Rocky Mountain Conference on Magnetic Resonance

Volume 55 *55th Annual Rocky Mountain Conference on Magnetic Resonance* Article 1

7-28-2013

55th Annual Rocky Mountain Conference on Magnetic Resonance

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Abstract

Final program, abstracts, and information about the 55th 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 28 - August 1, 2013.

55TH ANNUAL ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 28 – August 1, 2013

Crowne Plaza Denver

Denver, Colorado, USA

www.rockychem.com

55TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 28 – August 1, 2013

Crowne Plaza Denver • Denver, Colorado

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ORGANIZERS AND CHAIRPERSONS

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&
Society for Applied Spectroscopy

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ROCKY MOUNTAIN CONFERENCE INFORMATION

REGISTRATION

Admission to all technical sessions is by name badge only. Registration materials may be picked up at the RMCMR registration area located at the Crowne Plaza Denver between 1:00 p.m. and 5:00 p.m. on Sunday, July 28 or anytime 8:00 a.m. to 5:00 p.m., Monday, July 29 through Thursday, August 1.

CONFERENCE RECEPTION

Monday evening from 5:30 – 7:00 p.m., all attendees are cordially invited to join in on cocktails and hors d'oeuvres. Unwind from the day's events and continue the "Rocky Mountain Conference" experience.

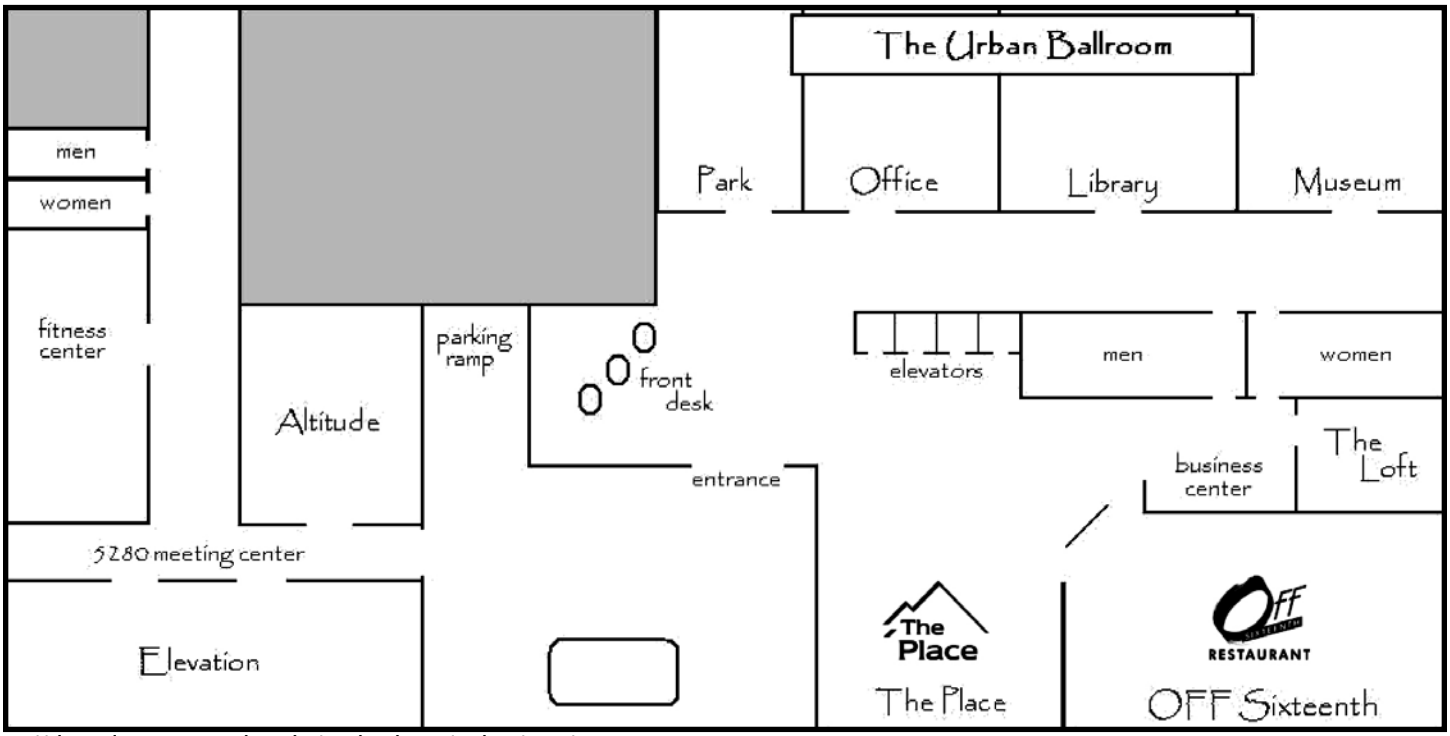
MESSAGES

Messages will be accepted and posted on the message board located next to the Rocky Mountain Conference registration desk. Call 800-996-3233 or 303-690-3233 to leave messages.

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.
EPR Lectures	*Library / Museum*										
EPR Posters	*Park / Office*										
Workshops	*University of Denver EPR Lab*										

CROWNE PLAZA DENVER MEETING SPACES



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36TH INTERNATIONAL EPR SYMPOSIUM

&

55TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 28 – August 1, 2013

Crowne Plaza Denver – Denver, Colorado

CONFERENCE CHAIR

Kurt W. Zilm

EPR SYMPOSIUM COMMITTEE

Gail Fanucci • Chair

Christoph Boehme, Howard Halpern, Fraser MacMillan,
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REGISTRATION

Register at www.rockychem.com

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EPR SYMPOSIUM – Oral Sessions

MONDAY, JULY 29, 2013

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8:00 a.m.		**Welcoming Remarks**. Gail Fanucci, EPR Symposium Chair
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8:50 a.m.	102	**Design and Use of Superconducting Resonators for Pulsed ESR.** David Cory, University of Waterloo
9:25 a.m.	103	**The Effect of ^{29}Si Spectral Diffusion on ^{31}P Neutral Donor Nuclear Spins.** Evan Petersen, Princeton University
9:40 a.m.	104	**Hole Injection in Fullerene Based Semiconductors.** Hiroki Morishita, University of Utah
10:00 a.m.		*Break*
10:30 a.m.	105	**Dramatic Increase of Electron Spin Decoherence Time for Bismuth Donors in Silicon at Clock Transition 7.0317 GHz.** Steve Lyon, Princeton University
10:50 a.m.	106	**Spin-Dependent Recombination in Organic Light-Emitting Diodes and the Effect of Phosphorescent Emitters.** T.L. Keevers, University of Sydney
11:05 a.m.	107	**Shuttling Electrons On and Off as Donor Atoms in Silicon.** Alexei Tyryshkin, Princeton University
11:25 a.m.	108	**TBA.** Amir Yacoby, Harvard University
12:00 p.m.		*Lunch*
SESSION II, MATERIALS, DANE MCCAMEY CHAIRING		
1:35 p.m.	109	**ODMR and EDMR in Organic Semiconductors and Devices.** Joe Shinar, Iowa State University
2:10 p.m.	110	**Overcoming Decoherence of Spin-based Qubits in Solid-state Systems.** Susumu Takahashi, University of Southern California
2:45 p.m.	111	**Theoretical *ab-initio* Modelling of P_b-like States at Silicon Related Interfaces.** Uwe Gerstmann, Universität Paderborn
3:00 p.m.		*Break*
3:20 p.m.	112	**Time-Resolved ESR Spectroscopy Investigation of Photoconduction Mechanism in Covalent Organic Framework (COF) Materials.** Toshikazu Nakamura, Institute for Molecular Science
3:40 p.m.	113	**EPR and Electrochemical Investigations on the Oxidation of Highly Crowded Organophosphines and Arsines.** Rene Boere, University of Lethbridge
4:00 p.m.	114	**Mystery of Non-equivalent Centers in Congruent and Stoichiometric $LiNbO_3$ and $LiTaO_3$.** Galina Malovichko, Montana State University
4:30 p.m.	115	**New Opportunities for High-field MR Spectroscopy to Study Oxide Heterostructures and Materials for Photovoltaic Applications.** Matthias Fehr, University of California, Santa Barbara
4:45 p.m.	116	**Temperature Dependent Magnetic and EPR Studies of Bulk and Nanoparticles of $Bi_{0.1}Ca_{0.9}MnO_3$.** Geetangali Singh, Indian Institute of Science
5:00 p.m.		**Group Discussion.**
5:30-7:00 p.m.		*Conference Reception*
SESSION III, POSTERS		
7:30-9:00 p.m.		**Authors Present for Posters Labeled A**

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TUESDAY, JULY 30, 2013

SESSION IV, METHODS, CHRISTOPH BOEHME CHAIRING		
8:05 a.m.	120	**Electrically Detected Magnetic Resonance – Basic Concepts and Applications.** Carlos Graeff, DF-FC-UNESP
8:40 a.m.	121	**Recent Progress in Pulsed EDMR.** Martin Brandt, Technical University of Munich
9:15 a.m.	122	**Spin Lattice Relaxation at High Fields and Low Temperatures.** Hans Van Tol, National High Magnetic Field Laboratory
9:35 a.m.	123	**Multi-Extreme THz ESR: Its Development and Application.** Hitoshi Ohta, Kobe University
9:55 a.m.	124	**Continuing Development of a Free Electron Laser-based EPR Spectrometer.** Devin T. Edwards, University of California, Santa Barbara
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10:30 a.m.	125	**Readout and Control of a Single Nuclear Spin with a Meta-stable Electron Spin Ancilla in Diamond.** Sang-Yun Lee, Universität Stuttgart
11:05 a.m.	126	**EPR Probeheads for Very Small Samples: Developments and Prospects.** Edward Reijerse, Max Planck Institute for Chemical Energy Conversion
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11:45 a.m.	128	**Signal Detection During Detector Dead Time with Arbitrary Waveform Generation in Pulsed EPR.** Ryan Barnes, University of California, Santa Barbara
12:00 p.m.		*Lunch*
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2:40 p.m.	131	**New EPR insights on the catalytic model for H_2 activation by the [FeFe]-hydrogenase H-cluster in HydA1 from *Chlamydomonas reinhardtii*.** David Mulder, National Renewable Energy Laboratory
2:55 p.m.	132	**Analysis of Metal-RNA Interactions by EPR Methods.** Vicki DeRose, University of Oregon
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3:50 p.m.	133	**Locating NO in the $\{FeNO\}^7$ Complex Using HYSCORE: A Structural Context for Locating Substrates in Non-heme Fe(II) Dependent Dioxygenases Using ESEEM.** Thomas Casey, Michigan State University
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WEDNESDAY, JULY 31, 2013

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8:45 a.m.	146	**Nitroxide and Trityl Radical Probes for Multifunctional in vivo EPR Spectroscopy and Imaging.** Valery Khramtsov, Ohio State University
9:20 a.m.	147	**Spin Dynamics of Concentrated "Finland" Trityl Radicals at Cryogenic Temperatures.** Mike Bowman, University of Alabama
9:40 a.m.	148	**250 MHz to 34 GHz Study of Nitroxide Relaxation Mechanisms.** Josh Biller, University of Denver
10:00 a.m.		*Break*
10:30 a.m.	149	**Diradicals and Polyradicals: Synthesis, Magnetism, and Spin-Spin Interactions.** Andrezj Rajca, University of Nebraska
11:05 a.m.	150	**The Amide Nitroxide: Coming to a EPR Spectrometer Near You.** Garland Marshall, Washington University
11:30 a.m.	151	**High-Field EPR Studies of Organic Radical Ferromagnets Under High Pressures.** Stephen Hill, NHMFL
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2:10 p.m.	153	**Five-pulse DEER: Improved Distance Range and Sensitivity.** Peter Borbat, Cornell University
2:30 p.m.	154	**Distances and Orientations with DEER/PELDOR at High EPR Frequencies.** Igor Tkach, Max Planck Institute for Biophysical Chemistry
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4:10 p.m.	156	**Distance Measurements in Biomolecules Using Gd^{3+} Spin Labels – Pros and Cons.** Daniella Goldfarb, Weizmann Institute of Science
4:45 p.m.	157	**Complex Docking Models – Elucidating Protein-protein Interactions With EPR.** Morgan Bye, University of East Anglia
5:00 p.m.	158	**A Single-stranded Junction Modulates Nanosecond Motional Ordering of the Substrate Recognition Helix of a Group I Ribozyme.** Phuong Nguyen, University of Southern California
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8:00-9:30 p.m.		**Authors Present for Posters Labeled B**

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THURSDAY, AUGUST 1, 2013

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9:55 a.m.	169	**Water Soluble Complexes of Xanthophyll Antioxidants: Aggregation vs. Complexation.** Adam Magyar, University of Alabama
10:10 a.m.	170	**Characterization of the Electronic Structure of P450 Compound I: Implications for Reactivity.** Alexey Silakov, Pennsylvania State University
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11:20 a.m.	172	**Interaction Between Anti-HIV Antibody 10E8 and its Lipid-embedded Epitope Defined by EPR.** Likai Song, National High Magnetic Field Laboratory
11:40 a.m.	173	**Effects of Lipid Bilayer Phase and Nanoscale Curvature on Surface Electrostatic Potential as Measured by Spin-probe EPR.** Amir Koolivand, North Carolina State University
11:55 a.m.	174	**Magnetic Interaction of Transition Ion Salts With Spin Labeled Lipid Membranes: Hofmeister Anion-driven Adsorption of Ions, Membrane Fluidity and Flexibility of Nitroxide Tethers.** Boris Dzikovski, Cornell University
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EPR SYMPOSIUM
Poster Sessions

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7:30–9:30 p.m. *(Poster Session A)*

TUESDAY, JULY 30, 2013
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A	182	**EPR Studies of Pressure induced Jahn-Teller Reorientation in the Coordination Polymer: [CuF2(H2O)2(pyrazine)].** C. C. Beedle, Florida State University
B	183	**Characterizing Lung Surfactant Peptide and Lipid Interactions in Different Timescales.** Otonye Braide, University of Florida
A	184	**Locating NO in the {FeNO}7 Complex using HYSCORE: A Structural Context for Locating Substrates in non-heme Fe(II) Dependent Dioxygenases using ESEEM.** Thomas M. Casey, Michigan State University
B	185	**Dipolar Relaxation of Trityl Radicals at Low Temperatures.** Hanjiao Chen, The University of Alabama
A	186	**Impurities and Spin Relaxations in Nanodiamonds.** Franklin H. Cho, University of Southern California
B	187	**Zero- and Low- Field Study of Spin Dependent Trap Assisted Tunneling in Amorphous SiC:H Thin Film Dielectrics.** C.J. Cochrane, The Pennsylvania State University
A	188	**EPR studies of Orthorhombic Jahn-Teller Effect in Cu(II) doped (NH4)2Cd2(SO4)3 (ACS) Single Crystals. Paper I.** Dilip Kumar De, Kaduna State University
B	189	**Applications of Portable Nuclear Magnetic Resonance Spectrometers.** Jacob Donohoue, Overland High School, Science Department, and National Aeronautics and Space Administration
A	190	**Synthesis and Frequency Dependence of Semiquinone Relaxation Times.** Hanan B. Elajaili, University of Denver
B	191	**SpecMan4EPR 2.0: Shaped Pulses using SpinCoreTM RadioProcessorTM and PulseBlasterDDSTM Boards** Boris Epel, University of Chicago
A	192	**Studying Conformational Changes In The Glycine Riboswitch Using Electron Paramagnetic Resonance Spectroscopy.** Jackie M. Esquiaqui, University of Florida
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A	200	**Site Localization and Rigid-body Docking in the MMM Software Package.** G. Jeschke, ETH Zürich
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A	202	**X-Band EPR Spectrometer with Customizable Arbitrary Waveform Generator for Precise Tailoring of Pulses as "Seen" by the Spins.** Timothy J. Keller, University of California Santa Barbara
B	203	**Effects of Lipid Bilayer Phase and Nanoscale Curvature on Surface Electrostatic Potential as Measured by Spin-probe EPR.** Amir Koolivand, North Carolina State University
A	204	**Electron Spin Relaxation Measurements of the Oxygen-Induced Radicals in neuronal Nitric Oxide Synthase.** Matthew D. Krzyaniak, The University of Alabama
B	205	**Orientation of Phospholamban in Lipid Bicelles Detected by Electron Paramagnetic Resonance.** Jesse E. McCaffrey, University of Minnesota
A	206	**Exploring the Catalytic Mechanism of Tyrosine Hydroxylase.** John McCracken, Michigan State University
B	207	**DEER Reveals that Single Point Mutations Modulate Seed Selection in Fibril Growth of Tau** Virginia Meyer, University of Denver
A	208	**Improving Sensitivity of Detection of Biologically-Generated Radicals by Rapid-Scan EPR.** Deborah G. Mitchell, University of Denver
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A	210	**Sucrose Radicals Induced by Low Dose Irradiation with X-ray.** K. Nakagawa, Graduate School of Health Sciences
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B	213	**A Spin Label Derived from Mannosamine.** Joseph T. Paletta, University of Nebraska-Lincoln
A	214	**EPR and FTIR Insights in to the Enzymatic Mechanism of H2 Activation by the [FeFe]-Hydrogenase HydA1 from *Chlamydomonas reinhardtii*.** Michael W. Ratzloff, National Renewable Energy Laboratory
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A	**222**	**Broadband Magnetic Resonance of Magnetic Nanoparticles.** Robert J. Usselman, National Institute of Standards and Technology
B	**223**	**Modulation of Intracellular Reactive Oxygen Species by External 7 MHz Radio Frequency Magnetic Fields.** Robert J. Usselman, National Institute of Standards and Technology
A	**224**	**Radical Model for Arsenic Toxicity: Experimental EPR Spin Trapping and Theoretical Studies.** Frederick A. Villamena, The Ohio State University
B	**225**	**Structure and Dynamic Properties of the Mesodomain Environment of the Protein, Ethanolamine Ammonia-Lyase, in Frozen Aqueous Sucrose Solutions.** Kurt Warncke, Emory University
A	**226**	**Optical Detection of Coherent Electron Spin States of Silicon Vacancy Defects in Silicon Carbide.** Matthias Widmann, Stuttgart University
B	**227**	**Super-absorbent Polymers as Matrices for EPR.** Zhelin Yu, University of Denver
A	**228**	**Effects of Fluorine on the Structure of Fluorohydroxyapatite: a Solid-State NMR Study.** Peizhi Zhu, Yangzhou University

ABSTRACTS

EPR SYMPOSIUM
Oral Sessions

101 **TBA.**
Patric Bertet, CEA Saclay

102 **Design and Use of Superconducting Resonators for Pulsed ESR.**
David G. Cory,[1,2,3] Olaf Benningshof,[1,4] Troy Borneman,[1,4] Guoxing Miao,[1] Hamid Resa Mohebbi,[1] Ivar Taminiau,[1] Chris Wood[1,4]

University of Waterloo, Waterloo, Ontario, Canada
1. Institute for Quantum Computing
2. Department of Chemistry
3. Perimeter Institute for Theoretical Physics
4. Department of Physics and Astronomy

We will report on the design, fabrication and applications of a range of superconducting resonators for X-band pulsed ESR. These resonators achieve high quality factors and low mode volumes for small 3-D and 2-D sample geometries. They enable improved S/N and can reach strong coupling when filled with sufficient numbers of spins. To use these effectively demands new pulse control methods that combine classical and optimal control, which we will describe. The resonators are an essential element of our design for a hybrid quantum information processor where electron spins are quantum actuators for nuclear spin qubits. This new architecture will be described.

ORAL SESSION
David Cory, Institute for Quantum Computing, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada
E-mail: dcory@uwaterloo.ca

103 **The Effect of ^{29}Si Spectral Diffusion on ^{31}P Neutral Donor Nuclear Spins.**
Evan S. Petersen,[1] A.M. Tyryshkin,[1] S.A. Lyon,[1] J.J.L. Morton,[2] S. Tojo, K.M. Itoh,[3] M.L.W. Thewalt,[4] H. Riemann, N.V. Abrosimov,[5] P. Becker,[6] H.J. Pohl[7]

1. Princeton University, Department of Electrical Engineering, Princeton, NJ 08544
2. University College London, London Centre for Nanotechnology, London WC1H 0AH, UK
3. Keio University, Department of Applied Physics and Physico-Informatics, Yokohama 223-8522, Japan
4. Simon Fraser University, Department of Physics, Burnaby, British Columbia V5A 1S6, Canada
5. Institute for Crystal Growth, 12489 Berlin, Germany
6. Physikalisch-Teknische Bundesanstalt, D-38116 Braunschweig, Germany
7. VITCON Projectconsult GmbH, 07743 Jena, Germany

Magnetic field fluctuations arising from nuclear spin flip-flops are often found to be the main source of *electron* spin decoherence in systems containing magnetic nuclei. Here we demonstrate that the same nuclear spin flip-flops can also be a source of *nuclear* spin decoherence. We use pulsed ENDOR (X-band) to measure ^{31}P nuclear spin decoherence[1] for neutral phosphorus donors in lightly-doped (~10^{15} /cm^3) silicon crystals with ^{29}Si magnetic nuclei concentrations of 1%, 4.7% (natural abundance), 10%, and 50%. The light donor doping and measurement temperature of 1.7 K ensure that neither electron spin flips nor flip-flops limit the nuclear T_2. We find that the resulting nuclear T_2 decays are non-exponential and are best described by $\exp(-(2t/T_2)^2)$, which is characteristic of spectral diffusion due to environmental (^{29}Si) nuclear spin flip-flops. The T_2 times extracted from fitting curves are found to scale inversely proportionally with ^{29}Si density in the silicon crystals. The nuclear decoherence time of neutral phosphorus donors in natural silicon is approximately 1 second, about 2000 times longer than donor electron spins in natural Si. *This research was supported by NSA/LPS through Lawrence Berkley National Laboratory (contract #100000080295).*

[1] J. J. L. Morton et al., Nature 455, 1085 (2008)

ORAL SESSION
Evan S Petersen, Princeton University, B417 Equad, Olden St., Princeton, NJ, 08544, USA
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104 **Hole Injection in Fullerene Based Semiconductors.** Hiroki Morishita, University of Utah
H. Morishita,[1] W. J. Baker,[1] D. P. Waters,[1] R. Baarda,[1] J. M. Lupton,[1,2] C. Boehme[1]
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Fullerene based semiconductor materials have been considered to be pure electron acceptors and conductors. Minority hole carriers are in the literature often considered to be irrelevant. Here, we present an experimental test of this hypothesis. Room temperature pulsed electrically detected magnetic resonance (pEDMR) measurements have been performed on [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) thin film devices. A current was applied to devices with unipolar and bipolar injectors. This current was then monitored transiently after a coherent (pulsed) magnetic resonant excitation was applied. The measurements did not reveal any signal for unipolar electron devices which suggests that spin-dependent transport mechanisms are not dominant in PCBM. However, under bipolar injection, at least two pronounced spin-dependent signals were detected whose magnitudes increased as the devices degraded upon exposure to air. Electrical detection of spin-Rabi beat oscillation revealed that one of these two signals is due to weakly coupled pairs of spins with s=1/2. We therefore attribute this signal to electron-hole recombination. This observation shows that while PCBM is a poor hole conductor, hole injection can be significant.

ORAL SESSION

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105 **Dramatic Increase of Electron Spin Decoherence Time for Bismuth Donors in Silicon at Clock Transition 7.0317 GHz.** Gary Wolfowicz,[1,2] Alexei M. Tyryshkin,[3] Richard E. George,[1] Helge Riemann,[4] Nikolai V. Abrosimov,[4] Peter Becker,[5] Hans-Joachim Pohl,[6] Mike L. W. Thewalt,[7] Stephen A. Lyon,[3] John J. L. Morton[1]
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A major challenge in using spins in the solid state for quantum technologies is protecting them from sources of decoherence. This can be addressed, to varying degrees, by improving material purity or isotopic composition for example, or active error correction methods such as dynamic decoupling, or even combinations of the two. However, a powerful method applied to trapped ions in the context of frequency standards and atomic clocks, is the use of particular spin transitions which are inherently immune to external perturbations. One example is so-called `clock transitions' (CTs) that are the points where an electron spin transition frequency, f, becomes independent of the applied magnetic field, B_0, e.g. $df/dB_0 = 0$. Here we show that such a CT can be observed for bismuth donors in silicon at 7.0317 GHz and magnetic field of 80.1 mT. By measuring Bi donors at this CT we observe a dramatic enhancement in electron spin decoherence time from 55 ms as measured at X-band to 2.7 s at 7.0317 GHz. We find that electron spins at the CT become about two orders of magnitude less sensitive to the local magnetic environment, including spin flip-flops of other donor electrons and also flip-flopping ^{29}Si nuclear spins as found in natural silicon. We expect the use of such CTs will be of additional importance for donor spins in future devices, mitigating the effects of noise arising from defects introduced device during processing or associated with nearby surfaces and interfaces.
This research was supported in part by NSF through the Materials World Network program (DMR-1107606) and the Princeton MRSEC (DMR-0819860) and by NSA/LPS through Lawrence Berkley National Laboratory (100000080295).

ORAL SESSION

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106 **Spin-Dependent Recombination in Organic Light-Emitting Diodes and the Effect of Phosphorescent Emitters.** T.L. Keevers,[1] A. Danos,[2] K. Weber,[3] S. Watkins,[3] D. R. McCamey[1]
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The low cost and flexibility of organic polymers makes them ideal for a range of opto-electric applications, including solar cells and organic light-emitting diodes (OLEDs)[1]. The latter relies on electroluminescence: oppositely charged polarons are

injected into the material, which form tightly-bound excitons via an intermediate polaron pair state and emit light through the singlet manifold. The spin-dependent nature of emission arises from spin-selection rules, and the weak spin-orbit coupling of these materials. Spin-degeneracy statistics suggest that fluorescent pathways should be limited to 25% efficiency; however this limit has repeatedly been exceeded experimentally[2]. The theoretical reasons for this high efficiency are still not well understood[3], suggesting that models of charge transport and capture are incomplete. Unfortunately, the efficiency of fluorescence is typically too poor for commercial purposes. The addition of heavy-metal impurities leads to strong spin-orbit coupling which rapidly mixes the singlet and triplet states, leading to greater overall emission through increased phosphorescence[4]. We aim to develop a more detailed understanding of the role of heavy-metal impurities by comparing iridium-doped phosphorescent OLEDs with fluorescence-based MEH-PPV and PDY-132 ("Super Yellow") OLEDs. We will discuss the development of experimental capabilities which allow us to investigate the low-field behaviour of these materials at a range of magnetic fields and temperatures (77 to 300K), using spin resonant techniques in conjunction with optical and electrical detection mechanisms[5]. This approach provides us with the ability to sensitively investigate the spin-dependent processes which impact device efficiency.

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ORAL SESSION

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107 **Shuttling Electrons On and Off as Donor Atoms in Silicon.**

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Hybrid quantum devices where electron spins are used for state initialization, fast manipulation, long range entanglement and detection, while nuclear spins are used for long term storage promise revolutionary advantages. Here we report our first experiments using a silicon-based device that utilizes electron and nuclear spins of arsenic donors. The device is a large-area, parallel-plate capacitor fabricated on a 100 nm silicon-on-insulator (SOI) wafer where the SOI layer is implanted with arsenic donors. A back gate is formed in the silicon below the buried oxide by a high-energy boron implant. The electrons can be controllably stripped from the donors and then reintroduced to the ionized donors by applying appropriate gate voltages. We use pulsed ESR/ENDOR experiments (X-band) to track the occupancy of the donors during these operations. The number of spins is small (~10^{11} donors) and we boost our ESR signal 10 fold with a HEMT low-noise microwave amplifier operating at liquid helium temperature. Pulsed ESR/ENDOR is used to characterize the electron and nuclear spin states of As donors, while removing and then reintroducing electrons from the donors, and also to measure electron and nuclear Stark shifts while applying non-ionizing gate voltages. For neutral As donors we find that both electron and nuclear T_2 are controlled by electric (Stark) field noise, probably arising from the voltages on the gates. We also find that shuttling the electron on and off the donor causes only a marginal effect on the nuclear spin state of the donor, with a nuclear state survival probability of 99.7% per electron removal-reintroduction cycle.

ORAL SESSION

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108 **TBA.**

Amir Yacoby, Harvard University

109 **ODMR and EDMR in Organic Semiconductors and Devices.**

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It is widely recognized that nonradiative quenching of excitons by other excitons and polarons become the dominant decay mechanism of these excitons at high excitation densities. These quenching processes cause the roll-off in the efficiency of organic light-emitting devices (OLEDs) and prevent lasing at high injection current densities. This review presents the optically- and electrically-detected magnetic resonance (ODMR and EDMR, respectively) evidence for these photoluminescence- and electroluminescence-quenching processes. And while it provides such evidence for quenching of singlet excitons by polarons and triplet excitons, it reveals the central role of the strongly spin-dependent annihilation of triplet excitons by polarons, since under normal excitation conditions the steady-state polaron and triplet exciton populations are 100 – 10,000 times the singlet exciton population. In addition, it also suggests that quenching of singlet excitons by bipolarons, likely stabilized by a counterpolaron or countercharge at specific sites, may also be a significant quenching mechanism that also affects the charge transport properties.

ORAL SESSION

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110 **Overcoming Decoherence of Spin-based Qubits in Solid-state Systems.**

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Quantum decoherence is a central concept in physics. Applications such as quantum information processing depend on understanding it. Many insulating electronic spin-based qubits in solid-state systems are currently the subject of intense experimental interest, notably in nitrogen-vacancy (NV) centers in diamond, large-spin molecular magnets and semiconductor quantum dots. In all these systems, three intrinsic environmental decoherence mechanisms are involved. The electronic spins couple locally to (1) phonons; (2) to large numbers of nuclear spins (a nuclear spin bath); and (3) to neighboring electron spins via dipolar interactions.[1,2] In this talk, I will present our investigation to overcome spin decoherence in molecular magnets and NV centers in diamond. *Supported by the Searle Scholar program.*

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ORAL SESSION

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111 **Theoretical *ab-initio* Modelling of P_b-like States at Silicon Related Interfaces.**

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The interface between silicon and SiO_2 and its defects, such as the P_b centers at (111) and (100) surfaces, play a key role in semiconductor industry. The same is true for the corresponding coordination defects at the interface between crystalline and amorphous silicon in solar cells. Despite a long history of scientific research [1,2], these interfaces are still intensively investigated by experiment and theory. Nowadays, advanced experimental techniques like electrical detected magnetic resonance (EDMR) [3] or electron spin echo envelope modulation (ESEEM) spectroscopy [4] lead to a deeper insight, but clear results require careful comparison with theoretically determined EPR parameters.

In this work, we calculate the paramagnetic fingerprint of interface states from first principles for a wide range of model systems. By this, we are able to refine the current models for the Pb_0 and Pb_1 centers at the (100) interface. Our calculations in the framework of density functional theory (DFT) are, however, not restricted to localised dangling-bond like states of the P_b family. For delocalised conduction band electrons and tail states we present a novel non-perturbative approach via the orbital magnetization [5]. Our theoretical investigations show (1) that hydrogenation and oxidation of Si surfaces does not change the g-tensor considerably if the surface atoms are coordinated in the same way. (2) This holds also for the c-Si/a-Si:H interface between crystalline and amorphous silicon where the predicted existence of P_b like centers is experimentally confirmed by EDMR [3]. (3) We identify the microscopic structure responsible for the quasi-delocalised tail states and present a microscopic model picture for an efficient, band-tail assisted electron transfer through the a-Si/c-Si:H heterojunction.

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ORAL SESSION

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112 **Time-Resolved ESR Spectroscopy Investigation of Photoconduction Mechanism in Covalent Organic Framework (COF) Materials.**

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Covalent organic framework (COF) materials are porus crystalline materials. They attracted much attention because of their functionalities. Recently, a variety of COF materials based on the Donor-Acceptor (D-A) system have been developed. Jiang and coworkers synthesized a variety of D-A type COFs such as NDI-ZnPc, PyDI-ZnPC and ZnPc-NDI-HHTP. While molecules are connected by tight covalent bonds within the two-dimensional layers, the molecules stack to form one-dimensional columns perpendicular to the planes. They show pronounced photo-conducting behavior. The possible photo-conduction origin is the electron transfer between donor and acceptor. However, the detail mechanism is an open question. We performed time-resolved photo-excited ESR spectroscopy for a series of D-A type COF materials to investigate the photo-conduction mechanism. After photo-excitation to D-A type COFs, an ESR signal originated from the charge-separated state was observed, which could not be observed in isolated molecules. As for ZnPc-NDI-COF, we can observe the charge-separated ESR signal even at R.T., indicating long lifetime of the photo-excited carriers. Actually, the lifetime of the photo-excited charge-separated states in ZnPc-NDI-COF are estimated as 865 μs at 80K and 1.8 μs at 280K. In this paper, we discuss the photoconduction mechanism of the D-A type COF materials.

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ORAL SESSION

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113 **EPR and Electrochemical Investigations on the Oxidation of Highly Crowded Organophosphines and Arsines.**

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Cation radicals of trivalent organophosphines and organoarsines are normally extremely reactive and have commonly been observed only in low-temperature matrix studies. However, recent work has shown that bulky aryl groups can dramatically stabilize such ion radicals.[1,2] Recently a crystalline radical cation, $Tripp_3P^{+\bullet}$ was isolated in several salts with crystallographic characterization.[3] We now report on the synthesis and structure determination of novel examples of bulky triarylpnictophines and tetraaryldipnictophines. The results of detailed studies on their one-electron and two-electron oxidations using chemical and electrochemical methods will be discussed. The use of EPR methods for the characterization of the cation radicals in mobile and rigid phases has been central to this undertaking. Significant structural changes that accompany the oxidation reactions have been examined using hybrid DFT computational methods which are used in conjunction with the EPR evidence for the structures of the radical cations. Short-lived species are investigated using EPR spectroelectrochemistry and we will report on the use of our novel low-temperature in situ EPR-electrochemical cell.

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ORAL SESSION

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114 **Mystery of Non-equivalent Centers in Congruent and Stoichiometric $LiNbO_3$ and $LiTaO_3$.**

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Lithium Niobate (LN) and Lithium Tantalate (LT) doped with transition and rare-earth ions are of great interest for both fundamental science and advanced applications. According to the Rutherford back scattering data, all trivalent ions substitute for Li and should create similar centers. Electron Paramagnetic Resonance, EPR and Electron Nuclear Double Resonance, ENDOR provides additional information about characteristics of impurity centers and their structures. Our EPR/ENDOR study has shown that transition and rare-earth ions create unexpected variety of completely different non-equivalent centers in both stoichiometric and lithium deficient congruent crystals. Two Er^{3+}, three Fe^{3+}, four Nd^{3+}, and nine Yb^{3+} centers were found and described in LN. Dominated Fe, Yb and Nd centers have C_3 point symmetry (axial center), whereas all others have lowest C_1 symmetry. Distant defects create small distortions of crystal field at the impurity site, which cause a line broadening, but do not change the C_3 symmetry. Defects in the near neighborhood can lower center symmetry from C_3 to C_1. The ENDOR observations for dominated axial centers allowed to determine their atomic structures, and to propose models for low symmetry centers: self-compensated Yb(Li)-Yb(Nb) pairs, different complexes of Me^{3+} and intrinsic defects. Our findings help to understand complicated spectra of optical absorption, emission, and site-selective spectroscopy. The determination of the lattice sites and charge compensators of non-isovalent impurities are vital for both defect structure calculation and tailoring material properties.

ORAL SESSION

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115 **New Opportunities for High-field MR Spectroscopy to Study Oxide Heterostructures and Materials for Photovoltaic Applications.**

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Magnetic resonance spectroscopy at high magnetic fields offers the opportunity to study the atomic and electronic structure of solids with high sensitivity and resolution. I will present recent results how these advantages can be utilized to shed light on the ferromagnetic properties of complex oxide materials. In addition, I will briefly summarize our development of high-field dynamic nuclear polarization spectroscopy for inorganic (a-Si:H) and electrically-detected magnetic resonance for organic photovoltaic applications. In complex oxide heterostructures magnetism is a critical phenomenon which often accompanies quantum phase transitions between a highly correlated metal and a Mott insulator. Applying Ferromagnetic Resonance (FMR) to heterostructures comprised of magnetic Mott insulators ($GdTiO_3$) and band insulators ($SrTiO_3$) opens the possibility to study the magnetic state of highly correlated two-dimensional electron gases at the Metal-insulator transition. I will show first high-field FMR measurements of the magnetization density of ferrimagnetic $GdTiO_3$ carried out at a microwave frequency of 240 GHz and at high magnetic fields (> 8 T) and discuss our strategy to investigate the magnetic state of a Mott insulator. *Work on complex oxides is supported by the MRSEC Program of the National Science Foundation (Award No. DMR 1121053). MF is grateful for support from the Alexander von Humboldt foundation.*

ORAL SESSION

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116 **Temperature Dependent Magnetic and EPR Studies of Bulk and Nanoparticles of $Bi_{0.1}Ca_{0.9}MnO_3$.**

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Here we studied the temperature dependent magnetic and EPR properties of nano and bulk samples of $Bi_{0.1}Ca_{0.9}MnO_3$ (BCMO). We prepared the nanoparticles of BCMO by standard sol-gel technique and bulk samples by solid state reaction method. We investigated magnetic ordering by doing temperature dependent magnetic and EPR studies on both the samples to compare the properties with each other. Earlier reports[1] say that antiferromagnetic and ferromagnetic orders coexist in the bulk sample of $Bi_{0.1}Ca_{0.9}MnO_3$ without any charge ordered state. Our magnetization and EPR results show the existence of

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ferromagnetism in the bulk sample which is present in the nano sample as well but with somewhat weakened strength with the size reduction.

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ORAL SESSION

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120 **Electrically Detected Magnetic Resonance – Basic Concepts and Applications.**

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Magnetic resonance techniques attract considerable attention in many research fields. Advantages compared to other techniques are among others, high sensitivity and selectivity. In general, the technique can be used to investigate local static and dynamic interactions, or in other words the microscopic surroundings of the spin. Among MR techniques Electrically Detected Magnetic Resonance (EDMR) is a powerful tool for materials and electronic device characterization. In this talk, we shall present a short review on the use of EDMR in different semiconductors: a-Si(Ge):H,[1,2] Si/SiGe heterostructures [3] and Alq_3 based OLEDs.[4,5] We will also present a brief introduction to the fundamental concepts of the technique.

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ORAL SESSION

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121 **Recent Progress in Pulsed EDMR.**

Martin Brandt
Technical University of Munich

122 **Spin Lattice Relaxation at High Fields and Low Temperatures.**

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At high fields and helium temperatures in the majority of spin systems, the main energy exchange of the spin system with the surroundings is through single phonon (direct) processes. The increase in phonon density with EPR frequency leads to a strong field dependence of the spin-lattice relaxation time T_1 in the low temperature regime and orders of magnitude changes in the T_1 from 10 to 400 GHz. Examples will be shown raniging from impurities in semiconductors to frozen solutions of free-radicals. This frequency dependence can have significant impact on PELDOR distance measurements at high fields, and low temperature Dynamic Nuclear Polarization. The roles of spectral diffusion, and non-equilibrium phonon distributions will be discussed as they can be of significant importance, and can sometimes lead to large nuclear polarizations.

ORAL SESSION

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123 **Multi-Extreme THz ESR: Its Development and Application.**

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Recent development of our multi-extreme THz ESR and its applications will be presented. First, our multi-extreme THz ESR has following specifications;

1) Frequency region between 0.03 and 7 THz[1]
2) Temperature region between 1.8 and 300 K[1]
3) Magnetic field region up to 55 T[1]
4) Pressure region up to 2 GPa[2,3]
5) Measurements of micrometer size single crystal using a micro-cantilever[4]

As we can achieve THz ESR under multi-extreme conditions, such as the high magnetic field, the high pressure and the micrometer size, we call it multi-extreme THz ESR. We have also developed the magnetization detected ESR using SQUID magnetometer (SQUID ESR).[4] The advantage of SQUID ESR is that the absolute intensity measurement is possible, and this SQUID ESR enables the millimeter wave ESR for all SQUID magnetometer users in the world and it has a high potential for the study of molecular magnets. Finally the application of our multi-extreme THz ESR to kagome antiferromagnet Cr-jarocite will be presented.

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ORAL SESSION

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124 **Continuing Development of a Free Electron Laser-based EPR Spectrometer.**

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The expansion of EPR to high magnetic fields has been driven by extensive research to exploit the advantages of sensitivity, and resolution, which are especially important. However, in EPR the lack of high-power sources operating above 100 GHz has limited the development of pulsed EPR at magnetic fields above ~3 Tesla. A new EPR spectrometer built using the high power available from the Free Electron Lasers (FELs) at UCSB has shown the capability to perform pulsed EPR at 8.5 Tesla with up to two, short (<10 ns) pulses for the first time ever. These short pulses dramatically improve sensitivity and time resolution, allowing measurements in systems that were previously difficult to measure due to weak signals or rapid spin relaxation, and helping push towards higher temperature measurements. The use of such short pulses for high-field EPR can yield interesting effects, such as the observation of sample magnetizations large enough to affect the spin system. While operational, the FELEPR is undergoing constant development to improve and expand its capabilities. Recent work has introduced full phase control using both pulses, despite the lack of phase control of the FEL, which greatly increases the versatility of the spectrometer. This talk will briefly introduce the FELEPR spectrometer, but focus on the latest advances in the spectrometer's capabilities and current experiments.

ORAL SESSION

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125 **Readout and Control of a Single Nuclear Spin with a Meta-stable Electron Spin Ancilla in Diamond.**

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Electron spins in solids can strongly interact with electrical charges and optical photons, thus the single spin states can be well detected both electrically and optically. This property makes the electron spins one of the promising solid state qubits for quantum technologies, such as quantum computing, quantum communication and quantum metrology. Strong interaction with the environment, however, limits their coherence times. Thus, hybrid quantum systems consisting of coupled electron and nuclear spins have been proposed. In these systems, the nuclear spins are used as long-lived quantum memories owing to their long coherence time, while the electrons spins serve as readout gates or ancillary qubits for initializing the nuclear spins. A particularly favorable electronic structure is a singlet ground state and metastable excited state. In this case, coupling between the electron and nuclear spin – that otherwise limits the nuclear spin coherence time – is switched off while the nuclear spin is in the electronic ground state for storage. This scheme has been achieved using ensemble spins of C_{60}[1] under cryogenic conditions and we will present that it is also possible to realize this scheme in a single molecule scale under room temperature conditions. We will use a newly found color center, the ST1 center, observed in diamond nano-pillars. This novel single spin defect has singlet ground and excited states and a meta-stable state which has a spin triplet manifold, and shows exceptionally high positive optical spin signal contrast (up to 45%) at room temperature. Using this, we demonstrate the initialization of a single nuclear spin with a metastable electron spin and readout of it in the spin free electronic ground state.[2]

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ORAL SESSION

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126 **EPR Probeheads for Very Small Samples: Developments and Prospects.**

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In the study of paramagnetic centers in radical- and metallo-proteins one of the main targets is the determination of all magnetic interaction tensors of the center including their relative orientations. This task can be best performed when single crystals are available. Since protein crystals are usually very small (i.e. typically 0.1-0.4 mm), the development of EPR probeheads adapted to very small samples is of key importance for such investigations. Our project in the German SPP1601 priority program aims to investigate the practical limits in sample size and sensitivity of EPR micro-resonators. Several designs will be analyzed, e.g. 1) Planar microresonators (PMR) operating at X-band[1,2], 2) loopgap resonators at 35 GHz,[3]3) Solenoid microcoils and planar microstrip probe-heads [4]. Each of these designs can be optimized for particular sample shapes and particular EPR experiments. Several of these options will be discussed and preliminary experiments on single crystals will be presented. We have constructed an X-band (cryogenic) PMR probehead (sample diameter 0.4 or 0.8 mm) and performed a systematic comparative study with standard EPR resonators using a nitroxide probe in a range of sample sizes. As expected, the PMR was superior in absolute sensitivity but some commercial resonators also performed remarkably well. The implications of these measurements with respect to further optimizations of the design will be discussed.

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ORAL SESSION

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127 **A Highly Sensitive and Tunable RF Sensor for Electron Paramagnetic Resonance Spectroscopy Applications.**

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A highly sensitive and tunable RF sensor is proposed and demonstrated for electron paramagnetic resonance (EPR) spectroscopy applications. The sensor is based on the interference of RF probing waves from two signal branches.[1, 2] One branch has paramagnetic samples and the other is a reference. A simple sensor is built and demonstrated. Microstrip lines and coplanar waveguides are used to hold paramagnetic samples. Tunable phase shifters and attenuators are used to tune the operating frequencies and sensor sensitivities. The sensor works from ~ 20 MHz to ~ 1 GHz. Its effective quality factor, which is defined as $Qeff=f0/\Delta f$ with center frequency $f0$ and 3dB bandwidth Δf obtained from transmission coefficients $S21$, is as high as ~ 10^5. Unlike conventional resonators, dielectric losses due to paramagnetic samples do not affect $Qeff$ significantly. Preliminary EPR measurements are conducted with DPPH powders and home-made magnetic coils. Dispersion and absorption EPR signals are obtained simultaneously. Further work is needed to achieve high EPR sensitivity. *Supported by NSF CHE1152892 and Gates Foundation OPP1058477.*

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[2] Yang et al., *Lab Chip*, 2010, 10, 553

ORAL SESSION

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128 **Signal Detection During Detector Dead Time with Arbitrary Waveform Generation in Pulsed EPR.**

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The inherent dead time caused by cavity ring down has presented a long standing challenge to the application of pulsed EPR to fast relaxing spin systems. This makes it nearly impossible to measure the *T2*'s, on the order of 10 ns, of biological nitroxide spin labels at room temperature, thus making the extraction of crucial spectroscopic information challenging. We demonstrate the ability to accurately measure *T2*'s that decay faster than the ring down. To do this we employ a recently developed 1 GHz arbitrary waveform generation platform (AWG) as part of a home built, versatile, X-band EPR spectrometer to synthesize a pulse designed to destructively and accurately cancel the ring down. We fine-tune the "cancellation pulse" by minimizing the residual from the destructive addition of the cancellation pulse and the ring down. We inject the cancellation pulse immediately before the detector. Because we use an independent pulse for cancellation we can detect signal at any time independent of the shape of our excitation pulse. With this technique we detected the EPR nutation during the pulse as well as the ring down. We also construct a *T2* curve composed of echoes acquired both during and after the ring down. This shows good agreement with the *T2* curve determined from echoes acquired entirely outside of the ring down, demonstrating our ability to measure a *T2* that decays faster than the cavity ring down. This showcases that AWG platforms can extend the scope of pulsed EPR to applications previously thought unattainable.

ORAL SESSION

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129 **EPR, ENDOR and ESEEM Spectroscopies in Metallobiochemistry.**

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EPR, ENDOR and ESEEM spectroscopic techniques, in combination with cryoreduction and annealing/relaxation methods, have been used to characterize the structures of intermediates in the complex, multi-step reaction pathways of metalloenzymes and biomimetic metal complexes. An area of particular interest has been hydrido species, that are associated with the metal centers. These species are key intermediates in the metal-mediated interconversion of protons and electrons with dihydrogen (H_2). Electronic and geometric structural information and mechanistic insights from biomimetic complexes plus enzymes, including the MoFe protein of the nitrogenase enzyme, will be presented.

ORAL SESSION

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130 **EPR Studies of [Fe-Fe] Hydrogenase H-cluster Assembly.**

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The catalytic "H-cluster" of the [FeFe] hydrogenase is a [6Fe-6S] unit consisting of a conventional [4Fe-4S] cluster linked to a unique [2Fe-2S] cluster that has two CN-and three CO ligands as well as a dithiolate bridge (DTMX), with the identity of the central atom X ambiguous in current structures. A set of Fe-S proteins, HydF and two radical SAM enzymes, HydE and HydG, are involved in H-cluster synthesis. We are using EPR to study the reaction mechanisms of these enzymes involved in building this H-cluster. Characterization of FeS signals and a radical intermediate signal detected in the HydG catalyzed reaction of CO and CN- production from tyrosine has led us to a new proposed mechanism for this specific radical SAM reaction, as well as new insights into the overall bioassembly process.

ORAL SESSION

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131 N**ew EPR insights on the catalytic model for H_2 activation by the [FeFe]-hydrogenase H-cluster in HydA1 from *Chlamydomonas reinhardtii*.**

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The [FeFe]-hydrogenases catalyze the activation of molecular H_2, which occurs at a unique metallo-cluster termed as the H-cluster. Composed of a [4Fe-4S] subcluster linked by a cysteine thiolate to an organometallic diiron subsite with CO, CN, and dithiolate ligands,[1] the H-cluster cycles between several electronic structural states during catalysis. While a mechanistic model for H_2 activation at the H-cluster has been developed from comprehensive studies of bacterial [FeFe]-hydrogenases,[2] it remains difficult to discretely define catalytic states due to the presence of auxiliary FeS clusters. Here, a combination of EPR and FTIR spectroscopy were used to characterize the algal HydA1 enzyme from *Chlamydomonas reinhardtii*, a minimal hydrogenase consisting of only the H-cluster domain, to further resolve the nature of the reaction intermediates of the H-cluster during catalytic proton reduction and H_2 activation.[3] Chemical reduction by NaDT versus reduction by H_2 resulted in unique EPR spectra, primarily with the appearance of a rhombic 2.08 signal (g = 2.077, 1.935, 1.880) or a broad 2.3-2.07 signal (g = 2.3-2.07, 1.863), respectively, for each reduction method. Corresponding FTIR spectra of NaDT and H_2 reduced samples also each displayed unique line shapes. Both EPR signals displayed relaxation properties similar to $[4Fe\text{-}4S]^{1+}$ clusters, suggesting the presence of several S = ½ H-cluster catalytic intermediates containing a $[4Fe\text{-}4S]^{1+}$ subcluster. Whereas the rhombic 2.08 EPR signal and FTIR spectra were similar to the "super-reduced" state reported in an earlier study[4] the other spectral features are consistent with extensive complexity and subcluster interactions during catalytic turnover.[2,5] This presentation will summarize our recent EPR results and proposed catalytic model for the [FeFe]-hydrogenase H-cluster.
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ORAL SESSION

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132 **Analysis of Metal-RNA Interactions by EPR Methods.**

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Functional RNA molecules are critical to biology and are remarkably dependent on metal ions, both for global structure and local interactions. Catalytic RNAs have metal-based active sites whose properties are tied to the requirement for global RNA folding. While dynamic RNA structure changes are critical in biology, there are few methods available for precision mapping of 3-dimensional complexes. DEER spectroscopy can be applied successfully to this problem when the influence of spin labels on RNA function can be assessed. The catalytic efficiency of the Hammerhead ribozyme provides a functional readout for RNA integrity, and this ribozyme provides a model system for EPR studies of RNA. Metal-based EPR methods have been applied to Mn(II) in this ribozyme, and DEER spectroscopy has been used to monitor a large-scale metal-dependent structural change. Power saturation studies report on metal ion clustering in this and other complex RNAs. In general, EPR methods are powerful when applied judiciously to structure-function studies of complex RNAs.

ORAL SESSION

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133 **Locating NO in the {FeNO}^{7} Complex Using HYSCORE: A Structural Context for Locating Substrates in Non-heme Fe(II) Dependent Dioxygenases Using ESEEM.**

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Non-heme Fe(II)/alpha ketoglutarate (α-KG) dependent dioxygenases are a large family of enzymes important in a wide range of biologically and medically relevant processes. These enzymes are believed to use a generally conserved mechanism and possess a common 2-histidine, 1-carboxylate Fe(II) coordination motif known as a "facial triad." Taurine Hydroxylase (TauD) is the archetype enzyme for this family and is an ideal subject for refining structural investigation methodologies due its abundance, stability, relative simplicity of substrate, and the existence of multiple crystal structures. By using nitric oxide (NO) as a surrogate to O_2, a S=3/2 {FeNO}^{7} complex amenable to EPR can be formed that closely mimics the Fe-O_2 complex native to the functioning enzyme. Conveniently, NO also defines the principal magnetic axes used for reference in structural studies using EPR. A method for measuring its exact location in the complex is highly desirable. Using Hyperfine Subevel Correlation (HYSCORE), the position of NO in the {FeNO}^{7} complex in TauD was observed by measuring the relative positions of the two histidine ligands. With this structural context, the measurement of the position and orientation of taurine using ^{2}H ESEEM was directly correlated to the ligands of the {FeNO}^{7} complex. Application of this methodology to Xanthine Hydroxylase (XanA), a poorly understood member of this family, is also presented. This study represents the first direct structural characterization of XanA and suggests the efficacy of this methodology for structural investigations of non-heme Fe(II) sites in general.

ORAL SESSION

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134 **Solving an Enzyme Mechanism by EPR.**

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Lipoxygenase enzymes initiate formation of mediators of inflammation. The structural basis of the mechanism is incompletely understood. At the active site, a water-iron center is activated for proton-coupled electron transfer. EPR studies to determine how a long lipid chain gets into the active site involve both strategically placed spin labels and the paramagnetic iron center. The aim in designing spin label targets in the structure was to find pockets just inside the surface in which the R1-spin label could be placed by modeling. Modeling was facilitated by existence of X-ray structures of four isoforms so that preferred χ angles are known.[1] All SDSL mutants were enzymatically active. The modeled positions of the spin labels agree well with experimental distances from DEER, between ten double-labeled proteins.[2] With five spin label sites established, then the location of the polar end of a lysolecithin, spin labeled on choline, was determined.[2] This result hinted to the general entrance of the substrate to buried iron, involving primarily helix-2 of the protein structure. A SDSL scan of helix-2 has been made, and in contrast to SDSL sites on other parts of the structure, helix-2 spins respond strongly to addition of a substrate analog or to pH variation. To determine structural changes involved, relaxation of side chains <2.5 nm from hs-ferrous iron has been examined by power saturation. The conclusion is that a portion of helix-2 moves outward, or "opens", when substrate binds.[3] Finally, a new bacterial lipoxygenase has been discovered that binds a complete phospholipid in the active site. The ferric form

of this enzyme has an EPR spectrum identical to one of two known ferric EPR spectra of plant lipoxygenases. *Support: NIH GM065268.*

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[3] Bradshaw Thesis in progress.

ORAL SESSION

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135 **Membrane Insertion and Interactions of Individual CesA Transmembrane Helices by Site-directed Spin-labeling EPR.**

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Cellular membranes represent a highly heterogeneous and anisotropic environment that subjects membrane proteins to rather large gradients of local polarity that drives inter- and intra-residue hydrogen bonding and hydrophobic interactions. Accurate determination of polarity gradients experienced by transmembrane helices (TMHs) provides both the means for evaluating the TMH membrane structure and essential data on physical interactions responsible for helix-to-helix interactions. Such experimental data are important in view of the emerging plant cellulose synthase complex (CesA) computational models and recently solved crystal structures of related bacterial BcsA and BcsB complexes. Here we report on the use of an arsenal of spin-labeling EPR methods to study membrane insertion and helix-to-helix interactions of CesA TMH 4 and 5. A series TMH 4 and 5 with single point Cys mutations and no connecting loop were prepared using solid-state peptide synthesis, covalently modified with an EPR-active side chains at selected positions of the peptide sequence, and inserted into bilayers prepared from long-chain (DOPC), short chain (DLPC), or mixed DOPC/DLPC lipids. Local polarity experienced by the nitroxide-labeled side chains was measured based on the exquisite sensitivity of EPR parameters (i.e., *g*-factor and A_{iso}) to dielectric and hydrogen-bonding effects. Further, we investigated effects of membrane-spanning a-helical WALP23 peptide on TMH 4 and 5 membrane insertion and helix-to-helix interactions. Polarity and depth parameter Φ profiles for bilayers of the same lipid compositions were separately calibrated using WALP. One of the conclusions of this work is that the specific lipid composition of the bilayers and the presence of other membrane-spanning helices appear to be an important requirement for proper insertion of individual CesA TMHs in lipid bilayers. Supported as a part of the Center for LignoCellulose Structure and Formation under DOE Award DE-SC0001090.

ORAL SESSION

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136 **The Central Cavity of ABCB1 Undergoes Alternating Access During Drug Translocation.**

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The molecular process underlying multi-drug recognition and efflux by P-glycoprotein (ABCB1) remains a biological enigma. Structural data has recently become available for the murine and *C. elegans* homologues of ABCB1. Both of these structures were obtained for protein in the basal conformation characterised by the absence of nucleotide or substrate. A striking feature of the structures was the presence of a central cavity that is inaccessible from the extracellular face of the protein. To determine the conformational dynamics of this region we mutated several residues in transmembrane helices 6 (331, 343 and 354) and 12 (980) to cysteine based upon structural predictions that these residues line or reside proximal to the central cavity of ABCB1. The inserted cysteine residues were labelled with a paramagnetic probe to enable spectral analysis by EPR. Spectra were recorded in the presence of hydrophobic (O_2) or hydrophilic (NiEDDA) quenching agents to ascertain the local environment of each residue. Molecular dynamic simulations were used to reconcile the EPR measurements (describing probe motility and local environment) from a structural perspective. ABCB1 was subsequently trapped in its nucleotide bound and post-hydrolytic conformations and EPR spectra recorded in the presence and absence of quenching agents. The alterations in spectral properties were used to provide information on the likely movements of the chosen residues within TMVI and XII.

The data suggest that the extracellular face of the cavity is converted to an open configuration following nucleotide binding. This is in agreement with the "power stroke" model of ABC transporters and provides evidence for an alternating access of the cavity to opposite sides of the membrane during drug translocation.

ORAL SESSION

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137 **Development of Redox Molecular Imaging of Free Radicals in Living Animal.**

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Dynamic nuclear polarization (DNP)-MRI, also called proton electron double resonance imaging (PEDRI) or Overhauser MRI, is a new imaging method for observing free radical species. MRI image intensities from water proton can be enhanced up to 10^2 fold by irradiating at the EPR resonance frequency of the free radical prior to applying the MRI pulse sequence. The major advantage of DNP-MRI is that the spatial resolution of free radical spectra is similar to that in MRI. We succeeded in simultaneous dual images by using nitroxyl radicals labeled with ^{14}N and ^{15}N nuclei and changing the external magnetic field for EPR irradiation in DNP-MRI.[1] Synthetic nitroxyl or trityl radicals have provided unique information regarding redox status,[2] vascular permeability/oxygen concentration[3] and whole body-pharmacokinetics[4] in living animals.

In the present study, two DNP-MRI scanners were developed. One is a DNP-MRI scanner using a commercial EPR spectrometer. The system operates at 20 mT with corresponding frequencies of 850 kHz and 565 MHz for NMR and EPR modes, respectively, and free radical distributions were visualized *in vitro* and *in vivo*. The large difference of gyromagnetic ratio between electron and proton spins restricted EPR excitation and the proton detection fields. By transporting the sample between EPR (20 mT) and MR magnets at 1.5 T (or 0.4 T), we have developed a high sensitive DNP-MRI scanner, the spacial resolution of which was less than 0.2 mm.

However, the development of DNP-MRI for human applications is still challenging. If endogenous free radical intermediates were used for imaging, DNP-MRI could become a promising technique to add metabolic/biochemical dimensions to anatomic images. Here, we demonstrate a novel redox molecular imaging (ReMI), which can simultaneously visualize various endogenous free radical intermediates derived from redox transformations in a single experiment. ReMI represents a novel molecular imaging methodology for redox metabolic imaging.

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ORAL SESSION

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138 **Uncovering secrets in membrane electrostatics, cell-signaling and transport using EPR spectroscopy.**

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Spin-labeling methodologies when combined with EPR spectroscopy have evolved into a powerful tool-set to examine a range of problems in macromolecular structure and dynamics. Much of our work has focused on biological membranes and membrane proteins, and we will discuss examples of how EPR spectroscopy has been used to characterize membrane electrostatics, the membrane association of proteins and protein conformational exchange. Recent developments in site-directed spin labeling provide an exciting approach to understand the molecular basis for membrane protein function, and are able to reveal conformational heterogeneity and conformational equilibria that are lacking in high-resolution crystal structures.

ORAL SESSION

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145 **Investigation of Spin-Trapping Artifacts Formed by the Forrester-Hepburn Mechanism.**

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Free radical detection with ESR spin trapping relies on the specific addition of the radical to nitrone/nitroso compounds. It has been proposed that spin traps can react with nucleophiles in biological system to give false-positive results. For nitrone spin traps, this reaction, first described by Forrester and Hepburn, has been discussed as the most critical source of artifacts.

For artifact identification, the ESR preincubation method may be used, which employs isotopically marked spin traps. Here we investigated the influence of fast sulfite-hydroxylamine equilibrium chemistry on the fidelity of this assay. Using the (faster) aspiration technique, we found that the Forrester-Hepburn mechanism also contributes to DMPO/$^{\bullet}SO_3^{-}$adduct formation during ferricyanide-mediated sulfite oxidation, but no evidence for artifactual DMPO/$^{\bullet}SO_3^{-}$formation was found if the more potent horseradish peroxidase was used. This is ESR evidence that the Forrester-Hepburn mechanism can occur under mild conditions, depending on the experimental details.

This technique can also be used to test for other artifact mechanisms. We investigated the known *ene* reaction of DBNBS and tryptophan in more detail. We found that a strong artifact signal is induced by light; however, with atypically long incubations, we found that the artifact is also formed thermally.

ORAL SESSION

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146 **Nitroxide and Trityl Radical Probes for Multifunctional in vivo EPR Spectroscopy and Imaging.**

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In recent years it came to realization that tissue microenvironment (TME) plays a key role in pathophysiology of living organisms. For two leading causes of mortality in the United States, cancer and ischemic heart disease, tissue *hypoxia* is well documented and is accompanied by changes in glycolysis resulting in tissue *acidosis* and tissue *redox* changes. Methods that monitor these parameters *in vivo* are of critical importance for diagnostics and optimization of treatment strategies of these and other diseases. Low-field EPR-based techniques provide sufficient depth of microwave penetration in living tissues and have advantage over NMR in functional specificity when applied in combination with paramagnetic probes. Here we discuss the recent advances in chemistry of functional paramagnetic probes[1,2] which make multifunctional monitoring of TME feasible. They include dual function pH & redox nitroxide probes[1], pH and oxygen trityl probes[2], and glutathione-sensitive nitroxide disulfide reagents[1]. The exemplified applications include concurrent monitoring of ischemia-induced myocardial oxygen depletion and acidosis in isolated rat hearts[3], and multifunctional (pH, redox, oxygen and glutathione content) monitoring of tumor TME[4], including pH mapping of living tissues using low-field EPR imaging and functional proton-electron-double-resonance imaging. *Supported by NIH grant* EB014542.

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ORAL SESSION

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147 **Spin Dynamics of Concentrated "Finland" Trityl Radicals at Cryogenic Temperatures.**

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The low-temperature electron spin dynamics of the symmetric triarylmethyl radical (TAM) known as Finland trityl was examined at the high concentrations used for dynamic nuclear polarization (DNP). The electron spin-lattice (T_{1e}) relaxation shows two new relaxation routes with different dependences on temperature and radical concentration. The phase memory or spin-spin (T_2) relaxation has large contributions from both spectral diffusion and instantaneous diffusion. The relaxation of electron spin dipolar order is temperature independent but concentration dependent at X-band (0.34 T) and W-band (3.4 T). The spin dynamics of TAMs at typical DNP conditions are a collective property of the sample and not a property of the individual radicals studied in typical EPR measurements.

ORAL SESSION

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148 **250 MHz to 34 GHz Study of Nitroxide Relaxation Mechanisms.**

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T_1 and T_2 have been measured by inversion recovery and spin echo decay from 250 MHz to 34 GHz for a range of nitroxyls in water, water:glycerol, toluene and di-ortho-xylyl-ethane mixtures at 295 K. Nitroxyls studied vary in isotopic substitution (both $^{14}N/^{15}N$ and H/D), ring structure and the presence or absence of gem dimethyl groups. Within this group isotropic nitrogen hyperfine ranges from 4.7 G to 23 G and the tumbling correlation times are 9 to 50 ps. The frequency dependence of $1/T_1$ is modeled as the sum of contributions from spin rotation, modulation of g and A-anisotropy and a thermal process. Below about 9 GHz $T_1 \sim T_2$ for most radicals, as expected in the fast tumbling regime. Between 34 and 3 GHz T_1 decreases with decreasing frequency. The shortest values of T_1 are observed at about 1 GHz, but values become longer again at 250 MHz. Specific molecular features drive these relaxation contributions. There are systematic differences between relaxation rates for radicals where the only difference is $^{14}N/^{15}N$ substitution. The thermal process appears to involve modulation of spin-orbit coupling via changes in the nitrogen geometry.

ORAL SESSION

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149 **Diradicals and Polyradicals: Synthesis, Magnetism, and Spin-Spin Interactions.**

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Diradicals and polyradicals are of interest for the development of a wide range of materials for technological and biomedical applications such as organic magnets, spin labels, and contrast agents for magnetic resonance imaging. These applications would benefit from the radicals with optimized spin-spin interactions which can be controlled at the molecular level by the design of well-defined structures. This presentation will provide an overview of the design, synthesis and study of nitroxide radicals, including spirocyclic nitroxides, annelated nitroxide diradicals, macrocyclic nitroxide tetraradicals and octaradical. The analysis of their magnetic properties and spin-spin interactions, such as exchange coupling and magnetic dipole-dipole coupling, as well as the modulation of these couplings, will be discussed.

ORAL SESSION

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150 **The Amide Nitroxide: Coming to a EPR Spectrometer Near You.**

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The synthesis, spectroscopic and computational characterization of a novel hydroxamic acid, spin-label probe is described. This nitroxide spin label is incorporated into the peptide amide bond and is thus anchored to the peptide backbone resulting in minimal steric and motional perturbations when incorporated into peptides. These features are advantageous in enhancing the precision in monitoring protein dynamics, conformational changes and long-range distance measurements with NMR, EPR/DEER spectroscopy. As a prototype, Ac-AibΨ[CONO*]Aib-OMe was prepared and its EPR spectra analyzed by DFT in terms of four rotameric states.

The synthetic approach has been adapted to SPPS, and double spin-labeled β-hairpin model peptides are currently being synthesized to measure their dynamic distance distributions by DEER EPR experiments.

ORAL SESSION

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151 **High-Field EPR Studies of Organic Radical Ferromagnets Under High Pressures.**

Stephen Hill, NHMFL

152 **Excitation and Detection in Ultra-Wideband EPR.**

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For most of its history, pulsed EPR has relied on excitation by monochromatic rectangular pulses, with bandwidth limited by available microwave power and typically being smaller than spectral width. Ultra-wideband pulses, as they can be generated by sufficiently fast arbitrary waveform generators, overcome this limit. An analysis of excitation by frequency-swept (chirp) pulses shows that for typical transverse relaxation times and typical microwave power supplied by a traveling wave tube amplifier, excitation bandwidths of more than 1 GHz are feasible at X- or Q-band frequencies. The main limitation now results from the decrease in detection sensitivity that results from a decrease in the quality factor of the resonator. We have analyzed excitation of two-level systems over bands that are comparable to or larger than resonator bandwidth, as specified by the 3 dB points, and have demonstrated that high inversion efficiency can be achieved by adiabatic chirp pulses.[1] The length of an excitation waveform may be limited not only by transverse relaxation, but also by the manipulation of spin dynamics that is required for separation of interactions. For instance, we found that DEER pump pulses achieve better broadband inversion if they are realized as fast passage rather than adiabatic passage pulses.[1] In general, time-extended broadband excitation of multi-level systems can lead to transverse and longitudinal interference effects.[2] Examples are presented for such effects in spin systems that are typical for current pulsed EPR applications.

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ORAL SESSION

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153 **Five-pulse DEER: Improved Distance Range and Sensitivity.**

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Pulsed electron spin resonance dipolar spectroscopy (PDS), mainly represented by double electron-electron resonance (DEER) and double quantum coherence (DQC), is a mature but still rapidly expanding technology for studying structure and function of biomolecules at the nanoscale by measuring distances and distance distributions between engineered or endogeneous paramagnetic centers via magnetic dipolar interactions. However, achieving high sensitivity and a long distance range in PDS, especially for low concentration samples of membrane proteins presents a challenge. The major problem encountered in long-distance (>4 nm) measurements is the signal decay due to several phase relaxation mechanisms, dominated by nuclear spin diffusion, as the evolution time increases. To address this challenge, partial or complete system deuteration is used. This may not always be practical or possible, especially in the case of membrane proteins. The five-pulse DEER sequence (DEER-5) alleviates the problems associated with nuclear spin diffusion, permitting the extension of the time for recording the dipolar evolution by nearly a factor of 2, or by about 1.4 in the case of deuterated solvents, or else it shortens the measurement time considerably. The 4-pulse DEER allows signal recording over a 4 to 8 μs time interval, depending on the extent of deuteration and spin-label exposure to the solvent. Using DEER-5 brings these numbers to the range of 8 to 12 μs, respectively. We find an improvement even in the case of complete deuteration. The advantages of this method go beyond the case of nitroxides, and, for example, distances in the range of 4 to 6 nm could be measured between Cu2+ sites. We illustrate the features of DEER-5 and compare it with DQC and standard DEER using several examples of organic biradicals, nitroxide spin-labeled proteins, and oligonucleotides. All PDS data were recorded with home-build spectrometers at a working frequency of 17 or 34 GHz.

ORAL SESSION

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154 **Distances and Orientations with DEER/PELDOR at High EPR Frequencies.**

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PELDOR spectroscopy is a well-known technique to measure inter-spin distances in a nanometer range. Besides this, if applied at high fields/frequencies (95 and 263 GHz), the method exhibits an enhanced orientation selectivity. Thus, it can be used to provide information on the relative orientation of spin-labels in a pair, assuming those are rigidly oriented in a studied bio-macromolecule.

However, general applicability of the method is hampered by two major difficulties:

First, at high fields, PELDOR performance is aggravated by a narrow bandwidth of a single mode resonator. This prompted us to develop a dual-mode resonator that allows performing dual-frequency experiments with a variable separation of pump and detection frequencies up to 800 MHz[1-3]. The design of the resonator will be presented and discussed.

Second, the inherent symmetry of the magnetic interactions complicates the analysis of the orientation selective PELDOR data. We attempt to refine the experimental data and its analysis by implementing the dual-mode approach and by increasing the frequency of the measurements. Our recent results on two representative biological systems, i.e. an RNA and an alpha-helical peptide, permit to explore the feasibility of the method[2]. We show how its performance can be improved by enhancing resolution toward orientation selectivity and by setting proper constraints for the orientation analysis.

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ORAL SESSION

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155 **The Molten Globule State of Maltose Binding Protein: DEER Measurements at pH 3.**

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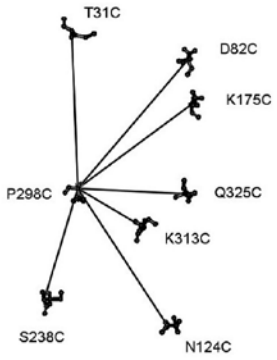

Maltose-binding protein (MBP) is in a molten globule state at pH 3 as characterized by ANS binding. DEER measurements of seven spin-labeled double mutants in the native state at pH 7 had shown excellent agreement with X-ray data. At pH 3 corresponding DEER measurements of all the mutants yield a broad distribution of distances. This was to be expected if there is no defined tertiary structure and the individual helices pointing into all possible directions.[1] However, as MBP still binds maltose as molten globule although more weakly, the native structure must be retained at or near the active site. This is now being investigated with a new set of mutants.

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ORAL SESSION

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156 **Distance Measurements in Biomolecules Using Gd^{3+} Spin Labels – Pros and Cons.**

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Methods for measuring nanometer scale distances between specific sites in biomolecules (proteins and nucleic acids) and their complexes are essential for analysis of their structure and function. In the last decade pulse EPR techniques, mainly pulse double-electron-electron resonance (DEER), has been shown to be a very effective for measuring distances between two nitroxide spin labels attached to a biomolecule. Recently we have introduced a new family of spin labels that are based on Gd^{3+} chelates attached to proteins using site directed spin labeling, similar to the common method of labeling proteins with nitroxide spin labels. Gd^{3+} spin labels are particularly attractive for high field DEER measurements such as W-band (95 GHz, ~3.5 T). The benefits such S=7/2 spin labels, in combination with high field, are the high sensitivity that reduces the amount of the biomolecule needed by more than an order of magnitude and the lack of orientation selection that allows straight forward data analysis. Here we will present Gd^{3+}- Gd^{3+} distance measurements in models compounds and their applications to study trans-membrane peptides in model membranes. The chemical and spin physics requirement for the ultimate Gd^{3+} label will be discussed.

ORAL SESSION

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157 **Complex Docking Models – Elucidating Protein-protein Interactions With EPR.**

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Recent focus in atomic resolution structure determination has shifted from viewing a protein in isolation to a more biologically relevant mechanistic fashion in how a protein interacts and combines with others to form complexes. Structure determination has previously been dominated by NMR and X-ray crystallography with development of both fields yielding ever more and better structures. However, they are hampered by limitations such as protein size or difficulties in crystallization; limitations by which EPR is unaffected. The site directed spin labelling of proteins in combination with EPR has potential to further determination of protein-protein as well as protein-membrane interactions. Power saturation studies give the spin labels accessibility to water and phospholipid environments. Which, when combined with labelling across the surface of the protein, allows for an orientation model to built. Spin labelling at several sites across a complex allows for a complex three dimensional model to be built using pulsed electron double resonance (PELDOR) measurements of intra- and inter-molecular distances. Through bespoke software solutions, these distances can be inserted into existing, extensively tested NMR focussed docking software packages[1] as additional parameters to enhance docking models. Using the well-characterised system of colicin E9 and its cognate inhibitor, Im9[2] we develop modelling methods to enhance existing NMR parameter based docking models before application to previously untested non-cognate colicin E9 inhibitors, Im2, Im7 and Im8.

[1] HADDOCK - nmr.chem.uu.nl/haddock

[2] Cascales et al., *MMBR* **2007** (71) 711158

ORAL SESSION

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158 **A Single-stranded Junction Modulates Nanosecond Motional Ordering of the Substrate Recognition Helix of a Group I Ribozyme.**

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In this work, the method of site-directed spin labeling was used to examine how the sequence and length of a single-stranded junction (J1/2) modulates nanosecond dynamics of the substrate recognition duplex (the P1 duplex) in a 120-kD folded RNA, the *Tetrahymena* group I ribozyme. Studies were carried out on a ribozyme state called the "open complex", in which the P1 duplex is linked to the folded ribozyme core via J1/2 but makes no tertiary contacts with the core. An advanced stable nitroxide radical probe, designated as **Ç**, was rigidly fussed with P1 duplex, and its X-band continuous-wave (cw) Electron Paramagnetic Resonance (EPR) spectrum was used to monitor rotational motions of P1 in the 0.5 – 50 nanosecond regime. As compared to a previously used flexible nitroxide probe, the rigid **Ç** provided enhanced sensitivity, and was able to detect dependence of P1 nanosecond dynamics on not only changes of J1/2 length, but also its sequence. The data revealed that intrinsic properties of the single-stranded J1/2, such as its persistence length and the propensity of base-stacking, modulate nanosecond motional ordering of the P1 duplex, which is one of the key factors impacting sampling of the conformational space. These studies establish an incisive method for examining the local nanosecond dynamics of specific secondary structural elements within a large folded RNA and the dependence of their dynamics on specific sequences, thus advancing our knowledge of dynamics in large RNA molecules.

ORAL SESSION

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159 M**easurement of Gd-Gd Distances by cw-EPR at 240 GHz.**

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Recent work has shown Gd^{3+} to be a promising candidate for measuring distances using EPR at high magnetic fields. This spin 7/2 ion has a nearly isotropic g tensor and negligible hyperfine coupling, greatly simplifying analysis of distance measurements. Additionally, the paramagnetic core is well shielded by other valence electrons, making it relatively insensitive to its local chemical environment and extremely robust even in vivo. At high magnetic fields, the spectrum is dominated by the $|-1/2> \rightarrow |1/2>$ transition, which can be as narrow as 5 G at 240 GHz. This intrinsically narrow line is very sensitive to dipolar broadening, giving increased sensitivity at high temperatures and extended interspin distances. Critically, this feature is maintained in Gd^{3+} chelating moieties that can be functionalized as spin labels. This combination of favorable characteristics presents enormous opportunities for EPR based distance analysis, allowing for the study of structure and dynamics of proteins in conditions close to their natural ambient environment. Measurements of frozen solutions of $GdCl_3$ have shown that dipolar broadening is visible out to interspin distances of ~4 nm. In order to develop analysis methods for quantitative distance determination, we have begun a study of specially synthesized "ruler" molecules which feature two Gd^{3+} spin labels bound by a rigid backbone. Lineshape measurements of a 2.9 nm ruler exhibit significant broadening compared to the monomer at temperatures from 10 K to 215 K. Numeric calculations of the broadening allow for extraction of interspin distances in these rulers. Further work will include validation and refinement of this technique using ruler molecules of various lengths and by comparison with DEER data. A Gd^{3+} spin labeled chemotaxis protein will serve as a test of this technique in a biologically relevant system. *This work is supported by the NSF MCB-1244651 grant and the USA-Israel Binational Science Foundation.*

ORAL SESSION

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165 ***In vivo*** **Imaging and Spectroscopy.**

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In vivo imaging and spectroscopy promise to provide new insights into the physiology of disease in addition to aiding diagnosis and guiding therapy. Instrumentation and methodology enhancements are required to encompass a wide range of resolutions – spatial, temporal, and chemical – and to measure a variety of probes. A perspective will be presented on the potential roles of CW, pulse, and rapid scan methods, and of digital technology in each of these methods. An introduction to rapid scan EPR will occur in the Workshop prior to the EPR Symposium. The relative advantages of each method for samples of different spectral extents and relaxation times will be discussed.

ORAL SESSION

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166 **Probes and Methods for Clinical Oximetry.**

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Oxygen is a critical determinant in the prediction of treatment outcome of several disease including surgical interventions, cancer therapy, tissue graft, and cell therapy. There is a great need for methods capable of reliable noninvasive measurement and monitoring of oxygen concentration in tissues. Although several methods are utilized to measure oxygen concentration, a suitable technique for noninvasive and repeated measurements of oxygen in the same tissue or cells on a temporal scale is warranted. While electrode techniques have evolved as the standard methods for measurement of oxygen, they generate analytical artifacts during assay procedures at the freshly probed sites. Near-infrared and nuclear magnetic resonance techniques are noninvasive methods. However, they do not report the absolute values of oxygen concentration, and lack the resolution of oxygen measurements. Electron paramagnetic resonance (EPR) oximetry enables reliable and accurate measurements of concentrations of molecular oxygen. EPR oximetry can measure directly and at the actual site of interest. The ability of EPR oximetry to make repeated measurements from localized sites provides a very important capability that can enable critical aspects of a number of biomedical applications. We have developed innovative approaches using oxygen-sensing nano/microcrystalline probes to perform noninvasive oximetry/imaging in a variety of applications including myocardial ischemia/reperfusion injury, cellular cardiomyoplasty (cell therapy), tumor angiogenesis, cancer therapy, and wound healing. Current developments in in vivo EPR methodologies enable a number of potential applications that could be very significant additions to clinical medicine. The current developments of oximetry probes and designs for clinical oximetry will be presented. S*upported by NIH grant R01 EB004031*

ORAL SESSION

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167 **Comparison of Pulse Sequences for Spin-lattice Relaxation Based *in Vivo* EPR Oxygen Imaging.**

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Spin-lattice relaxation (SLR) based imaging produces nearly absolute oxygen images. Unlike phase relaxation, SLR shows much weaker dependence on spin-probe concentration and thus gives more accurate oxygen partial pressure estimation. Therefore, it is of great interest to compare SLR imaging methodologies.

Application of imaging methodologies to live subjects requires a balance between image quality, oxygen precision, imaging time and radio frequency power deposition per unit time. We have evaluated imaging methodologies by obtaining 10 minute SLR images of a homogeneous phantom using a 250 MHz EPR in vivo imager.

Between spin echo based methodologies, the inversion recovery imaging showed the best oxygen precision and the highest power deposition, while imaging using 3 pulse stimulated echo sequence demonstrated the lowest power deposition. For free induction decay single point imaging, inversion recovery imaging demonstrated the best performance.

ORAL SESSION

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168 **Skin Structure of *Psoriasis Vulgaris* Investigated by EPR Spin-Probe Method.**

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EPR (electron paramagnetic resonance) spin-probe method was used to investigate structural aspects of *psoriasis vulgaris* SC (pv-SC). EPR spectra of the SC samples were analyzed using order parameter (S_0) and rotational diffusion rates. A little, broad three-line pattern of 5-doxylstearic acid (5-DSA, spin probe) in pv-SC was observed. The spectral pattern of pv-SC is quite different from those of control SC reported. The S_0-values obtained for the pv-SC and the control were approximately 0.20 and 0.49, respectively. The statistical analysis suggests that the 0.20 value of pv-SC is significantly smaller than the 0.49 value of the control ($p < 0.01$). The rotational diffusion rates for the probe motion in the SC were faster than those of the control. Moreover, there was no spectral difference of the glass-plate with the SC against the static magnetic field, except for the signal intensity.[1-3] The present results suggest that the pv-SC is less rigid of the structure than that of the control SC, indicating irregular architecture of pv-SC. *Supported by a Grant-in-Aid for Scientific Research (24650247) and (25282124) from JSPS (K.N.).*

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ORAL SESSION

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169 **Water Soluble Complexes of Xanthophyll Antioxidants: Aggregation vs. Complexation.**

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Xanthophyll carotenoids can self-assemble in aqueous solution to form J- and H-type aggregates. This feature significantly changes the photo-physical and optical properties of these carotenoids, and can be very important for various applications. In this study we have applied EPR spin trapping techniques and optical absorption spectroscopy to investigate how the complexation with water soluble oligosaccharides and polysaccharides can affect the aggregation of the xanthophyll carotenoids zeaxanthin, lutein and astaxanthin. Their photostability and antioxidant activity was also examined. It was shown that complexation with arabinogalactan and glycyrrhizin reduced the aggregation rate but do not inhibit aggregation completely. Moreover, these complexants form inclusion complexes with both monomer and H-aggregates of carotenoids. H-aggregates of carotenoids exhibit higher photostability in aqueous solutions as compared with monomers, but much lower antioxidant activity. It was found that complexation increases the photostability of both monomers and the aggregates of xanthophyll carotenoids.

ORAL SESSION

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170 **Characterization of the Electronic Structure of P450 Compound I: Implications for Reactivity.**

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We present the first detailed characterization of the electronic structure of P450 compound I (P450-I). P450s are thiolate-ligated heme proteins that excel at the activation of inert C-H bonds. In humans, these enzymes are responsible for the phase I metabolism of ~75% of all pharmaceuticals. A major goal of bioinorganic chemistry has been to elucidate factors that enable cytochrome P450 to activate inert hydrocarbons[1]. Central to these efforts have been attempts to define the geometric and electronic structures of the highly reactive intermediate, termed compound I, in which the ferryl iron (S=1) is antiferromagnetically coupled to a radical (S=1/2). Recently, our laboratory made a breakthrough on this front by developing a method to prepare P450-I in high yields[2]. This discovery has set the stage for investigations that could provide key insights into the factors that govern C-H bond activation. We have characterized the electronic structure of P450-I employing advanced pulse EPR methods. We have resolved the ^{33}S(Cys), ^{1}H(b-protons of Cys) and ^{14}N (porphyrin) hyperfine coupling interactions using ENDOR, HYSCORE and ELDOR detected NMR methods. These parameters are direct reporters for the degree of delocalization of the radical between the porphyrin and the axial thiolate ligand. Comparison of the obtained values to those of the chloroperoxidase (CPO) compound I provide important functional insight for understanding the factors

influencing the reactivity of the thiolate-ligated heme iron sites, especially since CPO's are structurally similar to P450's but cannot oxidize unactivated hydrocarbons.

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ORAL SESSION

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171 **Conformation of p53 Response Elements Deduced Using Site-directed Spin Labeling.**

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The tumor suppressor protein p53 regulates a large number of signaling pathways by specifically recognizing a diverse set of DNAs, called p53 response elements (REs). Details on DNA conformational changes upon p53 binding are limited, as currently there is no structure of any unbound RE available. Here site-directed spin labeling is used to probe solution conformations of REs regulating protein p21 and Bax (called p21-RE and BAX-RE, respectively). Using a nucleotide-independent nitroxide probe and Double-Electron-Electron Resonance, nanometer distances between various DNA sites were measured in unbound REs as well as that complexed to the p53 DNA binding domain (p53DBD). Models of the unbound REs, which were selected using the measured distances from a large pool generated by all-atom Monte-Carlo simulations, reveal conformational changes at the center region as compared to the bound DNA reported in crystal structures. However, the modes of deformation for both REs are different: p21-RE kundergoes major helix axis shift, while BAX-RE twists and unwinds slightly upon p53DBD binding. The methodology applied here will have general implications for studying protein-DNA recognition in the context of transcription regulation, and the results suggest a mechanism in which deformation of RE plays a role in regulating p53 target recognition and function.

ORAL SESSION

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172 **Interaction Between Anti-HIV Antibody 10E8 and its Lipid-embedded Epitope Defined by EPR.**

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HIV uses its trimeric envelope protein to mediate entry into human T lymphocytes. The membrane proximal ectodomain region (MPER) of the HIV envelope protein gp41 plays a critical role in virus-host cell fusion, and is a major target of anti-HIV antibodies, including a newly identified potent antibody - 10E8. How these antibodies bind to the MPER segment and mediate anti-viral activity are unclear. Here, EPR dynamics, spin-spin distance and power saturation techniques were used to define the manner in which these antibodies recognize their membrane-immersed epitopes. The MPER adopted a structurally conserved pair of helices connected by a short flexible hinge on the viral membrane. 10E8 induces large conformational changes in the MPER relative to the membrane, lifts up the hinge region and extracts buried residues from the lipids. Thus, anti-HIV antibodies disrupt virus entry into human T cells by perturbing a facile MPER hinge function during membrane fusion. These findings have significant implications for structure-aided HIV vaccine design.

ORAL SESSION

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173 **Effects of Lipid Bilayer Phase and Nanoscale Curvature on Surface Electrostatic Potential as Measured by Spin-probe EPR.**

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Surface electrostatic potential is an essential property of phospholipid membranes that governs many vital functions of living cells. Many proteins are known to have strong binding preferences to curved lipid bilayer surfaces. To assess the surface electrostatics of the lipid membrane experimentally, we employed EPR of a recently introduced phospholipid (IMTSL-PTE) bearing a pH-sensitive nitroxide covalently attached to the lipid head group. The p*K*a of the ionizable group of this nitroxide is a function of the bilayer surface electrostatics potential and was determined by analyzing EPR spectra of the nitroxide affected by changes in rotational dynamics and magnetic parameters upon the probe protonation. The magnitude of the negative surface electrostatic potential, Ψ, for POPG (1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol)) small unilamellar vesicles (SUV) in the fluid phase (17 oC) increased from -137 to -167 mV upon decrease in the vesicle diameter from 107 to 31 nm. This effect could be rationalized by assuming different lipid packing upon increase in the SUVs' curvature. Interestingly, there is no significant difference in zeta-potential for POPG SUVs of different diameters: -48 mV for 68 nm and -46 mV for 102 nm. For DMPG (1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol)) SUVs in the gel phase (17 oC) the effect of curvature on the surface electrostatic potential is not that pronounced. We speculate that biologically relevant fluid bilayer phase allows for a larger variability in the lipid packing density in the lipid polar head group region than a more ordered gel phase. To assure a complete pH equilibration of both inner and outer leaflets a gramicidine A (gA) proton channel was inserted into SUVs. The electrostatic potentials determined for vesicles of the same diameter both with and without gA were found to be nearly identical. It is likely that the lipid flip-flop is responsible for pH equilibration of IMTSL-PTE.
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ORAL SESSION

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174 **Magnetic Interaction of Transition Ion Salts With Spin Labeled Lipid Membranes: Hofmeister Anion-driven Adsorption of Ions, Membrane Fluidity and Flexibility of Nitroxide Tethers.**

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The large values of relaxation enhancement (RE) of T_1 and T_2 for PC spin labels in the phospholipid membrane induced by paramagnetic metal salts dissolved in the water phase can be explained by Heisenberg Exchange from vertical fluctuations of the nitroxide group due to membrane fluidity and flexibility of lipid chains. Other possible mechanisms, such as dipole-dipole interactions from the hydrophobic membrane core to the water phase, or permeation of ions into the membrane do not contribute significantly to the RE. Whether the magnetic interaction occurs predominantly via Heisenberg exchange (Ni) or by dipole-dipolar (Gd) mechanism, getting the paramagnetic ion into close proximity with the nitroxide moiety is essential for efficient RE. We show how the composition and the phase state of the membrane affect the RE values. For phosphatidylcholine membranes the dependence of the RE on the anion in general follows the anionic Hofmeister series and reflects adsorption of anions followed by anion-driven attraction of paramagnetic cations on the choline groups. This adsorption is caused by the chaotropic effect and higher for chaotropic ions, e.g. perchlorate. However, there is no anionic dependence of RE for model membranes made from charged lipids. We used Ni-induced RE to study competitive adsorption of different di- and monovalent ions and to get better insight into the thermodynamics and electrostatics of ion/membrane interactions. The effect of cholesterol on the RE is consistent with its known effects on the lipid acyl chain conformation and mobility. Our results also point to a relatively low viscosity in the hydrophobic core of the fluid lipid membrane, similar to that of bulk hexadecane.

ORAL SESSION

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180 **Reducing the Time Required for DEER Measurements by Addition of Rapidly Relaxing Metal Ions.**

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Nitroxide spin labels are used to measure distances in biomolecules with the electron paramagnetic resonance (EPR) method known as double electron-electron resonance (DEER). To slow molecular motions that enhance electron spin relaxation, DEER experiments are performed at temperatures at or below 80 K. The intensity of the signal is determined by the concentration of the sample and by the electron spin-spin relaxation rate, $1/T_2$. Signals are weak, so extensive signal averaging is required. The rate at which signal averaging can be performed is limited by the spin-lattice relaxation rate ($1/T_1$) of the nitroxide, which is very slow at temperatures at or below 80 K. Dipolar interaction between a rapidly-relaxing paramagnetic metal ion and nitroxide increases the nitroxide spin-lattice relaxation rate. We propose to add paramagnetic metal ions to reduce the time required for distance measurements and increase the signal to noise ratio that can be achieved in a shorter time. Therefore, the effect of rapidly-relaxing metal ions (lanthanides and Co^{2+}) on nitroxide T_1 and T_2 has been explored. The goal is to achieve minimal effect of the metal ion on nitroxide T_2 while maximizing the effect on T_1. The effect of Dy^{3}, Er^{3+}, Gd^{3+}, Tm^{3+}, and Co^{2+} in the range of 1 to 30 mM on the relaxation times of 0.2 mM tempone (2,2,6,6-tetramethyl-4-oxo-piperidin-1-oxyl) in 1:1 water: glycerol at pH 6 was studied. Nitroxide T_1 and T_2 in the presence and absence of paramagnetic metal ions were measured by inversion recovery and spin echo dephasing, respectively, between 30 and 295 K. The positive effects of Er^{3+} on nitroxide relaxation times between 30 and 80 K and of Co^{2+} between 50 and 80 K are promising. The effect of Er^{3+} and Co^{2+} is being tested for DEER experiments at 80 K.

POSTER SESSION

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181 **Probing the Hydrogen Bonding of the Ferrous-NO Heme Center of NOS by Pulsed EPR.**

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Mammalian nitric oxide synthases (NOSs) are enzymes oxidizing L-Arg to NO. The water molecule at the catalytic heme site has been proposed to form a hydrogen bond with the peroxo ligand and to supply proton(s) necessary for the conversion of L-Arg substrate to N^{G}-hydroxy-L-arginine (NOHA) (which is further converted to L-citrulline and NO). The specific H-bonding assignments are largely based on the positions of protons inferred from, but not directly observed in, the X-ray structures. Studying the heme active site by experimental techniques sensitive to protons can provide important insights regarding the H-bonding interactions. In this work, we used ^{1}H, ^{2}H, and ^{17}O ENDOR to study the H-bonding of the NO ligand of the heme center in ferrous-NO form of neuronal NOS (nNOS), which is a close mimic of the obligatory ferric (hydro)peroxo intermediate in NOS catalysis. The ^{1}H ENDOR spectra obtained for the samples without a substrate and with L-Arg revealed that no H-bond to the NO ligand is formed in both cases: the ^{1}H anisotropic hfi with $T_{//} \approx 3$ MHz corresponds to the shortest possible NO – H distance of > 3 Å. On the other hand, in the sample with NOHA a weak H-bond is formed: the ^{1}H hfi is characterized by $T_{//} \approx 5.7$ MHz (corresponds to the shortest possible NO – H distance of ~2.3 Å) and $a_{iso} = -0.6$ MHz. The ^{17}O ENDOR data support these conclusions and indicate that in the case of NOHA the H-bonding hydrogen belongs to NOHA. *Supported by NIH GM081811, NSF CHE-1150644, AHA 12GRNT11780019, NCRR 5P20RR016480-12, and NIGMS 8 P20 GM103451-12.*

POSTER SESSION

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182 **EPR Studies of Pressure induced Jahn-Teller Reorientation in the Coordination Polymer: [CuF2(H2O)2(pyrazine)].**

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In this work we focus on the magnetic coordination polymer [$CuF_2(H_2O)_2$(pyrazine)], which undergoes successive pressure-induced structural transitions, both of which involve re-orientations of the Jahn-Teller axes associated with the CuII ions [1,2]. Multi-high-frequency EPR measurements were carried out under pressures up to 34kbar employing a vector magnet system which enables polar mapping of the Landé g-tensor both below and above the first phase transition. The EPR measurements yield direct information on the disposition of the magnetic *dx2-y2*orbital, thereby providing insights into the nature of the electrononic structure in ambient and high-pressure phases [2].

POSTER SESSION

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183 **Characterizing Lung Surfactant Peptide and Lipid Interactions in Different Timescales.**

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KL4, a 21 residue mimetic of surfactant protein B, is effective in the treatment of infant respiratory distress syndrome (RDS) and functions by lowering aveolar surface tension and promoting oxygen exchange. Here we compare the results from previous NMR investigations to those of fluorescence characterization of the effects of KL4 on the lipid dynamics and organization in liposomes. We utilized a pyrene phospholipid analog to investigate the effect of KL4 on lipid organization and acyl chain dynamics by monitoring changes in excimer-to-monomer (Ie/Im) ratio. This experiment probes the environment of the hydrophobic core of DPPC/POPG and POPC/POPG liposomes. An average decrease of ~27-40% and ~0-10% in Ie/Im was observed in the DPPC/POPG and POPC/POPG LUVs, respectively, with increasing peptide concentration (0.5 to 5 mol%). This decrease is directly proportional to a lowered probability of excimer formation, which is highly dependent on proximal interactions of an excited monomer with a pyrene moiety at ground state. The ability of the peptide to modify membrane fluidity properties was studied via anisotropy measurements of a rhodamine-labeled phospholipid. A steady increase in the order was observed in the DPPC/POPG liposomes with relatively constant fluorescence intensity, while collisional quenching was observed in the POPC/POPG liposomes. These observations agree with NMR observations and proposed mechanisms of peptide-mediated lipid trafficking. Further studies on the orientation and penetration of the peptide were interrogated using power saturation SDSL EPR.

POSTER SESSION

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184 **Locating NO in the {FeNO}7 Complex using HYSCORE: A Structural Context for Locating Substrates in non-heme Fe(II) Dependent Dioxygenases using ESEEM.**

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Non-heme Fe(II)/alpha ketoglutarate (α-KG) dependent dioxygenases are a large family of enzymes important in a wide range of biologically and medically relevant processes. These enzymes are believed to use a generally conserved mechanism and possess a common 2-histidine, 1-carboxylate Fe(II) coordination motif known as a "facial triad." Taurine Hydroxylase (TauD) is the archetype enzyme for this family and is an ideal subject for refining structural investigation methodologies due its abundance, stability, relative simplicity of substrate, and the existence of multiple crystal structures. By using nitric oxide (NO) as a surrogate to O_2, a S=3/2 $\{FeNO\}^7$ complex amenable to EPR can be formed that closely mimics the Fe-O_2 complex native to the functioning enzyme. Conveniently, NO also defines the principal magnetic axes used for reference in structural studies using EPR. A method for measuring its exact location in the complex is highly desirable. Using Hyperfine Subevel Correlation (HYSCORE), the position of NO in the $\{FeNO\}^7$ complex in TauD was observed by measuring the relative positions of the two histidine ligands. With this structural context, the measurement of the position and orientation of taurine using ^{2}H ESEEM was directly correlated to the ligands of the $\{FeNO\}^7$ complex. Application of this methodology to Xanthine Hydroxylase

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(XanA), a poorly understood member of this family, is also presented. This study represents the first direct structural characterization of XanA and suggests the efficacy of this methodology for structural investigations of non-heme Fe(II) sites in general.

POSTER SESSION

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185 **Dipolar Relaxation of Trityl Radicals at Low Temperatures.**

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The relaxation and spin dynamics of *sym*-trityl-CH_3 or "Finland" trityl radical was measured by pulsed EPR at x-band and w-band between the temperatures 3 - 110K. The spin-lattice relaxation rates, $1/T_{1e}$, agree with those measured previously by the Eaton Lab. The relaxation of the dipolar field, $1/T_{1D}$, produced by the trityl radicals in the sample, was measured using a dipolar echo sequence published by Jeener and Broekaert in 1967. The dipolar field relaxation is limited by the T_{1e} at high temperatures, but has a non-exponential decay at low temperatures extending over three orders of magnitude in time. We measured the T_{1D} using a logarithmic variation in time in order to observe the entire dipolar decay. The $1/T_{1e}$ ranged from less than 1 s^{-1} at 3 K to 1000 s^{-1} near 100 K and followed closely an exponential kinetics.

The relaxation kinetics for T_{1D} at low temperatures is close to that expected for spin diffusion among the trityl radicals in the sample and appears to be temperature independent. These results suggest that the dipolar relaxation and spin diffusion become significant factors in saturation of the electron spin system and in DNP at low temperatures and high radical concentrations.

POSTER SESSION

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186 **Impurities and Spin Relaxations in Nanodiamonds.**

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A nitrogen-vacancy (NV) center in diamond has been proposed as a promising candidate for nanoscale magnetic sensing and imaging in biological systems because its ability to detect small magnetic moment nearby and biocompatibility of diamond.[1] The sensitivity of NV center as magnetic sensor depends on impurities and spin relaxations of defects in its surrounding environment, and it is important to fully understand them in order for successful application of NV center. In the present study, multi-frequency continuous-wave and pulsed electron paramagnetic resonance (EPR) measurements of different size nanodiamond powders will be presented. Continuous-wave EPR spectra taken with our home-built 230/115 GHz continuous-wave/pulsed EPR spectrometer reveals a presence of unknown paramagnetic impurity (Impurity X) in nanodiamond and a strong powder size dependence in the EPR intensity ratio between P1 center and Impurity X. Moreover, the size dependence of longitudinal relaxation time *T1* in nanodiamond powders will be discussed.

[1] E. E. Romanova, R. Akiel, F. H. Cho, and S. Takahashi, Submitted to J. Phys. Chem. (2013)

POSTER SESSION

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187 **Zero- and Low- Field Study of Spin Dependent Trap Assisted Tunneling in Amorphous SiC:H Thin Film Dielectrics.**

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We report on measurements utilizing a very sensitive zero- and low-field electrically detected magnetic resonance (EDMR) technique which allows for the detection of defects that are responsible for trap assisted spin dependent tunneling (SDT) in thin layer dielectric films. Our work indicates that zero- and low-field SDT/EDMR can be a very useful measurement for the study of defects involved in transport through technologically important dielectrics used in metal oxide semiconductor

field effect transistors (MOSFETs) and other various capacitor structures. In this study, we investigate low-field SDT transport through 5 nanometer SiC:H capacitors; the SiC:H system is of considerable interest for interlayer dielectrics in microprocessors. SDT allows direct detection of defects involved in the variable range hopping transport which dominates the leakage currents in these systems. This transport is almost certainly related to an important, but poorly understood, reliability problem called time dependent dielectric breakdown (TDDB). SDT in these films can be observed because the transport process involves tunneling between paramagnetic defect sites. Tunneling transport between these defects is spin thus dependent, allowing magnetic resonance at the defects to influence the device currents.

POSTER SESSION

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188 **EPR studies of Orthorhombic Jahn-Teller Effect in Cu(II) doped (NH4)2Cd2(SO4)3 (ACS) Single Crystals. Paper I.**

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This paper presents both the experimental and theoretical EPR studies of the orthorhombic JT effect in Cu(II):cadmium ammonium sulphate(**(NH4)2Cd2(SO4)3)** single crystal. Since the first experimental confirmation of axial Jahn-Teller effect in Cu(II) doped ZnSiF6.6H2O in 1950, the Orthorhombic Jahn-Teller Effect (OJTE) in solids has not been clearly observed experimentally even though a lot of conjectures have been made. This is the first report of clear experimental observation of orthorhombic Jahn-Teller EPR spectra with ^{2}E Cu(II) ion in a single crystal providing the direct confirmation of the OJTE. The simultaneous occurrence of three groups of well resolved Cu(II) hyperfine lines(I=3/2) in the direction of g_z correspond to all the three Jahn-Teller potential well minima being non-equivalent in energy. The detailed theoretical analysis and computer simulation of the EPR spectra led to evaluation of many spectroscopic parameters and their temperature dependence, suggesting possible applications of such systems.

POSTER SESSION

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189 **Applications of Portable Nuclear Magnetic Resonance Spectrometers.**

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Nuclear Magnetic Resonance (NMR) spectroscopy is arguably the most important analytical method of our time yet has until now been strictly relegated to the laboratory. However, recent commercial advances in NMR instrumentation have significantly reduced the size of NMR instrumentation and have made it reasonable to investigate the potential uses of NMR spectroscopy in the field. Miniature NMR spectrometers are much easier to transport (<5 kg) and do not require cryogens of any kind, which makes stationary field measurements fairly straight forward. A more exciting question is whether these instruments are capable of being utilized in mobile applications where vibration is constantly varying along with the magnetic environment itself. Utilizing a picoSpin45 miniature NMR spectrometer we acquired spectra in two challenging field environments; a remote mountain top at 14,278 feet above sea level, and on board NASA's microgravity aircraft. In these environments, the instrument was exposed to significant and rapid vibrational, temperature, gravitational, and magnetic field changes. Spectra were continuously acquired during the course of the flight and the spectral characteristics of both the individual and averaged spectra evaluated. Despite a 40 μT variation in the experienced magnetic field and resulting 950 Hz shift in the Larmor frequency during acquisition we observed only modest decreases in signal to noise and resolution, both of which were still within the manufacturer's factory specifications at the time. Our results give hope that utilization of NMR on the International Space Station may be feasible in the near future. Not only would a miniature NMR spectrometer on the ISS, but provide additional analytical capabilities to the station but its use on the ISS would provide additional insights into the feasibility of deploying low field MRI in space, an important capability for long duration missions.

POSTER SESSION

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190 **Synthesis and Frequency Dependence of Semiquinone Relaxation Times.**

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Semiquinone radicals are important in many biological systems. In the present work the goal is to study three semiquinone radicals that had been reported to be persistent enough for our proposed studies. In the syntheses several parameters were varied, including the presence or absence of oxygen, and the stoichiometry of the reaction between KOH and quinone or hydroquinone. The best condition for stability of the 2,5-di-t-butyl-1,4-benzosemiquinone (25DTBSQ) radical is to mix equal volumes of air-saturated solutions of 2,5-di-t-butyl hydroquinone (5mM) and KOH (5mM) in ethanol.[1] 2,6-di-t-butyl-1,4-benzosemiquinone (26DTBSQ) radical was prepared from 2,6-di-t-butyl-1,4-benzoquinone using the same procedure. 2,3,5,6-tetramethoxy-1,4-benzosemiquinone (TMBSQ) radical was prepared by mixing 10:1 mole ratio of 25mM KOH and 5mM tetra fluoro-1,4-benzoquinone in methanol in air, which is a higher ratio of hydroxide to quinone than was used in the literature.[2] X-band CW (continuous wave) spectra for the three radicals were obtained using a Bruker EMX spectrometer. Hyperfine coupling constants were in good agreement with literature values. T_1 and T_2 relaxation times were measured at frequencies from 34 GHz to 1.5GHz on a Bruker E580 or on locally-designed and built spectrometers. T_2 is shorter at higher frequencies due to increased effects of g-anisotropy. T_1 is shorter at lower frequencies. Prior studies of the temperature and viscosity dependence of T_1 for semiquinones provided evidence for contributions from spin rotation and a second process with an activation energy of about 1 kcal/mole.[3] Neither of those processes predicts a frequency dependence of T_1. Further studies are underway to define the additional contribution to relaxation at lower frequencies.

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POSTER SESSION

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191 **SpecMan4EPR 2.0: Shaped Pulses using SpinCoreTM RadioProcessorTM and PulseBlasterDDSTM Boards**

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Shaped radio frequency pulses are widely used in nuclear magnetic resonance and MRI. They allow efficient excitation of particular spectral lines and precise control of spin trajectories. This results in enhanced performance of pulse sequences. Applications of shaped pulses in EPR are rather rare, primarily in quantum computing and imaging; nevertheless those studies demonstrate clear advantage of this technique.

In the past, wide use of shaped pulses in EPR was inhibited by the high cost of arbitrary wave form generators operating at EPR frequencies. Advances of high frequency electronics have lifted this limitation and opened the door for budget solutions. During last 10 years SpecMan4EPR software was successfully used for spectrometer control in a variety of applications from radio frequency imaging to high-field DNP. SpecMan4EPR offers multifunctional and expandable software platform for EPR/NMR/DNP spectrometers and imagers.

Our poster presents the second generation of SpecMan4EPR. In addition to 'rectangular' pulses version 2.0 offers shaped pulses with predefined and user-generated envelope. The performance of the software was evaluated using SpinCore™ RadioProcessor™ and PulseBlasterDDS™ boards featuring radio frequency arbitrary waveform generators. In the future we plan to extend our support to devices operating at higher frequencies.

POSTER SESSION

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192 **Studying Conformational Changes In The Glycine Riboswitch Using Electron Paramagnetic Resonance Spectroscopy.**

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Electron Paramagnetic Resonance (EPR) spectroscopy is used to study dynamic conformational changes in the RNA glycine riboswitch. The dynamic role of the leader-linker interaction within glycine riboswitch conserved sequences is probed through site directed spin labeling and continuous wave EPR. Inter-aptamer and aptamer-expression platform interactions

are elucidated through double electron-electron resonance spectroscopy. Incorporation of spin labels is achieved through optimized ligation methodologies allowing synthetically modified RNA to be joined to larger RNA sequences. Expected folding and burial of riboswitch elements will lead to restricted motion of the spin label and, additionally, pulsed EPR experiments yield distance distribution profiles indicating conformational exchange between states in the absence and presence of glycine.

POSTER SESSION

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193 **Dense Functionalization of Graphene via Covalent Attachment of Nitroxide Radicals.**

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Electrochemical double layer capacitors (EDLC's) are devices that can store and release electrical energy quickly (high power density) with good cycling stability.[1] However, the amount of energy they can store (energy density) falls short of conventional Li-ion batteries. Devices that combine the high power density of EDLC's and the high energy densities of batteries are thus highly desirable, as they may provide a more efficient way of storing/delivering energy.[2] Nitroxides are stable organic free radicals which undergo a fast, reversible, one-electron oxidation at ≈ 0.8 V (vs. Ag/AgCl) to oxoammonium cations.[3] Herein, we demonstrate the covalent attachment of nitroxides to graphene and characterization of the resultant densely-functionalized graphene using EPR spectroscopy, electrochemistry, electrical conductivity, IR, TGA, etc. The nitroxide-functionalized graphene, when assembled into an EDLC, is expected to exhibit increased energy density over graphene alone, due to the fast, reversible redox reaction of the nitroxide radicals. *Supported by NSF CHE-1012578 and the Nebraska Center for Energy Sciences Research.*

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POSTER SESSION

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194 **EPR investigation of low-sized powders of KNbO3 and KNbO3:Fe.**

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Nanoscale undoped $KNbO_3$ powders exhibit a wide X-band EPR signal, which consists of several resonance lines having width from 200 to 1000 Oe. The lines broaden, decrease in peak-to-peak intensity and shift to lower fields with the temperature decrease. The effect of magnetization on the EPR signal was studied. It was found that individual lines are of a ferromagnetic nature. To define the origin of the ferromagnetism, the spectra of low-sized $KNbO_3$:Fe powders were studied. Two types of signals, a paramagnetic signal and one or more (depending on the Fe content) ferromagnetic lines, were revealed in the spectra. A paramagnetic signal originated from individual Fe^{3+} ions, is presented in the sample doped with 1at.% of Fe. Together with this signal, a ferromagnetic line is also registered in the powders with 1 at.% of Fe. The line is suggested to be from the impurity phase of α-Fe_2O_3. With iron concentration increasing, the intensity of the paramagnetic signal remains constant, whereas the intensity of the line from α-Fe_2O_3 increases. That indicates to a low solubility of iron in the $KNbO_3$ powder and the tendency of iron to the clusterization on the surface of particles. Another ferromagnetic line arises in the powders doped with more than 10 at.% of Fe. The signal is suggested to be from the clusters of α-Fe.

POSTER SESSION

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195 **Orphan Spin Operators Enable the Acquisition of Multiple 2D and 3D MAS Solid-State NMR Spectra of Proteins.**

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Solid-state NMR (ssNMR) is the method of choice for probing structure, dynamics, chemistry, and ligand binding of microcrystalline and membrane-bound proteins at the atomic resolution. In this work we present a new method MEOSIS[1](Multiple ExperIments via Orphan SpIn operatorS) that enables one to simultaneously acquire multiple multidimensional NMR spectra, resulting from four different polarization transfer pathways. This method utilizes simultaneous cross polarization (SIM-CP), long-living^{15}N polarization, and orphan (i.e. neglected) spin operators, to generate four phase-encoded coherence pathways that are decoded into four independent spectra using Hadamard transformations. To demonstrate the power of this method, we simultaneously acquired four 2D experiments DARR, NCO, CA(N)CO and N(CA)CX, and three 3D experiments NCACX, NCOCX, and CA(N)COCX, on a U-^{13}C, ^{15}N-labeled microcrystalline ubiquitin. Hadamard decoding the coherences into multiple independent experiments is a general concept in NMR and can be used to redesign many pulse sequences. The MEIOSIS method is based on our recently developed DUMAS (dual acquisition magic angle spinning) solid state NMR techniques.[2,3] Two examples of MEOSIS method are demonstarted for ubiquitin microcrystalline protein, and a membrane protein sarcolipin. Figure 1A shows the simultaneous acquisition of four 2D spectra using 2D MEIOSIS pulse sequence. The total experimental time for the four experiments acquired simultaneously with the MEIOSIS sequence was ~29 hours, cutting experimental time by more than 50%. Figure 1B shows the three 3D spectra NCACX, NCOCX, and CA(N)COCX, acquired simultaneously using 3D MEOSIS pulse sequence. DUMAS and MEIOSIS methods are general and can be used to combine several sets of multi-dimensional ssNMR experiments (see the uploaded file)

POSTER SESSION

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196 **Electron Magnetic Resonance Studies of Nanosized Sm0.35Ca0.65MnO3 Manganite.**

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Electron magnetic resonance (combining ferromagnetic resonance in the ferromagnetic phase and electron paramagnetic resonance in the paramagnetic phase) is known[1] to provide benchmark signatures of the charge ordered phase in doped rare earth manganites. Here the charge ordering refers to the real space ordering of the Mn^{3+} and Mn^{4+} ions occurring below a certain temperature in these mixed valent compounds. Reduction of the particle size of the manganites to nanoscale has drastic effects[2] such as disappearance of the charge order and appearance of a ferromagnetic phase instead of the antiferromagnetic phase present in the bulk sample. Here we report a systematic tracking of the effect of size reduction on magnetic properties and EPR parameters of electron doped $Sm_{0.35}Ca_{0.65}MnO_3$. The bulk form of this system is charge ordered below 270 K and antiferromagnetic below 160 K. Nanoparticles of various sizes (mean dia ~ 14, 18, 27, 45 nm) were prepared by sol-gel method. Magnetic and X-band EPR measurements were carried out on all the samples in the temperature range 10-300K. EPR signals were analysed by line shape fitting using double Lorentzian function accounting for both clockwise and anticlockwise rotating components of the microwave field. Magnetization measurements and the extracted EPR parameters, namely, the line width, intensity and the resonance field indicate that as the size of the particle reduces there is a gradual weakening of the charge order and its complete disappearance in the smallest of the particles. The nanoparticles also exhibit ferromagnetism with increasing strength as the particle size decreases. We discuss the origin of these effects in terms of the presently existing models[3].

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POSTER SESSION

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197 **Macroscopic and Microscopic Defects in KH2PO4 Cystals with Embedded TiO2 Nanoparticles.**

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High quality KH_2PO_4 (KDP) crystals with incorporated TiO_2 anatase nanoparticles show giant nonlinear optical susceptibility. Their characterization using several complementary methods is presented. Visual observations, transmission and scanning electron microscopy have shown that the anatase nanoparticles were captured mainly by the pyramidal growth sector and, to a considerably lesser extent, by the prismatic growth sector. Deciphering complicated electron paramagnetic resonance spectra in KDP:TiO_2 and comparison with published data permitted the identification of paramagnetic defects along with their associated g-factors and zero-field splitting parameters (in some cases for the first time). It was found that the dominant lines belong to four different centers Fe_A^{3+}, Fe_B^{3+}, Cr_R^{3+} and Cr_{GB}^{3+}. From analysis of line intensities it was concluded that the concentration of intrinsic defects like potassium and hydrogen vacancies in KDP:TiO_2 is comparatively small, that the concentration of non-controlled impurities in nominally pure KDP samples is several times larger than in KDP:TiO_2, and that the concentration of non-controlled impurities in the prismatic part of the KDP:TiO_2 boule is approximately twice as large as in the pyramid part. The study allowed the nature and distribution of macroscopic and microscopic defects in the KDP:TiO_2 crystals to be clarified. The relationship between these defects and the distribution of TiO_2 nanoparticles, and the influence of incorporated nanoparticles on the nonlinear optical properties of composite crystals in comparison with pure crystals were also elucidated.

POSTER SESSION

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198 **ESEEM and HYSCORE Analysis of the Allosteric Forms of Phenylalanine Hydroxylase: Evidence for Changes in H2O Coordination Following Substrate Addition.**

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Phenylalanine Hydoxylase uses tetrahydrobiopterin and molecular oxygen to catalyze the conversion of L-phenylalanine to L-tyrosine. Phenylalanine allosterically regulates the enzyme leading to a global conformational change that results in ligand rearrangement at the catalytic site. Electron Spin Echo Envelope Modulation (ESEEM) and Hyperfiine Sublevel Correlation (HYSCORE) studies of a series of $[FeNO]^7$-$N_2O_{1\text{-}3}$ model complexes were used to develop a means for detecting and quantifying water ligands bound to Fe(II). This methodology was then extended to studies of human Phenylalanine Hydroxylase (hPheH) to reveal the presence of two water ligands bound to the $[FeNO]^7$ paramagnetic center at the active site of the unactivated, or allosteric T-(Tense) state of the enzyme. Further addition of substrate, L-phe, to poise the enzyme in its fully active, or allosteric R-(Relaxed) state, resulted in the loss of one bound water ligand. Finally, addition of the cofactor 5-deaza-6-methyltetrahydropterin to activated, R-state, $[FeNO]^7$-hPheH, resulted in the loss of the remaining water ligand leaving the metal site void of bound water.

POSTER SESSION

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199 **Natural Occurring Polymorphisms Alter Flap Conformation and Backbone Dynamics of HIV-1 Protease.**

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HIV-1 Protease (HIV-1 PR) is an essential enzyme for generating infectious HIV virus particles and is a target in the fight against HIV infection. By using pulsed EPR studies, we have shown that natural polymorphisms alter HIV-1 PR conformation ensemble. Here, NMR relaxation technique was used to show that the natural polymorphisms also change the backbone dynamics. Furthermore, we selectively introduce some natural polymorphisms to the subtype B and utilized double electron-electron resonance to show that these mutations are responsible for the different flap conformation sampling in CRF_01 A/E. The close look at previous X-ray structures further indicate that the altered salt-bridge formation between these mutations may be the reason for CRF_01 A/E has more curled flap conformation compare to subtype B.

POSTER SESSION

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200 **Site Localization and Rigid-body Docking in the MMM Software Package.**

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The open-source Matlab-based software package MMM provides fast and reasonably accurate simulation of the conformational distribution of common nitroxide spin labels and of label-to-label distance distributions, including multi-spin effects for up to five labels. The graphical user interface allows for visualization of protein and nucleic acid structures and symmetry or lipid-bilayer related transformation of protein coordinates. Combined with the possibilities to read PDB structures and DEER/PELDOR experimental data or distance distributions, MMM can be used for testing whether structures or structure models are consistent with experimental label-to-label distance measurements.

Version 2013.2 of MMM includes new features for localizing label positions in only partially resolved structures where the label position is in an unresolved domain. Such localization is possible with two-fold ambiguity if three distances to known sites were measured and unambiguously if at least four distances were measured. Depending on the width of the label-to-label distance distributions and consistency of the experimental data, such trilateration or multilateration leads to position uncertainty, which decreases by including additional distance constraints. Such uncertainty is accounted for in MMM by computation of probability density surfaces. Relative positions in a network of labels can be computed without resorting to a structural template by a distance matrix geometry approach, similar to recent work from the Gaffney and Freed groups,[1] but also allowing for cases where not the full distance matrix is known. If a teamplate is available and at least three labelled sites are resolved in this template, the network can be fitted to it.

Finally, a full grid search protein-protein docking approach that we earlier introduced on the NhaA homodimer is generalized to symmetric homooligomers consisting of more than two protomers and to heterodimers.

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POSTER SESSION

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201 **Temperature Dependence of Magnetocrystalline Anisotropy in Bulk and Nanoparticles of La1-xSrxMnO3 (x=0.15, 0.125).**

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Ferromagnetic resonance (FMR) can provide information on magnetocrystalline anisotropy (MA) even in polycrystalline ferromagnetic materials in contrast with torque magnetometry, the standard technique of investigating MA, which requires single crystal samples. We have carried out FMR study of magnetocrystalline anisotropy in bulk and nanoparticles (dia ~ 20 nm) of $La_{1-x}Sr_xMnO_3$, x=0.15, 0.125 (LSMO) as a function of temperature in the range 4 K - 300 K. The nanoparticles were prepared by standard sol-gel technique and were characterized by XRD, EDS and TEM. The bulk LSMO samples were prepared by sintering the nanoparticles at high temperature. SQUID measurements showed that the nanoparticles of LSMO0.15 (LSMO0.125) underwent ferromagnetic transition at ~ 280 K (300 K) whereas the bulk did so at ~ 240 K (200 K). The FMR signals were recorded using a commercial EPR spectrometer between 4K - 300 K. FMR signal line shape is a definitive indicator of the nature and sign of magnetocrystalline anisotropy of the sample[1]. The signal shape of the LSMO bulk and nanoparticles of both the compositions at the lowest temperature used is indicative of negative anisotropy. As the

temperature is increased, for LSMO0.15, the line shape gradually changed and at ~ 205 K for the bulk and at ~ 250 K for the nanopartilces, signals characteristic of positive anisotropy are observed. We analyzed the signals using the 'ROKI'[2] simulation program and extracted the parameters. We have determined the uniaxial anisotropy constant vs. temperature which clearly shows the sign reversal of magnetocrystalline anisotropy. However, for the LSMO0.125 sample, FMR does not show any reversal of sign of MA. We believe that the co-operative Jahn-Teller (JT) transition occurring in the FM phase in LSMO0.15 drives the sign change in the magnetocrystalline anisotropy while in the LSMO0.125 sample FM transition occurs below the JT transition thus accounting for the absence of the sign reversal of MA.

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POSTER SESSION

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202 **X-Band EPR Spectrometer with Customizable Arbitrary Waveform Generator for Precise Tailoring of Pulses as "Seen" by the Spins.**

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We present arbitrary control over a homogenous spin system, demonstrated on a simple home-built EPR spectrometer operating at 8–10 GHz (X-band) and controlled by a 1 GHz arbitrary waveform generator (AWG) with 42 dB (i.e. 14-bit) of dynamic range. The spectrometer is built with a single DAC (digital to analog converter) board operating as the main control unit and a relatively small number of stock components, and it can capitalize on automated digital calibration and correction routines in order to generate shaped X-band pulses with precise amplitude and phase control. More importantly, it can precisely tailor the excitation profiles "seen" by the spins in the microwave resonator. We demonstrate the capability to generate a variety of pulse shapes, including rectangular, triangular, Gaussian, sinc, and adiabatic rapid passage waveforms. We then show that by finely adjusting for the distortion and broadening caused by transmission into the microwave cavity, one can optimize corrected waveforms that are distinctly different from the initial, uncorrected waveforms. The enhanced control over pulse phase and amplitude can be directly applied to excite spin systems more broadly and uniformly (e.g. broadband inversion and saturation) and will enable measurement of T_1 and T_2 in the absence of spectral or spin diffusion for samples with spectral bandwidths that span even several hundred MHz. Another related application of broad and tailored excitation can improve dynamic nuclear polarization (DNP) techniques by achieving uniform maximal saturation (s_{max}) for spin probes by simultaneously saturating all hyperfine lines. In this way we experimentally set $s_{max} = 1$ and remove the ambiguity in s_{max} which can vary dramatically for freely dissolved spin labels and those attached to highly mobile polymer chains.

POSTER SESSION

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203 **Effects of Lipid Bilayer Phase and Nanoscale Curvature on Surface Electrostatic Potential as Measured by Spin-probe EPR.**

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Surface electrostatic potential is an essential property of phospholipid membranes that governs many vital functions of living cells. Many proteins are known to have strong binding preferences to curved lipid bilayer surfaces. To assess the surface electrostatics of the lipid membrane experimentally, we employed EPR of a recently introduced phospholipid (IMTSL-PTE) bearing a pH-sensitive nitroxide covalently attached to the lipid head group. The p*K*a of the ionizable group of this nitroxide is a function of the bilayer surface electrostatics potential and was determined by analyzing EPR spectra of the nitroxide affected by changes in rotational dynamics and magnetic parameters upon the probe protonation. The magnitude of the negative surface electrostatic potential, Ψ, for POPG (1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol)) small unilamellar vesicles (SUV) in the fluid phase (17 oC) increased from -137 to -167 mV upon decrease in the vesicle diameter from 107 to 31 nm. This effect could be rationalized by assuming different lipid packing upon increase in the SUVs' curvature. Interestingly, there is no significant difference in zeta-potential for POPG SUVs of different diameters: -48 mV for 68 nm and -46 mV for 102 nm. For DMPG (1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol)) SUVs in the gel phase (17 oC) the effect of curvature on the surface electrostatic potential is not that pronounced. We speculate that biologically relevant fluid bilayer phase allows for a larger variability in the lipid packing density in the lipid polar head group region than a more ordered gel phase. To assure a complete pH equilibration of both inner and outer leaflets a gramicidine A (gA) proton channel

was inserted into SUVs. The electrostatic potentials determined for vesicles of the same diameter both with and without gA were found to be nearly identical. It is likely that the lipid flip-flop is responsible for pH equilibration of IMTSL-PTE. *Supported by U.S. DOE Contract DE-FG02-02ER15354.*

POSTER SESSION

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204 **Electron Spin Relaxation Measurements of the Oxygen-Induced Radicals in neuronal Nitric Oxide Synthase.**

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Nitric oxide(NO) is an important molecule in a number of physiological and pathophysiological processes. Through a pair of coupled mono-oxygenase reactions, nitric oxide synthase(NOS) catalyzes the formation of NO, L-citrulline, $NADP^+$ and H_2O from L-arginine(L-arg), NADPH and molecular oxygen. In addition to the substrates, NOS requires the cofactor tetrahydrobiopterin (BH_4) for enzymatic activity. In the absence of L-arg or the BH_4 cofactor the reactions uncouple and could lead to the formation of reactive oxygen intermediates such as superoxide, hydrogen peroxide or peroxynitrite. This work is a study of neuronal NOS under these uncoupled condition in order to gain an understanding of the regulatory mechanisms of L-arg and/or BH_4 on the production of radical species. In the absence of primary substrate L-arg, we trapped two different radicals which show very different relaxation behavior. In addition we were able to use electron spin relaxation measurements to determine the location of these radicals respect to the heme active site. *This work supported by NIH HL095820*

POSTER SESSION

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205 **Orientation of Phospholamban in Lipid Bicelles Detected by Electron Paramagnetic Resonance.**

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We have used electron paramagnetic resonance (EPR) to probe changes in transmembrane helix orientation of the integral membrane protein phospholamban (PLB), as a function of phosphorylation and addition of its regulatory target, the sarcoplasmic reticulum calcium ATPase (SERCA). We found previously that PLB remains bound to SERCA after phosphorylation, suggesting that a structural transition within the SERCA-PLB complex is responsible for relief of inhibition[1]. Our current goal is to elucidate this mechanism through orientation and accessibility EPR, in order to support rational design of therapies to improve calcium transport in muscle cells. We used solid-phase peptide synthesis to label the monomeric mutant AFA-PLB with the TOAC, a spin label attached rigidly to the α-carbon, within the transmembrane domain, and reconstituted the protein in lipid bicelles and vesicles[2]. EPR on aligned bicelles and spectral analysis with MultiComponent[3] showed that the PLB transmembrane domain changes its tilt relative to the membrane upon phosphorylation and upon binding to SERCA. *This work was funded by grants from NIH (R01 GM27906 and T32 AR007612).*

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POSTER SESSION

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206 **Exploring the Catalytic Mechanism of Tyrosine Hydroxylase.**

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Tyrosine Hydroxylase (TyrH) is a non-heme Fe(II) hydroxylase that catalyzes the hydroxylation of substrate tyrosine to produce 3,4 dihydroxy -L -phenylalanine, or L-DOPA. This reaction is the rate-limiting step in the biosynthesis of the catecholamine neurotransmitters and as such, dysfunction in TyrH is thought to lead to several neurological disorders. The chemistry requires the binding of substrate tyrosine, a cofactor, tetrahydrobiopterin and molecular oxygen to a

non-heme Fe(II)-based catalytic site. We have used NO as a surrogate for molecular oxygen to produce an $(FeNO)^7$, S=3/2, paramagnetic center amenable to EPR spectroscopy at the catalytic site. A combination of orientation-selective ^{2}H-ESEEM and ^{1}H-HYSCORE spectroscopies have been undertaken to address issues regarding allosteric regulation of the enzyme and structural aspects of pterin and tyrosine binding that are key to proper function.

POSTER SESSION

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207 **DEER Reveals that Single Point Mutations Modulate Seed Selection in Fibril Growth of Tau**

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Fibrils resulting from the aggregation of microtubule-associated protein tau are a characteristic of Alzheimer's disease and other neurodegenerative disorders. Small tau aggregates are believed to spread intracerebrally by transfer between neurons and template-assisted conversion of native tau monomers. The protein can be grouped into isoforms of three- and four-repeat tau based on the number of microtubule binding repeats in the amyloidogenic core region. The conformation of tau fibrils varies with isoform composition. Fibrils of three-repeat tau are structurally homogeneous, while fibrils of four-repeat tau are heterogeneous, composed of at least three distinct conformers. Here, we used double electron-electron resonance (DEER) spectroscopy, a technique that measures the distances between two spin labels, to gain molecular insights into the four-repeat tau fibril ensemble. We observe that single point mutations at key positions in the protein (ΔK280, P301S, P312I, and D314I) markedly change the distribution of fibril conformers after template-assisted growth, while other mutations in the protein (I308M, S320F, G323I, G326I, N336R) have little effect. These findings suggest that seed selection is sequence dependent with specific tau disease mutants showing selective preferences. The results reveal DEER spectroscopy as a powerful technique for investigating the conformational ensembles of amyloid fibrils.

POSTER SESSION

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208 **Improving Sensitivity of Detection of Biologically-Generated Radicals by Rapid-Scan EPR.**

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The low flux and short lifetime of superoxide *in vivo* makes detection challenging. Spin trapping with BMPO to form the BMPO-OOH adduct converts the very short-lived superoxide radical into a more stable spin adduct. In rapid-scan EPR, the magnetic field is scanned through resonance in a time that is short relative to electron spin relaxation times, and data are processed (deconvolved) to obtain the absorption spectrum. To validate the methodology, superoxide was generated by the reaction of xanthine oxidase and hypoxanthine with flux rates of 0.1 to 6.0 micromolar/min and trapped with BMPO. The technique was also used to detect superoxide produced by Enterococcus Faecalis. A factor of 40 improvement was observed with rapid scan for these systems relative to normal CW detection.

POSTER SESSION

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209 **Gate Potential and Field Dependence of Electrically Detected Magnetic Resonance in Amorphous SiO2 and SiOC:H on Si.**

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We report on x-band electrically detected magnetic resonance (EDMR) measurements as a function of gate potential and thus also oxide field in amorphous SiO_2 and SiOC:H films on Si. This response can be observed over a wide range of gate potential and oxide fields. EDMR measurements have been made at fields of as little as about 1 MV/cm to approximately 10 MV/cm. The EDMR is almost certainly the result of EPR mediated spin dependent trap assisted tunneling. Our observations indicate the involvement of several defects in electronic transport within these films. A comparison of EDMR amplitudes and

calculated metal/dielectric/silicon band diagrams versus gate potential allows us to draw admittedly crude conclusions with regard to the density of states of defects involved in electronic transport. Unfortunately the EDMR spectra observed to date have been essentially featureless Gaussians or in some cases a superposition of two featureless Gaussians. The spectra exhibit zero crossing g values ranging between 2.000 to 2.005. Peak-to-peak line widths vary between 10 and 20 Gauss. Our results, although preliminary in nature, suggest that EDMR has the potential to provide fundamental information about transport mechanisms in dielectric thin films.

POSTER SESSION

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210 **Sucrose Radicals Induced by Low Dose Irradiation with X-ray.**

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We investigated stable radical of sucrose and L-alanine radicals produced by heavy ions and X-ray irradiation at the same dose. Especially, sucrose radicals induced by low dose irradiation of X-ray were examined. The EPR (Electron Paramagnetic Resonance) spectral areas for the two compounds showed a linear relation with the absorbed dose.[1,2] The both irradiations of sucrose produces stable free radicals. EPR of sucrose radicals showed linear increase of the signal intensity as well as accumulation of dose. Based on the EPR spectral pattern obtained, the stable sucrose radicals are the same among helium (He) ion, carbon (C) ion, silicon (Si) ion, neon (Ne) ion, and X-ray irradiation. However, the radical production as a function of LET suggested that the smaller particle size can be more LET dependent than those for the larger particle size. Further analysis was carried out for the radical-production cross sections (s), which showed that stable radicals of the two compounds were produced through collisions of several particles with a single molecule. Considering the molecular sizes of sucrose and alanine, the s values are similar. In addition, a comparison of the EPR results for the C-ions and X-rays at 50 Gy dose was made. Sucrose spin concentrations produced by C-ions at LET 13 and X-rays were similar unlike alanine.[3] *Supported by a Grant-in-Aid for Scientific Research (24650247) and (25282124) from JSPS (K.N.).*

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POSTER SESSION

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211 **ATP Hydrolysis by Myosin Monitored with Pulsed EPR.**

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ATP binding and hydrolysis trigger myosin recovery stroke, priming myosin for interaction with actin and the force production. At the myosin active site Mg^{2+} coordinates γ and β phosphates of ATP and two amino acid residues, S237 and T186. Two mechanisms for phosphate abstraction are currently proposed: the direct mechanism, when one of the water molecules at the myosin active site donates a proton to the γ phosphate, abstracting it from the nucleotide, and indirect mechanism, when a proton is transferred to the γ phosphate through one of the neighboring residues, S236 or K185. Atomic structures and quantum mechanical calculations show a longer bond between β and γ phosphates when ATP is coordinated to Mg^{2+} at the myosin active site. It is hypothesized that phosphate gets released via the "back door", formed by switch I and switch II loops. The other product of hydrolysis, Mg.ADP, is released later. In this work we used a rapid freeze technique in combination with pulsed EPR to directly observe the process of the γ phosphate abstraction. We used paramagnetic manganese instead of diamagnetic magnesium, since myosin is a non specific enzyme, supporting Mn.ATPase activity. The samples containing spin-labeled myosin and Mn.ATP were rapidly mixed and frozen with different delays. Mn^{2+} binding to myosin was monitored using pulsed ELDOR. The number of phosphates coordinated to Mn^{2+} was measured by pulsed ENDOR as a function of the delay time. The EPR results are compared with the structural kinetics of myosin recovery stroke, measured with transient time-resolved FRET. *Supported by NIH AR59621.*

POSTER SESSION

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212 **Highly-Efficient Charge Separation and Polaron Delocalization in Polymer-Fullerene Bulk-Heterojunctions: A Comparative Multi-Frequency EPR & DFT Study.**

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The depletion of fossil fuels has led to an intensive search for renewable energy sources. Solar-based technologies could provide sufficient energy to satisfy the global economic demands in the near future.[1] Organic Photovoltaic (OPV) cells are promising devices for solar energy utilization, offering low-cost fabrication and tunability of electronic properties. Understanding the charge separation and charge transport at a molecular level is crucial for improving the efficiency of OPV materials. Light-induced EPR spectroscopy combined with DFT calculations is used to study the electronic structure of charge separated states in blends of the polymers P3HT, PCDTBT, and PTB7 with fullerene derivatives. Under illumination of these blends, two paramagnetic species are formed due to photo-induced electron transfer between the conjugated polymer and the fullerene derivative. They are the positive, P^+, and negative, P^-, polarons on the polymer backbone and fullerene cage, respectively, and correspond to radical cations and radical anions. Using the high spectral resolution of high-frequency EPR at 130 GHz, the EPR spectra of these species were resolved and principal components of the g-tensors were assigned. Pulsed ENDOR spectroscopy allowed the determination of ^{1}H hyperfine coupling constants of light-induced positive and negative polarons. The experimental results obtained for the different polymer-fullerene blends have been compared with DFT calculations, revealing that the three systems the positive polaron is distributed over distances of 40 - 60 Å on the polymer chain. This corresponds to about 15 thiophene units for P3HT, approximately three units PCDTBT, and about three to four units for PTB7.[2] Delocalization of the positive polaron on the polymer donor is an important reason for the efficient charge separation in bulk heterojunction systems as it minimizes the wasteful process of charge recombination. Advanced EPR spectroscopy in combination with DFT is a powerful approach for investigation of light-induced charge dynamics in OPV materials.

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POSTER SESSION

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213 **A Spin Label Derived from Mannosamine.**

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We have synthesized a nitroxide-functionalized *D*-mannosamine **1** and related monosaccharide derivatives for potential use as spin labels. Pyrrolidine nitroxides, with *gem*-diethyl groups adjacent to the nitroxide moiety, are remarkably resistant to reduction with ascorbate and related antioxidants,[1] and thus may have a sufficiently long half-life in living cells to be compatible with metabolic oligosaccharide engineering.[2] As various hydrophobic and sterically large *N*-acyl mannosamine derivatives have been shown to be incorporated onto the cell surface as the corresponding *N*-acyl-modified monosaccharide sialic acids,[2] spin label **1** could provide a new tool for targeting and imaging of the sialic acid pathway.[3] *Supported by NSF CHE-1012578.*

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POSTER SESSION

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214 **EPR and FTIR Insights in to the Enzymatic Mechanism of H2 Activation by the [FeFe]-Hydrogenase HydA1 from *Chlamydomonas reinhardtii.***

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[FeFe]-hydrogenases catalyze the reversible activation of H_2 via an organometallic cluster termed the H-cluster. The H-cluster comprises a [4Fe-4S] ferredoxin-like subcluster linked to a CO and CN ligated diiron subcluster via a cysteine bridging ligand[1]. During catalysis, the H-cluster cycles between several different electronic and vibrational intermediate conformers and a general model for catalysis has been derived mainly from the study of bacterial [FeFe]-hydrogenases[2]. Here, correlated EPR and FTIR spectroscopy were used to study the algal [FeFe]-hydrogenase HydA1 from *Chlamydomonas reinhardtii*[3], which contains solely the H-cluster domain and no accessory FeS cluster domains found in bacterial [FeFe]-hydrogenases that may complicate spectral interpretation and enrichment for particular intermediates. Steady-state reduction by either sodium dithionite or H_2 resulted in different EPR and FTIR spectra. EPR signals from both treatments suggest multiple H-cluster intermediates which contain a reduced $[4Fe\text{-}4S]^{+1}$ subcluster whereas the FTIR spectra indicate differing diiron subcluster configurations. While consistent with earlier experimental and theoretical studies[2,4,5], the spectra suggest a higher level of complexity than previously reported for the catalytic mechanism employed by these unique enzymes. This poster will summarize our recent spectroscopic results in the context of an expanded mechanistic model.

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POSTER SESSION

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215 **Recent Developments and Applications from the Center for Electron Paramagnetic Resonance Imaging of *in vivo* Physiology.**

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Oxygenation status is integral to many physiologic and biologic processes. Therefore, accurate and noninvasive oxygen images assume enormous importance. The Center for EPR Imaging *in vivo* Physiology works to develop and enhance EPR oxymetry.

Spin-lattice relaxation imaging using an inversion recovery pulse sequence (R_1-imaging), as opposed to previously used imaging (R_2-imaging), enables an essentially absolute measure of pO_2 due to significantly decreased confounding concentration-dependent self-relaxation effects.

Maximally spaced projection sequencing enables real-time reconstruction and post-acquisition temporal resolution image adjustment by optimization of acquired EPR projection data. It allows reconstruction of intermediate images from incomplete projection sets, more rapidly approximating the final image. This is applied for investigation of dynamic changes, such as acute hypoxia in mouse models.

Bimodal resonators with two orthogonal B_1 modes are proven to have exceptional isolation between excitation and detection components, as well as high efficiency. These bimodal resonators include an Alderman-Grant volume resonator, and a volume excitation/surface loop detection resonator for restricted field-of-view, high-resolution imaging.

The Center is also developing Rapid Scan EPR imaging, which utilizes the rapid passage effect and direct detection of EPR signal. In comparison with continuous wave imaging, this method allows faster projection acquisition and higher projection/image SNR.

The technology of the Center has been applied to investigate how local oxygen environment affects various biologic processes. This includes the effect of tumor oxygenation on radiotherapy resistance, the interplay between the BNip3 protein and tumor hypoxia, the roles of HIF-1α and HIF-2α in mediating responses of various organs to changes in breathing conditions (e.g., sleep apnea), as well as how premalignant tumor oxygenation status relates to progression to cancer from chromosomal aberrations and human papillomavirus.

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POSTER SESSION

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216 **Membrane Targeting and Binding of NOD Peptides.**

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A Sec 14p-nodulin domain phosphatidylinositol transfer protein has been shown to polarize membrane growth of root hairs. To understand the mechanism of regulation, we have synthesized peptides representing the sequence thought to be responsible for the targeted membrane binding. Three peptides investigated in this work are short, 11-12 aa, highly positively charged peptides, containing motif of seven lysine residues. We have tested a hypothesis that in addition to electrostatic interaction, binding to *PtdIns(4,5)P2* – containing membranes is more complex and specific to *PtdIns(4,5)P2*. Using spin-labeling EPR, ITC and DLS we have investigated binding of these peptides to liposomes of various compositions. The data were analyzed using a comprehensive model that includes description of electrostatic interaction using the Gouy-Chapman theory. Analysis of local polarity and accessibility of the EPR label for membrane-bound form of the peptides was used to assess the location of bound peptides. Substantial differences in binding behavior of these charged peptides were observed despite the similarity in sequences. Addition of NOD1 peptide to LUV containing 4 mol% of phosphatidylserine lipids or 1 mol% of *PtdIns(4,5)P2* lipids induced precipitation of liposomes at 1:50 peptide to lipid ratio and at 1:1000 peptide to lipid ratio for LUV containing 3 mol% of *PtdIns(4,5)P2*. Surprisingly, the precipitation was reversed upon overnight incubation of samples at 4 ^{o}C. DLS experiments confirmed formation of LUV of the original size upon prolonged exposure of precipitated sample at 4 ^{o}C. Fluorescence leakage experiments have shown that integrity of LUV is preserved upon precipitation and recovery. *The work was supported by NSF-0843632 to TIS.*

POSTER SESSION

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217 **Ligand-Induced Structural Change in a Cyclic Nucleotide-Regulated Ion Channel.**

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Hyperpolarization-activated cyclic nucleotide-modulated (HCN) ion channels are crucial for electrical signalling in the human body, including cardiac and neuronal pacemaker activity. These non-selective cation channels are activated by cell membrane hyperpolarization and depolarize the membrane upon opening. The gating from the closed to the open state is promoted by direct binding of cyclic nucleotides such as cyclic AMP. The underlying mechanism is not well understood. We present results of our investigation of the structural changes induced by cyclic AMP binding in a carboxy-terminal binding domain of the channel HCN2, using FRET and DEER spectroscopy. *Supported by NIH (R01 EY010329 and F32 EY018981).*

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POSTER SESSION

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218 **^{13}C HYSCORE Study of Methoxy Orientations in the QA and QB sites of the Photosynthetic Reaction Center from *Rb. sphaeroides*.**

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Ubiquinone is an almost universal, membrane-associated redox mediator. Its ability to accept either one or two electrons allows it to function in critical roles in biological electron transport. The redox properties of ubiquinone are substantially determined by its environment in the binding sites of proteins and by the dihedral angles of the methoxy groups relative to the ring plane.[1] In this work, we use the photosynthetic reaction center as a model system for understanding the role of methoxy conformations in determining the redox potential of the ubiquinone/semiquinone couple. Despite the abundance of X-ray crystal structures for the reaction center, quinone site resolution has thus far been too low to provide a reliable measure of the methoxy dihedral angles of the primary and secondary quinones, Q_A and Q_B. We have performed HYSCORE on isolated reaction centers with ubiquinones ^{13}C-labeled at the headgroup methyl and methoxy groups, and the isotropic and anisotropic hyperfine (HF) coupling constants were estimated. In contrast to FTIR studies,[2] our data in combination with quantum mechanical modeling shows that the 2-methoxy of Q_B is significantly more out of plane than that of Q_A, which we conclude provides a significant, if not essential role in establishing the driving force for electron transfer in reaction centers.

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POSTER SESSION

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219 **Spin Decoherence and Electron Spin Bath Noise of a Nitrogen-vacancy Center in Diamond.**

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A nitrogen-vacancy (NV) center in diamond is a promising candidate for sensitive magnetic sensing and imaging devices because of its ability to detect single spin nearby. The sensitivity of the NV center depends on spin decoherence of the NV center due to surrounding environments. We have recently investigated spin decoherence of a single NV center caused by surrounding nitrogen spin bath.[1] In this presentation, we will discuss about dependence of nitrogen spin concentration on the spin decoherence and noise spectrum of the nitrogen spin bath. *Supported by the Searle Scholar program.*

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POSTER SESSION

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220 **Background Subtraction Method for Sinusoidal Rapid Scan Spectra that Does Not Require Off-Resonance Measurements.**

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In a rapid scan experiment the magnetic field is scanned through a line in a time that is shorter than the spin-spin relaxation time. This method can significantly enhance the sensitivity of a CW EPR spectrometer. There are a number of factors that contribute to the improvement in signal-to-noise: (i) The full amplitude of the absorption spectrum is measured, which is larger than for the segment recorded with standard filed modulation. This becomes critically important for imaging. (ii) In the rapid scan regime one can substantially increase incident power without signal saturation. (iii) Averaging of a periodic signal is equivalent to using a comb filter that very efficiently filters out source noise. (iv) The scan rate can be optimized for a given resonator Q-factor given linewidth criteria.

The major problem in implementing the method is a periodic background signal. Experiments demonstrated that the background signal primarily consists of the first harmonic of the scan frequency with a small contribution of the second harmonic. A method has been developed to separate the EPR signal from the background. It is based on the principle that the

up-field scan can be separated from the down-field scan in the frequency domain. The uniqueness of this approach is that it does not require an additional off-resonance measurement.

POSTER SESSION

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221 **Does Green Coffee Really Have More Antioxidants Than Roasted Coffee?**

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TEMPOL is a heterocyclic compound used as a catalyst and a chemical oxidant. It can also be used to measure antioxidant concentrations in liquids by determining the rate at which its signal is lost. Many people have the perception that green beans have more antioxidants than roasted coffee beans. I wanted to see whether this was really true or not. To carry out this experiment, I used green coffee beans and TEMPOL. I placed the green coffee beans in 80 mL of distilled water, and set it on a hot plate. I let it boil for 10 minutes. I then removed 990 μL of the extract with a pipette. Next, I added 10 μL of 100 mM TEMPOL and mixed the coffee beans and water mixture. I put this mixture in a capillary tube in and measured the rate of TEMPOL reduction on a Bruker EScan spectrometer using the lag time program of WinAquisit. I repeated this several times but saw little if any loss of the TEMPOL signal. I was very surprised by this result, so I tried the same experiment again, but used coffee beans that I roasted at 250°C for different lengths of time. I saw that the coffee beans roasted for 5 minutes reduced the TEMPOL more quickly compared to the green coffee beans; roasting the green coffee beans for 12 minutes had an even greater effect. My results show that green coffee beans appear to have less antioxidants than roasted coffee beans.

POSTER SESSION

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222 **Broadband Magnetic Resonance of Magnetic Nanoparticles.**

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Magnetic resonance measurements have been used extensively to characterize magnetic nanoparticles. From the resonance line shape at low temperatures, one can obtain the magnitude and form of the magnetic anisotropy. At higher temperatures or lower fields one observes a narrowing of the resonance indicative of anisotropy melting. To separate inhomogeneous and intrinsic broadening effects and to obtain intrinsic damping properties of nanoparticles, one must use broad band resonance techniques. Fig. 1 shows a broad band resonance measurement of Feraheme (an FDA approved iron supplement drug) along with magnetization data. In the simplest model, the slope of the line-width versus frequency gives a Gilbert damping parameter of a = 0.008 and from the intercept one obtains an inhomogeneous field consistent with a uniaxial anisotropy of 45 mT. The damping parameter of 0.008 is less than that often reported in the literature. Much of the confusion has to do with the separation of the large inhomogeneous effects from the intrinsic damping and the lack of complete models. Here, we examine both numerical and analytical models to determine how accurately we can extract relevant parameters of nanoparticle ensembles that are relevant for biological applications, including Feraheme, Molday ion, and ferritin. Both the anisotropy energies and damping determine the RF absorption by the particle and the MRI T_1 and T_2 signatures. Fig. 2 shows calculated fluctuation spectra (proportional to the frequency times the imaginary susceptibility) for a typical ensemble of iron oxide nanoparticles with uniaxial anisotropy for two different values of damping. The longitudinal susceptibility shows behavior characteristic of two-state switching while the transverse susceptibility shows magnetic resonance response at microwave frequencies. By tailoring the anisotropy, particle size, and damping, the susceptibility can be engineered for a particular application. For MRI T_1 contrast, one wants a maximum of the spectral weight at the MRI field and proton resonance frequency. For MRI-based hyperthermia one wants a maximum in the transverse susceptibility at the proton resonance frequency.

POSTER SESSION

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223 **Modulation of Intracellular Reactive Oxygen Species by External 7 MHz Radio Frequency Magnetic Fields.**

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The effects of weak radio frequency magnetic fields on the production of intracellular superoxide and extracellular hydrogen peroxide (H_2O_2) were investigated *in vitro* on rat pulmonary arterial smooth muscle cells (rPASMC). Cells were exposed to Control 45 mT static magnetic field (Case I, static magnetic field (SMF) oriented vertical to the plane of growth of cells) and SMF combined with weak 7 MHz radio frequency (RF) magnetic fields of 10 mT_{RMS} intensity at 90° angle (Case II, correspondingly in the horizontal direction in the lab). Hydrogen peroxide was measured by fluorometric techniques by use of Amplex Ultra Red. Intracellular superoxide radical was detected by EPR technique by use of TM-H cyclic hydroxylamines. Cell numbers were enhanced by up to 35% on day 3 for cells exposed to Case II magnetic fields with concomitant extracellular H_2O_2 production increased by 45% on day 3. Case II exhibited a diminish in detected basal superoxide concentration, which implies either an increase in consumption or a decrease in proliferation of superoxide. The herbicide Paraquat and Diphenylene Iodonium were used to induce reactive oxygen species (ROS) in rPASMC. Paraquat had no effect on hydrogen peroxide production in rPASMC for both Case I and II. Case II further enhanced Paraquat suppression of superoxide concentration by 40% compared to Case I. Inhibition of the EPR spin probe signal by PEG-SOD demonstrated that TM-H targeted intracellular superoxide. DPI had no effect on H_2O_2 production for either Case I or II, but DPI-induced superoxide production was inhibited by Case II. Taken together, this study demonstrates the interplay between superoxide radical and hydrogen peroxide production modulated by RF magnetic fields.

POSTER SESSION

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224 **Radical Model for Arsenic Toxicity: Experimental EPR Spin Trapping and Theoretical Studies.**

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Arsenic is one of the most environmentally significant toxins and a great global health concern. Long known for its acute toxicity, arsenic has also been discovered to be a potent carcinogen. Evidence links arsenic toxic and carcinogenic actions to reactive oxygen species (ROS). In most animal including humans, arsenic undergoes a biomethylation to yield organic arsenic species, long assumed to be a process of detoxification. However, a growing body of evidence suggests that these organic arsenic species, particularly the reduced trivalent intermediates, may be just as if not more toxic than the inorganic analogs. Furthermore, current food safety regulations often monitor only inorganic arsenic levels. The European Food Safety Authority (EFSA) recently concluded that there is a dangerous lack of toxicological data and characterization of organic. There is, therefore, a clear need for more literature and empirical data concerning the toxic mechanisms of arsenic.

In this study, we examined organic and inorganic arsenites capacity to generate ROS when exposed to common oxidizing agents *via* EPR spectroscopy and spin-trapping with the cyclic nitrone 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO). We supplemented our experimental observations with theoretical studies of the structure and reactivities of possible arsenic radical intermediates.

POSTER SESSION

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225 **Structure and Dynamic Properties of the Mesodomain Environment of the Protein, Ethanolamine Ammonia-Lyase, in Frozen Aqueous Sucrose Solutions.**

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The microscopic structure of frozen aqueous sucrose solutions [0–75% (w/v], that contain the adenosylcobalamin-dependent ethanolamine ammonia-lyase (EAL) from Salmonella typhimurium, is characterized by using CW- and pulsed-EPR spectroscopic and relaxation techniques, and the paramagnetic probe, TEMPOL. The results extend previous studies [1] of the structure and dynamics of the mesoscopic domain (mesodomain), that forms upon freezing at water-ice crystallite boundaries, to address the influence of protein on the mesodomain. TEMPOL resides in the mesodomain.[1] The following approaches were applied: (a) CW-EPR spectroscopy of TEMPOL mobility was used to determine dynamical transitions (related to the effective glass transition temperature, Tg') in the mesodomain over 200-270 K. (b) ESEEM spectroscopy at

6 K was used to detect the hyperfine interaction of TEMPOL with 2H-labeled sucrose, as a probe of the relative volume of the mesodomain. (c) ESE–detected spin-lattice relaxation times (T1) at 6 K were used to determine the mesodomain concentration of TEMPOL, and the volume fraction of the mesodomain. (d) The ESE phase memory time (TM) at 6 K was also used as an indicator of the relative TEMPOL mesodomain concentration. Integrated interpretation of the results reveals that EAL creates a mesodomain in the absence of sucrose. Added aminoethanol substrate (small solute) and sucrose augment the mesodomain, leading to distinct structural and dynamical properties. The results inform mechanistic interpretations of the independently-measured kinetics of low-temperature reaction steps in EAL. *Supported by NIH R01 DK054514.*

[1] Chen et al., *Langmuir* **2013**, *29*, 4357.

POSTER SESSION

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226 **Optical Detection of Coherent Electron Spin States of Silicon Vacancy Defects in Silicon Carbide.**

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Electronic spins in semiconductors have attracted a great deal of interest, because they can be externally controlled and detected via optical and magnetic resonance techniques even on single spin scale. Among semiconducting materials, the diamond has been known as a hosting material in which an existing single spin system can be addressed optically at room temperature. Many key steps in quantum information technology, like single-shot readout, quantum register, have been shown by using the so called nitrogen-vacancy (NV) center in diamond[1,2]. However, other host materials which can be embedded more easily in existing electronic devices is highly demanded. Silicon carbide (SiC) can harbor equivalent defects to the NV center, and therefore it is regarded as on of key materials for silicon-based quantum technology.[3,4] Known as a wide band gap semiconductor, various deep point defects states can be found in the band gap, depending on the polytype structure. Among them, coherent spin manipulation of divacancies has been studied.[4,5] Our research is focused on the other well-known silicon vacancy (V_{Si}). V_{Si} is also attractable because it has a PL emission in shorter wavelength range (900 nm) which has advantages for future single spin detection. This relies on the fact that most commercially available single photon detectors provide decent single photon detection efficiency in this wavelength regime. Here we report that spin ensembles of silicon vacancies in the 4H-SiC can be optically detected, and their coherent motions can be observed as well at room temperature. In addition, the technical challenge for single spin detection will also be discussed.

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[4] Weber et al, *PNAS*, 2010, 107, 19
[5] Falk et al, *Nature Communications*, 2013, 4, 1819

POSTER SESSION

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227 **Super-absorbent Polymers as Matrices for EPR.**

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For in vivo EPR imaging phantoms and standards for EPR measurements with arbitrary orientations such as tooth dosimetry, it is desirable to have orientation-independent samples of rapidly tumbling radicals. This is difficult to achieve with aqueous solutions because the locations of air bubbles change when a sample is reoriented. Super-absorbent polymers (SAP) consist of cross-linked polyacrylic acid or polyacrylate salts. These polymers can absorb a large amount of water relative to the volume of the polymers. When an aqueous solution is mixed with SAP, a gel is formed. The pH of the gel can be adjusted by using a buffered solution. Although the macroscopic viscosity of the gel is high, the local microscopic viscosity is low. When an 1:10 ratio by mass of water to SAP (cross-linked polyacrylate sodium salt, Sigma-Aldrich #436364) was used to prepare samples containing ^{15}N-perdeuterated tempone (PDT), the X-band EPR signal was in the rapid tumbling regime although the gel was so viscous that centrifugation was used to force entrapped air bubbles to the surface. The spectrum of aqueous trityl-CD_3

radical in SAP also is in the rapid tumbling regime. Phantoms for 250 MHz in vivo imaging were prepared, with an air bubble at one end of the tube. The tube could be inverted for prolonged periods with no displacement of sample. These experiments indicate that SAP can be used to prepare EPR samples in which small molecule solutes are tumbling freely, but the sample does not flow readily within the tube.

POSTER SESSION

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228 **Effects of Fluorine on the Structure of Fluorohydroxyapatite: a Solid-State NMR Study.**

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Hydroxylapatite (HA) is the main mineral in teeth and bones within the human body. Especially, Tooth Enamel, the hardest and most highly mineralized substance in the human body, contains roughly 96 percent of hydroxylapatite. Fluorine-substituted hydroxyapatite (FHA) is chemically more stable than hydroxyapatite in acid environment.[1] Over recent years, fluorohydroxyapatite has been used as bioactive ceramic coatings due to its enhanced biostability as compared to the other ceramic coatings. Fluoride-containing bioactive glasses are of particular interest in many fields of dentistry and orthopedics because they are osteoconductive and can combine the benefits of fluorapatite with the bone-regenerative properties of bioactive glasses.[2] In FHA composition, part of the OH ions are substituted by F^- ions in order to improve material stability. However, most studies so far have focused on the preparation methods of FHA and its thermal and chemical stability.[3] The effects of different fluorine contents on the stucture have seldom been studied systematically. The resistance of fluorohydroxyapatite to acids depends largely on its chemical structure, it is of great interest to determine its structure that prevents the process of erosion. In this study, a series of FHAs with varying fluorine levels were synthesized and their structure were analyzed by ^{1}H, ^{43}Ca and ^{31}P MAS solid-state NMR to examine the effect of fluorine substitution on the hydroxyapatite structure. For the first time we observed the well-resolved Ca(I) and Ca(II) signal change in fluorohydroxylapatite with different fluorine contents. Compared with ^{31}P NMR, for which only small variations induced by incorporation of fluorine are observed, the significant change of ^{43}Ca(II) signal and 1H NMR of OH signal indicate that the fluorine perturbs the Ca(II) ion and OH group more than phosphorous one.

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POSTER SESSION

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