dynamics of the ligand binding process, pulsed electron-electron double resonance (PELDOR, also known as DEER) spectroscopy was applied to study the conformational changes in the N-acetylneuraminic acid-specific SBP VcSiaP. The protein is the SBP of VcSiaPQM, a sialic acid TRAP transporter from *Vibrio cholerae.* Spin-labeled double-cysteine mutants of VcSiaP were analyzed in the substrate-bound and -free state and the measured distances were compared to available crystal structures. The data were compatible with two clear states only, which are consistent with the open and closed forms seen in TRAP SBP crystal structures. Substrate titration experiments demonstrated the transition of the population from one state to the other with no other observed forms. Mutants of key residues involved in ligand binding and/or proposed to be involved in domain closure were produced and the corresponding PELDOR experiments reveal important insights into the open-closed transition.

EPR POSTER SESSION

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225 **Development of GaAs Switches for Advanced Pulse Sequences for EPR powered by a Free-Electron Laser.**

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EPR becomes more powerful at higher magnetic fields and frequencies, and with the application of high-power, short pulses. EPR powered by a free electron laser (FEL) at UCSB provides pairs of pulses with independently controllable power, duration (minimum pulse of 13 ns), separation, and phase. It enables a variety of EPR experiments such as FID, Hahn echoes, FID-detected Rabi oscillations, and FID-detected T_1 [1]. The FEL outputs pulses from 1 to 5 μs long which are sent to a quasi-optical pulse slicer to generate very short pulses useful for most EPR experiments. Currently, special Si switches driven by frequency doubled, Q switched Nd:YAG lasers (~100 mJ per pulse at 532 nm) generate two short 240 GHz pluses with tunable lengths and separations. However, Si switches are not suitable for generating more than two EPR pulses due to the long charge carrier life time (~ 1 μs). A new quasi-optical pulse slicer is under development which will use GaAs switches, which can be driven by lower power (10s of W) solid state diode lasers. The charge carrier life time of a few ns in GaAs enables more flexible switch design. This would yield switches capable of generating up to four EPR pulses to perform most advanced EPR experiments such as echo-detected saturation/ inversion recovery, stimulated echo, DEER, and with the possibility of ENDOR. Moreover, this switch technology could be applied to slicing any THz oscillator, including gyrotrons. *This work was supported by NSF-DMR 1626681*

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EPR POSTER SESSION

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226 **Powder and Single Crystal EPR Study of Metal-organic Framework $Cu_{2.931}Zn_{0.069}(btc)_2$.**

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Porous coordination polymers also known as metal-organic frameworks (MOF) compounds have a large application potential in areas such as adsorption, catalysis, gas separation and sensing. Many MOF materials contain paramagnetic ions and EPR investigations of such system are often feasible for powders, but difficult to perform for crystals because single crystals are only available in sub-millimeter size. However, for a detailed characterization of the structure of absorption complexes it is necessary to have knowledge about the orientation of magnetic tensors. This information can be obtained from single crystal investigations only. In the present work we show that the use of dielectric resonators may improve the sensitivity of the EPR experiments and provide the opportunity to investigate very small single crystals of porous materials such as MOFs at X- band frequencies.[1] We will present our latest studies of Cu(II) containing MOF single crystals. Here we explore the influence of the gas adsorption over $Cu_{2.931}Zn_{0.069}(btc)_2$ MOF single crystals on the orientation of the magnetic A – and g – tensor of paramagnetic Cu(II) ions with respect to the crystal axes. A detailed investigation of the angular dependence of the Cu(II) EPR signals allows for detailed characterization interaction mechanism between gas molecules and Cu(II) ions from MOF crystal structure.

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EPR POSTER SESSION

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227 **Pulsed EPR Studies of Spin-Spin Interactions in Trityl Radicals.**

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The effects of spin-spin interactions are an important consideration in studies using spin probes. They affect the relaxation and resolution of pulsed EPR measurements and can reveal the distribution of spins around the probe, which provides essential structural information in systems like proteins and membranes. The traditional way to measure spin-spin interactions is with instantaneous diffusion measurements that use two microwave pulses to measure the echo decay as a function of the delay between the pulses. The second microwave pulse manipulates dipolar fields from surrounding spins, and the data from this yields information about spin dimensionality and the distribution of dipolar interactions. However, the measurement is limited by the relaxation of the spin echo. There are also multiple phenomena contributing to the echo decay, making the dipolar interactions difficult to isolate. Double resonance techniques like double electron-electron resonance (DEER) measurements can also be used to probe spin-spin interactions. DEER measurements only probe the dipolar interaction between spins, but they are less sensitive. This study focuses on the spin-spin interactions in a variety of triarylmethyl (trityl) radicals. Trityl radicals are commonly used as spin probes because they have long relaxation times and narrow EPR lines. We use instantaneous diffusion and DEER measurements to reveal the dimensionality of a variety of substituted trityl radicals at various concentrations to probe spin dimensionality and compare it with relaxation properties. We have developed scripts written in the Python programming language to process and transform the data to reveal spin dimensionality. Together, these two measurements provide similar information that can help us to understand spin-spin interactions.

EPR POSTER SESSION

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228 **FD-FT THz-EPR as a Tool to Study Magneto-Structural Correlations in Single-Molecule Magnets: (Pseudo)-Tetrahedral Co^{II}Complexes with $[N_2O_2]$ Coordination Environment.**

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The unique magnetic properties that single-molecule magnets (SMMs) exhibit below their characteristic blocking temperature, i.e. slow relaxation of field-induced magnetization, renders them potential candidates used for spin-based nanoscopic data storage. As the energy barrier for relaxation of the magnetization scales linearly with the zero-field splitting (ZFS) parameter $|D|$, a large D is a critical property for the development of improved SMMs. The ZFS parameters D and E, as well as other spin-Hamiltonian parameters in paramagnets are ideally studied by EPR. However, for such high-spin states with large ZFS, EPR transition energies spread over a very wide frequency/field range, which often exceeds the microwave energies applied in conventional single-frequency EPR spectrometers. By using broadband sources in the THz and FIR range, frequency-domain Fourier-transform (FD-FT) THz-EPR[1] grants access to a largely expanded range of transitions energies. FD-FT THz-EPR at BESSY II represents a highly versatile setup, in which either coherent synchrotron radiation or a Hg-arc lamp, in combination with a superconducting high-field magnet enable measurements from 5-190 cm^{-1} and 0-10 T. Recently, we have studied several novel Co^{II} (S = 3/2) single ion magnets (SIMs), which in zero-field showed EPR transitions in the range of 40-180 cm^{-1}. Spin-Hamiltonian-based simulations of their field dependence allowed to precisely determine the ZFS energy $\Delta E_1 = 2(D^2 + 3E^2)$, providing crucial information to establish magneto-structural correlations. For a series of 5 (pseudo)-tetrahedral Co^{II} SIMs with a $[N_2O_2]$ donor environment, both experimentally and theoretically obtained D values were correlated with the structural parameter ε_T describing the elongation of the coordination environment,[2] which allowed for the deduction of design criteria to improve SIM behavior in (pseudo)-tetrahedral Co^{II} complexes.

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EPR POSTER SESSION

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229 Vanadyl Ligand Speciation Through High-Resolution ^{1}H ENDOR.

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The processing of crude oil into more useful products requires several refining steps. The efficiency of catalysts used in refining is reduced by the build-up of cokes and deposition of metals. Vanadium is a particularly problematic metal, which occurs in crude oil primarily in the form of vanadyl ions coordinated in petroporphyrins. The vanadyl petroporphyrins form thick aggregated layers that are non-trivial to separate. A separation-free method of analyzing crude oil could be useful in better understanding theses vanadyl petroporphyrins. We show that high-resolution ^{1}H ENDOR spectroscopy is useful for this purpose, as it is capable of differentiating between of a variety of vanadyl porphyrin ligands based on ^{1}H superhyperfine couplings. In addition, the ability to distinguish components within mixtures of vanadyl porphyrins is demonstrated.

EPR POSTER SESSION

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230 Trajectory-based Simulations of Electron Paramagnetic Resonance Spectra.

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The combination of EPR spectroscopy and site-directed spin labeling (SDSL) is a powerful tool for probing structure and dynamics in biological systems. However, the corresponding spectra can be complex and difficult to interpret due to the required use of spin labels as spectroscopic probes. To accurately model experimental data, user-friendly programs have been developed to simulate spectra, especially for continuous-wave (CW) EPR in the slow-motion regime (dynamical time scales of ≈10-100 ns for nitroxides at 9-10 GHz). The standard method is to simulate spectra in the frequency domain by numerically solving the stochastic Liouville equation. These programs are very fast, but are often restricted to specific simplified rotational diffusion models and limited to specific spin labels. When more complex models are needed, trajectory-based time domain simulation methods provide a promising alternative. Here we demonstrate our implementation of time domain methods in EasySpin, which allows us to simulate spectra using motional models that are difficult to implement using frequency domain methods. As a starting point, the program uses trajectories that are calculated either internally using stochastic dynamics, with an arbitrary orienting potential, or externally by molecular dynamics. The latter feature allows for detailed studies of how both spin label and protein dynamics contribute to EPR spectra.

EPR POSTER SESSION

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231 An EPR Examination of 3D Printing Materials.

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The potential to 3D print various components for EPR spectrometers is appealing owing to the ease of design and rapid prototyping. However, the potential for signals arising from the materials used and the printing process itself exists. The most common materials used for fused deposition 3D printing are PLA (polylactic acid), ABS (acrylonitrile butadiene styrene), and PETG (polyethylene terephthalate glycol-modified). In a typical 3D printer, the extrusion head is made of either brass or stainless steel, yielding the potential for metal contamination in the parts. A variable-temperature EPR study of the materials before and after extrusion will be presented along with a compilation of the various chemical and physical properties of the materials.

EPR POSTER SESSION

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232 **^{1}H-HYSCORE Reveals Details of the Coordination Chemistry at the Fe(II) Site of Taurine/2-Ketoglutarate Dioxygenase.**

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^{1}H-HYSCORE experiments have been used to study the coordination chemistry at the Fe(II) site of taurine/2-ketoglutarate (aKG) dioxygenase (TauD), a non-heme Fe(II) hydroxylase. To facilitate EPR experiments, Fe(II)-NO derivatives of the enzymes were studied. The NO serves as a substitute for molecular oxygen and binds to the integer spin Fe(II) to yield an S = 3/2 paramagnetic center with a nearly axial EPR spectrum characterized by g-perpendicuar = 4.00 and g-parallel = 2.00. Using the results of an X-ray crystallographic study of TauD crystallized under anaerobic conditions in the presence of both cofactor aKG and substrate taurine, together with the results of a previous ^{2}H-ESEEM study, we were able to assign the proton cross peaks detected in the orientation-selected HYSCORE spectra. Descrete contributions from the protons of two coordinated histidine ligands and one of the protons of substrate taurine were resolved. If substrate taurine is absent from the complex, orientation-selective HYSCORE spectra show crosspeaks that are less resolved. This finding is attributed to a decrease in local order at the Fe(II) site in the absence of substrate and is likely the reason that the protein can ony be crystallized in the presence of both taurine and aKG. HYSCORE studies of TauD in the absence of aKG, show additional ^{1}H crosspeaks assigned to two distinct bound water molecules that complete Fe(II)'s coordination sphere under these conditions. For these data, we found disparities in the predicted intensities of the the histidine proton cross peaks, and those due to coordinated water protons that may stem from the limited bandwidth of the HYSCORE pi-pulse.

EPR POSTER SESSION

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233 **Field-Stepped-Direct-Detection Electron Paramagnetic Resonance (FSDD-EPR) at Low Temperatures using a Metal Free Cryostat.**

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Abstract: Field Stepped Direct Detection has been employed for the measurement of wide field scans by rapid scan EPR at room temperature.[1] We now demonstrate rapid scan EPR at cryogenic temperatures. For this purpose, a cryostat with a metal free region has been developed by ColdEdge Industries/Bruker Biospin. A metal-free region allows homogeneous magnetic field scan coils to be mounted external to the cryostat, instead of using small scan coils inside the cryostat, thus minimizing interfering eddy current artifacts while maximizing the homogenous field region around the resonator. The sample is in a Bruker ER4118-MD5 dielectric resonator, which has a 10 mm long sample region. The sample is cooled by flowing He gas, using a "Stinger" closed-loop helium recirculation system also developed by ColdEdge/Bruker Biospin. Large diameter scan coils are required for the appropriate Helmholtz spacing of about 3 inches. Instrument stability and background impurity signals in the resonator are the greatest barriers to data acquisition when using the FSDD technique at low temperature. Data acquisition with a blank water/glycerol sample is needed to subtract signals from the dielectric resonator, which were previously too fast-relaxing to observe at room temperature. Frequency drift during the time required to obtain several field positions creates imperfections in the subtracted FSDD spectra. Proof of concept data is presented, demonstrating the viability of this technique to record very wide field scans at low temperatures despite these challenges. Recent improvements in rapid-scan background reduction are anticipated to improve FSDD-EPR at all temperatures.[2] Optimization of data acquisition and spectral reconstruction are the focus of future experiments.

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EPR POSTER SESSION

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234 An Algorithm to Calculate Polycrystalline Pulsed EPR Signals with Relaxation Rigorously in Liouville Space using Stochastic Liouville Equation.

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An algorithm is developed to calculate pulsed electron paramagnetic resonance (EPR) signals with relaxation in polycrystalline materials rigorously using Stochastic Liouville equation in Liouville space. It can be carried out within a reasonable time on a PC using Matlab, not requiring any sophisticated software. The flow chart for this kind of simulation is included. It is illustrated here numerically, as coded in Matlab, to calculate the spin echo correlation spectroscopy (SECSY) and echo-electron-electron double-resonance (echo-ELDOR) signals for a coupled electron-nuclear system with the electron spin S= ½ and nuclear spin I= ½. A software has been developed in Matlab, which only requires to input the parameters. It can be obtained from the authors upon request.

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235 Excitonic Transport in Amorphous Silicon Studied by Pulsed Electrically Detected Magnetic Resonance.

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Hydrogenated amorphous silicon (*a*-Si:H) is one of the prime examples of a disordered semiconductor. Today, a-Si:H is a key material for state-of-the-art thin-film solar cells or thin-film transistors (TFTs). Although extensively studied for more than 50 years, numerous questions regarding the detailed physical mechanisms of electronic transport in a-Si:H remain unanswered. Prominent examples concern the origin of light-induced degradation by means of the Staebler-Wronski effect (SWE)[1], or the prevailing charge-carrier transport and recombination channels through localized defect states[2], which impair the efficiency of *a*-Si:H-based devices.

The tool of choice for studying microscopic transport and recombination mechanisms in real devices is electrically detected magnetic resonance (EDMR) due to its high sensitivity and selectivity to spin-dependent transport processes. A series of studies on *a*-Si:H have utilized EDMR[2-6]. From these experiments, a picture comprising two principal transport processes has emerged: (i) at room temperature, spin-dependent recombination via mid-gap dangling bonds and, (ii) at low temperature ($T \leq 90$ K), spin-dependent transport of electrons and holes via band-tail states. We proof this picture incomplete by providing evidence for light-induced triplet excitons (TEs) making up a major contribution to spin-dependent transport at low temperatures. While the presence of TEs has already been proposed in early studies[2-4], to date, clear evidence has been missing due to the lack of modern pulsed EDMR (PEDMR) techniques. We now close this gap by an approach that combines PEDMR on fully processed *a*-Si:H solar cells with transient EPR (TR-EPR) experiments. Thereby, we will conclusively show that spin-dependent transport is governed by a three-particle process, where a TE is trapped at a paramagnetic band-tail state, from which an electron is released in an Auger-type process initialized through the light-generated TE.

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EPR POSTER SESSION

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236 **Low Magnetic Field Electrically Detected Magnetic Resonance Spectroscopy with Circularly Polarized RF Excitation.**
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Most electron paramagnetic resonance (EPR) experiments use linearly-polarized AC fields with amplitudes B_1 in order to drive spin excitations. For the description of EPR, linear polarization can be treated as a superposition of two circular polarized waves with opposite helicity [i.e., rotating wave approximation (RWA)[1]]. Under the typical EPR condition, $B_1 << B_0$, with B_0 representing the static magnetic Zeeman field, one of the two helicities is far out of magnetic resonance and can thus be neglected (EPR-inactive) while the other, EPR-active helicity allows for spin excitation. At high excitation powers when B_1 is large and/or at small excitation frequencies and magnitudes of B_0, the RWA breaks down and higher order EPR effects like the Bloch-Siegert shift[2], spin collectivity[3] and multiple photon transitions start to emerge. In order to scrutinize these effects and to study the limits of the RWA, we have built a radio frequency (RF) range low magnetic field (low mT-range) magnetic resonance setup which allows for the generation of circularly-polarized B_1 using a perpendicular four-coil arrangement where two pairs of RF coils are driven 90° out-of-phase. In order to observe magnetic resonance at room temperature and mT-range Zeeman splittings, we used a previously demonstrated[3] low-magnetic field electrically detected magnetic resonance (EDMR) spectroscopy scheme where permutation-symmetry sensitive (rather than polarization sensitive) electron-hole pair transitions in the Super yellow light-emitting PPV copolymer (SY-PPV) were probed. We show various measurements taken with different linear, elliptical, and circular polarized excitations as well as a variety of powers. The data reveals that both magnetic resonances that occur at positive and negative magnetic field strengths with equal intensity for linear polarized excitation, become unequal in intensity under application of elliptically polarized RF fields. In order to verify the isolation of the pure circular polarization states, we show the disappearance of each of the corresponding resonance peaks.

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EPR POSTER SESSION
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237 **Linear Prediction to Supplement FT-EPR of Transient Spin-Correlated Radical Pairs.**
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Fourier transform EPR (FT-EPR) is in the midst of a resurgence due to recent innovations in arbitrary waveform generation; however, challenges remain in signal processing, especially for transient radicals with relatively short-lived free-induction decays (FIDs). Linear prediction assisted by singular value decomposition (LPSVD) is a powerful tool in pulsed magnetic resonance spectroscopy because it leverages simplified, principal component modeling of the time domain signal as noiseless, damped complex exponential functions.[1] In our methods, we present a statistical analysis of a robust LPSVD algorithm with several approaches to determining the model order (M) and spectral parameter estimation (frequency, damping, phase, etc.).[2,3,4] In the context of experimental EPR spectroscopy, a major benefit of LPSVD is (1) lower or non-uniform point density than that required for discrete FT and (2) forward or backward prediction of portions of the signal corrupted by noise or instrument response.[5] To investigate this, we apply LPSVD to time-consuming 2D pulsed-EPR echo spectroscopy and to heavily truncated, damped FIDs of organic spin-correlated radical pairs. *This was supported by the US National Science Foundation under grant no. CHE-1565925.*

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EPR POSTER SESSION
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238 Electron Spin Relaxation Times of Spin Labels Without Gem-dimethyl Groups.

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Abstract: Distance distribution and conformations in biological molecules can be studied by labelling biomolecules with nitroxide spin labels and using Double Electron-Electron Resonance (DEER). Currently, nitroxide spin labels with gem-dimethyls are used for this purpose. However, rotation of the methyl groups at rates comparable to the anisotropy in hyperfine coupling to the methyl protons shortens T_m at T >80 K, thereby making DEER experiments difficult. We are synthesizing nitroxide spin labels devoid of gem-dimethyls to increase T_m above 80 K and permit DEER at higher temperatures [1]. One of these new spin labels is MTS-gem-diEster. We are studying its electron spin relaxation and its application to biological labeling. In trehalose glasses, $1/T_m$ for MTS-gem-diEster free or bound to T4L does not show the enhancement of $1/T_m$ at temperatures above 80 K that is characteristic of gem-dimethyl rotation. In rigid trehalose glasses, $1/T_m$ is approximately temperature independent up to 160 K. These observations indicate that spin labels with methyl groups far from the nitroxide moiety have much less impact T_m than the gem-dimethyls. The $1/T_1$ rates are similar to other spin labels ranging from 84 ms to 22 μs between 20 and 280 K, respectively. $1/T_m$and $1/T_1$ are frequency independent and T_m is orientation independent which facilitates observer and pump pulse placement during DEER. *Funding from NIGMS R01-GM124310-01 is gratefully acknowledged.*

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EPR POSTER SESSION

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239 *In Situ* Electron Paramagnetic Resonance Spectroscopy – Understanding Mechanisms in Lithium-Oxygen Batteries.

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Owing to its high theoretical specific energy density, the Lithium-Oxygen battery is one of the most promising energy storage systems, which has the potential to revolutionize electrical transportation.[1] Although advances in understanding the underlying mechanisms has opened up promising directions for Li-O_2 cells, major challenges remain in order to be able to access the true potential of Li-O_2 batteries. A deeper understanding of the decomposition reactions occurring during the cycle of Li-O_2 is needed to provide a solid foundation of fundamental understanding electrolyte degradation and carbon corrosion reactions which limit the cell-lifetime strongly.[2] One of the spectroscopy techniques that offers unprecedented opportunities to study the challenges we are facing in the development of Li-O_2 batteries is electron paramagnetic resonance (EPR) spectroscopy. We are developing a Li-O_2 spectroelectrochemical cell for in situ EPR spectroscopy examinations. This purpose-built cell is made up of material that are (i) compatible with all cell components in a Li-O_2 battery, (ii) transparent to microwave radiation and (iii) inactive for EPR. In situ EPR spectroscopy is a powerful tool for characterizing the formation and disappearance of unpaired electrons or radicals during the cycling of the battery.[3] It could therefore unravel the reactions potentially responsible for the battery's degradation and ultimately define directions for the exploration of more stable Li-O_2 batteries.

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EPR POSTER SESSION

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240 Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region.

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THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, has been developed 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] Wewill mainly focus on the recent developments of the torque magnetometry[5] and mechanically detected ESR[6] measurements using a commercially available membrane-type surface stress sensor, and its application to the metal protein systems.

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EPR POSTER SESSION

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241 Combining PELDOR and SAXS to Study the Solution Structure and Function of Type-III-effector Protein YopO from *Yersinia Pestis*.

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Yersinia pestis is the causative agent of plague and has caused several pandemics during human history. During infection, the bacterium is able to avoid innate immune defenses, e.g. phagocytosis, by utilizing a syringe-like type-three-secretion-system (T3SS). This molecular needle injects a set of six Yop proteins (Yersinia-outer proteins) into attacking phagocytes. After injection, the Yops interfere with several important cellular processes [1]. One of the effector proteins, YopO (also known as YpkA), is subject of this study. When injected into the host cell, YopO specifically interferes with the regulation of the actin cytoskeleton in different ways: 1) The C-terminus of YopO binds to Rac1 GTPases and acts as a guanidine nucleotide dissociation inhibitor. 2) YopO binds to monomeric actin, forming a stable 1:1 complex. This interaction leads to autophosphorylation and activation of the N-terminal kinase domain of YopO, which then in turn phosphorylates various cellular targets that are involved in cytoskeletal dynamics[2, 3].

A recent crystal structure of the YopO/actin-complex revealed how the bound actin molecule is used as a bait to recruit cellular proteins for phosphorylation[3], however, an important question remained unanswered: How is YopO structurally activated by actin binding? To answer this question, we have conducted PELDOR measurements on spin labelled apo-YopO and the YopO/actin-complex. Furthermore, we performed SAXS measurements on apo-YopO in solution and used mtsslDock[4] to combine these data with PELDOR distances to construct a structural model of apo-YopO. By serendipity, we found that the isolated kinase domain of YopO has a strong tendency to dimerize. Also here, SAXS and PELDOR were used to investigate the structure of this dimer and possible implications for the activation mechanism of YopO.

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EPR POSTER SESSION

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242 **Dextran-grafted Triarylmethyl Radicals.**

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Stable tetrathiatriarylmethyl (TAM) radicals are favorite spin probes used in biomedical EPR for the measurement of important physiological parameters, such as oxygen, pH and inorganic phosphate (Pi), *in vivo*. This particular family of water soluble trityl radicals exhibits an unprecedented stability in biological media in combination with long relaxation times, leading to extremely sharp EPR lines. The most representative members of this family are the oxygen probes cTAM, Ox063 and the multifunctional (pO_2, pH, Pi) pTAM probe (Figure 1).

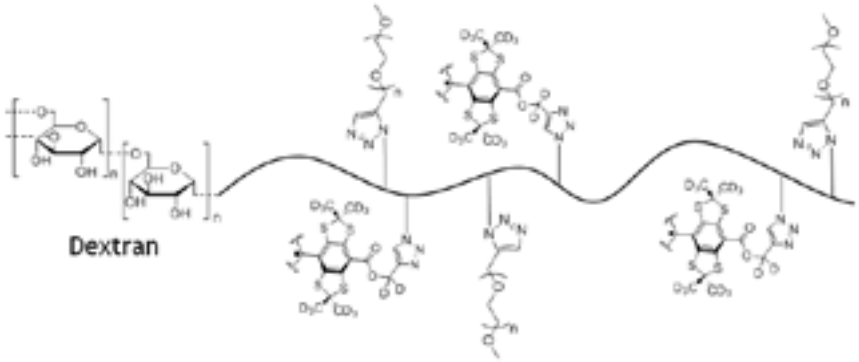

Figure 1

However, the binding of cTAM and pTAM to biomacromolecules of the plasma (such as albumin) through hydrophobic interactions limits their mode of administration to intra-tissue only. On the contrary, the more hydrophilic structure of OX063 prevents these interactions and therefore allows for its systemic delivery. However, the use of OX063 in EPR imaging has been proven to be challenging due to its rapid clearance. Hereby, we report new dextran-PEG-TAM biopolymers. These macromolecular spin probes were synthesized by grafting TAM radicals on an azide-modified dextran biopolymer using a click chemistry approach (Figure 2). A set of different dextrans with different spin probe loadings has been synthesized and their EPR properties are reported in this poster.

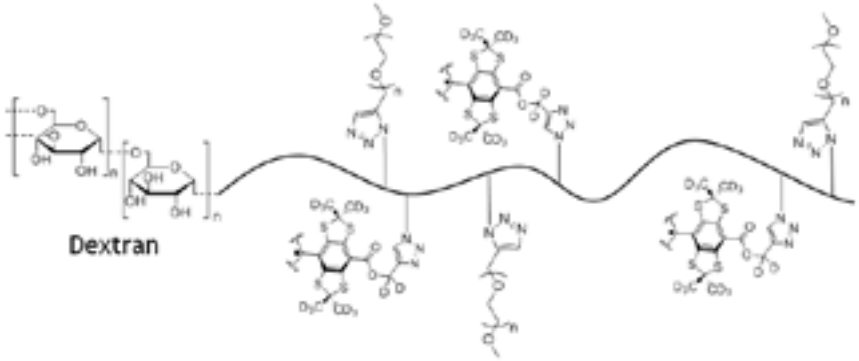

Figure 2

Supported by NIH grants R01CA194013, R01CA192064, U54GM104942 and K99EB02399

EPR POSTER SESSION

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243 **Fringe Field Measurements of Ferromagnetic NiFe Films using Electrically Detected Magnetic Resonance.**

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We report a study of fringe field effects of ferromagnetic thin NiFe films on adjacent layers of the organic semiconductor tris(8-hydroxyquinolinato)aluminium (Alq3) using electrically detected magnetic resonance (EDMR) spectroscopy. The study consisted of two parts: (i) The investigation of the qualitative and quantitative nature of spin-dependent charge carrier recombination in Alq3 under bipolar injection conditions. For this, we conducted multi-frequency continuous wave EDMR on bipolar injection devices, i.e. organic light emitting diodes (OLEDs) with active layers of Alq3. These measurements allow for the determination of hyperfine field distributions, the electronic g-factors, as well as the magnitude of g-strain of both, electron and hole states. (ii) EDMR measurements in OLED devices, with and without a NiFe adjacent to the Alq3 layer. The experiments reveal that the individual charge-carrier resonances become increasingly indistinguishable for increasing NiFe layer thicknesses. Similarly, we observe that the significantly different line widths of electron and hole polaron states also approach each other as the NiFe film thickness increases—the narrow resonance line becomes wider and the broad resonance line narrows. We use a rigorous statistical analysis[1,2] to assess the significance of these changes. We interpret these observations as effects caused by the ferromagnetic fringe field induced randomization of magnetic field which occurs on the order of the ferromagnetic domain sizes and thus, it is identical for adjacent electrons and holes. This effect is superimposed with the intrinsic random magnetic field distributions in Alq3 that are caused by unresolved hyperfine coupling between charge-carrier spin and the nuclear spin of hydrogen, and which fluctuate on the molecular scale and are distinct for electrons and for holes.

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EPR POSTER SESSION

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244 **Simulating Experiments with Shaped Pulses using EasySpin.**

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EasySpin now provides full support for the simulation of pulse EPR experiments with shaped pulses. This new functionality is based on the integration and extension of SPIDYAN[1] into EasySpin. Capabilities include predefined as well as user-defined shaped pulses, arbitrary multi-dimensional experiments with incrementation of any pulse or delay parameter, arbitrary spin systems, incorporation and compensation of resonator and amplifier distortions, phase cycling, detection during pulses, a variety of detection and excitation operators, and fully integrated treatment of relaxation. Compared to the original implementation[1], the user interface is much simpler and simulations run significantly faster. We illustrate the capabilities through a series of short examples.

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EPR POSTER SESSION

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245 **Two-Dimensional Distance Correlation Maps from Pulsed Triple Electron Resonance (TRIER) on Model Compounds and Proteins.**

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Recently we introduced the pulsed triple electron resonance (TRIER) experiment[1] as a complement to double electron-electron resonance (DEER). DEER is well known for its ability to provide distance distributions from doubly

labeled proteins. However, if the investigated biomolecule exists in more than one conformation, a problem with the one-dimensional DEER data arises: Peaks in the distance distribution cannot be unambiguously assigned to one conformation. By adding a third spin label, the TRIER sequence allows for correlation of dipolar frequencies that stem from the same molecule. This information can be used to solve the assignment problem.

As compared to our first publication[1], we have improved the sequence to increase sensitivity. Initially we were only able to obtain two-dimension TRIER spectra in frequency domain. With an improved data processing we can now present the first two-dimensional distance correlation maps. This was made possible by two-dimensional approximate Pake transformation of the two-dimensional time domain data and is applicable not only to model compounds. We were also able to obtain distance correlation maps of triply labeled. The data we obtained through TRIER were in good agreement with DEER and simulated inter spin distances.

Though TRIER still faces some challenges, we expect such maps to facilitate the interpretation of sets of DEER data and to give more insight into the structure of complex proteins. As TRIER requires pulses with three different excitation windows that must not overlap, we aim to extend our scope to compounds with two different types of spin labels such as the combination of nitroxide and gadolinium labels.

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EPR POSTER SESSION

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246 Software for Advanced and Global Analysis of EPR data: GloPel and SpecProFi.

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It is for us scientists an obligation to analyze our measurement data as meticulously as possible to draw sound conclusions based on them. Especially in EPR, where spectral parameters rarely can be read out directly from spectra or echo decay curves, and where many parameters influence the data, performing several independent experiments may be helpful to extract multiple magnetic-resonance parameters with high fidelity. To this end, global analysis proves to be very useful to analyze independent experiments by fitting two or more data curves simultaneously.

In this contribution, we present SpecProFi (Spectra Processing and Fitting), a comprehensive EPR data processing and fitting framework, that provides sophisticated analysis tools, such as the global analysis of multiple experimental data sets combined with semi-stochastic analysis. Such global analyses include the simultaneous examination of cw-EPR measurements at multiple microwave frequencies, as well as combinations of cw-EPR and ENDOR spectra, orientation selective ENDOR measurements recorded at different magnetic field positions, multiple harmonics, or liquid-state cw-EPR and solid-state cw-EPR data. SpecProFi relies on the well-established and powerful EasySpin simulation package[1] and is kept in the corresponding structure syntax, thus making it easy to use. Beside the fitting framework, SpecProFi provides various toolbox-independent functions for data processing, such as denoising methods (e.g. based on discrete wavelet transforms), automatic phase-correction for cw-EPR data, or differentiation of absorptive EPR data using Tikhonov regularization.

Furthermore, GloPel (Global analysis of PELDOR data), available as cross-platform Python GUI application, provides a comprehensive PELDOR/DEER data processing and analysis framework supporting global analysis[2]. Tikhonov regularization as well as multi-Gaussian fitting models are implemented. The analysis is highly optimized in terms of performance. The user-friendly GUI application offers spectra processing, fast data analysis, and validation tools to avoid potential misinterpretation of data.

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EPR POSTER SESSION

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247 Orienting the Dimerization of Retinal Guanylyl Cyclase Activating Protein 1 using DEER Derived Distances and Molecular Modeling.

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Retinal guanylyl cyclases (RetGCs) in vertebrate photoreceptors are regulated by guanylyl cyclase activator proteins (GCAP1 and GCAP2). Dimerization of the GCAPs has been implicated in function and regulation of RetGCs, however there is no previously determined structural evidence. To address this question, we employed EPR double electron-electron resonance (DEER) studies on GCAP1 by labeling different residues (E57C, E133C, and E154C) with MTSSL and measured intermolecular distances[1]. These DEER derived distances were used as restraints in molecular docking of a GCAP1 monomer structure to generate a dimeric model. The generated GCAP1 dimer model possesses intermolecular hydrophobic contacts involving the side chain atoms of H19, Y22, F73, and V77. The dimer structure was validated using NMR and size exclusion chromatography by GCAP1 mutations (H19R, Y22D, F73E, and V77E) at the dimer interface which lead to an abolishment of the dimer. These mutants have been shown previously to diminish or suppress the ability of GCAP1 to activate RETGCs. Thus, these results show a structural model for the dimerization of GCAP1 and that dimerization is important for the regulation of cyclase activity. *Supported by NIH R01GM065790 (GLM) and NIH R01EY012347 (JA).*

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EPR POSTER SESSION

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248 Imaging of Enzyme Activity by Electron Paramagnetic Resonance (EPR). Synthesis and Characterization of an Alkaline Phosphatase-sensitive Nitroxide Spin Probe.

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Enzyme activities are important biomarkers of many pathologies, such as cancers, Alzheimer's disease or diabetes. While reliable methods have been developed to measure enzyme concentration, expression and activity in vitro and ex vivo, the direct measurement of enzyme activity in vivo remains extremely challenging. Hereby we report the synthesis and characterization of an alkaline phosphatase (ALP) -sensitive nitroxide spin probe. As proof of concept the enzymatic dephosphorylation of the probe has been imaged in vitro using a homebuilt rapid scan EPR imaging system operated at 800 MHz. The concept will be extended using newly synthesized trityl probes, enabling in vivo imaging of the enzyme activity.

EPR POSTER SESSION

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249 An Equatorial Histidine Swap in the Prion Protein Copper Center is Essential for its Neuroprotective Self-Regulation.

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Using EPR and NMR, we demonstrate that two highly conserved histidines in the C-terminal domain of the prion protein are essential for the protein's copper-driven cis interaction, which potentially protects against neurotoxicity carried out by its N-terminus. We show that mutation of these histidines drastically weakens the *cis* interaction and

biases cultured cells towards toxic events. Mechanistically, we propose an equatorial swap – a copper bound histidine from the N- terminus of the prion protein is replaced by a histidine from its C-terminus, forming a tether that holds the two domains together. We also find that extra N-terminal histidines in pathological familial mutations inhibit this interaction by stealing copper from the C-terminus, suggesting a mechanism for the toxicity of these mutants.

EPR POSTER SESSION

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250 Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy.

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National Institutes of Health

With 25.3 million deaths and 38.1 million additional infections worldwide since 2000, the HIV/AIDS pandemic presents itself as a grave health crisis. Although, extraordinary progress has been made in understanding HIV, complete eradication remains elusive. HIV type I reverse transcriptase (HIV-1 RT) catalyzes the conversion of single-stranded, virally encoded RNA into double-stranded proviral DNA, which is the first step towards the integration of viral DNA into the host genome, a prerequisite for the HIV replication cycle. Active HIV-1 RT accommodates DNA as well as RNA through remarkable intrinsic dynamics in the finger and thumb subdomains as identified by variable intermolecular distances in crystallographically determined protein structures. Current drugs suppress such binding events but their inhibitory mechanisms are still under investigation. The configurational space sampled by the finger and thumb subdomains of free, DNA- or drug-liganded HIV-1 RT was investigated by Q-band double electron–electron resonance pulsed electron paramagnetic resonance spectroscopy, a method for determining long-range distances between pairs of surface-engineered nitroxide spin-labels in the finger and thumb subdomains. In the unliganded state, open and closed configurations for the finger and thumb subdomains are observed, which is in contrasts with the crystallographic data in which the unliganded state only adopts the closed conformation. Upon addition of double-stranded DNA, all constructs adopt open conformations consistent with previous crystallographic data in which the position of the thumb and finger subdomains is determined by contacts with the bound oligonucleotide duplex (DNA or DNA/RNA). Likewise, binary complexes with five different non-nucleoside RT inhibitors populate the open or partially open conformations, indicating that binding of the inhibitor to the palm subdomain indirectly restricts the conformational space sampled by the finger and thumb subdomains. The presented method and results describe the inhibitory restraints placed onto the finger and thumb domain of HIV-1 RT by non-nucleoside RT inhibitors, which render its polymerase function inactive, and hence arrests the HIV-1 replication cycle. Future studies will exploit this inhibitory mechanism to screen previously approved drugs of other treatments and improve known small molecular drugs.

EPR POSTER SESSION

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251 Automation of a Terahertz Frequency Rapid Scan ESR Spectrometer.

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A high effort is currently invested in development of pulsed high frequency/field electron spin resonance (HFESR) spectrometers, which can satisfy a high spectral resolution and are suitable for spin-dynamics studies.[1] However, their development has to overcome many challenges, mostly issued by generation, propagation and detection of terahertz waves.[2] Our aim is to build a multifunctional broadband ESR spectrometer, based on a terahertz frequency rapid scan method (European Research Council Starting Grant THz-FRaScan-ESR), which maximum achievable magnetic field in cryostat chamber will be 16 T, and a frequency range of a terahertz source will between 80 and 1100 GHz. By the rapid sweep of terahertz wave frequency, the spectrometer will allow to acquire information about broadband ESR spectrum as well as relaxation time.[3] A fast processing of acquired data is crucial, because a single scan can be done in a few microseconds and contain more than ten thousand points. For this reason, it is useful to do the most of a data preprocessing onboard by a field programmable gate array (FPGA).[4] This will unburden a processor of operating computer, which can be used for other utilities as semi-automated evaluation of results or drawing of ESR spectrum

maps.[5] An overall goal of the spectrometer automation is to make a measuring routine more pleasant by implementing of powerful algorithms along with easy-to-use user interface. *Supported by ERC-STG 714850 and FEKT-S-17-3934.*

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EPR POSTER SESSION

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252 Collaborative Research on Molecular Spins for Quantum Information Technologies in the Frame of the European COST Action "Molecular Spintronics".

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Molecular spins are quantum objects and, as such, they open the way to several applications: hybrid quantum architectures, quantum sensors, spintronics and quantum computation. The great advantages in the use of molecules lie in their extraordinary tunability, of relevance for the realization of quantum-gates,[1] for their scalability, and for their processing. The manipulation of their spin states, the operation as quantum gates and the realization of quantum simulators make large use of magnetic resonance techniques. The latter are therefore central to the research activity conducted in the frame of our European COST (European Cooperation in Science & Technology).

Action MolSPIN (www.icmol.es/molspin), whose third work-package is entirely dedicated to molecular spins for quantum technologie, comprises 24 COST countries, including Israel, and one COST Near Neighbour Country. International non-EU institutions also participate as International Partner Countries. As a first result of the trans-national cooperation promoted by COST, a collaborative research project has been funded in the frame of the European Quantum flagship (https://quantera.eu/news/projects-catalogue). The goals comprise the scaling up of quantum computation with molecular spins , the coupling with photons, as well as single spin addressing by scanning probe techniques.

We will review here most recent activities and achievements of the COST action in the area of relevance for the magnetic resonance community, as well as the possible means to enlarge the network of collaborations to other countries.

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EPR POSTER SESSION

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253 A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements.

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We report a novel gadolinium(III)-spin label complex [Gd.sTPATCN]-SL, developed from the previously published complex [Gd.TPATCN].[1] [Gd.TPATCN] has the narrowest reported CW EPR line in solution, with a peak-to-peak width of 13 G at X-band. [Gd.sTPATCN]-SL exhibits a small zero-field splitting, with the ability to tether to the natural

amino acid cysteine via a single, stable thioether bond using a 4-nitropyridine functionality. Here, we demonstrate its potential as a protein spin label for EPR by cysteine selective labeling of both a test peptide and protein, TRIM25cc. [Gd.sTPATCN]-SL is water soluble and offers high labeling efficiency under mild conditions, and is therefore highly desirable for protein systems. Importantly, we show the application of this new gadolinium(III) spin label to double electron electron resonance (DEER) by measuring the distance between a pair of [Gd.sTPATCN]-SL (5.85 nm, σ_r=0.55 nm) in addition to the distance between the gadolinium label and R1 on TRIM25cc. The label provides promising relaxation times at Q-band, allowing for long DEER measurement time windows. The narrow zero-field splitting, which has been shown to suit longer interspin distances,[2] also allows for increased sensitivity and greater modulation depths, expected only to improve when moving to higher fields.

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EPR POSTER SESSION

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254 Lipoxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure.

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Abstract: Hydrogen tunneling in enzymatic C-H activation requires a reactive ground-state enzyme-substrate conformation that can achieve a transient tunneling-ready state (TRS) through dynamical sampling.[1,2] It was recently shown that ^{13}C electron-nuclear double-resonance spectroscopy (ENDOR) provides high-precision information on substrate conformation in the H-tunneling enzyme, soybean lipoxygenase (SLO).[3] ENDOR here provides an exquisitely sensitive probe of enzyme control of substrate conformation, demonstrating the influence of subtle enzyme modifications either at a hydrophobic sidechain in contact with bound substrate or at a remote residue within a solvated network linked to H-transfer. The differential enthalpic barrier for deuterium and hydrogen transfer, ΔEa, serves as a selective ruler for effective wavefunction overlap at the TRS, and we report a remarkable correlation between the population of the reactive ground-state conformer as obtained from ENDOR spectroscopy and the magnitude of ΔEa, among seven SLO variants **(figure)**. This correlation shows the critical role of ground-state structural precision in achieving a TRS correspondingly optimized for quantum H-atom tunneling, and shows how very modest changes in a single amino acid alter and compromise tunneling. *Supported by National Institutes of Health (NIH): GM111097 to BMH; and GM025765 to JPK. ARO was supported by NIH GM11343 (F32) and startup funds from ECU.*

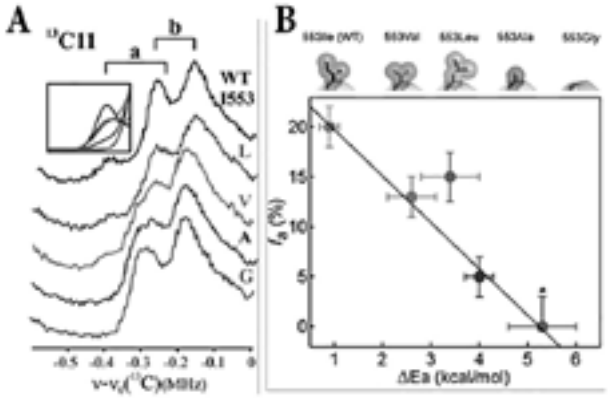

Figure (A) ^{13}C ENDOR spectra for I553X variants. *Inset:* overlay of simulations **(B)** Percentage of a conformer (f_a) versus ΔEa; I553X sidechains shown for reference; 553Leu removed from fitting (black line).

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EPR POSTER SESSION

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255 EPR Imaging at VHF with Field Reversal Background Correction.

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Understanding tumor physiology, including local oxygen and redox status, is crucial to the development of improved cancer therapies. Novel probe molecules have been developed by our collaborators and our group is developing improved EPR imaging methods to map the spatial variation of the spectral properties of the probe [1]. A background correction method based on reversal of B_0 is being developed in our lab [2]. Experiments are performed at low magnetic fields (~9 to 25 mT) that are required for studies in living systems. We now report results for EPR imaging experiments using this method. Imaging measurements were performed at room temperature with a locally-built spectrometer operating at 258 MHz (~9 mT) and a cross-loop resonator. Samples with nitroxide radical concentrations between 0.1 and 0.5 mM in a two compartment phantom were studied. Four types of experiments were performed: single-sweep sinusoidal scan, 2D spectral spatial imaging with sinusoidal scan, field-stepped linear scan, and 2D spectral-spatial imaging with field-stepped linear scans. The background subtraction method greatly reduced the background for both linear and sinusoidal scans. Signal-to-noise, linewidths in spectra and spectral slices through the images, and resolution of the separation between the two compartments of the phantom were compared.

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EPR POSTER SESSION

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256 Air Stable Triplet Ground State Diradical Dication and Radical Cation of Conjoined Double Helicene.

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Development of novel paramagnetic materials with inherently strong chiral properties could facilitate discovery of new organic optoelectronic materials and devices. To date, there are very few chiral organic radical building blocks for such development, due to the enormous challenge in the design and synthesis of molecules incorporating persistent organic radical within the helical p-systems. A π-conjugated double helicene, D_2-symmetric dihydrazine 1-D_2 that is configurationally stable, with a high isomerization barrier of ~35 kcal mol^{-1} (at 180 °C) to C_{2h}-symmetric structure (meso),[1] is a promising target for the development of chiral high-spin organic radical with robust stability. Here we present the progress report on computational and experimental studies of the radical cation and diradical dication derived from 1-D_2. The DFT calculations predict high isomerization barrier for neutral 1-D_2, radical cation $1^{\cdot+}$-D_2 and diradical dication $1^{2\cdot2+}$-D_2. Importantly, $1^{2\cdot2+}$-D_2 is predicted to possess triplet ground state with a modest singlet triplet energy gap, ΔE_{ST} » 0.8 kcal mol^{-1}. The racemic $1^{2\cdot2+}$-D_2 is prepared from racemic 1-D_2 using [NO][SbF_6] as an oxidant. Quantitative EPR spectra not only confirm triplet ground state for the racemic $1^{2\cdot2+}$-D_2 but also indicate that solution of $1^{2\cdot2+}$-D_2 in dibutyl phthalate is stable on air at room temperature. These results indicate the potential for achieving the first stable helicene-based high-spin diradical, such as chiral $1^{2\cdot2+}$-D_2. The next challenge is to obtain enantiomerically pure 1-D_2, precursors to chiral radical cations $1^{\cdot+}$-D_2 and diradical dications $1^{2\cdot2+}$-D_2. One of the approaches to chiral resolution, which we are exploring, relies on chiral salt [Me_2NH_2][Λ-BINPHAT].[2] *Supported by NSF grants: CHE-1362454 and CHE-1665256.*

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EPR POSTER SESSION

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257 Intermediate Excited States for Optical Excitation and Electrical Generation in Donor: Acceptor based OLEDs.

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The mechanism of thermally activated delayed fluorescence (TADF) emission in organic light emitting diodes (OLEDs) raised many questions about the mechanism of triplet-singlet up-conversion leading to emission. Yet, direct spin-sensitive measurements on OLED devices are scarce in literature. Here, we apply a combination of time-resolved optical spectroscopy and spin-sensitive magnetic resonance measurements based on electrical detection (EDMR), electroluminescence (ELDMR) and photoluminescence (PLDMR) to efficient TADF OLED devices based on several donor:acceptor systems. Our results show that the triplet state which is mainly responsible for the occurrence of TADF in donor:acceptor based systems is the exciplex triplet for both electrically driven devices as well as for optically excited samples. Molecular triplets however, appear only after optical excitation at low temperatures and don't play any role for electrical injection. We expect this picture to also be valid for further donor:acceptor exciplex emitters, which is why it is imperative to carefully distinguish between optical excitation and electrical generation as they may involve different intermediate excited states.

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EPR POSTER SESSION

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258 Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition.

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Pulsed Dipolar Spectroscopy (PDS) methods, such as Double Electron Electron Resonance and Double Quantum Coherence, are powerful methods for studying the structure and function of biological systems. In PDS, a dipolar signal is acquired from the interaction between a pair of spin labels, from which the distance distribution between them, P(r) may be obtained between the distance ranges of 1 to 10 nm. However, due to the ill-posed nature of the inversion of the dipolar signal to yield the P(r), one must resort to regularization or model fitting methods to obtain reasonable results. The method of Tikhonov regularization (TIKR) is commonly used, but it relies heavily on the choice of regularization parameter that yields a compromise between good resolution and stability of the P(r). Model fitting methods, on the other hand, require a priori model functions to estimate P(r), which may not accurately represent the actual distance distributions. This is especially true if the P(r) is multimodal. We developed a new and objective approach based on singular value decomposition (SVD) that yields an optimum approximate solution, obviating the need for regularization.[1] Instead of solving for the complete distance distribution all at once, the method finds the optimal distribution value at each distance or distance range by determining each of their different singular value cut-offs. The new method ensures optimal convergence at all distance ranges, while preventing a premature or unstable solution at some or all distance ranges. We tested the new SVD method on several model and experimental dipolar signals with unimodal and multimodal distributions. The method yields high resolution P(r) without any spurious peaks or negative P(r)'s and consistently performs better than TIKR. The new method can successfully reconstruct multimodal distributions, both overlapping and independent, with varying distribution widths.

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EPR POSTER SESSION

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259 Characterization of the Distribution of Spin-lattice Relaxation Rates of Lipid Spin Labels in Fiber Cell Plasma Membranes of Eye Lenses with a Stretched-exponential Function.

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Medical College of Wisconsin

The stretched-exponential function (SEF) was used in a novel way to analyze and interpret saturation recovery (SR) electron paramagnetic resonance (EPR) data obtained from spin-labeled intact eye-lens membranes. The SEF has two fitting parameters, the characteristic spin-lattice relaxation rate (T_{1str}^{-1}) and the heterogeneity parameter β. Because T_1^{-1}s are determined primarily by the rotational diffusion of spin labels, they are a measure of membrane fluidity. The heterogeneity parameter β describes the distribution of T_1^{-1}s and ranges between zero and one. When $\beta = 1$ the function is a single exponential; in that case T_{1str}^{-1} is the same as T_1^{-1}. The two parameters can be used to compute a probability density function that describes the multi-exponential decay curve without assumption of the number of exponentials, magnitudes, or T_1^{-1} values. The SEF was applied to analyze SR data obtained from intact cortical and nuclear fiber cell plasma membranes from two-year-old porcine eye lenses labeled with phospholipid- and cholesterol-analog spin labels. The analysis demonstrates that the lipid environment sensed by these molecules in nuclear membranes is less fluid and more heterogeneous than in cortical membranes. Multivariate analysis (samples are cross plotted according to T_{1str}^{-1} and β values) of stretched-exponential data obtained with phospholipid- and cholesterol-analog spin labels indicate that membrane samples can be grouped by origin in nuclear or cortical membranes and can be cleanly separated by quadratic discriminant lines. In future work, the SEF will be applied to analysis of samples from human eye lenses of donors with the different health histories.

EPR POSTER SESSION

Natalia Stein, Medical College of Wisconsin

260 Characterization of the Mechanism of Solvent-Protein Coupling to the Radical Rearrangement Reaction in B_{12}-Dependent Ethanolamine Ammonia-Lyase.

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Solvent-coupled protein motions have been shown to play a role in protein function[1]. These motions can be classified as either collective (α) or incremental (β) fluctuations. However, because these motions are typically on the ps – ns timescale at room temperature (T), specific motions are difficult to resolve. We have addressed contributions of protein configurational states and fluctuations to the substrate radical rearrangement reaction in B_{12}-dependent ethanolamine ammonia lyase (EAL), from *Salmonella typhimurium*, at cryogenic Ts by using full-spectrum, time-resolved CW EPR[2,3]. The reaction with aminoethanol as substrate shows a piecewise continuous Arrhenius dependence from 295 – 220 K (monoexponential) and 214 – 203 K (biexponential), delineated by a bifurcation (219 K) and kink (~217 K)[2]. This has been interpreted as a quenching of the collective fluctuations at a glass-like transition, followed by reaction supported by incremental fluctuations at lower Ts. More recently, using the spin probe TEMPOL, it was shown that 0.5-4.0 % v/v added DMSO depresses the solidification Ts of the protein-associated domain and mesodomain around EAL in the frozen polycrystalline solution by ≤20 K.[4] We thus hypothesize that addition of DMSO will lower the bifurcation and kink T values. In the presence of 2.0% v/v added DMSO, the Arrhenius dependence of the radical rearrangement reaction decay retains the same general form as seen previously[2], but the bifurcation and kink Ts are lowered by 10 K. The results indicate that the native reaction is maintained in the presence of DMSO and establishes that specific collective protein fluctuations involved in the rearrangement reaction are coupled to solvent a-fluctuations in the mesodomain. The ability to control the T of the bifurcation/kink transitions presents a unique platform with which to further characterize specific protein configurational contributions to catalytic steps in EAL.

Supported by NIH DK054514.

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EPR POSTER SESSION

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261 Structure and Mechanism of Assembly of the Ethanolamine Utilization (Eut) Bacterial Microcompartment (BMC) Shell Components.

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Bacterial microcompartments (BMCs) are self-assembling organelles that encapsulate enzymes of a specific metabolic pathway within a polyhedral protein shell[1]. The ethanolamine utilization (Eut) BMC plays a role in bacterial catabolism in the human gut and confers a fitness advantage for pathogenic *Salmonella and Escherichia coli*[2]. The structures of shell proteins of Eut and other BMCs have been explored by X-ray crystallography and electron microscopy[3,4], however, the molecular mechanisms of assembly and functional interactions among shell proteins, and with internal enzymes, are poorly understood. Here, we use analytical gel filtration and spin-label electron paramagnetic resonance (EPR) spectroscopy to characterize the affinities and oligomeric states of the BMC shell and shell-associated proteins from the Eut operon of *S. typhimurium*. The proteins self-associate to form trimers (Eut Q, K, L) and hexamers (Eut M, N, S) which appear to represent fundamental shell-tiling units. Gel filtration-mixing experiments identified an interaction between the principal shell structure protein, Eut M, and the BMC count-enhancing Eut Q, but failed to detect an interaction between the signature encapsulated enzyme, ethanolamine ammonia-lyase (EAL), and either Eut M or Eut Q. Reaction of Eut M, S, and Q with 4-maleimido-TEMPO shows that the 1-3 native Cys residues per monomer are inaccessible, consistent with X-ray structure predictions[3]. Site-directed mutagenesis is being used to introduce Cys at selected surface sites of Eut M to determine the intra-hexamer structure and inter-hexamer interactions in higher-order structures. The results advance toward BMC-based therapeutics and repurposing the Eut BMC for alternative metabolic and materials applications. *Supported by NIH DK054514.*

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EPR POSTER SESSION

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262 Precise Determination of Spin Concentration using Double Electron-electron Resonance.

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Precise determination of spin concentration is critical in many fields from quantum physics and condensed matter physics to biochemistry. Unfortunately, currently available techniques have limitations. For example, lineshape analysis of EPR spectroscopy has been applied to determine the concentration of paramagnetic impurities, however the method remains challenging for wide applications as it highly depends on the choice of the reference sample, position of the samples in the cavity, spin relaxations and so on. Here we discuss a method to determine a wide range of spin concentrations using a wide-band high-frequency electron spin resonance and double electron-electron resonance spectrometer [1]. We also shows the study of spin decoherence time T_2 of the nitrogen impurities in diamond as a function of the spin concentration. The method developed in this work is applicable for various spin systems and can be implemented in other EPR related techniques. Possible applications will also be discussed.

This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).

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EPR POSTER SESSION

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263 Computational Modeling of the Cytotoxic PLA2, ExoU, using SDSL EPR.

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Computational protein modeling methods can be powerful tools for studying protein structure, function and conformational changes. Coupling these techniques with experimental data can significantly improve modeling efficency and resolution. As a result, these high-resolution models can be used to inform and accelerate hypothesis driven research and structure-based drug design. Site Directed Spin Labeling (SDSL) Electron Paramagnetic Resonance (EPR) is a powerful technique that can provide a wealth of structural information that can be used to develop, test and refine computational models. We utilize several computational techniques, including molecular dynamics simulations and Monte Carlo search-based software, to study the structure and conformational changes of the bacterial cytotoxin, ExoU. ExoU is a highly cytotoxic phospholipase. Pseudomonas aeruginosa injects ExoU directly into host cell cytoplasm, where it associates with the eukaryotic protein cofactor, ubiquitin. Once in complex with ubiquitin/substrate, ExoU undergoes a conformational change that promotes the cleavage of host membrane phospholipids, resulting in cellular lysis. Two crystal structures of ExoU have been published, and both are postulated represent an inactive conformation. Additionally, over 20% of the amino acid residues are unresolved, including a critical catalytic residue, D344. We recently modeled the non-covalent ExoU-ubiquitin interaction using the Rosetta protein modeling suite, facilitated by data from continuous wave (CW) EPR and Double Electron-Electron Resonance (DEER) distances. Here we utilize computational modeling and SDSL EPR to expand our studies to mapping missing electron density in the ExoU crystal structures as well as conformational changes required for activation.

EPR POSTER SESSION

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264 4-pulse Nitroxide-nitroxide Q-band DEER Revisited.

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Double Electron-Electron Resonance (DEER) in combination with site-directed spin labeling is a versatile electron paramagnetic resonance (EPR) technique for obtaining high precision distance information in proteins. The sensitivity of this two-frequency technique is strongly dependent on the achievable excitation bandwidth of the microwave pulses with respect to the available spectral width of the spin probes.

The introduction of arbitrary waveform generator (AWG) technology and the availability of high power amplifiers at Q band mark a "new era" in pulse EPR due to significant sensitivity improvements and the possibility to perform novel types of experiments. While sequences like CP (Carr-Purcell) DEER[1,2,3] offer advantages like a prolongation of the dipolar time evolution, it is still worth to revisit the 4-pulse DEER experiment.

We present an optimized 4-pulse DEER setup that uses Gaussian observer pulses (GaussDEER) in connection with a hyperbolic pump pulse. Gaussian pulses allow to experimentally remove the "2+1" pulse train ESE[4] artifact which is intrinsically present in any DEER experiment using rectangular pulses. Hyperbolic pump pulses can significantly increase the modulation depth of the DEER experiment due to their box-like excitation bandwidth. However, 4-pulse GaussDEER with a hyperbolic pump pulse has limitations regarding its sensitivity for high frequencies in the dipolar spectrum[5], but it does not require the measurement of multiple time traces or any post-processing of the time-domain data to remove artifacts from lower order experiments, while still offering a reasonable sensitivity improvement and providing straightforward expandability to additional pump pulses if a longer dipolar time evolution is required.

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EPR POSTER SESSION

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265 Anesthesia Free Pre-Clinical Rapid Scan Oximetry.

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Anesthesia is routinely used in pre-clinical EPR spectroscopy and imaging. However, this procedure is known to affect animal metabolism, which may skew results of the conducted studies. Pulsed EPR was used to address the problem of anesthesia influencing oxygen partial pressure in tumors and normal tissues [1]. Measurements were done on the sub-second time scale using conscious mice. Here we present rapid scan EPR [2] measurement at 800 MHz in mice without anesthesia. To solve the problem of radiofrequency reflection due animal motion, we developed a discrete auto-frequency control (DACF) method. The DACF periodically produces short (10-100 μs) and wide (up to 5 MHz) frequency scans to find and lock into the resonance frequency for a few tens of milliseconds, during which hundreds of RS spectra measured and averaged. RS anesthesia free method permits fast and repetitive measurements using a wide range of functional probes.

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EPR POSTER SESSION

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266 Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in B_{12}-dependent Ethanolamine Ammonia-Lyase Catalysis Revealed by Multiple EPR Techniques.

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Protein configurational fluctuations involved in the core chemical step in the B_{12}-dependent ethanolamine ammonia-lyase enzyme from *Salmonella typhimurium*, and the role of solvent as a stochastic, bi-directional dynamical modulator, are addressed by using multiple electron paramagnetic resonance (EPR) techniques that probe the successive "spheres of influence," which are, from bulk solvent to protein interior: (*1*) nitroxide spin-probe EPR to resolve temperature (*T*) -dependent dynamics of mesodomain (bulk) and protein-associated domain (PAD, hydration layer) solvent phases,[1,2] with *T*-dependence of the solvent dynamics tuned by using cosolvents, (*2*) nitroxide spin-label EPR to resolve protein surface dynamics at specific sites,[3] and (*3*) time-resolved, full-spectrum EPR spectroscopy to measure first-order kinetics of the substrate radical rearrangment reaction.[4,5] Cryo-*T* conditions (173-250 K) render protein configurational transitions rate-determining, and transform collective atom displacements into localized, incremental displacements, thus revealing the contributions of native collective protein configurations and fluctuations to reaction chemistry.[6] The *T*-dependences of spin probe and spin label motional parameters are compared to the *T*-dependence of the rearrangement reaction kinetics under the different solvent conditions, to identify and characterize the molecular mechanisms of solvent-protein-reaction coupling. The results progress toward dynamics-based molecular therapeutic approaches in medicine and bio- and materials-catalyst design principles. *Supported by NIH R01DK054514.*

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267 Field-reversal Method for Rapid Scan Background Correction.

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Rapid Scan is a continuous wave technique in which the magnetic field is scanned through the spectrum at kHz to MHz rates. This method gives substantially improved signal-to-noise relative to CW spectra, for a wide range of samples [1]. The rapid scans induce a background signal that may be larger than the EPR signal and increases with increasing scan width. A magnetic field-dependent component of the background is attributed to eddy currents induced in the resonator. The usual background correction by subtraction an off-resonance signal does not work well at low fields where a step off-resonance may be a significant fraction of the center field. A new procedure has been developed that uses two sets of data that are arbitrarily labeled as scan 1 and scan 2 [2]. The experiments are made possible by the use of a CAEN bipolar power supply. In scan 2 the external field B_0 is reversed and the data acquisition trigger is offset by one half cycle of the scan field relative to the settings used in scan 1. For data acquired with a cross-loop resonator the two scans exhibit the same background signal, but the EPR signal in scan 2 is inverted relative to that in scan 1. Upon subtraction of scan 2 from scan 1 the background cancels and the signal is amplified. This method has been tested for samples containing nitroxide radicals, a trityl radical, a dinitroxide, and a nitroxide in the presence of a magnetic field gradient. This method has the advantage that no assumption is made about the shape of the background signal, and it provides an approach to automating the background correction. It has been shown to be effective for background signals with multiple harmonics of the scan frequency and ones that are unsymmetrical.

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268 Trityl Radicals for EPR Spectroscopic Measurements on Oligonucleotides.

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Tris(2,3,5,6-tetrathiaaryl)methyl (Trityl) radicals are currently under development as spin probes for EPR spectroscopic applications such as distance measurements and dynamic investigations of biological systems. In comparison to the more common nitroxide spin-labels[1] they show several complementary features, in particular longer relaxation times T_1 and T_2 in the liquid state at room temperature[2,3] as well as their persistence in reducing environments[4]. These attributes give rise to the hope for high quality EPR spectroscopic measurements of biomacromolecules under native conditions such as room temperature[5,6,7] and within living cells[4].

Here, we present a synthetic approach to Trityl spin labels for oligonucleotides and corresponding labeling procedures. The Trityl compounds were mono-functionalized with an alkyne group by statistical esterification reactions. The alkyne moiety allows a bioconjugation with an Iodo-modified Uridine nucleotide through a palladium catalyzed coupling reaction. To achieve a more facile labeling-procedure we further synthesis a Trityl spin label functionalized with an azide for copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC). The properties and applications of the labels in EPR spectroscopic measurements will be discussed.

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