Rocky Mountain Conference on Magnetic Resonance

Volume 61 *60th Annual Rocky Mountain Conference on Magnetic Resonance* Article 1

7-21-2019

60th Annual Rocky Mountain Conference on Magnetic Resonance

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Abstract

Final program, abstracts, and information about the 60th 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 Denver, Colorado, July 21-25, 2019.

FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 21–25, 2019

Crowne Plaza Denver
Denver, Colorado

www.rockychem.com

60TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 21–25, 2019
Crowne Plaza Denver
Denver, Colorado

Endorsed by:
Colorado Section – American Chemical Society
&
Society for Applied Spectroscopy

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

CONFERENCE CHAIR:

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DOI: https://doi.org/10.56902/RMCMR.2019.61.1

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 Crowne Plaza Denver between 12:00 p.m. and 5:00 p.m. on Sunday, July 21 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 22 through Thursday, July 25.

EXHIBITION SCHEDULE

Monday, July 22

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

Tuesday, July 23

10:00 a.m. – 4:00 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.

CONFERENCE BANQUET & AWARDS CEREMONY

Wednesday evening from 7:00 p.m. to 9:00 p.m. in The Range Ballroom. Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required. Speeches by Christoph Boehme, Gareth Eaton and Harold Swartz, moderated by Thomas Prisner, followed by EPR Poster Awards.

MESSAGES

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

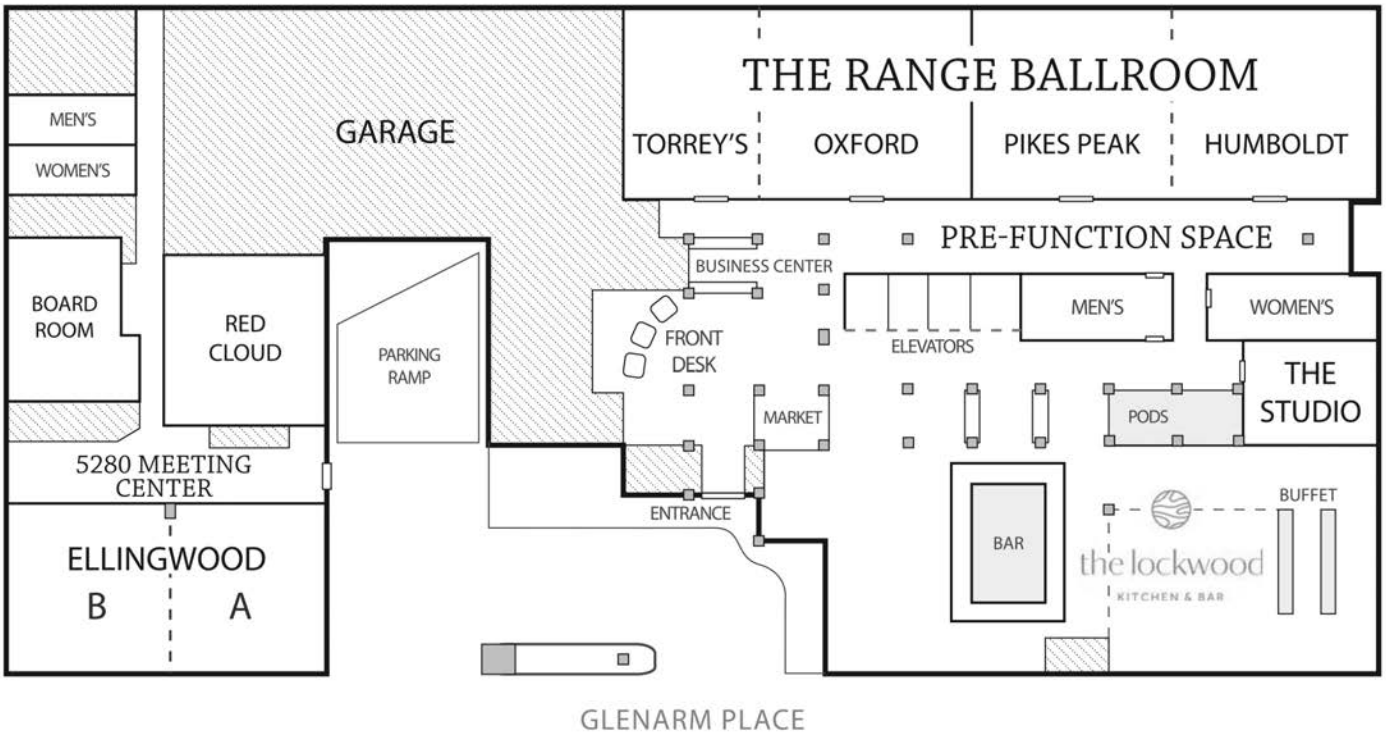
SOCIAL MEDIA

Follow us on Facebook (rockymtnconf) or Twitter (@rockymtnconf) and join in the conversation.

CONFERENCE-AT-A-GLANCE

EVENT	LOCATION	Sunday		Monday		Tuesday		Wednesday		Thursday	
		a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
Bruker EPR Users' Meeting	***University of Denver (Olin Hall)***										
Conference Banquet & Awards Ceremony	***The Range Ballroom***										
EPR Lectures	***Oxford/Pikes Peak/ Humboldt***										
EPR Posters	***Torrey's/Oxford***										
Exhibition	***Ballroom Pre-Function***										

CROWNE PLAZA DENVER MEETING SPACE



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Phone: 508-532-8699
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Bridge12 offers complete, quasi-optical, high-field EPR solutions, instrumentation for Overhauser DNP spectroscopy in addition to active and passive high-frequency microwave components and systems such as gyrotrons, power meters and frequency measurement systems. The company has an international customer base in the US, Europe and Asia.

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42ND INTERNATIONAL EPR SYMPOSIUM

July 21–25, 2019

60TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 21–25, 2019

Denver, Colorado

CONFERENCE CHAIR

Kurt W. Zilm

EPR SYMPOSIUM COMMITTEE

Susumu Takahashi (Chair)

Fraser MacMillian (Co-Chair 2019, Chair 2020)

Ania Bleszynski-Jayich, Christoph Boehme, Enrica Bordignon, Boris Epel, Gail Fanucci, Songi Han, Stephen Hill, Dane McCamey, Chandrasekhar Ramanathan

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Register at www.rockychem.com

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 Crowne Plaza Denver between 12:00 p.m. and 5:00 p.m. on Sunday, July 21 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 22 through Thursday, July 25.

EVENTS

Bruker EPR Users' Meeting:
Sunday, July 21

Meeting followed by a mixer
(University of Denver – Olin Hall)

Shuttle bus departs Crowne Plaza Denver at 5:00 p.m.

For information and registration access:
https://www.bruker.com/events/rmc.html

Poster Sessions:
Monday, July 22
7:00 p.m. – 9:00 p.m. (Torrey's/Oxford)
and
Tuesday, July 23
7:00 p.m. – 9:00 p.m. (Torrey's/Oxford)

Conference Banquet & Awards Ceremony:
Wednesday, July 24

7:00 p.m. – 9:00 p.m. (The Range Ballroom)

Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.

- **Banquet Speakers:**
  Thomas Prisner – Moderator (Goethe University Franfurt)
  Christoph Boehme (University of Utah)
  Gareth Eaton (University of Denver)
  Harold Swartz (Dartmouth College)
- **EPR Poster Awards**

EPR SYMPOSIUM ORAL SESSIONS AGENDA

MONDAY, JULY 22, 2019

8:10 AM	**Welcoming Remarks.** Susumu Takahashi, EPR Symposium Chair	
Materials I. Christoph Boehme, Chair		
8:15 AM	100	**Electrical Control of Quantum Spins.** Arzhang Ardavan, Oxford University
8:45 AM	101	**Photodriven Quantum Teleportation of an Electron Spin State in a Covalent Donor-Acceptor-Radical System.** Michael R. Wasielewski, Northwestern University
9:00 AM	102	**Probing Spin Decoherence Mechanisms in Cr7Mn Molecular Nanomagnets using an Atomic Clock Transition.** Gajadhar Joshi, Amherst College
9:15 AM	103	**Divalent Lanthanide Complexes as Molecular Spin Qubits.** Lydia Nodaraki, University of Manchester
9:30 AM	104	**An Integrated Magnetic Resonance Investigation of Metal-Metal Bonded Systems: Potential New Routes to Single-Molecule Magnets.** Stephen Hill, Florida State University and National High Magnetic Field Laboratory
9:45 AM	*Break*	
Materials II. Stephen Hill, Chair		
10:25 AM	105	**Chemical Design of Qubits.** Danna E. Freedman, Northwestern University
10:55 AM	106	**Photogenerated Spin-Correlated Radical Pairs as Spin Qubit Pairs for Quantum Information Science.** Matthew D. Krzyaniak, Northwestern University
11:10 AM	107	**Magnetic Interactions and Coherence Transfer in Magnetic Graphene Nanoribbons.** Michael Slota, Oxford University
11:25 AM	108	**Surprising Manifestations of the Isotropic Exchange Interactions in High-Field EPR.** Andrew Ozarowski, National High Magnetic Field Laboratory
11:40 AM	109	**Bioinspired Systems for Solar Fuel Production: Advanced EPR/DFT Biohybrid Characterization.** Oleg G. Poluektov, Argonne National Laboratory
12:00 PM	*Lunch*	
Biomacromolecules I. Fraser MacMillan, Chair		
1:30 PM	110	**The Structure of the Central 'Janus' Intermediate of Nitrogenase: A Novel Integration of Experiment and Computation.** Brian M. Hoffman, Northwestern University
2:00 PM	111	**Allosteric Gating in Cyclic Nucleotide-gated Ion Channels: New Insights from DEER Spectroscopy.** Eric G. B. Evans, University of Washington
2:15 PM	112	**From Conditions to Conformations via Components. Unraveling Functional Dynamics from DEER Data.** Eric J. Hustedt, Vanderbilt University
2:30 PM	113	**Unveiling the Mechanics of a Tc Toxin in Action: An Integrative EPR and EM Approach.** Svetlana Kucher, Ruhr University Bochum
2:45 PM	114	**Site-directed Spin Labeling of Proteins using NcAA-mediated Conjugation Techniques and a Photocaged Nitroxide.** Anandi Kugele, University of Konstanz
3:00 PM	*Break*	
Biomacromolecules II. Songi Han, Chair		
3:40 PM	115	**Advanced EPR Study of Intermediates of Water Oxidation Catalysis.** Sun Hee Kim, Korea Basic Science Institute
4:10 PM	116	**Determining Structural Features and Elucidation of Mechanisms in Membrane-associated Transport Proteins.** Fraser MacMillan, University of East Anglia
4:25 PM	117	**Vanadyl Porphyrin Speciation Through High-Resolution ^{1}H Mims ENDOR Spectroscopy.** Donald Mannikko, University of Washington
4:40 PM	118	**Structural Dynamics of Biomolecules through Atomistic Simulations Guided by DEER Measurements.** Fabrizio Marinelli, National Institutes of Health
IES Fellow Award Presentation		
5:00 PM	Thomas Prisner (IES President) to Lawrence Berliner (University of Denver)	
5:30-7:00 PM	*Conference Reception (included with registration)*	
Posters		
7:00–9:00 PM	***Authors Present for Posters Labeled A***	

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DOI: https://doi.org/10.56902/RMCMR.2019.61.1

TUESDAY, JULY 23, 2019

Methods I. Chandrasekhar Ramanathan, Chair		
8:15 AM	125	**In-cell Distance Measurements.** Daniella Goldfarb, Weizmann Institute of Science
8:45 AM	126	**Perks and Pitfalls of Nitroxide-Metal Ion RIDME for Distance Measurements.** Irina Ritsch, ETH Zürich
9:00 AM	127	**High-field ENDOR Spectroscopy at 263 GHz.** Igor Tkach, Max Planck Institute for Biophysical Chemistry
9:30 AM	128	**High-Q Resonators for mm-Wave EPR Just Got Bigger.** Alex I. Smirnov, North Carolina State University
9:45 AM	*Break*	
Methods II. Chandrasekhar Ramanathan, Chair		
10:25 AM	130	**Binding of Tetracycline to its Aptamer Probed by Pulsed Dipolar and Hyperfine EPR Spectroscopy.** Thomas Prisner, Goethe University Frankfurt
10:55 AM	131	**Multi-frequency Rapid-scan HFEPR Spectroscopy.** Petr Neugebauer, Brno University of Technology
11:10 AM	132	**Development of Photo-Activated Switches for Advanced Pulse Sequences for EPR powered by a Free-Electron Laser.** Marzieh Kavand, University of California Santa Barbara
11:25 AM	133	**Application of Pulse Shaping in Double Electron-Electron Resonance Spectroscopy at 115/230 GHz.** Zaili Peng, University of Southern California
11:40 AM	134	**Double Resonance Calibration of g Factor Standards: Carbon Fibers as a High Precision Standard.** Konstantin Herb, ETH Zürich
12:00 PM	*Lunch*	
Exotic Topics. Susumu Takahashi, Chair		
1:30 PM	135	**Quantum Sensing at High Pressures using Spin Defects in Diamond.** Satcher Hsieh, University of California Berkeley
2:00 PM	136	**Multi-Extreme THz ESR: Developments on High-Pressure ESR and Mechanically Detected ESR.** Hitoshi Ohta, Kobe University
2:15 PM	137	**Suppressing Spectral Diffusion in Phosphorus-doped Silicon via Optical Excitation in High Magnetic Fields.** Chandrasekhar Ramanathan, Dartmouth College
2:30 PM	138	**Multi Frequency ESR Measurements of Organic Low-dimensional Antiferromagnets.** Toshikazu Nakamura, Institute for Molecular Science
2:45 PM	139	**A New Design Paradigm for Improved Q-factors in Microresonators with Nanoliter Active-Volumes.** Nandita Abhyankar, University of Maryland and National Institute of Standards and Technology
3:00 PM	*Break*	
Spin Devices. Ania Bleszynski-Jayich, Chair		
3:40 PM	140	**Electron Spin Characteristics Unveiled by Resistively-detected NMR.** Yoshiro Hirayama, Tohoku University
4:10 PM	141	**Realizing Two-dimensional NMR using Diamond Quantum Sensors in a Microfluidic Platform.** Joshua T. Damron, University of New Mexico
4:25 PM	142	**Three-dimensional Distance Measurements of Nuclear sSpins in Diamond.** Jonathan Zopes, ETH Zürich
4:55 PM	143	**Adiabatic Pulse Control of NV Center Spin States at 115 GHz.** Benjamin Fortman, University of Southern California
Posters		
7:00–9:00 PM	***Authors Present for Posters Labeled B***	

WEDNESDAY, JULY 24, 2019

Spin Centers I. Enrica Bordignon, Chair		
8:15 AM	**150**	**Decay, Decoherence, Diffusion - Understanding the Dynamics of Large Spin Ensembles.** Stefan Stoll, University of Washington
8:45 AM	**151**	**Spin-probe EPR of Nanoheterogeneous Media: MOFs and ILs.** Matvey V. Fedin, Novosibirsk State University
9:00 AM	**152**	**Cu^{2+}-ion as a ESR Probe of Protein/DNA Structure and Flexibility.** Sunil K. Saxena, University of Pittsburgh
9:30 AM	**153**	**Electrostatics of Silica Nanoparticle - Water Interface by EPR of pH-Sensitive Spin Probes.** Vladislav Perelygin, North Carolina State University
9:45 AM	*Break*	
Spin Centers II. Gail Fanucci, Chair		
10:25 AM	**155**	**High Field EPR Studies of Ferromagnets and Anti-ferromagnets for Spintronics.** Johan van Tol, Florida State University and National High Magnetic Field Laboratory
10:55 AM	**156**	**New Spin Labels and Spin Labeling Methods.** Janet E. Lovett, University of St Andrews
11:10 AM	**157**	**Determining the Relative Orientation of Rigidly-Bound Cu^{2+} Spin Labels in Biomolecules by Electron Paramagnetic Resonance.** Austin Gamble Jarvi, University of Pittsburgh
11:25 AM	**158**	**Precisely Determining Changes in Shape and Flexibility of DNA using Copper-Based EPR Techniques.** Shreya Ghosh, University of Pittsburgh
11:40 AM	**159**	**Copper-Copper and Copper-Nitroxide Distance Measurements for Uncovering Conformations of Multi-copper Binding Cellular Prion Protein PrPc.** Tufa E. Assafa, University of California Santa Cruz
12:00 PM	*Lunch*	
Biomacromolecules III. Enrica Bordignon, Chair		
1:30 PM	**160**	**Spin-Labeling EPR Applications in Polymeric Macromolecules: Biomimetic Polymers and Block Copolymer Systems.** Gail E. Fanucci, University of Florida
2:00 PM	**161**	**CRISPR-Cas Mediated DNA Unwinding Detected using Site-directed Spin Labeling.** Peter Z. Qin, University of Southern California
2:15 PM	**162**	**Probing the Structure of the Immature HIV-1 Reverse Transcriptase (RT) Homodimer using Double Electron– Electron Resonance EPR Spectroscopy.** Thomas Schmidt, National Institutes of Health
2:30 PM	**163**	**Turning Charges "On" and "Off" in Transmembrane Protein Domains: A Spin-Labeling EPR Study.** Tatyana I. Smirnova, North Carolina State University
2:45 PM	**164**	**Correlating Light-Induced Conformational Changes and Photointermediate States in Proteorhodopsin Detected by Time-Resolved 240 GHz EPR.** C. Blake Wilson, University of California Santa Barbara
3:00 PM	*Break*	

Biomacromolecules III *(continued)*. Fraser MacMillan, Chair		
3:40 PM	**165**	**Orthogonal Biocompatible Labels for In-cell EPR at Physiological Concentrations: Milestones and Challenges Ahead.** Enrica Bordignon, Ruhr University Bochum
3:55 PM	**166**	**From Structure to Function: Multifrequency Pulsed EPR Investigations of Assembly Intermediates in Mn/Fe R2lox.** Effie K. Miller, The Ohio State University
4:10 PM	**167**	**Beyond Pairwise Distance Determination: Resolving Dynamic Conformational Change in CDF Regulatory Domains.** Jenny Hall, University of East Anglia
7:00–9:00 PM	***Conference Banquet & Awards Ceremony*** *(Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.)*	
7:55 PM	**Welcoming Remarks.** Thomas Prisner, Chair	
8:00 PM	**Physics/Material Science.** Christoph Boehme, University of Utah	
8:15 PM	**Biology/Medicine.** Harold Swartz, Dartmouth College	
8:30 PM	**Chemistry/Instrumentation.** Gareth Eaton, University of Denver	
8:45 PM	**EPR Poster Awards**	

THURSDAY, JULY 25, 2019

EPR Imaging-clincal. Boris Epel, Chair		
8:15 AM	**170**	**Oxygen Diffusion in Microencapsulated Live Cells, Studied by Electron Spin Resonance Microscopy.** Aharon Blank, Technion, Israel Institute of Technology
8:45 AM	**171**	**Biologic Validation of Pulsed Spin Lattice Relaxation Based EPR pO_2 Images.** Howard J. Halpern, University of Chicago
9:05 AM	**173**	**Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.** Benoit Driesschaert, West Virginia University
9:25 AM	**174**	**Clinical Applications of EPR: using Results to Date to Predict the Future Course of Clinical Uses of EPR.** Harold M. Swartz, Dartmouth College
9:45 AM	*Break*	
Session XV: EPR Materials II. Christoph Boehme, Chair		
10:25 AM	**175**	**Engineering Coherent Defects in Diamond.** Nathalie de Leon, Princeton University
10:55 AM	**176**	**The Dynamics of Spin-dependent Charge Carrier Recombination in Tris(8-hydroxyquinolinato) Aluminium (Alq3).** Henna Popli, University of Utah
11:10 AM	**177**	**Controlling Electron Spin Relaxation Times via Molecular Design.** Joseph M. Zadrozny, Colorado State University
11:25 AM	**178**	**Advancing Liquid-State Overhauser DNP Instrumentation and Applications.** John M. Franck, Syracuse University
11:40 AM	**179**	**Electrically Detected Electron Paramagnetic Resonant Multi-photon Transitions.** Hans Malissa, University of Utah
11:55 AM	**Closing Remarks.** Susumu Takahashi, EPR Symposium Chair	

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61ST ANNUAL

ROCKY MOUNTAIN CONFERENCE

ON MAGNETIC RESONANCE

July 20–24, 2020

Copper Conference Center

Copper Mountain, Colorado

60TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

42ND INTERNATIONAL EPR SYMPOSIUM
POSTER PRESENTATIONS

MONDAY, JULY 22 • 7:00–9:00 p.m.
(Authors Present for Posters Labeled A)

TUESDAY, JULY 23 • 7:00–9:00 p.m.
(Authors Present for Posters Labeled B)

A	**200**	**Photochemical Electron Doping of Colloidal $SrTiO_3$Nanocrystals: Effect of Hole Quencher and Carriers Densities.** Muhammad Abdullah, University of Massachusetts Amherst
B	**201**	**A Closer Look at Confined Water: Use of Overhauser Dynamic Nuclear Polarization to Study Nanoscale Water Dynamics in Aerosol-OT Reverse Micelle Model Systems.** Alec A. Beaton, Syracuse University
A	**202**	**A Multimodal Method for the Investigation of Complex Protein Systems with Site-Directed Spin-Labeling.** Samantha M. Betts, Syracuse University
B	**203**	**Decoherence of Molecular Spin Qubits in Solution.** Elizabeth R. Canarie, University of Washington
A	**204**	**Characterization of Expansible Argilominerals in Reservoir Rocks by Relaxometry.** Gilson Da Silva Júnior, Federal University of Rio de Janeiro
B	**205**	**Development of a New and Greener Calibration Reaction for Use with Rapid-Freeze-Quench Apparatus for EPR Spectroscopy.** Peter E. Doan, Northwestern University
A	**206**	**Hydration Environment Characterizations of the Folding of IA_3, an Intrinsically Disordered Protein.** Katie M. Dunleavy, University of Florida
B	**207**	**Redox Regulation by Extracellular Superoxide Dismutase (EC-SOD) Due to the R213G Variant in Bleomycin-induced Lung Injury.** Hanan Elajaili, University of Colorado Anschutz Medical Campus
A	**208**	**Allosteric Gating in Cyclic Nucleotide-gated Ion Channels: New Insights from DEER Spectroscopy.** Eric G.B. Evans, University of Washington
B	**209**	**Measuring, Processing and Analysing Non-Uniform Sampled HYSCORE with Hyscorean.** Luis Fábregas Ibáñez, ETH Zürich
A	**210**	**Spin-probe EPR of Nanoheterogeneous Media: MOFs and ILs.** Matvey V. Fedin, International Tomography Center SB RAS
B	**211**	**Pulsed Dipolar EPR Distance Measurements using Orthogonal Labeling with Triplet Fullerene and Nitroxide or Triarylmethyl Radicals.** Matvey V. Fedin, International Tomography Center SB RAS
A	**212**	**Understanding Linewidth of ESR Spectrum Detected by a Single NV Center in Diamond.** Benjamin Fortman, University of Southern California
B	**213**	**Effect of Freezing Method on Polarizability of Finland Trityl.** Benjamin R. Fowler, University of Alabama

A	214	**Advancing Liquid-State Overhauser DNP Instrumentation and Applications.** John M. Franck, Syracuse University
B	215	**Determining Protein-DNA Interaction using Copper-based EPR Techniques.** Shreya Ghosh, University of Pittsburgh
A	216	**Beyond Pairwise Distance Determination: Resolving Dynamic Conformational Change in CDF Regulatory Domains.** Jenny Hall, University of East Anglia
B	217	**Hyperpolarization and Bath Spectroscopy of Individual ^{13}C Nuclei in Diamond via ODMR.** Konstantin Herb, ETH Zürich
A	218	**Development of Enzyme Responsive Spin Probes for Non-Invasive Imaging of Enzyme Activity by EPR.** Justin Huffman, West Virginia University
B	219	**Protein and Solvent Dynamical Contributions to the Radical Rearrangement Catalysis of 2-Aminopropanol in the B12-Dependent Ethanolamine Ammonia-Lyase.** Alina Ionescu, Emory University
A	220	**Nuclear-Spin-Pattern Control of Electron-Spin Dynamics in a Series of V(IV) Complexes.** Cassidy E. Jackson, Colorado State University
B	221	**Simulating Electronic Decoherence in Glassy Samples via Cluster Expansion Methodologies.** Samuel M. Jahn, University of Washington
A	222	**Tailored Nuclear Spin Dynamics in a Coordination-Complex Vessel.** Spencer Johnson, Colorado State University
B	223	**Adjustable Frequency and Variable Coupling EPR Probe with Loop-Gap Resonators for Spectroscopy up to X-Band.** Gajadhar Joshi, Amherst College
A	224	**Experimental Validation of the ALLNOX Program for Studying Protein–Nucleic Acid Complexes.** Venkatesan Kathiresan, University of Southern California
B	225	**Progress Towards Time-Resolved Measurements of Light-Induced Conformational Changes in Gd^{3+} Spin-Labeled Proteins by cw-EPR at 240 GHz.** Marzieh Kavand, University of California Santa Barbara
A	226	**X-band EPR Studies on Ion Beam Irradiated YIG Thin Films; Reconfiguration of Structural and Magnetic Properties.** Bijoy Kumar Kuanr, Jawaharlal Nehru University
B	227	**Modulation of Radical Reaction-Protein-Solvent Coupling in the B12-Dependent Ethanolamine Ammonia-Lyase Enzyme by using Sucrose in the Low-Temperature Mesodomain System.** Wei Li, Emory University
A	228	**Studying Drug-Drug Interactions in Cytochrome P450 3A4 with EPR.** Molly Lockart, University of Alabama
B	229	**New Spin Labels and Spin Labeling Methods.** Janet E. Lovett, University of St Andrews
A	230	**EPR Spectroscopy Across the Spectrum – From Coordination Complexes to Whole Cells.** Heather R. Lucas, Virginia Commonwealth University
B	231	**Electrically Detected Electron Nuclear Double Resonance in a Fully Processed Bipolar Junction Transistor.** Brian R. Manning, Pennsylvania State University
A	232	**An Improved Adaptive Signal Averaging Approach for Optimizing Signal to Noise in Continuous Wave Magnetic Resonance Measurements.** Brian R. Manning, Pennsylvania State University
B	233	**Evaluation of Aromatic Rings Hydrogenation in Hidrocarbon Resins by NMR Spectroscopy.** Antonio Marchi Netto, Braskem
A	234	**Structural Dynamics of Biomolecules through Atomistic Simulations Guided by DEER Measurements.** Fabrizio Marinelli, National Institutes of Health

B	**235**	**Fast Full-spectrum Kinetics Experiments by Rapid Scan EPR at X-band.** Joseph E. McPeak, University of Denver
A	**236**	**Calculation of Polycrystalline Pulsed EPR Signals with Relaxation by Phonon Modulation of Hyperfine and g Tensors Rigorously in Liouville Space using Stochastic Liouville Equation.** Sushil K. Misra, Concordia University
B	**237**	**Lineshape Analysis of NV-detected Nanoscale EPR Spectroscopy.** Laura Mugica, University of Southern California
A	**238**	**Protein Cofactor Control of H2 Catalysis by [FeFe]-hydrogenase as Studied by Correlated Spectroscopy.** David W. Mulder, National Renewable Energy Laboratory
B	**239**	**The Quintet State Generation Process via Inter- and Intra-molecular Singlet Fission.** Hiroki Nagashima, Kobe University
A	**240**	**Multi Frequency ESR Measurements of Organic Low-dimensional Antiferromagnets.** Toshikazu Nakamura, Institute for Molecular Science
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ABSTRACTS

100 **Electrical Control of Quantum Spins.**

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Magnetic fields are challenging to localise to short length scales because their sources are electrical currents. Conversely, electric fields can be applied using electrostatic gates on scales limited only by lithography. This has important consequences for the design of spin-based information technologies: while the Zeeman interaction with a magnetic field provides a convenient tool for manipulating spins, it is difficult to achieve local control of individual spins on the length scale anticipated for useful quantum technologies. This motivates the study of electric field control of spin Hamiltonians[1].

Mn^{2+} defects in ZnO exhibit extremely long spin coherence times and a small axial zero-field splitting. Their environment is inversion-symmetry-broken, and the zero-field splitting shows a linear dependence on an externally-applied electric field. This control over the spin Hamiltonian offers a route to controlling the phase of superpositions of spin states using d.c. electric field pulses, and to driving spin transitions using microwave electric fields[2].

Experiments on Mn defects in ZnO provide insights into how to achieve manipulation of individual spins on surfaces using a scanning tunnelling microscope. A high-frequency voltage applied to the tip can drive electron spin resonance in Fe atoms on MgO surfaces via modulation of the crystal field experienced by the Fe atom[3].

It has been proposed theoretically that frustrated exchange-coupled molecular clusters might offer sensitivity to externally-applied electric fields[4]. Experiments on an antiferromagnetically-coupled Cu_3 compound reveal a small linear electric field effect. A comparable sensitivity is exhibited by the heterometallic $S = 1$ antiferromagnetic ring Cr_7Mn, but no effect is found for the $S = 1/2$ Cr_7Ni[5].

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EPR ORAL SESSION

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101 **Photodriven Quantum Teleportation of an Electron Spin State in a Covalent Donor-Acceptor-Radical System.**

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Quantum teleportation is essential to the development of many aspects of quantum information science (QIS). Toward this goal, we demonstrate electron spin state teleportation in an ensemble of covalent organic donor-acceptor-stable radical (D-A-R•) molecules. Following preparation of a specific electron spin state on R• in a magnetic field using a microwave pulse, photoexcitation of A results in the formation of an entangled electron spin pair $D^{\bullet+}$-$A^{\bullet-}$. The spontaneous ultrafast chemical reaction $D^{\bullet+}$-$A^{\bullet-}$-R• -> $D^{\bullet+}$-A-R^- constitutes the Bell state measurement step necessary to carry out spin state teleportation. Quantum state tomography of the R• and $D^{\bullet+}$ spin states using pulse electron paramagnetic resonance spectroscopy shows that the spin state of R• is teleported to $D^{\bullet+}$ with high fidelity. This result affords the possibility that chemical synthesis can create complex nanostructures for QIS applications.

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102 **Probing Spin Decoherence Mechanisms in Cr7Mn Molecular Nanomagnets using an Atomic Clock Transition.**

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Atomic clock transitions can significantly enhance the coherence time (T_2) in molecular nanomagnets (MNMs), making them promising spin qubits.[1, 2] To further improve the T_2 requires identification and amelioration of the dominant mechanisms of decoherence. The dephasing of spins by dipolar interactions between molecules can be mitigated by diluting the MNMs in diamagnetic solvents. The use of clock transitions allows one to isolate the decohering effects of field fluctuations from other mechanisms of decoherence. We find that at the clock transitions, Hahn-echo coherence times reach values as high as ~3.5 μs. We have done a systematic study to investigate the role of phonons and spin-spin interactions on spin decoherence in dilute samples of Cr_7Mn MNMs using electron-spin-echo spectroscopy making use of the clock transition taking place at zero magnetic field. Our measurements are done using a home built spectrometer with loop-gap resonators at cryogenic temperatures. We have measured the temperature-dependent decoherence rates at the clock transition and away from the clock transition. These measurements indicate that phonon-mediated spin decoherence plays a significant role at the clock transition, while (30-50 Oe) away from the clock transition both phonon and spin fluctuations govern the decoherence of the MNMs. Experiments using a Carr-Purcell-Meiboom-Gill pulse sequence significantly enhance T_2 to ~8 μs at the clock transition, indicating that a substantial source of the decoherence is slow, taking place on the ~1 μs timescale. Efforts to further enhance T_2 using chemical-engineering techniques will be discussed.

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EPR ORAL SESSION

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103 **Divalent Lanthanide Complexes as Molecular Spin Qubits.**

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Molecular systems exhibiting robust quantum coherence are considered to be excellent candidates for quantum bits (or qubits), regarded as the elementary unit of information in quantum computing.[1] A unique property of qubits is their ability to exist in superposition states; simultaneously in a combination of the 'spin-up' and 'spin-down' states of classical bits. One limitation of molecular qubits is the necessity to maintain a certain quantum state for long enough to perform logic functions. Current efforts are focused towards designing molecules that exhibit long superposition state lifetimes, which can be measured via pulse EPR as the phase memory time (T_M).[2, 3]

Herein we present a family of low-valent lanthanide complexes, with the general formula $[K][Ln(Cp')_3]$, in which Ln can be any of Y, La, Lu and Cp' = $C_5H_4SiMe_3$.[4] We have used various advanced pulse EPR techniques, such as ESEEM and ENDOR, to characterize these compounds investigating not only their coherence properties but also the interactions between the electron and the nuclear spins. One of the most commonly utilized strategies for maximizing the phase memory time is to eliminate surrounding spin active nuclei as they act as a source of decoherence. Despite the very rich nuclear spin environment (^1H, ^{13}C) present in these compounds they display long-lived quantum coherence, as demonstrated by accessible Rabi oscillations probing their potentials as molecular spin qubits.

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EPR ORAL SESSION

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104 **An Integrated Magnetic Resonance Investigation of Metal-Metal Bonded Systems: Potential New Routes to Single-Molecule Magnets.**

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Interest in metal-metal bonding stems from both fundamental and practical perspectives. On the fundamental side, interacting metal centers offer a challenging environment to test electronic structure models and explore relationships between structure and function. From a practical perspective, metal-metal bonded systems offer a rich source of electrons for multi-electron redox reactions and, more recently, have been proposed as building-blocks for molecular nanomagnets. We will review several recent examples involving the application of advanced magnetic resonance methods to study metal-metal bonded transition metal complexes. This represents part of a broader strategy for developing polynuclear single-molecule magnets (SMMs) with increased blocking temperatures. The first example concerns an Fe-V triply bonded species [V(^{i}PrNPPh$_2$)$_3$FeI] (**1**), [1, 2] investigated using high-frequency EPR (HFEPR), ^{57}Fe Mössbauer spectroscopy, and high-field electron double resonance detected NMR (ELDOR-NMR). This suite of methods enables determination of the effective g-tensors as well as the Fe/V hyperfine tensors of the spin S = ½ ground state. We rationalize these tensors via ligand-field theory supported by quantum chemical calculations, which suggest that the S = ½ ground state originates from a single unpaired electron localized on the Fe site. We then discuss compounds featuring Fe-Fe bonds, [Fe(^{i}PrNPPh$_2$)$_3$FeR] (R = ≡N^{t}Bu and PMe$_3$) (**2**).[3] Insights gained from studies of these compounds suggest a strategy for designing SMMs based on polymetallic compounds linked via direct metal-metal bonds. Finally, we present recent HFEPR results for a Fe$_6$ SMM, [4] featuring direct Fe-Fe bonds. The results suggest that the high-spin ground state is well isolated in comparison to polynuclear transition metal complexes coupled via superexchange interactions. This superior isolation reduces spin-state mixing, which shuts down quantum-tunneling pathways that are detrimental to magnetization blocking.

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EPR ORAL SESSION

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105 **Chemical Design of Qubits.**

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Over the past several decades considerable research has been devoted to understanding electronic spin dynamanics, and manipulating electronic spin via pulse EPR. This research continues to demonstrate tremendous impact across fields, ranging from biology to spintronics. An emerging area of research, quantum information science, harnesses this research and pushes it in a new direction - control of qubits for computing and sensing applications. Here, it is possible to use chemical control of synthesis to create and understand qubits. Our lab uses synthetic chemistry to construct, modify, and understand chemical qubits. Research on extending coherence time, creating and understanding arrays of qubits, and polarizing qubits will be presented.

EPR ORAL SESSION

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106 **Photogenerated Spin-Correlated Radical Pairs as Spin Qubit Pairs for Quantum Information Science.**

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Spin-correlated radical pairs (SCRP) generated through photo-driven electron transfer reactions from excited singlet states in covalent organic donor-acceptor (D-A) molecules generate a radical pair (RP) in which the two spins are initially entangled and, in principle, can serve as a two-qubit pair in quantum information science (QIS) protocols. As a testbed for this we used a D-A molecule consisting of a tetrathiafulvalene (TTF) donor, a 4-amino-1, 8-naphthalimide (ANI) chromophoric primary acceptor, and a pyromellitimide (PI) as a secondary acceptor (TTF-ANI-PI), photoexcitation of ANI results in sub-nanosecond formation of TTF+•-ANI-PI-•. This molecule provides spectral addressability due to differences in the g-tensors of TTF+•, [2.01566 2.00783 2.00306], and PI-•, [2.00558 2.00598 2.00338], [1] which was further enhanced through ordering in 4-cyano-4'-(n-pentyl)biphenyl (5CB), a nematic liquid crystal, which aligns with the magnetic field prior to freezing to preserve the alignment. A major requirement for any physical qubit for QIS is preparation of a pure initial state.[2] The sub-nanosecond separation of two spin-paired electrons originating from the same molecular orbital producing the SCRP results in a well-defined initial state, which can be further manipulated using transition selective microwave pulses to generate a pure starting state. A second major requirement for any physical qubit is the implementation of a set of universal quantum gates. Any unitary operation can be approximated with just 4 quantum gates, three single qubit gates, namely, the Hadamard, phase, and π/8 gates and the two-qubit CNOT gate.[3] We will present results that apply these four quantum gates to TTF+•-ANI-PI-•, and the fidelity of the qubit gate operations will be probed using quantum state tomography.

These results provide the first steps toward understanding how SCRP's might be used as qubit pairs for QIS applications.

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EPR ORAL SESSION

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107 **Magnetic Interactions and Coherence Transfer in Magnetic Graphene Nanoribbons.**

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Graphene, a well-defined two-dimensional honeycomb network of carbon atoms, shows impressive electrical and mechanical properties[1]. Quasi-onedimensional nanoribbons of graphene have emerged particular interest. For example, by introducing magnetic edges in graphene nanoribbons, ferromagnetic couplings and superior spin filtering are predicted[2,3], making them promising materials for future spintronic devices. Conventional techniques such as unzipping of carbon nanotubes, however, do not deliver the necessary degree of purity to design such systems. By utilising an ultra-clean synthetic bottom-up approach, we were able to create graphene nanoribbons with great purity[4]. We were furthermore able to functionalize the ribbon edges with nitronyl-nitroxide radicals, which serve as magnetic sites. Via electron paramagnetic resonance spectroscopy, we gain a comprehensive picture of the interactions between the magnetic radicals and the nuclei. The coherence time reaches microseconds at W-band frequencies at liquid nitrogen temperature, and sub-microseconds at room temperature. Using a combination of continuous-wave and DEER spectroscopy, we obtained evidence of the existence of a magnetic edge state in the nanoribbon earlier[5], and now unravel its interaction with nuclei using hyperfine spectroscopic techniques. We show HYSCORE spectroscopy results, which reveal interesting interaction patterns. Spectra will be compared to simulations in order to gain a full picture on electron-nuclei interactions.

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EPR ORAL SESSION

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108 **Surprising Manifestations of the Isotropic Exchange Interactions in High-Field EPR.**

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The isotropic exchange interactions in bi- or polynuclear transition metal complexes give rise to a series of states characterized by the total spin, S_T, of a coupled system. The isotropic exchange manifests itself typically in the magnetic susceptibility. Quite often, spectra coming from several coupled spin states can be observed in EPR and the isotropic exchange determines the relative intensities of such spectra, while there is no effect of the exchange magnitude on the EPR resonance fields. The positions of the EPR features may become dependent on the isotropic exchange when it is sufficiently small, so that the microwave quantum energy can cause transitions between various S_T states. This is more likely to occur in HF EPR than in X or Q Bands, owing to much higher frequencies used. Transitions between different S_T states are nominally forbidden, but the zero-field splitting on interacting moieties mixes different S_T states and relaxes the selection rules. This offers an interesting possibility of studying the exchange interactions which are too weak to affect the bulk magnetic properties. Systems consisting of dimeric copper(II) molecules interacting with other copper(II) dimers or monomers, [1] as well as a quasi-dimer of two high-spin Co(II) ions[2] will be discussed.

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EPR ORAL SESSION

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109 **Bioinspired Systems for Solar Fuel Production: Advanced EPR/DFT Biohybrid Characterization.**

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Solar fuels research aims to mimic photosynthesis and devise integrated systems that can capture, convert, and store solar energy in high-energy molecular bonds. Currently, we are designing both synthetic supramolecular photocatalytic systems as well as biohybrids based on natural photosynthetic proteins that photochemically produce hydrogen. Molecular hydrogen stands out among the solar fuels, since it can be utilized essentially pollution-free. The two electrons needed to reduce protons to one hydrogen molecule can be provided by natural and artificial photosensitizers. Using natural photosystems allows taking advantage of nature's optimized light-harvesting and electron-transfer capabilities, while artificial photosensitizers provide a larger choice of chromophores. Independently, the incorporation of the metalorganic hydrogen catalysts in protein surrounding has the potential to protect and stabilize them and thus overcome one of their weaknesses – low stability in acidic environment. To achieve sustainable hydrogen generation, the catalysts should not be rare and expensive, but use earth abundant elements like first row transition metals. Both cobaloximes and Ni-bis(diphosphine) complexes are among the best molecular transition metal complexes for the reduction of protons to molecular hydrogen. The catalytic properties of these systems depend not only on the chemical structure of the complexes but also on the local surrounding and on the direct ligands to the central metal ion. Knowledge of the electronic properties is important for an in-depth understanding of the catalytic properties of the complexes. Multi-frequency Electron Paramagnetic Resonance (EPR) spectroscopy at X-band (9 GHz), Q-band (34 GHz), and D-band (130 GHz) has been used to investigate these cobaloxime and Ni-bis(diphosphine) complexes, allowing us to determine the electronic g-tensors and hyperfine interaction with various magnetic nuclei like ^{59}Co, ^{14}N, ^{1}H and ^{31}P. The experimental results are supplemented with an extensive set of DFT calculations. The knowledge gained by these model studies is used to characterize the binding of the hydrogen catalyst to proteins as well as mechanism of hydrogen generation. The associated complexes are capable of light-induced molecular hydrogen generation with high yield. Further development and improvement of these systems relies on understanding the inherent, fundamental mechanisms for coupling captured photons to fuel generation.

EPR ORAL SESSION

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110 **The Structure of the Central 'Janus' Intermediate of Nitrogenase: A Novel Integration of Experiment and Computation.**

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Our team, comprising the laboratories of Lance Seefeldt and Dennis Dean, and Dmitriy Lukoyanov in our laboratory, has shown that the key state in N_2 reduction to two NH_3 by the enzyme nitrogenase is the $E_4(4H)$, 'Janus' intermediate, which has accumulated four [e^-/H^+] and is poised to undergo reductive elimination of H_2 coupled to N_2 binding and activation. Initial ^1H and ^{95}Mo ENDOR studies of freeze-trapped $E_4(4H)$ revealed the catalytic multi-metallic cluster (FeMo-co) binds two Fe-bridging hydrides, [Fe-H-Fe]. However, the analysis failed to provide a satisfactory picture of its structure - the relative spatial relationships of the two [Fe-H-Fe]. Our recent density functional theory (DFT) study with Simone Raugei yielded a lowest-energy form, denoted $E_4(4H)^{(a)}$, with two parallel Fe-H-Fe planes bridging pairs of 'anchor' Fe on the Fe2, 3, 6, 7 face of FeMo-co. However, the relative energies of structures $E_4(4H)^{(b)}$, with one bridging and one terminal hydride, and $E_4(4H)^{(c)}$, with one pair of anchor Fe supporting two bridging hydrides, were not beyond the uncertainties of the calculation. Moreover, a structure of V-dependent nitrogenase resulted in a proposed structure analogous to $E_4(4H)^{(c)}$, and additional structures have been proposed by DFT studies of others. To resolve the nature of hydride binding to the Janus intermediate, we performed exhaustive, high-resolution CW-stochastic ^1H-ENDOR experiments using improved instrumentation, Mims ^2H ENDOR, and a pulsed-ENDOR protocol ('PESTRE') to obtain absolute hyperfine-interaction signs. These measurements are coupled to DFT structural models through an analytical point-dipole Hamiltonian for the hydride electron-nuclear dipolar coupling to its 'anchoring' Fe ions, an approach that overcomes limitations inherent in both experimental interpretation and computational accuracy. The result: the freeze-trapped, lowest-energy Janus intermediate structure is $E_4(4H)^{(a)}$.

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111 **Allosteric Gating in Cyclic Nucleotide-gated Ion Channels: New Insights from DEER Spectroscopy.**

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Cyclic nucleotide-gated (CNG) ion channels generate the primary electrical responses in vertebrate visual and olfactory signal transduction. CNG channels assemble as four-fold symmetric tetramers with a central ion-conducting pore that is gated by the direct binding of cyclic nucleotides (cAMP/cGMP) to a cytoplasmic cyclic nucleotide-binding domain (CNBD). Cyclic nucleotide-dependent conformational changes in the CNBD are thought to be allosterically coupled to the pore by the so-called C-linker domain, but the molecular mechanism by which this is achieved is not understood. Here we employ double electron-electron resonance (DEER) spectroscopy to measure select inter-subunit distance distributions in SthK, a prokaryotic CNG channel from *Spirochaeta thermophila*. DEER distributions recorded both in detergent micelles and in lipid nanodiscs reveal a rearrangement of the C-linker in the presence of activating cAMP, resulting in an outward movement of the C-linkers relative to the channel pore. The amplitude of this radial movement is particularly large at the C-terminal segment of the B'-helix. Our structural results are linked with functional states of the channel through electrophysiological recordings from giant *E. coli* spheroplasts. Finally, we use restraints from the DEER distributions in combination with a closed-state cryoEM structure to generate molecular models of the resting and activated channel. Our results reveal a previously unseen agonist-dependent structural rearrangement of the C-linker domain of a CNG channel and provide new insight into the allosteric gating mechanisms of this important class of channels.

EPR ORAL SESSION

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112 **From Conditions to Conformations via Components. Unraveling Functional Dynamics from DEER Data.**

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Few techniques match the ability of DEER spectroscopy to investigate proteins as they cycle between functionally relevant conformational states. DEER data collected under different conditions (e.g. apo versus ligand-bound) can be globally analyzed with a unified model to reveal the shifting equilibrium between different protein conformations. The Matlab program GLADDvu has been developed for the global analysis of DEER data using a GUI-based interface. In GLADDvu the distance distribution, P(R), for each conformation is modeled using one or more Gaussian components linked across data for different conditions. Model-based global analysis of data from the membrane transporters LmrP, BmrCD, and Pgp will be demonstrated. The results will be compared to those obtained using a model-free approach. For the proton-dependent multidrug transporter LmrP, DEER collected at 8 different pH values has been analyzed to determine a pK for the transition from the outward-closed to outward-open states. For the ATPbinding cassette (ABC) multidrug transporter BmrCD, the global analysis of DEER data collected under four different ligand conditions reveals three distinctly different conformations. For the mammalian ABC multidrug transporter Pgp, DEER data collected under multiple ligand conditions for wild-type (cys-less) and three functionally impaired mutants has been globally analyzed to investigate the mechanistic origin of the nucleotide binding site asymmetry. Together, these three examples demonstrate the benefits of the simultaneous analysis of multiple DEER data sets using a global model-based approach.

EPR ORAL SESSION

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113 **Unveiling the Mechanics of a Tc Toxin in Action: An Integrative EPR and EM Approach.**

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Tc toxins are 1.7 MDa protein complexes that are found in insect- and human-pathogenic bacteria. After endocytosis, Tc penetrates the membrane of the host's cells and translocates a deadly enzyme into the cytosol. The complex consists of three subunits: the 1.4 MDa TcA pentamer, which mediates target cell association, membrane insertion and toxin translocation, and two smaller subunits, TcB and TcC, which form a 250 kDa cocoon that encapsulates the toxic enzyme. TcA contains a ~40 residue long, stretched linker between the outer shell and the toxin translocation channel, [1] which contracts upon the pH-triggered shell opening of TcA and drives membrane permeation.[2] However, the exact sequence and the kinetics of the prepore-to-pore transition are unknown. Here we present cw EPR and DEER kinetics, corroborated by ODNP data, on two crucial steps of pore formation: shell opening and linker contraction of TcA. Both steps are triggered by basic pH and proceed slowly with half-lives in the 10 hours range, with no indications of enrichment of an open, non-contracted intermediate. Moreover, we found that mutations in the TcA subunit, which prevent membrane insertion, caused an acceleration of pore formation by at least three orders of magnitudes and modified the pH-dependency of the reaction such that pores are also formed at acidic pH values *in vitro*. A cryo-EM structure of the membrane-integration-deficient TcA variant shows a slight opening of the outer shell, which indicates that a structural rearrangement that might be caused by receptor binding *in vivo*, has to precede the prepore-to-pore transition to activate Tc.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2033 – Projektnummer 390677874.

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EPR ORAL SESSION

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114 **Site-directed Spin Labeling of Proteins using NcAA-mediated Conjugation Techniques and a Photocaged Nitroxide.**

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The post-translational conjugation of non-canonical amino acids (ncAA) with spin-labels allows for bioorthogonal reaction schemes. However, the potential for nitroxide labelling is underexplored. In the present study, we report spin labelling via Suzuki-Miyaura coupling of a nitroxide boronic acid label with the genetically encoded amino acid 4-iodo-L-phenylalanine.[1] The resulting spin label bears a rigid biphenyl linkage with lower flexibility than spin label R1. It is suitable to obtain defined electron paramagnetic resonance distance distributions and to report protein-membrane interactions and conformational transitions of the intrinsically disordered protein alpha-synuclein. Moreover, we developed a Photoactivatable Nitroxide for DAinv reaction (PaNDA spin label), which enables shielding of the EPR-active radical in biological, i.e. reducing conditions.[2] Our strategy features high reaction rates combined with high selectivity, and the possibility to deprotect the nitroxide in *E. coli* lysate.

Supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant Agreement number: 772027 – SPICE – ERC-2017-COG) and by the Deutsche Forschungsgemeinschaft (SFB 969, Project B5 and C3).

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EPR ORAL SESSION

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115 **Advanced EPR Study of Intermediates of Water Oxidation Catalysis.**

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Great efforts have been devoted for the development of water oxidation catalysts for renewable energy source. However, making efficient water oxidation catalysts requires the knowledge of the mechanism of this difficult catalytic reactions. To fully understand working mechanisms for water oxidation, we have been investigating the intermediates of the catalytic water oxidation reactions by using both homogenous molecular catalysts and heterogeneous metal oxide nanoparticles.

Metal-oxo species has been known to play a vital role as an intermediate of difficult catalytic reactions such as C-H activation and water oxidation reactions. In addition, it is implicated that the electronic structure of metal-oxo species can be an important determinant for those catalytic reactions, thus, extensive efforts have been devoted to characterizing metal-oxo species. To explore the electronic structure of metal-oxo species, we employed advanced EPR spectroscopy, i.e. multi-frequency, multi-technique pulse EPR along with ^{17}O isotope labeling experiments. Advanced EPR spectroscopy provides accurate spin Hamiltonian values which can be used for in-depth analysis to elucidate the electronic structure of high-valent metal-oxo species. In particular, ^{17}O isotope labeling is very helpful to provide magnetic parameters of oxygen atom of metal-oxo species. I will present the recent multi-frequency, multi-technique EPR spectroscopic results in conjunction with ^{17}O isotope labeling experiments on these species. The EPR spectroscopic results will offer the experimental evidence for understanding of the electronic structure of metal-oxo species.

EPR ORAL SESSION

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116 **Determining Structural Features and Elucidation of Mechanisms in Membrane-associated Transport Proteins.**

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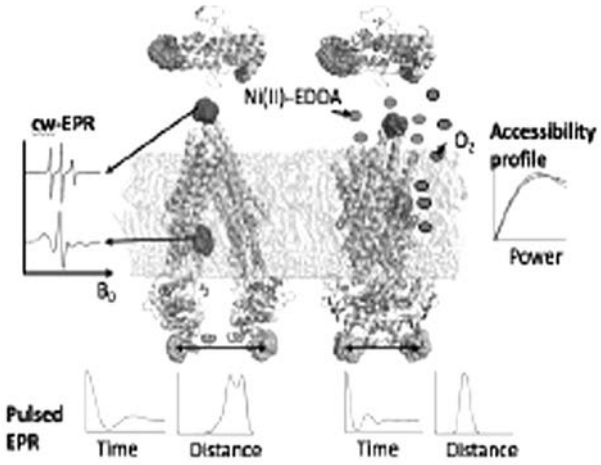
Current research in the Henry Wellcome Unit for Biological EPR at UEA focuses on the architecture and functional dynamics of membrane proteins, many medically relevant with a special interest on membrane transport systems and their interaction with intra-cellular signalling pathways. Using EPR spectroscopy together with intrinsic parmagnets as well as site-directed spin labelling (SDSL) opens up these transport systems to a wide range of different magnetic resonance experiments making EPR a powerful technique for both qualitative and quantitative investigations into the dynamic processes membrane transport systems undergo.



Here I will use examples from our recent collaborative work on membrane and metallo-proteins, multidrug efflux pumps, membrane transporters and bacterial pathogens to demonstrate the power of this technique to deliver key mechanistic insight into e.g. how to resolve multiple distances in complex macromolecular complexes, how to observe conformational change within membrane proteins at a molecular level and finally to identify the molecular determinants of substrate binding and the potential implications for e.g. host-pathogen interactions.

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EPR ORAL SESSION

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117 **Vanadyl Porphyrin Speciation Through High-Resolution ^{1}H Mims ENDOR Spectroscopy.**

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We use high-resolution ^{1}H Mims Electron Nuclear DOuble Resonance (ENDOR) spectroscopy to resolve superhyperfine couplings from distant ligand protons on a series of model vanadyl (VO^{2+}) porphyrins. The couplings (down to 0.16 MHz) reveal the distance distribution of protons (up to 8 Å) from the central vanadyl ion and thereby the protonation pattern, allowing speciation of the porphyrin ligand. We show that it is possible to determine the composition of vanadyl porphyrin mixtures. Therefore, the approach has potential as a separation-free method for vanadyl porphyrin speciation. This is an area of interest in petroleomics, as crude oil contains significant amounts of vanadyl porphyrins, which are toxic to catalysts used in oil processing and refining.

Mannikko, D; Stoll, S, Energy Fuels, 2019, accepted, 10.1021/acs.energyfuels.9b00867

EPR ORAL SESSION

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118 **Structural Dynamics of Biomolecules through Atomistic Simulations Guided by DEER Measurements.**

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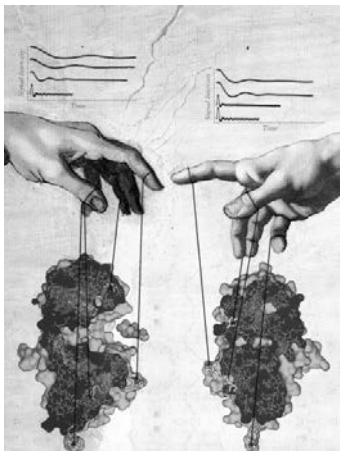
Double Electron-Electron Resonance (DEER) detects long-range distances between spin-labels attached to a biomolecule and it is widely used to assess its structural dynamics in a native environment. This notwithstanding, DEER measurements reflect an ensemble of states that accounts for biomolecular dynamics as well as the intrinsic spin-labels flexibility, therefore they do not provide high-resolution structural and dynamical information. To tackle this problem, we introduce the restrained-average dynamics method[1]; a minimally biased simulation technique to sample a structural ensemble that reproduces directly the raw experimental data within the experimental uncertainty.

The methodology is implemented in the Colvars module[2] and is freely available in the NAMD[3] and LAMMPS[4] programs.



We first illustrate the performance of this methodology on a benchmark protein system (T4-Lysozyme), we then show the practical application of the proposed technique for the molecular interpretation of recent DEER data[5] on membrane transporter substrate-binding protein (VcSiaP). In particular, our simulations underscore the large scale open-to-close conformational transition that occurs upon ligand binding and reveal that the unbound VcSiaP is more open in solution than suggested by its X-ray structure. Overall, the results support an induced-fit binding mechanism in which conserved protein residues play a crucial role.

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EPR ORAL SESSION

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125 **In-cell Distance Measurements.**

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Recent demonstrations of in-cell distance measurements on proteins by EPR techniques has opened up new opportunities for exploring conformational equilibria and conformational changes in proteins in their natural environment. The motivation for such studies is the notion the cellular environment is different than that of a dilute buffer solution and therefore the conformational equilibrium maybe different as well. To realize the potential of such measurements spin labels' properties in terms of chemical stability, EPR sensitivity and distance resolution have to be optimized along with increasing measurement sensitivity, allowing measurements as close at physiologically relevant concentrations. We have been using Gd(III) chelates as spin labels for in-cell measurements because of their high chemical stability and the high sensitivity they exhibit at W-band frequencies. We will present a number of Gd(III) tags and compare their in-cell performance in terms of stability, sensitivity and distance resolution, showing that through tuning of the chemical structure of the Gd(III) chelate all these properties can be optimized. To increase sensitivity we implemented the use of chirp pulses.[1, 2] Finally we will demonstrate the feasibility of the methodology using on the BIR1 domain of the X-linked inhibitor of apoptosis protein (XIAP), which shows some difference between in the distance distributions measured in frozen solution and frozen cells.

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EPR ORAL SESSION

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126 **Perks and Pitfalls of Nitroxide-Metal Ion RIDME for Distance Measurements.**

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Distance measurements by Pulsed Dipolar Spectroscopy (PDS) have become a valuable tool in structure determination of biomolecules. Based on the success of PDS methods also for the structural investigation of complex biomolecular assemblies, and building on new developments in spin labels, there is a strong interest in robust PDS methods that perform well with spectroscopically orthogonal spin pairs. A popular choice for PDS with orthogonal spin labels is the Relaxation Induced Dipolar Modulation Enhancement (RIDME)[1, 2] experiment. It was early recognised that RIDME performs especially well for spectroscopically orthogonal spin pairs with different longitudinal relaxation properties, such as nitroxide – metal ion pairs.[2, 3, 4] We present a systematic RIDME study with nitroxide-metal ion molecular rulers that improves the accuracy and reliability of the method for distance determination. The water soluble molecular rulers were loaded with different metal ions (Cu(II), Gd(III), Mn(II)), and several sources of artifacts in the low spin rulers (Cu(II)-nitroxide) could be identified.[5] Orientation selection was observed with the Cu(II)-nitroxide rulers at Q-band, which lead to the development of RIDME with coherent frequency-swept pulses for one-step orientation averaging. This FT-EPR correlated RIDME variant additionally allows correlation of the dipolar coupling spectra to the nitroxide orientation. In the rulers loaded with the high spin metal ions Gd(III) and Mn(II) we observed the expected higher harmonics of the dipolar coupling frequency, which need to be considered for data analysis. The build-up of the overtones, which is important for the potential application to distance measurements in samples with unknown distance distributions, was studied similarly to the calibration procedure for high spin metal-metal RIDME.[6]

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EPR ORAL SESSION

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127 **High-field ENDOR Spectroscopy at 263 GHz.**

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Pulsed ENDOR is a well-established technique which plays an important role in a variety of applications and can be applied at any magnetic field. However, if recorded at higher fields, ENDOR gains several advantages not attainable in low-field experiments. In particular, the spectral resolution for pulse excitation is increased, hence the technique can be used to selectively excite only a small fraction of molecular orientations and thus evaluate hyperfine tensors needed for structural analysis. Other valuable features at higher fields are the increased nuclear Zeeman resolution, higher sensitivity, and the 'first-order' hyperfine spectra, which are easier to interpret. We discuss the performance of high-field ^{1}H-ENDOR by employing the latest results obtained with a prototype Bruker spectrometer operating at 263 GHz (9.4 T). We use a protonated bis-diphenylene-phenyl-allyl (BDPA) radical as a model system with two distinct hyperfine couplings to validate the efficiency of the setup in terms of proton detection. Furthermore, to verify the applicability of high-field ENDOR to orientation-selective studies, we use the protein ribonucleotide reductase (RNR) from *E. Coli* with a native Y_{122} radical. Davies ENDOR spectra recorded at 5 K on approximately 15 picomoles of the protein sample reveal previously obscured spectral features, which have never been observed at lower frequencies but are reasonably interpreted by spectral simulations aided by DFT. Our analysis shows that seven internal proton couplings are detectable for this specific radical due to high orientation selectivity and profitable g-strain, not counteracting the expected narrowing of the ENDOR powder pattern. The results prove both high stability of the equipment and fidelity of 263 GHz experiments in reporting orientation-selected ^{1}H ENDOR data, thereby demonstrating that new significant information can be uncovered in complex molecular systems by using high-field/high-frequency approach[1].

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EPR ORAL SESSION

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128 **High-Q Resonators for mm-Wave EPR Just Got Bigger.**

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Many EPR experiments at mm-wave (mmW) resonant frequencies are carried out with non-resonant sample holders, though Fabry-Perot and single- and over-moded cylindrical cavity resonators are also employed. While non-resonant structures allow for larger sample volumes, resonator cavities offer higher mm-wave B_1 fields and constitute the preferred configuration for the best EPR sensitivity at X- and Q-band. However, the main problem with adapting conventional EPR resonator technology to higher frequencies stems from increased non-resonant absorption of mm-waves by the metal surfaces of the resonator cavity. Moreover, the dimensions of single-mode resonators scale down with the wavelength, thus, making sample tubes/holders exceedingly small and, perhaps, even impractical to handle. Last year we have introduced a radically new line of EPR resonators that is based on placing a defect within one-dimensional photonic band gap (PBG) dielectric crystal. The prototype PBG resonators were assembled from λ/4 low-loss dielectric layers with alternating dielectric constants and demonstrated experimental Q≈520 at 94.3 GHz. A nanoporous ceramic disc of 50 μm thickness was employed as an aqueous sample holder allowing for ca. 2-3 μl sample volume. Here we report on the next generation of PBG EPR resonators designed to significantly increase both the sample volume and Q-factors while minimizing dielectric losses even for liquid aqueous samples. A series of smooth and corrugated Gaussian 95 GHz launchers were tested to improve the flatness of the mmW front. The resonator Q-factor was further improved by increasing the sample diameter from 12 to 36 mm yielding a 9-fold sample volume increase. Experimental Q≈3, 300 has been observed for eight (8) alternating λ/4 layers of alumina and air gaps. Experimental tests of the new resonators for aqueous and thin film samples are also reported. The PBG resonator design is readily scalable to higher mmW frequencies.

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EPR ORAL SESSION

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130 **Binding of Tetracycline to its Aptamer Probed by Pulsed Dipolar and Hyperfine EPR Spectroscopy.**

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In the present study, we use dipolar and hyperfine methods to investigate the magnesia ion mediated binding of the antibiotic tetracycline (TC) to a tetracycline-binding RNA aptamer (TC-aptamer). Orientation selective PELDOR experiments were performed using cytidine analogue spin labels[1] rigidly incorporated into double stranded parts of the aptamer. We determined the structural changes of the aptamer induced by the binding of the TC ligand as a function of the magnesia concentration[2]. By replacing Mg with Mn^{2+} ions PELDOR spectroscopy between a single spin label located on the aptamer and the paramagnetic Mn^{2+} ions was used to investigate the metal binding sites. Hyperfine spectroscopy of the paramagnetic Mn^{2+} ion was used to investigate the TC binding site in more detail. We used 2D-correlated hyperfine techniques, as 2D-EDNMR and THYCOS, to correlate the ^{31}P peaks from the RNA to the ^{13}C peaks from the TC ligand, thus confirming the formation of a ternary RNAMn^{2+}-TC complex.

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EPR ORAL SESSION

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131 **Multi-frequency Rapid-scan HFEPR Spectroscopy.**

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The development of the rapid scan technique was historically connected to the problem of the enhancement of the signal-to-noise ratio in NMR, [1-2] but it did not find wide application in NMR or EPR due to the rapid development of high power radio-frequency and microwave sources for pulse methods. However, the past decade is marked by the intense development of solid-state THz instruments, which has made it possible to perform EPR spectroscopy at very high frequencies and fields.[3-5] Unfortunately, the output power of such tunable THz sources is not sufficient for the implementation of pulse methods. Consequently, the rapid scan is the only affordable technique for multi-frequency investigation of spin dynamics at THz frequencies. To our best knowledge, this EPR technique was demonstrated at frequencies up to 94 GHz only.[6] Here we present results of the first successful implementation of multi-frequency rapid-scan EPR in the (sub)millimeter frequency range with access to extremely short relaxation times (several nanoseconds). The experiments were performed using a home built HFEPR spectrometer (University of Stuttgart) operated in induction mode.[4] The spectrometer does not require any resonator, and therefore, we are able to use frequency sweeps instead of magnetic field sweeps as it was done previously in the majority of experiments.[7-9] The main advantages of the frequency domain are the extremely high sweep rates (thousands of THz/s) and absence of eddy currents in the sample holder and/or resonator.[10] The new HFEPR spectrometer in the Central European Institute of Technology (Brno) will further extend the frequency range and sensitivity of the rapid scan technique.

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EPR ORAL SESSION

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132 **Development of Photo-Activated Switches for Advanced Pulse Sequences for EPR powered by a Free-Electron Laser.**

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High field and high power EPR is limited by the lack of technology such as high power sources and switches. The UCSB free electron laser (FEL) is a high power terahertz (THz) source capable of producing THz pulses with durations of 1 to 5 μs and peak powers of a few kWs. EPR powered by the UCSB FEL at 240 GHz is currently configured to generate a pair of THz short pulses (minimum pulse of 13 ns) with independently tunable duration, power, separation, and phases.[1, 2] Si photo-activated switches are used to slice a pair of short ns pulses from the long μs output pulse of the FEL. Si photo-activated switches driven by high power Nd:YAG lasers have sub-nanosecond rise times, but the ~μs long carrier life times in Si makes a single Si switch unsuitable for ns pulse shaping. Currently, photo-activated Si switches must be used in pairs to generate fast and short ns pulses at 240 GHz. To perform more advanced pulsed EPR experiments with current pulse-slicing technology additional pairs of photo-activated Si switches and Nd:YAG lasers would be needed, which would have large space requirement and complexity and would provide limited flexibility. To address these challenges, we are studying and developing other semiconductor switching technologies, such as InP and GaAs, with shorter carrier life times (a few ns) to make fast, compact, and low cost THz switches. In parallel, a lower power and low cost solid state laser array is under development to provide enough laser power for driving the InP and/or GaAs photo-activated switches. Our data promises the generation of InP photo-activated switches for slicing any THz oscillators such as FELs and gyrotrons to perform advanced EPR experiments at high field such as echo-detected saturation/inversion recovery, stimulated echo, DEER, and with the possibility of ENDOR.

This work was supported by NSF-DMR 1626681.

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EPR ORAL SESSION

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133 **Application of Pulse Shaping in Double Electron-Electron Resonance Spectroscopy at 115/230 GHz.**

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Double electron-electron resonance (DEER) spectroscopy is widely used to investigate structure information of biological samples by measuring distance and relative orientation of functional groups (paramagnetic centers and spin labels) in the molecule and their hyperfine coupling. High frequency DEER spectroscopy enables increasing spectral resolution and spin polarization, thus potentially allowing to improve the sensitivity and the accuracy of the determination of the molecular orientation. However, HF DEER spectroscopy is still often challenging because of a low microwave power compared with low frequency EPR systems and difficulty to control pulse amplitude and phase for optimization of DEER experiment. For example, optimum control of the excitation bandwidth enables improvement of the DEER signal intensity as well as accuracy of the molecular orientation determination. In this presentation, we present the implementation of pulse shaping using arbitrary wave generator in DEER on our 115/230 GHz EPR spectrometer at USC. We employ Cu^{2+}-based spin labels and DEER to explore the orientation-dependence in biomolecules.

EPR ORAL SESSION

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134 **Double Resonance Calibration of g Factor Standards: Carbon Fibers as a High Precision Standard.**

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The precise determination of the g factor is important in many applications of EPR spectroscopy. Unfortunately, the magnetic field B_0 at the sample position is usually not known with sufficient precision for determining the absolute g factor. Therefore, a sample with known g factor ("the standard") is measured either shortly before or together with the sample of interest. Established standards like DPPH, Mn:MgO or Li:LiF show difficulties in handling, reproducibility or precision. We propose high-performance carbon fibers as a new general-purpose g factor standard1. Carbon fibers show exceptional ESR properties like a perfectly Lorentzian and narrow line (0.4 G @ 4.2 K), a g=2.002644(30) factor near gfree and a rather strong signal. Moreover, carbon fibers meet the requirements in practice because they are easy to handle, inert and very cheap. However, what counts most is that carbon fibers are absolutely and independently calibratable by internal protons. We measured the proton nuclear resonance and the ESR transition frequency simultaneously with high precision to determine the g factor. The nuclear resonance is detected via the Overhauser shift which is considerably enlarged due to DNP. Our double resonance experiments enabled us to determine the g factor up to a relative uncertainty of ±15 ppm. We believe that research along our lines will open the door to a whole class of new g factor standards where the precision can be pushed even further. The calibrated high-performance carbon fibers are fully operational and satisfy todays demands on precision for many experiments. The easy handling, the "inertness" and the strong signal make them an ideal standard for the day-to-day usage in many laboratories worldwide even in cases where such high absolute precision is not needed.

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EPR ORAL SESSION

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135 **Quantum Sensing at High Pressures using Spin Defects in Diamond.**

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Pressure alters all physical, chemical and electronic properties of matter. The development of the diamond anvil cell (DAC) enables tabletop experiments to investigate a diverse landscape of high pressure phenomena ranging from the properties of planetary interiors to transitions between quantum mechanical phases. We introduce and utilize a novel nanoscale sensing platform, which integrates nitrogen-vacancy (NV) color centers directly into the culet (tip) of diamond anvils. We demonstrate the versatility of this platform by performing diffraction-limited imaging of both stress fields and magnetism, up to pressures ~30 GPa and for temperatures ranging from 25-340 K. For the former, we quantify all six (normal and shear) stress tensor components, offering unique new capabilities for characterizing the strength and effective viscosity of solids and fluids under pressure. For the latter, we demonstrate vector magnetic field imaging, enabling us to measure the pressure-driven $\alpha \leftrightarrow \varepsilon$ phase transition in iron as well as the complex pressure-temperature phase diagram of gadolinium. In addition to DC vector magnetometry, we highlight a complementary NV-sensing modality using T1 noise spectroscopy; crucially, this demonstrates our ability to characterize phase transitions even in the absence of static magnetic signatures. By integrating an atomic scale sensor directly into DACs, our platform enables the in *situ* imaging of elastic, electric and magnetic phenomena at high pressures.

EPR ORAL SESSION

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136 **Multi-Extreme THz ESR: Developments on High-Pressure ESR and Mechanically Detected ESR.**

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THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, has been developed in Kobe. It covers the frequency region between 0.03 and 7 THz, [1]the temperature region between 1.8 and 300 K, [1]the magnetic field region up to 55 T, [1]and the pressure region is extended from 1.5 GPa[2]to 2.7 GPa using the hybrid-type pressure cell.[3]Recent development of high-pressure THz ESR up to 25 T[4]and its application to Cs_2CuCl_4will be discussed[5]. Moreover, wewill focus on the recent developments of the torque magnetometry[6]and mechanically detected ESR[7]measurements using a commercially available membrane-type surface stress sensor, which is the extension from our micro-cantilever ESR[8], and its application to the microliter solution sample (myoglobin)[9].

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EPR ORAL SESSION

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137 **Suppressing Spectral Diffusion in Phosphorus-doped Silicon via Optical Excitation in High Magnetic Fields.**

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The phosphorus donor impurity in silicon is a promising candidate for spin-based quantum devices. Recent experiments have shown that above-band gap optical excitation can result in strong hyperpolarization of the donor nuclear spins[1, 2.] Here we show that low-power above-band-gap excitation can also *extend* the phase memory time of the donor electron spins in a low-concentration (~3.3 - 3.5 × 10^{15} cm^{-3}) phosphorus-doped natural abundance silicon sample. A two-pulse Hahn echo experiment at 8.5 T and 4 K was used to measure the decay of the echo amplitude with time. The non-exponential decays (~exp(-(t/T_{SD})^2) suggest that the phase memory time is dominated by spectral diffusion due to the ^{29}Si spins[3]. T_{SD} was measured to be 110 μs in the dark and with sub-bandgap excitation, rising to over 180 μs with 1050 nm laser excitation. With 980 nm excitation, T_{SD} was observed to increase with applied laser power, saturating at 200 μs.

Part of the work was done at the National High Magnetic Field Laboratory, which is supported by the NSF (DMR-1644779) and the State of Florida.

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EPR ORAL SESSION

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138 **Multi Frequency ESR Measurements of Organic Low-dimensional Antiferromagnets.**

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Magnetic investigations were carried out for two-related organic low-dimensional antiferromagnets, α-(BEDT-TTF)$_2$$PF_6$ and ζ-(BEDT-TTF)$_2$$PF_6$(THF). The macroscopic behaviors of these salts are very similar to each other and the spin susceptibility of them seems to follow that of typical paramagnetic insulators with low-dimensional antiferromagnetic interaction. The absolute values of the macroscopic antiferromagnetic interaction, J/k_B, are also very close. Several obvious differences are, however, observed as follows: ζ-(BEDT-TTF)$_2$$PF_6$(THF) undergoes an antiferromagnetic transition at around 5 K, while α-(BEDT-TTF)$_2$$PF_6$ shows no long-range magnetic ordering down to 2 K. The ESR linewidth behaviors with temperatures are quite different between these two salts. The ESR linewidth of ζ-(BEDT-TTF)$_2$$PF_6$(THF) is almost temperature independent in the paramagnetic region, while that of α-(BEDT-TTF)$_2$$PF_6$ gradually decreases as the temperature decreases. In order to clarify the manner of the development of the spin-spin correlation at low-temperatures, we performed multi frequency, *i.e.* X-, Q-, and W-band ESR measurements for these salts. We discuss the low temperature electronic phases of these salts from the microscopic point of view.

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EPR ORAL SESSION

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139 **A New Design Paradigm for Improved Q-factors in Microresonators with Nanoliter Active-Volumes.**

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2. Amit Agrawal, a. Institute for Research in Applied Physics and Electronics, University of Maryland, College Park, MD 20740, USA, b. National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
3. Robert McMichael, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
4. Veronika Szalai, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

A new approach for designing microresonators is reported, which results in experimental quality factors (Q-factors) in the range of 100 to 300 for sub-microliter mode volumes at room temperature. These values are up to an order of magnitude higher compared to previously reported experimental Q-factors of 10 to 50 for similar mode volumes.[1, 2, 3] Our inverse anapole microresonator design is based on a metamaterial structure that minimizes radiation losses, resulting in higher Q-factors.[4] Resonators with frequencies of 9 GHz and 34 GHz have been fabricated and tested. Facile coupling to the feedline is accomplished by adjusting the position of the microresonator with respect to the

feedline. The resonant frequency is tunable over a frequency range of approximately 500 MHz. The combination of high Q-factors and facile coupling increases the potential for applicability of microresonators to the study of a variety of volume-limited samples, including liquids, microcrystals, and thin films. We report sensitivity tests conducted using a concentration series of thin films of BDPA in a polystyrene matrix.

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EPR ORAL SESSION

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140 **Electron Spin Characteristics Unveiled by Resistively-detected NMR.**

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NMR provides us versatile tool to clarify electron spin characteristics in semiconductor quantum systems. Although conventional NMR suffers low sensitivity, resistively-detected NMR enables us to get enough NMR signal even for single layer- and single nano-structures, especially GaAs based structures. Knight-shift gives us information of electron spin polarization and nuclear relaxation (T_1 time) includes information of electron spin fluctuation. Many interesting physics are unveiled in two-dimensional electron systems, especially in the quantum Hall regime.[1] The clear difference between ground and second Landau- level is clarified by Knight-shift measurements up to high temperature regime where fractional quantum Hall effect disappears.[2] A combination of scanning gate control and resistively-detected NMR results in successful two-dimensional mapping of electron spin polarization using quantum Hall breakdown phenomena as an example.[3] Recently, such measurements have been applied to one-dimensional systems like quantum point contact[4] and other materials like InSb quantum systems.[5]

Supported by KAKENHI Grants Nos. 18H01811 and 15H05867.

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EPR ORAL SESSION

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141 **Realizing Two-dimensional NMR using Diamond Quantum Sensors in a Microfluidic Platform.**

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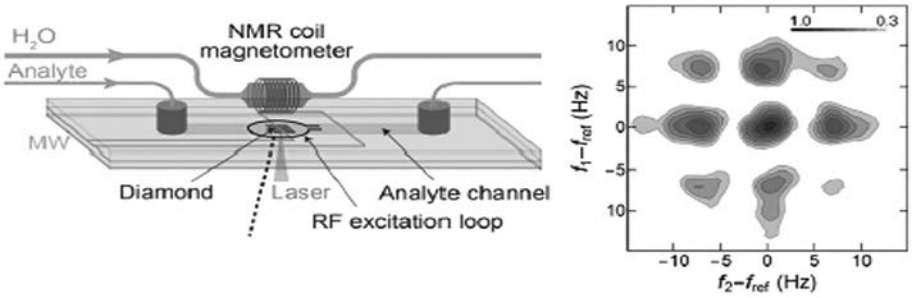
Quantum sensors based on nitrogen-vacancy centers in diamond have emerged as a promising detection modality for nuclear magnetic resonance (NMR) spectroscopy. The micron-scale volume and non-inductive based detection of the NV platform have the potential to enable new applications in NMR, including the detection of metabolites at physiological concentrations in single cell systems. For this to be realized, high spectral resolution and sufficient concentration sensitivity must be achieved, particularly for multidimensional NMR analysis of picoliter sample volumes.

In this talk, I will discuss our recent progress in pursuing this goal. By utilizing separate pre-polarization and detection phases in a microfluidic platform, we realize a spectral resolution of 0.65 ± 0.05 *Hz* and concentration sensitivity of 27M $s^{1/2}$ (for signal-to-noise ratio of 3) with an effective ~ 40 picoliter detection volume. The achieved sensitivity and spectral resolution of our platform enabled us to perform the first two-dimensional NMR experiments using NVs. The use of diamond quantum sensors in conjunction with in-line microfluidic NMR detectors demonstrates a significant step towards applications in mass-limited chemical analysis and single cell biology.



EPR ORAL SESSION

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142 **Three-dimensional Distance Measurements of Nuclear sSpins in Diamond.**

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Nitrogen Vacancy (NV) centers in diamond are sensitive quantum sensors for local magnetic fields. In our group we use single NV centers to detect nuclear magnetic resonance (NMR) signals of small nuclear spin ensembles in its vicinity. Using high-resolution spectroscopy of the magnetic resonance signals, we aim to determine the location of individual nuclei via their spectroscopic signature. Here, the long-term goal is to image individual molecules that are attached to the diamond surface. In this presentation, we will introduce spectroscopy techniques that enable the reconstruction of the full three-dimensional location of individual nuclei with high spatial resolution (below 0.5 Angstrom) by using the dipole field of the NV center as the imaging gradient. The imaging protocol requires active manipulation of the nuclei, which we realize with micro coils that generate strong and high-bandwidth radio-frequency pulses. High-precision localization critically depends on the accurate, in-situ calibration of the field vector and temporal shape of the radio-frequency pulses. In this context we will also present our recent results to directly, that is reconstruction-free, detect magnetic fields in the time-domain with both high field and time resolution using the NV center.

EPR ORAL SESSION

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143 **Adiabatic Pulse Control of NV Center Spin States at 115 GHz.**

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Pulsed electron paramagnetic resonance (EPR) spectroscopy at high magnetic fields offers higher spectral resolution and greater spin polarization than measurements at lower magnetic fields. However, the shift to high fields requires a high frequency microwave source whose output power is often much lower than that of a low frequency microwave source. This results in narrow excitation bandwidth and incomplete population inversion due to long pulse times and small signal amplitude. Adiabatic frequency sweeps have the capability to control spin states over a wide bandwidth despite weak and inhomogeneous microwave field across the sample volume. This property has triggered the development of adiabatic pulses that have recently been applied to EPR with the development of high temporal resolution (~ns) arbitrary waveform generators. Within low field EPR, adiabatic pulses have been utilized to demonstrate broadband control over wide frequency ranges and shown sensitivity improvements for multi-frequency double electron electron resonance (DEER) measurements. For high frequency EPR, the reduction in power limits excitation bandwidth, but has distinct advantages for specific systems.

Within this talk I present our recent development and application of adiabatic pulses to control the spin states of single nitrogen vacancy (NV) centers at high magnetic field. Nanoscale magnetic resonance is possible through NV-detected EPR and has the potential for high spectral resolution and insight into structure that is not seen within conventional

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EPR.[1, 2] Shaped pulses offer wider spectral excitation, an ability to correct pulse imperfections, and generally higher fidelity than rectangular pulses. For the NV center spin states, implementation of these pulses generates coherent echoes and corrects for nuclear spin flips from the hyperfine coupled nucleus. Further applications to NV-based DEER and improvements enabled by optimal control theory are also discussed.

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

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EPR ORAL SESSION

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150 **Decay, Decoherence, Diffusion - Understanding the Dynamics of Large Spin Ensembles.**

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Large spin ensembles play important roles in several areas of EPR spectroscopy, including the application of DEER spectroscopy in biostructural research and the development of molecular spin qubits for quantum information processing. Here, we present two recent results about the fundamental physics in large spin ensembles. (1) We show that, at low temperatures, the exponentially decaying background signal in DEER spectroscopy acquires an out-of-phase component due to spin polarization. (2) We demonstrate that the model of nuclear spin diffusion can predict decoherence times (phase memory times) of spin centers in frozen aqueous solutions from first principles. Both results provide insight into the dynamics of large spin ensembles.

EPR ORAL SESSION

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151 **Spin-probe EPR of Nanoheterogeneous Media: MOFs and ILs.**

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Nanoheterogeneous media find numerous applications in catalysis, separations, smart materials etc., but characterization of their properties at the nanoscale is often challenging. We overview our recent developments and applications of spin-probe EPR to the two types of such systems: metal-organic frameworks (MOFs) and ionic liquids (ILs). Most of MOFs and ILs are EPR silent, therefore we use the traditional and advanced nitroxides, triarylmethyls and photoexcited triplet probes to obtain information on the surrounding nanoenvironment. In particular, embedding of nitroxides into the pores of MOFs provides opportunities to monitor stimuli-induced structural rearrangements, adsorption and separation of gases and liquids.[1] Our most recent work demonstrated a huge potential of nitroxides in MOFs as multifunctional agents for kinetic EPR studies of liquid-phase separation processes. In many cases doped paramagnetic ions also provide unique information on functional properties of catalytically-active MOFs.[2] The media of the second type, ILs, are known to self-organize at molecular level and form various nanosized heterogeneities. In addition to common continuous wave (CW) EPR of nitroxide probes, we developed time-resolved (TR) EPR approaches for studying nanostructures in ILs using photoexcited porphyrins and fullerenes. Finally, pulse EPR of advanced nitroxides and triarylmethyls allows probing local rigidity/softness of ILs in a wide temperature range. This approach relies on monitoring the stochastic molecular librations, and, in particular, allowed the first observation of structural anomalies in ILs near their glass transitions.[3] Apart from fundamental interest, this promotes ILs as unique media with nanosized heterogeneities tunable by temperature. The developed complex of CW, TR and pulse EPR techniques provides versatile information on nanostructuring in ILs.

IL studies were supported by RSF (19-13-00071), MOF studies by RFBR (18-29-04013).

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EPR ORAL SESSION

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152 **Cu^{2+}-ion as a ESR Probe of Protein/DNA Structure and Flexibility.**

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Pulsed -ESR techniques that reliably measure interspin separations in the order of 1.5-16 nm - even in non-crystalline samples - to ultimately provide an "amino-acid-level" picture of structure and structural transitions, have impacted biophysical research. The talk will discuss our efforts in developing Cu^{2+}-ion based pulsed-ESR distance methods and illustrate how they are used to understand structure-function relationships. The talk will describe recent efforts to bind Cu^{2+}-ions site selectively in proteins and in DNA. In proteins, the spin probe is assembled in situ from natural amino acid residues and a metal salt, and requires no post-expression synthetic modification. Initial results show that the resultant Cu^{2+}-probe potentially provides distance distributions that are five times narrower than the common protein spin label – the approach, thus, potentially overcomes the inherent limitation of the current technology, which relies on a spin label with a highly flexible side-chain. We describe the use of this approach to resolve protein conformational dynamics, to locate native paramagnetic ions in proteins, and to resolve relative orientations of different protein segments. In DNA, the incorporation of a 2, 2'-dipicolylamine into DNA creates a nucleotide-independent, site-specific Cu^{2+} binding site within the interior of the DNA helix Cu^{2+}-based distance measurements directly measure the most-probable backbone distance. Together the data demonstrate the utility of Cu^{2+} based distance measurements as a probe of biomolecular structure and function.

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EPR ORAL SESSION

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153 **Electrostatics of Silica Nanoparticle - Water Interface by EPR of pH-Sensitive Spin Probes.**

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Silica nanoparticles (SiNPs) are among, perhaps, some of the most widely studied and used nanomaterials today. SiNPs are currently employed in heterogeneous catalysis, composite nanomaterials, separation phases, biosensors, and as carriers for drug delivery - to name a few practical uses. Further progress in these fields requires detailed physicochemical understanding of the SiNP surfaces as well development of chemical and physical methods to tailor interfacial properties to specific applications. For the latter, spectroscopic methods capable of characterizing nanoparticle interface and, particularly, interfacial electrostatic properties, become indispensable. Here we report on the first spin labeling EPR study of local dielectric and electrostatic properties of the SiNP-water interface by means of covalently attaching two pH-sensitive nitroxides with different pKa's to silica surface through a short linker. Such covalent attachment ensures that the spectroscopic EPR readout originates from a well-defined location at the SiNP-water interface. Monodispersed SiNPs of ca. 116 nm in diameter were synthesized and decorated with silane ligands terminated by thiol groups. Such ligands were covalently modified by nitroxides through methanethiosulfonate chemistry. Two pH-sensitive nitroxides were employed to provide a broader pH range for characterization of the surface electrostatic potential. The EPR titration data for these two probes allowed for differentiating the dielectric and electrostatic contributions to the interfacial properties of SiNPs. From such titrations an effective local dielectric constant at the silica nanoparticle-water interface was found to be e=70.8±5.0. EPR titration of nitroxide-labeled nanoparticles revealed an approximately linear dependence of the surface potential on pH, demonstrating that the surface potential associated with the silanol deprotonation develops over a wide pH range starting at pH≈4 and increasing in magnitude up to pH ≈ 8 – 9 where pH-sensitive nitroxide reaches its sensitivity limit.

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EPR ORAL SESSION

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155 **High Field EPR Studies of Ferromagnets and Anti-ferromagnets for Spintronics.**

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Magnetic materials are increasingly used for spintronics applications and information storage. Recently, ferromagnetism was discovered in 2D van der Waals crystals such as CrI_3, and this intrinsic 2D ferromagnetism is of potential interest for various spintronic applications. The detailed anisotropic interactions that enable ferromagnetism in these 2D materails and determine the Curie temperature are not well understood. A study of the orientation dependence of the ferromagnetic resonance in combination with theoretical calculations allow to quantify the anisotropic spin interactions in what turns out to be predominantly a Kitaev ferromagnetic material.[1] While ferromagnetic materials are already currently used for spintronics applications and spin injection into materials, they do have limitations in density and speed. Anti-ferromagnetic materials could have the advantage of much faster operations, as the exchange interaction tends to be much larger than the anisotropy energy in ferromagnetic materials. We have measured the antiferromagnetic resonance of MnF_2 which has a Neel temperature of 67K and a spin gap around 260 GHz. Through the inverse spin hall effect (ISHE) the spin currents injected into a thin metal film can be characterized, showing the creation of electrostatic potential at resonance condition under irradiation with millimeter waves, showing promise for the use of AF materials for spintronics applications.

[1] Lee, I. et al. https://arxiv.org/abs/1902.00077

EPR ORAL SESSION

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156 **New Spin Labels and Spin Labeling Methods.**

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Spin labels are intrinsically required for many applications of EPR to biological systems. Tuning their properties is therefore essential for both increasing the efficiency of the EPR experiment and/or labelling chemistry and broadening the scope of the systems that can be investigated. One aspect of these improvements is to label a wider range of proteins by overcoming issues associated with too many cysteines that would be labelled with conventional labels such as MTS (R1). New work on chemical modification of the protein or adaptations of the labels will be presented.[1] A second approach is to change the paramagnetic center away from the conventional nitroxyl radical, [2] to this end a Gd(III) label with a narrow central linewidth will be demonstrated.[3] Finally, the findings of a robust study to understand how a spin label at the 2' position[4] associates with DNA using NMR, X-ray crystallography and molecular dynamics simulations will be shown.

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EPR ORAL SESSION

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157 **Determining the Relative Orientation of Rigidly-Bound Cu^{2+} Spin Labels in Biomolecules by Electron Paramagnetic Resonance.**

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In this work, we demonstrate the versatility of a rigid, Cu^{2+} based spin label in conjunction with Q-band electron paramagnetic resonance (EPR) to report on the relative orientations of the spin labels. We show that the double histidine (dHis) motif, a rigid Cu^{2+} labelling technique[1], provides distinct advantages over alternative spin-labelling methods for orientational analysis. The dHis-Cu^{2+} system exhibits orientational selectivity at Q-band when performing double electron-electron resonance (DEER) such that data collected at discrete magnetic fields produced distinct DEER signals. Using the high sensitivity and resolution afforded by Q-band EPR, DEER data was collected over a wide range of magnetic fields. This data was then simulated in order to extract the relative orientations of the two Cu^{2+} centers[2]. The rigidity of the dHis Cu^{2+} motif provides unambiguous orientational information and allows clear correlation of the orientations as determined by EPR to the protein crystal structure. These results demonstrate a new method by which Cu^{2+} based EPR may be used to elucidate conformational changes within proteins.

This work is supported by NSF MCB-1613007 and NSF MRI-1725678.

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[2] A. Gamble Jarvi, et al., *J. Phys. Chem.* B, **2018**, 122, 10669.

EPR ORAL SESSION

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158 **Precisely Determining Changes in Shape and Flexibility of DNA using Copper-Based EPR Techniques.**

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Site-directed spin labeling in DNA using a Cu^{2+}-chelating ligand, called 2, 2'-dipicolylamine (DPA), was previously reported[1]. The methodology provided ESR distance which reported directly on the DNA backbone, with the measured distance being within an Å of the backbone distance. However, it was not clear why this distance was so close as the position of the DPA with respect to the helix was not known. We were also intrigued to see if such methodology would work for any number of base pair separations and sequentially report on the DNA backbone. To answer these questions, we designed four DNA duplexes with the two Cu^{2+}-DPA motifs present at varying separations. For each of these separations, the most probable DEER distance was in reasonable agreement with the expected distance for a B-DNA duplex. Furthermore, we performed molecular dynamics (MD) simulations on an unmodified DNA duplex. The most probable distance from the MD simulations also agreed with the ESR distance within 1-2 Å. This proved two things: first, the Cu^{2+}-DPA motif is present inside the DNA helix and second, this motif can directly report on the DNA backbone without the need for extensive modelling. Going forward, this robust technique can be used to monitor the different shape adaptations that the DNA undergoes when interacting with a protein.

Supported by NSF MCB- 1613007 and NSF MRI- 1725678. S.G. thanks University of Pittsburgh for the Andrew Mellon Predoctoral Fellowship and the Pittsburgh Quantum Institute for the PQI Fellowship.

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EPR ORAL SESSION

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159 **Copper-Copper and Copper-Nitroxide Distance Measurements for Uncovering Conformations of Multi-copper Binding Cellular Prion Protein PrPc.**

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Cellular prion protein PrPc is a multi-copper binding protein. The copper binding modes of the PrPc N-terminus have been studied by EPR in detail with Cw-EPR and hyperfine spectroscopy[1], with high copper occupancy state component 1 being composed of a single octarepeat segment requiring residues HGGGW[2]. Until recently, there have been challenges in using Copper as a paramagnetic centre for distance measurements. At the University of California, Santa Cruz, we recently upgraded our spectrometer to operate at Q band with a commercial 300 W TWT amplifier and

arbitrary waveform generator (AWG). The AWG can be used to create chirp pulses which excite a much larger fraction of the copper signal, potentially avoiding orientation selection in double electron-electron resonance measurements. Copper-nitroxide distance measurements can be conducted at Q Band using relaxation-induced dipolar modulation enhancement (RIDME), utilising the difference in T1 relaxation times of the two spins, and creating modulation depth regardless of spectrometer bandwidth[3]. Here, 2x-dHis-Cu^{2+} GB1 protein[4] and an octarepeat-MTSL helical peptide were used as model systems to calibrate these distance measurements. With Cu-Cu and Cu-NO distance measurements we aim to characterise and localise PrPc's relatively disordered N-terminus in full length PrPc.

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EPR ORAL SESSION

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160 **Spin-Labeling EPR Applications in Polymeric Macromolecules: Biomimetic Polymers and Block Copolymer Systems.**

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Site-directed spin labeling approaches are most commonly utilized to characterize local mobility, environment, and conformational changes in biological macromolecules such as proteins, nucleic acids, lipid membranes as well as complexes among these species. Recently we have embarked upon incorporating nitroxide spin-labels into homopolymers and self-assembled block copolymer systems with stimuli-responsive biomimetic polymers. We will present our efforts that target characterization of mobility and induced local polarity associated with structural transitions in pH-responsive polymers – including synthetic strategies for spin-label incorporation, as well as our results in micellar/liposomal polymers and polypeptide systems where we have been interested in characterizing pH-induced changes in alterations in local water penetration, mobility and dielectric fields.

EPR ORAL SESSION

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161 **CRISPR-Cas Mediated DNA Unwinding Detected using Site-directed Spin Labeling.**

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CRISPR-Cas systems [Clustered regularly interspaced short palindromic repeats (CRISPR) and CRISPR-associated (Cas) proteins] have been adapted to precisely edit genomes in a large variety of organisms, leading to a revolution in genome engineering. For Cas9 and Cas12a, the two main systems for CRISPR-based developments, specific recognitions of DNA duplexes rely on DNA unwinding and formation of an R-loop structure in which the DNA target strand hybridizes with a guide of the CRISP RNA while the DNA non-target strand is unwounded. We present here work on investigating CRISPR-Cas mediated DNA using the method of site-directed spin labeling and Electron Paramagnetic Resonance (EPR) spectroscopy. Specifically, we have demonstrated direct detection of Cas9-mediated DNA unwinding by a combination of site-directed spin labeling and Molecular Dynamics simulations (Tangprasertchai, et.al, ACS Chem. Biol. 2017, 1489-93). Our results support a model in which the unwound non-target strand is stabilized by a positively-charged patch located between the two nuclease domains of Cas9, and reveal uneven increases in flexibility along the unwound non-target strand upon scissions of the DNA backbone. The study establishes the synergistic combination of spin-labeling and Molecular Dynamics to directly monitor Cas9-mediated DNA conformational changes, and yields information on the target DNA in different stages of Cas9 function. Together with the use of spin-labeling to monitor conformational changes of Cas9 protein (Vazquez Reyes, et.al., Cell Biochem Biophys 2017), the method will aid in deciphering the mechanisms of CRISPR–Cas recognition and specificity, thus advancing mechanistic understanding of CRISPR-Cas and aiding future technological development.

EPR ORAL SESSION

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162 **Probing the Structure of the Immature HIV-1 Reverse Transcriptase (RT) Homodimer using Double Electron–Electron Resonance EPR Spectroscopy.**

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Human immunodeficiency virus type I reverse transcriptase (HIV-1 RT) catalyzes the conversion of single-stranded virally encoded RNA into double-stranded proviral DNA, a pivot point in HIV replication. Prior to maturation, HIV-1 RT forms a homodimer (p66/p66) of unknown structure, which subsequently is proteolytically cleaved by HIV protease to remove a RnaseH domain from one of the p66 subunits. The domain configuration sampled by the immature p66/p66' homodimer was investigated by pulsed Q-band DEER EPR, a method for determining long-range distances between pairs of nitroxide spin-labels introduced via surface-engineered cysteine residues. The combination of inter- and intra-subunit distances reveals that the p66/p66' dimer is asymmetric with a configuration fully consistent with that of the crystal structures of the mature p66/p51 heterodimer. In addition, the finger and thumb domains of one of the p66 subunits corresponds to the closed conformation of the p66 subunit of the p66/p51 heterodimer, while the other corresponds to the configuration seen in the p51 subunit of the p66/p51 heterodimer. Addition of non-nucleoside reverse transcriptase inhibitors shifts the configuration of the closed p66 subunit to the open form, fully consistent with what is also observed for the p66/p51 heterodimer. In addition, we were able to delineate the conformational space of the RNase H domain of p66/p66 that is cleaved by HIV-1 protease, such revealing the structural inner workings of the p66/p66' homodimer.

EPR ORAL SESSION

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163 **Turning Charges "On" and "Off" in Transmembrane Protein Domains: A Spin-Labeling EPR Study.**

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The ionization states of individual amino acid residues of membrane proteins are difficult to decipher or assign directly in the lipid membrane environment. The effective pK(a) values of protein groups are determined by a complex interplay between local polarity, Coulomb interactions, and a structural reorganization. The analysis is further complicated by the dearth of information about gradients in polarity, electric potentials, and hydration at the protein-membrane interface. The goal of our work is to develop spin-labeling EPR methods for assessing effects of membrane surface potential, local environment at the protein-membrane interface, and water penetration along this interface on effective pK(a) of membrane-burred ionisable groups. In this work we report on developing pH-sensitive ionizable EPR labels and related methods to 1) profile a heterogeneous dielectric environment along the α-helix of a WALP peptide integrated in a lipid bilayer and 2) asses the effect of solid support, specifically silica nanoparticles, on effective pK(a) of membrane-burred ionisable sidechains. pH-sensitive EPR labels were attached to cysteine residues positioned at various depth within bilayer at the peptide-lipid interface. We have shown that effective pK(a) of membrane-burred sidechain can be significantly shifted by varying the membrane surface charge density. The silica support exerted pronounced effects on WALP dynamics and the effective pKa of the ionizable probe. It was demonstrated that the silica nanoparticles shift the effective pKa of the ionizable nitroxide probe in a membrane depth-dependent manner. Upon protonation of the membrane-burred model ionisable sidechain the silica support caused significant changes in the membrane association of WALP peptide that are not observed when WALP is integrated into unilamellar phospholipid vesicles of similar curvature.

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EPR ORAL SESSION

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164 **Correlating Light-Induced Conformational Changes and Photointermediate States in Proteorhodopsin Detected by Time-Resolved 240 GHz EPR.**

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Proteorhodopsin (PR) is a retinal-binding, seven alpha helical trans-membrane (7TM) protein found in a range of bacterioplankton, and which functions as a light activated proton pump. Green PR function is triggered by the absorption of a 520 nm photon at the retinal chromophore. After absorbing a green photon, PR undergoes a characteristic photocycle which has been characterized by time-resolved UV-vis absorption, [1] which results in the transport of a proton across the cellular membrane. Proton transport in PR is accompanied by large-scale conformational changes, [2] which have been studied using time-resolved EPR together with site-directed spin labeling at X-band frequencies in PR suspended in micelles.[3] Time-resolved EPR at higher frequencies offers greatly enhanced spectral resolution, allowing for better modeling and understanding of spin label and protein dynamics, and offers sensitivity to different motional timescales. We present 240 GHz time-resolved EPR of nitroxide labeled PR, which reports on conformational changes, which we correlate with the growth and decay of photocycle intermediates characterized by time-resolved UV-vis spectroscopy. We present measurements of PR in detergent micelles, as well as liposomes, in order to probe the effects of protein-lipid interactions on PR motion and photocycle. Our results represent a promising step towards detecting time-resolved pair-wise distance changes at room temperature using EPR lineshape analysis of pairs of gadolinium spin labels.

This work is supported by NSF MCB grant 1617025.

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EPR ORAL SESSION

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165 **Orthogonal Biocompatible Labels for In-cell EPR at Physiological Concentrations: Milestones and Challenges Ahead.**

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Gadolinium is the most promising spin type for in cell studies of spin-labeled proteins. However, the availability of other bioresistant spin labels could aid the development of structural studies of biomolecules in a cellular context. The relatively small and flexible nitroxide label could offer many advantages in this area of research, because it is less prone to affect proteins' structure/function at most sites, extraction of interspin distances can be corroborated by dynamics and water accessibility data, and it can be used orthogonally to gadolinium. We characterized iodoacetamide- and maleimide-functionalized nitroxide spin labels based on the gem-diethyl pyrroline structure using cw and DEER. We compared their chemical resistance to reducing agents in ascorbate solutions, oocytes, *E. coli* and mammalian cells and found a remarkable cell- and concentration-specific behavior.

Spin/protein concentration is an important issue when addressing the possibility to perform in-cell EPR. In fact, low micromolar concentrations may already be the upper limit for physiologically relevant concentrations of most proteins in cells. We therefore also compared the concentration sensitivity of Q-band DEER for Gd- and NO-labeled proteins, to identify the lowest concentration at which reliable DEER data can be still extracted in vitro and in cell. We found that submicromolar concentrations are accessible for DEER measurements in cellular context.

To test the potential of biocompatible orthogonal labels in a complex protein system, we investigated apopotic Bax oligomers, in which protomers spin-labeled with Gd or gem-diethyl NO labels were mixed in vitro. We successfully detected NO-NO and Gd-Gd distances using two different spectroscopic DEER channels at Q band at different temperatures but we observed a residual Gd-Gd signal in the Gd-NO channel due to channel cross-talk, that prompted us to analyze in detail this unwanted contribution in order to be able to distinguish it from the real signal. Unfortunately, spin-labeled Bax did not localize properly into the cytosol when inserted into mammalian cells, thereby preventing DEER measurements under physiological conditions.

Despite many challenges are still ahead, in-cell DEER with orthogonal labels is within reach.

EPR ORAL SESSION

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166 **From Structure to Function: Multifrequency Pulsed EPR Investigations of Assembly Intermediates in Mn/Fe R2lox.**

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As one of only four classes of Mn/Fe proteins found in nature, the R2-like ligand-binding oxidase (R2lox) spontaneously and selectively forms a Mn/Fe cofactor *in vitro*, going against the commonly accepted Irving-Williams series for metal-binding affinities.[1] As well, R2lox is found primarily in pathogens and extremophiles, and represents one of the 10 most up-regulated proteins in *Mycobacterium tuberculosis (Mt)*, making it a potential therapeutic target.[2] R2lox is capable of executing multi-electron chemistry, as the protein performs C-H bond oxidation upon O_2 activation to generate an unprecedented tyrosine-valine crosslink within its scaffold,[1,3] achieving this reaction with impressive control and selectivity.[3] The final state of the R2lox cofactor after O_2 activation is as well-characterized, spin-coupled $Mn^{III}(\mu\text{-}OH)Fe^{III}$ center.[1,4] Further examination of the Mn/Fe R2lox assembly mechanism has resulted in identification of multiple reaction intermediates with distinct kinetic profiles and optical and electronic signatures; however, much work remains in isolating, assigning, and characterizing these transient species.[5] In this presentation, we emphasize the use of electron paramagnetic resonance (EPR) spectroscopy to examine the nature of two novel, spin-coupled Mn/Fe intermediates in R2lox (Figure 1). These species exhibit unique spectral and relaxation profiles, and spin Hamiltonian simulations confirm both intermediates as likely residing in the Mn^{III}/Fe^{III} state. Taking advantage of the increased anisotropy and spectral breadth of one of the species, orientation-selective, multi-frequency pulsed EPR techniques, including Q-band ENDOR, three-pulse ESEEM, HYSCORE, and W-band ELDOR detected NMR (EDNMR). At least one strongly-coupled, anisotropic proton is identified, along with multiple signals deriving from cofactor-bound nitrogen atoms. Taken together, this work provides the first structural characterization of reaction intermediates along the Mn/Fe R2lox assembly pathway and will aid the continued investigation of the intrinsic chemical reactivity possessed by these Mn/Fe cofactors. Ultimately, this knowledge will provide insight connecting structure with function in R2lox, shedding light on the potential role of R2lox in *Mt* virulence.

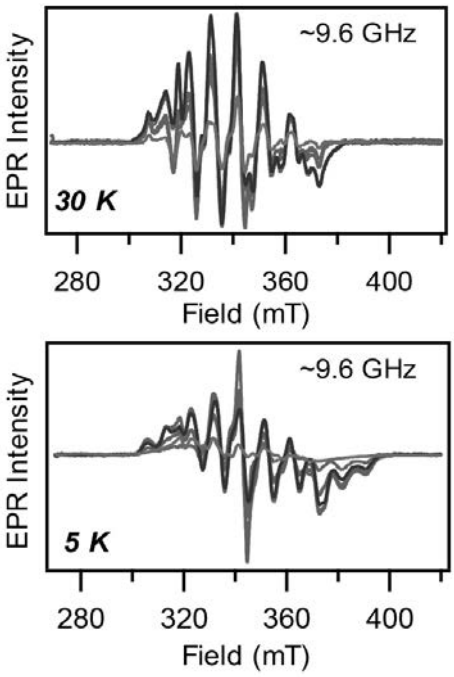

Figure 1. Time-resolved CW EPR showing kinetic profiles of two intermediates observed at 5 K (top) and 30 K (bottom). Samples were quenched at timepoints from 5 s (red) to 100 s (blue).

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EPR ORAL SESSION

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167 **Beyond Pairwise Distance Determination: Resolving Dynamic Conformational Change in CDF Regulatory Domains.**

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Many cellular functions are reliant on the presence of heavy divalent metal cations at low cellular levels. High concentrations of metal ions including Zn^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+} and Fe^{2+} can quickly lead to cytotoxic condi-tions, and so tight regulation of these levels is essential for cellular function. Cation di˙usion facilitator (CDF) proteins are a family of transmembrane transporters found within all domains of life responsible for the e˜ux of such heavy-metal ions, thereby regulating cellular metal-ion homeostasis.[1] Structural studies undertaken on such transporters have mainly focused on the cytoplasmic *C*-terminal domains (CTDs), of which a number of crystal structures have been solved. CDF CTDs

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are predicted to act as the regulatory domain, in which metal binding and subsequent conformational change of the transmembrane domain (TMD) for transport only occurs in the presence of high cellular metal ion levels.[2] However, protein-metal binding is not well understood in the CDF family of proteins.

Here, site directed spin labelling in conjunction with EPR spectroscopy has been undertaken on the CTD from MamM - isolated from *Magnetospirillum gryphiswaldense*. MamM is a bacterial homolog of the mammalian CTDs and is currently used as a model for the further understanding of this protein class. DEER studies have a˙orded the elucidation of conformational change between apo and metal-bound forms of the protein, as well as indicating the number of metal ions bound.[2] Further a variety of divalent metal cations have been tested for their binding and to help determine the specificity of this protein for particular metals. Additionally, iDEER experiments[3] using both spin-labelled and/or metal binding site variant MamM in the presence of Cu^{2+} has allowed for the determination of three dimensional structural information, providing more insight into the nature of metal binding and the associated dynamic conformational changes that occur.

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EPR ORAL SESSION

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170 **Oxygen Diffusion in Microencapsulated Live Cells, Studied by Electron Spin Resonance Microscopy.**

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Cell therapy has long been suggested as a promising solution for numerous pathological conditions and diseases, where the continuous and regulated delivery of a therapeutic factor is required. Non-autologous cell transplantation (in which the cells have not been sourced from the host itself), however, could lead to immune rejection by the recipient and consequently, to graft failure. Cell microencapsulation technology was developed primarily to overcome this barrier. In this technology, cells that secrete therapeutic products are immobilized in the confines of a semipermeable membrane and transplanted at the desired site for the controlled and continuous delivery of the therapeutic molecule. The immunobarrier permits inward diffusion of nutrients and oxygen, and secretion of waste and the therapeutic product, but prevents the access of the host immune system components. This technology has been vastly investigated for the past three decades as a treatment for a wide variety of diseases and dysfunctions such as diabetes, Alzheimer's, liver failure, cancer, anemia and others. One of the most important properties of the material comprising the capsule is its oxygen penetrability. The current techniques to quantify oxygen diffusion in the microcapsule and image possible oxygen gradients generated in the presence of cells have significant limitations that make them suboptimal. In this work, we make use of unique ESR spectroscopy and ESR micro-imaging tools to study the oxygen diffusion properties in single microcapsules containing live cells, intercalated with stable free radicals. We first measure by time-resolved ESR the diffusion coefficient of O_2 in/out of a single empty microcapsule, without any live cells, thereby learning about the basic materials' properties of these 3D gel structures. Following that, we employ 3D ESR micro-imaging to learn about the time-dependent oxygen distribution in a single microcapsule with live oxygen-consuming cells inside them.

EPR ORAL SESSION

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171 **Biologic Validation of Pulsed Spin Lattice Relaxation Based EPR pO_2 Images.**

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Purpose: Pulsed Spin Lattice Relaxation (SLR) based EPR pO_2 images reduce the spin probe self-relaxation and increase the accuracy of these images by an order of magnitude. Maintenance of effectiveness despite spatial resolution, pO_2 resolution issues was tested with images directing doses of additional radiation to either sensitive well oxygenated or to resistant poorly oxygenated (hypoxic) tumor regions.

Methods: Two syngeneic tumor types, a sarcoma (FSa) and a carcinoma (MCa4) were grown in the legs of C3H mice and cast in dental mold with embedded fiducial tubes for multi-image registration. Registered T2 MRI determined the entire tumor surface. EPR pO_2 images were based on inversion recovery relaxation rates from OX63d24 trityl infused IV via tail vein. Tumors were intially treated with whole tumor radiation to a dose sufficient to cure 15% of tumors using an XRAD225Cx isocentric animal CT/radiator. MRI, CT and EPR pO_2 images were registered and hypoxic regions in the tumor were selected as all voxels with $pO_2 \leq 10$ torr. During the whole tumor radiation, tungsten loaded PLA plastic blocks were fabricated with MakerGear M3 3D printers to provide opposed oblique radiation randomly chosen to treat to all hypoxia plus a 1.2 mm margin or an equivalent volume of well oxygenated tumor. Tumors were followed for 90 days (FSa) or 180 days (MCa4). Kaplan-Meier survival analysis determined significance of differences in tumor control vs time for extra treatment of EPR pO_2 image based hypoxic or well oxygenated tumor.

Results: Both tumor types showed significant doubling in local tumor control from boost radiation of hypoxic rather than well oxygenated tumor (FSa: $p=0.04$, MCa4: $p=0.013$).

Conclusion: EPR provides the first biologically significant pO_2 images in mammalian tumors, despite a century of hypoxic resistance to radiation. It demonstrates potential effectiveness of dose painting in human cancer treatment.

EPR ORAL SESSION

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173 **Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.**

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Water-soluble triarylmethyl (TAM or Trityl) radicals represent a unique family of stable paramagnetic probes which have found numerous in vivo biomedical magnetic resonance applications. Their use as hyperpolarizing agents of ^{13}C labeled metabolites (such as [^{13}C]-pyruvate) allows to monitor in real time the biochemistry of living organisms, including humans, by MRI/MRS. They possess long relaxation times (narrow linewidths), high stability in biological media and depending on their particular structure, show sensitivities to important physiological parameters such as oxygen, pH, inorganic phosphate (Pi), enzymatic activities, etc. In this talk, we will describe the recent synthetic developments of TAM paramagnetic probes carried out in our laboratory such as the PEGylation in other to increase biocompatibility, the synthesis of a highly hydrophilic sulfonated TAM or enzyme responsive TAMs.

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EPR ORAL SESSION

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174 **Clinical Applications of EPR: Using Results to Date to Predict the Future Course of Clinical Uses of EPR.**

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The clinical use of EPR has evolved from being considered to be a logical impossibility to potentially being the next MRI with widespread use. Now that we have several years of actual experience of making EPR measurements in human subjects, the reality, predictably, is somewhere in-between. The potential for being an approach with significant impacts on several important areas remains and is being implemented. But on the basis of experience we also now recognize that while there is a subset of the potential applications that will be realized and be very impactful, there is another subset that while it seems intriguing and potentially very valuable, for very practical reasons is less likely to be realized. The principal limitations revolve around regulatory/financial barriers for niche clinical uses. The limitations are where there is a need to utilize drug-like soluble materials (e.g. spin traps, nitroxides) because the cost to get these approved for use in humans would be too great. The two main areas of clinical applications still are oximetry and dosimetry after a large unplanned exposure to radiation. Within oximetry in vivo spectroscopy (including multisite spectroscopy) for guiding cancer therapy and peripheral vascular disease (especially in diabetes) with repeated direct measurements in tissues are the most likely to result in widespread clinical use. It seems increasingly likely that the applications for cancer will especially rely on the use of the implantable resonator, because of the need to make the measurements at deeper sites than can be probed with surface resonators. For repeated measurements of oxygen in peripheral vascular disease measurements from the surface are likely to be quite sufficient. For dosimetry measurements based on stable free radicals in the teeth and the finger/tor nails are very promising, with some significantly enhanced value of the measurements in nails because of the feasibility for measurements from all four limbs to provide information on the homogeneity of the exposure.

EPR ORAL SESSION

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175 **Engineering Coherent Defects in Diamond.**

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Engineering coherent systems is a central goal of quantum science and quantum information processing. Point defects in diamond known as color centers are a promising physical platform. As atom-like systems, they can exhibit excellent spin coherence and can be manipulated with light. As solid-state defects, they can be produced at high densities and incorporated into scalable devices. Diamond is a uniquely excellent host: it has a large band gap, can be synthesized with sub-ppb impurity concentrations, and can be isotopically purified to eliminate magnetic noise from nuclear spins. Specifically, the nitrogen vacancy (NV) center has been used to demonstrate basic building blocks of quantum networks and quantum computers, and has been demonstrated to be a highly sensitive, non-invasive magnetic probe capable of

resolving the magnetic field of a single electron spin with nanometer spatial resolution. However, realizing the full potential of these systems requires the ability to both understand and manipulate diamond as a material. I will present two recent results that demonstrate how carefully tailoring the diamond host can open new opportunities in quantum science.

First, currently-known color centers either exhibit long spin coherence times or efficient, coherent optical transitions, but not both. We have developed new methods to control the diamond Fermi level in order to stabilize a new color center, the neutral charge state of the silicon vacancy (SiV) center.[1, 2] This center exhibits both the excellent optical properties of the negatively charged SiV center and the long spin coherence times of the NV center, making it a promising candidate for applications as a single atom quantum memory for long distance quantum communication.

Second, color centers placed close to the diamond surface can have strong interactions with molecules and materials external to the diamond, which makes them promising for nanoscale sensing and imaging. However, uncontrolled surface termination and contamination can degrade the color center properties and give rise to noise that obscures the signal of interest. I will describe our recent efforts to stabilize shallow NV centers within 5 nm of the surface using new surface processing and termination techniques.[3] Specifically, we are able to demonstrate reversible and reproducible control over the top layer of atoms. These highly coherent, shallow NV centers will provide a platform for sensing and imaging down to the scale of single atoms.

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EPR ORAL SESSION

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176 **The Dynamics of Spin-dependent Charge Carrier Recombination in Tris(8-hydroxyquinolinato) Aluminium (Alq3).**

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We have studied the dynamics of room temperature spin-dependent charge carrier recombination in Tris(8-hydroxyquinolinato) aluminium (Alq_3)[1] thin film with continuous wave[2] and pulsed[3] electrically detected magnetic resonance (EDMR) spectroscopy under electrical injection conditions. The measurements revealed transverse charge carrier spin relaxation times, T_2 shorter, but of the same order of magnitude to those previously observed in other organic semiconductors thin films such as various π-conjugated polymers. Multi-frequency continuous wave EDMR spectroscopy revealed the local hyperfine field distributions for both mobile electron and hole states, as well as their respective spin-orbit coupling related g-factors and g-strain values. Our measurements show that, qualitatively, the nature of spin-dependent recombination in Alq_3 film is similar to that of the polymer materials and metal-organic complexes, i.e. Zinc phthalocyanine (ZnPc)[4]. Both continuous wave and pulsed EDMR measurements independently reveal strong evidence of additional spin-dependent process on top of the polaron-pair process.

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EPR ORAL SESSION

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177 **Controlling Electron Spin Relaxation Times via Molecular Design.**

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Understanding the dependence of electronic spin relaxation times on the magnetic environment – the spin bath – is vital toward next generation applications of magnetic molecules. [1]In this presentation, we will discuss recent results in the application of pulsed electron paramagnetic resonance (EPR) spectroscopy to understanding the interaction between environmental nuclear spins and open-shell metal ions. Our focus on metal-based molecules enables the use of the chemists's toolkit – molecular tuning – to test fundamental hypotheses about the probe-to-spin-bath interaction. [2]The presentation will focus on two different routes to understanding said interaction. First, we will present results demonstrating a new design principle of modulating nuclear spin dynamics in the coordination shell to impact the metal spin relaxation times. [3, 4]Here, we show for the first time that specific patterns of nuclear spins on the molecular shell can have dramatic impact on the spin dynamics of the contained metal ion. Second, we will show how venturing to uncommon EPR frequencies alters the nature of the EPR transition in a metal ion, and, hence, the relaxation times.

Supported by NSF (CHE-1836537).

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EPR ORAL SESSION

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178 **Advancing Liquid-State Overhauser DNP Instrumentation and Applications.**

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Over the past decade, liquid state Overhauser-Effect Dynamic Nuclear Polarization (ODNP) has experienced a renaissance. In particular, the combination of ODNP with careful spin labeling strategies has transformed it into a tool uniquely poised to directly observe the hydration water around biological macromolecules and soft materials. The simple, non-perturbative labeling strategy, versatility in opaque, viscous, and other "dirty" systems, and sensitivity to translational motion offer a unique advantages over several other techniques both in the field of hydration water studies and as a robust analytical tool for macromolecular study.

Of particular interest, lipids, nucleic acids, proteins, and man-made soft materials all exhibit hydration layers, and the heterogeneity of the hydration layer at the nanoscale (a length-scale of hundreds of molecules) is generally believed to stabilize macromolecular structures and to modulate functional motions of these macromolecules. However, when applying ODNP to the study of such systems, it remains unclear whether one can more productively interpret experimental results as a measure of solvent accessibility[1,2] or as a measure of dynamics[3,4]. Here we discuss our strategy of advocating a nuanced interpretation of ODNP experiments as a measure of the accessibility of a site to rapidly translating water. We employ this common theme as we summarize our progress along three related avenues: (1) Hardware and software capable of integrating sensitive 2D NMR relaxometry techniques into ODNP permit the study reverse micelles and other unique systems with controlled molecular dynamics. (2) A multi-modal magnetic resonance and simulation strategy that allows us to leverage transmembrane protein samples we have generated by standard site-directed spin-labeling techniques. (3) Integration of several unique strategies from literature that we deploy to enable routine temperature measurements for the extraction of thermodynamic information.

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EPR ORAL SESSION

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179 **Electrically Detected Electron Paramagnetic Resonant Multi-photon Transitions.**

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We have studied electron paramagnetic resonant (EPR) monochromatic radio frequency multi-photon transitions, in particular the $g = 1$ two-photon transition using electrically detected magnetic resonance (EDMR). The electronic devices used for these experiments were bipolar injection devices, essentially polymer-based organic light emitting diodes in which the π-conjugated polymer 'super-yellow' poly-phenylenevinylene (SY-PPV) was sandwiched between an electron injection layer (Ca) and a hole injection layer (polystyrene-sulfonate doped polyethylene-dioxythiophene, PEDOT:PSS). The detection of EPR took place by measurement of spin-dependent recombination rates of weakly spin-coupled charge-carrier pairs. The experiments were carried out under low excitation frequency/magnetic field (B_0 ~ 3mT), yet high magnetic resonant drive amplitudes B_1 that was on the same order of magnitude as B_0[1,2]. We also studied these processes theoretically using Floquet-Theory, which showed that, while two-photon magnetic resonance requires that the orientation of B_1 of one of the two photons is parallel to B_0 (the so-called π photon), two-photon transitions could occur nonetheless when B_1 is perpendicular to B_0 due to the unresolved hyperfine coupling between the charge-carrier spin and the surrounding nuclear spins of protium,3 which yields a weak admixture of π-photons. We analyze the dependence of these multi-photon transitions on the strength and helicity of the driving field B_1.

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EPR ORAL SESSION

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200 **Photochemical Electron Doping of Colloidal $SrTiO_3$Nanocrystals: Effect of Hole Quencher and Carriers Densities.**

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Manipulating charge carriers in colloidal semiconducting nanocrystals has recently gained lot of interests for solar-energy conversions, optoelectronics and quantum computing devices. Herein, a photochemical method for electron doping of colloidal strontium titanate nanocrystals ($SrTiO_3$NCs) is discussed. Photoexcitation of $SrTiO_3$NCs in the presence of a sacrificial hole quencher yields extra electrons that are stable indefinitely under anaerobic conditions. Unlike delocalized electrons in conduction band observed in Nb-doped TiO_2 and photodoped ZnO, the extra electrons in $SrTiO_3$NCs localize at Ti^{3+}trap sites that are observed by EPR spectroscopy and by a distinct color change. Kinetic studies show that rate of electron accumulation in the conduction band is sensitive to the nature of the hole quencher. An attractive aspect of this photochemical reduction is that the whole process can be completely reversed upon exposure of the colloidal suspensions to air. Taking the advantage of this reversibility, we estimate the average carrier densities per nanocrystal by chemical titration and find it exceeds that found for other TiO_2 and ZnO based semiconductors by about a factor of two. The interaction of these metastable Ti^{3+}defects to other paramagnetic defects will also be presented.

EPR POSTER SESSION

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201 **A Closer Look at Confined Water: Use of Overhauser Dynamic Nuclear Polarization to Study Nanoscale Water Dynamics in Aerosol-OT Reverse Micelle Model Systems.**

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Experimental studies of interfacial water are complicated by the inescapable presence of bulk water. Over the past decade, Overhauser Dynamic Nuclear Polarization (ODNP) has demonstrated remarkable aptitude for overcoming this problem. ODNP relies on chemistry to place a spin probe in a known location and on spin physics to read out the dynamics of water within 5-15 Å of that location, thereby extracting the interfacial water signal from the bulk.[1] As a simple but important model system, we have selected AOT (Aerosol-OT, dioctyl sulfosuccinate sodium salt) reverse micelles (RMs) employing ODNP with the amphiphilic spin label CAT-16 (4-(N,N'-dimethyl-N-(hexadecyl)) ammonium-2,2',6,6'-tetramethylpiperidine-1-oxyl salt) to extract the interfacial water signal and TEMPO-sulfate to extract the RM core water signal. These results will offer a unique perspective on nanoscale water dynamics and provide benchmark measurements important to ODNP analysis of confined water in other, more complex material systems with less defined morphology.[2] Here we present the development of specialized ODNP instrumentation, including a home-built NMR spectrometer and probe designed for ODNP measurements, as well as the design of a Python library that permits facile implementation of complex pulse sequences. Finally, to increase the capabilities of our ODNP NMR instrumentation, we present the extension of our standard data-processing library with an efficient, parallel implementation of the 2-Dimensional Inverse Laplace Transform (2D-ILT) algorithm.[3] We demonstrate via the 2D-ILT the ability to observe resonances for water and for other chemical species such as isopropyl alcohol simultaneously, thus opening up new possibilities for ODNP measurements.

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EPR POSTER SESSION

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202 **A Multimodal Method for the Investigation of Complex Protein Systems with Site-Directed Spin-Labeling.**

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Hydration water plays an essential role in biological function that encompasses both the stabilization of macromolecular structure and the modulation of conformational motion. The investigation of hydration water therefore leads to important macromolecular discoveries. However, rapid motion (10-100s of picoseconds) of most hydration water molecules and the presence of bulk water molecules, which vastly predominate in solution and rapidly exchange with hydration water, make investigation inherently challenging. Overhauser Dynamic Nuclear Polarization (ODNP) has been developed for use in tandem with site-directed spin-labeling to probe hydration water in a sensitive and localized manner, however a satisfactory method for interpretation remains undetermined. We advocate for using a quantitative ODNP method where we extract the accessibility to fast-moving hydration water at a specific site via measurement of cross-relaxivity and in a rigorous manner that relies on cross-validation with various experimental and computational observations. We employ proteorhodopsin, a retinal-binding proton pump with 7 transmembrane alpha-helices and the target of previous ODNP and NMR studies, as a model system. We optimize expression in *E. coli* for spin-labeling with MTSL along the E-F loop, as has been previously addressed, and down the F-helix to map the full transmembrane environment.We simulate spin-labeled samples with Rosetta – an open-access, self-contained biological modeling scaffold, widely used for structural prediction; it performs large-scale sampling with a realistic all-atom scoring function, and includes spin labeling and coarse membrane modeling. Our studies offer insight into the possible utility of integrating Rosetta's capabilities into existing ESR-focused tools like MMM (Multiscale Modeling of Macromolecules).We focus on optimizing the use of Rosetta-based algorithms with a wide sampling of conformational space and employ the conformational flexibility of the MTSL-Cys tether. Despite Rosetta offering structural (not dynamic) predictions, we also investigate possible links between simulations of cw ESR spectra and ensembles of reasonable Rosetta-generated conformations.

EPR POSTER SESSION

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203 **Decoherence of Molecular Spin Qubits in Solution.**

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Molecular spin qubits are potential materials for quantum information processing applications due to their tunability, scalability, and processability. Currently, their major drawback is that decoherence times are often on a timescale that is much too short for any practical application. We present experimental data on the low-temperature decoherence of a series of spin centers across the periodic table, from carbon- and nitrogen-centered radicals to transition metal complexes. We present a phenomenological analysis of the observed coherence decays that reveals two components. We then show that one of the components can be modeled quantitatively by nuclear spin diffusion.

EPR POSTER SESSION

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204 **Characterization of Expansible Argilominerals in Reservoir Rocks by Relaxometry.**

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The increasing search for oil and the characterization of reservoirs is increasingly important and makes the acquisition of data on rocks present in potential reservoirs important and necessary. For this characterization, basic analyzes on porosity, permeability, specific mass of grains and also determination of the pore distribution are made so as to the calibration of resonance profiles and delimitation of the free fluid boundary that can be produced. One of the reasons that can alter these determinations, in the reservoir rocks, is the presence of clay minerals. In this work, a non-destructive laboratory technique was proposed to identify the presence of expandable clay minerals in samples of sandstones and carbonate rocks. The technique is based on the measurement of short relaxation times in samples that have been dried under controlled humidity, thus keeping the water absorbed and adsorbed on the clays. The water found between the layers of the expandable clay minerals presents, in principle, a decay of the faster transverse magnetization, due to the more intense interactions to which the hydrogen nuclei are subjected. It was also tried to establish a relation between the amplitudes of the signals, obtained in the NMR, with the concentration of expandable argilominerais present in the sample, for that the SEM was used. Samples of sandstones and carbonate rocks were characterized by petrography, X-ray diffraction, scanning electron microscopy and NMR relaxometry. The T_2 distributions measured for sandstones with only non-expandable clays are centered between 0.1 and 1ms. For samples with expandable clays, such distributions are located around 0.1 ms. This result is consistent with the hypothesis that absorbed water has less relaxation times than adsorbed water, and indicates that the technique is able to perceive this contrast and detect the two classes of minerals. In addition, the amplitudes of the signals corresponding to the expandable minerals are much larger than the non-expandable ones, consistent with the fact that the volume of water absorbed is generally greater than the adsorbed volume. With the use of SEM, an equation was also obtained for correlation between the concentration of the expandable clay minerals and the amplitudes found in NMR. Although the profiling tools do not have the ability to detect the contrast capable of differentiating the absorbed waters from the adsorbed ones (due to electronics and the presence of noise in the well), the technique presents itself as a promising option to complement mineralogical analysis by means of a non-destructive test.

EPR POSTER SESSION

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205 **Development of a New and Greener Calibration Reaction for Use with Rapid-Freeze-Quench Apparatus for EPR Spectroscopy.**

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Rapid-Freeze Quench (RFQ) is a commonly used method for trapping transient species on time scales on the order of 10^{-4} to 10 s. The most frequently used reaction for calibrating mixing times of RFQ apparatus is the venerable binding of azide to aquometmyoglobin. This reaction requires the use of high concentrations (> 30 mM) of the highly toxic azide ligand in order to calibrate times of 10 ms and below. We have examined the use of the reaction of $Ca(EDTA)^{2-}$ + Cu^{2+} -> Ca^{2+} + $Cu(EDTA)^{2-}$ as a simple and non-toxic replacement for the Mb + azide reaction. By using buffers in

the 6 - 7.5 pH range with high concentrations of imidazole (Im), we find that this reaction provides changes on the millisecond time scale in the electronic spectrum that can be followed by stopped-flow absorption measurements. We have developed a method to quantitatively separate the contributions from the two EPR-active species in solution ($Cu(Im)_4^{2+}$ and $Cu(EDTA)^{2-}$) during the progress of the reaction that is accurate to 5-10%. This reaction and EPR quantitation method have been tested using an RFQ apparatus calibrated with the Mb + azide and yielded nearly identical results. We show that this simple reaction can provides a number a different ways to scale the reaction rates both faster and slower with little change without the use of large excesses of chemicals.

EPR POSTER SESSION

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206 **Hydration Environment Characterizations of the Folding of IA_3, an Intrinsically Disordered Protein.**

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IA_3 is an intrinsically disordered protein (IDP), found in Sacchoromyeces cerevisiae, that has been previously shown to adopt α-helical secondary structure when bound to yeast proteinase A (YPRA). The α-helical structure of IA_3 can be stabilized in the absence of YPRA, by using 2,2,2-trufluoroethanol (TFE). Site-directed spin-labeling (SDSL) along with electron paramagnetic resonance (EPR) has been used to characterize the TFE induced folding of IA_3. Here we report results from cysteine scanning through the N- termini, which reveals evidence for the degree of unfolded-ness of the region. Additionally, results demonstrate a sensitivity of the N-terminal region to amino acid substitution. Particularly, sites V8 and S9 are sensitive to SDSL, where alterations in amino acid structure are shown to limit or strengthen the TFE induced structural transition, respectively. We find that site S14C-SL behaves similarly to WT in TFE-induced folding, making S14 a useful spin-label reporter site to probe the impact of mutations at V8 and S9. Results from circular dichroism, EPR and Overhauser dynamic nuclear polarization (ODNP) will be presented. ODNP is used to further understand hydration effects on protein folding. Hydration effects impact proper folding of proteins, and the study of IA_3's hydration when disordered or ordered in structure using mutants of IA_3, with WT deviating behavior, can lead to a clearer representation of the secondary structure characteristics of this model IDP. ODNP will help us to understand the changes in this model system upon SDSL or residue mutation. Through the use of circular dichroism, SDSL-EPR, and ODNP, a clearer representation of the disordered and ordered states of IA_3will be determined. This model system can further be used to hypothesize about other functional IDPs and their structural transition upon protein function.

EPR POSTER SESSION

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207 **Redox Regulation by Extracellular Superoxide Dismutase (EC-SOD) Due to the R213G Variant in Bleomycin-induced Lung Injury.**

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Mice harboring knock in of a single nucleotide polymorphism (SNP) in the matrix binding region of EC-SOD (R213G mice) exhibit increased active plasma EC-SOD. The R213G mice are protected against intratracheal bleomycin-induced lung injury with enhanced resolution of inflammation. We hypothesized that the redistribution of R213G EC-SOD will modulate superoxide levels and the thiol redox state in different compartments, and these changes will promote protection with activation of the redox sensitive transcription factor, Nrf2 in circulating monocytes.

Methods Wild type (WT) and R213G mice were treated with intratracheal bleomycin (0.1 U/mouse) and blood and lungs collected 7 days post treatment. $O_2^{\bullet-}$ was measured by EPR using CMH or CPH spin probes. Reduced and

oxidized glutathione were measured by HPLC, and the redox potential (Eh) calculated. PBMC were isolated 7 days post-Bleo and ROS production evaluated using CMH. Nrf2 dependent genes were evaluate in recruited alveolar macrophages and circulating PBMC.

Results At 7 days post-bleomycin, blood $O_2^{\bullet-}$ levels increased in WT but not R213G mice, though lung $O_2^{\bullet-}$ level increased in both strains. Plasma EhGSSG was oxidized in R213G mice but reduced in WT. Lung EhGSSG was more oxidized in WT compare to R213G mice. Given the difference in plasma redox potential between WT and R213G and the role of the recruited monocyte in populating alveolar compartment and driving inflammation, we sought to explore differences in PBMC between the strains. Total PBMC $O_2^{\bullet-}$ production was higher in R213G mice. (n=5-6). Selected Nrf2 dependent genes were increased, suggesting Nrf2 activation in R213G mice.

Conclusion. The changes in $O_2^{\bullet-}$ levels and thiol redox status were regulated differently in blood and lung. We speculate that the oxidizing environment in the plasma induced elevated ROS production in the circulating monocyte, which activated Nrf2 and promoted resolution of inflammation.

EPR POSTER SESSION

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208 **Allosteric Gating in Cyclic Nucleotide-gated Ion Channels: New Insights from DEER Spectroscopy.**

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EPR POSTER SESSION

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209 **Measuring, Processing and Analysing Non-Uniform Sampled HYSCORE with Hyscorean.**

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Non-uniform sampling (NUS) provides a considerable reduction of measurement time especially for multidimensional experiments. This comes at the cost of additional signal processing steps to reconstruct the complete signal from the experimental data points. Despite being routinely employed in NMR for many experiments, NUS has not been employed in EPR applications due to the lack of a straightforward implementation to perform NUS in common commercial spectrometers. A new method to implement NUS HYSCORE experiments on commercial Bruker EPR spectrometers as well as new processing software tools for NUS HYSCORE signals are presented. These new developments come in the form of a free-software package: Hyscorean. The reconstruction methods are benchmarked for an experimental NUS HYSCORE spectrum of an Fe(III)-myoglobin variant[1] acquired on a commercial Bruker spectrometer.

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210 **Spin-probe EPR of Nanoheterogeneous Media: MOFs and ILs.**

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211 **Pulsed Dipolar EPR Distance Measurements using Orthogonal Labeling with Triplet Fullerene and Nitroxide or Triarylmethyl Radicals.**

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Distance measurements by pulsed EPR play crucial role in structural studies of biomolecules and their complexes. In parallel with growing applications of this approach, a significant attention has been paid to the search for new spin labels whose spectroscopic properties would overcome current limitations. In particular, recently a new direction of using the photoexcited spin-polarized triplet states as spin labels has emerged, where porphyrins were employed as first examples.[1,2]

In this work we propose and validate the use of the other type of photoexcited triplets for pulsed dipolar (PD) EPR – the photoexcited fullerenes. Stronger electron spin polarization and narrower spectrum of fullerenes compared to other triplets (e.g., porphyrins) enhance the sensitivity, and superior relaxation properties allow PD EPR measurements up to a near-room temperature. The capabilities of new labels were demonstrated using fullerene-nitroxide and fullerene-triarylmethyl pairs, as well as supramolecular complex of fullerene with nitroxide-labeled protein. We have reliably demonstrated that photoexcited triplet fullerenes can be considered as new potent spin labels with outstanding spectroscopic properties for future structural studies of biomolecules.

This work3 was supported by RSF (18-73-00292).

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212 **Understanding Linewidth of ESR Spectrum Detected by a Single NV Center in Diamond.**

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The nitrogen-vacancy (NV) center in diamond is an excellent candidate for quantum sensing because of its high sensitivity to magnetic fields, a capacity for optical spin state readout, and sub-nanometer spatial profile. These traits make the NV center a promising candidate for applications of electron spin resonance (ESR) with single spin sensitivity.[1] As the position, intensity, and line-shape of the ESR spectrum provide information on the spin system, understanding the NV-detected ESR spectrum is critical for nanoscale ESR.

Within this presentation, I present our recent study of the lineshape of NV-detected ESR using a double electron electron resonance technique (DEER) on substitutional nitrogen centers in diamond.[2] By studying the dependence of the DEER excitation bandwidth on the NV-ESR linewidth, we find that the spectral resolution is improved significantly and eventually limited by inhomogeneous broadening of the detected ESR. The resolved NV-detected ESR linewidth is shown to be as narrow as 0.3 MHz.

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

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213 **Effect of Freezing Method on Polarizability of Finland Trityl.**

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Triarylmethyl radicals, commonly referred to as trityls, are employed in biological applications due to their favorable stability and narrow spectral widths. One promising application is the use of trityls as polarizing agents for dynamic nuclear polarization (DNP). However, in order to tune radicals for optimal DNP enhancement it is important to understand the spin dynamics of these polarizing agents. Pulsed electron paramagnetic resonance (EPR) techniques provide insight on the complex interactions in the spin system and reveal how variations in sample preparation affect the spin system. We show that the rate at which samples are frozen during preparation affects the distribution of trityls and their interactions in the frozen state. In particular, spin-lattice relaxation (T_{1e}) measurements are correlated to the DNP efficiency of trityl solutions frozen via different methods. Samples were prepared in a manner which allows for both EPR and DNP measurements to be carried out on the same sample without further preparation. The results show large deviations in spin dynamics as a result of different freezing rates, emphasizing the importance of establishing reproducible methods of sample preparation.

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214 **Advancing Liquid-State Overhauser DNP Instrumentation and Applications.**

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See Oral Session #178

EPR POSTER SESSION

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215 **Determining Protein-DNA Interaction using Copper-based EPR Techniques.**

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EPR POSTER SESSION

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216 **Beyond Pairwise Distance Determination: Resolving Dynamic Conformational Change in CDF Regulatory Domains.**

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EPR POSTER SESSION

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217 **Hyperpolarization and Bath Spectroscopy of Individual ^{13}C Nuclei in Diamond via ODMR.**

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70 years ago, Erwin Hahn published the first experimental demonstration of a Free Induction Decay (FID) experiment[1]. Advances in quantum optics and material science enable us today to record the free precession signal of single ^{13}C nuclear spins inside a diamond crystal[2]. The experimental instrumentation to achieve this sensitivity is not of a classical and macroscopic scale as in Hahn's experiment, but rather of a microscopic scale. Indeed, the sensor is an electron spin: the electron spin of the Nitrogen-Vacancy (NV) center in diamond. Standard EPR microwave pulses can be used to manipulate it and laser pulses provide an optical manipulation path to read-out the spin state and to polarize the NV center at room temperature. This makes the NV platform a very promising candidate for single spin imaging. In this talk, we focus on two key challenges towards single molecule NMR spectroscopy: the hyperpolarization of single nuclei in the vicinity of the NV center at room temperature and the detection scheme. We use the hyperfine coupling of the nuclei to the NV center to transfer electron spin polarization in a ramped-amplitude NOVEL-like scheme. By modulating the amplitude of the spin-lock pulse, we improved the robustness and the efficiency of the protocol for polarizing multiple nuclear spins with *a priori* unknown hyperfine couplings. To detect the nuclear spins, we propose the use of periodic weak measurements. This allows a continuous FID detection at the single spin level. By that, we demonstrate sensitive, high-resolution NMR spectroscopy of multiple individually resolvable nuclear spins in the vicinity of the NV center.

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EPR POSTER SESSION

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218 **Development of Enzyme Responsive Spin Probes for Non-Invasive Imaging of Enzyme Activity by EPR.**

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In this work, we report on the development of nitroxide and trityl radicals to measure enzyme activity directly in vivo using EPR imaging. This new concept is based on a modification of the EPR spectra of a spin probe substrate of a particular enzyme upon enzymatic transformation. The shift in EPR resonance between the enzyme substrate and product can be used to image both substrate and enzyme independently using 4D spectral-spatial EPR imaging. Our first example depicts a nitroxide-based radical whose spectrum is sensitive to alkaline phosphatase (ALP). This radical was used to image ALP activity in vitro using a homemade rapid-scan EPR imager operating at 800 MHz.[1] However, the in vivo use of nitroxide radicals are limited by their fast bioreduction. Therefore, we are developing the first trityl radicals sensitive to enzyme activity. Indeed, trityl radicals are well known for their extraordinary stability in biological media, the narrow linewidth of trityl radicals also increases the sensitivity of detection and the spectral resolution between substrate and product. We report on the synthesis and characterization of a matrix metalloproteinase 2/9 sensitive trityl spin probe.

EPR POSTER SESSION

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219 **Protein and Solvent Dynamical Contributions to the Radical Rearrangement Catalysis of 2-Aminopropanol in the B12-Dependent Ethanolamine Ammonia-Lyase.**

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The signature enzyme B_{12}-dependent ethanolamine ammonia lyase (EAL) of the gut homeostatic ethanolamine metabolism, and ethanolamine utilization pathway in pathogenic strains of *Salmonella* and *Escherichia coli*,[1] isolated from *Salmonella typhimurium* has been studied by electron paramagnetic resonance (EPR) spectroscopy to gain insights into the fundamental aspects of its molecular mechanism and modulation by the surrounding environment. The cryotrapped cob(II)alamin-aminoethanol substrate radical pair decays to diamagnetic products upon temperature (T) -step initiation in the range of 295 – 203 K. The kinetics of the radical decay measured by time-resolved, full-spectrum EPR exhibits a piecewise-linear Arrhenius dependence punctuated by a transition in the kinetics from mono- to biexponential over $220>T\geq217$ K.[2] Solvent dynamics studies done by using TEMPOL spin-probe EPR revealed a correspondence of the T of the kinetic transition with an order/disorder transition (ODT) in the protein-associated domain that surrounds EAL, which can be tuned (T decreased) by using added (0.5- 4.0% v/v) dimethylsulfoxide (DMSO).[3] In contrast, the native rearrangement reaction kinetics of 2-aminopropanol substrate (~10^3-fold slower decay rate constants[4]) are twin-biexponential from 220-250 K, and show parallel native and non-native (destructive) radical rearrangement pathways. To address the role of protein-solvent coupling in the reaction, we hypothesized that the presence of DMSO, and consequent lowering of the ODT, would guide the reaction of EAL with 2-aminopropanol fully to the native pathway. The observed persistence of the native and non-native processes indicates a decoupling of the 2-aminopropanol substrate radical reaction from the solvent dynamics. For 2-aminopropanol, intrinsic chemical or conformational factors mimic the protein configurational barrier to reaction, at physiological T-values. The results distinguish protein configurational and reactant-intrinsic contributions to reactivity in B_{12}-dependent EAL enzyme catalysis.

Supported by NIH DK054514.

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EPR POSTER SESSION

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220 **Nuclear-Spin-Pattern Control of Electron-Spin Dynamics in a Series of V(IV) Complexes.**

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Designing molecular systems with long electron spin relaxation times is a major obstacle hindered by the dynamics of nuclear spins in the local environment.[1] To address this challenge, we tested whether the specific arrangements of nuclear spins in a molecular complex influence coherence time for a V(IV) ion ($S = {}^1/_2$). For this study, we chose to pattern catecholate ligands with interstitial $^{79/81}$Br nuclear spins in the canonical V(IV) triscatecholate complex.[2,3] We measured the influence of nuclear-spin patterning with high-frequency/field pulsed electron paramagnetic resonance spectroscopy which reveals a 2 μs difference in the phase memory relaxation times. Notably, two molecules have starkly different phase memory relaxation times despite the same chemical composition, which we ascribe to specific patterned arrangements of nuclear spins in the ligand shell. These results are the first to demonstrate a nuclear spin pattern design principle for modulating relaxation times in molecules.

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EPR POSTER SESSION

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221 **Simulating Electronic Decoherence in Glassy Samples via Cluster Expansion Methodologies.**

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Nuclear spin diffusion is the dominant effector of electronic decoherence at low temperatures. The decoherence timescale limits the duration for experiments requiring coherent spin manipulation, from DEER measurements to quantum information processes. *A priori* knowledge of the decoherence timescale could expedite system selection by the *in silico* elimination of systems with an unfavorable coherence time. Spin diffusion is a quantum process and classical models cannot fully capture or predict the decoherence dynamics. We show that a clustering method from solid-state physics can approximately solve the quantum evolution for a reasonable *ab initio* prediction of the coherence decay function for glassy samples.

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222 **Tailored Nuclear Spin Dynamics in a Coordination-Complex Vessel.**

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Interstitial patterning of nuclear spins is a central design process for engendering coherence in solid state qubits. Herein we provide the first test of the extent to which atomic patterning in ligands modulates nuclear spin dynamics in a molecular platform by characterizing the T_1 and T_2 times of protium nuclei using NMR spectroscopy with inversion-recovery and CPMG pulse sequences. We prepared and studied a series of un-, mono-, di-, tri-, and tetra-brominated catechols, revealing T_1 values in the range of 11.0-40.8 s and T_2 values in the range of 2.1-10.3 s for the ^{1}H nuclei. These catechol species were then used to form Ti(IV) species, $(Me_2NH_2)_2[Ti(C_6H_{4-n}Br_n)_3]^{2-}$ (n = 1, 2, 3, and 4). When complexed, the nuclear spin relaxation rates increase markedly, down to 1.3 s for T_1 and 0.43 s for T_2. Yet, the comparative rates between the complexes match the ligands – namely, that ^{1}H relaxation times increase by a factor of three or more for interstitially substituted arrangements of ^{1}H and $^{79/81}$Br spins on the ligand. Hence, the design parameter for controlling relaxation times in the individual ligands is indeed conferred to the complex.

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223 **Adjustable Frequency and Variable Coupling EPR Probe with Loop-Gap Resonators for Spectroscopy up to X-Band.**

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Electron paramagnetic resonance (EPR) spectroscopy is an indispensable tool in several branches of science as well as in industry. Several commercial spectrometers exist at certain well-defined frequency bands to perform standard EPR spectroscopy. Typically, the frequency of an experiment is set and the spectrum is acquired using magnetic field as the independent variable. There are cases in which it is desirable instead fix the field and tune the frequency such as when studying zero-field splittings. For example, to observe atomic-clock transition behavior in the Cr_7Mn molecular nanomagnet, the frequency has to be tuned to match the zero-field splitting[1]. We have designed and tested an adjustable frequency and variable coupling EPR probe with loop-gap resonators (LGRs) that works at temperatures down to 1.8 K. The frequency is tuned by adjusting the height of dielectric piece of sapphire inserted into the gap of an LGR; coupling of the microwave antenna is varied with the height of antenna from the LGR. Both coupling antenna and dielectric piece are located within the cryogenic sample chamber, but their motion is controlled with external micrometers located outside the cryostat. The frequency of the LGR can be adjusted by up to 1 GHz depending on the resonator. To cover a wide range of frequencies, different LGRs can be designed to cover the 1-10 GHz range. The quality factor (Q) of these resonators easily reaches >2000 at cryogenic temperatures, which is ideal for continuous wave EPR spectroscopy. For the pulsed EPR, the antenna can be over-coupled to reduce the Q of resonators below 100. We have used this dynamic and versatile EPR probe to study pulsed ESR of molecular nanomagnets at cryogenic temperatures.

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224 **Experimental Validation of the ALLNOX Program for Studying Protein–Nucleic Acid Complexes.**

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Measurement of distances between spectroscopic labels (e.g., spin labels, fluorophores) attached to specific sites of biomolecules is an important method for studying biomolecular complexes. ALLNOX (Addition of Labels and Linkers) has been developed as a program to model interlabel distances based on an input macromolecule structure. Here, we report validation of ALLNOX using measured distances between nitroxide spin labels attached to specific sites of a protein–DNA complex. The results demonstrate that ALLNOX predicts average interspin distances that matched with values measured with pairs of labels attached at the protein and/or DNA. This establishes a solid foundation for using spin labeling in conjunction with ALLNOX to investigate structure-function relationships in protein-nucleic acid complexes, such as the CRISPR-Cas systems being developed for genome editing. With its high degree of flexibility for the label or the target biomolecule, ALLNOX also provides a useful tool for studying a large variety of biological molecules.

EPR POSTER SESSION

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225 **Progress Towards Time-Resolved Measurements of Light-Induced Conformational Changes in Gd^{3+} Spin-Labeled Proteins by cw-EPR at 240 GHz.**

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EPR in combination with site-directed spin labeling can be used to study protein structure and motion under biologically relevant conditions. Unlike pulsed EPR experiments such as DEER that require cryogenic temperatures, distance measurements by cw-EPR can be applied under closer to physiological conditions. However, distance measurement by cw-EPR using nitroxide-based spin labels is limited to inter-spin distances below 1.6 nm while longer distance ranges will dramatically benefit the characterization of proteins. High spin (S= 7/2) Gd^{3+} spin labels have emerged as sensitive probes for cw and pulsed EPR based distance measurements at high fields. The central (-1/2) to (1/2) transition of Gd^{3+} becomes narrower at higher fields and at lower zero-field splitting parameters, and hence provide higher concentration and distance sensitivity by resolving dipolar broadening of the EPR line shape[1]. We are making progress with cw EPR relying on Gd^{3+} based spin labels for the study of distances in protein systems, with the aim to resolve conformational changes in proteins induced by light activation at biologically relevant temperatures. The two systems that we have chosen are green-absorbing proteorhodopsin (PR)[2] and a light sensing light-oxygen-voltage (LOV) protein variant[2]. PR is a retinal binding transmembrane protein which marine bacteria use as light-activated proton pump to generate a proton gradient across the membrane bilayer. We have spin labeled PR at a variety of residues with two Gd^{3+}spin labels: Gd-ADO3A and Gd-TPATCN. Because zero-field splitting in Gd-TPATCN tag is weaker than in Gd-ADO3A, we have observed significantly narrower cw-EPR linewidth at 240 GHz for Gd-TPATCN, but for now the spin labeling efficiency with Gd-ADO3A is higher. Moreover, in contrast with MTSL, the Gd-ADO3A lineshape is independent of the local environment and the tagged site. Finally, we have detected cw EPR line shape broadening due to intra-molecular dipolar coupling in doubly Gd-ADO3A spin labeled PR. Among the different photoreceptor classes, the blue LOV proteins that are conserved in plants, bacteria, fungi, and archaea, can detect blue light via a Flavin cofactor and undergo conformational changes. We have synthesized and spin labeled the LOV domain from CreiLOV with Gd-ADO3A spin label, and performed cw-EPR at 240 GHz. We will present progress towards "filming" PR and CreiLOV in action through time-resolved cw EPR measurements of dipolar broadening to study light-induced conformational changes.

This study is supported by NSF MCB 1617025 and NIH R01GM116128

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EPR POSTER SESSION

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226 **X-band EPR Studies on Ion Beam Irradiated YIG Thin Films; Reconfiguration of Structural and Magnetic Properties.**

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We have investigated the change in saturation magnetization (M_s), magnetic damping, microstructure and surface morphology of yttrium iron garnet (YIG) thin films using nickel (Ni) ion beam irradiation. The structural variation was found to be enhanced with ion beam energy and fluence. X-band EPR studies gives information about the tuning of saturation magnetization as a function of ion beam fluence (10^{13} – 10^{15} ions/cm^3). EPR studies also confirms decrease of effective magnetization with increase in ion beam fluence. We observed the change in magnetic anisotropy and enhancement in higher order resonance modes. The study was performed on different YIG films deposited on variety of substrates (Quartz, Silicon and Gadolinium Gallium Garnet (GGG)). Fascinating results were observed at high ion fluence on GGG substrate i.e about 15% decrement in M_s and enhanced magnetic damping. These results evidence the applicability of ion beam irradiation for the fabrication of efficient micro and nano-sized magnetic crystals for magnonic applications.

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227 **Modulation of Radical Reaction-Protein-Solvent Coupling in the B12-Dependent Ethanolamine Ammonia-Lyase Enzyme by using Sucrose in the Low-Temperature Mesodomain System.**

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The adenosylcobalamin (coenzyme B_{12}) –dependent ethanolamine ammonia-lyase (EAL) is the signature enzyme in the sequence of ethanolamine utilization (eut) associated with microbiome homeostasis, and *Salmonella*- and *Escherichia coli*-induced disease conditions, in the human gut.[1] Characterization of the molecular mechanism of the EAL from *S. typhimurium* advances toward therapeutic modulation of the eut pathway. Full-spectrum, time-resolved electron paramagnetic resonance (EPR) spectroscopy[2] at low temperature (*T*) has revealed two sequential substrate radical intermediate states, distinguished by distinct protein configurations (**S_1•**, radical pair stabilization function; **S_2•**, rearrangement reaction-enabling), whose interconversion is latent at physiological *T*.[3, 4] Here, we use sucrose to resolve protein-solvent interactions that shape the reaction free energy landscape (FEL) in the concentric protein-associated domain (hydration layer) and mesodomain that surround EAL in frozen aqueous system.[5, 6] As shown by the power-law fits to **S_1•** and **S_2•** decay reactions at 217 K (Figure 1), increasing sucrose from 1 to 5% *w/v* up-shifts the mean observed rate constant (k_{obs}) for decay from **S_2•**, substantially down-shifts the mean k_{obs} for S1•, creates distributions in k_{obs} with approximately uniform widths, and shifts population from **S_2•** to **S_1•**. The results indicate that preferential protein solvation,[7] owing to hydrogen-bonding with sucrose,[8] ramifies the existing FEL into a continuum of trajectories, that nevertheless preserve the two-state reaction topography. The sucrose-concentration-independent distribution in k_{obs} suggests a site-specific effect. The progressive up/down shift in k_{obs} for decay from **S_2•**/**S_1•** with increased sucrose suggests an origin in relief of ice-boundary confinement of protein motions. The slowing of the decay, and growth in population of, **S_1•** is consistent with a selective kinetic stabilization6 of this state by sucrose. Overall, fundamental features of reaction-protein-solvent coupling are revealed, which inform effector design for EAL and other protein catalysts.

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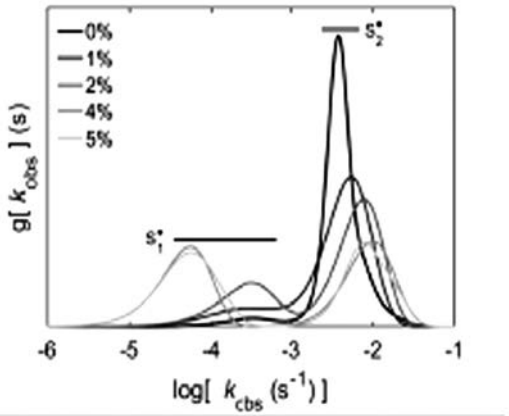

Figure 1. Sucrose dependence of the distribution of observed rate constants for the two-channel substrate radical decay at different added sucrose concentrations

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228 **Studying Drug-Drug Interactions in Cytochrome P450 3A4 with EPR.**

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Cytochrome P450s are monooxygenase enzymes present in nearly every living organism. In humans, they are responsible for the metabolism of the majority of all drugs on the market. Of the various drug-metabolizing CYPs, CYP3A4 is the most abundant and metabolizes the largest proportion of drugs. CYP3A4 has a dynamic active site that is able to accommodate multiple types and multiple copies of substrates, which leads to cooperativity and altered kinetics. This cooperativity is often at the center of drug-drug interactions that lead to unintended and potentially harmful drug metabolism. Electron paramagnetic resonance (EPR) spectroscopy can shed light on these interactions because it can identify and probe CYP-drug binding modes, including multiple binding modes that coexist in solution. In this study, we develop a method for characterizing drug-drug interactions with EPR. We examine two drug combinations, acetaminophen with caffeine and midazolam (MDZ) with carbamazepine (CBZ) binding to CYP3A4, both of which are known to exhibit cooperativity. We use continuous wave (CW) and pulsed EPR to characterize the binding of each individual drug as well as to monitor changes upon the addition of other drugs. These results contribute new details about the binding of acetaminophen, caffeine, MDZ, and CBZ to CYP3A4. In particular, they show that these drugs do not replace the axial water, and that the combination of two drugs perturbs the water-bridged complexes with only a single drug added. In addition, this work provides a framework for studying drug-drug interactions with EPR.

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229 **New Spin Labels and Spin Labeling Methods.**

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230 **EPR Spectroscopy Across the Spectrum – From Coordination Complexes to Whole Cells.**

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The coordination environment surrounding a metallocenter has a drastic effect on the EPR signal, whether comprised within a ligand scaffold, protein matrix, or the cellular milieu. The coordination sphere also has a direct effect on the reactivity preferences and/or behavior of the metallocenter. For example, the stability and reactivity patterns of metal-dioxygen adducts can be steered by the donating ability and structural restrictions imposed by their ligand framework. Although the electronic properties of metal-dioxygen binding modes found within coordination complexes can be tuned to facilitate difficult organic transformation reactions, the identity of the reactive species can often only be defined by a collection of advanced spectroscopic techniques - including EPR - and synthetic tricks that provide insight into the mechanistic pathway. In many cases, different metals can be housed within identical coordination spheres, altering the O_2 binding preferences and the subsequent reactivity. Such metal switching is not only controlled by synthetic preference and/or the scope of the researcher, but also by environmental factors within a natural system, which can affect protein folding

and/or protein translocation. In this work, the characterization of novel metallocomplexes comprised of earth abundant metals such as nickel, cobalt, and copper, will be discussed, along with their catalytic potential. Additionally, the effect of biometals such as iron and copper on protein folding, aggregation, and protein-membrane interactions will be described within the context of alpha-synuclein, a dynamic protein implicated in Parkinson's disease.[1-3] Finally, insights into the impact of manganese and iron transport and of redox speciation on bacterial virulence in the case of the opportunistic human pathogen *Streptococcus sanguinis* will be discussed.[4] Overall, the scope of this research will highlight the reach of EPR from bioinspired catalysis to metal-dependent biological pathways.

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EPR POSTER SESSION

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231 **Electrically Detected Electron Nuclear Double Resonance in a Fully Processed Bipolar Junction Transistor.**

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We have developed a sensitive electron nuclear double resonance (ENDOR) spectrometer in which the detection takes place through electrically detected magnetic resonance. We demonstrate that the spectrometer can provide reasonably high signal to noise spectra of ^{14}N interactions with deep level centers at the base-emitter junction of a fully processed heavily nitrogen doped 4H-SiC bipolar junction transistor at room temperature. The number of paramagnetic defects in this region is almost certainly less than 10^7. The electrically detected electron nuclear double resonance (EDENDOR) spectrometer utilizes a single loop non-resonant antenna that is placed within a TE_{102} microwave cavity adjacent to the transistor to generate the nuclear magnetic resonance (NMR) oscillating magnetic field. A frequency sweep is supplied to the NMR coil loop via an arbitrary waveform generator. To maintain constant power to the loop, a proportional-integral-derivative controller has been used to feedback a real time measurement of the power through the loop and adjust the output. This suppresses the non-resonant background which otherwise obscures the EDENDOR response. To the best of our knowledge this is the first time ENDOR measurements have ever been made within a fully processed transistor.

EPR POSTER SESSION

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232 **An Improved Adaptive Signal Averaging Approach for Optimizing Signal to Noise in Continuous Wave Magnetic Resonance Measurements.**

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We have significantly refined an adaptive signal averaging approach developed primarily for continuous wave electron paramagnetic resonance (EPR) and electrically detected magnetic resonance (EDMR) measurements.[1] This refinement overcomes several limitations in choosing the appropriate values for parameters utilized in the earlier approach.[2] The improved upper-diagonal (UD) decomposition recursive least-squares (RLS) algorithm with an exponential sliding window (UD-SWRLS) has been implemented. This algorithm updates the autocorrelation matrix via UD decomposition, thereby virtually eliminating the likelihood of the filter becoming unstable as well as essentially eliminating the possibility of introducing artifacts that are not present in the signal. Additionally, the filter has the ability to track statistical changes in the signal with greater accuracy due to the implementation of an exponential sliding window. The UD-SWRLS implantation in adaptive signal averaging utilizes averaged data sets to recursively

calculate filter coefficients on which will be applied to new incoming data. The filtered data of each scan is averaged thus reducing the time needed to resolve a clean signal trace. The UD-SWRLS algorithm provides significant improvements in resolving relatively small features in magnetic resonance spectra, while displaying an improvement in signal to noise. The alogrithm can also be used in both real-time processing as well as post processing situations.

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EPR POSTER SESSION

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233 **Evaluation of Aromatic Rings Hydrogenation in Hidrocarbon Resins by NMR Spectroscopy.**

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C9 hydrocarbon resins (HCR) are thermoplastic resins produced from aromatic petroleum feedstock polymerization; different levels of aromatic ring content may be obtained through variations in the feedstock prior to polymerization and/or further hydrogenation processes. The aromatic content is direct related to the product's performance and properties. Therefore, it is important to define proper tools for evaluating HCR aromatic content.

Present in the main organic chemistry labs, ^{1}H-NMR spectroscopy is a powerful analytical tool, quantitative under certain conditions. As already present in the literature[1-3] the NMR spectrum can be clearly split among two regions related to the respective protons: the aliphatic from about 0.5 to 3 and the aromatics from about 6 to 9 ppm (ethylenic protons were not detected).

Several HCR were tested by ^{1}H-NMR and a quantitative model was demonstrate to calculate aromatic and saturated protons content. Those numbers correlates very well with the cloud point in aniline/methylcyclohexane, a property that measures the resin's compatibility in that solvent system and can indicate the aromatic/aliphatic content present in this type of sample. The proposed NMR method is been widely used by the researchers. In a short future, the fully chemical composition of those HC resins by advanced NMR experiments will be implemented.

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234 **Structural Dynamics of Biomolecules through Atomistic Simulations Guided by DEER Measurements.**

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235 **Fast Full-spectrum Kinetics Experiments by Rapid Scan EPR at X-band.**

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Rapid-scan EPR has been shown to yield increased signal-to-noise ratios in less acquisition time than traditional continuous wave EPR .[1]Prior studies have demonstrated the effectiveness of RS-EPR to study spin-trapped reactive oxygen species.[2]The study of rapid kinetics by CW-EPR usually requires monitoring intensity changes at constant magnetic field.[3]In RS-EPR, the main field is held constant while scan coils sweep the field, which permits much faster acquisition of spectra than traditional CW-EPR. This study extends RS-EPR methodology to acquire kinetic data with spectral resolution to improve detection of dynamic processes while monitoring spectral changes that occur on the acquisition timescale. A comparison of data-acquisition techniques is presented. Data will be shown for reductions of nitroxides by common antioxidants, bromine-mediated carbonyl formation from frequently used spin trapping agents, and dinitroxyl exchange coupling via disulfide reduction. The use of RS-EPR allows molecular dynamics to be observed on a timescale of seconds which is significantly shorter than the CW-EPR timescale of tens of seconds when using commercially available digitizers and realistic spectral acquisition parameters. Faster RS-EPR data acquisition will be possible as digitizers are improved and spectrometer overhead is decreased in the future.

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EPR POSTER SESSION

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236 **Calculation of Polycrystalline Pulsed EPR Signals with Relaxation by Phonon Modulation of Hyperfine and g Tensors Rigorously in Liouville Space using Stochastic Liouville Equation.**

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Stochastic Liouville equation has been used to calculate pulsed electron paramagnetic resonance (EPR) signals rigorously in Liouville space taking into account relaxation by phonon modulation of hyperfine and g tensors in polycrystalline materials. The calculations can be carried out within a reasonable time on a PC using Matlab. The flow chart for this simulation is included. It is illustrated for a coupled electron-nuclear system with the electron spin S= ½ and nuclear spin I= ½ to calculate the spin echo correlation spectroscopy (SECSY) and echo-electron-electron double-resonance (echo-ELDOR) signals. The flow chart for this simulation is included A software has been developed in Matlab, which only requires to input the parameters. It can be obtained from the authors upon request.

EPR POSTER SESSION

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237 **Lineshape Analysis of NV-detected Nanoscale EPR Spectroscopy.**

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Lineshape analysis of electron paramagnetic resonance (EPR) spectrum is a powerful method for characterization of paramagnetic centers employed in various fields including chemistry, physics, materials science and structural biology. For example, EPR analysis has led the identification of radical intermediates in chemical reactions by distinguishing EPR spectra with different g-values, the observation of dynamics of molecules in solution through analysis of the rotational correlation times and the determination of coordination geometry of metal ion sites by detecting hyperfine coupling of surrounding nuclear spins.

The nitrogen vacancy (NV) center is an atomic-scale fluorescent defect in diamond. EPR detection of a single spin using a NV center has been demonstrated at room temperature through measurement of a dipole magnetic field produced by the target spin located several nanometers away from the NV sensor. Therefore NV-detected EPR (NV-EPR) spectroscopy is potentially an ultimate method to perform EPR analysis of various systems with single spin sensitivity and careful lineshape

analysis of NV-EPR spectrum [1] will enable characterization of a small population of spin species, inhomogeneous nanoscale environments and dynamics of individual target spins which are hindered in ensemble EPR experiment. In this presentation we discuss lineshape analysis of NV-EPR spectroscopy to extract dynamics of target spins.

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EPR POSTER SESSION

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238 **Protein Cofactor Control of H2 Catalysis by [FeFe]-hydrogenase as Studied by Correlated Spectroscopy.**

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[FeFe]-hydrogenases catalyze one of the simplest PCET reactions in biology through the activation of molecular hydrogen from protons and electrons. We have been studying the reaction chemistry of the active-site H-cluster and how outer-sphere interactions enable coordinated movement of electrons and protons for rapid catalysis.[1] Using the algal HydA1 [FeFe]-hydrogenase and a combination of EPR, FTIR, and Mössbauer spectroscopy, we have shown that the catalytic hydride state (H_{hyd}) can be trapped when the proton-transfer kinetics are altered through modification of a nearby cysteine residue to serine.[2] Potentiometric titrations show that stabilization of H_{hyd} correlates with a shift in the midpoint potential, and fine-tuning of hydride binding through extended hydrogen-bonding demonstrates how the protein structure interacts with the H-cluster to control PCET.[3] Analogous studies on more complex [FeFe]-hydrogenases from *Clostridium pasteurianum* are probing how directional catalytic rates are controlled to favor either proton reduction or H_2 uptake reactions. These are leading to new observations on how the relative stabilization of redox states through secondary interactions can modulate catalytic reactivity and are revealing common principles for cofactor tuning relevant to other multi-electron redox reactions such as N_2 and CO_2 reduction. Related to this, we are developing photochemical techniques for probing mechanisms of electron-transfer and tracking electron-flux by EPR in redox enzymes and pathways for biological energy conversion.[4,5]

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EPR POSTER SESSION

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239 **The Quintet State Generation Process via Inter- and Intra-molecular Singlet Fission.**

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Singlet fission is a spin allowed process which a singlet exciton produces two triplet excitons. The singlet fission is potentially useful to improve the efficiency of photovoltaics, photodetectors and light emitters. Weiss et al. and Tayebjee et al. reported the time-resolved electron paramagnetic resonance (TREPR) spectra of the correlated triplet pair in the quintet state. The mechanism of spin conversion from singlet to quintet is significant for applications by prohibiting unwanted triplet-triplet annihilation which is the reverse reaction of the singlet fission.

In this study, we prepared aggregates of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn) and 2-phenyl-6,11-bis(triisopropylsilylethynyl)tetracene (TIPS-Ph-Tc) which undergo the intermolecular singlet fission. A tetracene dimer conjugated by an adamantane linker (Tc-Ad-Tc) which undergoes the intramolecular singlet fission.

Both aggregates showed similar TREPR signals except the peak separations due to the different zero-field splittings between tetracene and pentacene. The spin polarization patterns were well reproduced by the spectral simulation assuming that Q-2, Q-1 and Q0 states of five quintet sublevels are preferentially populated. The quintet generation mechanism is described by the fast triplet exciton migrations in the ordered area in aggregates. In contrast, the TREPR spectra of quintet state Tc-Ad-Tc generated by the intramolecular SF was described by the modulation of exchange interactions due to the molecular motions. This mechanism was also validated by the magnetophotoselection experiment. In the presentation, detailed spin dynamics in the singlet fission will be discussed.

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240 **Multi Frequency ESR Measurements of Organic Low-dimensional Antiferromagnets.**

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241 **Synthesis and Electron Spin Relaxation of Bis-Spirooxetane Nitroxide.**

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MTSL is the nitroxide that is used most commonly for double electron-electron resonance (DEER) measurements of the distance between paramagnetic sites in proteins. The longest distances that can be obtained by DEER are limited by the spin echo dephasing time T_m, which determines the length of the time window during which the dipolar evolution curve can be monitored. For MTSL and most other common nitroxides, there are gem-dimethyl groups on the two carbons adjacent to the nitroxide N-O moiety. Rotation of these methyl groups at rates that are comparable to the inequivalences in hyperfine couplings to the methyl protons is a very effective dephasing mechanisms that shortens T_m at temperatures between about 80 and 273 K. To perform DEER at temperatures above 80 K and eventually at ambient temperatures we are designing spin labels without methyl groups on the alpha carbons.[1,2] To keep the size and hydrophobicity of the nitroxide as small as possible we now report the synthesis of a bis-spirooxetane pyrroline nitroxide 1. The structure was confirmed by X-ray crystallography. The temperature dependence of T_m and T_1 in a trehalose glass were determined between 10 and 293 K. Relaxation times are compared with those for other methyl-free nitroxides.

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EPR POSTER SESSION

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242 **Positron Emission Tomography - Electron Paramagnetic Resonance Coimaging System: First Development Steps.**

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Positron Emission Tomography (PET) - Electron Paramagnetic Resonance (EPR) real-time co-imaging system[1] is being developed in West Virginia Health Sciences Center. PET and EPR major hardware components, such as scintillation crystals, magnet, scan coils, gradients will form a coaxial structure with the EPR resonator in its empty core of about 5 cm in diameter. The development of a bi-modal rapid scan (RS) resonator together with a mouse bed and RS coils that fit within the system core will be described. The PET/EPRI system will be used to study breast cancer mice models. Provided the spatial constraints and sensitivity requirements for high quality high-resolution imaging, a design for the excitation resonator is proposed that is somewhat in between a Helmholtz and butterfly configurations. In Helmholtz coils, two loops are parallel to each other. The butterfly configuration is flat. In the proposed design, the loops are angled at 45 degrees. The detection resonator is a standard surface loop. The detection loop can be positioned in a way that minimizes magnetic coupling with the detection resonator. In addition, a radiofrequency signal can be injected using a coupler to cancel out the residual transmission between the modes.

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EPR POSTER SESSION

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243 **Application of Pulse Shaping in Double Electron-Electron Resonance Spectroscopy at 115/230 GHz.**

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EPR POSTER SESSION

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244 **Combination of DFT Calculation and Solid State ^{13}C NMR in the Evaluation of Efavirenz Polymorphs.**

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Much attention has been focused on the study of the pre-disposition of some pharmaceutical solids to crystallize in various crystalline forms. Different forms of drugs may exhibit distinct chemical and physical properties, the most important being stability, dissolution and bioavailability. The thermodynamically stable form is generally chosen for the pharmaceutical development of the final commercial product.[1] Efavirenz ([4S] -6-chloro-4- [2-cyclopropylethynyl]-4-[trifluoromethyl]-2,4-dihydro-1H-3,1-benzoxazin-2-one, EFZ) is one of the drugs used in the anti-HIV cocktail.[2] In this work, two EFZ polymorphic forms reported in the literature were studied by electronic structure calculations (EFZII and EFZIII) and ^{13}C CPMAS NMR. The calculations were based on the density functional theory (DFT), with periodic boundary conditions and using flat-wave functions as basis, implemented in the Quantum-Espresso (QE) free access program. The electronic correlation and the terms of trade were used through the GGA-PBE functional. The results of geometry optimization obtained for the EFZII and EFZIII samples showed that DFT-D2 was the most adequate compared with PBE and vdW data. ^{13}C CPMAS NMR spectra obtained for forms I, II and III showed that the three forms are different. Based on these results, this work discussed the correlation among experimental, computational and literature data. The results evidenced some mistakes in the literature data for EFZ solid-state ^{13}C NMR assignment.

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245 **Electrostatics of Silica Nanoparticle - Water Interface by EPR of pH-Sensitive Spin Probes.**
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EPR POSTER SESSION
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246 **Frequency-Chirped Millimeter-Wave Control of ^{13}C-DNP in Diamond.**
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Electron and nuclear spins in diamond have long coherence and relaxation times at room temperature, making them a promising platform for applications such as biomedical and molecular imaging and nanoscale magnetic field sensing. While the optically-active nitrogen-vacancy (NV) defect has received a great deal of attention, the substitutional nitrogen (or P1) center also exhibits long coherence and relaxation times. These P1 centers are typically present at significantly larger concentrations (about an order magnitude larger) than NVs, allowing us to explore the role of P1-P1 interactions in mediating DNP. The system can, in principle, show DNP via the solid effect (SE), cross effect (CE) and Overhauser effect (OE) depending on the P1 concentration and the field.

Here, we show enhancement of natural abundance ^{13}C nuclei found within the diamond, using the unpaired electron of the P1 center (concentration 110-130 ppm) in particles with a 15-25 μm diameter, under static conditions at room temperature and 3.4 T. From the DNP spectrum we conclude that both the SE-DNP and OE-DNP mechanisms are active. The OE, in our case, results in negative enhancement, in contrast to previous results reporting positive OE enhancements. A negative OE implies that zero-quantum relaxation is more effective than double-quantum relaxation, likely due to strong anisotropic hyperfine interactions. We also explore the effect of frequency modulation (FM) of the DNP mechanism. Preliminary results suggest that the OE benefits from faster FM (>100 kHz) whereas the SE does not. This suggests that we can control which DNP mechanism is effective using FM parameters such as frequency, amplitude and shape.

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247 **Radical Clouds: Determining How Light Generates Free Radicals in Cloud Droplets in the Atmosphere.**
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Recent studies have found that brown carbon, or organic matter from the soil, has been found in high concentration in fogs, clouds, rainwater, and other atmospheric areoles.[1] Brown carbon is made from organic matter in the air called polycyclic aromatic hydrocarbons (PAH) which react with light, but the exact molecular reaction is not understood. PAH are products generated from burning fuel. Additionally, this reaction allows atmospheric metals, such as iron, to easily dissolve into surrounding water such as clouds, lakes, and other water sources.[2] Both the creation of brown carbon and solubility of iron in water result in the creation of reactive oxygen species (ROS). These free radicals cause adverse human health effects when inhaled or ingested, and furthermore should be prevented. To begin action against the production of brown carbon in the atmosphere, it is vital to learn how it is made. In this study, we mimicked the environment in which free radicals are formed in the atmosphere by placing an anthracene suspension under a simulated sun. X-band EPR spin trapping experiments were used to observe the ROS produced. Through this study, we aim to understand the chemical reaction on a molecular level and suggest a mechanism for the production of brown carbon and the formation of soluble iron.

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[2] *Atmos. Environ.*, **2010**, 44, 5165-5173

EPR POSTER SESSION
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248 **A THz ESR Study under High-Pressure using Hexaaqua Complex Salt Containing High-Spin Metal Ion.**

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Recently, the function of proteins is much more attract attention and measurement of high-pressure NMR about proteins showed many remarkable results in this field.1We reported the hemin as a model compound of metalloprotein using ESR employing terahertz light and high–pressure (HP–THz ESR)2, and zero–field splitting (ZFS) parameter D term was increased depending on load pressure raise. On the other hand, gz value was shown significant decreases in especially almost 0 to 1 GPa region, inversely. However, calibration of pressure in this system is not enough and estimated pressure value from the outer load is conceiving with containing some volume of errors. Because pressure standard marker like as DPPH as magnet field marker was not reported. Hence, Tutton's salt (TS) studied usability as a pressure standard marker.TS could understand from simple crystal field theory and precise ZFS parameters of various TS could be got from recent reports of Prof. Dr. Rudowicz group. A TS with Fe^{2+} ion (also called Mohr's salt) was measured in the region of up to 1.8 GPa and 0.4 THz. The result showed significant pressure dependence of E term (H//y) as increase of E = 3.7782 cm^{-1} (0 GPa) to E = 4.8345 cm^{-1} (1.8 GPa). This increase of E term had assigned from the decrease of symmetry of orthorhombic crystal structure depending pressure rise. Especially, referencing similar study without pressure,3increase of E term conclude as decrease of symmetry along x- and y-axis direction. In the presentation of the day, we will show the result in detail.

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EPR POSTER SESSION

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249 **Rapid Scan EPR Imaging of a Multi-sample Phantom.**

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As a demonstration of the application of rapid scan EPR to imaging at low frequency and field, a multi-compartment phantom containing six different samples was imaged. Samples include nitroxide radicals, trityl (triarylmethyl) radicals, and the oxygen-sensitive solid lithium phthalocyanine (LiPc), all of which are useful for in vivo imaging. The 2D spectral-spatial image demonstration was performed at 260 MHz, with samples in sealed tubes of various sizes arranged in a 3D-printed plastic holder. The importance of proper selection of resonator bandwidth and scan rate for obtaining various information about the spin system is demonstrated for a case in which the sample is composed of species with different signal bandwidths. For nitroxide, a 50 G sweep width is needed to include the three lines, while for narrow line samples such as trityl and LiPc, small sweep width (5 G) and slow scan frequency (2.5 kHz) are needed to avoid line broadening for the resonator Q of 70. Experiment showed that increasing the number of projections and increasing the number of data points digitized for each projection decrease the linewidth in spectral slices of the image, especially for trityl and LiPc.

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250 **Absorption and Dispersion Component Selection in a Non-Resonant Interferometric ESR Spectrometer.**

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A recent work has detailed the utilization of an interferometric microwave bridge for sensitive ESR detection using non-resonant microwave probes[1]. This highly adaptable non-resonant probe and sensitive bridge is capable of measurement on a wide range of materials and microwave frequencies without sensitivity penalties. However, the non-resonant arrangement is sensitive to both amplitude and phase and thus can measure both absorption and dispersion information. Automatic frequency control schemes used in the conventional resonant cavity for such line shape selection is largely incompatible with the interferometric bridge setup. Since the line shape analysis conveys a

significant amount of information[2] it is quite important to remedy this shortfall. In the non-resonant interferometric measurement, this problem is typically treated by iterating the difference between local oscillator phase and the bridge output until a reference sample line shape transitions to the desired component (absorption/dispersion). An unfortunate consequence of the interferometric bridge is that further tuning to improve cancelation (and overall sensitivity) can shift the phase difference between the local oscillator and the bridge output.

In this work, we detail an experimental technique which links the DC component of the mixer intermediate frequency output to the absorption/dispersion phase adjustment. A single calibration of this DC component to the phase adjustment removes the need for iterative line shape analysis to select pure absorption and dispersion. Moreover, it eliminates the experimental patience required to conduct such a line-shape analysis when observing a weak signal. An experimental approach to automate this calibration process will also be discussed.

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EPR POSTER SESSION

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251 **Magnetic Interactions and Coherence Transfer in Magnetic Graphene Nanoribbons.**

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252 **Ultra High Vacuum Transfer Chamber for High Field – Electron Paramagnetic Resonance.**

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Motivated by the broad area of application including quantum computing, optoelectronics, or sensor technology, the interest in a detailed description of microscopic processes in molecular nanomagnets (MNMs) deposited on surfaces has been increasing continuously.[1] Unfortunately, many MNMs on surfaces are sensitive to oxidation and decomposition under normal ambient conditions.[2] Therefore, minimizing the detrimental effects and preventing the formation of products of decomposition is a crucial step in the fabrication and characterization process. In this work, we present the set up and development of a general multi-purpose transfer system that will allow transporting air sensitive samples from an evaporation chamber to a spectrometer probe without exposure to atmospheric conditions. The transfer system connects our home-built high field electron paramagnetic resonance (HF-EPR) spectrometer with the in-house ultra-high vacuum (UHV) cluster located within the Nanofabrication and Characterization Facilities of the Central European Institute of Technology (CEITEC). Our HF-EPR spectrometer is based on rapid frequency scans that operate at frequencies between 80 GHz to 1100 GHz, at temperatures from 1.8 K to 300 K, and at magnetic fields up to 16 T. The high sensitivity of our EPR setup allows detecting small concentrations of paramagnetic molecules, and confirming the successful deposition and intactness of molecules on surfaces based on their magnetic properties. The design consists of a portable vacuum suitcase dedicated EPR airlock and an EPR sample holder that allows sample transferring from any UHV chamber with ConFlat (CF) flange into our highly precise HF-EPR spectrometer. Furthermore, our sample holder design contains electric contacts, temperature sensor, and heater for complex EPR experiment. The high spectral resolution achieved by higher magnetic fields and higher frequencies along with the proposed here handling

system enables exploring spin dynamics and other phenomena not accessible by the current commercially available technologies.

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[2] Caneschi, A et al., *Coord. Chem. Rev.*, **2015,** 178, 357-378.

EPR POSTER SESSION

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253 **Dipolar Linewidth and Decay of a Homogenous Distribution of Polarized Spins.**

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Double electron-electron resonance (DEER) spectroscopy is commonly used for distance measurements between spin labels attached to proteins or other biological macromolecules. The DEER signal consists of a product of a contribution from the desired intra-protein distance and a background decay due to coupling of observer spins on one protein with pumped spins on other proteins, which are uniformly and randomly distributed in 3D space. DEER experiments are commonly conducted in the high-temperature limit at low fields. In this regime, the DEER background has the form of a single exponential decay with constant phase. Outside this limit, i.e. in the presence of significant spin polarization, the background decay shows a phase that is linear in the dipolar evolution time and in the spin polarization. We derive this linear phase theoretically, confirm it with Monte Carlo simulations, and present experimental data at several fields and temperatures. The effect highlights an unexamined aspect of the fundamental spin physics underlying DEER spectroscopy.

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EPR POSTER SESSION

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254 **Effects of Natural Polymorphisms of Subtypes F and H HIV-1 Protease on Protein Conformations: A DEER and MD Investigation.**

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HIV-1 protease (PR) is essential to the maturation of HIV-1 virus as it post-translationally cleaves the viral polyproteins gag and gag-pol. Inhibition of HIV-1 PR leads to non-infectious and immature virus making it a drug target for HIV infection. The flaps of HIV-1 PR play an important role in its catalytic activity as they control access of substrate as well as inhibitor to the catalytic pocket of the protease. The flaps of HIV-1 PR adopt different conformations: closed, semi-open, wide-open, and curled/tucked.[1] Our previous studies show drug-pressure selected mutations shift conformational ensemble of HIV-1 PR to open-like conformations.[2,3] Natural polymorphisms are mutations naturally occurring in non-B variants compared to the widely studied subtype B. Natural polymorphisms can also shift conformational ensemble of non-B HIV-1 PR compared to subtype B.[4] In this study, double electron-electron resonance (DEER) and molecular dynamics (MD) simulations are utilized to study how natural polymorphisms affect protein conformational ensembles of subtypes F and H. Flap distance of nitroxide spin labeled PR measured by DEER show F and H predominantly adopt closed conformation as opposed to semi-open conformation as observed for subtype B. MD simulations show D60E and I62V mutations shift conformational ensembles to higher closed population.

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EPR POSTER SESSION

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255 **A New Insight into Stereolithography: EPR Mapping of Oxygen in 3D Printed Objects.**

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Oxygen plays a crucial role in the process of photopolymerization of many resins, especially in stereolithography (STL) 3D printing applications. The light induces the activation of photoinitiator to split into the free radical fragments which start the polymerization process of the resin. Resin dissolved oxygen acts both as photoinitiator quencher and free radical propagation termination agent. Therefore, an oxygen concentration in the resin governs the speed of the polymerization kinetics and the polymer quality (e.g., length of polymer chains, softness/hardness of resulting material[1]. Here we are presenting an electron paramagnetic Rapid Scan technique[2] for imaging of oxygen concentration during photopolymerization of acrylamides (STL polymerization). The mixture of commercially available acrylamide based resin (FLGPCL04 for Form2 3D printer by FormLabs) and oxygen sensitive octa-n-butoxynaphthalocyanine (LiNc-BuO) microcrystals was used to study the oxygen concentration profile during the light-activated polymerization process. The images of oxygen concentration and probe distribution for various time of light illumination show the applicability the methods for live monitoring of oxygen content/polymerization degree of the resin. Considering fast-growing area of application 3D printed techniques in medicine, dentistry, prosthetic, and bioprinting, we imply this method can be used for 3D material property and quality monitoring.

Acknowlegement: this work was supported by NIH grants EB022775 (M.T.), EB023888 (M.T.), U54GM104942, and P20GM121322 (A.B.). The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health.

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256 **Comparative EPR and Structural Analysis of $MgFe_2O_4$-ZnO Nanocomposite and its Constituents.**

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EPR and optical studies of pure $MgFe_2O_4$ and ZnO nanoparticles and $MgFe_2O_4$-ZnO nanocomposite have been done in order to explore its electronic and magnetic properties. Effect of incorporating zinc oxide in pure $MgFe_2O_4$ nanomatrix on structural properties was investigated using X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) techniques. UV-Visible and Photoluminescence spectra are used to determine band gap of composite for photocatalytic applications. FTIR spectra indicate the presence of absorption bands in the range 390–561 cm^{-1}, which is a common feature of spinel ferrite. The Energy Dispersive Spectroscopy (EDS) analysis confirms the composition of specimen. Further, the investigation of electronic and magnetic properties of the synthesized samples is done using Electron Paramagnetic Resonance (EPR) Spectroscopy. EPR parameters g value, peak-to-peak line width (Hpp), resonant field (Hr), and spin–spin relaxation time (T_2) were calculated and useful information drawn. Role of magnetic dipolar interaction and super exchange interaction in the EPR spectra also discussed.

EPR POSTER SESSION

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257 **Control of Solvent Dynamics and Confinement Effects Around the B_{12}-Dependent Ethanolamine Ammonia-Lyase in Frozen Aqueous Solutions by using Dimethyl Sulfoxide Adjustment of Mesodomain Volume.**

Benjamen Nforneh, Kurt Warncke
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The temperature-dependent structure and dynamics of two concentric solvent phases, the protein-associated domain (PAD, akin to the hydration layer) and mesodomain, that surround the protein, ethanolamine ammonia-lyase (EAL) from *Salmonella typhimurium* in frozen polycrystalline aqueous solution[1] are addressed by using electron paramagnetic resonance (EPR) spectroscopy of the paramagnetic nitroxide spin probe, TEMPOL, over the temperature (*T*) range, 195–265 K. Dimethyl sulfoxide (DMSO; added at 0.5, 2.0 and 4.0 % v/v), and present at the maximum freeze concentration at $T \leq 245$ K, varies the volume of the interstitial aqueous-DMSO mesodomain (V_{meso}), relative to a fixed PAD volume (V_{PAD}). The increase in V_{meso}/V_{PAD} from 0.8 to 6.0 is quantified by the partitioning of TEMPOL between the two phases. As V_{meso}/V_{PAD} is increased, Arrhenius parameters for activated TEMPOL rotational motion in the mesodomain remain uniform, while the parameters for TEMPOL in the PAD show a progressive transformation toward the mesodomain values (higher-mobility). An order-disorder transition (ODT) in the PAD is detected by exclusion of TEMPOL from the PAD into the mesodomain upon decreasing *T*. The ODT *T* value is systematically lowered by increased V_{meso}/V_{PAD} (from 215 to 200 K), and PAD ordering kinks the mesodomain Arrhenius dependence. Thus, there is reciprocity in PAD-mesodomain solvent coupling. The results are interpreted in terms of a dominant influence of ice-boundary confinement on PAD solvent structure and dynamics, that is transmitted through the mesodomain. This influence decreases with mesodomain volume at increased added DMSO. The systematic conntrol of PAD and mesodomain solvent dynamics by variation of added DMSO is the basis for an approach to resolution of contributions of protein-solvent dynamical coupling to EAL catalysis, through correlations of the ODT with the *T*-dependence of rates of single reaction steps.[2,3]

Supported by NIH R01 DK054514.

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EPR POSTER SESSION

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258 **Investigating the Oxidative Potential of Secondary Organic Aerosols on Polyunsaturated Fatty Acids and Lipid Membranes.**

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Airborne particulate matter found in industrial byproducts can promote lung, cardiovascular, and even cerebrovascular diseases. Much attention has been given to PM 2.5, a particulate matter found to penetrate the human lung barrier. A large fraction of PM 2.5 consists of secondary organic aerosols (SOAs), a gas-to-particle conversion of oxidized hydrocarbon vapors found in the atmosphere.

For the first time, we identify SOAs ability to oxidize polyunsaturated fatty acids (PUFAs) and cellular membranes of live mammalian carcinoma cells. In our study, three developed strategies were used to probe and assess the oxidative potential of SOA on several different lipid membrane systems. (1) Electro-Paramagnetic Resonance (EPR) with the usage of 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) spin trapping identifies the presence of carbon-based radicals in SOA-DMPO samples. We additionally show *in vitro* evidence for fatty-acid free radical formation using spin trap 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) with oxidized PUFAs in organic solvent. EPR spectra demonstrates an increase in radical adduct formation upon reaction of DMPO and SOA-oxidized PUFAs. (2) A Diphenyl-1-pyrenyphosphhine (DPPP) fluorescent probe employed in both PUFAs and live-mammalian cells showed a significant increase in DPPP oxide fluorescence when exposed to SOA, compared to controls. Our data further supports the production of free radicals in secondary organic aerosols, and their oxidative effect on different cellular membranes. (3) A 2',7'- Dichlorodihydrofluorescein diacetate (DCFH-DA) fluorescent probe was assayed to measure intracellular reactive oxygenated species (ROS) formation via flow cytometry. Our results demonstrated a larger shift in fluorescent cell population upon incubation with SOA. Microscopy imaging further supports a significant increase in green fluorescence denoting an increase in ROS production upon incubation of SOA. Our results demonstrate the oxidative potential of secondary organic aerosols and its profound oxidative damage in both *in vivo* and *in vitro* experiments.

Results from this study will be used assess oxidative damage upon SOA exposure to pulmonary and cardiovascular cell strains, as well as various compositions of PUFA-derived liposomal membranes.

EPR POSTER SESSION

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259 **A Cyclic Disulfide Bridged Dinitroxide Probe for Determining Tissue Redox Status.**

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Methods to measure tissue physiology including oxidation-reduction (redox) status are important for the characterization and treatment of diseases such as cancer or traumatic brain injury. Elajaili et al. previously described a dinitroxide for which cleavage of a disulfide linkage disrupted the exchange interaction between two nitroxide moieties and converted the five-line dinitroxide spectrum into a three-line monoradical spectrum.[1] It was shown later in vivo by Epel et al. that this dinitroxide could be utilized in imaging to determine redox status in murine tumors.[2] For these initial experiments the redox status was characterized by the rate of cleavage of the disulfide linkage. Here we present an improved version of this disulfide dinitroxide system and its reactions with select thiol species. In its oxidized form, a cyclic structure prevents interaction of the two nitroxide centers. The resulting spectrum is the typical three lines expected for a mono-radical. After reduction, the dinitroxide can adopt conformations that allow for significant exchange, producing a five-line spectrum. The redox reaction is reversible, so the new probe is designed to monitor the in vivo redox status based on both the kinetics and the equilibrium populations of the oxidized and reduced forms of the dinitroxide indicator molecule. A crucial step for utilizing a system such as this is the quantitative determination of the contribution of each conformation to the spectrum. To accomplish this goal, a previously described EasySpin simulation function that was developed for these experiments was used.[3] Results will be discussed for reactions with several thiols.

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EPR POSTER SESSION

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260 **H/D Isotope Effects: Experimental Evidence for the Key Role of Intramolecular Vibrations in Spin Dynamics.**

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3. National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA.

Recent years, the applications of single-ion magnets (SIMs) in quantum computing magnetic molecules become an exciting research topic for both chemists and physicists.[1,2] We report two low spin Co(II) complexes, {[CoL](CH_3CN)}$[BPh_4]_2$·CH_3CN (**1-H**, L = 1,5-bis(2pyridylmethyl)-1,5-diazacyclooctane) and {[CoL](CD_3CN)}$[BPh_4]_2$·CD_3CN (**2-D**), with only CH_3CN and CD_3CN difference. They show distinct slow magnetic relaxation at low temperature. Time-domain THz spectra indicate that the slow magnetic relaxation mechanism is from intramolecular vibration/spin-vibration (phonon) coupling. The *ac* susceptibility under different external *dc* field demonstrates that the vibration modes coupled with spin are magnetic field dependent, which gives a clear picture to help understanding the spin-phonon coupling. Quantum coherence was detected with the 240 GHz high field pulsed EPR in both 100% and 5% samples. The spin decoherence time is up to *ca* 1.2 μs at 1.6 K with undiluted complex, which is surprisingly long for a spin in a nuclear spin rich surrounding. Comparing the magnetic dynamics and quantum coherence properties of **1-H** and **2-D**, H/D isotope effects provide direct experimental evidence for the key role of intramolecular vibrations both in spin-lattice relaxation and spin-spin relaxation processes.

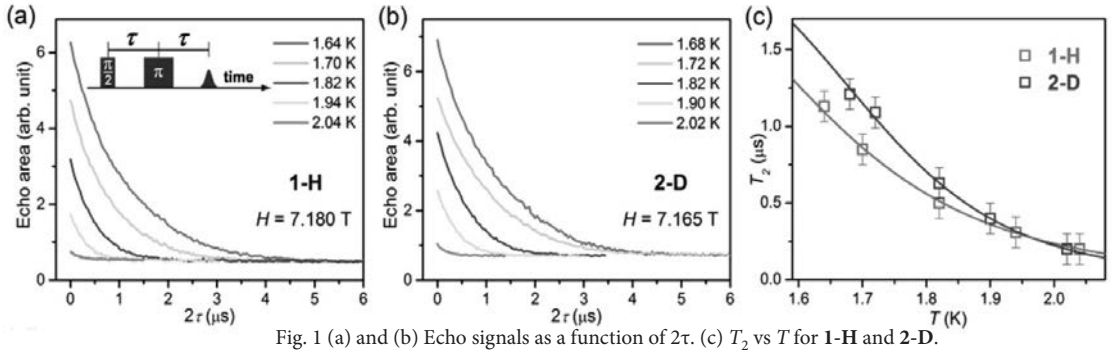

Fig. 1 (a) and (b) Echo signals as a function of 2τ. (c) T_2 vs T for **1-H** and **2-D**.

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261 **Mapping Out the Degree of Freedom of Hosted Enzymes in Confined Spatial Environments using EPR Spectroscopy.**

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Unraveling the relation between the spatial environment of a host material and performance of encapsulated enzymes is of fundamental importance for a wide range of applications. A detailed understanding of the underlying structure-property relationships between host-guest interactions and the resulting enzymatic performance, expressed in terms of the mobility of the enzymes, though of great interest for biocomposite development, is still lacking. Here, we present a comprehensive elucidation of the impact of confined spatial environments on the degree of freedom of the hosted enzymes and consequently, their accompanying reactivity. Site-directed spin labeling in combination with electron paramagnetic resonance spectroscopy (SDSL-EPR) allows direct detection of the host-guest interactions at atomic resolution in the presence of complexities caused by the background signals from the host materials and host-guest interactions. Meanwhile, the tailorable synthesis of covalent organic frameworks (COFs) enables an evaluation of the factors affecting such interactions. Specifically, the enzyme is found to be more constrained and less active along with the increased hydrophilicity of the COF materials. These results support the establishment of a connection between the hydrophilicity of the spatial environment and the resulting biocomposites' reactivity, enabling the prediction of the enzymatic activity for unknown biocomposites. This study provides unique insight into the mechanistic pathways underpinning biocatalysis and allows for the development of COF materials to mimic the confined cellular environments so that complex in-cell structure and function studies for sophisticated enzymes can be performed in a cell-free platform.

EPR POSTER SESSION

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262 **ESR and Magnetization Studies on $Cu_4(OH)_6FCl$: An Antiferromagnet with Kagome Lattice**

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Geometrically frustrated magnets have attracted considerable interests due to their exotic ground states especially the quantum spin liquid state. The herbertsmithite $ZnCu_3(OH)_6Cl_2$ is one of the best materials for realizing spin liquid state. However, a small amount of Cu^{2+} ions is diluted by Zn^{2+} in the kagome layers and accordingly interkagome Zn^{2+} can be replaced by Cu^{2+}. Recently, the barlowite $Cu_4(OH)_6FBr$ with kagome motif has been synthesized and it is thought

as a new spin-liquid candidate. While, antiferromagnetic (AFM) ordering appears at 15 K accompanying with a week ferromagnetic (FM) moment. In this work, we have successfully synthesized the claringbullite $Cu_4(OH)_6FCl$, a related polymorph to clinoatacamite $Cu_2(OH)_3Cl$, isostructural with the barlowite. The magnetic susceptibility gives Curie-Weiss temperature θ_{CW} = 135 K and two magnetic anomalies at T_1 = 15 K and T_2 = 4.8 K with weak ferromagnetism. The empirical frustration factor is about $f = |\theta_{CW}|/T_1 = 9$, implying a strong frustration in this system. The nearest-neighbor exchange coupling J is estimated to be $J/k_B = -166$ K by fitting the data between 125 K and 300 K according to the tenth-order high-temperature series expansion (HTSE). The anomalies at T_1 and T_2 can be further observed in specific heat data at zero field. However, no λ-like peaks expected for long-range magnetic order. The high-field ESR data are strongly correlated with the magnetism. The ESR linewidth is broadened with decreasing temperature. No significant peak shift is observed until T_1 = 15 K, below which the resonance field shifts to lower field. At 4.2 K, the resonance splits into three peaks, 1, 2 and 3. A gapless mode 1 observed at all temperatures. Two gapped modes 2 and 3, corresponding to different temperature regions: $T<T_1$ (= 15 K) and $T<T_2$ (= 4.8 K), respectively.

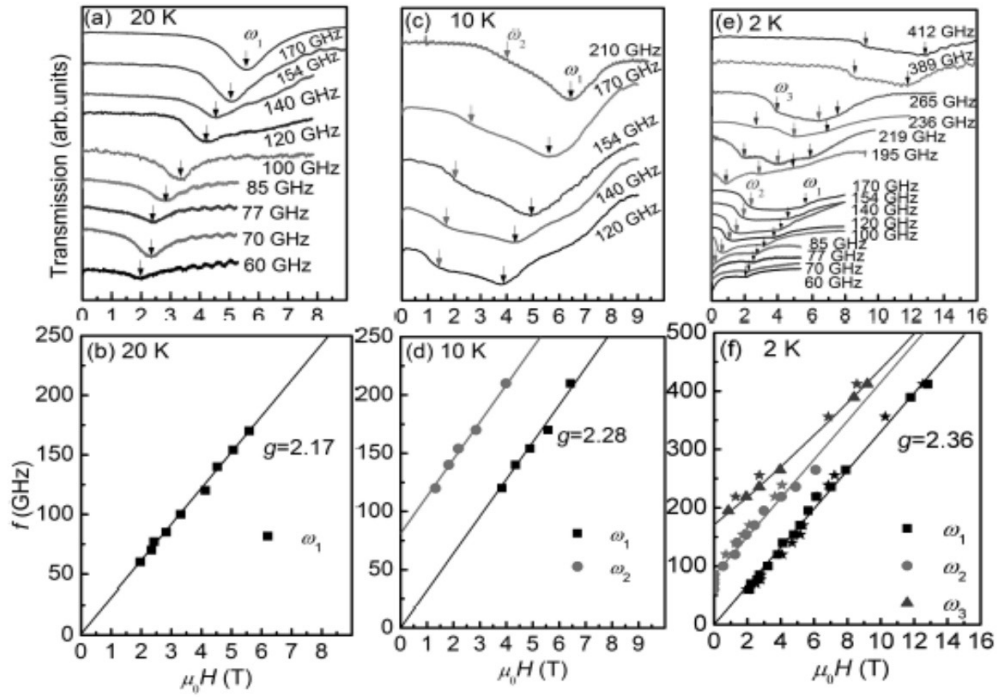

Fig. 1 Frequency-dependent ESR spectra and the corresponding *f-H* relations measured at 20, 10 and 2 K for $Cu_4(OH)_6FCl$. The red line is the calculated curve based on the FM-like resonance. In (f), the asterisks stand for the data for the barlowite. The black and blue lines are guides to the eyes for AFM-like resonances with easy-plane anisotropy.

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263 **Steady State and Time Resolved Electron Paramagnetic Resonance Investigations of Structured Fluids.**

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Electron paramagnetic resonance (EPR) is a spectroscopic technique commonly used for the investigation of the structure, dynamics, and reactivity of any paramagnetic species. EPR spectra of free radicals can provide information about their molecular environment, such as polarity and viscosity. In this project, structured fluids based on silica-based Aerosils suspended in organic solvents have been studied using nitroxide free radical spin probes. Steady state EPR and Time Resolved EPR (flow system) were used to better understand the fluid dynamics and photochemistry dynamics at molecular level. Spectra of Aerosil/n-octane solutions using the TEMPONE spin probe have revealed that the rotational correlation time is very sensitive to the % loading of the Aerosil. Besides, on this project research, we did the Temperature dependent research. Through TREPR spectra, the dynamics of radical pairs (RPs), the structural and dynamic parameters are explored.

EPR POSTER SESSION

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264 **Site-directed Spin Labeling of Proteins using NcAA-mediated Conjugation Techniques and a Photocaged Nitroxide.**

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265 **Quantum Sensing at High Pressures using Spin Defects in Diamond.**

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EPR POSTER SESSION

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266 **Determining the Relative Orientation of Rigidly-Bound Cu^{2+} Spin Labels in Biomolecules by Electron Paramagnetic Resonance.**

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- Automated systems for emergency dosimetry for large events (radiation triage)

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- Small animal systems
- Large animal systems

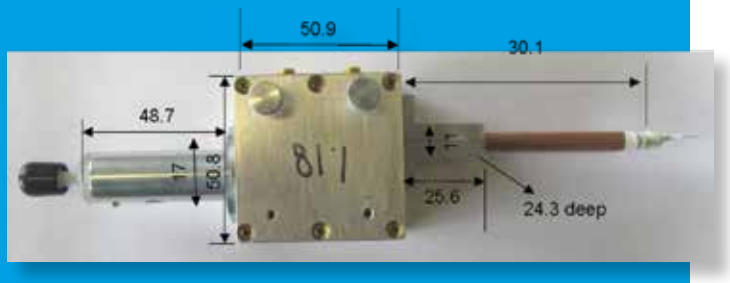
Components for Applications in Humans and Animals (L-Band)

CLINICAL:

- Surface probes for measurements of oxygen or free radicals
- Flexible resonators to minimize effects of pressure and motion artifacts
- Implantable resonators (Developmental for clinical use – currently preclinical only)
- Intraoral (for tooth dosimetry)

PRECLINICAL RESEARCH:

- Surface probes
- Implantable resonators



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