Rocky Mountain Conference on Magnetic Resonance

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57th Annual Rocky Mountain Conference on Magnetic Resonance

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57th Annual Rocky Mountain Conference on Magnetic Resonance

Abstract

Final program, abstracts, and information about the 57th annual meeting of the Rocky Mountain Conference on Magnetic Resonance, co-endorsed by the Colorado Section of the American Chemical Society and the Society for Applied Spectroscopy. Held in Snowbird, Utah, July 26-31, 2015.

57TH ANNUAL

ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 26-31, 2015

Snowbird Resort & Conference Center

Snowbird, Utah, USA

www.rockychem.com

57TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 26–31, 2015

Snowbird Resort & Conference Center

Snowbird, Utah

Endorsed by:

Colorado Section – American Chemical Society
&
Society for Applied Spectroscopy

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ORGANIZERS AND CHAIRPERSONS

ENDORSED BY:
Colorado Section — American Chemical Society
&
Society for Applied Spectroscopy

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ROCKY MOUNTAIN CONFERENCE INFORMATION

REGISTRATION

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCMR registration area located at the Snowbird Conference Center between 10:00 a.m. and 5:00 p.m. on Sunday, July 26 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 27 through Friday, July 31.

EXHIBITION SCHEDULE

Monday, July 27

10:00 a.m. – 7:00 p.m.
(Conference Reception 5:30 p.m. – 7:00 p.m.)

Tuesday, July 28

10:00 a.m. – 4:00 p.m.

ALTITUDE

Snowbird is approximately 8,100 feet above sea level. The acclimatization process is inhibited by dehydration, over-exertion, alcohol and other depressant drugs. Please take the following precautions regarding high altitude:

- Take it easy; don't over-exert yourself.
- Light activity during the day is better than sleeping because respiration decreases during sleep, exacerbating the symptoms.
- Avoid tobacco, alcohol and other depressant drugs including, barbiturates, tranquilizers, and sleeping pills.
- Eat a high carbohydrate diet
- Drink three to four times more water than usual.

CONFERENCE LUNCH

A complimentary lunch is being provided July 27, 28 and 29 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with any other day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The lunch will be served in Golden Cliff each designated day from 12:00 noon – 1:00 p.m.

CONFERENCE RECEPTION

Monday evening from 5:30 p.m. to 7:00 p.m., all attendees are cordially invited to join in on beverages and hors d'oeuvres. Unwind from the day's events and continue the "Rocky Mountain Conference" experience. Check out all of the latest products and services as the reception is held right in the exhibition area.

MESSAGES

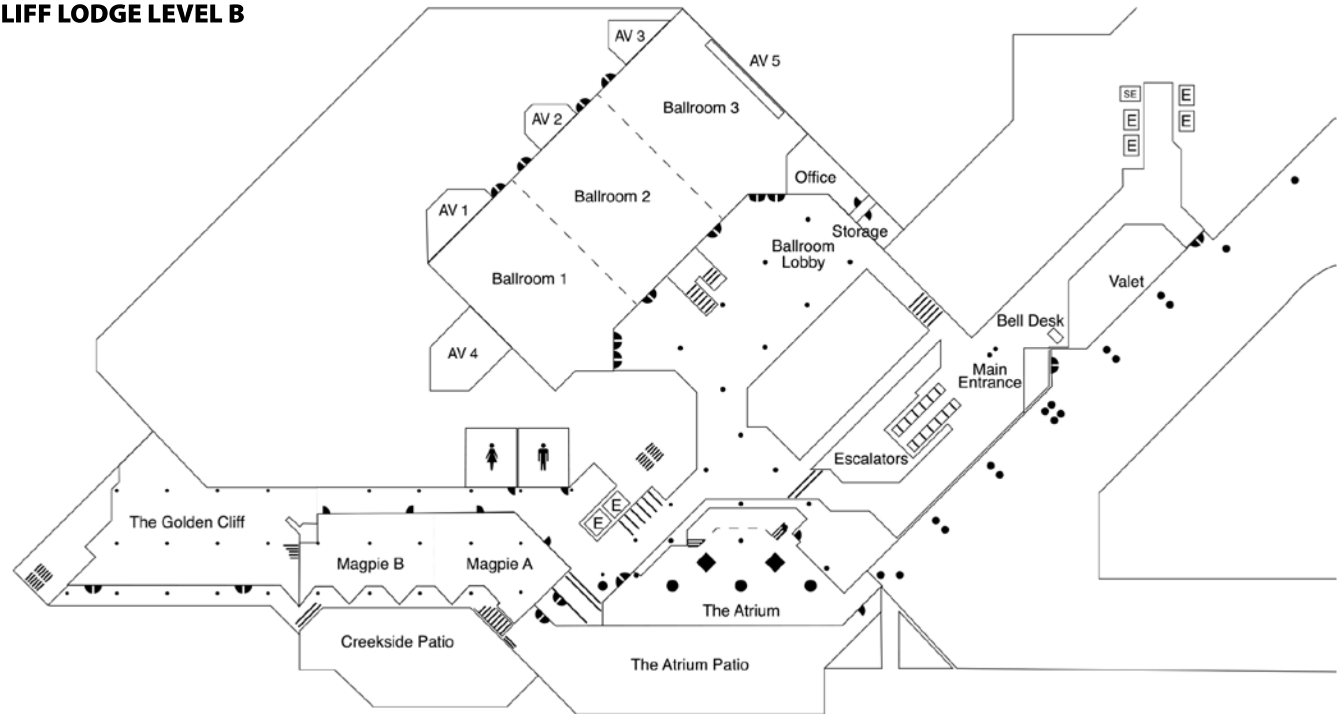
Messages will be accepted and posted on the message board. Call 800-996-3233 or 303-690-3233 to leave messages.

CONFERENCE-AT-A-GLANCE

EVENT	LOCATION	Sunday		Monday		Tuesday		Wednesday		Thursday		Friday	
		a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
Bruker Users Meeting	*Primrose*		▨										
EasySpin Workshop	*Ballroom 1*		▨										
EPR Lectures	*Ballroom 1*			▨	▨	▨	▨	▨	▨	▨			
EPR Posters	*Magpie*			▨	▨	▨	▨	▨	▨	▨			
Exhibition	*Ballroom 1 Foyer*			▨	▨	▨	▨						
GCW Lectures	*Maybird*										▨	▨	

SNOWBIRD CONFERENCE CENTER MEETING SPACE

CLIFF LODGE LEVEL B



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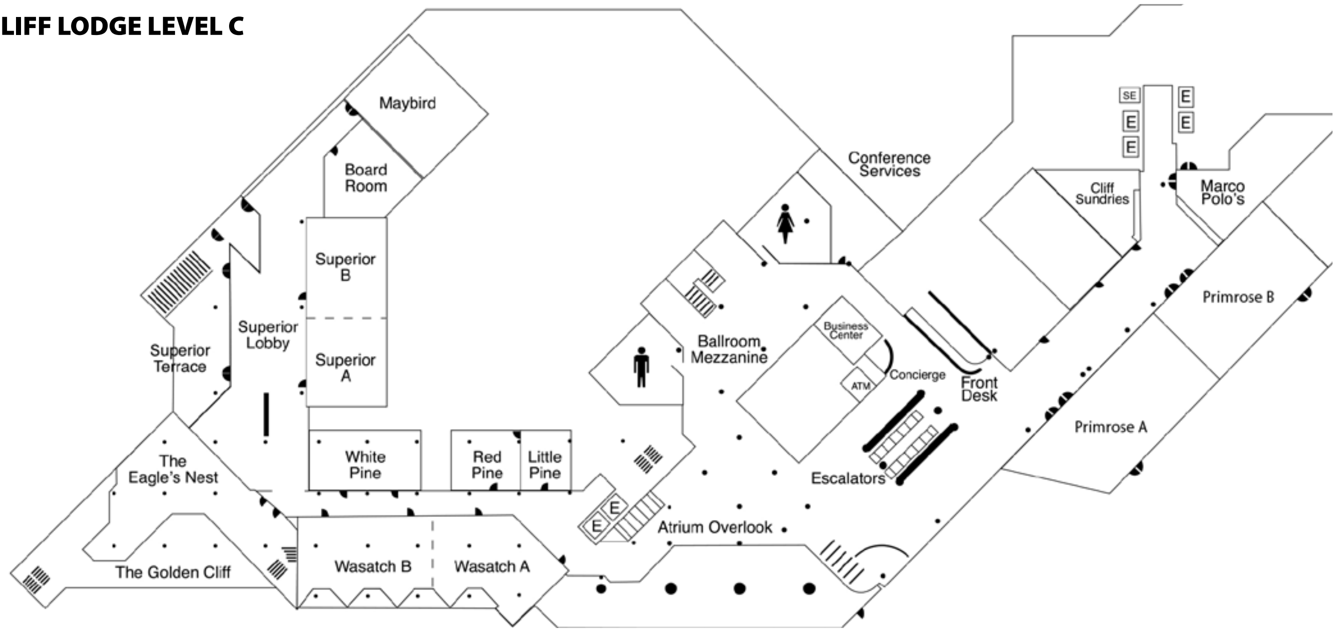

38TH INTERNATIONAL EPR SYMPOSIUM

July 26–30, 2015

57TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 26–31, 2015

Snowbird Resort & Conference Center
Snowbird, Utah

CONFERENCE CHAIR

Kurt W. Zilm

EPR SYMPOSIUM COMMITTEE

Kurt Warncke (Chair)

John Morton (Co-Chair 2015, Chair 2016)

Ania Bleszynski-Jayich, Christoph Boehme, Boris Epel, Fraser MacMillan, John McCracken, Susumu Takahashi

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EVENTS

EasySpin EPR Simulation Tutorial:

Sunday, July 26
4:00 p.m. – 6:00 p.m.
(presented by Stefan Stoll)

Bruker EPR Users' Meeting:

Sunday, July 26
Starts at 6:30 p.m., followed by a mixer.
For information and registration access https://www.bruker.com/events/users-meetings/mr/epr-us/registration-north-american-epr-users-meeting.html

Poster Sessions:

Monday, July 27
7:30 p.m. – 9:00 p.m.
and
Tuesday, July 28
7:30 p.m. – 9:00 p.m.

EPR Banquet:

Wednesday, July 29
7:00 p.m. – 9:00 p.m.
Enjoy an evening of comradeship and fine food in the scenic Aerie Private Dining Room in Cliff Lodge.
(Pre-registration required – additional fee for dinner)

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DOI: https://doi.org/10.56902/RMCMR.2015.57.1

EPR SYMPOSIUM
ORAL SESSIONS AGENDA

SUNDAY, JULY 26, 2015

Pre-Conference Activities	
4:00–6:00 PM	**EasySpin EPR Simulation Tutorial.** Stefan Stoll, University of Washington
6:30–10:00 PM	**Bruker EPR Users' Meeting** *Meeting followed by Mixer*

MONDAY, JULY 27, 2015

8:10 AM	**Welcoming Remarks.** Kurt Warncke, EPR Symposium Chair	
Session I: Spin Devices I. Ania Bleszynski-Jayich, Chair		
8:15 AM	100	**Purcell-Enhanced Relaxation of Electron Spins.** John Morton, University College London
8:45 AM	101	**Optical Hyperpolarization of Donor Electron Spins in Silicon Using a Tunable DBR Laser.** Brendon Rose, Princeton University
9:00 AM	102	**Inverse Spin Hall Effect From a Pulsed Ferromagnetic Resonance Driven Spin Current in Organic Semiconductors with Tunable Spin-Orbit Coupling.** Marzieh Kavand, University of Utah
9:15 AM	103	**Pulsed Electron Spin Resonance of Shallow Donors in Germanium.** Anthony Sigillito, Princeton University
9:30 AM	104	**Spins in a Semiconductor Quantum Dot.** Richard Warburton, University of Basel
10:00 AM	*Break*	
Session II: Methods I. Unconventional EPR. Susumu Takahashi, Chair		
10:30 AM	105	**Induction-Detection Electron Spin Resonance With Single Spin Sensitivity.** Aharon Blank, Israel Institute of Technology
11:00 AM	106	**Non-Resonant Near-Field EPR Scanning Probe Spectroscopy.** Jason Campbell, National Institute of Standards and Technology
11:20 AM	107	**Differentiating Between Hyperfine and Spin-Orbit Coupling in Magnetic Resonance Spectral Broadening of Organic Semiconductors.** Hans Malissa, University of Utah
11:40 AM	108	**Multi-Extreme THz ESR: Application to Shastry-Sutherland Model Substance $SrCu_2(BO_3)_2$.** Hitoshi Ohta, Kobe University
12:00 PM	*Lunch (included with registration)*	
Session III: Biological Macromolecules I and II. John McCracken, Chair		
1:30 PM	109	**EPR Analysis of Ligand Binding to Chlorite Dismutase From *Magnetospirillum* sp.** Sabine Van Doorslaer, University of Antwerp
2:00 PM	110	**Understanding the Active Site of [FeFe] Hydrogenases.** Agnieszka Adamska-Venkatesh, Max Planck Institute, Mühlheim
2:15 PM	111	**Electronic Structure Characterization of a Cu^{II} Alkoxide Complex.** Ellen Hayes, University of Washington
2:35 PM	112	**Insights into the Catalytic Mechanism of Bacillus subtilis Oxalate Decarboxylase: An Electron Paramagnetic Resonance Investigation.** Umar Twahir, University of Florida
2:50 PM	113	**Development of New Spin Labelling Strategies for Cysteine Rich Proteins.** Bouchra Hajjaj, University of St. Andrews
3:05 PM	*Break*	
3:35 PM	114	**Conformational Behavior of an Ion Channel, and the Quantification of Uncertainty in DEER.** Stefan Stoll, University of Washington
4:05 PM	115	**DEER and NMR Reveal the Structural Regulation of HCN Ion Channels by TRIP8b.** Hannah DeBerg, University of Washington
4:25 PM	116	**How the Prion Protein Folds – from the Copper's Perspective**. Glenn Millhauser, University of California Santa Cruz
4:45 PM	117	**Chemistry in Warm Little Ponds: On the Application of ESR Spectroscopy for the Identification of Copper Species and Assessing Molecular Fitness for Chemically-Evolving Solutions.** Christopher Bender, Fordham University
5:00 PM	118	**Determination of the Zero-Field Splitting Parameters of Novel Gd^{3+} Complexes by Very High Frequency EPR.** Jessica Clayton, University of California Santa Barbara
5:30–7:00 PM	*Conference Reception*	
Session IV, Posters		
7:30–9:00 PM	**Authors Present for Posters Labeled A**	

TUESDAY, JULY 28, 2015

Session V: Spin Devices II. Ania Bleszynski-Jayich, Chair		
8:15 AM	125	**Exploration of Spin Qubits in Silicon and Diamond.** Thomas Schenkel, Lawrence Berkeley National Laboratory
8:45 AM	126	**High-Frequency Optically Detected Magnetic Resonance of Nitrogen-Vacancy Centers in Diamond.** Viktor Stepanov, University of Southern California
9:05 AM	127	**Towards Bioimaging on the Nanoscale Using Single Spins in Diamond**. Tim Eichhorn, University of California Santa Barbara
9:25 AM	128	**High Precision Vector Magnetometry With Uniaxial Quantum Centers in Silicon Carbide**. Andreas Sperlich, Julius-Maximillian University, Würzburg
9:45 AM	129	**Development of a Spin-Selection Rule based Single-Electron Spin Resonance Microscope**. Kapildeb Ambal, University of Utah
10:00 AM	*Break*	
Session VI: Materials I. Christoph Boehme, Chair		
10:30 AM	130	**Electrically Detected Magnetic Resonance in 4-H SiC Transistors**. Patrick Lenahan, Pennsylvania State University
11:00 AM	131	**Probing Carrier-Pair Spin-Spin Interactions in a Conjugated Polymer by Detuning of Electrically Detected Beating of Spin-Rabi Oscillations**. Kipp van Schooten, University of Utah
11:15 AM	132	**Estimation Of The Exciton-Polaron Coupling In Organic Semiconductors Through Pulsed Electrically Detected Magnetic Resonance.** Thomas Keevers, University of New South Wales
11:30 AM	133	**Dynamics of Charge Separation in Polymer-Fullerene Bulk Heterojunctions as Revealed by Time-Resolved EPR/ENDOR and DFT**. Oleg Poluektov, Argonne National Laboratory
11:45 AM	134	**Spin-Dynamics in Vicinity of Spin-Gap and Antiferromagnetic Phase Transition of Low-Dimensional Organic Conductors (TMTTF)$_2X$**. Toshikazu Nakamura, Institute for Molecular Science
12:00 PM	*Lunch (included with registration)*	
Session VII: Biological EPR I. Fraser MacMillan, Chair		
1:30 PM	135	**Room-Temperature Distance Measurements of Immobilized Spin-Labeled Protein by DEER/PELDOR**. Sandra Eaton, University of Denver
2:00 PM	136	**Using Pulsed EPR to Explore Loop Dynamics of the TonB-Dependent Transporter ButB in Native Membranes.** Arthur Sikora, University of Virginia
2:15 PM	137	**smFRET and DEER Distance Measurements as Applied to Disordered and Structured Protein**. Tatyana Smirnova, North Carolina State University
2:30 PM	138	**Distances and Orientations with Low and High-Field/Frequency PELDOR/DEER**. Igor Tkach, Max Planck Institute, Fassberg
2:50 PM	*Break*	
Session VIII: Dynamic Nuclear Polarization. Susumu Takahashi, Chair		
3:20 PM	139	**Development of High-Field DNP Instrumentation for Magic-Angle Spinning ^{13}C NMR at 16.4 T and 30 K.** Toshimichi Fujiwara, Osaka University
3:50 PM	140	**Comparing Frequency Modulation Schemes for Improving DNP Enhancements.** Mallory Guy, Dartmouth College
4:05 PM	141	**Optimizing Frequency-Modulated CW EDMR in Silicon.** Lihuang Zhu, Dartmouth College
Session IX: IES Awards. Stephen Hill, Chair		
4:20 PM	142	**Electronic Structure of Novel Paramagnetic Actinide Complexes.** Eric McInnes, University of Manchester
4:40 PM	143	**CW and Pulsed EPR Study of Complex Coacervation of the Mussel Foot Protein Inspired Adhesives.** Ilia Kaminker, University of California Santa Barbara
Session X: Posters		
7:30–9:00 PM	**Authors Present for Posters Labeled B**	

WEDNESDAY, JULY 29, 2015

Session XI: Biological EPR II. Fraser MacMillan, Chair		
8:15 AM	150	**Genetically Encoded Spin Labels and In-Cell EPR.** Malte Drescher, University of Konstanz
8:45 AM	151	**New Approaches for Distance Measurements in Nucleic Acids Using Nitroxyl and Trityl Spin Labels.** Matvey Fedin, International Tomography Center, Novosibirsk
9:05 AM	152	**Spin-Labeling Magnetic Resonance Studies of Conformational Dynamics and Flexibility of the 232 nt Glycine Riboswitch.** Gail Fanucci, University of Florida
9:25 AM	153	**Electrostatics of Bio-Interfaces by EPR of Proteins and Phospholipids Labeled with pH-Sensitive Nitroxides.** Alex Smirnov, North Carolina State University
9:45 AM	154	**G-Quadruplex Targeting by Pt(II) Complexes Studied Using Site-Directed Spin Labeling.** Peter Qin, University of Southern California
10:05 AM	*Break*	
Session XII: Methods II: Pulse and Detection Optimization, and EPR Simulation. Susumu Takahashi, Chair		
10:35 AM	155	**Optimal Control of Spin Dynamics**. Steffen Glaser, Technical University, Munich
11:05 AM	156	**Considerations on Frequency-Swept Excitation Pulses.** Andrin Doll, ETH Zürich
11:20 AM	157	**Field-Stepped Direct Detection Electron Paramagnetic Resonance.** Zhelin Yu, University of Denver
11:40 AM	158	**Adiabatic Pulses for Improved Electrically and Optically Detected Magnetic Resonance.** Joanna Guse, University of New South Wales
12:00 PM	*Lunch (included with registration)*	
Session XIII: In Vivo EPR. Boris Epel, Chair		
1:30 PM	159	**In Vivo EPR Profiling of the Tumor Microenvironment Using Multifunctional Nitroxide and Trityl Probes.** Valery Khramtsov, The Ohio State University
2:00 PM	160	**Nitroxides as Biological Sensors.** Joseph Kao, University of Maryland
2:30 PM	161	**Multifunctional Probing of Microenviroment by Monophosphonated Trityl Radical Using FT and ESE Pulsed EPR Technique.** Andrey Bobko, The Ohio State University
2:45 PM	162	**Field Modulated Pulse EPR Spectroscopy and Imaging.** Mark Tseytlin, University of Denver
3:00 PM	163	Skin Structure of Psoriasis Vulgaris Investigated by CW EPR and 9 GHz EPR Imaging. Kouichi Nakagawa, Hirosaki University
Piette Award. Introduction by Sandra Eaton		
3:20 PM	164	**Melanin – An Important Biological Pigment with Unique Physico-chemical Properties.** Lawrence H. Piette Memorial Lecture, Tadeusz Sarna, Jagiellonian University
RMC General Business Meeting		
5:00 PM	Kurt Warncke, Chair	
IES General Business Meeting		
5:30 PM	Hitoshi Ohta, Chair	
EPR Banquet		
7:00–9:00 PM	*Enjoy an evening of comradeship and fine food. (Pre-registration required)*	

THURSDAY, JULY 30, 2015

Session XIV: Methods III: Noble Methods for Biology & HF EPR. Susumu Takahashi, Chair		
8:15 AM	170	**Pulsed Dipolar EPR Spectroscopy with Broadband Microwave Pulses.** Thomas Prisner, Goethe University
8:45 AM	171	**ESR of Spin-Labeled Lipid Bilayers Directly Tethered to a High Sensitivity Non-Resonant ESR Probe.** Pragya Shrestha, National Institute of Standards and Technology
9:00 AM	172	**EPR Spectroscopy on Mixed Phase Samples under Flow Conditions.** Eric Walter, Pacific Northwest Laboratory
9:20 AM	173	**Electron Spin Interactions and Electron Spin Relaxation at High Field.** Johan van Tol, National High Magnetic Field Laboratory
9:40 AM	174	**Electron-Spin-Echo Decay of Low- and High-Spin species at 240 GHz**. Blake Wilson, University of California Santa Barbara
9:55 AM	*Break*	
Session XV: EPR Materials II. Christoph Boehme, Chair		
10:25 AM	175	**Probing Single Electron Spins.** Jörg Wrachtrup, University of Stuttgart
10:55 AM	176	**Quantum Coherence in Mn-Based Single Molecule Magnets.** Susumu Takahashi, University of Southern California
11:15 AM	177	**Magnetic Phase Transition in Ferroelectric Lithium Niobate Doped with Erbium.** Galina Malovichko, Montana State University
11:35 AM	178	**Simulation of Magnetic Resonance Spectra of Low-Symmetry Systems**. Valentin Grachev, Montana State University
11:55 AM	**Closing Remarks.** Kurt Warncke, EPR Symposium Chair	

38TH INTERNATIONAL EPR SYMPOSIUM POSTER SESSIONS AGENDA

MONDAY, JULY 27 • 7:30–9:00 p.m.

(Authors Present for Posters Labeled A)

TUESDAY, JULY 28 • 7:30–9:00 p.m.

(Authors Present for Posters Labeled B)

A	**200**	**Electrically Detected Magnetic Resonance Measurements via Spin Dependent Charge Pumping and Other Detection Schemes in SiC Metal-Oxide-Semiconductor Field-Effect Transistors.** Mark Anders, Penn State University
B	**201**	**EPR of Di-and Tri-Nuclear Mixed-Valence Copper Amidinate Complexes from Reduction of Iodine.** William E Antholine, Medical College of Wisconsin
A	**202**	**Morphology and Photoexcitation Dependence of Optically Detected Magnetic Resonance in MEH-PPV Thin Films.** Douglas L Baird, University of Utah
B	**203**	**Solution State Overhauser Dynamic Nuclear Polarization at 10 mT.** Joshua R. Biller, National Institute of Standards and Technology
A	**204**	**Pulse Shaping at L-band using an Arbitrary Waveform Generator.** Laura A Buchanan, University of Denver
B	**205**	**Fast Frequency Swept EPR for Optimizing Microwave Efficiency in DNP NMR of Small Samples.** Anne M Carroll, Yale University
A	**206**	**Advantages of the Rotated and Modulated Magnetic Field Gradient in 2d Spatial and Spectral-spatial EPR Imaging.** Tomasz Czechowski, noviLET
B	**207**	**DEER Measurements of Copper Porphyrins Stacked on Guanine Quadruplexes.** Matthew P Donohue, National Institute of Standards and Technology
A	**208**	**Bayesian Uncertainty Quantification For DEER Spectroscopy.** Thomas H Edwards, University of Washington
B	**209**	**250 MHz in vivo Rapid Scan Images of pH and Thiol Reductive Status.** Boris Epel, University of Chicago
B	**210**	**Acceleration of Pulse EPR pO_2 Imaging using Low-Rank Tensor Imaging.** Boris Epel, University of Chicago
A	**211**	**Center for Electron Paramagnetic Resonance Imaging In Vivo Physiology—Tissue pO_2 as a Determinant of Tumor Biology.** Boris Epel, University of Chicago
B	**212**	**Solitons in Phthalocyanine Chromophores: Fundamental Study and Implications for Organic Spintronics.** Gregory P Eyer, University of Wisconsin-Madison

A	213	**Two-Dimensional Electron-Electron Double Resonance and Molecular Motions: The Challenge of Higher Frequencies.** John M Franck, ACERT
B	214	**Multiplex Detection of Magnetic Resonance for π-conjugated Polymer Electronics Devices.** Kunito Fukuda, Gunma University
A	215	**SHARED EPR: A Network of EPR Researchers.** Gary J. Gerfen, Albert Einstein College of Medicine
B	216	**Influence of Synthesis Route on Magnetic Ordering of SmxCa1-xMnO3(x=0.35, 0.65) Manganites: EMR Studies.** Lora Rita Goveas, Dr. Ambedkar Institute of Technolog/St. Joseph College
A	217	**EM Simulation Methods to Facilitate Design and Development of Custom Resonators.** Alexander Gunn, Independent Consultant, Active Spectrum
B	218	**Investigation of Radical Distribution in Foodstuffs by X-band ESR Imaging.** Hideyuki Hara, Bruker Biospin K.K.
A	219	**A Modular Low Frequency EPR Spectrometer for Studying Objects with Cultural Heritage Significance.** Joseph Hornak, RIT
A	220	**Low Frequency EPR of Ceramic and Marble Objects with Cultural Heritage Significance.** Joseph Hornak, RIT
B	221	**Low-Frequency EPR Imaging of Planar Objects with a Surface Coil.** Joseph Hornak, RIT
A	222	**Spin Dynamics of Strongly-Coupled Photogenerated Triradicals.** Noah E Horwitz, Northwestern University
B	223	**Electrically Detected Magnetic Resonance Spectroscopy on Monolithic Organic Light Emitting Diodes with built-in Lithographically Defined Microwave Excitation/Magnetic Field Modulation Structures.** Shirin Jamali, University of Utah
A	224	**Multi-Harmonics Electrically Detected Magnetic Resonance Spectroscopy of Organic Light Emitting Diodes Using Capacitively Coupled Coplanar Waveguide Resonators.** Gajadhar Joshi, University of Utah
B	225	**ESEEM Study of the Initial Stages of Tau Protein Aggregation.** Timothy J Keller, University of California Santa Barbara
A	226	**Characterization of the Free Energy Landscape for Radical Rearrangement Catalysis in B12-Dependent Ethanolamine Ammonia-Lyase.** Meghan Kohne, Emory University
B	227	**Spin Dynamics of Radical Pairs in Electron Donor-Acceptor Systems using Fourier Transform EPR Methods.** Matthew D Krzyaniak, Northwestern University
A	228	**Interaction Between the Influenza HA Fusion Peptide and Transmembrane Domain Affects Membrane Structure.** Alex L Lai, Cornell University
B	229	**Simulating Slow-Motion Continuous Wave EPR Spectra for General Spin Systems Using the Stochastic Liouville Equation.** Jeremy D Lehner, University of Washington

A	**230**	**Structural Changes at the Ferrous Active Site of Phenylalanine Hydroxylase Resulting from Allosteric Activation by Substrate.** John McCracken, Michigan State University
B	**231**	**Low Frequency Electrically Detected Magnetic Resonance and Near-Zero Field Magnetoresistance in a Variety of Amorphous Semiconductors and Dielectrics.** Michael J Mutch, Pennsylvania State University
A	**232**	**Distributions of C-ion and X–ray Induced Sucrose Radicals Investigated by CW EPR and 9 GHz EPR Imaging.** Kouichi Nakagawa, Hirosaki University
B	**233**	**Protein Surface Dynamics and Coupling to Solvent Dynamical Transitions Probed by Using EPR Spectroscopy of Spin-labeled B_{12}-dependent Ethanolamine Ammonia-lyase.** Benjamen Nforneh, Emory University
A	**234**	**EPR Studies of PCBM Derivatives.** Saralyn Ogden, University of Washington
B	**235**	**Rapid Scan Electron Paramagnetic Resonance at L-band of γ-irradiated Organic Solids.** Yilin Shi, University of Denver
A	**236**	**Characterization of a Radical Intermediate in Lipoyl Cofactor Biosynthesis.** Alexey Silakov, Pennsylvania State University
B	**237**	**EasySpin 5.** Stefan Stoll, University of Washington
A	**238**	**Pulse EPR 25 mT Magnetometer with 0.1 µT Resolution.** Subramanian Vadathavoor Sundramoorthy, University of Chicago
B	**239**	**Triplet State Delocalization in Multi-porphyrin Systems.** Claudia E. Tait, University of Washington
A	**240**	**Achieving Control with High-Q Superconducting Resonators in Pulsed Electron Spin Resonance.** Grum Teklemariam, Infinite Potential Labs
B	**241**	**EPR study of KH2PO4 Crystals with Embedded TiO_2 Nanoparticles.** Romand Tse, Montana State University
A	**242**	**Full Spectrum Rapid Scan 4D Spectral-Spatial EPR Imaging with Nitroxide Probes at 250 MHz.** Mark Tseytlin, Dartmouth College
B	**243**	**The Effects of Environmental Conditions On Free Radical Levels In Olive Oil.** Jagjeet T Wani, Steppingstone MAgnetic Resonance Training Center
A	**244**	**Brain Tissue Oxygen Measured by Electron Paramagnetic Resonance in Vascular Cognitive Impairment and Methamphetamine Abuse.** John M Weaver, University of New Mexico
B	**245**	**Electron Spin Resonance as a Probe for Antioxidant Mechanisms in Lubricants: ESR Signatures of Some Common Additives.** James R White, Active Spectrum
A	**246**	**High-field ESR Measurements of S=1/2 Frustrated J_1-J_2 Chain System $NaCuMoO_4(OH)$ as a Candidate Substance which Shows a Spin Nematic Phase.** Kitahara Yoko, Kobe University

GRAND CHALLENGE WORKSHOP

July 30–31, 2015

57TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 26–31, 2015

Snowbird Resort & Conference Center
Snowbird, Utah

CONFERENCE CHAIR

Kurt W. Zilm

GRAND CHALLENGE WORKSHOP ORGANIZATION

Gary Gerfen – Chair

Organized by the Research Coordination Network (RCN), "Supporting, Highlighting and Advancing Recent Developments in EPR" (SHARED EPR), funded by the National Science Foundation

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National Science Foundation
WHERE DISCOVERIES BEGIN

GRAND CHALLENGE WORKSHOP AGENDA

THURSDAY, JULY 30, 2015

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2:00 PM	276	**High Sensitivity ESR with High Spatial Resolution: Methodologies and Applications.** Aharon Blank, Technion – Israel Institute of Technology
2:45 PM	277	**Single-chip Electron Paramagnetic Resonance Transceivers in Silicon.** Aydin Babakhani, Rice University
3:30 PM	*Break*	
3:45 PM	278	**Resonating (and non-resonating) Microstructures for Broad-band Electrically and Optically Detected Magnetic Resonance Spectroscopy.** Christoph Boehme, University of Utah
4:30 PM	279	**Pushing the Sensitivity Limits for EPR of Small Samples with Micro-fabricated Planar Resonators.** Dieter Suter, Technical University of Dortmund
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FRIDAY, JULY 31, 2015

9:00 AM	280	**Single Spin Sensors: The New Paradigm in Ultrasensitive EPR and NMR?** Jörg Wrachtrup, University of Stuttgart
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ABSTRACTS

EPR SYMPOSIUM – ORAL SESSIONS

100 **Purcell-Enhanced Relaxation of Electron Spins.**

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Observing spontaneous emission in spins is challenging. Nuclear spins in 800 MHz NMR exhibit a free space spontaneous emission rate of ~10^{-22} s^{-1}, while for electron spins at a typical X-band frequency this rate is ~10^{-12} s^{-1}. Spontaneous emission therefore presents a negligible contribution to the spin relaxation time T^1, which is instead driven by a variety of other processes, such as spin-phonon interactions. When a two-level system is placed in a resonant cavity, spontaneous emission is enhanced through the Purcell effect [1], which has been observed for several decades for optical transitions in a variety of atomic and solid state systems [2]. Nevertheless, for typical cavity Q-factors and mode volumes in conventional ESR, even this enhanced relaxation rate remains on the order of a year^{-1}.

By coupling an ensemble of Bi donors in Si to a 7.3 GHz micron-scale superconducting resonator with Q > 10^5, we achieve a Purcell-enhanced relaxation rate of up to 3 Hz, well in excess of the natural spin relaxation rate of this system (observed to be 10 s at 3.5 K [3] and expected to be even longer at 10 mK used here). We find that the measured spin relaxation rate ($1/T_1$) follows the square of the cavity-spin coupling constant, as expected. In this way, the Purcell effect provides a possible mechanism to engineer spin relaxation, thus making mK ESR feasible in systems which would otherwise possess impractically long relaxation times.

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EPR ORAL SESSION

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101 Optical Hyperpolarization of Donor Electron Spins in Silicon Using a Tunable DBR Laser.

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We report on measurements of isotopically enriched silicon samples (45 ppm ^{29}Si) with very low donor densities (1E12-1E14/cm^3). Pushing the donor density to these low levels leads to very small signals and necessitates optimizing the experimental sensitivity and enhancing spin polarization. Donor spin polarization greater than Boltzmann (hyperpolarization) can be established by optically exciting the no-phonon bound exciton transitions followed by Auger recombination[1,2]. We established significant donor spin hyperpolarization using a distributed Bragg reflector (DBR) diode laser, tunable across all shallow donors in silicon, including ^{31}P and ^{209}Bi. For phosphorus doped silicon we observed both electron and nuclear spin polarization. Polarization of up to 100%-200% are measured (200% implies full polarization of both the electron and ^{31}P nuclear spins), depending on donor density, which is as much as a 13x boost in signal intensity compared to the 15% thermal spin polarization at 2 K. For bismuth donors at a clock transition (B = 80.6 mT), we observed about 50% spin polarization, and 500% away from the clock transition. This increase in spin polarization allows for a single shot measurement of low doping density samples (4E12/cm^3 for P and 1E14/cm^3 for Bi). Coherence times obtained from Hahn echo decays while polarizing with the laser are consistently shorter than those obtained with Boltzmann equilibrium. This is true even when operating at a magnetic field clock transition in bismuth doped silicon, indicating that this extra decoherence is not of magnetic origin. This excess noise can be mostly suppressed by shining a small amount of above gap light subsequent to laser illumination. With this technique we have measured Hahn echo decay times of ~4.5 seconds at a clock transition in Si:Bi (1E14/cm^3).

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EPR ORAL SESSION

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102 Inverse Spin Hall Effect From a Pulsed Ferromagnetic Resonance Driven Spin Current in Organic Semiconductors with Tunable Spin-Orbit Coupling.

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The inverse spin-Hall effect (ISHE) is typically referred to a voltage that appears across condensed matter in which a spin current experiences spin-dependent scattering that translates into charge separation, and thus, an electric field, through mediation by spin-orbit coupling (SOC) [1]. Experimentally, the ISHE has been observed only within the past decade [2] and it has been utilized in recent years for the exploration of spin-transport and spin-injection phenomena. Spin current needed for the detection of an ISHE can be generated in a wide range of materials via the process of spin-pumping from a ferromagnetic substrate subjected to ferromagnetic resonance [3].

Here we introduce a novel experimental approach for the generation of very strong ISHE signals using pulsed ferromagnetic resonance which allows the detection of 2 to 3 orders of magnitude stronger ISHE signals compared to continuous wave driven ferromagnetic resonance. The strong pulsed ISHE response enables us to investigate a variety of organic semiconductors with tunable, but overall weak, SOC, ranging from π-conjugated polymers containing intra-chain platinum atoms (producing the highest SOC within the group of weakly SOC materials) to fully-carbon based organic C60 films which exhibit SOC strengths between the Pt-doped and undoped polymers (due to curvature of the Fullerene cages). Our experiments offer a route for the exploration of efficient injection and detection schemes for pure spin currents at room temperature, and thus, the study of spin-orbit controlled spintronics device concepts in plastic materials.

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EPR ORAL SESSION

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103 Pulsed Electron Spin Resonance of Shallow Donors in Germanium.

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The presence of magnetic nuclei are one of the major sources of decoherence in semiconductor quantum devices. Germanium, like silicon, has been identified as a promising material for hosting donor-spin qubits because it has stable isotopes with no nuclear spin. In its natural form, Ge contains 7.7% ^{73}Ge (nuclear spin 9/2) but isotopically enriched material with reduced ^{73}Ge exists. However, until now, the prospect of using germanium for quantum devices has remained largely unstudied.

In this presentation we report pulsed spin resonance measurements of the coherence (T_2) and relaxation (T_1) times for ^{75}As and ^{31}P donors in natural and isotopically enriched (4% and 0.1% ^{73}Ge) germanium down to He-3 temperatures. Below 2 K we find that T_1 is limited by a single-phonon process whereas a two-phonon Raman process dominates at higher temperatures. We observe anisotropies in the linewidth and T_1 that depend on the magnetic field direction relative to the Ge crystal. This is explained using a valley repopulation model. We also report the first T_2 measurements for donors in Ge and find that in isotopically enriched material, T_2 is limited by T_1 to 1.2 ms at 350 mK for $B_0 \parallel (100)$ at X-band frequencies. This is compared to a ^{73}Ge limited T_2 of 55 ms for natural germanium. Other orientations are expected to show longer spin coherence.

EPR ORAL SESSION

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104 Spins in a Semiconductor Quantum Dot.

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A semiconductor quantum dot is a potential host for a spin qubit. On the one hand, dealing with the nuclear spin noise is an important issue. On the other hand, the nuclear spins in a self-assembled quantum dot are decoupled to all extents and purposes from the other nuclear spins in the material and an opportunity arises to explore the properties of a nano-sized nuclear spin ensemble. We show here how frequency-swept NMR can be applied to manipulate the quantum dot nuclear spins and to determine their key parameters (initial temperature following polarization, the indium concentration and the isotope-specific quadrupole frequency distributions). We go on to determine the coherence associated with the central transition (-1/2 to +1/2). The Hahn echo T2 is a few milliseconds for an unoccupied quantum dot but falls by about a factor of 100 on occupying the quantum dot with a single electron, evidence for a RKKY-like decoherence process whereby all nuclear spins couple via a common interaction with the electron spin. This interaction ultimately limits the electron spin coherence. We show how the coupling to the nuclear spins can be turned off by switching to a hole spin and applying a transverse magnetic field.

EPR ORAL SESSION

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105 Induction-Detection Electron Spin Resonance With Single Spin Sensitivity.

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ESR has many applications, ranging from semiconductor characterization to structural biology and even quantum computing. While being very powerful and informative, ESR traditionally suffers from low sensitivity, requiring many millions of spins to get a measureable signal with commercial systems using the Faraday induction-detection principle. In view of this disadvantage, significant efforts were made recently to develop alternative detection schemes based, for example, on force, optical, or electrical detection of spins, all of which achieve single electron spin sensitivity. This sensitivity, however, comes at the price of limited applicability and usefulness to address real scientific and technological issues facing modern ESR, as conventional induction-detection ESR does on a daily basis. In the talk we present the most sensitive experimental induction-detection ESR setup and results ever reordered that show the detection capability of the magnetization of just a single electron spin.[1] This was achieved thanks to the development of an ultra-miniature micrometer-sized microwave resonator that was operated at ~34 GHz at cryogenic temperatures in conjunction with a unique cryogenically-cooled low noise amplifier. The experiment employed as a test sample isotopically enriched phosphorus-doped silicon, which is of significant relevance to spin-based quantum computing. The sensitivity was experimentally verified with the aid of a unique high-resolution ESR imaging approach. These new results represent a paradigm shift with respect to the capabilities and possible applications of induction-detection-based ESR spectroscopy and imaging. Details of the experimental set-up will be provided and future directions leading to further improved sensitivity will be discussed.

1. Applied Physics Letters 106, (2015) 084104

EPR ORAL SESSION

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106 Non-Resonant Near-Field EPR Scanning Probe Spectroscopy.

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EPR has demonstrated itself as a crucial tool for understanding a wide variety of biochemical interactions. However, EPR is relatively insensitive and thus requires a large number of spin active species in order to produce a signal. This presents a significant challenge for studying many biological systems as synthesizing the needed volume of spin-labeled biomolecules to produce a spectrum is often unfeasible.

Here, we demonstrate continuous wave spectroscopic X-band EPR via a non-resonant near field microwave probe1. The key innovation is replacing a standard resonant structure with a geometrically-scaled shorted coaxial termination with $Q \approx 1$. The degraded sensitivity associated with using a non-resonant structure is more than compensated for by the gains in filling factor upon geometric scaling. The net sensitivity is improved by more than 20000x over conventional systems. These sensitivity gains are demonstrated at ambient conditions by measuring 140 attomoles of TEMPO in an approximately 593 femtoliter liquid cell. The experimental arrangement associated with this detection approach is amenable to a wide variety of samples (solids/liquids) and eliminates many of the sample restrictions dictated by resonator base experiments. In addition, the form factor is akin to a scanning probe measurement in which the sample surface can be EPR imaged with relative ease. The experimental form factor is highly suitable for examining biochemical interactions at relevant ambient conditions with great fidelity.

J.P. Campbell, J.T. Ryan, P.R. Shrestha, Z. Liu, C. Vaz, J. Kim, V. Georgiou, and K.P. Cheung, “Electron Spin Resonance Scanning Probe Spectroscopy for Ultrasensitive Biochemical Studies,” Analytical Chemistry, in press (2015). DOI: 10.1021/acs.analchem.5b00487.

EPR ORAL SESSION

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107 Differentiating Between Hyperfine and Spin-Orbit Coupling in Magnetic Resonance Spectral Broadening of Organic Semiconductors.

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The conductivity of organic semiconductors is strongly influenced by nuclear spins of the all-abundant hydrogen atoms. This effect can be observed for instance by comparative magnetoresistance measurements of organic semiconductor devices which are nominally identical except for the different hydrogen isotopes[1]. These nuclear spins are hyperfine coupled to the spins of charge carriers (so called polaron states). We have investigated nuclear-spin control mechanisms of the electronic materials properties using various pulsed electrically detected magnetic resonance (pEDMR) spectroscopy techniques[2,3]. In order to experimentally distinguish nuclear spin effects from spin-orbit effects, we have conducted pEDMR experiments on charge carrier (polaron) spins over a broad range of frequencies and magnetic fields ranging from the low-field (several MHz) up to the quasi-optical (hundreds of GHz) regime. As expected, at low magnetic fields, the polaron resonance line width is dominated by the nuclear spin-electron interaction (the so-called hyperfine fields), whereas at high magnetic fields it is governed by the weak, but non-zero spin-orbit coupling induced distribution of the Landé-factor, with width Δg, of electron and hole polaron resonances[2]. The comparison of the data obtained in the different frequency domains allows us to accurately determine both the magnitude of the random hyperfine fields as well as Δg.

This work was funded by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Sciences and Engineering under Award DESC0000909.

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EPR ORAL SESSION

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108 Multi-Extreme THz ESR: Application to Shastry-Sutherland Model Substance $SrCu_2(BO_3)_2$.

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Development of THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, is the main target in Kobe recently. 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 the pressure region up to 1.5 GPa.2 Recently we achieved 2.7 GPa using the hybrid-type pressure cell.3Our micro-cantilever ESR also enables the measurements of micrometer size single crystals.4Development on the magnetization detected ESR using SQUID magnetometer (SQUID ESR) has been also achieved.5 As an application high pressure THz ESR results of Shastry-Sutherland Model Substance $SrCu_2(BO_3)_2$ up to 2 GPa at 2 K will be presented and the possible phase transition under high pressure will be discussed.

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EPR ORAL SESSION

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109 EPR Analysis of Ligand Binding to Chlorite Dismutase From *Magnetospirillum* sp.

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Perchlorate reducing bacteria have the ability of transforming toxic perchlorate in chloride ions and therefore offer the possibility of perchlorate removal via bioreactors. In the perchlorate pathway, the heme protein chlorite dismutase (Cld) catalyzes the splitting of chlorite in chloride and oxygen. The EPR spectrum of ferric wild-type Cld of *Magnetospirillum* sp. (*Ma*Cld) exhibits a variety of ferric heme centers. Addition of an axial ligand, such as azide, nitrite or imidazole, removes this heterogeneity almost entirely. This is in line with the two existing high resolution crystal structures of *Ma*Cld obtained in the presence of azide and thiocyanate that show the coordination of the ligands to the heme iron. The crystal structure of the *Ma*Cld-azide complex reveals a single well defined orientation of the azide molecule in the heme pocket. EPR shows, however, a pH-dependent heme structure, probably due to acid-base transitions of the surrounding amino-acid residues stabilizing azide. For the azide, nitrite and imidazole complex of *Ma*Cld the hyperfine and nuclear quadrupole interactions with the nearby ^{14}N and ^{1}H nuclei are determined using pulsed EPR. These values are compared to the corresponding data for the low-spin forms observed in the ferric wild-type MaCld and to existing EPR data on similar complexes of other heme proteins.

EPR ORAL SESSION

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110 Understanding the Active Site of [FeFe] Hydrogenases.

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In the green algae Chlamydomonas reinhardtii photosynthesis under sulfur deprivation results in the release of a byproduct, H_2, a possible future renewable energy carrier. This is due to its highly efficient [FeFe] hydrogenase that contains an active site called the “H-cluster”. This consists ofa “classical” [4Fe-4S] cluster and a unique $[2Fe]_H$ sub-cluster with CN^- and CO ligands and a dithiolate bridging ligand. We have recently shown that the apo-protein of [FeFe] hydrogenase, which contains only the [4Fe-4S] part of the H-cluster, could be maturated and activated by a synthetic precursor of the diiron sub-cluster ($[Fe_2(CO)_4(CN)_2(adt)]^{2-}$) [1, 2]. This approach allows not only the production of large amounts of highly active enzyme but also to modify and selectively isotope label the precursor of the $[2Fe]_H$ sub-cluster. Additionally, we could insert many different biomimetic complexes into the enzyme and identify structural motifs which are essential for catalytic activity [3]. Using FTIR spectro-electrochemistry new intermediate states could be identified both in native and hybrid versions of the H-cluster [4]. A combination of isotope labeling (^{57}Fe, ^{13}C and ^{15}N) and the use of hybrid enzyme allowed us to study in great detail the electronic structure of the H-cluster by multi-frequency pulse EPR methods [5, 6].

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EPR ORAL SESSION

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111 Electronic Structure Characterization of a Cu^{II} Alkoxide Complex.

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A unique four coordinate Cu^{II} alkoxide complex structurally reminiscent of the galactose oxidase active site has been synthesized[1] and the electronic structure characterized. The galactose oxidase enzyme is known to oxidize primary alcohols to aldehydes through a four coordinate Cu^{II} alkoxide intermediate. The oxidation is believed to occur via a one-electron transfer to Cu^{II} and a hydrogen atom transfer from the α-C-H bond of the alkoxide ligand to a coordinated 3'-(*S*-cysteinyl)tyrosine radical.[2,3] The model compound $Tp^{tBu}Cu^{II}\text{-}OCH_2CF_3$ (Tp^{tBu} = (3-t-butyl-pyrazolyl)-borate) contains a trifluoroethoxide ligand and exhibits an almost axial EPR spectrum with a uniquely large $g_{||}$ value of 2.45 and small copper hyperfine coupling $A_{||}$ of $39{\bullet}10^{-4}$ cm^{-1} or 118 MHz. To determine the electronic structure yielding these unique parameters, optical absorption, single crystal Q-band EPR and ENDOR (electron nuclear double resonance), MCD (magnetic circular dichroism), and rR (resonance Raman) spectroscopies have been employed. Single crystal EPR experiments reveal a d_{x2-y2} ground state (LUMO) with the orbital plane perpendicular to a long Cu-N$_{axial}$ bond and ENDOR experiments reveal the spin density on the ethoxide ligand. The optical absorption spectrum shows a weak d orbital manifold transition at 900 nm and an intense charge transfer transition at 420 nm which is assigned to an ethoxide lone pair to LUMO transition based on MCD and rR results. These data, supported by DFT calculations, will be used to compare the electronic structure of this unique model complex to the existing literature on small molecule and biological copper active sites.[4,5]

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EPR ORAL SESSION

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112 Insights into the Catalytic Mechanism of Bacillus subtilis Oxalate Decarboxylase: An Electron Paramagnetic Resonance Investigation.

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Oxalate Decarboxylase from Bacillus subtilis is a Mn-dependent enzyme that catalyzes the degradation of oxalate to carbon dioxide and formate. OxDC is a member of the bicupin superfamily of enzymes, with a mononuclear Mn (II) coordinated in each of its two domains. The proposed mechanism employs oxygen a co-catalyst necessary to drive the initial oxidation step in the catalytic cycle, suggesting Mn (III) is present while superoxide is generated. Superoxide production was studied utilizing both spin trapping EPR and mass spectrometry.[1] Mn (III) has also been seen in related enzymes,[2,3] where the Mn ion cycles through oxidation states during turnover, suggesting that OxDC might follow a similar trend. In the present study the enzyme was chemically oxidized in order to observe Mn (III) directly, using parallel- mode X-band and Mn (II) oxidation using High-Field/Frequency EPR. The observed Mn (III) EPR signature was then also observed in as-prepared enzyme, and exhibits a strong pH dependency which was observed on the same enzyme preparation using an enzyme immobilization technique. OxDC is only active at low pH where the majority of the Mn(III) signal was observed and shows a pH dependence of its Mn (II) signals indicative of conformational changes.[4]

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EPR ORAL SESSION

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113 Development of New Spin Labelling Strategies for Cysteine Rich Proteins.

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EPR ORAL SESSION

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114 Conformational Behavior of an Ion Channel, and the Quantification of Uncertainty in DEER.

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This presentation consists of two parts. (A) HCN is a hyperpolarization-activated ion channel that is involved in the regulation of the heartbeat. HCN contains an intracellular ligand-binding domain that regulates the channel's activation. The structural basis for this regulation is unknown. We present a structural model for the conformational transition induced by ligand binding. The model is based on multiple DEER distance distributions in combination with coarse-grain elastic network modeling. We also show results on the topology of the complex between the HCN ligand-binding domain and TRIP8b, a structurally uncharacterized accessory protein. For this, we used DEER-based probabilistic trilateration.

(B) Although most experimental DEER data are contaminated by noise, the commonly applied Tikhonov regularization (TR) delivers a noise-free distance distribution P(r), without any error bars. In addition, the DEER workflow includes systematic biases such as the particular choice of the regularization parameter. Commonly, neither the effect of noise nor the impact of biases on P(r) is fully analyzed. This can potentially lead to over-interpretation and to erroneous structural conclusions. We present first results on a promising approach for quantifying the uncertainty in TR-based P(r) due to noise and biases. The approach is based on Bayesian inference and intends to facilitate more reliable data interpretation.

EPR ORAL SESSION

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115 DEER and NMR Reveal the Structural Regulation of HCN Ion Channels by TRIP8b.

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Hyperpolarization-activated cyclic nucleotide-gated (HCN) ion channels play an important role in regulating pacemaking activity in the heart and brain. They are regulated by adenosine 3',5'-cyclic monophosphate (cAMP). cAMP binds to a conserved intracellular cyclic nucleotide binding domain (CNBD) in the channel, increasing the rate and extent of activation of the channels and shifting activation to less hyperpolarized voltages. TRIP8b is an auxiliary subunit that regulates HCN channel localization and, when bound to HCN, reduces their cyclic nucleotide dependence. The structure of TRIP8b is unknown. We show that TRIP8b binds to the apo state of the cyclic nucleotide binding domain (CNBD) of HCN2 channels without changing the overall domain structure through cw-EPR and double electron-electron resonance (DEER) experiments. Furthermore, we use 1H, 15N HSQC nuclear magnetic resonance to identify the binding surface for TRIP8b on HCN. We apply intermolecular DEER to measure distances between HCN and TRIP8b and map the topology of the TRIP8b and HCN channel complex. These data provide a structural framework for understanding how TRIP8b regulates the cyclic nucleotide dependence of HCN channels.

EPR ORAL SESSION

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116 **How the Prion Protein Folds – from the Copper's Perspective**.

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The cellular prion protein (PrP^C) is a membrane-anchored glycoprotein consisting of two domains: a flexible N-terminal domain that participates in Cu^{2+} and Zn^{2+} binding, and a mainly helical C-terminal domain that converts to β-sheet structure in the course of prion disease. These two domains have traditionally been thought of as non-interacting; however, recent cellular and biophysical evidence has forced a reconsideration of this view. Using NMR, we recently reported a novel tertiary fold in which the Zn^{2+}-bound octarepeat domain contacts the exposed surface of helices 2 and 3.[1] We now wish to approach this with the copper bound protein. The inter-domain structure in Cu^{2+}-bound recombinant PrP is examined using site-directed spin labeling of the genetically incorporated unnatural amino acid pAcPhe and Cu^{2+}–nitroxide DEER EPR. Distance measurements show that the Cu^{2+}-bound PrP octarepeats interact with a negatively charged surface defined by helices 2 and 3. Our results are supported by molecular dynamics simulations, which indicate that the observed *cis* interaction is stabilized by electrostatics. Our findings suggest that metal-induced tertiary structure may be a general property of PrP^C, important for protein processing[2] and function,[3] and that disruption of this interaction may be a contributing factor in prion disease pathology.

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EPR ORAL SESSION

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117 **Chemistry in Warm Little Ponds: On the Application of ESR Spectroscopy for the Identification of Copper Species and Assessing Molecular Fitness for Chemically-Evolving Solutions.**

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The Miller-Urey experiments of the 1960s demonstrated how a mixture of inorganic gas can be induced to form a condensate of fundamental organic building-blocks that coincide with the molecules of metabolic importance. Thus were posited scenarios of a primeval sequence in which molecular complexity evolves through directed stepwise syntheses. Geochemical origins of an ordering principle associated with these syntheses have been suggested, and we are examining the leaching of copper and formation of coordination complexes with small organic molecules in saline solutions that are formulated to mimic geochemical systems. The parametric information obtained from the cw-ESR spectra is sufficiently precise to make distinctions among coexisting copper(II) species in the saline solutions, and for the interactions of a given specific ligand with copper, we are able to observe changes in speciation as we alter the prevailing conditions in the solution. By systematically comparing the ESR spectra of copper coordinated by ligands that are members of a homologous series, we are observing binding trends that may be interpreted and used as a gauge of molecular fitness in chemical evolution processes that eventually lead to structural motifs that are familiar to peptide and protein chemists.

The work to be presented was peformed at Brooklyn College, and the author gratefully acknowledges Richard S. Magliozzo for the use of the ESR spectrometer.

EPR ORAL SESSION

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118 Determination of the Zero-Field Splitting Parameters of Novel Gd^{3+} Complexes by Very High Frequency EPR.

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Site-directed spin-labeling (SDSL) combined with electron spin resonance has proven to be a very powerful tool for elucidating the structure of biomolecules in a variety of environments. With technological developments making high-field EPR ever more accessible and versatile, SDSL has naturally been extended to the high-field. Due to limitations of stable nitroxide radicals for high-field work a new family of spin-labels based on S=7/2 Gd^{3+} compounds have been introduced.[1] Previous work using Gd^{3+}-based spin labels for distance measurements with high-field DEER and CW-EPR have largely ignored effects of zero-field splitting (ZFS), which is typically 3+-labeled systems has shown that the effects of ZFS must be considered, and hence accurate knowledge of the ZFS parameters is required.[1,2,3] Very-high frequency EPR conducted at low temperatures is particularly well-suited to extracting ZFS parameters.[4] We investigate the ZFS parameters of six Gd^{3+} complexes, including Gd(Py-MTA), Gd(DOTA), Gd(Py-DTTA), and Gd(TAHA) in 300 μM glassy solutions using low-temperature EPR spectra recorded at 240 GHz. These results are confirmed by additional spectra recorded at W-band and X-band. Experimental spectra are fit to two models for the axial and rhombic ZFS parameters (D and E) from literature: (1) uncorrelated single-Gaussian distributions of D and E and (2) a bimodal distribution of D values with the distribution of E/D taken to be $P(E/D) \propto (E/D) - 2 \cdot (E/D)^2$.[4,5]

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EPR ORAL SESSION

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125 Exploration of Spin Qubits in Silicon and Diamond.

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Electron and nuclear spins of donors in silicon and of color centers in diamond are being explored as quantum bit candidates and for emerging sensor applications. Ion implantation is one standard method for the placement of donor atoms into silicon devices. I will present results from EDMR (electrical detection of magnetic resonance) studies of ion implanted silicon transistors and discuss challenges and opportunities for device integration of donor spin qubits.

In diamond, color centers such as nitrogen-vacancy (NV) centers can be formed by implantation of nitrogen ions into high purity synthetic diamond, followed by thermal annealing. But the reliable formation of high quality color centers has proven challenging. I will discuss emerging techniques for the formation of color center qubit arrays in diamond by ion implantation and local electronic excitation.

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126 **High-Frequency Optically Detected Magnetic Resonance of Nitrogen-Vacancy Centers in Diamond.**

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A nitrogen-vacancy (NV) center is a paramagnetic center in diamond with unique electronic, spin, and optical properties. Electron spin resonance (ESR) of a single NV center is observable by measuring changes of the FL intensity, a magnetic resonance technique known as optically detected magnetic resonance (ODMR) spectroscopy. A NV center in diamond is a promising candidate for applications to high sensitive magnetic resonance (MR) spectroscopy and magnetic sensing because of its ODMR signals are extremely sensitive to their surrounding electron and nuclear spins. For example, detection of a single or a small ensemble of electron and nuclear spins surrounding a NV center has been demonstrated using electron spin echo envelope modulation (ESEEM), double electron-electron resonance (DEER) and electron-nuclear double resonance (ENDOR) spectroscopies of a single NV center at low magnetic fields. In addition, spin relaxometry based on the longitudinal relaxation time (T_1) measurement of a single NV center has been employed to detect several electron spins. Here we discuss high-frequency (HF) ODMR spectroscopy of NV centers. The HF ODMR system consisting of two high-frequency high-power solid-state sources, a quasioptical system, a 12.1 Tesla cryogenic-free superconducting magnet, and a ^{4}He cryostat[1] is capable of performing ODMR, DEER and other MR spectroscopies. We present investigations of ODMR of a single NV at 4.2 Tesla at room temperature and the magnetic field dependence of T_1 of NV centers in nanodiamonds.[2] In addition, DEER techniques at high magnetic fields will be discussed.

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EPR ORAL SESSION

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127 **Towards Bioimaging on the Nanoscale Using Single Spins in Diamond**.

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Ania Bleszynski Jayich[1]
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Nitrogen vacancy (NV) centers in a diamond crystal are quantum defects that have unique physical properties of their electronic spin system. NV centers allow highly-sensitive magnetic field imaging with nanometer-scale resolution since the spin system exhibits long quantum coherence and is optically prepared and read out. Due to its atomic-scale size, individual and optical addressability, excellent photostability, biocompatibility, and noninvasiveness, the NV center is a particularly promising and versatile nanoscale sensor of biological signals under ambient conditions.

Here we report on our approach to widefield imaging of the electric activity of two types of excitable cells, namely neurons and cardiac myocytes, using a home-built total internal reflection fluorescence (TIRF) microscope and optically detected magnetic resonance (ODMR) protocols. Assuming 100-nanometer proximity of NV centers to the cell, we expect magnetic field amplitudes of a few nano-Tesla within tens of milliseconds that are associated with the cell's electric activity[1,2]. We discuss the prospects of meeting these demanding conditions with NV center sensors and we present results of ongoing measurements. We also present our efforts aimed at enhancing the NV sensors' sensitivity via ensemble magnetometry using custom-made diamond samples[3] with high NV density.

The work is supported by SNF grant P2ELP2_158879.

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EPR ORAL SESSION

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128 **High Precision Vector Magnetometry With Uniaxial Quantum Centers in Silicon Carbide**.

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We show that uniaxial color centers in silicon carbide with hexagonal lattice structure can be used to measure not only the strength but also the orientation of the external magnetic field with high precision. The method is based on the optical detection of multiple spin resonances in the silicon vacancy defect with quadruplet ground state. We achieve a perfect agreement between the experimental and calculated spin resonance spectra without any fitting parameters, providing angle resolution of a few degrees in the magnetic field range up to several millitesla. Our approach is suitable for ensemble as well as for single spin-3/2 color centers, allowing for vector magnetometry on the nanoscale at ambient conditions.

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EPR ORAL SESSION

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129 **Development of a Spin-Selection Rule based Single-Electron Spin Resonance Microscope**.

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Paramagnetic point defects in semiconductors are among the most coherent qubits found in nature[1], yet using them for quantum applications will require the detection and readout of single electrically isolated paramagnetic states with atomic scale spatial resolution and independent addressability. More than two decades after the first single-electron spin resonance experiments[2], the spatial resolutions of various electrical[3], optical[4] and even scanning probe based single spin detection techniques[5] are still either well above the atomic scale or require conducting substrates in which fluctuating charges can induce significant decoherence. Thus, a reliable single-spin detection technique with atomic scale resolution and access to individually isolated qubit states is needed.

This presentation outlines a concept for a scanning-probe based single-spin resonance experiment[6] that allows for atomic scale spatial resolution. The experiment is based on electrostatic force detection[7] of spin-selection rule controlled single-electron tunneling transitions that utilizes a low temperature scanning probe microscope with a dielectric substrate and a crystalline silicon probe that has a silicon dioxide surface layer with very high densities of paramagnetic centers. A center at the tip of the probe is aimed to be used as probe spin for single spin detection. We report on progress towards the implementation of this experiment, including the observation of individual surface defects, the observation of random charge carrier telegraph noise-detected single electron tunneling transitions and the preparation of silicon dioxide layers with an unprecedented density of paramagnetic silicon dangling bond states.

This work was supported through the Utah MRSEC center, grant #1121252. The acquisition and development of the low-temperature AFM was supported by the National Science Foundation through MRI project #0959328. A.P. was supported by the Army Research Office, grant #W911NF-10-1-0315.

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EPR ORAL SESSION

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130 Electrically Detected Magnetic Resonance in 4-H SiC Transistors.

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We have utilized electrically detected magnetic resonance (EDMR) via spin dependent recombination (SDR) in 4H SiC metal oxide semiconductor field effect transistors. We have exploited the near frequency and field independence of SDR/EDMR to make EDMR observations from 16GHz, down to 85MHz indentifying several important point defects in these devices. In addition, the very wide range of frequencies utilized allow us to explore the paramagnetic centers in ways which have rarely, if ever, been utilized in semiconductor device physics studies. Perhaps the most interesting observations involve an SDR/EDMR response at half the resonance field caused by the mixing of states by magnetic dipole-dipole coupling of paramagnetic centers.[1,2,3] Since the half field response scales with the reciprocal of defect separation to the sixth power, the response provides information about the distance between the defects. [1,2] Because the half field response scales with the reciprocal of the resonance frequency squared,[1,2] the very low frequency measurements are sensitive at technologically relevant concentrations. Also of interest is the close correlation between the near zero magnetic field magnetoresistance response and the EDMR which provide a direct demonstration that the low field magnetoresistance effects are due to spin dependent recombination. [4] Another observation of interest is the likely SDR/EDMR detection of nitrogen complexes in SiC devices. [5] The is of interest because of their relevance to device operation and quantum computation.

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EPR ORAL SESSION

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131 Probing Carrier-Pair Spin-Spin Interactions in a Conjugated Polymer by Detuning of Electrically Detected Beating of Spin-Rabi Oscillations.

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Radical pair reactions can explain phenomena ranging from avian magnetoreception to spin-dependent charge-carrier recombination and transport rates in semiconductor materials. Central to the radical pair model are weakly-coupled electron spin pairs in a matrix with weak spin–orbit interactions. However, while it has been known that the magnetic-dipolar and spin-exchange interaction strengths within these pairs are weak, specific values within their native operating environment (e.g. within organic light emitting diodes) have been experimentally difficult to obtain. To probe intra-pair coupling strengths *in situ* for an organic semiconductor diode under operating conditions, we use electrically detected magnetic resonance to measure the detuning behavior of spin-Rabi nutation frequencies [1]. In the limit of negligible exchange and dipolar coupling, a fundamental Rabi frequency is analytically predicted to be accompanied by a first harmonic at exactly twice the fundamental frequency. Deviations from this analytical prediction are due to finite values of exchange and dipolar interactions, as anticipated by Rajevac et al., [2] and Limes et al. [3]. By comparing these measured deviations with those obtained from an accurate numerical simulation of various combinations of finite coupling, constraints on both the exchange ($|J| < 30$ neV) and dipolar ($|D| = 23.5 \pm 1.5$ neV) coupling energies are formulated. Further, by considering the dipolar portion alone, a mean intercharge separation of 2.1 ± 0.1 nm is implied, describing the distance over which carrier-pair entanglement persists.

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EPR ORAL SESSION

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132 Estimation Of The Exciton-Polaron Coupling In Organic Semiconductors Through Pulsed Electrically Detected Magnetic Resonance.

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Exciton-charge reactions have been invoked to explain the substantial magnetic field effects observed in organic semiconductors at room temperature. There are several candidates for explaining organic magnetoresistance (OMAR) and unambiguous differentiation between these mechanisms often proves challenging[1]. Pulsed Electrically Detected Magnetic Resonance[2] provides a strong avenue for future investigation as the charge carriers can be microscopically manipulated and different spin processes can more readily be disentangled. We develop a general time domain theory which quantitatively describes the role of exciton-charge reactions in electrically-detected setups, which we verify through comparison with full and half field Rabi oscillations[3]. We propose exciton-polaron exchange as the microscopic mechanism for exciton-polaron reactions. We are able to bound the exchange strength as well as the intersystem crossing and exciton-polaron dissociation rates by examining the transient behaviour and the shape of the Rabi oscillations. Our model provides a general platform for future analysis of the triplet exciton-polaron quenching mechanism in the time domain. In the future, multi-pulse schemes such as the Hahn echo and inversion recovery will allow the direct investigation of the relaxation processes.

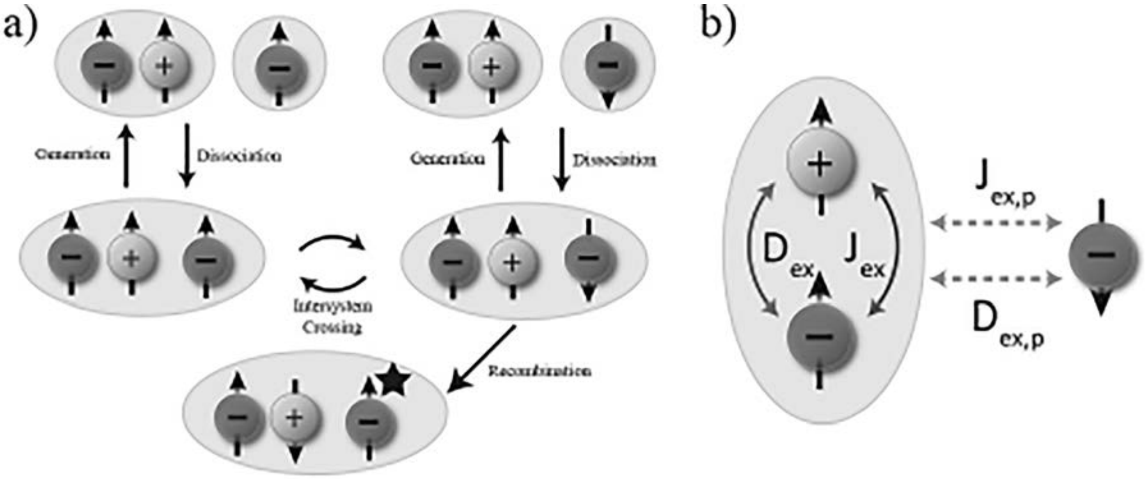

Figure 1: We develop a general time domain theory to describe triplet-polaron reactions in organic semiconductors. a) The microscopic states involved in the reaction and the possible electronic transitions. B) The Triplet-exciton polaron spin Hamiltonian. D_{ex} and J_{ex} are the dipolar and exchange coupling within the exciton, and $J_{ex,p}$ and $D_{ex,p}$ are the exchange and dipolar coupling between the exciton and polaron.

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EPR ORAL SESSION

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133 Dynamics of Charge Separation in Polymer-Fullerene Bulk Heterojunctions as Revealed by Time-Resolved EPR/ENDOR and DFT.

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At present, fossil fuels are the predominant source of energy driving world technological development. Due to the increasing world-wide demand for energy, new renewable and clean energy sources are needed to supplement, and eventually replace, the environmentally harmful and finite supply of fossil fuels. Solar energy provides one of the most promising sources of energy to meet future energy needs. Two possible pathways convert solar energy to useful forms of energy. The first, a "solar to fuel" approach, stores captured solar energy in high energy chemical bonds of molecules such as hydrogen. This approach is inspired by Nature's photosynthetic solar energy conversion processes. A second approach involves "solar to electricity" conversion. Both approaches include light harvesting and light-induced charge separation (CS) steps. In natural photosynthesis, light-induced long-lived charge separation occurs with a quantum yield that approaches 100%. This efficiency is so far unmatched by any man-made artificial system. To this end, we use light-induced EPR/ENDOR spectroscopy combined with DFT calculations to study mechanisms of charge separation and charge stabilization in active organic photovoltaic materials (OPV) based on the composites of multiple and fullerene derivatives. Time-resolved EPR spectra show a strong polarization pattern for all polymer-fullerene blends under study, which is caused by non-Boltzmann population of the electron spin energy levels in the radical pairs. Similar polarization patterns were first reported in molecular donor-acceptor systems, such as natural and artificial photosynthetic assemblies, and comparison with these systems allow us to better understand CS processes in OPVs. The spectral analysis presented here, in combination with DFT calculations, shows that charge separation processes in OPV materials are similar to that in natural and man-made organic photosynthetic systems.

EPR ORAL SESSION

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134 Spin-Dynamics in Vicinity of Spin-Gap and Antiferromagnetic Phase Transition of Low-Dimensional Organic Conductors $(TMTTF)_2X$.

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The spin dynamics in the vicinity of the spin-gap phase transition of the organic conductor $(TMTTF)_2PF_6$ were examined by pulsed-ESR spectroscopy, comparing conventional spin-Peierls phase in $MEM(TCNQ)_2$. An anomaly in the relaxation time was observed in this intermediate region between the ground state and the high-temperature phase and was associated with the charge re-orientation originating in the transverse magnetic interaction. Considering the inter-chain interactions, the transverse magnetic interaction (triangular frustration network) plays an important role of the spin-gap phase transition in $(TMTTF)_2PF_6$.

We also investigated antiferromagnetic resonance (AFMR) of $(TMTTF)_2Br$. Curious temperature dependence of AFMR was observed below the Neel temperature. Possible sub-phases in the antiferromagnetic state are discussed.

EPR ORAL SESSION

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135 Room-Temperature Distance Measurements of Immobilized Spin-Labeled Protein by DEER/PELDOR.

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Nitroxide spin labels that are commonly used for Double Electron-Electron Resonance (DEER) measurements contain gem-dimethyl groups. T_m for these nitroxides decreases rapidly at temperatures above 80 K due to rotation of the methyl groups at rates comparable to the anistropy in the electron-proton hyperfine coupling. A spin label has been prepared in which the gem-dimethyl groups are replaced by spirocyclohexyls. This label has longer T_m between 80 and 295 K in immobilized samples than conventional labels [1]. Two of the spirocyclohexyl spin labels were attached to sites on T4 lysozyme (T4L) introduced by site-directed spin labeling. Interspin distances up to about 4 nm were measured by DEER at temperatures up to about 160 K in water:glycerol glasses. For measurements at ambient temperature the doubly-labeled T4L sample was immobilized in glassy trehalose. In this matrix T_m for the doubly-labeled T4L was long enough to measure an interspin distance of 3.2 nm at 295 K, which could not be measured for the same protein labeled with a conventional methyl-containing label [2].

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EPR ORAL SESSION

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136 Using Pulsed EPR to Explore Loop Dynamics of the TonB-Dependent Transporter ButB in Native Membranes.

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Outer-membrane TonB-dependent transporters function in the uptake of essential nutrients, and are important for the success of many pathogenic bacteria These proteins consist of a 22 stranded β-barrel where the N-terminal 130 to 150 residues form a core domain that fills the barrel. During transport, these proteins undergo a cycle of binding and unbinding to the inner membrane protein TonB, through an interaction that is mediated by the Ton box, an energy-coupling segment near the transporter N-terminus. Over 50 high-resolution crystal structures have been obtained for 12 different TonB-dependent transporters, however the mechanisms of substrate transport remain unclear. Determination of membrane protein structure or dynamics with high resolution in whole cells is an attractive way to solve transport mechanisms but yet to be demonstrated.

In this work, the cobalamin transporter BtuB was overexpressed and spin labelled in whole cells and outer membranes and interspin distances were measured to a spin labelled cobalamin using pulse EPR. This represents the first example of double electron-electron resonance (DEER) preformed in whole E. coli cells. A comparative analysis of the data reveals a similar interspin distance distribution between whole cells, outer membranes and synthetic vesicles. We then take advantage of these native lipid environments to study the conformational heterogeneity of BtuB outer loops. The data indicate that there is a strong calcium mediated ordering of the 1-2 loop. We also see evidence of allosteric loop modulation, the binding of TonB to the Ton box on the periplasmic surface of BtuB alters the configuration of these extracellular loops. This approach provides an elegant way to study conformational changes or protein-protein/ligand interactions for large outer membrane protein complexes in whole cells and native membranes, and provides a method to validate high-resolution structures of membrane proteins in their native environment.

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137 **smFRET and DEER Distance Measurements as Applied to Disordered and Structured Protein**.

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FRET and DEER are two spectroscopic methods that are widely applied for biophysical studies of protein structure. Both methods are based on measuring dipolar interactions – electrical dipoles in case of FRET and magnetic dipoles in case of DEER - between specifically labeled protein sites. The experimental data are then analyzed to derive the distance between the interacting dipoles and relate this distance to the structure of biomacromolecule(s). Another common aspect of these two methods is the sample preparation involving mutation of selective protein residues to cysteine and the consequent covalent modification of cysteines with molecular labels, spin labels for DEER and fluorescent labels for FRET. Molecular volume of EPR labels is generally smaller vs. that of the fluorescent probes and DEER experiments can be carried out by labeling cysteines with identical molecular tags whereas FRET typically relies on orthogonal labeling with distinct donor and acceptor fluorophores. Another essential difference is that FRET can be performed under physiological conditions, but DEER typically requires cryogenic or near cryogenic temperatures because of short phase memory time for nitroxides at ambient conditions. Finally, single molecule (sm) FRET reports on conformation of individual protein molecules whereas DEER provides information on ensemble average. While the distance ranges of these two methods overlaps the direct comparison of FRET and DEER data is rarely found in the literature. Here we report on the distance measurements using both smFRET and DEER on the same protein system. We attached probes to a unique pair of cysteines in the neuronal SNARE protein SNAP-25. SNAP-25 is highly disordered in isolation, but it folds into a stable alpha-helix bundle upon forming SNARE complex with syntaxin and synaptobrevin. Results of smFRET and DEER distances and distance distribution are compared for disordered SNAP-25 and folded SNAP-25 within the SNARE complex.

EPR ORAL SESSION

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138 **Distances and Orientations with Low and High-Field/Frequency PELDOR/DEER**.

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The common “low” field (0.3 T/9 GHz) pulsed electron-electron double resonance (PELDOR/DEER) is a routinely used technique for distance measurements and structural studies on biomolecules. If applied at higher fields and frequencies (35, 95 and 263 GHz), the method is increasingly affected by orientation selectivity. This feature is usually considered as a nuisance that prevents an accurate distance measurement. However, in many cases, high-frequency PELDOR delivers information inaccessible at low fields. For example, if distances are known, high-frequency PELDOR permits to extract information needed to correlate the mutual orientation of spin labels or natural paramagnetic centres[1,2]. Furthermore, the absolute sensitivity at high fields/frequencies is increased and allows performing experiments on limited sample volumes. Besides, distance measurements with metal centers are facilitated[3]. However, PELDOR at high frequencies is more difficult to execute. The limited available power and increased microwave losses render excitation pulses longer and therefore the signal weaker. This, combined with a broader EPR spectrum, predicts weaker modulation depths than those observed at X-band frequencies. Furthermore, the “out-of-phase” signal observable at high fields[4,5] must be considered and adequately analysed. Here, we present comparative multifrequency (9, 35, 95 and 263 GHz) PELDOR studies on a model RNA systems containing rigid[6] and flexible nitroxides and discuss the advantages and possible bottlenecks of the high field measurements. We show that at high fields/frequencies still considerable modulation depths can be observed and orientation selectivity is significant, which is particularly important for orientation selective studies.

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EPR ORAL SESSION

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139 Development of High-Field DNP Instrumentation for Magic-Angle Spinning ^{13}C NMR at 16.4 T and 30 K.

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The sensitivity of magnetic resonance is the crucial factor for studying the structures of large biomolecules. We are improving the instrumentation for high-field dynamic nuclear polarization (DNP) to increase the sensitivity of high-resolution solid-state 13C NMR by using elelctron spin polarization. Our previous experiments showed that DNP at about 30 K provided much higher polarization than those at about 90 K. These magic-angle-spinning (MAS) DNP experiments were performed by boiling liquid helium[1]. Thus the large liquid He consumption made the routine DNP experiments difficult. To minimize the He consumption, we have developed a closed He-gas circulation system with an electrical gas chiller for MAS experiments at about 30 K. This circulation system not only reduced the operation cost but also stabilized the gas flow over an experimental time of a week for multidimensional NMR experiments. The large Boltzmann polarization and reduced thermal noise at the low temperature increased the NMR sensitivity. We developed a high-power submillimeter wave irradiation system with two gyrotrons to saturate electron spin resonances of paramagnetic compounds efficiently at 16.4 T[2]. One second-harmonics gyrotron generates a high-intensity 460-GHz wave with a continuously tunable range of about 1 GHz. The other gyrotron provides the submillimeter wave with frequency modulation at the rate about 10 kHz. The submillimeter waves are transmitted to a sample rotor through a diplexer connected to corrugated waveguides. This system can be used for double resonance experiments in a submillimeter wave range which should improve the high-field DNP experiments.

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EPR ORAL SESSION

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140 Comparing Frequency Modulation Schemes for Improving DNP Enhancements.

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Triangular and sinusoidal frequency modulation of the applied microwaves during a dynamic nuclear polarization (DNP) experiment have recently been shown to yield higher DNP enhancements when compared to fixed frequency microwave irradiation[1,2]. These techniques are particularly useful for samples with a broad ESR line, since the frequency modulation increases the number of electrons contributing to the initial polarization transfer step between the electrons and the nuclei. However, there is no a priori reason that the modulation schemes that have been experimentally demonstrated (triangular and sinusoidal) are best for improving DNP enhancements. In the present study, we investigate a variety of amplitude and frequency modulation schemes for increasing DNP enhancement. Using an LOD-ESR setup in the same system[3], we are also able to measure the ESR spectrum of the sample, and adapt the modulation scheme accordingly. We show DNP enhancement results obtained using a modulation scheme based on an LOD-ESR spectrum of 10 mM 4-amino TEMPO in 60/40 glycerol/water, and we compare these enhancements to those obtained using triangular modulation.

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EPR ORAL SESSION

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141 **Optimizing Frequency-Modulated CW EDMR in Silicon.**

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In this study we investigate the detection sensitivity of frequency-modulated CW-EDMR to study paramagnetic spin defects in silicon. Frequency modulation can potentially minimize the relative contribution of microwave-induced currents in the EDMR technique. We measure the relative intensities of both the dangling bond and phosphorus dopant signals as a function of multiple experimental parameters such as microwave power, modulation amplitude and frequency and optical excitation. Our experiments are performed on phosphorus-doped natural silicon wafers in a home-built system at 2.3 GHz (~80 mT) at 5 K. Our observation of rapid passage effects at higher modulation frequencies suggests that it might be possible to adapt rapid-scan techniques to EDMR.

EPR ORAL SESSION

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142 **Electronic Structure of Novel Paramagnetic Actinide Complexes.**

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Over the last decade or so there have been remarkable advances in low-valent actinide (An) chemistry, including novel chemical (e.g. catalysis, small molecule activation) and physical (e.g. magnetic materials) properties.[1] These advances are also enabling fundamental studies of the electronic structure of An complexes, with key questions being addressed including the nature of metal-ligand bonding and the extent of covalency. EPR should therefore be an important tool where the An ion is in a paramagnetic oxidation state. However, EPR of 5f elements is much less developed than that of d-block or 4f-block; early studies focused on An(III)-doped CaF_2,[2] while in terms terms of molecular systems there are important studies of organometallics, e.g. the work of Edelstein, Ephritikhine and others.[3] In this lecture we will examine the electronic structure of a family of related uranium(III) and (V) complexes by EPR spectroscopy, and complementary methods and theory. The species studied include complexes containing new uranium-ligand multiple bond motifs, e.g. terminal nitrides with a formal UN triple bond,[4] low coordination numbers,[5] and dimers where there is direct spectroscopic evidence of exchange coupling.

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EPR ORAL SESSION

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143 CW and Pulsed EPR Study of Complex Coacervation of the Mussel Foot Protein Inspired Adhesives.

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Marine mussels are exceptional at rapid and permanent adhesion to solid surfaces in wave-swept seashores. To form an adhesive plaque on the underwater surface mussels utilize complex fluids to deliver the necessary components at high concentrations. Detailed, molecular level, understanding of this process is of great importance for guiding synthetic approaches towards artificial under-water adhesives – a grand challenge.[1] A family of complex fluids termed complex coacervates are thought to be an important wet adhesive delivery mechanism. In complex coacervates a mixture of oppositely charged polymers phase separates to form droplets of a dense phase within a dilute solution. This is, for example, observed when mixing mussel foot protein 3 fast (mfp3f), a polycation, and hyaluronic acid (HA), a polyanion. Interestingly a related less charged but more hydrophobic variant, mussel foot protein 3 slow (mfp3s) has been shown to form a coacervate phase without any polyanion counterpart.[2] For the in-situ study of such complex fluids and macromolecular assemblies in solution analysis methods are extremely scarce often limited to light scattering and optical microscopy.These do not provide an insight on the molecular level interactions and dynamics. Here we demonstrate that application of modern pulsed and CW EPR methods can provide unique insight into the molecular structure of this unique phases behavior of the mfps and other related biomimetic materials. For example, we show that the dense phases formed by mfp3s and mfp3f + HA, respectively, reveal highly distinct local environments. Mp3s forms much denser and very rigid coacervate phase while mfp3f + HA form substantially more mobile phase similar to other complex coacervates observed in similar systems.[3] Such insight provides guidance to the development of novel under-water adhesive candidate materials.

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EPR ORAL SESSION

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150 Genetically Encoded Spin Labels and In-Cell EPR.

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In-cell EPR in combination with site-directed spin-labeling is a very powerful tool to monitor the structure and dynamics of bio-macromolecules in their natural environment.[1] We have demonstrated that the Gd(III) based spin label Gd-PyMTA is suitable for in-cell EPR. It is cell compatible, inert in-cell extracts of Xenopus laevis oocytes for more than 24 h, and can be used for precise intracellular distance measurements as proven by a model compound, which consists of a spacer of well-known stiffness. An oligoproline peptide was site-directedly spin labeled with Gd-PyMTA at two cysteine moieties for EPR distance measurements. To analyze the intracellular peptide conformation, a rotamer library was set up to take the conformational flexibility of the tether into account. The results suggest that the spin labeled peptide is inserted into cell membranes, coinciding with a conformational change of the oligoproline from a PPII into a PPI helix.[2] The most elegant approach for site-directed spin labeling is the genetic encoding of a noncanonical, spin-labeled amino acid. This enables the intracellular biosynthesis of spin-labeled proteins and obviates the need for any chemical labeling step usually required for protein EPR studies. We have developed a genetically encoded spin label that can be introduced at multiple, user-defined sites of a protein and is stable in E. coli even for prolonged expression times. It can report intramolecular distance distributions in proteins by double-electron electron resonance measurements.[3] This provides elegant new perspectives for in-cell EPR studies of endogenous proteins.

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EPR ORAL SESSION

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151 New Approaches for Distance Measurements in Nucleic Acids Using Nitroxyl and Trityl Spin Labels.

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Pulsed dipolar EPR spectroscopy (PELDOR/DEER and DQC) is nowadays widely applied for distance measurements in biologically-important systems. Although significant progress has been achieved in this field, a number of challenges still remain. One of them is site-directed spin labeling (SDSL) of long (exceeding 50-70 base pairs) natural nucleic acids that is not feasible using common solid-phase synthesis. In this work, we propose and validate novel SDSL approach suitable for long RNAs.[1] It is based on the complementary-addressed reaction between the target RNA residue and the oligodeoxyribonucleotide agent, allowing site-specific attachment of nitroxide at the next step. First, the new approach was tested using model 10-mer RNA duplex with known structure, where the distances obtained by Q-band DEER corresponded well to the expected ones. Next, SDSL of the Hepatitis C Virus IRES RNA consisting of up to 350 nt and having complicated spatial structure has been demonstrated, again with reasonable distances obtained by DEER. Another current challenge in pulsed dipolar EPR is a design of spin labels and SDSL strategies for distance measurements at room/physiological temperatures. In this work, we report the first physiological-temperature distance measurement in DNA, exemplified using trityl-labeled immobilized DNA duplex.[2] We succeeded in development of optimal trityl-based labels, approach for SDSL and efficient immobilization procedure that, working together, allowed us to measure as long distances as ~4.6 nm with high accuracy at 310 K (37 °C). Moreover, comparison of distance distributions obtained using trityl/trityl, trityl/nitroxyl and nitroxyl/nitroxyl pairs of labels at 80 K shows that better accuracy can be achieved for trityls, regardless the type of the linker used. Further applications of trityl labels for DEER measurements are discussed.

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EPR ORAL SESSION

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152 Spin-Labeling Magnetic Resonance Studies of Conformational Dynamics and Flexibility of the 232 nt Glycine Riboswitch.

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Site-directed spin-labeling (SDSL) coupled with electron paramagnetic resonance (EPR) is a popular tool for characterizing conformational flexibility and dynamics in protein and lipid assemblies. In recent decades the utility of SDSL EPR has been applied to the study of RNA molecules. Here, we show our achievements in developing a suite of spin-labeling based magnetic resonance (MR) approaches for characterizing dynamics, conformational sampling, and local hydration environment of the large RNA glycine riboswitch. A series of singly and doubly spin-labeled 232 nt RNAs were prepared via optimized splinted ligation methods and spin labels were incorporated at modified backbone or base locations. Continuous wave (CW) EPR line shapes and distance distribution profiles from double electron-electron resonance (DEER) EPR spectroscopy reveal changes in backbone dynamics and conformational sampling of the kink-turn motif under various environmental conditions such as changes in ionic strength or presence of magnesium and cognate ligand – glycine. Results are consistent with trends of biochemical studies and show the utility of DEER applications to characterize conformational sampling of large RNAs. Additionally, we have assembled a custom microwave transmitter that is interfaced with our existing EPR/NMR equipment for performing novel, low-field (0.35 T), Overhauser dynamic nuclear polarization (ODNP) enhanced NMR spectroscopy. The ODNP NMR technique allows one to probe changes in dynamic motions of H_2O in the spin-labeled regions and interrogate the hydration landscape. Therefore, changes in conformational sampling, which are obtained from CW EPR and DEER, can be studied together with local hydration dynamics, under varying environmental conditions, to understand RNA folding. Taken together this work represents one of the first SDSL MR characterizations of large SL-riboswitch constructs prepared by splinted ligation methods; nicely laying the foundation for more in-depth investigations into the structure, dynamics, and folding of the glycine riboswitch to elucidate molecular mechanisms of regulation and function.

EPR ORAL SESSION

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153 Electrostatics of Bio-Interfaces by EPR of Proteins and Phospholipids Labeled with pH-Sensitive Nitroxides.

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Electrostatic interactions are known to play one of the major roles in the myriad of cellular and molecular biology processes ranging from protein folding to insertion of proteins, toxins, and viruses into membranes as well other more complex events such as membrane fusion. Here we describe a site-directed spin-labeling method to probe local electrostatic potentials of proteins and lipid bilayer systems that is based on observation of reversible ionization of protonable nitroxides by EPR. Two types of the electrostatic probes have been synthesized. The first type includes methanethiosulfonate derivatives of protanable nitroxides that could be used for highly specific covalent modification of the cysteine's sulfhydryl groups. Such spin labels are very similar in magnetic parameters and chemical properties to conventional MTSL making then suitable for studying local electrostatic properties of protein-lipid interfaces. The second type of EPR probes was designed as spin-labeled phospholipids having a protonatable nitroxide tethered to the polar head group. The probes of both types report on their ionization state through changes in magnetic parameters and a degree of rotational averaging, thus, allowing one for extracting the electrostatic contribution to the interfacial pK_a of the nitroxide, and, therefore, determining the local electrostatic potential. Due to their small molecular volume these probes cause a minimal perturbation to the bilayer while securing the position of the reporter nitroxides, and, hence, the location of the measured electric potentials precisely at the lipid bilayer interfaces. We present the most recent results on i) calibration of these nitroxide probes in aqueous, mixed aqueous-organic and detergent solutions, and ii) their application for probing the surface electrostatics in multi- and unilamellar vesicles of various sizes and lipid compositions, different phase states, and along the protein-lipid bilayer interface.

EPR ORAL SESSION

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G-Quadruplex Targeting by Pt(II) Complexes Studied Using Site-Directed Spin Labeling.

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Guanine-rich oligonucleotides (either DNA or RNA) can adopt a unique stacked tetrad structure called G-quadruplex. Formation of G-quadruplexes can be detected in vivo, and it is known to exert important biological functions. As such, G-quadruplexes are targets in therapeutic developments, and various classes of small molecules targeting G-quadruplexes, including metal complexes, are being investigated as potential new drugs. However, G-quadruplexes process a very high degree of structural polymorphism, which rendering it difficult to obtain detailed information on the modes of interaction between G-quadruplexes and small molecules. Here, we report work on using the technique of site-directed spin labeling to investigate interaction between G-quadruplex and Pt(II) complexes. A new compound (designated as 1) has been synthesized, in which a nitroxide radical (TEMPO) is covalently tagged onto a multi-nuclear Pt(II) compound. 1 preferably binds to DNA G-quadruplexes against the duplexes. Using the TEMPO moiety as a spin label, electron paramagnetic resonance spectroscopy (EPR) was carried out to characterize the mode of binding between 1 and a known G-quadruplex forming DNA sequence found in the human telomeres (hTel22). Measurements revealed that two molecules of 1 bind to one hTel22. The inter-spin distance measured between the two bound 1, together with Molecular Docking analyses, allowed identification of the two binding sites on the G-quadruplex. The results demonstrate a new strategy for investigating small molecule binding to G-quadruplexes. With the expanded capability provided by the tagged nitroxide, these Pt(II) compounds may provide a new class of molecules for targeting G-quadruplex.

EPR ORAL SESSION

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Optimum Control of Spin Dynamics in Magnetic Resonance.

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Optimal Control Theory offers powerful analytical and numerical tools to explore the ultimate performance limits of pulse sequences. These tools not only provided pulse sequences of unprecedented quality and capabilities, but also new analytical and geometrical insight and a deeper understanding of pulse optimization problems. Efficient numerical algorithms, such as the GRAPE algorithm [1,2], make it possible to develop robust time-optimal or relaxation-optimized pulse sequences, taking into account experimental limitations and imperfections, such as maximum pulse amplitudes, maximum pulse power, pulse inhomogeneity as well as transient effects associated with the switching of pulse amplitudes and phases. Examples will be shown for applications in EPR and NMR spectroscopy [3,4]. These include broadband [9] and band-selective pulses, coherence transfer experiments, and novel ultra-broadband decoupling sequences [5]. In addition to individually optimized pulses, simultaneously optimized gains, by exploiting cooperative effects [6] and novel cooperative Hahn echo sequences, will be presented.

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EPR ORAL SESSION

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156 Considerations on Frequency-Swept Excitation Pulses.

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The excitation bandwidth of monochromatic pulses is on the order of the field strength ν_1, which is often not sufficient to excite the entire EPR spectrum. This limitation can be relaxed by using frequency-swept pulses. For this class of pulses, excitation bandwidths on the order of the frequency sweep range Δf are achievable. Moreover, adaptation of the frequency sweep to the spectrometer's frequency response allows for population inversion[1] and coherence excitation[2] beyond the physical excitation bandwidth. If the pulse is short compared to relaxation times, the effective flip angle can be predicted by quantification of the adiabaticity factor Q_{min}. At the extremities of the frequency sweep, edge truncation alters the predicted flip angle, unless adiabaticity is maintained by prolonged edge truncation. Using Q_{min}, the characteristics of these pulses for (i) population inversion, (ii) coherence excitation, and (iii) coherence refocusing are outlined. Particular emphasis is laid on spatial inhomogeneities in ν_1. These are most delicate for coherence excitation, but virtually insignificant for population inversion. Contrary to population inversion, inversion of coherence (refocusing) is hampered by spatial inhomogeneity of Bloch-Siegert phase shifts, which is to substantial extent compensated in a refocused echo.[3] These fundamental considerations are complemented with relevant examples, such as FT-EPR of nitroxides in frozen glassy solution and 2D EPR/ESEEM correlation spectroscopy of oriented Cu(II) centers.

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EPR ORAL SESSION

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157 Field-Stepped Direct Detection Electron Paramagnetic Resonance.

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The widest scan that we have previously demonstrated for rapid scan EPR was a 155 G sinusoidal scan[1]. As the scan width increases, the voltage requirements increase dramatically and the background signal induced by the rapidly changing field increases. An alternate approach is needed to achieve wider scans. We have now developed field-stepped direct detection EPR, which is based on the rapid scan technology, to generate scan widths up to 6200 G. A linear scan frequency of 5.12 kHz was generated with the scan driver described in[2]. The field was stepped at intervals of 10 mG to 1 G. At individual field points scan widths were up to 11.5 G. Data were combined by matching DC offsets. This approach has the advantages that (i) sweep range can be widely extended as needed; (ii) rapid-passage oscillations that occur when the time of scan through the resonance is shorter than electron relaxation times can be deconvolved; (iii) quadrature signal detection permits deconvolution and phase correction in post processing; (iv) the signal to noise ratio (S/N) and field resolution are potentially better than conventional continuous wave EPR in the same acquisition time.Field-stepped direct detection EPR spectra were obtained for ^{14}N-perdeuterated tempone (^{14}N-PDT) in sucrose octaacetate, Mn^{2+} doped in CaO, Cu^{2+} doped in Ni(diethyldithiocarbamate)$_2$, Cu^{2+} doped in Zn tetraphenyl porphyrin, vanadyl doped in a parasubstituted Zn tetraphenylporphyin, and an oriented crystal of Mn^{2+} doped in Mg(acetylacetonate)$_2$(H_2O)$_2$. A degased lithium phthalocyanine sample was used to demonstrate that the linear deconvolution procedure[3] can be integrated with field-stepped direct detection EPR.

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EPR ORAL SESSION

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158 Adiabatic Pulses for Improved Electrically and Optically Detected Magnetic Resonance.

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Improving the fidelity of the coherent control required form pulsed used in EPR can significantly increase spectroscopic sensitivity. This is especially true in organic materials whose spin-dependant behaviour (including recombination, photoluminescence and transport) depends on the permutation symmetry of the spin pairs in the system. The singlet/ triplet content can be probed directly using pulsed electrically and optically detected magnetic resonance (p E/ODMR). The visibility of such a signal is directly related to the fidelity spin rotations. High fidelity coherent control over spins in room temperature devices can be exploited to create new devices, such as sensitive magnetic resonance based magnetometers, which may find widespread application[1,2,3].

Adiabatic pulses used widely in NMR provide a means of achieving high fidelity control. Unfortunately, for a wide range of experiments there is no trivial mapping of these techniques to EPR spectroscopy because of the qualitative difference in nuclear vs electron spin disorder $S_n<<S_e$. Typical excitation bandwidths easily encompass nuclear spectral widths; however they are often not sufficient to excite the whole electron spin ensemble at reasonable operating conditions (room temperature, accessible microwave power etc.).

A numerical investigation of various broadband adiabatic pulse schemes on typical electron spin ensembles under practical operational conditions will be presented. We find that adiabatic pulses improve fidelity for pulse lengths in excess of ~30 ns, which makes them suitable for use on materials with reasonable phase coherence times, including organic semiconductors. Results on the concatenation of adiabatic pulses specifically designed and optimized for pulsed electrically- and optically-detected magnetic resonance will be presented.

Finally, technical details associated with implementing such schemes in a commercial spectrometer will be discussed.

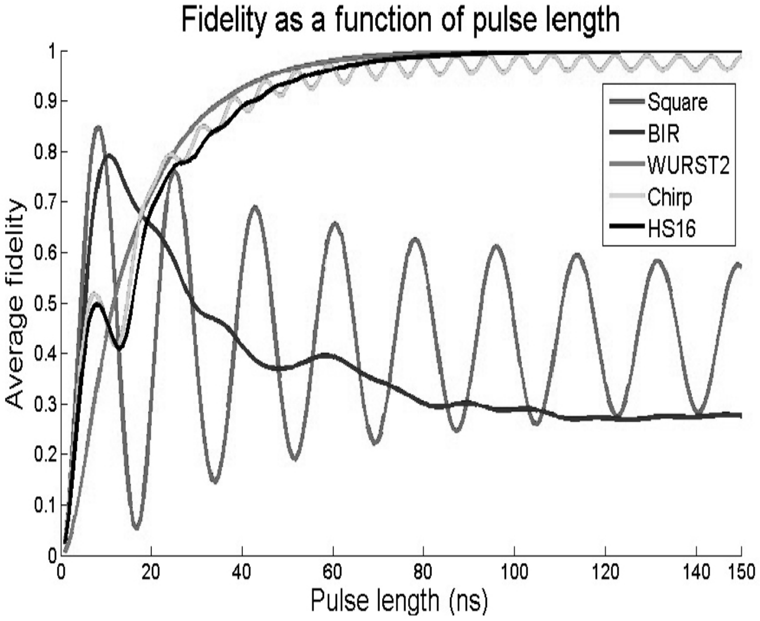

Figure 1: Fidelity of a π rotation about the x-axis as a function of pulse length for a range of different adiabatic schemes, with B1= 2 mT , Se = 1 mT (FWHM) and microwave bandwidth = 500 MHz. For pulse durations exceeding 30 ns, adiabatic approaches provide improved fidelity.

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EPR ORAL SESSION

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159 In Vivo EPR Profiling of the Tumor Microenvironment Using Multifunctional Nitroxide and Trityl Probes.

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Tumor microenvironment (TME) is now widely recognized as a major contributor to cancer aggression and treatment resistance and as a target for therapeutic intervention. Tissue hypoxia, extracellular acidosis, elevated levels of inorganic phosphate (Pi), high reducing capacity and high concentrations of major component of intracellular redox buffer, glutathione (GSH), are among the crucial TME parameters of importance for tumorigenesis. Noninvasive in vivo assessment of the TME parameters provides important knowledge for advanced TME-targeted anticancer therapies.[1] To this aim we developed a set of paramagnetic probes for multifunctional profiling of chemical TME using electron paramagnetic resonance (EPR)- and nuclear magnetic resonance (NMR)-based techniques. Specifically we utilize trityl probes[2,3] for concurrent in vivo monitoring of tissue oxygenation (pO_2), extracellular pH (pH_e) and Pi, and nitroxide probes[4, 5] for pH_e, GSH and reducing capacity measurements, using in vivo L-band EPR spectroscopy and MRI-based functional proton-electron double-resonance imaging [5]. The in vivo studies performed in breast tumor-bearing mice show that all the measured parameters, pO_2, pH_e, Pi, redox and GSH, tend to deviate from the pattern characteristic of normal tissue upon progression to malignancy. Normalizing the TME parameters may decrease the selection pressure for malignant phenotypes, therefore providing a tool for TME-targeted anticancer therapy. A capacity of specific TME pattern to be used as a prognostic factor in tumorigenesis and the approaches for normalizing chemical tumor microenvironment for anticancer TME-targeted therapeutic interventions will be discussed.

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EPR ORAL SESSION

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160 Nitroxides as Biological Sensors.

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161 Multifunctional Probing of Microenviroment by Monophosphonated Trityl Radical Using FT and ESE Pulsed EPR Technique.

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Recently we synthesized monophosphonated trityl (pTAM) probe with multifunctional sensitivity to local microenvironment and demonstrated its applicability for simultaneous monitoring of interstitial oxygenation (pO_2) and extracellular acidity (pH_e) in biological systems using CW EPR[1]. Here we show that the shape of FT-EPR[2] spectrum and ESE decay is dependent on parameters of local microenvironment, namely, pH, pO_2, buffer and probe concentration. Analysis of FT-EPR spectra and ESE decay shapes allowed us to extract the values of T_1, T_2, fraction of protonated and deprotonated forms of pTAM, and the rates of chemical and self-exchange, therefore, providing information about local pH, pO_2, inorganic phosphate and probe concentrations. Finally we provide the comparative analysis of CW, FT and ESEEPR techniques for characterization of local microenvironment using pTAM probe with some examples of in vivo and in vitro application in biological and chemical systems.

Supported by NIH grants EB014542 and CA194013.

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EPR ORAL SESSION

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162 Field Modulated Pulse EPR Spectroscopy and Imaging.

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Bi-modal resonators are currently used for in vivo EPR spectroscopy and imaging to decouple radiofrequency (RF) bridge excitation and detection pathways with the goal to reduce after-pulse dead time[1,2]. Isolation up to 60 dB can be achieved due to geometric orientation of the orthogonal resonators, which are tuned to the same frequency. The detection and excitation resonators can be decoupled even stronger if they are tuned to different frequencies. To ensure resonance conditions for both resonators, we have used sinusoidal magnetic field modulation that changed the Larmor frequency of the spins during free evolution. We have used excitation RF pulses at the frequency of the first resonator (246 MHz) and detection resonator is tuned to the frequency (259 MHz) different from the frequency of excitation resonator by ¾ of the peak-to-peak amplitude of the magnetic field modulation. Because the field modulation is constantly affecting precession of the spins, the measured signals demonstrate passage effects similar to those observed in rapid scan EPR [3]. To restore the 'normal' echo shape, numerical transformation into the reference frame associated with the changing Larmor frequency of the spins has been performed.

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EPR ORAL SESSION

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163 Skin Structure of Psoriasis Vulgaris Investigated by CW EPR and 9 GHz EPR Imaging.

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We investigated skin structure in relation to radical locations in various types of skin using continuous wave (CW) electron paramagnetic resonance (EPR) and 9 GHz EPR imaging. For EPR imaging, a Bruker E500 ELESYS system was used. Spin probe (5-doxylstearic acid, 5-DSA) was used to investigate structural aspects of psoriasis vulgaris SC (PV-SC). A small, broad three-line pattern of 5-DSA in PV-SC was observed.1, 2 The spectral pattern of PV-SC was quite different from those of the control SC.Two-dimensional (2D) imaging using a 9 GHz EPR imager showed that radical locations vary between control and PV skin. The PV skin showed a stronger intensity than that of the control. The intensity may be due to the structural aspects of PV skin. The results showed that spin probe 5-DSA can easily penetrate the PV-SC. The present EPR results suggest that PV skin has a less rigid structure than that of the control SC, indicating the irregular architecture of PV skin. The 9 GHz EPR imaging easily showed the identity of the less rigid structure of PV-skin.

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EPR ORAL SESSION

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164 Melanin – An Important Biological Pigment with Unique Physico-chemical Properties.

Lawrence H. Piette Memorial Lecture

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In humans, melanin is normally present in the skin, hair, eyes, inner ear and midbrain. In spite of considerable research efforts, the molecular structure of this unusual pigment, its biological functions and the exact mechanism of the proposed action in pigmented cells remain only partially understood. The paper will review selected results that demonstrate antioxidant and photoprotective action of melanin from retinal pigment epithelium (RPE) both in model systems and in cells in vitro. Using X-band and W-band EPR spectroscopy, saturation recovery EPR, EPR-spin trapping, EPR-oximetry, and chemical analysis of characteristic melanin degradation products, it has been shown that human RPE melanosomes undergo significant age-related changes that modify their physicochemical properties. Compared to control RPE melanosomes from young donors, melanin granules from human donors of older age and in vitro photoaged bovine RPE melanosomes contain oxidatively degraded melanin, exhibit higher photoreactivity and lower metal-ion binding capacity. Such pigment granules have reduced ability to protect unsaturated lipids against photoinduced and iron ion-induced peroxidation. In cultured cells, photoaged melanin is even phototoxic as demonstrated in ARPE-19 cells containing phagocytized pigment granules. The data collectively suggest that with aging melanin in the human RPE becomes less efficient in protecting these postmitotic cells against oxidative stress, which has been postulated to play an important role in the pathology of age-related macular degeneration, which is the major cause of blindness in people over 60 in developed countries.

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EPR ORAL SESSION

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170 Pulsed Dipolar EPR Spectroscopy with Broadband Microwave Pulses.

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Goethe University

171 ESR of Spin-Labeled Lipid Bilayers Directly Tethered to a High Sensitivity Non-Resonant ESR Probe.

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ESR along with site-directed spin-labelling[1] has been recognized as a powerful tool to study dynamic membrane structures and functionalities[2]. Unlike X-ray diffraction of crystallized proteins, the ESR method is able to probe dynamic structures in solution without the size limitations inherent in NMR spectroscopy. However, the technique is plagued by low sensitivity that limits the utility to high concentration samples and consequently excludes the possibility of single membrane layer observations.

Here we demonstrate a non-resonant near-field ESR detection scheme which allows us to observe spin-labeled lipid bilayers tethered to a microfabricated ESR probe[3]. A microfluidic channel is bonded directly to the micro-fabricated ESR probe to form a disposable ESR sample holder that keeps the lipid bilayer in a controllable liquid environment. We measured a hybrid bilayer of 10% tempo-labeled dipalmitoyl phosphaticholine in diphytanol phosphocholine tethered to an octadecanethiol self-assembled monolayer on gold electrode surface. With a probe surface area of ≈ 0.125 mm^2, we achieved a signal-to-noise ratio > 5 in less than 30 minutes of data acquisition time using CW X-band ESR. It is expected that measurements on concentration < 1% can be done by simply increasing the probe size. Such measurement are made possible in our X-band system by the > 20000x boost in sensitivity compared to conventional ESR systems. The ability to measure low-spin concentrations in a single lipid layer leads to two major advantages. First, low concentration helps avoid spin-spin interactions (interference and background signals). Second, this method can be used for detection of various motions of the spin labels ranging from the fast rotational isomerism to slower protein motion[4].

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EPR ORAL SESSION

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172 EPR Spectroscopy on Mixed Phase Samples under Flow Conditions.

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3. Department of Chemistry and Biochemistry, University of California Santa Cruz, Santa Cruz, CA

Investigations of mixed phase reaction systems under operando conditions can require flow to provide the appropriate species in the necessary concentration. Here we report continuous flow EPR cells for both gas and liquid mobile phases, with designs capable of temperatures ranging from cryogenic to >300 C, and pressures from ambient to 150 Bar, and with access for electrochemistry. Examples include copper and iron loaded catalysts used for reduction of NOx in exhaust gas. With the appropriate gas flow and temperature ramp, an EPR-detected version of the TPx (x=R for reduction; O for oxidation, etc.) can be performed. Because the spectrum is recorded, rather than just amplitude, specific chemical species are correlated with a reaction. We also introduce a new fluorinated spin trap analog of FDMPO which can be tethered to a solid support. This solid phase spin-trap media can be packed in an EPR flow cell and used to detect radicals in the out flow of a reaction cell. Radical species that cannot be directly observed (i.e. superoxide in liquids), or are at very low concentration at any single time point in a flow experiment, are trapped on the column where the EPR spectrum can build up to a detectable level.

EPR ORAL SESSION

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173 Electron Spin Interactions and Electron Spin Relaxation at High Field.

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At high fields and low temperatures both the Spin Lattice Relaxation time (T_1) and Spin-Spin Relaxation time (T_2) can change dramatically with respect to those at lower fields, with the T_2 increasing and T_1 decreasing. Relaxation in spin systems is of crucial interest with respect to various possible applications like quantum information processing and storage, spintronics, and dynamic nuclear polarization (DNP). Many of the proposed spin systems for quantum information have relatively short spin-spin distances and frozen solutions used in DNP involve relatively concentrated spin systems, and the electron dipolar spin-spin interactions tend to become the dominating decoherence mechanism. High frequencies and fields in combination with low temperatures polarize the electron spins, and allow for considerably longer spin memory times at high fields and frequencies as compared to X-band[1]. On the other hand, high frequencies lead to a significantly increased contribution from direct single phonon processes in the Spin Lattice Relaxation. This can lead to orders of magnitude shorter T_1 times at high frequencies as compared to low frequencies.

This contribution will provide a review of the existing relaxation measurements and will attempt a quantitative comparison of both spin-lattice and spin-spin relaxation with theory/theories.

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EPR ORAL SESSION

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174 Electron-Spin-Echo Decay of Low- and High-Spin species at 240 GHz.

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Mechanisms leading to electron-spin-echo (ESE) decay are investigated at high magnetic field. At 8.6 T and at low temperatures, the high temperature approximation breaks down, and the electron spin bath polarization approaches 100%. Polarizing the spin bath leads to a dramatic lengthening of the phase memory time *Tm* in environments with few proton spins.[1] This effect can be used to extract inter-electron distances,[2] as well as study the effects of electron- and nuclear-induced spectral diffusion on ESE decay. Assuming a dipolar spin flip-flop model,[3] this effect can be used to extract average distances as well as to probe the geometrical arrangement of S=1/2 spins.[2] We report quantitative differences in ESE decay kinetics for S=1/2 and S>1/2 reporter spins in the presence of a polarized spin bath. S=1/2 ESE decay in this regime typically follows a stretched exponential $\propto\exp(-(2\tau/\tau_m)^x)$, while low temperature ESE decay measurements of Gd^{3+} (S=7/2) in frozen solutions follow an exponential decay. We report low temperature *Tm* and spin-lattice relaxation time *T1e* measurements at 240 GHz for Gd^{3+} complexes as a function of temperature, inter-electron distance, and magnetic field, extending work conducted on S=1/2 species to high-spin species of great interest for applications in studying biological systems.[4]

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EPR ORAL SESSION

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175 **Probing Single Electron Spins.**

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Increasing the sensitivity of EPR towards single spin detection is a long standing quest. Diamond spin detectors appear to be a big leap forward as they have demonstrated single spin detection of electrons as well as nuclear spins. Quite remarkably this has been achieved under a wide variety of environments including room temperature and ambient conditions. The talk will describe recent achievements including detection of single nitroxide spin labels on proteins [1] as well as approaches towards imaging [2] single spins. I will discuss limitations in signal to noise and spectral and spatial resolution.

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EPR ORAL SESSION

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176 **Quantum Coherence in Mn-Based Single Molecule Magnets.**

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Molecular nanomagnets, also known as single molecule magnets (SMMs), are a unique class of spin systems, which possess large magnetic moments (the high-spin states) and an anisotropic energy barrier between their spin-up and spin-down states at the molecular level. The nanomagnetism and spin physics of SMMs have been investigated on large ensembles of SMMs extensively. In addition, it has been demonstrated that an individual or a small ensemble of SMMs can be transferred to surface with retention of their magnetic behavior, therefore SMMs are fertile testing ground for potential applications to dense quantum memory and molecular spintronics. Various types of SMMs have been synthesized, including widely studied Mn- and Fe-based SMMs and newly discovered single-ion-SMMs based on the lanthanides. In spite of diverse interests on quantum properties in SMMs, decoherence properties that ultimately limit such behaviors have not fully been understood yet. Until now, coherent manipulation of spin states in SMMs has been experimentally demonstrated only in a few SMMs including Fe_8 [1,2], V_{15}, Fe_4, and Cr_7Ni systems. Here we present quantum coherence in Mn-based SMMs for the first time [3]. Single crystals of Mn_3 SMMs are investigated using high-frequency electron paramagnetic resonance (HF EPR) spectroscopy. The HF EPR study reveals decoherence processes in Mn_3 SMMs that limit the spin decoherence time (T_2) to be < 300 ns [3]. In addition, we will discuss a pathway to further improve the coherence in Mn_3 SMMs.

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EPR ORAL SESSION

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Magnetic Phase Transition in Ferroelectric Lithium Niobate Doped with Erbium.

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Due to multilevel structure of energy levels, lithium niobate (LN) crystals doped with Er^{3+} are promising material for quantum electronics and telecommunication. However, required understanding of fundamental features of centers created by Er^{3+} is not achieved yet. The EXAFS analysis and Rutherford back scattering have shown that Er^{3+} ions substitute only for Li, whereas six or more different centers were distinguished in congruent samples by optical absorption/emission and site-selective spectroscopy. According to previously proposed center models, the charge excess of Er^{3+} substituted for Li^+ is compensated by lithium vacancies in different positions, and axial centers should give dominant lines of EPR. In order to clarify reasons of contradictions of published data, we made extended study of congruent and stoichiometric samples doped with relatively small amount of Er^{3+} (less than 0.5% wt% in the melt). We found unusual behavior of magnetic system in classical ferroelectric. After fast cooling to liquid helium temperatures there was no internal magnetic field in the samples. This allowed observing unperturbed EPR spectra. No axial Er^{3+} centers were registered in both congruent and stoichiometric LN; two found low-symmetry centers have very strong anisotropy of g-tensor (gmax»15, gmin<1). After 10 hours the magnetic moments of Er ions started to reveal an ordering, and after several days an internal magnetic field in the plane perpendicular to crystal axis approached several hundred Gauss: usual 180° repetitions of EPR spectra disappeared. The internal field appeared also during slow cooling of samples. It is concluded that due to huge magnetic moment of Er^{3+} ions, they have a tendency to magnetic ordering. Most of Er^{3+} ions create self-compensating pairs or complexes with even number of ions. Such complexes are invisible in EPR, but reveal themselves in optical experiments. Isolated Er^{3+} ions are only a visible top of huge iceberg under water.

EPR ORAL SESSION

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Simulation of Magnetic Resonance Spectra of Low-Symmetry Systems.

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Material characterization with the help of magnetic resonances (EPR, NMR, ENDOR etc.) is equally important for many natural sciences: chemistry, biochemistry, physics, biology, medicine etc. Various electron-nuclear systems were investigated with the help of these methods: ions and molecules, radicals, excitons, electron and hole traps, etc. Key elements for successful application of these methods are fast procedure of quantum mechanical calculation of magnetic properties on the base of proper hypothesis and model of the system, and efficient procedure for the determination of numerous model characteristics based on comparison of predicted and measured spectra. Both procedures strongly rely on computer treatments and require development of corresponding computational methods. Most existed computer programs can be successfully used for treatment of low-spin high-symmetry systems, but meet with difficulties or simply fail if applied to high-spin or multi-spin low-symmetry systems. Several ideas for program improvement are proposed and discussed in this talk. The consideration includes: hidden symmetry in commonly used spin-Hamiltonians that leads to inseparable combinations of spin-Hamiltonian parameters and makes these spin-Hamiltonians unsuitable for computer calculations, double spiral partition method for acceleration of calculation and smoothening spectra of disordered materials, reasonable combination of exact diagonalization and perturbation theory for multi-spin systems, scaling of multicomponent lines for spectrum simulation, interactive fitting of both multicomponent spectrum and its angular dependencies etc. An implementation of these ideas in our “Visual EPR” program package is illustrated using examples of spectra for crystalline, powder, and organic materials. The proposed algorithms and programs enhance trustworthiness of obtained results, improve accuracy of determined characteristics, and facilitate and accelerate spectra treatment. Convenient interface of the programs allows easily integrate them in student education.

EPR ORAL SESSION

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200 Electrically Detected Magnetic Resonance Measurements via Spin Dependent Charge Pumping and Other Detection Schemes in SiC Metal-Oxide-Semiconductor Field-Effect Transistors.

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We report on low field/frequency and high field/frequency electrically detected magnetic resonance (EDMR) measurements made on SiC lateral metal-oxide-semiconductor field-effect transistors (LMOSFETs) and double diffused MOSFETs (DMOSFETs). The measurements utilized several detection schemes; the most notable is spin dependent charge pumping.[1] Charge pumping is a now standard purely electrical measurement in which a periodically varying potential is applied to the gate of a MOSFET,[2] cyclically flooding the semiconductor/oxide interface with electrons and then holes. The process can be carried out over a wide range frequencies and gate potentials. These frequency and potential combinations allow for extraction of energy levels and physical position of defects at/near the SiC/SiO_2 interface. Additionally, by utilizing different device geometries, we can explore the SiC/SiO_2 interface (using LMOSFETS) and the SiC bulk (using DMOSFETs) regions of fully processed devices. LMOSFET geometry allows us to use the bipolar amplification effect biasing scheme which is very sensitive to the MOSFET channel.[3] DMOSFET geometry allows us to either strongly accumulate or invert the channel which turns off recombination in that area. Forward biasing the drain/body junction allows exploration of the bulk SiC. Among other results, the most surprising is the detection of a physical change in defect structure almost certainly via some reaction with hydrogen in the SiC bulk when the gate oxide is subjected to electric fields of a few MV/cm at moderately elevated temperature (150°C). To the best of our knowledge, this result has not been anticipated anywhere within the extensive literature dealing with instabilities in these devices.

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EPR POSTER SESSION

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201 EPR of Di-and Tri-Nuclear Mixed-Valence Copper Amidinate Complexes from Reduction of Iodine.

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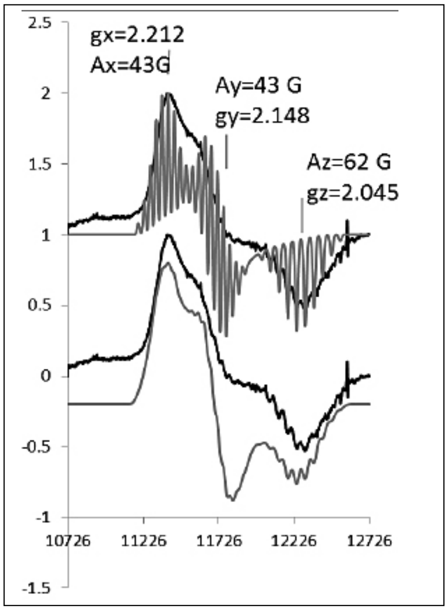
The reaction of the bimetallic Cu(I) complex, $[(2,6\text{-}Me_2C_6H_3N)_2C(H)]_2Cu_2$, with I_2 in THF, CH_3CN, and toluene affords three new mixed-valent copper complexes, $[(2,6\text{-}Me_2C_6H_3N)_2C(H)]_2Cu_2(\mu_2\text{-}I_3)(THF)_2$, $[(2,6\text{-}Me_2C_6H_3N)_2C(H)]_2Cu_2(\mu_2\text{-}I)(NCMe)_2$, and $[(2,6\text{-}Me_2C_6H_3N)_2C(H)]_3Cu_3(\mu_3\text{-}I)_2$, respectively. All three compounds have been characterized by EPR spectroscopy. A Q-band spectrum and a simulation for a $Cu_3(amidinate)_3(I)$ mixed valence complex with Cu(1.33)Cu(1.33)Cu(1.33) is shown in the insert. In addition, spectra for di-nuclear mixed valence complexes and simulations will be presented.



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EPR POSTER SESSION

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202 Morphology and Photoexcitation Dependence of Optically Detected Magnetic Resonance in MEH-PPV Thin Films.

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For poly(2-methoxy-5-(2-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV), photoexcitation of thin films results predominantly in the formation of strongly coupled singlet excitons which subsequently undergo geminate recombination, producing photoluminescence. However, due to disorder in these materials there is also always a small fraction of excitations which undergo charge separation. In absence of an electric field, these charge carriers will ultimately recombine non-geminately by formation of weakly spin-coupled excitonic precursor pairs, (so-called polaron pairs) which then undergo transitions into either singlet- or triplet-excitons. The manipulation of polaron pairs with electron spin resonance leads to a change of the ratio between singlet and triplet-exciton generation rates and because triplet excitons recombine predominantly non-radiatively, it leads to optically detectable changes of the photoluminescence intensity. Thus, the net-magnitude of an optically detected magnetic resonance (ODMR) signal of the photoluminescence relative to the overall photoluminescence is a measure for the fraction of charge carriers that recombine non-geminately (even though the two ratios are not the same).

Here, we present a study of the strength of the room temperature ODMR signal of MEH-PPV as a function of the deposition (which directly controls the film morphology), thin-film device parameters and the intensity and photoexcitation energy. We find that the fraction of the charge carriers that recombine non-geminately decreases with laser intensity, disappearing into the noise floor at around 500μW/mm^2 for excitation wavelength of 405nm, suggesting that for low charge carrier densities, the ability of charge carriers to leave geminate pairs is suppressed. For a high excitation density of 15mW/mm^2 we find that a higher fraction of non-geminate pairs exists for samples prepared with drop-cast films vs. those that were dip-cast. For spin-cast MEH-PPV films, we generally could not detect ODMR. However, by application of an aluminum electrode onto these films, an ODMR signal could be reintroduced.

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EPR POSTER SESSION
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203 Solution State Overhauser Dynamic Nuclear Polarization at 10 mT.

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At room temperature and in fluid solution the Overhauser mechanism dominates for the transfer of electron polarization to surrounding protons. At very low magnetic fields, the hyperfine interaction plays an increasingly important role in the magnitude of DNP enhancement. To explore and characterize the impact of the hyperfine interaction at very low magnetic fields, a small DNP spectrometer has been constructed, currently operating at 10 mT. The goal is characterization of radical molecules with differeing hyperfine interactions from 10 mT to 100 μT. Coverig a regime where enhancement changes from a dependence on the applied static magnetic field (ratio of gyromagnetic constants) to a dependence on hyperfine will increase understanding of how to optimize selection of polarizer molecules for solution DNP experiments. In addition, the information gained will be used for future experiments in an ultra-low-field MRI (ULF-MRI) system currently under construction at NIST.

EPR POSTER SESSION
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Pulse Shaping at L-band using an Arbitrary Waveform Generator.

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Pulsed EPR imaging with magnetic field gradients require larger excitation bandwidths than spectra in the absence of gradients. To obtain the highest-quality projections it is important to maximize the bandwidth and uniformity of the excitation. Pulse shaping is a powerful tool for improving excitation,[1,2] but is difficult to implement with analog devices. The use of arbitrary waveform generators as the source for EPR spectrometers provides the opportunity to define radiofrequency pulses with nanosecond phase and amplitude precision.[3, 4] In the present study, the excitation profiles produced with rectangular, composite, exponential sine, or rectangular pulse shapes are compared. Simulation of the resonator response to shaped pulses, taking account of the resonator Q, was used to select the parameters required for uniform excitation. Experimental tests of the predictions were obtained by recording the FID for an aqueous solution of the triarylmethyl radical, trityl-CD3, as a function of magnetic field offset. Uniformity of excitation, excitation bandwidth, and power requirements are compared.

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EPR POSTER SESSION

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205

Fast Frequency Swept EPR for Optimizing Microwave Efficiency in DNP NMR of Small Samples.

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DNP has proven very helpful in increasing sensitivity for the investigation of large biomolecules by solid state NMR. It is also potentially useful in applications where small samples are required for very fast magic angle spinning, or are only available in limited quantities. When microliter sized samples are used, gryotrons are not necessary to provide the required microwave power density for DNP. In this instance a diode based microwave source can be employed, providing several advantages in frequency agility, modulation capability, and cost. However, efficiently coupling the microwave power into such small samples can be challenging. We describe a rudimentary frequency swept EPR capability that can be used to assess microwave delivery to a MAS sample volume. Using a synthesizer and amplifier multiplier chain from Virginia Diodes Inc. (VDI) on a 7T system, we are able to optimize the alignment of the microwave components in real time by sweeping over the 195-201 GHz range. EPR spectra of several suitable probe samples will be presented, including single crystal HPHT diamond. Support for this work by Agilent Labs and the NSF Chemical Measurement and Imaging program under grant CHE-1413096 is gratefully acknowledged.

EPR POSTER SESSION

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206 Advantages of the Rotated and Modulated Magnetic Field Gradient in 2d Spatial and Spectral-spatial EPR Imaging.

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Methods for fast 2D spectral and spectral-spatial electron paramagnetic resonance imaging (EPRI) are presented. The aim of the measurements was to reduce acquisition time of the sinogram by combining rapid scan of Zeeman magnetic field using high frequency sinusoidal modulation with simultaneously applied magnetic field gradient, which orientation or amplitude are changed at low frequency. The correctness of the method is confirmed by studies carried out on a phantom consisting of two LiPc samples. The images from the acquired data are reconstructed using iterative algorithms. The proposed methods allows to reduce the image acquisition time up to 10 ms for 2D spatial [1], and 200ms for 2D spectral-spatial EPRI [2]. The linewidths obtained from 2D spectra-spatial imaging and phantom shapes obtained from 2D spatial imaging were in excellent agreement with the values expected for the phantoms used.

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EPR POSTER SESSION

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207 DEER Measurements of Copper Porphyrins Stacked on Guanine Quadruplexes.

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Aside from a double helix, DNA folds into non-canonical structures, one of which is the guanine quadruplex. Cationic porphyins bind guanine quadruplexes[1-2], but the effects of ligand binding on the structure of guanine quadruplexes with more than four guanine quartets remain to be fully elucidated. In this work, double electron electron resonance (DEER) spectroscopy conducted at X-band is used to measure the distances between copper porphyrins bound to parallel-stranded guanine quadruplexes with increasing numbers of guanine quartets. The topology of these systems presents a unique model with one-dimensional spatial control over the distance between metal ions. To overcome the low modulation depths exhibited by transition metals as a result of their broad absorption spectra, a substantial gain in bandwidth excitation at the pumping frequency is observed through the use of a partially adiabatic pulse[3]. The extracted copper-copper distance distributions increase as the number of guanine quartets increases, but is not consistent with the predicted guanine quadruplex lengths. This inconsistency may arise from either (a) a decreasing copper porphyrin-guanine quartet stacking distance or (b) a compression of the guanine quadruplex.

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EPR POSTER SESSION

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Bayesian Uncertainty Quantification For DEER Spectroscopy.

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Double Electron-Electron Resonance (DEER), also known as Pulsed Electron Double Resonance (PELDOR), is an increasingly important biophysical pulsed Electron Paramagnetic Resonance (EPR) technique for structural characterization of biomacromolecules. Notably, DEER reports a distribution of distances corresponding to protein conformational ensembles in frozen glassy solutions. The predominant method for extracting this distribution from the acquired DEER time-domain data is non-negative Tikhonov regularization. Due to the ill-conditioned, inverse nature of the problem, a robust method for quantifying uncertainty in DEER distance distributions obtained from Tikhonov regularization does not currently exist. This significantly complicates interpretation, as missing error estimates can lead to overinterpretation. Here we show how Bayesian statistical methods can be used to quantify uncertainty in DEER distance distributions arising from the noise of the time-domain signal and from the bias introduced by regularization parameter selection. We generate corresponding Bayesian credible intervals to visualize uncertainty and guide interpretation.

EPR POSTER SESSION

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209

250 MHz in vivo Rapid Scan Images of pH and Thiol Reductive Status.

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Rapid Scan EPR (RS EPR) is an innovative approach to obtaining EPR spectra with higher signal to noise ratio. RS EPR opens door for efficient imaging of injectable spin probes in vivo. We present experimental procedures and in vivo images of pH and thiol reductive status. The change in these environmental parameters from their normal values is indicative for determination of cancer proliferation and aggressiveness and can be used for treatment optimization.

For the image we have used intratumoral injection of pH and PxSSPx probes. pH-sensitive nitroxide exhibited a change in hyperfine coupling as a function of extracellular pH and was imaged using 4D spectral-spatial methodology. The dissociation kinetics of PxSSPx due to reaction with intracellular glutathione was observed using 35 s 3D spatial images.

This work complements our previous studies of tissue oxygenation and broadens our knowledge of the tumor cell microenvironment. This work is supported by NIH grants P41 EB002034, R01 CA98575 and K25 EB016040.

EPR POSTER SESSION

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210 Acceleration of Pulse EPR pO_2 Imaging using Low-Rank Tensor Imaging.

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We have developed a low-rank tensor image model for performing dynamic pO_2 mapping from highly undersampled (k,t)-space data. This model represents a set of dynamic images collected with different pulse sequence parameters in a low-dimensional, time-varying parameter subspace. This model captures the correlations between images across both time and the parameter space, and is an extension of our previous work on accelerated parameter mapping using low-rank models [1,2] and accelerated dynamic imaging using low-rank models [3].

This model was applied for 250 MHz in vivo pulse EPR imaging of spontaneous and induced oxygen fluctuations in mouse tumors and provided 30s pO2 temporal resolution with spatial and pO_2 resolution comparable to those derived from the standard 10 min pO_2 image. This resulted in factor of 20 acceleration in image acquisition.

This work is supported by NIH grants P41 EB002034, R01 CA98575.

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EPR POSTER SESSION

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211 Center for Electron Paramagnetic Resonance Imaging In Vivo Physiology—Tissue pO_2 as a Determinant of Tumor Biology.

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The molecular oxygen concentration or partial pressure in tumor tissue is an important determinant in cancer development that may be used for tumor prognosis and therapy. In vivo oxymetry is a main focus of the Center for Electron Paramagnetic Resonance Imaging In Vivo Physiology. pO_2 images developed by the Center give detailed insight into physiology of living tissue in non-invasive and accurate manner. Registration with the MRI and CT images provides complimentary information about anatomy of the investigated region.

The Center is an ideal place for the researchers interested in oxygen biology. A number of collaborators are already benefiting from the resources provided by our Center. The Center developed technologies for oxygen guided intensity-modulated radiation therapy; for correlation of hypoxia, gene function (e.g. BACH1) and protein expression (e.g. VEGF, HIF1a, Ca9); for imaging small objects such as in situ ductal carcinoma. We welcome new collaborators to join our quest.

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EPR POSTER SESSION

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212 Solitons in Phthalocyanine Chromophores: Fundamental Study and Implications for Organic Spintronics.

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A series of organic chromophores which are commonly used in organic photovoltaic devices have been studied using X-Band CW EPR spectroscopy of powders to quantify the presence of an intrinsic sub-gap radical state (soliton) at room temperature which has been previously studied extensively in cis- and trans-poly(acetylene) films.[1-3] In addition to CW EPR, we use pulse EPR methods to identify the spin states in ClAlPc and AlPc TEMPO powders (PEANUT)[4] and to quantify the nature of electron-^{14}N hyperfine interactions using powder ESEEM. These pulse EPR studies highlight the potential importance of electron-nuclear spin-spin interactions for the relative stability and magnitude of soliton states in organic chromophores. We envision using this suite of EPR experiments as an analytical technique to better understand design principles for organic spintronic devices.

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EPR POSTER SESSION

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213 Two-Dimensional Electron-Electron Double Resonance and Molecular Motions: The Challenge of Higher Frequencies.

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The Freed lab pioneered the use of the Stochastic Liouville Equation (SLE) for extracting molecular information from ESR spectra, and subsequently, the ACERT center has presented many advances in the field of 2D ELDOR (electron-electron double resonance spectroscopy) as well as multi-frequency, multi-field ESR. These studies have offered insight into the dynamics of proteins, as well as the dynamics of ordered fluids, including lipid membranes. At ACERT, we are currently pioneering the development of multi-frequency 2D ELDOR. The most challenging aspect of this development involves the implementation of W-band 2D ELDOR for biologically relevant samples. Correctly processing the resulting datasets and fitting them to simulations that offer information on the molecular dynamics and ordering also involves significant efforts. In this poster, we offer an overview of the progress in these areas and outline, in particular: (1) the current performance of the W-band ELDOR instrument, and the types of spectral information that can already be acquired; (2) our success with employing 3D EM modeling to dramatically increase the available B_1 field without increasing the transmitter power and our progress towards employing similar modeling to reduce the dead-time; as well as (3) upgrades to the NLSL software that improve user interaction and allow for a more seamless interface with experiments.

EPR POSTER SESSION

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214 Multiplex Detection of Magnetic Resonance for π-conjugated Polymer Electronics Devices.

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Molecular dynamics often causes time fluctuation on physical properties of π-conjugated polymer electronics devices. We have tried to develop a variable frequency C-band electron spin resonance (ESR) instrument to measure spectral density of molecular dynamics. Furthermore, magnetic resonance experiments with versatile spin generations including optical and electric field and also with several detection methods were implemented in order to identify spin dependent phenomenon that couples carrier transports. Variable frequency C-band ESR experiments were performed using a variable size microwave cavity equipped with custom waveguide windows. We will show the simultaneous measurements of electrically detected magnetic resonance (EDMR) and ESR for a complex sample of a silicon diode with DPPH powder and also for an organic photovoltaic cell of ITO/pentacene/Al. The simultaneous ESR/EDMR measurements could be helpful to identify mobile and trapped carriers.

EPR POSTER SESSION

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215 SHARED EPR: A Network of EPR Researchers.

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This poster will describe an NSF-supported Research Coordination Network named "Supporting, Highlighting and Advancing Recent Developments in Electron Paramagnetic Resonance" (SHARED EPR) to promote the development and dissemination of innovative instrumentation and techniques in the area of EPR spectroscopy. EPR is of central importance to scientific research in the disciplines of Chemistry, Physics, Biology, Medicine, and Materials Science. It is crucial to the overall growth of the field of EPR that advances achieved in one discipline be communicated to researchers in the other disciplines. The SHARED EPR network is designed to ensure these advances are translated from the lab in which they are developed to the labs in which they are needed, no matter what discipline is involved. The Primary Goals of the network will be 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 Network will achieve these goals by spearheading the following network activities. An annual Grand Challenge Workshop will be organized in conjunction with a national scientific meeting, which will bring together a diverse range of EPR researchers to identify and address major issues facing the field of EPR spectroscopy. A web portal will be developed which will provide a centralized location for information regarding EPR research and resources and serve as a gateway to the EPR community for non-specialists. The Network will sponsor EPR Technology Transfer Experiences in which students and postdocs spend time doing experiments in other labs to learn new EPR techniques which they will bring back and implement in their home labs. And international collaboration will be fostered through the interaction of the SHARED EPR Network with the German Priority Program titled "New Frontiers in Sensitivity for EPR Spectroscopy."

EPR POSTER SESSION

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216 Influence of Synthesis Route on Magnetic Ordering of SmxCa1-xMnO3(x=0.35, 0.65) Manganites: EMR Studies.

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Here we report Electron Magnetic Resonance (EMR) investigation of influence of fabrication process on magnetic ordering in bulk samples of Sm0.65Ca0.35MnO3 and Sm0.35Ca0.65MnO3 prepared by two different routes, viz., solid state reaction (SS) and sol-gel (SG) methods. The solid-state reaction route is the commonly used method for the preparation of polycrystallinesolids from a mixture of solid starting materials, where in solid-solid diffusion is accelerated by high temperature. Sol-gel is a wet chemical synthetic method in which the phase formation is accelerated by using liquid media. The different fabrication routes can result in different dislocations, vacancies, and defects at grain boundaries and variations in the concentration of the dopant content in a compound impacting the structure, magnetic and electric properties of the sample. The crystal structure and microstructure studies of the synthesised samples are done by X-ray diffraction, surface morphology by field emission scanning electron microscope (FESEM) and elemental analysis by energy dispersive X-ray analyzer (EDAX) coupled with FESEM. The magnetization measurement was carried out with a SQUID magnetometer under a field of 100 Oe from 4 -300 K. The samples were further subjected to detailed EMR spectroscopy studies using a Bruker EMX X-band (9.4 GHz) spectrometer in the temperature range 5 -300 K. Our results show that though the two different techniques result in phase-pure samples with similar crystal structure, through the temperature variation of the EMR parameters viz, intensity, linewidth and g-factor we could detect minute differences in the spin environment confirming that EMR is a powerful tool to study static and dynamic magnetic correlations on a microscopic level.

EPR POSTER SESSION

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217 EM Simulation Methods to Facilitate Design and Development of Custom Resonators.

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Electromagnetic (EM) simulation software is an important tool in prototype development for laboratories that have a need for customized probes or bridge components. Unlike analytical and academic research laboratories, that must accommodate a wide variety of samples and experimental conditions, many industrial or educational applications require the same measurement or procedure to be performed repeatedly or even continuously. Custom probes for each application can be, therefore, tailored to a specific routine measurement. EM simulation methods and post-processing for resonator design will be presented.

EPR POSTER SESSION

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218 Investigation of Radical Distribution in Foodstuffs by X-band ESR Imaging.

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ESR imaging is widely used for in-vivo samples such as mouse or rat with L-band or lower frequencies. However using strong field gradient coil, material imaging at X-band became possible. At X-band imaging, we could not measure large sample volume but could high sensitivity measurements with small sample.

In this work, we show some X-band imaging data of foodstuffs samples. We applied it to investigate the distribution of crystallized sucrose in gamma irradiated dried mango. There are many crystalized sucrose on the surface of the dried mango but not inside of the mango. Fig. 1 shows the radical distribution of the gamma irradiated dried mango. This result indicates that the EPR signal is generated only from crystallized sucrose but no non-crystalline sucrose. Then we investigate radical locations in various sesame seeds. The ESR imaging showed that free radicals were located surface region and hilum region and not inside the black sesame seed. The most intense signal was detected at the hilum part. The very weak image for the white sesame (light-roasted) was observed. In addition, the imaging for the irradiated white sesame showed that free radicals were located at the hilum and whole region of the seed. Thus, the X-band EPR imaging showed the exact location of radical species in various sesame seeds for the first time.

EPR POSTER SESSION

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219 A Modular Low Frequency EPR Spectrometer for Studying Objects with Cultural Heritage Significance.

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We report on a laboratory built, modular, low frequency electron paramagnetic resonance (LFEPR) spectrometer used to study objects with cultural heritage significance. The term modular implies that the continuous wave spectrometer bridge, detector, control program, and magnet are readily reconfigured to perform a new experiment. The magnet can accommodate 15 cm diameter/wide objects up to a few meters in length and is thus suitable for studying medium sized ceramic objects. The spectrometer can operate at frequencies between $150 < \nu < 450$ MHz, and scan the magnetic field between $-27 < B_o < +27$ mT. Samples can be examined using one of seven single turn solenoid (STS) resonators operating at 150, 204, 240, 300, 355, 406, and 440 MHz; or two surface coils (SC) operating at 250 and 270 MHz. The 2 cm diameter 3 cm long STSs accommodate 1.5 cm diameter sample tubes and are used to study the effects of firing temperature on clay samples, and the frequency dependence of the EPR signal of complex spin systems such as S=5/2 Mn(II) in marble. The surface coils have sensitive diameter/depth of 20/5 and 2.9/0.5 mm and could be used to nondestructively and noninvasively study large, intact objects up to 15 cm in diameter, and the spatial distribution of paramagnetic materials on 15 cm wide piece of paper or painting. The magnet, radio frequency synthesizer, and lock-in amplifier on the spectrometer are controlled by LabView code.

EPR POSTER SESSION

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220 Low Frequency EPR of Ceramic and Marble Objects with Cultural Heritage Significance.

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Low frequency electron paramagnetic resonance (LFEPR) is used primarily for in vivo applications. We report on a new application of LFEPR to study ceramic and marble objects with cultural heritage significance. Conventional high field EPR has been used for this purpose by unobtrusively removing a small sample from the object. LFEPR is capable of looking at the EPR signal from large cultural heritage objects non-invasively and non-destructively. We have examined intact objects as large as 15 centimeters in diameter using 250 MHz LFEPR. These include a Ming dynasty porcelain bowl (ca. 1500), a Meissen contemporary Böttger red stoneware candlestick (ca. 1920), a Wedgwood rosso antico jug (ca. 1850), a Saxon Notgeld coin (ca. 1921), a terracotta clay flower pot (ca. 2010), and white marble tiles. The spectra of ceramics show features of $S=5/2$ Fe(III) displaying a $g\approx4$ peak (Fe(III) substituting for Al in aluminosilicate lattices), a $g\approx2$ peak (Fe(III) in iron oxide) or orientation-dependent ferro/ferrimagnetic resonance behavior. We also report on the dependence of these signals on firing temperature and the signals from pigments used in coloring ceramics and paintings. We have also studied the LFEPR spectrum of $S=5/2$ Mn(II) in marble between 150 and 450 MHz. This ability is important when trying to understand LFEPR in systems where the high-field approximation breaks down due to comparable Zeeman and hyperfine interactions. Examples of spectra from representative samples will be presented.

EPR POSTER SESSION
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221 Low-Frequency EPR Imaging of Planar Objects with a Surface Coil.

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We present the use of low frequency electron paramagnetic resonance (LFEPR) spectroscopy to image electrophotographically printed text on paper using a rastered surface coil approach. Electrophotography or xerographic toner is known to contain ferri/ferromagnetic materials which become fused to the copy paper. These materials possess a signal when examined with an LFEPR spectrometer. A LFEPR spectrometer was equipped with a two dimensional translational stage to move #72 (1.9 cm high) font Arial text under a 2.9 mm diameter, 271 MHz surface coil probe. The magnetic field was fixed at 7.5 mT and the spectrometer recorded the signal while the text was moved under the surface coil in 17 parallel lines, each separated by 2 mm. The resultant 561 point spectra were plots of the signal as a function of distance along the raster line. Spectra were baseline corrected and used to create 17 rows of an image which was expanded to 204x561 square pixels using a bicubic interpolation. The text could easily be read in the image with a signal-to-noise ratio of 11 without further image processing. This technique has potential for imaging the distribution of paramagnetic materials in paintings and illuminated manuscripts.

EPR POSTER SESSION
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222 Spin Dynamics of Strongly-Coupled Photogenerated Triradicals.

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Organic donor-acceptor systems that undergo photoinduced electron transfer reactions have attracted interest due to their potential applications in solar energy conversion and spintronics. The charge separation and recombination processes that govern the efficiency of organic photovoltaics are dependent on the spin states of the electrons involved, and manipulation of these spin states can potentially improve the efficiency of such devices. We present the synthesis and characterization of an organic donor-acceptor system coupled to a stable radical. The effects of the radical on the rates of photoinduced charge separation, charge recombination, and competing processes are measured using transient optical absorption spectroscopy. Transient EPR spectroscopy is used to follow spin polarization within the system, providing information on the mechanisms behind the observed changes in rates.

EPR POSTER SESSION

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223 Electrically Detected Magnetic Resonance Spectroscopy on Monolithic Organic Light Emitting Diodes with built-in Lithographically Defined Microwave Excitation/Magnetic Field Modulation Structures.

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Magnetic resonance of charge carrier (so called polaron) spin states in thin solid films made of π-conjugated polymers can be observed through the measurement of charge carrier recombination currents in diode devices that allow for both electron and hole polaron injection. Such electrical detection of magnetic resonance (EDMR) is significantly more sensitive than inductively detected magnetic resonance as the resonantly measured sample current is only weakly dependent of the polaron ensemble magnetization, and thus, it is not directly dependent on the applied temperature, the magnetic field, or the sample volume. For this reason EDMR on polymer-thin film diodes has been used in the past for magnetic resonance based absolute magnetometry of mid to low magnetic field domains.[1]

Following this idea, we report here on the fabrication of monolithic copper-based lithographically defined wires for broadband (low-Q) EPR excitation located 1micron beneath organic light emitting diode (OLED) stacks with a circular surface area of 57um diameter. For the fabrication of these integrated resonator/OLED devices, we deposited crossed wires on top of a quartz substrate, followed by the deposition of a 1micron thick dielectric insulator stack below an OLED back contact. These template structures where brought into an inert glovebox environment where the OLED device layers were deposited.

The integrated devices allow for EDMR spectroscopy over broad frequency ranges with high driving field B_1 to square-root-of-power ratios as well as thin film induced magnetic field modulation. In the RF range (f≈ 100MHz) the structures allow for the continuous-wave application of B_1>1mT without any recognizable heating effect. We discuss the applicability of these structures not just for magnetometry but also for non-linear EDMR spectroscopy at high B_1 and low frequency/B_0 conditions.

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EPR POSTER SESSION

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224 Multi-Harmonics Electrically Detected Magnetic Resonance Spectroscopy of Organic Light Emitting Diodes Using Capacitively Coupled Coplanar Waveguide Resonators.

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Coplanar waveguide (CPW) resonators have a wide range of applications for quantum optics, radiation detectors, parametric amplifiers and magnetic resonance spectroscopy. However, most of the works found in the literature reports on superconducting CPW resonators at low temperatures [1]. We have designed and implemented CPW resonators for which one end is capacitively coupled to the feed line while the other end is connected to the ground plane in order to allow for room temperature electrically detected magnetic resonance (EDMR) spectroscopy of organic light emitting diodes (OLEDs) over a wide frequency range from about 1GHz to about 20 GHz [2]. The fundamental frequency of the resonator design is determined by the resonator length in the wave propagation direction and dielectric constant of the substrate. We implemented six resonators with fundamental frequency approximately spaced equally between 1 and 6 GHz. We have used these to observe EDMR spectra not only at the fundamental modes but also at higher harmonic modes predicted by the formula, $f_{2n-1}=(2n-1)f_0$. We found that the amplitude of the observed EDMR signals, and thus, the effective resonant driving field B_1 decreases. This may be attributed to the inhomogeneity in the distribution of B_1 over the device geometry and associated decrease of quality factor with higher resonance modes [3].

The simulation, development and implementation of CPW resonators presented here were supported through a National Science Foundation CAREER Project (#0953225) by support of G.J., K.A., and C.B. The preparation of organic semiconductor devices was supported by the Department of Energy Grant (#DESC0000909) through support of H.M. and M.K.

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EPR POSTER SESSION

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225 ESEEM Study of the Initial Stages of Tau Protein Aggregation.

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The aggregation of the microtubule stabilizing protein tau has been identified as an important constituent in the formation of amyloid plaques characteristic of neurodegenerative diseases such as Alzheimer's disease. Monomeric tau protein is an intrinsically disordered protein, which has a propensity to aggregate at three (or four depending on isoform) microtubule binding regions eventually forming beta-sheet strands. While the characteristics/structure of tau protein before and after aggregation has been characterized by a number of methods, the transient intermediate states have been far more difficult to study. In particular, we are interested in whether the hydration water is restructured or relinquished before or during oligomer formation, and whether this is correlated with the microtubule binding regions of tau protein. We have used pulsed EPR to characterize the initial stages of tau protein aggregation; including T_M relaxation measurements to monitor oligomer formation and ESEEM to characterize the hydration water upon aggregation of tau protein. We find that immediately after inducing aggregation, we observe a dramatic decrease in T_M which is caused by the association of tau protein into oligomers. These oligomers are not yet beta-sheet strands, but the decrease in T_M is an indication that tau protein has associated from a monomeric state into dimers or higher order oligomers. In addition, we find that the water accessibility is decreased immediately upon inducing aggregation, however, only at sites which are adjacent to microtubule binding regions. This result indicates that the association of tau protein into oligomers is driven by interactions at the microtubule binding regions.

EPR POSTER SESSION

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226 Characterization of the Free Energy Landscape for Radical Rearrangement Catalysis in B12-Dependent Ethanolamine Ammonia-Lyase.

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The Co^{2+}-substrate radical pair intermediate in the reaction cycle of ethanolamine ammonia-lyase (EAL) from *Salmonella typhimurium* accumulates during steady-state turnover, and can be stably cryotrapped. Upon annealing at temperatures (T) of 197-230 K, the radical pair formed by using aminoethanol substrate decays to diamagnetic products.[1] The decay is measured by using time-resolved, full-spectrum continuous-wave electron paramagnetic resonance (CW EPR) spectroscopy. The radical decay exhibits two regimes: (*i*) High temperature range, $220 \leq T \leq 230$ K; monoexponential decay with rate constant, *khigh*, and (*ii*) Low temperature range, $197 \leq T < 220$; biexponential decay with rate constants, k_{fast} and k_{slow}. The *k*-values represent the substrate-to-product radical rearrangement reaction. The *khigh* values display an Arrhenius T-dependence that extrapolates to values for rearrangement-determined *kcat* at $T \geq 277$ K. Both the *kfast* and k_{slow} populations diverge from the *khigh* relation at $T_{div}=220$ K, and follow distinct Arrhenius dependences for $T < T_{div}$. The T_{div} is comparable to the glass transition temperature (T_g’) of the solvent mesodomain[2] that envelopes EAL in the frozen polycrystalline samples (Chen, Sun, Warncke, unpublished). Based on these results, we propose that the native radical reaction coordinate includes a subset of the collective motions of protein and coupled solvent atoms (α-fluctuations), that are revealed by the effective quenching of the collective dynamics at $T_{div} \approx T_g'$. The reaction of the substrate radical at $T < T_{div}$ indicates secondary channels for reaction. We have developed a multi-state, T-dependent free energy landscape model for simulation of the EPR-monitored decay kinetics. The results indicate that the protein samples the wide substrate radical configuration state space[3] at high T, but at T

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EPR POSTER SESSION

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227 Spin Dynamics of Radical Pairs in Electron Donor-Acceptor Systems using Fourier Transform EPR Methods.

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Covalently-linked organic donor-acceptor (D-A) molecules are a category of systems with intriguing possibilities for use in quantum information processing (QIP). Fast photo-initiated electron transfer within a D-A molecule can result in the formation of a spin-correlated radical pair (SCRP) with a well-defined initial spin configuration. These SCRPs systems have displayed coherent spin motion for ~100 ns[1, 2], which could provide a basis for the development of new QIP strategies based on this spin coherence. Before these strategies can be exploited, a greater understanding of the factors controlling spin coherence dephasing is necessary.

Both the intrinsic properties of SCRPs and their surrounding environment play a role in the dephasing of the initial photo-generated spin coherence. In order to quantitate these effects, a series of rigid donor-acceptor molecules were studied under several different solvent conditions. The characterization of the spin dynamics in this series of molecules was performed using Fourier transform EPR methods.

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EPR POSTER SESSION

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228 Interaction Between the Influenza HA Fusion Peptide and Transmembrane Domain Affects Membrane Structure.

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Viral glycoproteins, such as influenza hemagglutinin (HA) and HIV gp41, are anchored by a single helical segment transmembrane domain (TMD) on the viral envelope membrane. The fusion peptides (FP) of the glycoproteins insert into the host membrane and initiate membrane fusion. Our previous study showed that the FP or TMD alone perturbs membrane structure. Interaction between the influenza HA FP and TMD has previously been shown, but its role is unclear. We used PC spin labels DPPTC (on the head group), 5PC and 14PC (5-C and 14-C positions on the acyl chain) to detect the combined effect of FP-TMD interaction by titrating HA FP to TMD-reconstituted DMPC/DMPG/Chol lipid bilayers using ESR. We found that the FP-TMD increases the lipid order at all positions, which has a greater lipid ordering effect than the sum of the FP or TMD alone, and this effect reaches deeper into the membranes. Although HA-mediated membrane fusion is pH dependent, this combined effect is observed at both pH5 and pH7. In addition to increasing lipid order, multiple components are found for 5PC at increased concentration of FP-TMD, indicating that distinct domains are induced. However, the mutation of Gly1 in the FP and L187 in the TMD eliminates the perturbations, consistent with their fusogenic phenotypes. ESR on spin-labeled peptides confirms that these observations. We suggest that this interaction may provide a driving force in different stages of membrane fusion: initialization, transition from hemifusion stalk to transmembrane contact, and fusion pore formation.

EPR POSTER SESSION

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229 Simulating Slow-Motion Continuous Wave EPR Spectra for General Spin Systems Using the Stochastic Liouville Equation.

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A general stochastic Liouville equation solver has been implemented to simulate slow-motion cw-EPR spectra for any general spin system given the spins in the system and the spin Hamiltonian interaction tensors or parameters. Example simulations over a range of rotational correlation times are shown for a variety of model spin systems with $S > \frac{1}{2}$ and with several interactions, including multiple hyperfine interactions and zero field splitting. This general slow-motion implementation is used to extract rotational correlation times from X-band cw-EPR spectra of a high spin [Gd(III)-DOTA]Cl_3 solution in glycerol/water.

EPR POSTER SESSION

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230 Structural Changes at the Ferrous Active Site of Phenylalanine Hydroxylase Resulting from Allosteric Activation by Substrate.

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Structural changes that occur at the catalytic Fe^{2+} site of rat Phenylalanine Hydroxylase (PheH) in response to allosteric activation of the enzyme by substrate, L-phe, were studied using the Electron Paramagnetic Resonance method of Hyperfine Sublevel Correlation spectroscopy (HYSCORE). Nitric Oxide was used as a surrogate for molecular oxygen to poise the enzyme in an S=3/2, $\{FeNO\}^7$ state amenable to EPR spectroscopy. Three different forms of the enzyme were studied: Δ-PheH, a fully-active, truncated form of the protein where the regulatory domain has been removed; $PheH^T$ – a non-activated, full length form of the enzyme treated with a low concentration of L-phe; and $PheH^R$, an allosterically activated full-length form of the enzyme that results from treatment with a 50-fold excess of substrate. HYSCORE spectra collected for Δ-PheH and enzyme poised in the T-, or non-activated state showed well-resolved ^1H cross peaks providing evidence for the coordination of two distinct water molecules in a facial arrangement with NO. For enzyme poised in the R- or allosterically activated state, changes in ^1H-HYSCORE and 3-pulse ESEEM spectra show that only a single water ligand remains bound to the $\{FeNO\}^7$ paramagnetic center. Complications that arise from the electronic structure of the $\{FeNO\}^7$ center will be discussed.

EPR POSTER SESSION

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231 Low Frequency Electrically Detected Magnetic Resonance and Near-Zero Field Magnetoresistance in a Variety of Amorphous Semiconductors and Dielectrics.

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We report on low frequency ($\nu \approx 50$ MHz, 80 MHz, 150 MHz, 300 MHz, and 500 MHz) and X-band electrically detected magnetic resonance (EDMR) and near zero magnetic field magnetoresistance in amorphous inorganic semiconductor and dielectric systems of technological importance. The inorganic materials explored include diamond-like carbon, a-Si:H, a-C:H, a-SiN:H a-SiC:H a-SiOC:H and a-SICN:H. EDMR, almost certainly detected via spin dependent variable range hopping, and near zero field magnetoresistance are observed in all of these systems corresponding to large, roughly comparable current changes approaching one percent in some cases. We find several important advantages of multi-frequency EDMR measurements. As anticipated, EDMR line widths are consistently smaller at low frequencies. The narrower line widths sometimes allow for the straightforward observation of superhyperfine interactions which are completely obscured in high frequency measurements. One particularly important superhyperfine interaction is that of nearby hydrogen in a-SiOC:H films; these films play important roles in present day microprocessors. EDMR measurements on a-SiOC:H films before and after bias temperature stressing show quite significant changes in line width almost certainly indicating changes in the presence of nearby hydrogen atoms. These changes in hydrogen location are also almost certainly important factors in performance changes in these films in state-of-the-art-microprocessors. Another technologically relevant aspect of these EDMR measurements involves EDMR amplitude as a function of dielectric electric field. A comparison of EDMR response versus band diagrams allows for a fairly rough, yet straightforward, calculation of the energy levels of the observed paramagnetic defects. Perhaps the most interesting low frequency observation is the generation of a half-field response which scales with the reciprocal of the measurement frequency squared. This half-field response allows for a determination of the distance between the observed defects.

EPR POSTER SESSION

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Distributions of C-ion and X–ray Induced Sucrose Radicals Investigated by CW EPR and 9 GHz EPR Imaging.

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Although electron paramagnetic resonance (EPR) detects stable organic radicals, it cannot verify the location of the radicals in a sample. In addition, most stable organic radicals appear around the g = 2.002 region of the spectrum. The 9 GHz EPR imaging can nondestructively verify the stable radicals in a sample. We investigated the stable radicals of crystalline sucrose radicals produced by C ion and X-ray irradiation at the same dose. The radicals were measured using electron paramagnetic resonance (EPR, a JEOL RE-3X) and 9 GHz EPR imaging (a Bruker E500 ELESYS system).[1,2] Both irradiations of sucrose produce stable free radicals. EPR of sucrose radicals showed a linear increase of the signal intensity as well as accumulation of the dose. EPR imaging suggests that the radical distribution can vary with changes in LET and absorbed dose. The EPR and 2D EPR imaging results suggested that radical species were mostly located inside the sucrose crystal. Fewer radicals were found at surface region of the sucrose crystal. Therefore, we confirmed that the CW EPR and 9 GHz EPR imaging were sufficient for the determination of the spatial distribution of paramagnetic species in C ion irradiated sucrose.

Partly supported by Research Project with Heavy-ions at NIRS-HIMAC(K.N.), a Grant-in-Aid for Exploratory Research (15K12499) and for Scientific Research (B) (25282124) from the Japan Society for the Promotion of Science (JSPS), and Japan Science and Technology (JST) A-Step (AS262Z00876P) (K.N.).

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EPR POSTER SESSION

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Protein Surface Dynamics and Coupling to Solvent Dynamical Transitions Probed by Using EPR Spectroscopy of Spin-labeled B_{12}-dependent Ethanolamine Ammonia-lyase.

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The mobility of protein surface-attached spin labels was studied over the temperature (T) range of 190-265 K in the ethanolamine ammonia-lyase (EAL) from Salmonella typhimurium, and compared with the T-dependent mobility of a spin probe present in the mesodomain solvent environment around the protein [1], with the goal of characterizing the coupling of protein surface and solvent dynamics. EAL was spin-labeled specifically at the solvent-accessible, native Cys37 site on the EutC subunit, and non-specifically at global solvent-accessible sites, by using 4-maleimido-TEMPO (4MT). Continuous-wave, X-band electron paramagnetic resonance (EPR) spectroscopy was used to observe the degree of motion of the 4MT label as a function of T, as revealed by the EPR line shape. The mobility of the 4MT label was quantified by the rotational correlation time (τ_c) by using EPR simulations. From 190-220 K, the spin label is detectably immobile on the X-band EPR timescale (τ_c>5×10-7 s), which is consistent with the solid state of the solvent mesodomain [1]. Over the T range of 220-225 K, the 4MT label undergoes a mobility transition. At T>225 K, the spin label displays activated mobility behavior. The spin label mobility transition T range on EAL overlaps with the TEMPOL spin probe-detected transition in mesodomain solvent mobility [L. Sun, H. Chen, K. Warncke, unpublished]. The results indicate that the protein surface and hydration layer dynamics and mesodomain solvent dynamics are interdependent.

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EPR POSTER SESSION

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234 EPR Studies of PCBM Derivatives.

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Phenyl-C61-butyric acid methyl ester (PCBM) is a popular fullerene for the charge separation layer of organic photovoltaics. It acts as an efficient acceptor and has increased solubility when compared with buckminsterfullerene. Despite its widespread use, it has been shown[1] that the fullerene forms crystallites upon phase separation which lead to decreased charge separation. A triphenyl amine (TPA) moiety has been added to the PCBM by our collaborators in the Alex Jen group which prevents the formation of these crystallites. The intensity of the triplet CW-EPR spectrum of the TPA-PCBM is significantly decreased when compared with PCBM. Furthermore, the changes in populations, D, and E values are seen indicating changes in spin-orbit coupling and symmetry of the triplet state. It is assumed that this change is due to the TPA moiety acting as the acceptor and the fullerene as the donor leading to an excited charge transfer state.

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235 Rapid Scan Electron Paramagnetic Resonance at L-band of γ-irradiated Organic Solids.

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The radicals in six γ-irradiated organic solids: malonic acid, glycylglycine, 2,6 di-t-butyl 4-methyl phenol, L-alanine, dimethyl malonic acid, and 2-amino isobutyric acid, were studied by rapid scan electron paramagnetic resonance at L-band (~1.04 GHz) using a customized Bruker Elexsys spectrometer and a locally-designed dielectric resonator. Sinusoidal scans with widths up to 182 G were generated with the recently described coil driver and Litz wire coils [1]. Deconvolution of the rapid-scan signal gives the absorption spectrum [2, 3]. The results showed that the linear regions of the power saturation curves extend to higher B_1 for rapid scan than for CW. Absorption spectra obtained by rapid scan have substantially higher S/N than standard CW spectra when data are acquired for the same time. The improvements in S/N are large enough to open new vistas in measuring radiation defects in organic materials.

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EPR POSTER SESSION

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236 **Characterization of a Radical Intermediate in Lipoyl Cofactor Biosynthesis.**

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Lipoyl synthase (LipA) catalyzes the final step in the biosynthesis of the lipoyl cofactor, which is the insertion of two sulfur atoms at C6 and C8 of an n-octanoyl chain. LipA is a member of the radical S-adenosylmethionine (SAM) superfamily of enzymes, and uses two [4Fe–4S] clusters to catalyze its transformation. One cluster binds in contact with SAM and donates the requisite electron for the reductive cleavage of SAM to generate two 5´-deoxyadenosyl 5´-radical intermediates, which abstract hydrogen atoms from C6 and C8 of the substrate. By contrast, the second, auxiliary [4Fe-4S] cluster, has been hypothesized to serve as the sulfur donor in the reaction. Such a sacrificial role for an iron–sulfur cluster during catalysis has not been universally accepted. Use of a conjugated 2,4-hexadienoyl-containing substrate analogue has allowed the substrate radical to be trapped and characterized by continuous-wave and pulsed electron paramagnetic resonance methods such as Hyperfine Sublevel Correlation spectroscopy (HYSCORE). Here we present an observation of a ^{57}Fe hyperfine coupling interaction with the substrate-based radical, which indicates that the iron-sulfur cluster of LipA and its substrate are within bonding distance.Therefore, the obtained results confirm the first part of the proposed mechanism, in which formation of a cross-linked species initiates the oxidation of one of the bridging μ-sulfido ions, that in turn results in the loss of one of the iron ions and addition of the sulfur atom to the substrate carbon.

EPR POSTER SESSION

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237 **EasySpin 5.**

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We present a new version of EasySpin, a software package for the simulation and analysis of EPR spectra. EasySpin is based on Matlab and is freely available at easyspin.org. New features include: (1) simulation of frequency-domain EPR spectra for all regimes (fast limit, slow motion, rigid limit) and all levels of theory including perturbation theory and matrix diagonalization, (2) simulation of steady-state time-domain cw EPR signals for rapid-scan EPR, (3) general excitation geometries for beam EPR experiments, (4) more general Stochastic Liouville equation solver for slow-motion simulation, (5) data imports for spectrometer data from Adani, Magnettech, ActiveSpectrum, and JEOL spectrometers, (6) greatly improved user interface for crystal simulations, (7) direct import of results from quantum chemical calculations with ORCA.

EPR POSTER SESSION

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238 Pulse EPR 25 mT Magnetometer with 0.1 μT Resolution.

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Development of magnets and magnetic field gradient systems for in vivo EPR imaging requires precise (0.1-0.2 μT) measurements of the magnetic field with high spatial resolution of ~5 mm. Commercial high resolution magnetometers utilizing NMR principle are available only for the fields above 40mT, while the lower field range of 10-30 mT is mostly covered by Hall Effect Magnetometers. The disadvantage of these Magnetometers is in the directionality of their measurements and the lower temperature stability and accuracy.

Availability of high spin density narrow line spin probes such as LiPC allows construction of pulse EPR Magnetometers. In the device built at the University of Chicago, the deoxygenated spin probe was located in a 2.2 mm ID, 3 mm long, 4Turns of #20 AWG wire RF micro coil, tuned to 700MHz with a Q of ~20, and the micro coil loaded with LIPC sample is located at the tip of the measurement probe. The RF Bridge was built using classic homodyne scheme. General purpose RF source Analog devices ADF4351 was used, pulse generator was built using Arduino platform, Minicirsuits ZPUL-30P for power amplifier (20dBm @1GHz), and the PICO 3402A scope was used for signal detection. Custom software receives FID signals from the spin probe excited by 62.5 ns pulse and Fourier transform them to obtain offset from the base Magnetometer frequency which can be set in the range of 700 MHz ± 30MHz. This allows achieving approximately 2 mT operational range. Different signal averaging time from 0.1 ms to 1 s can be set to achieve desired field resolution. For LiPC with ~3 μT line width, the precision of the line center determination of 0.1 μT can be achieved.

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239 Triplet State Delocalization in Multi-porphyrin Systems.

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Supramolecular multi-porphyrin structures are of significant interest for applications in molecular engineering, artificial photosynthesis and spintronics.[1-3] Electronic communication between the porphyrin units in these assemblies is essential for these purposes and has been investigated in a series of linear and cyclic porphyrin arrays by probing the extent of triplet state delocalization. The properties of the photoexcited triplet states of butadiyne-linked zinc porphyrin arrays with up to six porphyrin units and of a cyclic six-membered porphyrin ring were investigated using a combination of photoexcited time-resolved EPR, ENDOR and magnetophotoselection experiments. The observed changes in zero-field splitting parameters, spin polarisations and ^{1}H hyperfine couplings as a function of the number of porphyrin units and the geometry of the porphyrin system were interpreted in terms of changes in the extent of delocalization of the triplet state. The magnetophotoselection experiments provided information on the relative orientation of the optical and magnetic axes and revealed a reorientation of the zero-field splitting tensor in linear arrays with two or more porphyrin units, resulting in an alignment of the Z axis of the zero-field splitting tensor with the principal optical axis. In the linear porphyrin arrays, the extent of delocalization of the excited triplet state was found to depend on the conformation of the porphyrin chain. Excitation-wavelength dependent transient EPR and ENDOR experiments were used for preferential excitation and investigation of different conformations.

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EPR POSTER SESSION

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240 Achieving Control with High-Q Superconducting Resonators in Pulsed Electron Spin Resonance.

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Superconducting resonators offer enhanced measurement sensitivity for pulsed electron spin resonance spectroscopy by enabling high quality factors and small mode volumes. We present a variety of novel superconducting resonators and devices that exhibit small mode volumes ($\sim 100\ \mu m^3$), high quality factor ($\sim 10^4 - 10^5$), and excellent homogeneity over planar 2D samples. Additionally, we discuss the development of high fidelity control sequences that account for the distortions of an ideal applied waveform that are present in such superconducting devices. The presented control sequences are optimized by including a circuit model of the resonator transient response and ringdown suppression in standard optimal control theory algorithm to directly optimize pulse superoperators. In this way, non-invertible hardware distortions, such as resonator kinetic inductance non-linearity, may be accounted for.

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241 EPR study of KH2PO4 Crystals with Embedded TiO_2 Nanoparticles.

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Results from the successful growth of high quality KH_2PO_4 (KDP) crystals with incorporated TiO_2 anatase nanoparticles and the characterization of these crystals using several complementary methods are presented. Visual observations, transmission and scanning electron microscopy have shown that the anatase nanoparticles were captured mainly by the pyramidal growth sector and, to a considerably lesser extent, by the prismatic growth sector. Energy dispersive x-ray analysis was able to confirm that the growth layer stacks contain the TiO_2 particles. Deciphering complicated EPR spectra in KDP:TiO_2 and comparison with published data permitted the identification of paramagnetic defects along with their associated g-factors and zero-field splitting parameters (in some cases for the first time). It was found that the dominant lines belong to four different centers Fe_A^{3+}, Fe_B^{3+}, Cr_R^{3+}, and Cr_{GB}^{3+}. From analysis of line intensities it was concluded that the concentration of intrinsic defects like potassium and hydrogen vacancies in KDP:TiO_2 is comparatively small, that the concentration of non-controlled paramagnetic impurities in nominally pure KDP samples is several times larger than in KDP:TiO_2, and that the concentration of non-controlled impurities in the prismatic part of the KDP:TiO_2 boule is approximately twice as large as in the pyramid part. EPR spectra drastically change for samples grown with concentration of TiO_2 nanoparticles above 10^{-2} wt.% in liquor. Lines of all Fe^{3+} and Cr^{3+} centers disappear, probably due to their recharge to non-paramagnetic states Me^{4+}. Instead, four lines of K^0 centers and broad asymmetric line with $g \approx 2.18$ appear. The study helped clarify the nature and distribution of macroscopic and microscopic defects in the KDP:TiO_2 crystals. The relationship between these defects and the distribution of TiO_2 nanoparticles, and the influence of incorporated nanoparticles on properties of composite crystals in comparison with pure crystals were also elucidated.

EPR POSTER SESSION

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242 Full Spectrum Rapid Scan 4D Spectral-Spatial EPR Imaging with Nitroxide Probes at 250 MHz.

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Novel two-dimensional spectra-spatial EPR imaging algorithm was reported previously 1-3. It is based on direct solution of the system of linear equations Ax=p, in which image is a vector of unknowns x, A is a matrix describing geometry of the experiment, and p is a vector representing data. Tikhonov regularization is used to obtain a stable solution-image. Direct reconstruction of 4D spectral-spatial images would require terabytes of computer memory. To reduce the use of computational resources, the algorithm solves the 4D imaging problem as a series of decoupled 3D problems, which can be accomplished on a regular computer with 64 GB RAM. The major advantages of the direct reconstruction are: (i) arbitrary set of projections can be used for image reconstruction, (ii) compared to the standard filtered backprojection reconstruction the new method does not limit spectral width in 4D images. The latter is very important for EPR imaging using multi-line nitroxide spin probes with spectra that span over 50 G. Joint use of rapid scan EPR to improve spectrometer sensitivity and the new multi-line 4D reconstruction method enabled full spectrum spectral-spatial imaging of various types nitroxide spin probes. The algorithm was tested on phantoms and in vivo on mouse tumor models.

This work is supported by NIH grants P41 EB002034, R01 CA98575, R01CA177744, and K25 EB 016040.

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EPR POSTER SESSION

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243 The Effects of Environmental Conditions On Free Radical Levels In Olive Oil.

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The wonders of the EPR always boggled my mind. Its uses and applications to my personal life always seemed miniscule...until one day. While cooking dinner, my mom complained that the oil we were using had gone bad and was not usable. This made me wonder, "Can I test the shelf life of a bottle of oil using EPR?" It seems likely as others had done something like this before[1]. That is when I began my research project with Dr. Morse. We followed the general procedure described by Bruker Biospin. We first made a 2M solution of PBN to trap any free radicals in the oil. We mixed 20ml of it with 300ml of California Olive Ranch Extra Virgin Olive oil[2]. We then took the sample, put it in a 50ml capillary tube, placed it in the EPR spectrometer (Bruker EScan), and measured the intensity of the signal as a function of time. After each scan we heated the sample at 70°C for five minutes in a water bath, and then ran another scan. We repeated this cycle eight times. We measured the signal intensity as a function of time and concluded that a strong EPR signal appeared during the time of the experiment. Therefore, it is clear that heat is one major factor that affects the free radicals in olive oil. One problem is that age or storage conditions of the PBN may affect the results because in some cases, under identical experimental conditions, no signal was seen. With further variations of experiments, we can continue to find out the factors that affect oils shelf life and experimental reproducibility.

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244 Brain Tissue Oxygen Measured by Electron Paramagnetic Resonance in Vascular Cognitive Impairment and Methamphetamine Abuse.

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Oxygen (O_2) is central to normal brain physiology and in vivo EPR oximetry is a useful method for sensitive and repetitive measurements of brain tissue O2 (pO_2). Methamphetamine (METH), given its widespread use, is a major medical and societal problem in the US, and vascular cognitive impairment (VCI) is widely viewed as the second leading cause of dementia in the elderly. Brain injury associated with both METH and VCI are suggested to depend on O_2 and oxidative stress; however, how brain pO_2 may contribute to each are less known. Using in vivo EPR oximetry, we measured changes in brain pO_2 in a mice model for METH abuse and a spontaneously hypertensive-stroke prone (SHR-SP) rat model for VCI, were they to occur. We determined that acute METH exposure resulted in a significant decrease in brain pO_2 accompanied with a decrease in cerebral blood flow, suggesting an ischemic condition, and preliminary measurements suggest hypoxia related blood brain barrier damage. We also present novel findings that EPR oximetry can make repeated measurements in the white matter (WM) of SHR–SP rats. WM Brain pO_2 changes in SHR–SP rats were dependent on the stage of the disease, and decreased WM pO_2, in the latter stages, was accompanied with WM damage and hemorrhages in the brain. We conclude that decreases in brain pO_2 after exposure to METH may play a significant role in METH-induced brain damage, and that changes in WM pO_2 in SHR-SP rats may contribute to VCI brain injury.Taken together, these experiments may offer further insight into neurotoxic drugs of abuse such as METH and neurodegenerative damage associated with VCI.

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245 Electron Spin Resonance as a Probe for Antioxidant Mechanisms in Lubricants: ESR Signatures of Some Common Additives.

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Most all lubricants on the market today contain some kind of antioxidant additive to prolong the useful life of the product. These additives are generally phenols, amines, or a combination of both. It is known that the thermal oxidative degradation of lubricants involves free radicals, so ESR/EPR is an ideal tool to get a better understanding of this reaction mechanism, and to help develop even more effective radical scavengers. We used plain light mineral oil for a solvent, added a common antioxidant, and heated the mixture. Aliquots were taken periodically, and run on the Micro-ESR. Many of the additives produced identifiable radicals that were stable enough to observe without a spin trap. The phenols were more likely to produce observable radicals than the amines.

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246 High-field ESR Measurements of S=1/2 Frustrated J_1-J_2 Chain System $NaCuMoO_4(OH)$ as a Candidate Substance which Shows a Spin Nematic Phase.

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Recently, new quantum state which is called as the spin nematic phase at just below the saturation field, is proposed theoretically in frustrated one-dimensional chain with a ferromagnetic and an antiferromagnetic interactions in the nearest and the next-nearest neighbors, respectively[1]. On the other hand, in the experimental research, observation of the spin nematic phase from a microscopic view points is failed in the previous candidate substance $LiCuVO_4$ due to the high saturation field at 44T[2]. New candidate substance $NaCuMoO_4(OH)$, which consists S=1/2 frustrated J_1-J_2 chain (J_1=-51K, J_2=36K), had been reported recently by Nawa. Existence of the spin nematic phase is expected in $NaCuMoO_4(OH)$ with a lower saturation field[3]. To investigate magnetic properties of frustrated J_1-J_2 chain system under high magnetic field from a microscopic view point, high fields ESR measurements of aligned fine $NaCuMoO_4(OH)$ crystals have been performed using pulsed magnetic field up to 35T. The measured temperature range is from 1.9K to 265K, and the frequency range is from 140GHz to 800GHz. We prepared the aligned sample with 200 pieces of small singe crystals to investigate the magnetic anisotropy. The temperature dependence ESR measurements revel new quantum magnetic phase below 7K over 300GHz region. High field ESR mode at around the spin nematic phase (26T) from frequency dependence measurements will be reported.

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