Rocky Mountain Conference on Magnetic Resonance

Volume 53 *53rd Rocky Mountain Conference on Analytical Chemistry* Article 1

7-24-2011

53rd Rocky Mountain Conference on Analytical Chemistry

53rd Rocky Mountain Conference on Analytical Chemistry

Abstract

Final program, abstracts, and information about the 53rd annual meeting of the Rocky Mountain Conference on Analytical Chemistry, co-endorsed by the Colorado Section of the American Chemical Society and the Society for Applied Spectroscopy. Held in Snowmass, Colorado, July 24-28, 2011.

53RD ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

FINAL PROGRAM AND ABSTRACTS

ENDORSED BY:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 24–28, 2011

Snowmass Conference Center • Snowmass, Colorado, USA

www.rockychem.com

53RD ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 24–28, 2011

Snowmass Conference Center • Snowmass, Colorado

TABLE OF CONTENTS

www.rockychem.com

Milestone Presentations, LLC • 4255 South Buckley Road, #118 • Aurora, CO 80013
Ph: 800-996-3233 or 303-690-3233 • Fax: 888-996-3296 or 303-690-3278

E-mail: info@milestoneshows.com • Web: www.milestoneshows.com

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

ORGANIZERS AND CHAIRPERSONS

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

CONFERENCE CHAIR

Kurt W. Zilm, Yale University, Department of Chemistry
PO Box 20817 • New Haven, CT 06520-8107
Ph: 203-432-3956 • Fax: 203-432-6144 • kurt.zilm@yale.edu

EPR SCIENTIFIC COMMITTEE:

Alex Angerhofer – Chair, University of Florida

Christoph Boehme – Co-Chair, University of Utah

Gail Fanucci – Co-Chair, University of Florida

Howard Halpern, University of Chicago

Frederick Villamena, Ohio State University

Kurt Warncke, Emory University

CONFERENCE SUPPORTERS

(As of July 15, 2011)

Active Spectrum

Bruker BioSpin

James and Karen Hyde Foundation

Jules Stein Professorship Endowment, UCLA

Medinox, Inc.

National High Magnetic Field Laboratory

Wilmad-LabGlass

ROCKY MOUNTAIN CONFERENCE INFORMATION

REGISTRATION

Admission to all technical sessions is by name badge only. Registration materials may be picked up at the RMCAC registration area located at the Snowmass Conference Center between 1:00 p.m. and 5:00 p.m. on Sunday, July 24 or anytime 8:00 a.m. to 5:00 p.m., Monday, July 25 through Thursday, July 28.

ALTITUDE

Snowmass is approximately 8,500 feet above sea level. The acclimatization process is inhibited by dehydration, over-exertion, alcohol and other depressant drugs. Please take the following precautions regarding high altitude:

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

CONFERENCE LUNCH

A complimentary lunch is being provided July 25, 26 and 27 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with another day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The lunch will be served in the Roof Garden Tent each designated day from 12:15 – 1:15 p.m.

CONFERENCE RECEPTION

Monday evening from 5:00 – 6:30 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.

CYBER LOUNGE

The RMCAC Cyber Lounge will be available.

Monday, July 25	Tuesday, July 26	Wednesday, July 27	Thursday, July 28
8:00 a.m. – 7:00 p.m.	8:00 a.m. – 5:00 p.m.	8:00 a.m. – 2:00 p.m.	8:00 a.m. – noon

The Cyber Lounge is located next to registration in the Conference Center foyer. Attendees may use the Cyber Lounge to access the internet/e-mail. Please limit your use to no more than 5 minutes at a time.

MESSAGES

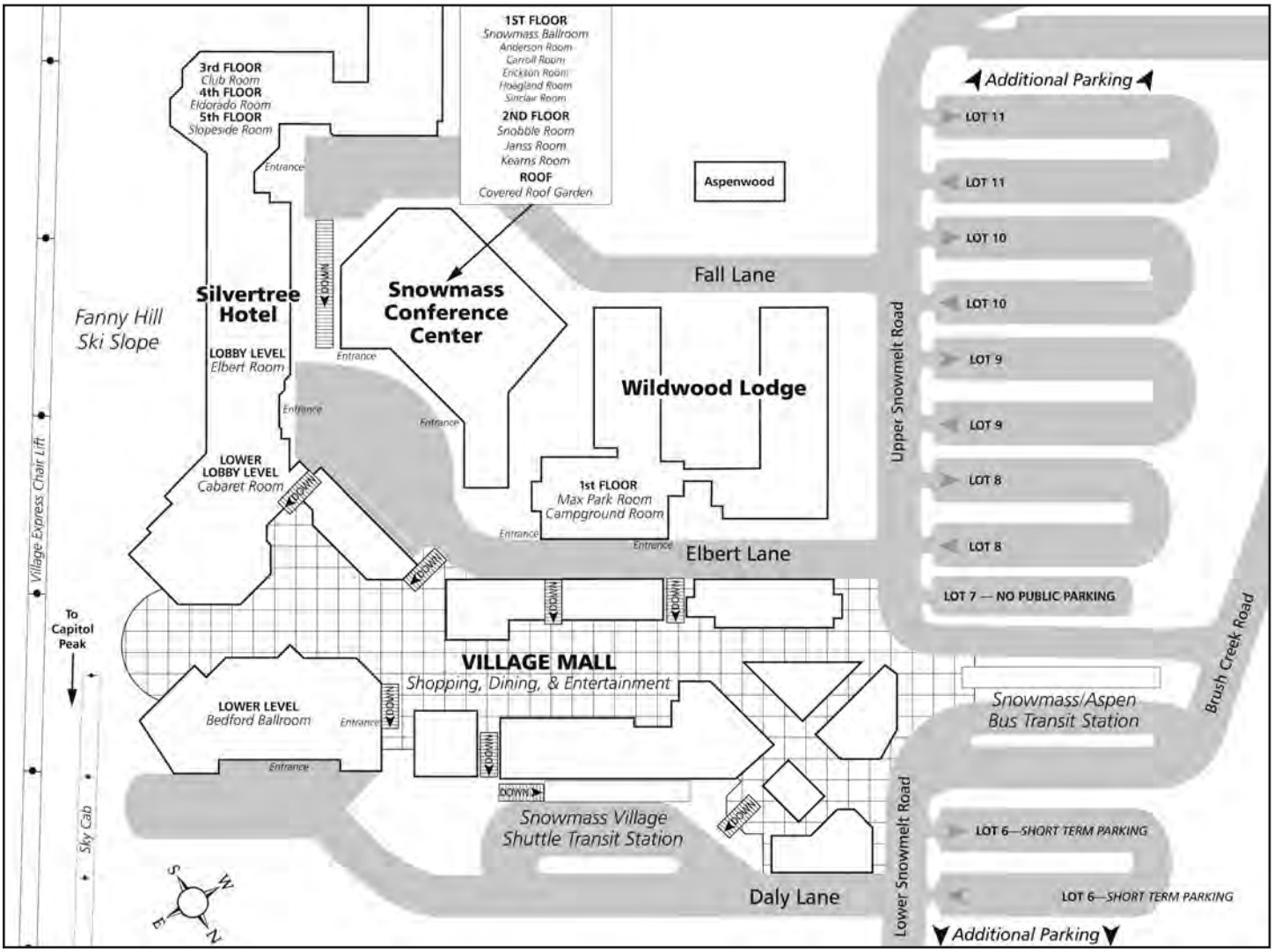
Messages will be accepted and posted on the message board located next to the Rocky Mountain Conference registration desk. Call 800-996-3233 or 303-690-3233 to leave messages.

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

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	*Anderson*										
EPR Posters	*Carroll / Sinclair*										
Speaker Prep	*Snobble*										
Workshops	*Erickson*										

SNOWMASS MEETING SPACES



34TH INTERNATIONAL EPR SYMPOSIUM

&

53RD ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 24–28, 2011

Snowmass Conference Center - Snowmass, Colorado

CONFERENCE CHAIR

Kurt W. Zilm

EPR SYMPOSIUM COMMITTEE

Alex Angerhofer, Christoph Boehme and Gail Fanucci, (Co-Chairs)

Howard Halpern, Frederick Villamena, Kurt Warncke

EPR SYMPOSIUM SPONSORS

Bruker BioSpin, EPR Division

James and Karen Hyde Foundation

Jules Stein Professorship Endowment, UCLA

Medinox, Inc.

National High Magnetic Field Laboratory

Wilmad-LabGlass

REGISTRATION

Register at www.rockychem.com

Admission to all technical sessions is by name badge only.

Registration materials may be picked up at the RMCAC registration area located at the Snowmass Conference Center from 1:00-5:00pm on Sunday, July 24 or anytime 8:00am-5:00pm Monday, July 25 through Thursday, July 28.

Complimentary lunches are being provided July 25, 26 and 27 to all registered symposia attendees.
You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk.
Tickets are date-specific and cannot be interchanged with another day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day. The lunch will be served each designated day from 12:15-1:15pm.

Workshops will be held Sunday, July 24 from 3:30-6:00pm (Spectral Simulation)
and Tuesday, July 26 from 2:00-3:30 pm (Spin Trapping).
If you are registered for the Rocky Mountain Conference and would like to attend one or both workshops, please send an email to alex@chem.ufl.edu to confirm which workshop(s) you would like to attend.

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

EPR SYMPOSIUM

Oral Sessions

SUNDAY, JULY 24, 2011		
3:30–6:00 p.m.	100	*Spectral Simulation Workshop* • Stefan Stoll
6:30–7:30 p.m.	101	*Bruker Annual Progress and Products Report*
7:30–10:00 p.m.	102	*Bruker Reception*

MONDAY, JULY 25, 2011		
Session I, Materials & Methods – Christoph Boehme, Chairing		
8:20 a.m.	*Welcoming and Introductory Remarks.* Alex Angerhofer and Christoph Boehme	
8:30 a.m.	101	**Electrical Readout of a Coherent Nuclear Spin Quantum Memory in Silicon.** Dane R. McCamey, University of Sydney
9:05 a.m.	102	**Device Limiting Defects in Amorphous Silicon Solar Cell Materials: An Advanced EPR Study.** Alexander Schnegg, Helmholtz-Zentrum Berlin
9:40 a.m.	103	**Multi-Frequency EPR Studies of Coherent Electron-Nuclear Spin Dynamics in a Rare Earth Molecular Nanomagnet.** Stephen Hill, National High Magnetic Field Laboratory
10:05 a.m.	*Break*	
10:25 a.m.	104	**Free-Electron Laser-Based Pulsed EPR.** Mark Sherwin, University of California Santa Barbara
10:50 a.m.	105	**Development of Submillimeter Wave Micro-Cantilever ESR-Possible Application to Biological Systems.** Hitoshi Ohta, Kobe University
11:15 a.m.	106	**Controlling the Defect Centers in ZnO Nanoparticles by In-Situ Light-Induced and High Field EPR Spectroscopy.** Emre Erdem, Albert-Ludwigs Universität Freiburg
11:30 a.m.	107	**Electrostatics of Bio- and Nano-Materials' Interfaces by EPR of pH-Sensitive Nitroxides.** Alex I. Smirnov, North Carolina State University
11:55 p.m.	108	**Probing Tau Protein's Site-Specific Hydration Water Dynamics to Unravel Early Events in Fibrillar Aggregation Mechanism.** Anna Pavlova, University of California Santa Barbara
12:20 p.m.	*Lunch (included with registration)*	
Session II, Spin Trapping – Frederick Villamena, Chairing		
2:00 p.m.	*Introductory Remarks.* Frederick Villamena	
2:10 p.m.	110	**Probing Heterogeneous Reactions with Spin Traps.** Victor Chechik, University of York
2:45 p.m.	111	**Spin Trapping in the Hydrogen Economy.** Shulamith Schlick, University of Detroit Mercy
3:20 p.m.	*Break*	
3:40 p.m.	112	**Surface-Mediated Production of Hydroxyl Radicals as a Mechanism of Iron Oxide Nanoparticle Biotoxicity.** Tatyana I. Smirnova, North Carolina State University

4:05 p.m.	113	**Synthesis, Physical-Chemical and Biological Properties of Sugar-Based Amphiphilic Nitrones and Nitroxides.** Grégory Durand, Université d'Avignon et des Pays de Vaucluse
4:30 p.m.	114	**Direct Evidence of DMPO Spin-Trapping Artifact Originated from Forrester-Hepburn Mechanism.** Fabian Leinisch, National Institutes of Health
5:00–6:30 p.m.	*Conference Reception*	
Session III, Posters		
7:30-9:30 p.m.	**Authors Present for Posters Labeled A**	

TUESDAY, JULY 26, 2011

Session IV, Metals in Biology – Kurt Warncke, Chairing		
8:20 a.m.	*Introductory Remarks.* Kurt Warncke	
8:30 a.m.	116	**Exploring Structure-Function Relationships at the Active Site of Tyrosine Hydroxylase using EPR Spectroscopy.** John McCracken, Michigan State University
9:05 a.m.	117	**EPR Up Close and From Afar: Elucidation of Short and Long Range Structural Information in Macromolecular Metalloprotein Complexes.** Fraser MacMillan, University of East Anglia
9:40 a.m.	118	**Determination of EPR Parameters Using a Spin-Orbit Coupled Complete Active Space Self-Consistent Field Approach.** Dmitry Ganyushin, Universität Bonn
10:15 a.m.	*Break*	
10:35 a.m.	119	**Effects of Ca^{2+} Binding to the Axial Ligation Geometry and Magnetic Properties of the Catalytic Diheme Center in MauG.** Aimin Liu, Georgia State University
11:00 a.m.	120	**Advanced Pulsed EPR Investigation of Biomimetic Model Complexes of the [FeFe] Hydrogenase Active Site in H_{ox}–CO and H_{ox} States.** Özlen F. Erdem, Max Planck Institute for Bioinorganic Chemistry
11:25 a.m.	121	**Cobaloxime Catalyst for Biomimetic Hydrogen Production: Multifrequency EPR and DFT Study of Cobaloxime's Electronic Structure.** Oleg G. Poluektov, Argonne National Laboratory
11:50 a.m.	122	**Double Electron-Electron Resonance Between Gd^{3+} Ions and Nitroxide Radicals.** Maxim Yulikov, ETH Zurich
12:15 p.m.	*Lunch (included with registration)*	
2:00–3:30 p.m.	123	**Spin Trapping Workshop** – Frederick Villamena
Session V, Award Lecture		
7:00 p.m.	*Introduction*	
7:05 p.m.	125	***Piette Lecture*** **– Redox Sensitive Switches Regulating Superoxide and Nitric Oxide from eNOS.** Jeanette Vasquez-Vivar, Medical College of Wisconsin
Session VI, Posters		
7:50-9:50 p.m.	**Authors Present for Posters Labeled B**	

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

WEDNESDAY, JULY 27, 2011

Session VII, Structure and Dynamics of Proteins – Gail Fanucci, Chairing

8:20 a.m.	*Introductory Remarks.* Gail Fanucci	
8:30 a.m.	127	**Tertiary Contacts in the Prion Protein and the Connection to Inherited Disease.** Glenn Millhauser, University of California Santa Cruz
9:05 a.m.	128	**Multiple DEER EPR Measurements to Estimate the Entropy of Complex Formation.** Garland Marshall, Washington University
9:40 a.m.	129	**Antibody-Mediated Mechanics on HIV-1 Envelope Protein gp41 at the Membrane Interface.** Likai Song, National High Magnetic Field Laboratory
10:05 a.m.	*Break*	
10:25 a.m.	130	**A Partially Structured Molten Globule Protein.** Wofgang E. Trommer, TU Kaiserslautern
10:50 a.m.	131	**The Affinity and Stability of Immobilized Biomolecules: Time-Resolved EPR Detection During Mobile Phase Gradients.** Eric Walter, Pacific Northwest National Laboratory
11:15 a.m.	132	**EPR Society Presentation.** Michael Bowman, University of Alabama
11:25 a.m.	133	**EPR Studies of Carotenoid Radicals and Their Significance in Photosynthesis.** Lowell D. Kispert, University of Alabama
11:50 p.m.	134	**The Magnetic Structure of Tryptophan Radicals.** Stefan Stoll, University of California Davis
12:15 p.m.	*Lunch (included with registration)*	

Session VIII, Young Investigator – Alex Angerhofer, Chairing

2:00 p.m.	*Introductory Remarks.* Alex Angerhofer	
2:10 p.m.	136	**Opportunities of High Field EPR: Extending the Distance Range with Gd^{3+}-Based Probes.** Devin Edwards, University of California Santa Barbara
2:25 p.m.	137	**EPR Study of Electron-Hole Asymmetry in Bulk and Nanoparticles of $Bi_{1-x}Ca_xMnO_3$(x = 0.4, 0.6): A Comparison.** Geetanjali Singh, Indian Institute of Science Bangalore
2:40 p.m.	138	**Progress And Challenges in Measuring the Orientational Dependence of DEER For Transition Metals In Model Systems And Proteins.** Alice M. Bowen, University of Oxford
2:55 p.m.	139	**Cu^{2+}Coordination Site Structure in Soluble and Fibrillar Forms of the Amyloid-β Protein.** Bill Gunderson, Emory University
3:10 p.m.	140	**Fitting the Puzzle Together: Spin Transitions in the New Class of Paramagnetic Labels – The Cage Complexes With Encapsulated Cobalt(II) Ion.** Valentin Novikov, Nesmeyanov Institute of Organoelement Compounds RAS
3:25 p.m.	*Break*	

3:45 p.m.	141	**Magnetic Resonance Studies of Dynamics to Decipher the Structure and Light-Activated Conformational Changes of Proteorhodopsin's E-F Loop.** Sunyia Hussain, University of California Santa Barbara
4:00 p.m.	142	**Global Structure of a 3-Way Junction in a Phi29 Packaging RNA Dimer Complex Determined Using Site-Directed Spin Labeling.** Xiaojun Zhang, University of Southern California
4:15 p.m.	143	**Simulating the Dynamics and Orientations of Spin Labeled Side Chains in the Restriction Endonuclease EcoRI.** Jessica Sarver, University of Pittsburgh
4:30 p.m.	144	**Characterization of the Semiquinone Intermediate in Cytochrome bc_1 Complex.** Preethi R. Vennam, University of Alabama
Session IX, In Vivo EPR – Howard Halpern, Chairing		
4:45 p.m.	145	**Structural Investigation of Stratum Corneum Lipid Using Electron Paramagnetic Resonance.** Kouichi Nakagawa, Hirosaki University
5:30 p.m.	*EPR General Business Meeting*	

THURSDAY, JULY 28, 2011

Session IX, In Vivo EPR – Howard Halpern, Chairing *(continued)*		
8:20 a.m.	*Introductory Remarks.* Howard Halpern	
8:30 a.m.	148	**Rapid Electron Spin Echo Imaging of Oxygen in Vivo.** Boris Epel, University of Chicago
9:05 a.m.	149	**Tumor Oximetry and Radiation Sensitivity of Experimental Gliomas.** Huagang Hou, Dartmouth Medical School
9:40 a.m.	150	**Digital EPR at Low Frequency.** Mark Tseitlin, University of Denver
10:15 a.m.	*Break*	
10:35 a.m.	151	**Multisite EPR Oximetry using Multiple Field Modulation Harmonics.** Rizwan Ahmad, The Ohio State University
11:10 a.m.	152	**Enhanced Dynamic Electron Paramagnetic Resonance Imaging of Cycling Hypoxia in Vivo Using Principal Component Analysis for Low-Order Approximation of Projections.** Gage Redler, University of Chicago
11:25 a.m.	*Closing Remarks.* Alex Angerhofer, Chair 2011 EPR Symposium and Christoph Boehme, Chair 2012 EPR Symposium	

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

EPR SYMPOSIUM
Poster Sessions

MONDAY, JULY 25, 2011
7:30–9:30 p.m. *(Poster Session A)*

TUESDAY, JULY 26, 2011
7:50–9:50 p.m. *(Poster Session B)*

A	155	**Distance Between Mo(V) and Fe(III) Heme Centers of Sulfite Oxidase Determined by Pulsed EPR.** Andrei V. Astashkin, University of Arizona
B	156	**Relaxation Times of Isotopically-Substituted Nitroxide Radicals in Aqueous Solution.** Joshua R. Biller, University of Denver
A	157	**Site Directed Spin Labeling Studies of Radical Catalysis in Oligomeric B12-Dependent Ethanolamine Ammonia-Lyase.** Adonis Bovell, Emory University
B	158	**Identification of V_{si}- Centers in 4H SiC MOSFETs.** C.J. Cochrane, Pennsylvania State University
A	159	**Spin Trapping of Radicals in Irradiated TiO_2 Nanoparticles.** Alex Cruce, University of Alabama
B	160	**A Simple Method to Extract Hyperfine Signs From Random-Hopped Davies ENDOR Data.** Peter Doan, Northwestern University
A	161	**Lipid Membrane-Associated Alpha Synuclein Copper Binding Characterization.** Chris Dudzik, University of California Santa Cruz
B	162	**Parameter Sensitivity of Multicomponent Magnetic Resonance Spectra.** Keith A. Earle, University at Albany (SUNY)
A	163	**Probing Interdomain Structure in the Prion Protein by Pulsed Dipolar Spectroscopy.** Eric G. Evans, University of California Santa Cruz
B	164	**Deprotonation of Open Chain Carotenoid Radical Cations: Mims ENDOR and DFT Studies.** A. Ligia Focsan, University of Alabama
A	165	**Effect of Glucose on EPR of Spin Label in Blood From Healthy and Diabetic.** Asako Kawamori, AGAPE-Kabutoyama Institute of Medicine
B	166	**Physical Properties of Membrane Models of the Eye-Lens Fiber-Cell Plasma Membrane for Animals of Different Life Spans: Saturation-recovery EPR Spin-Labeling Studies.** Alexey A. Konovalov, Medical College of Wisconsin
A	167	**The EPR Characterization of the Oxygen Induced Radical Intermediates in Neuronal Nitric Oxide Synthase.** Matthew D. Krzyaniak, University of Alabama
B	168	**ENDOR of Axial Centers of Nd^{3+} and Yb^{3+} in Lithium Niobate.** Galina Malovichko, Montana State University
A	169	**Investigations Into Cu^{2+}-Cu^{+} Redox Cycling in PrP Using CW X-band EPR.** Alex J. McDonald, University of California Santa Cruz
B	170	**Hyperbolic-Cosine Waveguide Tapers and Oversize Rectangular Waveguide for Reduced Broadband Insertion Loss in W-Band EPR Spectroscopy.** Richard R. Mett, Medical College of Wisconsin
A	171	**Resonator for Optimization of Liquid-Phase EPR Concentration-Sensitivity for Spin Labels at Q-Band: Practical Considerations.** Richard R. Mett, Medical College of Wisconsin
B	172	**Characterization of the Relaxation Processes of DPPH.** Virginia Meyer, University of Denver
A	173	**Nonselective Excitation of Pulsed ELDOR Using Multi-Frequency Microwaves.** Hiroyuki Mino, Nagoya University

B	174	**X-Band Rapid-Scan EPR.** Deborah G. Mitchell, University of Denver
A	175	**Irradiated Quartz Standard Samples for Pulsed EPR.** Deborah G. Mitchell, University of Denver
B	176	**Next Generation Software Solutions for EPR Spectroscopists.** Reef Morse, Scientific Software Services
A	177	**Structural Change of Circadian Clock Protein KaiB.** Risa Mutoh, Nagoya University
B	178	**Photolysis Studies of CO-inhibited Nitrogenase.** W.K. Myers, University of California Davis
A	179	**EPR Investigation of Sucrose and L-Alanine radicals Produced by Various Irradiations.** Kouichi Nakagawa, Hirosaki University
B	180	**Nucleotide Coordination to Mn^{2+} at the Myosin Active Site as Detected by Pulsed EPR.** Yuri E. Nesmelov, University of North Carolina
A	181	**Light-Induced Charge Separation in Polymer-Fullerene Bulk-Heterojunctions: A Multi-Frequency EPR Study of Cations, Anions, and Radical Pairs.** Jens Niklas, Argonne National Laboratory
B	182	**A Multi-Frequency EPR Spectroscopy Investigation of Conformational Changes in the Intrinsically Disordered Protein, IA_3.** Natasha L. Pirman, University of Florida
A	183	**Microwave Surface Resonator Array for In Vivo Electron Paramagnetic Resonance Spectroscopy.** Jason W. Sidabras, Medical College of Wisconsin
B	184	**Resonator Advances for W-band Pulse Spectroscopy.** Jason W. Sidabras, Medical College of Wisconsin
A	185	**Shifts in Conformational Populations of HIV-1PR Due to Primary and Secondary Mutations Measured by Double Electron-Electron Resonance Spectroscopy.** Adam N. Smith, University of Florida
B	186	**New Features in EasySpin.** Stefan Stoll, University of California Davis
A	187	**The Magnetic Structure of Tryptophan Radicals.** Stefan Stoll, University of California Davis
B	188	**DEER Reveals Conformational Changes Upon Substrate Binding in Cytochrome P450cam.** Stefan Stoll, University of California Davis
A	190	**Tau Fibril Conformation Probed by Double Electron-Electron Resonance at Q-Band.** Michael A. Swanson, University of Denver
B	191	**Power Saturation EPR on Both Surfactant Protein-B C- Terminus & Peptide Mimic KL4 Using Spin-labeled Peptide and Lipid in DPPC and POPC Enriched Vesicles.** Austin L. Turner, University of Florida
A	192	**Formation of Free Radicals in Coffee During Roasting.** Shreya Uppal, Steppingstone MAgnetic Resonance Training Center
B	193	**Determining the Binding Modes of Mtb CYP51B1 Inhibitors Using Pulsed EPR.** Preethi R Vennam, University of Alabama
A	194	**Room Temperature Charge Carrier Spin Quantum Phase Coherence in Organic Semiconductors.** W. J. Baker, University of Utah, Dept of Physics and Astronomy
B	195	**Characterization of the Semiquinone Intermediate in Cytochrome bc_1 Complex.** Preethi R. Vennam, University of Alabama
A	196	**Characterization of Phosphorus Donors in Silicon with Low Magnetic Field.** H. Morishita, School of Fundamental Science and Technology, Keio University

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

ABSTRACTS

EPR SYMPOSIUM
Oral Sessions

101 **Electrical Readout of a Coherent Nuclear Spin Quantum Memory in Silicon.**

Dane R. McCamey, School of Physics, University of Sydney, Sydney, 2006, Australia

Whilst spin resonance is an extremely powerful technique, the conventional implementation is incompatible with accessing small numbers of spins. This significantly hampers our ability to investigate the spin properties of a wide range of systems – in particular, nanoscale systems including nanoelectronics, thin film transistors and even single electron devices. Alternative approaches to detecting spin resonance allow this limitation to be overcome; for example, detecting the impact of spin on the electrical current flowing through an electronic device can allow detection of single spins.

In this talk, I will present a series of recent work investigating electrical readout of electronic and nuclear spins of phosphorus donors in silicon. I will discuss a spin trap mechanism that allows information about the donor electron spin state to be measured electrically.[1] I will then show how this technique can be used to electrically readout nuclear spins with lifetimes exceeding 100 seconds[2] and phase coherence times exceeding 2ms, with single-shot sensitivity. In doing so, I will discuss some modifications to conventional pulse sequences which are required to make them compatible with electrical readout.

By using both the phosphorus nuclear spin, as well as the spins of silicon nuclei near the donor, a memory register can be implemented which provides a way to store at least a byte of information in the nuclear spins coupled to a single donor [2]. The ability to electrically access spin phase coherent phenomena of nuclear spins in silicon is an important step toward implementation of spin memory devices for both classical and quantum information processing systems.

1. G. W. Morley et al., *Physical Review Letters* **101**, 207602 (2008)
2. D. R. McCamey et al., *Science* **330**, 1652-1656 (2010)

EPR ORAL SESSION

Dane McCamey, School of Physics, University of Sydney, Sydney NSW 2006 Australia.
Ph: +61 2 9036 6008, dane.mccamey@sydney.edu.au

102 **Device Limiting Defects in Amorphous Silicon Solar Cell Materials: An Advanced EPR Study.**

M. Fehr [1], Alexander Schnegg*[1], B. Rech[1], C. Teutloff[2], R. Bittl[2], G. Pfanner[3], C. Freysoldt[3], J. Neugebauer[3]
O. Astakhov[4], F. Finger[4] and K. Lips[1]
1. Helmholtz-Zentrum Berlin für Materialien und Energie, Institut für Silizium-Photovoltaik, Berlin, Germany
2. Fachbereich Physik, Freie Universität Berlin, Berlin, Germany
3. Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany
4. Forschungszentrum Jülich, Institute of Energy Research-Photovoltaic, Jülich, Germany

In order to improve the performance thin film photovoltaic (PV) devices optimum material properties are required, which can only be realized with the aid of tailor made simulation and characterization tools. In PV materials, where paramagnetic states determine charge transport and loss mechanisms, a unique probe is provided by unpaired electron spins. This renders Electron Paramagnetic Resonance (EPR) the method of choice to quantify the total number of defects and obtain nanoscopic insight into their structural properties. This is especially true for thin-film Si materials where defect states can drastically influence the solar conversion efficiency. In spite of the success of EPR spectroscopy in Si PV research, recent EPR studies were limited by insufficient resolution as well as detection sensitivity. This situation changed with the advent of advanced EPR, which, in many cases proved to be able to lift these restrictions. Recently, in Germany the dedicated research network "EPR-Solar" was established with the aim to exploit the power of advanced EPR methods to shed new light onto function-determining defects in thin-film Si materials. Here we report on recent advances achieved within the network.

Light-induced degradation of hydrogenated amorphous silicon (a-Si:H), referred to as the Staebler-Wronski Effect (SWE), was investigated on a microscopic level by studying native and light-induced defects using multi frequency EPR and electron nuclear double resonance (ENDOR). As a starting point we investigated native paramagnetic defects in as-deposited a-Si:H

samples. The g- and hyperfine interaction (hfi)-tensors are determined by multifrequency EPR with a precision superior to previous studies.[1,2] By comparing the experimental values with those obtained from density-functional theory (DFT) calculations, we test the hypothesis that coordination defects in a-Si:H arise due to threefold-coordinated Si atoms (dangling bonds).[3] In a second step we studied changes in the a-Si:H defect structure upon light-induced degradation. Based on our findings we discuss the structural properties of defect structures in a-Si:H and possible mechanisms explaining light induced defect formation.

This work was supported by the German Federal Ministry of Education and Research (BMBF network project EPR-Solar 03SF0328).

1. M. Stutzmann and D. K. Biegelsen, *Phys. Rev. B* 40, 9834 (1989).
2. T. Umeda, S. Yamasaki, J. Isoya and K. Tanaka, *Phys. Rev. B* 59, 4849 (1999).
3. M. Fehr, A. Schnegg, K. Lips, B. Rech, O. Astakhov, F. Finger, G. Pfanner, C. Freysoldt, J. Neugebauer, R. Bittl and C. Teutloff, submitted to Phys. Rev. B.

EPR ORAL SESSION

Alexander Schnegg, Helmholtz-Zentrum Berlin für Materialien und Energie, Institut für Silizium-Photovoltaik, Berlin, Germany. E-mail: alexander.schnegg@helmholtz-berlin.de

103 **Multi-Frequency EPR Studies of Coherent Electron-Nuclear Spin Dynamics in a Rare Earth Molecular Nanomagnet.**

Stephen Hill, S. Ghosh, Department of Physics and National High Magnetic Field Laboratory, Tallahassee, FL 32310; S. Datta and J. Krzystek, National High Magnetic Field Laboratory, Tallahassee, FL 32310; E. del Barco, Department of Physics, University of Central Florida, Orlando, FL 32816; S. Cardona-Serra and E. Coronado, Institute of Molecular Sciences, University of Valencia, Spain.

Continuous-wave, multi-high-frequency, and pulsed X-band EPR studies will be presented for a series of bulk single-crystal samples containing different dilutions of a recently discovered mononuclear Ho^{3+} ($4f^{10}$) molecular nanomagnet encapsulated in a highly symmetric polyoxometallate (POM) cage.[1] The encapsulation offers the potential for applications in molecular spintronics devices, as it preserves the intrinsic properties of the nanomagnet outside of the crystal, e.g., on surfaces or in field effect devices. A significant magnetic anisotropy arises in these complexes due to a splitting of the Hund's coupled $J = 8$ ground state in the POM ligand field. High-frequency EPR studies reveal a highly anisotropic eight line spectrum corresponding to transitions within the lowest $m_J = \pm 4$ doublet, split by a very strong hyperfine interaction with the $I = 7/2$ Ho nucleus (100% abundance). X-band electron-spin-echo measurements allow detailed studies of the coherent, coupled electron-nuclear spin dynamics, including Rabi oscillations, ESEEM, and evaluation of T_2. Results are compared for different hyperfine transitions (different Dm_I selection rules) and $[Ho_xLn_{1-x}]$ dilutions. Remarkably, relatively long T_2 times are found at X-band, even for the most concentrated samples. Multi-frequency studies reveal the presence of an appreciable tunneling gap between the mJ = ±4 doublet states having the same nuclear spin projection, leading to a highly non-linear field-dependence of the spectrum at low-frequencies. It is this property that can account for the unusually long T_2 values found in the concentrated samples.

1. Al Damen et al., *JACS*, **2008**, 130, 8874-8875.

EPR ORAL SESSION

Stephen Hill, Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310. Ph: 850-644-1647, E-mail: shill@magnet.fsu.edu

104 **Free-Electron Laser-Based Pulsed EPR.**

Mark Sherwin, University of California, Department of Physics, and Institute for Terahertz Science and Technology (ITST), Santa Barbara CA 93106; Susumu Takahashi, University of Southern California, Department of Chemistry, Los Angeles CA 90089; Devin Edwards, University of California, Department of Physics and ITST, Santa Barbara CA 93106; Louis Claude Brunel, University of California, ITST, Santa Barbara CA 93106; Gerald Ramian, University of California, ITST, Santa Barbara CA 93106; Songi Han, University of California, Department of Chemistry and ITST, Santa Barbara CA 93106

The work presented will detail the ongoing development of a high-powered 240 GHz pulsed EPR spectrometer capable of one and two pulse measurements on short timescales. NMR spectroscopy has developed commercial, pulsed spectrometers operating at fields up to 23.5T, the limit that is currently achievable with low TC superconductors. By comparison, pulsed EPR instruments with high power and short pulses have been only recently achieved at 3.5T, and only with impressive, home-built spectrometers. The lack of sources limits high-field spectrometers (home built and commercial) to low powered (<50 mW) pulsed and CW experiments. By utilizing the unique Free Electron Lasers (FELs) at UCSB to deliver pulses with power>100

W, we have achieved sub-10ns π/2 pulses with excitation bandwidths >100 MHz at 8.5 T. Recently, we have implemented robust two-pulse experiments, enabling measurement of spin memory loss times T_2<100 ns. We have measured echo signals of Gd^{3+} near 200K, roughly doubling the temperature range accessible with a low powered source. Work is ongoing to improve spectrometer performance in terms of sensitivity and dead time as well as developing techniques for phase-cycled experiments. FEL-based pulsed EPR is scalable to the highest existing and foreseeable DC magnetic fields.

EPR ORAL SESSION

Mark Sherwin, University of California, Department of Physics, Santa Barbara CA 93106.
Ph: 805-893-3774, E-mail: sherwin@physics.ucsb.edu

105 **Development of Submillimeter Wave Micro-Cantilever ESR-Possible Application to Biological Systems.**

Hitoshi Ohta, Kobe University, Molecular Photoscience Research Center, Kobe 657-8501, Japan; Eiji Ohmichi, Shuya Hirano, Yuki Tokuda, Kobe University, Graduate School of Science, Kobe 657-8501, Japan

Development of submillimeter wave micro-cantilever ESR in Kobe is presented. In order to gain the sensitivity of our submillimeter wave ESR, we have developed a micro-cantilever ESR system using a torque method, which enables the ESR measurement of micrometer size single crystal.[1] Recently we have succeeded in making the measurement of microgram Co-Tutton salt up to 369 GHz and the achieved sensitivity is about 10^{10} spins/G. Submillimeter wave ESR has advantages, such as the high spectral resolution and the ESR observation of the system with zero field gap, and the possible applications of our submillimeter wave micro-cantilever ESR to the biological systems will be discussed.

1. H. Ohta et al., AIP Conference Proceedings 850 (2006) 1643-1644: E. Ohmichi et al., Rev. Sci. Instrum. 79 (2008) 103903/1-5: E. Ohmichi et al., Rev. Sci. Instrum. 80 (2009) 013904/1-5: H. Ohta, E. Ohmichi, Appl. Magn. Reson. 37(1-4) (2010) 881-891: E. Ohmichi et al., J. Low Temp. Phys. 159 (2010) 276-279.

EPR ORAL SESSION

Hitoshi Ohta, Kobe University, Molecular Photoscience Research Center, Kobe 657-8501, Japan.
Ph: +81-78-803-5646, Fax: +81-78-803-5770, E-mail: hohta@kobe-u.ac.jp

106 **Controlling the Defect Centers in ZnO Nanoparticles by In-Situ Light-Induced and High Field EPR Spectroscopy.**

Peter Jakes,[1] Rüdiger-A. Eichel,[1] Stefan Weber,[1] Andrew Ozarowski,[2] Hans van Tol,[2] Emre Erdem[1]

[1]Albert-Ludwigs Universität Freiburg, Institut für Physikalische Chemie I, Albertstrasse 21, D-79104 Freiburg Germany
[2]National High Magnetic Field Laboratory, Center for Interdisciplinary Magnetic Resonance, Florida State University, Tallahassee, Florida, USA, 32310

Comprehensive understanding of the defect centers in zinc oxide (ZnO) nanoparticles invokes an important issue of controlling the nanoscopic properties of ZnO compounds. Due to its wide band gap (3.4 eV), ZnO possesses extraordinary electronic and optical properties, which make it a very attractive material for technological applications – particularly for thin film printable electronics.[1,2] Doping ZnO with transition metal ions, like Fe, Co, or Mn leads to materials with diversified behavior towards magnetic and optical excitation.[3] Even relatively small concentrations of defects and impurities can significantly affect the electronic, magnetic and optical properties of semiconductors. Therefore, understanding the role of defect centers (i.e. vacancies, interstitials, and antisites) and the incorporation of stable or meta-stable defects is a key tool toward controlling the electronic properties of ZnO. EPR is well suited for this task since it provides a direct method to monitor different paramagnetic states of vacancies and, thus, complements other experimental techniques such as photoluminescence. In this sense, EPR does not only work very well on the identification of defects but also one may obtain reliable correlation to the luminescence properties of bound excitons. Nonetheless, just from the basic principles of defect formation, it is hard to understand or predict what kind of defects will be present in the sample. From the EPR point of view, so far different EPR spectra have been assigned to the same defect site, or the same spectrum has been assigned to the different paramagnetic centers in ZnO. Thus, the nature of the defects and the interpretation of the defects are still controversial issues. In this work, undoped ZnO nanoparticles were synthesized by decomposition of zinc oximate[1] and the doped samples were synthesized by coprecipitation method. In order to characterize the ZnO defect structure, both light induced X band and high field EPR has been applied. To understand the behavior of defects in ZnO nano-particles under light, we imposed in-situ laser light with wavelengths of 445 nm (2.78 eV) and 532 nm (2.33 eV) on the samples during the X band EPR measurements. This is crucially important since defect structures may show different properties under different wavelength. High frequency EPR measurements over the temperature range 2 K-300 K were performed on the 15/17 T transmission instrument at the NHMFL. EPR measurement at 208 GHz allowed resolve small

differences in the *g*-values. The two different *g*-factors of 2.0028 and 2.0000 originated from different defect centers located at the *surface*. The defect center with a g factor of 2.0000 has escaped observation by standard X band (9.5 GHz) EPR in previous works. [1] Moreover, the 406 GHz EPR result showed that the signal from the *surface* was due to three different paramagnetic defect centers. This indeed demonstrates the power of high field EPR in resolving defect centers characterized by slightly different *g* factors, which are not possible to detect by standard continuous wave X band EPR.[3] At 406 GHz, also the core signal (g~1.96)[1] revealed a shoulder indicating an anisotropic EPR line.

Acknowledgements: Financially supported by DFG (Grant Er 662/1-1). We would like to thank Dr. R. Hoffmann and Prof. Dr. J. J. Schneider for supplying some of the nanosized samples.

1. Schneider, J.J., et al., Journal of Materials Chemistry, 19, 1449-1457 (2009).
2. Schneider, J.J., et al., Chemistry of Materials, 22, 2203-2212 (2010).
3. Jakes, P., et al. phys. Stat. sol. b-RRL 5, 56-58 (2011)

EPR ORAL SESSION

Emre Erdem, Albert-Ludwigs Universität Freiburg, Institut für Physikalische Chemie I, Albertstrasse 21, D-79104 Freiburg Germany

107 **Electrostatics of Bio- and Nano-Materials' Interfaces by EPR of pH-Sensitive Nitroxides.**

Alex I. Smirnov and M. A. Voynov, Department of Chemistry, North Carolina State University, 27695-8204

One of the essential aspects of nanostructures is the vastly increased surface-to-volume ratio that makes their interfacial and surface properties the main determinants of chemical reactivity, as well as interactions with biological systems. Here we show that the nitroxide-based EPR methods coupled with custom-synthesized probes are uniquely capable for providing molecular level data on structure, dynamics, and electrostatics of interfacial layers. We report on surface electrical potentials for both small unilamellar monodisperse lipid vesicles (SUMV) with diameters ranging from 30 to 100 nm and also lipid tubules that are stabilized by confining these structures within rigid homogeneous nanopores of similar diameters. These measurements were carried out using recently synthesized lipids having pH-reporting nitroxides covalently tethered to the lipid polar head. For example, for SUMVs composed of negatively charged lipids the magnitude of the surface potential increased with bilayer bending from ca. -106 mV for 100 nm SUMV to -166 mV for 30 nm SUMV. For nanopore-confined bilayers we observed shift in the surface potential by ca. 52 mV that was attributed to lipid interactions with the alumina surface. Overall, the data indicate that the bilayer bending affects the local electrostatic potential and lipid fluctuation properties to a rather large degree and is likely associated with a mechanism for cellular machinery function.

Supported by U.S. DOE Contract DOE DE-FG02-02ER15354.

EPR ORAL SESSION

Alex I. Smirnov, Department of Chemistry, 2620 Yarbrough Drive, North Carolina State University, 27695-8204, USA.
Ph: 919-513-4377, Fax: 919-513-735, E-mail: Alex_Smirnov@ncsu.edu

108 **Probing Tau Protein's Site-Specific Hydration Water Dynamics to Unravel Early Events in Fibrillar Aggregation Mechanism.**

Anna Pavlova, Department of Chemistry and Biochemistry, University of California-Santa Barbara, 93106-9510;
Songi Han, Department of Chemistry and Biochemistry and Materials Research Laboratory, University of California-Santa Barbara, 93106-9510

Probing the mechanistic details of the early events in tau protein fibrillar aggregation is necessary to gain a complete understanding of pathogenic effects during the aggregation process. Especially as blocking the formation and maturation of the toxic aggregates may be the clearest point of therapeutic intervention. Unfortunately, characterization of the events and protein oligomers that occur early in fiber formation has been elusive due to their transient nature. Here, we will present the site-specific probing of protein hydration dynamics as an ultra-sensitive experimental paradigm to capture the structural evolution of tau proteins as they undergo early conformational changes, oligomerization and fiber formation. Our methodology employs the Overhauser Effect Dynamic Nuclear Polarization (OE-DNP) to investigate the translational dynamics of biological hydration water at relevant time-scales (~ 10-1000 ps). This is possible by measuring the OE-DNP Enhancement of the 1H NMR signal (15MHz) of liquid water in the presence of continuous microwave irradiation in the classical X-Band (10GHz) EPR cavity. We have developed a unique set of experimental tools and techniques to test existing and develop new hypotheses on how the water-protein coupled interactions and the hydrophobic effect drive protein

aggregation. We first show that the bulk-like properties of the hydration shell of monomeric tau modulates its solubility and intrinsically unfolded nature. We then show that tau monomers undergo sudden and specific conformational changes upon heparin addition, followed by exposure of hydrophobic protein segments to solvent and subsequent formation of parallel beta sheets via solvent expulsion. We further provide evidence that annealing of stabilized insoluble tau oligomers is the main mechanism of fiber elongation. Finally, we will discuss our observation that hydration water structurally stabilizes the mature amyloid fibers of tau protein by forming regions of bound water near hydrophobic fibrillar core.

1. Armstrong et al., *J Am Chem Soc*, 131, 4641,2009.
2. Pavlova et al., *Phys. Chem. Chem. Phys.*, 11(31),6833, 2009.

EPR ORAL SESSION

Songi Han, Department of Chemistry and Biochemistry and Materials Research Laboratory, University of California-Santa Barbara, CA 93106-9510. Ph: 805-893-4858, E-mail: songi@chem.ucsb.edu

110 **Probing Heterogeneous Reactions with Spin Traps.**

Victor Chechik, Department of Chemistry, University of York, York YO10 5DD, UK

Heterogeneously-catalysed reactions often proceed via formation of radical intermediates. These reactive species can either be free radicals, or radicals adsorbed on the catalyst surface. As spin traps can abstract radicals from the catalyst surface, heterogeneous reactions can be studied using spin trapping technique.[1] We used spin trapping to explore reactivity of Au nanoparticles. Despite being very inert in the bulk form, nanoparticulate gold is quite reactive, particularly in oxidation reactions. Trapping reactive intermediates made it possible to establish reaction mechanisms. Oxidation of substrates possessing labile hydrogens (e.g., aldehydes) was shown to proceed via hydrogen atom abstraction, whereas alcohol oxidation involved hydride transfer to the catalyst surface.[2] In the second part of the talk, detection of free radicals in the gas phase is discussed. In order to monitor heterogeneously-catalysed processes, we built a reactor which traps the gas phase radicals shortly after they leave the catalytic bed. The reactor was used to monitor oxidation of aldehydes and cyclohexane. A mixture of spin adducts was detected which helped clarify the radical oxidation mechanisms.[3]

1. B. Mile, Curr. Org. Chem., 2000, 4, 55.
2. M. Conte, H. Miyamura, S. Kobayashi, V. Chechik, J. Am. Chem. Soc. 2009, 131, 7189.
3. M. Conte, V. Chechik, Chem. Commun., 2010, 46, 3991.

EPR ORAL SESSION

Victor Chechik, Department of Chemistry, University of York, York YO10 5DD, UK.
Ph: +44-1904-324185, E-mail: victor.chechik@york.ac.uk

111 **Spin Trapping in the Hydrogen Economy.**

Shulamith Schlick, M. Spulber, M. Danilczuk, Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, MI 48221-3038

The fragmentation of perfluorinated membranes used in fuel cells (FC) has been studied by spin trapping ESR using DMPO, PBN, and NMP as spin traps. The method was applied to the study of adducts generated in model compounds (ex situ experiments),[1] and in a fuel cell inserted in the resonator of the ESR spectrometer.[2] The stability of Nafion, stabilized Nafion, and 3M and Aquivion membranes to attack by the hydroxyl radical, HO•, was compared in their aqueous dispersions at 300 K; the HO• radicals were generated by UV-irradiation of hydrogen peroxide, H2O2, and radicals were detected by spin trapping with DMPO.[3] The competitive kinetics (CK) approach that has been adapted for ranking the polymer stability leads to the determination of their reaction rate constant with hydroxyl radicals. Recently we have used _-cyclodextrin (_-CD) encapsulation of the spin adducts as a method to increase the lifetimes and enhance the stability of initially generated spin adducts detected in the fragmentation of model compounds for the perfluorinated membranes.[4,5]

Supported by grants from the Polymers Program of NSF, DOE7 (DE-FG36-07GO17006), GM, and Ford Motor Company.

1. Danilczuk, M.; Coms, F.D.; Schlick, S. *Fuel Cells* **2008**, 8(6), 436-452.
2. Danilczuk, M.; Coms, F.D.; Schlick, S. *J. Phys. Chem. B* **2009**, 113, 8031-8042.
3. Danilczuk, M.; Perkowski, A.J.; Schlick, S. *Macromolecules* **2010**, 43, 3352-3358.
4. Spulber, M.; Schlick, S. *J. Phys. Chem. A* **2010**, 114(21), 6217-6225.
5. Spulber, M.; Schlick, S., to be submitted.

EPR ORAL SESSION

S. Schlick, Ph: 1-313-993-1012; Fax: 1-313-993-1144; E-mail: schlicks@udmercy.edu

112 **Surface-Mediated Production of Hydroxyl Radicals as a Mechanism of Iron Oxide Nanoparticle Biotoxicity.**

Maxim A. Voinov, Jason O. Sosa Pagán, Alex I. Smirnov, Tatyana I. Smirnova, Department of Chemistry, North Carolina State University, 2620 Yarbrough Dr., Raleigh, North Carolina 27695-8204

Rapidly developing nanotechnology is introducing many new nanomaterials into the human environment today. Among the diverse array of such materials, the nanosized iron oxides are, perhaps, the most widely employed, because of promising applications in catalysis, magnetic data storage, multimodal biomedical imaging, targeted drug delivery, medical diagnostics and therapy. Here, for the first time we demonstrate that Fe_2O_3 nanoparticles produce highly reactive hydroxyl radicals (OH•) under conditions of the biologically relevant superoxide-driven Fenton reaction. Production of the short-lived OH• radicals has been assessed by Electron Paramagnetic Resonance (EPR) spin-trapping technique. By carrying out comparative spin-trapping studies it was found that the free radical production is attributed primarily to the reactions at the nanoparticle surface rather than to dissolved metal ions as previously thought. Moreover, it was determined that under conditions of the superoxide-driven Fenton reaction the catalytic centers on the nanoparticle surface are at least 50-fold more effective in OH• radical production compared to the dissolved ions. We also show that passivating the surface with oleate has little effect on the catalytic production of free radical while coating of the nanoparticles with bovine serum albumin (BSA) eliminates characteristic spin-adduct EPR signal almost entirely. We speculate that the catalytic pathway of radicals' formation directly at the nanoparticle surface could be the one responsible for biological toxicity of bare nanostructured iron oxides. The experimental protocol developed in this study could be employed as an analytical assay for assessing potential toxicity of nanomaterials.

The authors acknowledge partial support from NIH 1R01GM072897 to A.I.S. and NSF Grant MCB-0451510 to T.I.S. J.S.P. is thankful to the NSF Alliances for Graduate Education and the Professoriate grant 0450102 for support.

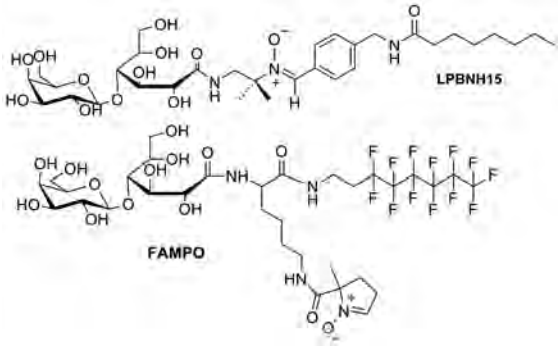
EPR ORAL SESSION

Tatyana I. Smirnova, Department of Chemistry, North Carolina State University, 2620 Yarbrough Dr., Raleigh, North Carolina 27695-8204

113 **Synthesis, Physical-Chemical and Biological Properties of Sugar-Based Amphiphilic Nitrones and Nitroxides.**

Grégory Durand, Université d'Avignon et des Pays de Vaucluse, F-84000 Avignon & Institut des Biomolécules Max Mousseron, F-34093 Montpellier, France

Amphiphilic compounds possessing both hydrophilic and lipophilic groups are expected to exhibit improved bioavailability and membrane crossing ability. Therefore, our work over the past 15 years has been devoted to the design of amphiphilic nitrones and nitroxides that can be used either as therapeutics or probes.[1-5] The synthesis of amphiphilic conjugates of nitrones and nitroxides as well as their self-aggregation properties in aqueous media determined by dynamic light scattering and EPR will be presented. Their protective effects in cells cultures exposed to toxic concentrations of oxidotoxins will be discussed as well.



1. Durand et al. *J. Med. Chem*, 2003, 46, 5230.
2. Ortial et al. *J. Med. Chem*, 2006, 49, 2812.
3. Durand et al. *Chem. Res. Toxicol*., 2009, 22, 1570.
4. Durand et al. *New J. Chem*, 2010, 34, 1909.
5. Durand et al. *J. Med. Chem*, 2010, 53, 4849.

EPR ORAL SESSION

Grégory Durand, Université d'Avignon et des Pays de Vaucluse, Equipe Chimie Bioorganique et Systèmes Amphiphiles, 33 rue Louis Pasteur, F-84000 Avignon & Institut des Biomolécules Max Mousseron (UMR 5247), 15 avenue Charles Flahault, F-34093 Montpellier Cedex 05, France, Ph: + 33 4 9014-4445, Fax: + 33 4 9014-4441, E-mail: vgregory.durand@univ-avignon.fr

114 **Direct Evidence of DMPO Spin-Trapping Artifact Originated from Forrester-Hepburn Mechanism.**

Fabian Leinisch, Kalina Ranguelova, Eugene DeRose, JinJie Jiang, Ronald Mason, NIEHS/NIH, Research Triangle Park, NC

With nitrone spin traps such as the commonly used 5,5-dimethyl-1-pyrroline N-oxide (DMPO) , proven artifacts are rare, but the fidelity of free radical detection is still of concern.[1] One possible pathway of ESR artifact formation is the Forrester-Hepburn mechanism. The same type of nitroxide radical as obtained from regular spin trapping may be formed by nucleophilic attack of the substrate on DMPO, forming a hydroxylamine intermediate that is subsequently oxidized to form the spin adduct. This artifact would not be revealed by standard spin-trapping control measurements, but utilization of isotopically labeled spin traps allows for direct and unambiguous detection in an advanced spin-trapping experiment.[2] ^{15}N-DMPO was synthesized and used to investigate the role of the Forrester-Hepburn mechanism in spin-trapping experiments with DMPO, horseradish peroxidase and nucleophilic substrates such as azide, cyanide, cysteine, glutathione and sulfite. Our experiments show that DMPO can indeed be prone to the Forrester-Hepburn artifact when cyanide is the substrate. Virtually the entire ESR signal has to be attributed to this artifact. The NMR-detectable intermediate was identified as cyano hydroxylamine by means of 2D-NMR experiments. However, with sulfite, the spin-trapping experiment is not affected, despite the known presence of a NMR-detectable intermediate.[3] So far, no indication of artifact formation has been found with other substrates.

1. Ranguelova et al., *Magn. Reson. Chem*., 2011, 49, 152
2. Timmins et al., *Redox Rep.*, 1997, 3, 225
3. Potapenko et al., *Magn. Reson. Chem*., 2003, 41, 603

EPR ORAL SESSION

Fabian Leinisch, PhD, Free Radical Metabolism Group, National Institute of Environmental Health Sciences, National Institutes of Health, MD F0-01, P.O. Box 12233, Research Triangle Park, NC 27709.
E-mail: leinischf@niehs.nih.gov, Fax: +1 919 541 1043

116 **Exploring Structure-Function Relationships at the Active Site of Tyrosine Hydroxylase using EPR Spectroscopy.**

John McCracken, Matthew D. Krzyaniak, Department of Chemistry, Michigan State University, East Lansing, MI 48824; and Paul F. Fitzpatrick, Department of Biochemistry, University of Texas Health Science Center, San Antonio, TX 78229

Tyrosine Hydoxylase (TyrH) catalyzes the hydroxylation of the aromatic side chain of tyrosine to form L-dopa (3,4-dihydoxyphenylalanine). Because this reaction is the rate-limiting step in the biosynthesis of the catecholamine neurotransmitters, epinephrine, norepinephrine and dopamine, it is vital to the proper functioning of the nervous system. Dysfunction of TyrH has been implicated in several neurological diseases including Parkinson's disease, bipolar disorder, and Segawa's syndrome. The hydroxylation chemistry is carried out at a non-heme Fe(II) that is bound to the enzyme by two histidyl imidazoles and one glutamate side chain arranged facially. Catalysis requires the binding of the primary amino acid substrate, tyrosine, a tetrahydropterin cosubstrate and molecular oxygen, and is thought to proceed through a two-step mechanism that yields 4a-hydroxytetrahydropterin and L-dopa as sequential products. Previous x-ray crystallographic studies, x-ray absorption and variable temperature - variable field MCD spectroscopic studies show that neither primary substrate nor the reduced pterin cosubstrate bind directly to the iron. Rather, they bind in the active site pocket and are positioned in a fashion that directs the hydroxylation chemistry through the discrete steps mentioned above. To characterize the structural relationship between the Fe(II) center and cosubstrates tyrosine and pterin, we have used NO as a surrogate for molecular oxygen to create an S=3/2 $\{FeNO\}^7$ paramagnetic center amenable to EPR studies. We will present ^{2}H-ESEEM and ^{1}H-HYSCORE data that reveal structural relationships between the metal center, tetrahydropterin and tyrosine for the first time. Parallel studies of a TyrH variant, E332A, show that positioning the reduced pterin cofactor for the first step of catalysis is crucial in the production of L-dopa.

EPR ORAL SESSION

John McCracken, Michigan State University, Department of Chemistry, East Lansing, MI 48824.
Ph: 517-355-9715 (ext. 269), Fax: 517-353-1793, E-mail: mccracke@msu.edu

117 **EPR Up Close and From Afar: Elucidation of Short and Long Range Structural Information in Macromolecular Metalloprotein Complexes.**

Fraser MacMillan, Matt Bawn, Jessica H van Wonderen & Fraser MacMillan, Henry Wellcome Unit for Biological EPR, School of Chemistry, University of East Anglia, Norwich, UK

Metal-containing and especially heme containing proteins are ubiquitous throughout nature, and are vital to many important biological reactions and mechanisms such as the transportation of diatomic gases, chemical catalysis, diatomic gas detection and electron transfer. Despite the great amount of scientific interest and research into these proteins, much about their function in many critical biological processes is still not fully understood. To address this we employ an EPR-based approach to probe both the local environment of paramagnetic centres as well as resolving long-range structural constraints both within and between macromolecular protein complexes. These approaches include a wide range of multi-dimensional, multi-frequency EPR spectroscopies such as ESEEM, HYSCORE (including matched-pulse HYSCORE and DONUT-HYSCORE), REFINE, PELDOR and ENDOR. Here I will illustrate our progress on various heme- and metal-containing proteins using examples from myoglobin, the cytochrome bc^1 complex, cytochrome cd^1, nitrite reductase and cytochrome c oxidase to address an array of research questions relating to the modes of action of these proteins.

EPR ORAL SESSION

Fraser MacMillan, Henry Wellcome Unit for Biological EPR, School of Chemistry, University of East Anglia, Norwich, UK. E-mail: fraser.macmillan@uea.ac.uk

118 **Determination of EPR Parameters Using a Spin-Orbit Coupled Complete Active Space Self-Consistent Field Approach.**

Dmitry Ganyushin, Frank Neese, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn, Germany

For nearly degenerate electronic states or transition metal complexes single-determinant approaches do not lead to a satisfactory 0th order description of the electronic structure. The only remedy for such situations is the utilization of multi-configurational ab-initio methods such as CASSCF, MRCI, or SORCI.[1] The spin-orbit coupling (SOC) effects are then usually treated using second-order perturbation theory or quasi-degenerate perturbation theory.[2] To describe the SOC interaction, the Breit-Pauli Hamiltonian or its mean field approximation (spin-orbit mean field, SOMF) is employed.[3] The accuracy of accounting for the SOC contribution on the ab-initio level can be further improved by employing a relativistic quantum chemical method that treats the SOC self-consistently. The majority of approaches that consider the SOC along with the electron-electron repulsion in the SCF framework employ two-component approaches in which the orbitals become complex valued linear combinations of spin-up and spin-down orbitals. This is best referred to as a molecular 'jj-coupling' approach. Here we propose a different method that is the analogue of 'LS-coupling' for the general molecular case. The first-order CASSCF equations can be rewritten in a way that the CI coefficients appear complex due to inclusion of the SOC Hamiltonian, but the orbitals remain real. Such an approach requires only partial modifications of the existing first-order CASSCF code. Scalar relativistic corrections for the SOC and Zeeman operators are acounted for using the second-order Douglas-Kroll-Hess scheme.[4] This new method is implemented into the CASSCF module of the ORCA program[5] and allows to obtain fast and accurate estimations of ZFS parameters and g-tesnors for molecules of a moderate size including second- and third-row transition-metal complexes.

1. Neese, *J. Chem. Phys.* 2003, 119, 9428.
2. D. Ganyushin and F. Neese, *J. Chem. Phys.* 2006, 125, 024103.
3. B. A. Hess, C. M. Marian, U. Wahlgren, and O. Gropen, *Chem. Phys. Lett.*1996, 251, 365.
4. M. Douglas and N. M. Kroll, Ann. Phys. (NY), 1974, 82, 89; B. A. Hess, R. J. Buenker, and P. Chandra, *Int. J. Quantum Chem.* 1986, 29, 737.
5. F. Neese. ORCA - an ab initio, Density Functional and Semiempirical program package, Universität Bonn, Bonn, Germany, 2010.

EPR ORAL SESSION

Dmitry Ganyushin, Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn, Germany. Ph: +49228-733834, Fax: +49228-739066, E-mail: ganyushin@thch.uni-bonn.de

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

119 **Effects of Ca^{2+} Binding to the Axial Ligation Geometry and Magnetic Properties of the Catalytic Diheme Center in MauG.**

Aimin Liu, Yan Chen, Sunil G. Naik, William H. Nelson, Shenghui Xue, Jenny. J. Yang, Departments of Chemistry, Physics and Astronomy, Georgia State University, P.O. Box 4098, Atlanta, GA, 30303; Sooim Shin, Victor L. Davidson, Department of Biochemistry, University of Mississippi Medical Center, Jackson, MS 39216; J. Krzystek, The National High Magnetic Field Laboratory, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310

MauG is a diheme enzyme possessing a five-coordinate high-spin (HS, S = 5/2) heme with an axial His ligand and a six-coordinate low-spin (LS, S = 1/2) heme with His-Tyr axial ligation.[1] A calcium ion is linked to the two hemes via H-bond networks and the enzyme activity depends on its presence. Removal of Ca^{2+} alters the EPR signals of each ferric heme such that they are significantly broadened.[2] Addition of Ca^{2+} back to the sample restored the original EPR signals and enzyme activity. The basis for this unusual Ca^{2+}-dependent behavior was characterized by multifrequency EPR and Mössbauer spectroscopy, and proton NMR relaxometry. In the Ca^{2+}-depleted MauG, the HS heme is converted to low-spin and the original LS heme exhibits a change in relative orientations of its two axial ligands. The properties of these two hemes are each different than in native MauG and now similar to each other. The EPR spectrum of Ca2+-depleted MauG appears to describe one set of six-coordinate low-spin ferric heme signals with a large g_{max} and g-anisotropy and a greatly elevated magnetic relaxation property. Both multifrequency EPR and Mössbauer spectroscopic results show that the two ferric hemes are present as unusual highly rhombic low-spin (HRLS) hemes in Ca^{2+}-depleted MauG along with altered magnetic properties. The original LS heme displays a dramatic change in the angle between the two axial ligand planes (Df, from 72˚ to ~ 20˚). These findings provide insight into the correlation of the enzyme activity with the orientation of axial heme ligands, and describe a new regulatory role for Ca^{2+} in metalloenzymes.

1. Jensen et al. Science, 2010, 327, 1392.
2. Shen et al., Biochemistry, 2011, 50, 144.

EPR ORAL SESSION

Aimin Liu, Georgia State University, Department of Chemistry, PO. Box 4098, Atlanta, GA 30303.
Ph: 404-413-5532, Fax: 404-414-5505, E-mail: feradical@gsu.edu

120 **Advanced Pulsed EPR Investigation of Biomimetic Model Complexes of the [FeFe] Hydrogenase Active Site in H_{ox}–CO and H_{ox} States.**

Özlen F. Erdem, MPI for Bioinorganic Chemistry, Mülheim/Ruhr, Germany; Lennart Schwartz, Department of Photochemistry and Molecular Science, Uppsala University, Sweden; Matthias Stein, MPI for Dynamics of Complex Technical Systems, Magdeburg, Germany; Alexey Silakov, MPI for Bioinorganic Chemistry, Mülheim/Ruhr, Germany; Michael Singleton, Texas A&M University, College Station, Texas, USA; Sascha Ott, Department of Photochemistry and Molecular Science, Uppsala University, Sweden; Edward Reijerse, MPI for Bioinorganic Chemistry, Mülheim/Ruhr, Germany; Marcetta Y. Darensbourg, Texas A&M University, College Station, Texas, USA; Wolfgang Lubitz, MPI for Bioinorganic Chemistry, Mülheim/Ruhr, Germany

Ever since the crystallization of the [FeFe] hydrogenases,[1] biomimetic and bioinspired model compounds of the active site have attracted great attention. Numerous model compounds have been reported,[2] e.g. by varying the bridging dithiolate ligands, applying asymmetric ligand substitution, thus, hoping to obtain proton reduction at lower overpotentials. We have performed a detailed pulsed EPR investigation on two types of model compounds: a) Compounds structurally resembling the CO-inhibited (H_{ox}-CO) state, with a nitrogen in the bridge (*azadithiolate*-nitrogen, *adt*-N), and b) Compounds structurally resembling the H_{ox} state, having an open coordination site vacant, with a bulky bridge (2,2-dimethyl-1,3-propanedithiolate), or with a bulky ligand (N-heterocyclic carbenes). In this presentation we will use a combination of EPR, ENDOR and HYSCORE experiments as well as DFT calculations to show that i) For the H_{ox}-like complexes the spin density distribution, surprisingly, doesn't drastically change depending on having neither a bulky ligand nor a bulky bridge; ii) For the H_{ox}-CO-like complexes, the magnetic coupling parameters obtained for the amino nitrogen in the azadithiolate bridge are quite similar to those for the native system at the H_{ox} state[3] indicating that the spin density in the native binuclear sub-cluster can indeed extent up into the amino group of the bridging adt., thus providing convincing evidence for the presence of an *adt*-N in the dithiolate bridge of the active site of native [FeFe] hydrogenase.[4] The confirmation of this amino function in the bridge is of relevance to the proposed mechanism of [FeFe] hydrogenases since it may act as proton donor/acceptor.

1. Peters et al., Science, 1998, 282, 1853; Fontecilla-Camps et al, *Nature*, 2009, 460, 814.
2. Tard et al., *J. Chem. Rev.*, 2009, 109, 245.
3. Silakov et al., *Phys. Chem. Chem. Phys.*, 2009, 11, 6592.
4. Erdem et al., *Angew. Chem. Int. Ed.*, 2011, 123, 1475.

EPR ORAL SESSION

Özlen F. Erdem, Max Planck Institute for Bioinorganic Chemistry, Stiftstrasse 34-36, Mülheim an der Ruhr, D-45470, Germany, Ph: 00492083063526, Fax: 0492083063955, E-mail: erdem@mpimuelheim.mpg.de

121 **Cobaloxime Catalyst for Biomimetic Hydrogen Production: Multifrequency EPR and DFT Study of Cobaloxime's Electronic Structure.**

Oleg G. Poluektov, Jens Niklas, Lisa M. Utschig, Karen L. Mulfort, David M. Tiede Argonne National Laboratory, Argonne, IL 60439; Rakhim R. Rakhimov, Norfolk State University, Norfolk, VA 23463; Kristy L. Mardis, Chicago State University, Chicago, IL 60628

Solar fuels research aims to mimic photosynthesis and devise integrated systems that can capture, convert, and store solar energy in high-energy molecular bonds. Currently, we are designing both synthetic supramolecular photocatalytic systems as well as Photosystem I—catalyst biohybrids that photochemically produce hydrogen. Further development and improvement of these systems relies on understanding the inherent, fundamental mechanisms for coupling captured photons to fuel generation. To this end, we are applying advanced spectroscopic techniques such as multifrequency pulsed EPR to elucidate important structure-function relationships in our artificial and biochemical complexes. The catalysts of choice for our research are cobaloxime derivatives. The catalytic properties of cobaloximes depend on the local surrounding and on the direct ligands to the central metal ion. The knowledge of the electronic properties is essential for understanding the catalytic activity of the molecule. EPR is an excellent tool to achieve this goal. In case of PS I, the other essential component of our biohybrid system, EPR spectroscopy has contributed tremendously to the current understanding of its electronic structure and function. In this work, difluoroboryl cobaloxime $Co(dmgBF_2)_2$ has been investigated in a variety of solvents with multi-frequency EPR spectroscopy at X-band (9 GHz), Q-band (34 GHz), and D-band (130 GHz) microwave frequencies. DFT modeling of the experimental data allows us to distinguish between different stable conformers and validate the structure of the axial ligand(s)-$Co(dmgBF_2)_2$ complexes.

This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-AC02-06CH11357.

EPR ORAL SESSION

Oleg Poluektov, Argonne National Laboratory, Chemical Sciences and Engineering Department, Argonne, IL 60439.
Ph: 630-252-3546, E-mail: Oleg@anl.gov

122 **Double Electron-Electron Resonance Between Gd^{3+} Ions and Nitroxide Radicals.**

Maxim Yulikov, Petra Lueders and Gunnar Jeschke, ETH Zurich, Laboratory of Physical Chemistry, Wolfgang Pauli Str. 10, 8093 Zurich, Switzerland

Double Electron-Electron Resonance (DEER) in orthogonal spin pairs, consisting of Gd^{3+} ions and nitroxide radicals is an interesting alternative approach for distance determination in macromolecules.[1] The technique is experimentally tested on model systems and provides rather good modulation depth and adequate distance information. It can be used as an alternative to common DEER on nitroxide-nitroxide spin pairs[2] or to Gd^{3+}-Gd^{3+} DEER, which is currently under development.[3] An important example to be presented here is a study of functionalized gold nanoparticles, where Gd^{3+}-nitroxide, nitroxide-nitroxide and Gd^{3+}-Gd^{3+} DEER measurements can be selectively performed on the same sample, thus supplementing each other. We also show that even at X band Gd^{3+}-nitroxide DEER can be performed on biologically relevant model systems with concentrations of spin-labeled macromolecules in the range of 100 – 200 mM. DEER measurements on Gd3+-nitroxide spin pairs are best performed at low temperatures (5-10 K) with detection on the central peak of the Gd3+ EPR spectrum and pump frequency at the maximum of nitroxide absorption. The typical offset between pump and observer frequencies is 80 MHz at X band and 300 MHz at Q band. The strength of ZFS for Gd^{3+} ions changes significantly with the type of chelate complex used. This influences the sensitivity of the technique but does not affect obtained distance information.

1. Lueders P., Jeschke G., and Yulikov M., *J. Phys. Chem. Lett.* 2011, 2, 604.
2. Jeschke, G.; Polyhach, Ye. *Phys. Chem. Chem. Phys*. 2007, 9, 1895.
3. Raitsimring, A. M. et.al., *J. Am. Chem. Soc.* 2007, 129, 14138.

EPR ORAL SESSION

Maxim Yulikov, ETH Zurich, Laboratory of Physical Chemistry, Wolfgang Pauli Str. 10, 8093 Zurich, Switzerland.
Ph: +41 44 632 3118, E-mail: maxim.yulikov@phys.chem.ethz.ch

123 **Spin Trapping Workshop**

Frederick A. Villamena, Department of Pharmacology and Davis Heart and Lung Research Institute, College of Medicine, The Ohio State University, Columbus, OH 43210

It has been a little over 40 years ago when spin trapping was first introduced for the detection of free radicals using electron paramagnetic resonance spectroscopy.[1-4] The use of both the linear nitrone, ·-phenyl-*tert*-butyl-nitrone (PBN), and the cyclic one, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), have shown successes for the identification of radicals in both chemical and biological systems. In spite of the limitations of PBN and DMPO for the detection of superoxide such as the short adduct half-life, slow rate of reactivity and non-target specificity to cellular compartments, they have contributed significantly toward the understanding of some of the most important chemical and biological processes. In this workshop, a historical overview of spin trapping, technical details for successful identification of radicals in various systems and current advances in the field will be presented. The aim of this presentation is to introduce (or reintroduce) the spin trapping technique to novice and seasoned spin trappers alike.

Supported by NIH RO1-HL60008412 and ARRA-HL60021301.

1. Iwamura, M.; Inamoto, N. Bull. *Chem. Soc. Jpn.* **1967**, 40, 703.
2. Janzen, Edward G.; Blackburn, Barry J. *J. Am. Chem. Soc.* **1968**, 90, 5909.
3. Harbour, J. R.; Chow, V.; Bolton, J. R. *Can. J. Chem.* **1974**, 52, 3549.
4. Janzen, E. G. *Acc. Chem. Res.* **1971**, 4, 31.

EPR ORAL SESSION

Frederick A. Villamena, The Ohio State University, Department of Pharmacology, Columbus, OH 43210.
Ph: 614-292-8215, Fax: 614-688-0999, E-mail: villamena.1@osu.edu

125 ***Piette Lecture* – Redox Sensitive Switches Regulating Superoxide and Nitric Oxide from eNOS.**

Jeanette Vasquez-Vivar, Department of Biophysics, Medical College of Wisconsin, Milwaukee, WI 53226

Nitric oxide and superoxide anion radical mediate several endothelial cell processes that are essential for vascular homeostasis. These radicals are produced under defined conditions by the endothelial constitutive isoform of nitric oxide synthase. Superoxide measurements by EPR-spin trapping methodologies proved essential to the discovery of a role for tetrahydrobiopterin (BH_4) cofactor in inhibiting the release of superoxide from the heme-oxygenase domain of eNOS. A redox switch control mediated by the ratio of BH_4:BH_2 was suggested to account for increased superoxide in a cellular context. Other redox sensitive switches regulating oxidant production from eNOS are $NADP^+$:NADPH, GSH:GSSG and NOx:RNO. In this presentation, I will discuss the impact of EPR methodologies and reagents in discerning the significance of these modifications to endothelial cell dysfunction.

EPR ORAL SESSION

Jeannette Vasquez-Vivar, Department of Biophysics, Medical College of Wisconsin, 8701 Watertown Plank Road Milwaukee, WI 53226. Ph: 414-955-8095, Fax: 414-456-6512, E-mail: jvvivar@mcw.edu

127 **Tertiary Contacts in the Prion Protein and the Connection to Inherited Disease.**

Glenn Millhauser, University of California, Santa Cruz, Department of Chemistry & Biochemistry, Santa Cruz, CA 95064

Misfolding of the prion protein (PrP) is responsible for the transmissible spongiform encephalopathies, which include mad cow disease, scrapie in goats and sheep, and the human disorders Kuru and Creutzfeldt-Jakob disease. PrP's N-terminal domain takes up both copper and zinc suggesting that the protein plays an important role in metal regulation within the central nervous system. Experiments over the last 15 years find little interaction between the protein's N-terminal domain and the folded, helical C-terminal domain. Here, we reinvestigate this issue using both NMR and EPR. We identify previously uncovered interactions that not only point to higher order structure in PrP, but also provide insight into inherited prion disease.

Supported by NIH grant GM065790.

1. Stevens et al. *PLoS Path.* 2009 5, e1000390.
2. Walter et al. *JACS* 2007 129, 15440.
3. Millhauser Ann. *Rev. Phys. Chem.* 2007 58, 299.

EPR ORAL SESSION

Glenn Millhauser, University of California, Santa Cruz, Department of Chemistry & Biochemistry, Santa Cruz, CA 95064

128 **Multiple DEER EPR Measurements to Estimate the Entropy of Complex Formation.**

Garland Marshall, Washington University, Department of Chemistry, St. Louis, MO 63130

DEER EPR spectroscopy can resolve the sets of distances between two nitroxide labels on a protein. Quantitation of abundance of the conformers giving rise to the different distances provides a means of estimating a simplified partition function for the system. By examining the changes in the DEER spectra upon complex formation, the entropy of complex formation can be estimated. By examining multiple pairs of spin labels distributed around the protein, a better estimate of the conformation ensemble can be determined. In the case of a double-labeled undecapeptide binding to photoactivated rhodopsin,[1] the conformational ensemble of the spin-labeled peptide was essentially reduced to a single conformer consistent with the bound conformer of the same peptide deduced by transfer NOE studies.[2] In order to improve the precision of distances measured by DEER, novel spin-labeled constrained amino acids will be incorporated into proteins biosynthetically,[3] or by chemical synthesis. The amide nitroxide is an example of a novel spin label under investigation.[4]

1. Van Eps et al., *Biochemistry*, 2010, 49, 6877.
2. Kisselev et al., *Proc. Natl. Acad. Sci. USA.* 1998, 95, 4270.
3. Murakami et al., Nature Meth. 2006, 3, 357.
4. Kullis et al. (unpublished).

EPR ORAL SESSION

Garland Marshall, Washington University, Department of Chemistry, St. Louis, MO 63130.
Ph: 314-935-7911, E-mail: garlandm@gmail.com

129 **Antibody-Mediated Mechanics on HIV-1 Envelope Protein gp41 at the Membrane Interface.**

Likai Song, National High Magnetic Field Laboratory, Tallahassee, FL; Zhen-Yu J. Sun, Harvard Medical School, Boston, MA; Mikyung Kim, Dana-Farber Cancer Institute, Boston, MA; Gerhard Wagner, Harvard Medical School, Boston, MA; Ellis L. Reinherz, Dana-Farber Cancer Institute, Boston, MA

A vaccine capable of stimulating protective anti-viral antibody responses is needed to curtail the global Acquired Immunodeficiency Syndrome (AIDS) epidemic caused by HIV-1. The membrane proximal ectodomain region (MPER) of the HIV-1 gp41 envelope protein subunit is the target of three human broadly neutralizing antibodies (BNAbs): 4E10, 2F5 and Z13e1. How these BNAbs bind to their lipid-embedded epitopes and mediate anti-viral activity are unclear. Here, EPR and NMR techniques were used to define the manner in which theses BNAbs differentially recognize viral membrane-encrypted residues configured within the L-shaped helix-hinge-helix MPER segment. Both 4E10 and 2F5 induce large conformational changes in the MPER relative to the membrane. However, while 4E10 straddles the hinge and extracts residues W672 and F673, 2F5 lifts up residues N-terminal to the hinge region, exposing L669 and W670. In contrast, Z13e1 affects little change in membrane orientation or conformation, but rather immobilizes the MPER hinge through extensive rigidifying surface contacts. Thus, BNAbs disrupt HIV-1 MPER fusogenic functions critical for virus entry into human T cells either by preventing hinge motion or by perturbing MPER orientation. HIV-1 MPER features important for targeted vaccine design have been revealed, the implications of which extend to BNAb targets on other viral fusion proteins.

EPR ORAL SESSION

Likai Song, National High Magnetic Field Laboratory, Tallahassee, FL 32310.
Ph: 850-644-6153, Fax: 850-644-4628, E-mail: song@magnet.fsu.edu

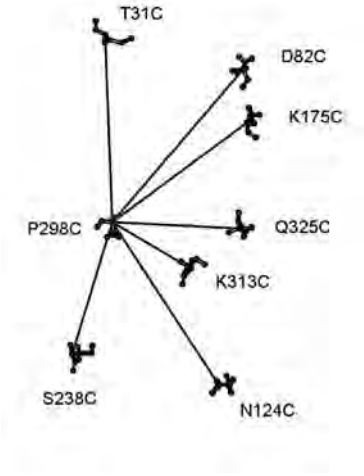
https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

130 **A Partially Structured Molten Globule Protein.**

J. Reichenwallner, M. Chakour, Wofgang E. Trommer, Department of Chemistry, TU Kaiserslautern, Kaiserslautern, Germany; S. Indu, R. Varadarajan, Molecular Biophysics Unit, Indian Institute of Science, Bangalore, India

Maltose binding protein (MBP) from E. coli was shown to bind maltose even in its molten globule state, although with substantially reduced affinity.[1] The native protein of which the X-ray structure is known, is devoid of cysteines. We have seven different mutants with two cysteines each, which have been labeled with the MTS-SL. Distances from the active site as derived from the X-ray structure vary from 14 to 31 Å as summarized and depicted below. DEER measurements have so far shown very good agreement between the X-ray data and the native structure. Now we want to compare distances in the native protein with those in the molten globule state.

Double Cys mutant	C_-C_ distance [_]
P298C T31C MBP	27.5
P298C D82C MBP	28.0
P298C N124C MBP	27.2
P298C K175C MBP	31.3
P298C S238C MBP	19.7
P298C K313C MBP	14.1
P298C Q325 MBP	19.7



1. Prajapati, R. S., Indu, S., Varadarajan, R., *Biochemistry*, "*Identification and Thermodynamic Characterization of Molten Globule States of Periplasmic Binding Proteins*", 46, pp. 10339-10352, 2007

EPR ORAL SESSION

Prof. Dr. Wolfgang E. Trommer, TU Kaiserslautern, Department of Chemistry, P.O. Box 3049, D-67653 Kaiserslautern, Germany. Ph: +49-631-205 2045, Fax: +49-631-205-3419, E-mail: trommer@chemie.uni-kl.de

131 **The Affinity and Stability of Immobilized Biomolecules: Time-Resolved EPR Detection During Mobile Phase Gradients.**

Eric Walter, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352; Glenn Millhauser, University of California Santa Cruz, 1156 High St., Santa Cruz, CA 95064

The parameters governing the interaction between chemical binding partners are of fundamental interest to chemists, biochemists and chemical engineers. Techniques that can determine the affinity, kinetics, structural change or chemical reactions due to interactions (NMR, CD, Fluorescence), usually require that both the analyte and the ligand be in solution. Here we report on the development of a new technique that employs affinity beads (or other chromatography column materials) as the solid phase and Electron Paramagnetic Resonance as the detection spectroscopy. This concept is realized by replacing the normal EPR aqueous sample cell with a fritted column of the same dimensions. The sample column contains the molecule of interest tethered to a solid phase resin and a mobile phase is continuously renewed via a binary gradient pump. The stability of a tethered protein can be monitored via a site-directed spin-labeling – the mobility of the label can be monitored while the content of the mobile phase is changed, i.e. a gradient change in pH or concentration of chaotrope. The affinity of the tethered molecule for a labeled ligand in solution can also be determined by build-up of the label signal with time. This method is compatible with a wide variety of attachment schemes – both covalent and affinity based – that can be chosen for compatibility with the experiment. Examples presented include the interaction of metals in solution with immobilized melanin and with fusion proteins, the binding of spin-labeled carbohydrates by proteins and the stability of covalently attached proteins.

EPR ORAL SESSION

Eric Walter, Pacific Northwest National Laboratory, 902 Battelle blvd., P.O. Box 999, K8-98, Richland, WA 99352. Ph: 509-371-6873, Fax: 509-371-6555, E-mail: eric.walter@pnl.gov

133 **EPR Studies of Carotenoid Radicals and Their Significance in Photosynthesis.**

Lowell D. Kispert, A. Ligia Focsan, The University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487-0336

Carotenoids are intrinsic components of reaction centers and pigment-protein complexes in photosynthetic membranes. They play a photoprotective role in plants, algae and cyanobacteria by quenching reactive photoinduced radicals and dissipating the excess energy. During this process radical cations and neutral radicals are formed.[1] Various EPR techniques,[2, 3] including X and Q band, CIDEP (Chemical Induced Dynamic Electron Polarization), cw and pulsed ENDOR, ESEEM, high frequency EPR, spin trapping, SEEPR and pulsed EPR relaxation methods have been used to characterize the structure of the carotenoid π-radical intermediates, their reactivity, electron transfer character, addition products, host guest complex formation, inclusion complexes, dependence of oxidation potential on host and relevance to photosynthesis. Examples will be presented where mixtures of carotenoid π-radicals with similar EPR isotropic hyperfine couplings ranging from 1 to 16 MHz have been resolved. Simultaneous electrochemical and EPR techniques (SEEPR) have identified carotenoid neutral radicals in solutions and measured their equilibrium constants with carotenoid radical cation and dication. Spin trapping studies have measured the relative ability of carotenoids to scavenge $^{\Sigma}$OOH radicals which shows a nonlinear dependence with carotenoid oxidation potential. CIDEP studies show that the electron transfer to the solvent occurs from the excited single state of the carotenoids. In arabinogalactan hosts the carotenoids showed enhanced photostability, and from ESEEM measurements interspin distances were measured between host metal ions and the carotenoid radicals.

This work was supported by the Office of Basic Energy Sciences, US Department of Energy.

1. Gao, Y.; Shinopoulos; Tracewell, C. A.; Focsan, A. L.; Brudvig, G. W.; Kispert, L. D., *J. Phys. Chem. B*, 2009, 113, 9901-9908.
2. Kispert, L.; Focsan, L.; Konovalova, T. Applications of EPR spectroscopy to understanding carotenoid radicals in Part III. Applications of spectroscopic methodologies to carotenoid systems of *"Carotenoids: Physical, Chemical, and Biological Functions and Properties*" edited by J. T. Landrum, CRC Press, 2010, p. 159-189.
3. Kispert L.D. and Polyakov N.E., *Chem. Lett*., 2010, 39, 148-155.

EPR ORAL SESSION

Lowell D. Kispert, The University of Alabama, Department of Chemistry, 250 Hackberry Lane, Tuscaloosa, AL 35487-0336, USA. Ph: 205-348-7134, E-mail: lkispert@bama.ua.edu

134 **The Magnetic Structure of Tryptophan Radicals.**

Stefan Stoll,[1] Hannah S. Shafaat,[2] Jurek Krzystek,[3] Andrew Ozarowski,[3] Michael J. Tauber,[2] Judy E. Kim,[2] R. David Britt[1]
1 Department of Chemistry, University of California Davis, Davis, CA 95616
2 Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093
3 National High Magnetic Field Laboratory, Tallahassee, FL 32310

Tryptophan radicals serve as relays in multi-step electron transfer and as redox mediators in biotechnologically relevant enzymes that can oxidize high-reduction-potential organic substrates such as lignin. Little is known how proteins control these radicals. We use multi-technique EPR to elucidate the structure of two model tryptophan radicals, photogenerated in the electron-transfer protein azurin. One radical is located in a solvent-exposed region close to the protein surface, and the other in a hydrophobic pocket in the core of the protein. Q-band ^{1}H ENDOR gives spin density distributions and side chain conformations. ^{1}H/^{2}H exchange and ^{2}H ENDOR probe the presence of hydrogen bonds. CW EPR at uniquely high field and frequency (25 T, 700 GHz) is used to completely resolve the very narrow g tensors (g_{max}-g_{min} < 0.0015) and determine the g values using endohedral atomic hydrogen as a field standard. The g tensor anisotropy correlates with the presence/absence of a hydrogen bond to the tryptophan radical.

EPR ORAL SESSION

Stefan Stoll, Department of Chemisty, University of California Davis ,One Shields Ave., Davis CA 95616.
Ph: 530-752-2964

136 **Opportunities of High Field EPR: Extending the Distance Range with Gd^{3+}-Based Probes.**

Devin Edwards, University of California, Department of Physics, Santa Barbara CA 93106; Daniella Goldfarb, Department of Chemical Physics, Weizmann Institute of Science, Israel; Songi Han, University of California, Department of Chemistry, Santa Barbara CA 93106; Mark Sherwin, University of California, Department of Physics, Santa Barbara CA 93106

In this work we detail development of Gd^{3+} as a spin probe to enhance distance measurement techniques by capitalizing on the advantages of high frequency EPR. The potential exists to investigate systems, timescales and distances at 240 GHz which are not easily realizable at lower fields. While high frequency instrumentation and techniques have developed rapidly, nitroxide based spin labels remain the standard, even though superior features of other spin systems emerge in this new regime. Impressive work has demonstrated the promising application of Gd^{3+} for DEER at W-Band(Potapov et al, *J. Amer. Chem. Soc.*, **2010**, 132, 9040). By working at higher frequencies, we further amplify the benefits of these new probes in both CW and pulsed applications. In spectral measurements, the central $|-1/2> \rightarrow |1/2>$ transition of Gd^{3+} shrinks to nearly 10 Gauss at 240 GHz—2.5 times narrower than at 95 GHz—making it an extremely sensitive probe of dipolar broadening and therefore distances with long distances limited by the unbroadened linewidth. Preliminary lineshape measurements using $GdCl_3$ in solution show changes in the central width down to 2.5mM, indicating sensitivity to ~5 nm, greater distances than are accessible in CW spectra of nitroxides at lower fields. While this presents enormous opportunities for cw EPR based distance analysis, pulsed EPR at high fields shows promise to stretch the capabilities of Gd^{3+} even further. The limitations of the intrinsic linewidth may be eliminated by observing interspin distance through temperature dependence of the decoherence time by quenching the Gd^{3+} spin bath at high fields. Such measurements of $GdCl_3$ show concentration dependence down to 300_M, suggesting the potential to push the sensitivity of EPR to distances approaching 10nm. Development of theory and methods, as well as applications are being carried out in order to move towards quantitative distance determinations and their validation.

EPR ORAL SESSION

Devin Edwards, University of California, Department of Physics, Santa Barbara CA 93106.
Ph: 805-893-2032, E-mail: dedwards@physics.ucsb.edu

137 **EPR Study of Electron-Hole Asymmetry in Bulk and Nanoparticles of $Bi_{1-x}Ca_xMnO_3$(x = 0.4, 0.6): A Comparison.**

Geetanjali Singh, Indian Institute of Science, Department of Physics, Bangalore, Karnataka, 560012; S V Bhat, Indian Institute of Science, Department of Physics, Bangalore, Karnataka, 560012

Electron-hole asymmetry.[1] which refers to the asymmetry in the phase diagram across x = 0.5 in doped rare earth manganites such as $Re_{1-x}A_xMnO_3$ is shown[2] to vanish on reducing the size of the particles to a few nanometers. Bismuth based manganites provide an interesting model system for comparison: e.g. though the doped rare earth manganites show disappearance of charge order (CO) on size reduction to nanoscale,[3] CO in Bi manganites is found to be more robust. Here we study the effect of size reduction on EPR parameters of electron (x = 0. 6, BCMOE) and hole (x = 0.4, BCMOH) doped $Bi_{1-x}Ca_xMnO_3$. Nearly spherical nanoparticles (d ~ 18 nm) of BCMO were prepared by sol-gel synthesis and the bulk samples using the solid state reaction route. X-band EPR was carried out between 4 and 300 K. Lineshape fitting was carried out using double Lorentzian function accounting for clockwise and counterclockwise rotating components of the microwave field. The extracted EPR parameters, namely, the linewidth, intensity and the resonance field for the bulk and the nano samples indicate that the differences observed in the EPR parameters for the electron and hole doped bulk samples persist in the nanosamples as well in contrast with the results on $Pr_{1-x}Ca_xMnO_3$[2]. We understand this in terms of the presence of the highly polarizable $6s^2$ lone pairs on bismuth which is understood to cause many interesting departures from the behavior of rare earth manganites.

1. Janhavi P. Joshi, A.K. Sood, S.V. Bhat, Sarathy, Vijay, C.N.R. Rao, *J.Phys. Cond. Matter.* 16, 2869 (2004)
2. K.G. Padmalekha and S.V. Bhat, arxiv-cond-mat/1010.3556.
3. S. S. Rao, S. Tripathi, D. Pandey and S. V. Bhat, *Phys. Rev, B* 74, 144416 (2006)

EPR ORAL SESSION

Geetanjali Singh, Department of Physics, Indian Institute of Science, Bangalore, Karnataka, India – 560012.
Ph: 91-80-22932727, Fax: 91-80-23602602, E-mail: geetanjali@physics.iisc.ernet.in

138 **Progress And Challenges in Measuring the Orientational Dependence of DEER for Transition Metals In Model Systems And Proteins.** Alice M. Bowen, Michael W. Jones, Janet E. Lovett, Jeffrey Harmer, John R. Dilworth and Christiane R. Timmel. Center for Advanced Electron Spin Resonance, University of Oxford, Inorganic Chemistry Department, South Parks Road, Oxford, OX1 3QR

This work presents a complete study, including measurement and analysis, of the orientational selectivity in DEER spectra recorded between two copper(II) centres in the protein homodimer of copper amine oxidase from *Arthrobacter globiformis* as well as model chemical systems with differing inter-copper distances. Spectra were recorded at X-band on a commercial Brucker Elexys spectrometer and simulated spectra were fitted to the experimental data using a least-squares algorithm. The degree to which orientational selectivity affects the shape of the resultant DEER trace differs across the EPR spectrum with regard to the selected pump and probe positions (Fig. 1). Therefore in order to observe and interpret significant orientational effects some prior knowledge of the system is required. Orientationally selective DEER spectra were simulated using Matlab based home-written software (J. E. Lovett, A. M. Bowen, et al., *Physical Chemistry Chemical Physics*, 2009, 11, 6840-6848). This program requires an initial structural input; in the case of the copper amine oxidase this was an X-ray structure of the protein. However for the model systems it was necessary to use a combination of Density Functional Theory (DFT) calculations and X-ray structures of chemical precursors to predict likely conformers of the molecular structure. In order to verify the structural model used for the model systems similar Copper-Nitroxide and Nitroxide-Nitroxide compounds were also studied. The bi-nitroxide systems were further analysed using DEERAnalysis (G. Jeschke, V. Chechik, et al., Applied Magnetic Resonance, 2006, 30, 473-498). However such analysis is not correct when significant orientational selection is present. DFT calculations were also employed to confirm the orientation of the g-matrix with respect to the molecular structure for both the model systems and the protein.

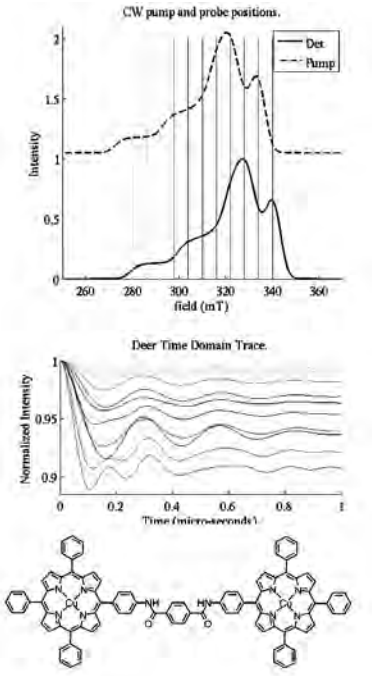


Fig. 1
a) DEER Pump and probe positions across the copper spectrum, for a di-copper model system, with a 200 MHz separation.
b) Resultant simulated DEER spectra showing orientational selectivity.
c) Structure of the di-copper model system.

EPR ORAL SESSION

Alice M. Bowen, Center for Advanced Electron Spin Resonance, University of Oxford, Inorganic Chemistry Department, South Parks Road, Oxford, OX1 3QR.
Ph: +44 1865 272641, Fax: +44 1865 272690, E-mail: alice.bowen@chem.ox.ac.uk

139 **Cu^{2+}Coordination Site Structure in Soluble and Fibrillar Forms of the Amyloid-β Protein.**
Bill Gunderson,[1] Jessica Hernandez-Guzman,[2] Jesse W. Karr,[3] Veronika A. Szalai,[4] Kurt Warncke[1]
1 Department of Physics, Emory University, Atlanta, GA 30322
2 Department of Physics, Adams State College, Alamosa CO 81102
3 Department of Chemistry, Boston University, Boston, MA 02215
4 National Institute of Standards and Technology, Gaithersburg, MD 20899

Aggregation of the amyloid-_ (A_) protein is associated with the development of Alzheimer's disease (AD). The transition metal ion, Cu^{2+}, is found at high concentrations in A_ plaques and neurofibrillary tangles in vivo, binds site-specifically to A_ in vitro, and has been reported to increase A_ toxicity. Understanding Cu^{2+} involvement in AD etiology requires characterization of metal site speciation and its effects on A_ aggregation properties. We use continuous-wave-electron paramagnetic resonance (EPR) and powder and orientation-selection electron spin echo envelope modulation (ESEEM) spectroscopies to characterize fundamental features of the S=1/2 Cu^{2+} coordination environment in vitro in soluble and fibrillar A_(1-40) [including natural isotopic abundance and ^{13}C-,^{15}N-histidine (His)-labeled A_(1-40)]. The ESEEM technique sensitively detects the remote (non-coordinated) ^{14}N in the imidazole side chain(s) of His that are equatorially-ligated to Cu^{2+}. Model equatorial bis-*cis*-, bis-*trans*-, and tris-imidazolyl-Cu^{2+} complexes, and the soluble monomeric Cu^{2+}-A_(1-16) complex, are also examined. Analysis and comparisons of the ^{14}N ESEEM, and in particular, the histidine imidazole remote ^{14}N Dm_I=±2 "double quantum" feature and harmonics,[1] is used to determine the number and geometry of equatorially-coordinated histidine imidazole ligands in the soluble and fibrillar Ab states. The $^{15}N/^{14}N$ isotope editing is used to identify the degree of involvement of the three His side chains (residues 6, 13, and 14) in Cu^{2+} binding. The results provide insights into the influence of aggregation state on Cu^{2+} coordination structure in Ab.

1. Sun et. al., *J. Magn. Reson*, **2009**. 200, 21.

EPR ORAL SESSION

William A. Gunderson, Emory University, Department of Physics, N201 MSC, Atlanta, GA 30322-2430
Ph: 404-727-4287, Fax: 404-727-0873, E-mail: wgunderson@physics.emory.edu

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

140 **Fitting the Puzzle Together: Spin Transitions in the New Class of Paramagnetic Labels – The Cage Complexes With Encapsulated Cobalt(II) Ion.**

Valentin Novikov, A. Lebedev, Y. Voloshin, Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia

Macrobicyclic tris-dioximate complexes with encapsulated cobalt(II) ion are perspective paramagnetic labels owing to the complete isolation of an encapsulated paramagnetic ion and hence the stability of the complex and the independence of its magnetic characteristics from the environment (Voloshin et el., Angew. Chem. Int. Ed., 44, 3400). The functionalization of such complexes by six ribbed and two apical substituents gives a room for fine tuning the characteristics of an encapsulated ion to achieve the features desired. In particular, the molecular design allowed obtaining macrobicyclic complexes with a high affinity to proteins (for example, T7 RNA polymerase). At the same time, the choice of dioximate ribbed groups affects tremendously the magnetic properties of an encapsulated ion, enabling the spin transition in these complexes. Those in a low-spin state demonstrate dynamic Jahn-Teller distortion, which results in the shift of an encapsulated cobalt(II) ion from the center of the macrobicyclic ligand's cavity, while the high-spin complexes have a C3 symmetry. The high-spin cobalt(II) complexes exhibit the EPR signal at the temperatures as high as 100K. The pseudocontact interactions with the cobalt(II) ion leads to the paramagnetic shift of distant (>2.5 nm) nuclei signals in NMR spectra, paving the way for the use of the cobalt(II) cage complexes as non-covalent paramagnetic tags.

The study was supported by Russian Foundation for Basic Research (10-03-00837) and Council of the President of the Russian Federation for young scientists (MK-3161.2010.3).

EPR ORAL SESSION

Valentin Novikov, Nesmeyanov Institute of Organoelement Compounds RAS, 28 Vavilova str., 119991, Moscow, Russia.
Ph: 7-903-742-7652, Fax: 7-499-135-50-85, E-mail: novikov84@ineos.ac.ru

141 **Magnetic Resonance Studies of Dynamics to Decipher the Structure and Light-Activated Conformational Changes of Proteorhodopsin's E-F Loop.**

Sunyia Hussain, University of California, Santa Barbara, Dept. of Chemical Engineering, Santa Barbara, CA 93106-5080;
Song-I Han, University of California, Santa Barbara, Dept. of Chemistry & Biochemistry, Santa Barbara, CA 93106-9510

The proteorhodopsin (PR) proton pump, recently discovered in marine bacteria, uses light to facilitate the transport of a proton across the cell membrane due to a conformational "switch". The resulting pH gradient can be used to generate chemical energy—a function distinguishing PR for the development of biological solar cells. PR belongs to the class of seven transmembrane (7TM) proteins, diverse and important biomolecules that are notoriously difficult to characterize due to their association with lipids and proteins. The model system of PR in a synthetic membrane therefore provides a way to study important dynamics, structure and function for both technological and biophysical applications. In this study, we employ continuous and light-triggered electron paramagnetic resonance (EPR) and dynamic nuclear polarization (DNP) spectroscopy to study the conformational dynamics of the PR E108Q mutant, with a slowed down photocycle that stabilizes the "M" photointermediate. These methods provide insight into the protein segment mobility and local hydration water dynamics of an amino acid residue spin-labeled with nitroxide-based radicals. DNP is a novel tool developed in the Han lab, and here is applied to examine protein movements through changes in hydration dynamics. We find an interesting structural feature of PR's third cytoplasmic (E-F) loop revealing an intimate interplay between structure and dynamics: the loop consists of a short α-helical segment that experiences conformational change upon photoactivation. The buried residues making tertiary contact with the protein experience increased mobility and water dynamics, demonstrating a slight lifting up of the interhelical E-F loop segment. The interfacial and exposed residues experience more complex changes that indicate a stiffening of the loop's water-exposed face and a twisting motion. These spectroscopic signatures of conformational change and structural dynamics give us unprecedented insight into activated 7TM protein movement from the complementary perspectives of amino acid side-chain flexibility and hydration changes.

EPR ORAL SESSION

Song-I Han, University of California, Santa Barbara, Dept. of Chemistry & Biochemistry, Santa Barbara, CA 93016-9510.
Ph: 805-893-4858, Fax: 805-893-4120, E-mail: songi@chem.ucsb.edu

142 **Global Structure of a 3-Way Junction in a Phi29 Packaging RNA Dimer Complex Determined Using Site-Directed Spin Labeling.**

Xiaojun Zhang, University of Southern California, Department of Chemistry, Los Angeles, CA, 90089; Peter Z. Qin, University of Southern California, Department of Chemistry, Los Angeles, CA, 90089

The condensation of bacteriophage phi29 genomic DNA into its preformed procapsid requires the DNA packaging motor, which is the strongest known biological motor. The packaging motor is an intricate ring-shaped protein/RNA complex, and the RNA component, called the packaging RNA (pRNA), is indispensable for motor function. Current structural information on pRNA is limited, which hinders our effort on understanding motor function. Here, we use site-directed spin labeling and pulse EPR spectroscopy to map the conformation of a 3-way junction in the context of a pRNA dimer, which has been shown to be a functional intermediate in assembling the ring-shaped pRNA complex in the packaging motor. A phosphorothioate labeling scheme was used to attach a stable nitroxide radical (R5) at specific sites within a pRNA monomer. The labeled pRNA was assembled into dimers without interfering with RNA folding and RNA/RNA interactions, and a total of 17 inter-R5 distances spanning the 3-way junction were measured using Double Electron-Electron Resonance spectroscopy. The measured distances, together with steric chemical constraints, were used to evaluate 65 billion of models of the 3-way junction where the spatial relationship between three corresponding A-form helices was systematically varied. The studies revealed a very small fraction of viable models, and all those viable models fall into a similar conformation, in which two of the helices (H_T and H_L) adopt an acute bend with the angle between their helical axes being ~ (88 ± 14)°. This contrasts to a recently reported pRNA tetramer crystal structure,[1] in which H_T and H_L stack onto each other linearly. The results demonstrate versatility in conformations of pRNA assemblies, which may be beneficial to pRNA function within the DNA packaging machinery.

Supported by NSF Career MCB 0546529 (PZQ).

1. Ding et al. PNAS, 2011, April 6 Epub ahead of print.

EPR ORAL SESSION

Peter Z. Qin, University of Southern California, Department of Chemistry, Los Angeles, CA, 90089.
Ph: 213-821-2461, Fax: 213-740-0930, E-mail: pzq@usc.edu

143 **Simulating the Dynamics and Orientations of Spin Labeled Side Chains in the Restriction Endonuclease EcoRI.**

Jessica Sarver, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260; Katherine Stone, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260; Jacque Townsend, University of Pittsburgh, Department of Biological Sciences, Pittsburgh, PA 15260; Paul Sapienza, University of Pittsburgh, Department of Biological Sciences, Pittsburgh, PA 15260; Linda Jen-Jacobson, University of Pittsburgh, Department of Biological Sciences, Pittsburgh, PA 15260; Sunil Saxena, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260

Molecular dynamics (MD) simulations were carried out in explicit solvent to investigate the preferred conformers and dynamics of the methanethiosulfonate spin label at sites 131, 180, and 249, as well as, to provide insight into the backbone contribution at these spin labeled sites of the restriction endonuclease EcoRI. Sites 131 and 180 are located on a loop and β-strand of the EcoRI arm region, respectively. The arm region of EcoRI is believed to play a major role in the extreme binding specificity of this DNA-binding enzyme. Site 249 resides on an α-helix in the stable, main domain of EcoRI. Ten parallel simulations were run starting with different initial orientations of the spin label derived from a rotamer search prior to MD simulation. The simulations were performed in an explicit waterbox for 30 nanoseconds (ns). The simulated results were validated by comparing the distance distribution between the nitrogen atoms of the spin label from the MD trajectories to experimental distance distributions obtained previously using the electron spin resonance Double Electron Electron Resonance technique.[1] The MD results were found to agree well with experiment for several of the parallel simulations. Detailed analysis of the last 20 ns of simulation, where the system is fully equilibrated, has provided insight into the preferred orientations and dynamics of the spin label at three different secondary structural regions of EcoRI. Additionally, insight into the position and dynamics of the backbone at these sites of EcoRI was obtained.

This work is supported by NSF (MCB 0842956).

1. Stone, K., et al. Angew. Chem. Int. Ed., 2008, 120, 10346-10348

EPR ORAL SESSION

Jessica Sarver, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260.
Ph: 412-624-8123, E-mail: jls144@pitt.edu

144 **Characterization of the Semiquinone Intermediate in Cytochrome bc_1 Complex.**

Preethi R. Vennam,[1] Matthew D. Krzyaniak,[1] Savannah P. Whitted,[3] Alexander G. Maryasov[4], Xu Quiang,[2] Jonathan L. Cape,[2] David M. Kramer,[2] Michael K. Bowman[1]

1 Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336;
2 Institute of Biological Chemistry, Washington State University;
3 Department of Chemistry, Union University
4 Institute of Chemical Kinetics & Combustion, Russian Academy of Science.

The cytochrome bc1 and related complexes are essential energy transduction components in the respiratory and photosynthetic electron transport chains of a wide range of organisms. The cyt *bc*[1] catalyzes the ubiquinol oxidation by forming a semiquinone (SQ) radical intermediate in close proximity to the hemes of the cyt b subunit and the Rieske FeS cluster. SQ radical has been trapped in cyt *bc*[1] by rapid freeze quench technique in 7 ms which is detected by CW and pulsed EPR measurements. Ubisemiquinone (USQ) radical anion and neutral USQ radical in cyclohexanol solution which is fairly hydrophobic, have been prepared and later characterized using pulsed EPR techniques. The slight difference in the g-tensor values of SQ trapped in cyt *bc*[1] and chemically prepared SQ is due to the difference in the SQ environment. Mims ENDOR spectra of chemically prepared USQ radical anion have 3 sets of proton hyperfine couplings where as the neutral USQ radical have 4 sets. Mims ENDOR spectra of the SQ trapped in the enzyme have similar hyperfine coupling values as that of radical anion in solution. Lack of 4th set of hyperfine coupling values and lack of Nitrogen modulation in ESEEM and HYSCORE indicates that there is neither H-bonding nor strong interaction with amides or Histidine. The electron spin echo (ESE) decay rate has been used to probe the interactions of SQ and fast relaxing metal centers of heme and/or Reiske. ESE decay of the trapped semiquinone in cyt *bc*[1] is strongly enhanced relative to that of ubisemiquinone radical anion at X-band by a fast relaxing metal like Fe of heme. Measured dipolar interactions indicate distance of about 10 Å between SQ and Heme.

This work is supported by NIH GM 061904.

EPR ORAL SESSION

Preethi R Vennam, The University of Alabama, department of Chemistry, Tuscaloosa Al 35487-0336.
Ph: 205-348-8457, E-mail: prvennam@crimson.ua.edu.

145 **Structural Investigation of Stratum Corneum Lipid Using Electron Paramagnetic Resonance.**

Kouichi Nakagawa, S. Hamakake, Department of Radiological Life Sciences, Graduate School of Health Sciences, Hirosaki University, 66-1 Hon-Cho, Hirosaki 036-8564, Japan

Electron paramagnetic resonance (EPR) in conjunction with a slow-tumbling simulation was utilized for defining stratum corneum (SC) lipid structure. We found that ordering calculated from the simulation is an appropriate index for evaluating SC lipids structure.[1, 2] The SC from two sites (mid-volar forearm and lower-leg) of human volunteers and cadaver was stripped consecutively from one to three times using a glass plate coated with a cyanoacrylate resin. Aliphatic spin probes, 5-doxylstearic acid (5-DSA) and 3β-doxyl-5α-cholestane (CHL), were used to monitor SC ordering. The SC samples were incubated in the probe aqueous solution at 37 °C for ~60 minutes. EPR spectrum of 5-DSA incorporated in the SC demonstrated a characteristic peak for the first strip. However, EPR spectra of CHL in the SC did not show a clear difference for each strip, except for the peak intensity. The results imply that CHL is not incorporated into the lipid phase as easily as is 5-DSA. A slow-tumbling simulation of the EPR spectrum was performed to analyze the lipid structure. The simulation results for 5-DSA show differences in values of the SC ordering. Thus, these results along with the simulation analysis provide detailed SC layer structure.[3]

Supported by a Grant-in-Aid for Scientific Research (C) (21500410) from JSPS (K.N.).

1. K. Nakagawa, et al., *Spectrochim. Acta Part A*, 63, 816 (2006).
2. K. Nakagawa and K. Anzai, *Lipids*, 45, 1081-1087 (2010).
3. K. Nakagawa, *Skin Res. Technol.*, 17, 245-250 (2011).

EPR ORAL SESSION

Kouichi NAKAGAWA, Department of Radiological Life Sciences, Graduate School of Health Sciences, Hirosaki University, 66-1 Hon-Cho, Hirosaki, 036-8564 JAPAN.
Ph. & Fax: 0172-39-5921, E-mail: nakagawa@cc.hirosaki-u.ac.jp

148 **Rapid Electron Spin Echo Imaging of Oxygen in Vivo.**

Boris Epel, Payam Seifi, Gage Redler and Howard J. Halpern, University of Chicago, Department of Radiation and Cellular Oncology, Chicago, IL 60637

Hypoxia (absence of oxygen) is a crucial determinant of the success of radiation treatment of solid tumors because it dramatically reduces the sensitivity of tumor cells to radiation. Hypoxia is commonly observed in solid tumors and determined as one of the major factors that promote the survival of malignant cells, as we have demonstrated. Recent studies have demonstrated that biological effect of hypoxia may be more pronounced in areas subjected to transient, varying hypoxia.

We have successfully applied Electron Spin Echo (ESE) to static imaging of pO_2, oxygen partial pressure in animals. Those studies demonstrated dramatic differences in the outcome of radiation treatment depending on the chronic hypoxic status of tumors. In the present work we apply ESE to the observation of time-dependent oxygen fluctuations. To accelerate image acquisition we use (i) partially deuterated OX063 spin probe with twice narrower EPR line width as compared to protonated OX063; and (ii) Principal Component analysis (PCA) filtration of projections prior to image reconstruction. This allowed us to decrease image acquisition to 75 s with no compromise in oxygen precision.

We present time-resolved oxygen images of mouse leg bourn tumors. In the first set of experiments the animal inhaled air and the fluctuations of pO_2 in tissues were observed. In the second set of experiments the breathing gas was switched multiple times between air and the gas mixture containing 95 % O_2 and 5% CO_2 with periods ranging from 6 to 30 minutes. These experiments demonstrated that ESE imaging can resolve time fluctuations of pO_2 in tissues. The analysis of tissue pO_2 response to change of pO_2 of the inhaled gas provides information on oxygen delivery.

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

EPR ORAL SESSION

Boris Epel, Center for EPR Imaging In Vivo Physiology, University of Chicago, Department of Radiation and Cellular Oncology, MC1105, 5841 S. Maryland Avenue, Chicago, IL 60637-1463 USA.
Ph: 773-702-2006, Fax: 773-702-5940, E-mail: bepel@uchicago.edu

149 **Tumor Oximetry and Radiation Sensitivity of Experimental Gliomas.**

Huagang Hou, Siriam. Mupparaju, Jean P. Lariviere, Harold M. Swartz, Nadeem. Khan. EPR Center for the Study of Viable Systems, Dartmouth Medical School, Hanover, NH 03755

Tumor hypoxia adversely affects the sensitivity of malignant cells to radiotherapy. Consequently, several methods to increase tumor pO_2 have been evaluated in an attempt to enhance the radiosensitivity for the treatment of gliomas. Recent clinical findings indicate that glioma pO_2 varies in patients with similar pathology and also among tumor types and grade. Therefore, it is vital to assess glioma pO_2, if therapeutic optimization has to be achieved. Unfortunately, therapeutic optimization has been restricted due to lack of appropriate methods that can provide repeated assessments of tumor pO_2 during therapies. We have focused on the development of in vivo Electronic Paramagnetic Resonance (EPR) oximetry using particulates for the repeated assessment of tumor pO_2.

The methodology for oximetry and the results of repeated pO_2 measurements of ectopic 9L and C6 tumors for five consecutive days are presented. We have investigated the effect of single dose irradiation with 4.8, 5.7, 7, and 9.3 Gy on 9L and C6 tumor pO_2. The changes in the tumor pO_2 were used to schedule the subsequent dose when an increase in pO_2 was observed after irradiation with 4.8 Gy and the results are compared with those irradiated with 2 Gy x 5. The tumor pO_2 and volumes were followed for 5 and 14 days respectively.

The 9L tumors had a baseline pO_2 of 8.0 ± 0.9 mmHg, while C6 tumors were relatively hypoxic, with a pO_2 of 5.5 ± 1.1 mmHg. The tumor pO_2 of C6 tumors significantly increased from day 2 to day 5 after single dose irradiations, however, no change in the pO_2 of 9L tumor was evident. The tumors treated with 4.8 Gy $Õ_2$ had a significant growth delay from day 5 to day 14 and day 3 to day 5, compared to the control and 2 Gy Õ5 treatment groups, respectively.

These results highlight the tumor specific effect on the tissue pO_2 and their response to hypofractionated radiotherapy. Furthermore, therapeutic outcome could be significantly improved if irradiations are scheduled at times of increase in tumor oxygenation. In vivo multi-site EPR oximetry could be a useful tool to monitor tumor oxygenation repeatedly to optimize fractionated radiotherapy. EPR oximetry technique is currently being used to assess tissue pO_2 of superficial tumors in patients undergoing chemoradiation.

This work was supported by National Cancer Institute (CA120919) and PPG (PO1EB2180).

EPR ORAL SESSION

Huagang Hou, EPR Center for the Study of Viable Systems, Dartmouth Medical School, Hanover, NH 03755.
Ph: 603-653-3591, Fax: 603-650-1717, E-mail: Huagang.Hou@Dartmouth.edu

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

150 **Digital EPR at Low Frequency.**

Mark Tseitlin, Sandra S. Eaton, and Gareth R. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, CO 80208; George A. Rinard, Richard W. Quine, School of Engineering and Computer Science, University of Denver, Denver, CO 80208.

Rapid increases in processing speed and memory of digital electronics as well as decreasing price/performance ratios provide exciting opportunities for EPR. A digital spectrometer could be less expensive, more robust, and more versatile. Suitable digital electronics are already available at the low frequencies required for in-vivo EPR. By using sub-sampling multiple harmonics of the field modulated CW signal can be obtained in one measurement.[1,2] Digital detection with time-locked subsampling in saturation recovery EPR enables ideal quadrature detection, and eliminates low-frequency distortions.[1] The present study demonstrates direct detection at the carrier frequency (250 MHz, 1 GHz) using sampling rates larger than the Nyquist frequency. For rapid scan EPR and pulse techniques, which involve real-time on-board averaging of short periodic EPR signals, the data size is small enough for fast transfer and processing. Excitation waveforms were produced by an arbitrary waveform generator (AWG) that is time-locked with the digitizer. This enables signal averaging and digital phase sensitive detection. Changing the excitation waveform in the AWG permits different kinds of experiments, such as FID, echo, rapid frequency sweep EPR, and magnetic field scan EPR without hardware changes. Those methods were tested on a variety of samples that are used for in-vivo EPR: LiPc, trityls, and nitroxyls. A major problem for digital detection using a reflection resonator is digitization of a small EPR signal in the presence of a large reflection signal. Separation of detection and excitation in a cross-loop resonator decreases this problem. The residual 'leakage' between excitation and detection resonators can be reduced using a directional coupler.

1. Hyde, J. S.; Camenisch, T. G.; Ratke, J. J.; Strangeway, R. A.; Froncisz, W. *Biol. Magn. Reson*. **2005**, *24*, 199-222.
2. Ahmad, R.; Som, S.; Kesselring, E.; Kuppusamy, P.; Zweier, J. L.; Potter, L. C. *J. Magn. Reson.* **2010**, *207*, 322-331.

EPR ORAL SESSION

Mark Tseitlin, Department of Chemistry and Biochemistry, University of Denver, 2101 E. Wesley Ave., Denver, CO 80208.
Ph: 303-871-2980, Fax: 303-871-2254, E-mail: Mark.Tseytlin@du.edu

151 **Multisite EPR Oximetry using Multiple Field Modulation Harmonics.**

Rizwan Ahmad, The Ohio State University, Davis Heart and Lung Research Institute, Columbus, OH 43210; Lee C. Potter, The Ohio State University, Department of Electrical and Computer Engineering, Columbus, OH 43210; Periannan Kuppusamy, The Ohio State University, Department of Internal Medicine, Columbus, OH 43210

A method is presented to use continuous wave electron paramagnetic resonance (EPR) imaging for rapid measurement of oxygen concentrations. A particulate EPR probe is employed to create a spatially sparse distribution of spins in a region of interest. A recently developed quadrature digital receiver is utilized to simultaneously collect multiple field modulation harmonics of EPR projection data. The presented data processing approach exploits parametric nature of the EPR lineshape, the spatial sparseness of the EPR probe, and collective information across multiple quadrature harmonics to estimate linewidths at multiple probe sites from a small number of projections. The proposed oximetry method is tested using simulation and has been experimentally demonstrated for a lithium octa-n-butoxy naphthalocyanine (LiNc-BuO) probe using an L-band digital receiver. We observed over an order of magnitude reduction in data acquisition time compared to spectral-spatial imaging using traditional tomographic reconstruction.

EPR ORAL SESSION

Periannan Kuppusamy, The Ohio State University, Davis Heart and Lung Research Institute, Columbus, OH 43210.
Ph: 614-292-8998, Fax: 614-292-8454, E-mail: kuppusamy.1@osu.edu

152 **Enhanced Dynamic Electron Paramagnetic Resonance Imaging of Cycling Hypoxia in Vivo Using Principal Component Analysis for Low-Order Approximation of Projections.**

Gage Redler, Boris Epel, and Howard J. Halpern, University of Chicago, Department of Radiation and Cellular Oncology, Chicago, IL 60637

Low concentration of oxygen (hypoxia) in tumors has been shown to strongly affect their malignant state. Hypoxia in regions of a tumor tends to promote mutagenesis, abnormal signaling and proliferation, increased metastasis, and resistance to radiation therapy. Recently, studies have shown that these effects may be enhanced in regions undergoing cycling hypoxia. Traditionally, electron paramagnetic resonance imaging (EPRI) has provided a non-invasive, quantitative imaging modality to investigate static pO_2 in vivo. However, in order to image cycling hypoxia in vivo, EPRI images with high temporal resolution (better than 1 minute) are required. There is a tradeoff between decreasing imaging time and the signal-to-noise ratio (SNR) of an EPRI image, thus the EPRI images with imaging time necessary to resolve relevant cycling hypoxia have rather low SNR. To allow for accelerated image acquisition with acceptable SNR, principal component analysis (PCA) is presented as a

method for filtering out noise in the projection data before reconstructing, while preserving the important information in a dynamic EPRI study. PCA produces an orthonormal expansion of the dynamic EPRI projection data through singular value decomposition of the covariance matrix. The data can be approximated by projecting it onto a subspace defined using only the first few eigenvectors or principal components. This low-order approximation reduces noise while retaining relevant information from the dynamic EPRI study investigating cycling hypoxia. Simulated and experimental results show that, in many cases, PCA filtering of EPRI projection data results in images with SNR increased by a factor of over 3.5. This can allow for dynamic EPRI studies with the necessary temporal resolution and SNR to investigate cycling hypoxia and its physiological implications more effectively.

EPR ORAL SESSION

Gage Redler, Center for EPR Imaging In Vivo Physiology, University of Chicago, Chicago, IL 60637-1463 USA.
Ph: 773-702-0006, Fax: 773-702-5940, E-mail: Gage@uchicago.edu

EPR SYMPOSIUM
Poster Sessions

155 **Distance Between Mo(V) and Fe(III) Heme Centers of Sulfite Oxidase Determined by Pulsed EPR.**

Andrei V. Astashkin, Asha Rjapakshe, Matthew Cornelison, John H. Enemark, Department of Chemistry & Biochemistry, University of Arizona, Tucson, AZ 85721; Kayunta Johnson-Winters, Department of Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, TX 76019

The sulfite oxidation taking place at the Mo active center of vertebrate sulfite oxidase (SO) depends on the electron transfers (ET) between the Mo and heme centers, and therefore knowledge of the distance between these centers, R_{MoFe}, is necessary for better understanding of the SO mechanism. The X-ray crystallographic distance R_{MoFe} = 32.3 Å appears to be in contradiction with the rapid ET rates of ~ 500 s^{-1} observed in liquid solution. The ET kinetics were rationalized by suggesting that dynamic motion of the interdomain loop joining the Mo and heme domains brings them closer together and allows for faster ET. However, no direct distance measurements for SO in solutions that would agree with or contradict this model exist so far. In this work, pulsed electron-electron double resonance (ELDOR) and relaxation induced dipolar modulation enhancement (RIDME) techniques were used to obtain the information about R_{MoFe} in the Mo(V)Fe(III) state of wild type (wt) human SO and in mutant human SO where three residues were deleted from the interdomain loop. In wt SO, the distance was found to be 32.5 Å, the same as in the X-ray structure, and the orientation of R_{MoFe} was fixed with respect to the heme g-frame. Surprisingly, in the loop-deletion mutant the distance was the same, although the R_{MoFe} orientation was statistically distributed in wide limits. The implications of these findings for the flexible loop model will be discussed.

EPR POSTER SESSION

Andrei Astashkin, University of Arizona, Department of Chemistry and Biochemistry, Tucson, AZ 85721.
Ph: 520-621-9968, E-mail: andrei@u.arizona.edu

156 **Relaxation Times of Isotopically-Substituted Nitroxide Radicals in Aqueous Solution.**

Joshua R. Biller,[1] Virginia Meyer,[1] Hanan Elajaili,[1] Sandra S. Eaton,[1] Gareth R. Eaton,[1] Gerald M. Rosen[2]
1 Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208
2 Department of Pharmaceutical Sciences, University of Maryland School of Pharmacy, Baltimore, MD 21201

T_2 by pulsed electron spin echo decay and T_1 by inversion recovery and saturation recovery have been measured for three nitroxide radicals at X-Band (ca. 9.4 GHz). Analysis of degassed 50 to 300 μM samples in aqueous solution indicate **(a)** the dominant contribution to T_1 are spin rotation and modulation of nitrogen hyperfine anisotropy **(b)** T_1 is the dominant contribution to T_2 for small radicals at room temperature **(c)** T_1 is dependent on mI **(d)** T_1 is longer for ^{15}N substituted than ^{14}N nitroxides and (e) both $T_1 \sim T_2$ and τc = 9-19 ps indicate that these nitroxides are near the rapid tumbling limit at X-band. Since the dominant anisotropic interaction is frequency-independent nuclear hyperfine, relaxation times at VHF (ca. 250 MHz) are predicted to be similar to those observed at X-band. Thus, studies at X-band for nitroxides in aqueous solution at room temperature are relevant for selection and design of nitroxide probes for low frequency in vivo experiments. Extension of these experiments to lower and higher frequencies will aid in understanding the relaxation mechanisms of these nitroxides in the fast tumbling regime.

EPR POSTER SESSION

Joshua R. Biller, Department of Chemistry and Biochemistry, University of Denver, 2101 E. Wesley Ave, Denver, CO 80208.
Ph: 303-871-2642, E-mail: jbiller77@gmail.com

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

157 **Site Directed Spin Labeling Studies of Radical Catalysis in Oligomeric B12-Dependent Ethanolamine Ammonia-Lyase.**
Adonis Bovell, Kurt Warncke, Emory University, Atlanta, GA 30322

The coenzyme B^{12}-dependent ethanolamine ammonia-lyase (EAL) from *Salmonella typhimurium* catalyzes the deamination of ethanolamine by using highly reactive radical species. Time-resolved, full-spectrum CW-EPR studies have determined the kinetics of selected steps in the reaction cycle of EAL.[1,2] We aim to probe the coupling of protein and solvent dynamics to the adiabatic reactions, by using the technique of site directed spin labeling (SDSL). Accessible native cysteine (C) residues in EAL were identified for mutation by using our *Salmonella* catalytic subunit (EutB) model[3] and the oligomeric ($EutB_6$ $EutC_6$; 16 total C per EutBEutC, αβ pair) structure from *Escherichia coli* (PDB: 3ABO). Five C-to-alanine (A) mutations generated EAL5C–, in which rapidly reacting, high mobility sites of 4-maleimido-TEMPO (4MT) and methanethiosulfonate spin label (MTSSL) reaction were eliminated while maintaining enzymatic activity. EAL5C– displayed identical k_{cat} and 3-fold larger K_M enzyme kinetic parameters, relative to wild type (WT). Single point mutations introduced targeted C labeling sites on the solvent-accessible surface of EutB (αD207C, αM434C, αN62C). Labeling of these sites with either 4MT or MTSSL gave heterogeneous, multi-component spectra. This suggests that the spin label adopts multiple conformations at these sites, or that there is background reactivity with native cysteines. Mass spectrometry (MALDI-MS) and EPR power saturation studies are underway to test the mobility models and to distinguish labeling sites. The results represent progress towards protein constructs for SDSL studies of reaction-dynamics coupling in EAL, and approaches to the challenges of selective C-labeling in a large, oligomeric, multi-C protein.

Supported by NIH DK54514.

1. Wang, M., Warncke, K. *J. Am. Chem. Soc.* **2008**, *130*, 4846.
2. Zhu, C., Warncke, K. *Biophys. J.* **2008**, *95*, 5890; *J. Am. Chem. Soc.* **2010**, 132, 9610.
3. Sun, L. et al., *Biochemistry* **2008**, *47*, 5523.

EPR POSTER SESSION
Adonis Bovell, Department of Physics, Emory University, 400 Dowman Drive, Atlanta, GA 30322.
Ph: 404-727-4274, E-mail: abovell@physics.emory.edu

158 **Identification of V_{si}- Centers in 4H SiC MOSFETs.**
C.J. Cochrane,[1] P.M. Lenahan,[1] A.J. Lelis[2]
1 The Pennsylvania State University, University Park, Pennsylvania 16802
2 US Army Research Lab, 2800 Powder Mill Road, Adelphi, Maryland 20783

There is great current interest in novel material systems for metal oxide semiconductor field effect transistors (MOSFETs). Arguably, the most promising new MOSFET material system is SiC/SiO_2. A major problem with SiC MOSFET technology is the existence of interface trap defects at the SiC/gate oxide interface. The large concentration of interface trap defects leads to shifts in threshold voltage and low channel mobility. We have utilized electrically detected magnetic resonance (EDMR) to identify one of the most important defects. We report on measurements utilizing a very sensitive electrically detected electron paramagnetic resonance (EPR) technique, spin dependent recombination (SDR), which allows us to detect point defects within fully processed 4H SiC MOSFETs. In our previous studies, we had tentatively linked the dominating defect to a negatively charged silicon vacancy. However, due to an inability to clearly resolve hyperfine interactions of the paramagnetic sites with nearly ^{13}C and ^{29}Si nuclei, we were not able to conclude with certainty that this defect structure was the dominating deep level. We have been able to overcome this problem to a considerable extent due to multiple improvements in hardware sensitivity and resolution as well as the exploitation of fast passage effect. We have identified hyperfine interactions with nearest neighbor ^{13}C nuclei. Our results are in close agreement with earlier studies of V_{Si-} reported in large volume samples in conventional EPR. Our suggests the presence of considerable disorder in the near SiC/SiO_2 interface region.

EPR POSTER SESSION
Corey Cochrane, The Pennsylvania State University, Department of Engineering Sciences and Mechanics, 212 EES Bldg., University Park, PA 16802. Ph: 814-863-4630, E-mail: cjc203@psu.edu

159 **Spin Trapping of Radicals in Irradiated TiO_2 Nanoparticles.**
Alex Cruce, Jon Brauer, Greg Szulczewski, Michael K. Bowman, Department of Chemistry, The University of Alabama, Box 870336, 35487-0336, Tuscaloosa, Alabama, USA

Titanium dioxide has many properties that are of interest to areas such as solar energy conversion and photocatalysis. Pure TiO_2 absorbs UV shorter than about 390 nm. Doping TiO_2 with nitrogen and fluorine creates new TiO_2 materials that absorb light in the visible range. The photocatalytic activity of N/F TiO_2 materials was measured by the photodegradation of

methylene blue. The chemical mechanism of the degradation of methylene blue is unclear. Free radicals formed by irradiation are one proposed mechanism. We have used EPR spin trapping with *t*-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) to study the formation of radicals at the surface of pure and nitrogen doped TiO_2 nanoparticles at neutral pH. Hydroxyl, superoxide, and a carbon centered radical were detected. The deoxygenation of the solution dramatically decreased the amount of superoxide adduct. Hydroxyl radicals readily react with methylene blue, and we have detected their products by mass spectrometry.

Thanks to G. M. Rosen for the BMPO

EPR POSTER SESSION

Alex Cruce, The University Alabama, Department of Chemistry, Box 870336, 35487-0336, Tuscaloosa, Alabama, USA.
Ph: 205-348-8457, E-mail: aacruce@crimson.ua.edu

160 **A Simple Method to Extract Hyperfine Signs From Random-Hopped Davies ENDOR Data.**

Peter Doan, Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, IL, 60208-3113

One of the most exciting recent developments in Pulsed ENDOR has been the ability to assign the absolute signs of hyperfine interactions (HFI) in systems studied at higher magnetic field and low temperatures.[1] We developed a multi-sequence technique, Pulsed-ENDOR SaTuration and REcovery (PESTRE),[2] that can be used to assign HFI signs by observing the effects of a series of Davies ENDOR pulse sequences on the spin system. The PESTRE technique relies on shifts in the apparent baseline of the ENDOR measurements that are attributable to polarization differences created by resonant NMR transitions. We now demonstrate that by maintaining the entire data set generated in a standard, random-hopped Davies ENDOR experiment, this data set can be reprocessed to extract a spectrum of baseline shifts. These baseline shifts can be interpreted identically to those seen in PESTRE experiments. This new technique is called Raw-Data PESTRE or RD-PESTRE. We have applied the RD-PESTRE technique in unraveling the overlapping patterns of the 57Fe ENDOR from an important reaction intermediate in the 7-iron FeMo-cofactor of nitrogenase.3 This work is supported by NIH HL-13531 (Brian Hoffman, Northwestern University).

1. Epel et al., *J. Magn. Reson.*, **2001**, 148, 388.
2. Doan, J*J. Magn. Reson.*. **2011**, 208, 76.
3. Doan et al. *J. Am. Chem. Soc.* submitted.

EPR POSTER SESSION

Peter Doan, Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, IL 60208-3113.
Ph: 847-491-4488, Fax: 847-491-7713, E-mail: ped131@northwestern.edu

161 **Lipid Membrane-Associated Alpha Synuclein Copper Binding Characterization.**

Chris Dudzik, University of California Santa Cruz, Department of Chemistry and Biochemistry, Santa Cruz, California, 95064; G.L. Millhauser, University of California Santa Cruz, Department of Chemistry and Biochemistry, Santa Cruz, California, 95064

Alpha Synuclein (AS) is a 140 residue, intrinsically disordered protein that is often discussed in the context of its role in neurological diseases such as Parkinson's and Alzheimer's disease. However, its true function and/or role in disease pathology remains the subject of much debate. Sequence analysis of AS shows a series of 11-mer imperfect repeats from residues 10-90 that have been demonstrated to form an alpha-helix in the presence of lipid vesicles, similar to apolipoproteins. Indeed, further evidence has shown that AS associates with synaptic vesicles and plays a role in modulating vesicular trafficking to and fusion with the synaptic cleft membrane and protection of the vesicles from oxidative stress. Several studies have indicated that there is an abundance of stress on synaptic vesicles from Reactive Oxidative Species (ROS) and Cu(II) ions, particularly in the substantia nigra, which is strongly effected by Parkinson's disease. Indeed Cu(II) levels have been shown to be higher there than in other parts of the brain. Furthermore, Cu(II) has shown to decrease lag time in AS fibril formation and there have been numerous studies demonstrating the peptides affinity for Cu(II) ions. Perhaps then AS serves as a first line of defense against the ingress and damage of Cu(II) ions in the cell by sequestering these ions for later disposal. Elucidation of the mode(s) of AS-Cu(II) binding in the presence of lipid bilayers and/or their role in facilitation of fibril formation can therefore lead to further understanding of the natural function of AS.

This work was generously funded by NIH grant GM65790.

EPR POSTER SESSION

Chris Dudzik, University of California Santa Cruz, Department of Chemistry and Biochemistry, Santa Cruz, California, 95064
Ph: 831-459-3390, Fax: 831-459-2935, E-mail: cdudzik@chemistry.ucsc.edu

162 **Parameter Sensitivity of Multicomponent Magnetic Resonance Spectra.**

Keith A. Earle, University at Albany (SUNY), Physics Department, 1400 Washington Ave., Albany, NY 12222;
David J. Schneider, USDA Agricultural Research Service, Cornell University, Ithaca, NY 14853

Multicomponent spectra often arise in the study of complex systems. Entropic methods offer an unbiased way to reliably determine model parameters and their uncertainties. These methods are particularly useful for determining the relative amounts of the components comprising the mixture. We note that these techniques are applicable to NMR and ESR, and indeed are generic. A particular advantage of the methods described here is that noise is treated in a consistent way,[1] and represents an advance over previous methods, which did not take noise into account quantitatively.[2] In order to demonstrate the methods we have developed, we give examples of multicomponent spectra arising from mixtures of ^{14}N and ^{15}N spin labels, as well as NMR multicomponent multiplet structure.

Supported by a Faculty Research Award Program grant from the University at Albany. The computational resources of ACERT are also acknowledged.

1. Earle, et al., *Appl. Magn. Reson.*, **2010**, 37, 865.

2. Earle and Schneider, AIP Conference Proc., **2011**, 1305, 357.

EPR POSTER SESSION

EPR Symposia Poster Session Keith A. Earle, University at Albany (SUNY), Physics Department, 1400 Washington, Av., Albany, NY 12222.
Ph:: 518 442-4521, E-mail: kearle@albany.edu

163 **Probing Interdomain Structure in the Prion Protein by Pulsed Dipolar Spectroscopy.**

Eric G. Evans and Glenn L. Millhauser, University of California Santa Cruz, 1156 High Street, Santa Cruz, CA 95064

The prion protein (PrP) is a membrane-anchored glycoprotein present in the central nervous system of all avian and mammalian species. The conversion of the normal cellular isoform, termed PrP^{C}, into a misfolded and infectious form, PrP^{Sc}, is implicated in the rare but fatal class of diseases known as the transmissible spongiform encephalopathies (TSEs). Despite high conservation of PrP, the precise function of the protein in vivo is largely unknown. PrP binds Cu^{2+} in a multi-component fashion through its unstructured N-terminal domain, an action that is essential for PrP endocytosis and neuronal protection. Recent evidence in our lab suggest that this N-terminal domain interacts with the structured C-terminal domain in a metal ion dependent fashion. To further investigate this interaction, site-directed spin labeling (SDSL) and double electron-electron resonance (DEER) EPR spectroscopy were employed to probe inter-domain distances in response to metal ion binding. Doubly labeled PrP constructs were generated by site-specific genetic incorporation of the unnatural amino acid p-acetyl phenylalanine (pAcF). Unlike traditional cysteine-based SDSL, substitution of pAcF into the PrP sequence does not interfere with native disulfide bond formation during oxidative refolding. pAcF PrP mutants were then reacted with a nitroxide radical bearing an alkoxyamine functional group to generate ketoxime-linked spin labeled protein. Inter-domain double mutant constructs were analyzed by DEER and distance distributions were obtained by Tikhonov regularization. The data confirm an inter-domain interaction in PrP, in which the N-terminal domain becomes ordered relative to the C-terminal domain upon metal ion binding, with some inter-nitroxide distances of less than 30Å measured. Inter-domain distance constraints such as these will enable a more complete characterization of this interaction and may ultimately provide insight into the role of metal binding in prion function and disease.

EPR POSTER SESSION

Eric Evans, Millhauser Research Group, University of California, 1156 High Street, Santa Cruz 95064.
Ph: 831-459-3390, E-mail: evans@chemistry.ucsc.edu

164 **Deprotonation of Open Chain Carotenoid Radical Cations: Mims ENDOR and DFT Studies.**

A. Ligia Focsan, Preethi R. Vennam, Alex Cruce, Michael K. Bowman and Lowell D. Kispert, The University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487-0336

In the light harvesting center II (LHCII) of plant's photosynthetic membrane, carotenoid radical cations serve to dissipate the excess energy by formation of a charge transfer complex of carotenoid with chlorophyll, which then undergoes charge separation. During this process, deprotonation of the generated radical cations would lead to formation of neutral radicals that could be very effective quenchers of the chlorophyll's excess energy. Previous Mims ENDOR studies on carotenoids adsorbed on artificial matrices in combination with DFT studies have shown that carotenoid radical cations containing terminal rings deprotonate at the methylene and methyl groups of the terminal rings, while the presence of functional groups like epoxy,

carbonyl and allene on the terminal rings prevents this loss. Furthermore, the occurrence or prevention of proton loss at the terminal rings is in accordance with the quenching or non-quenching abilities of the carotenoids present in LHCII suggesting that it might be important that proton loss occurs at the terminal rings rather than at positions situated on the conjugated polyene chain. To examine this dependence we focused our attention on open chain carotenoids (n=9-15 conjugation length) present in photosynthetic bacteria and we found that the addition of protons and functional groups like methoxy or carbonyl to a fully-conjugated polyene chain causes a preferential proton loss from a methylene group of the radical cation that extends the conjugation. After deprotonation, a change in the unpaired electron spin distribution produces larger hyperfine coupling constants for the neutral radicals than for the radical cations as determined by DFT. This permits identification of these radicals in a mixture adsorbed on an artificial matrix and analyzed by using Mims ENDOR techniques.

This work was supported in part by the U.S. DOE grant DEFG02-86ER-13465 (LDK), by the NSF for EPR instrument grants CHE-0342921 and CHE-0079498 and by the NIH grant GM61904 (MKB).

EPR POSTER SESSION

A. Ligia Focsan, The University of Alabama, Department of Chemistry, 250 Hackberry Lane, Tuscaloosa, AL 35487-0336, USA.
Ph: 205-348-8457, E-mail: focsa001@crimson.ua.edu

165 **Effect of Glucose on EPR of Spin Label in Blood From Healthy and Diabetic.**

Asako Kawamori, and Wataru Hattori, AGAPE-Kabutoyama Institute of Medicine, Nishinomiya, 662-0001, Japan

EPR signal of spin label in blood was investigated at X-band. The rate of decay of TEMPO for diabetic was faster than for healthy oneÅ@below the glucose quantity 150 mg/dL. The rate is lower for the glucose quantity higher than 150 mg/dL. We will report about the effect of added glucose on the rate of reduction of these spin labels in healthy and diabetic. To compare the result from the blood of human in vitro, the same experiment was repeated for the blood in tails of mice in vivo. A handy EPR for measurement of blood sugar of human will be planned based on these data. We will report the result for model system consisting of ascorbate and variable quantity of glucose in the buffer for blood with two concentrations of TEMPO (0.1mM and 2 mM). The decrease in the rate of reduction of TEMPO was found in glucose addition.

EPR POSTER SESSION

Asako Kawamori, AGAPE-Kabutoyama Institute of Medicine, Kabutoyama-cho 53-4, Nishinomiya 662-0001 Japan.
Ph. & Fax: 81-798-61-8402, E-mail: agape-kawa@nifty.com

166 **Physical Properties of Membrane Models of the Eye-Lens Fiber-Cell Plasma Membrane for Animals of Different Life Spans: Saturation-recovery EPR Spin-Labeling Studies.**

Alexey A. Konovalov, Ivana Krpan, Marija Raguz, Witold K. Subczynski, Medical College of Wisconsin, Department of Biophysics, 8701 Watertown Plank Road, Milwaukee WI, 53226

Model-membrane systems of the eye lens were investigated in the following three animal groups: mice, pigs, and humans, which have life spans of 3, 25, and 70 years, respectively. Phospholipid compositions of the model membranes resembled those of intact membranes, while cholesterol contents varied. Three cholesterol contents were chosen: membranes without cholesterol, membranes saturated with cholesterol (the condition in membranes of the eye cortex), and membranes oversaturated with cholesterol (the condition in the eye nucleus, where an excess of cholesterol forms pure immiscible cholesterol bilayer domains [CBDs]). Profiles of membrane properties across the phospholipid-bilayer portion of the model membrane were obtained using phospholipid-analogue spin-labels. CBDs were discriminated and characterized using cholesterol-analogue spin-labels and the discrimination by oxygen transport (DOT) method, which is based on the saturation-recovery EPR technique. Profiles of the oxygen transport parameter (oxygen diffusion-concentration product) for membranes saturated with cholesterol and membranes oversaturated with cholesterol were different from those of membranes without cholesterol in all membrane models. Cholesterol significantly decreased oxygen permeation from the membrane surface to the depth of the ninth carbon (the depth to which the rigid ring-structure of cholesterol is immersed), but did not affect oxygen transport in the membrane center. Oxygen transport within the CBD was strongly restricted. Conclusions: (1) A saturating amount of cholesterol is responsible for the unique properties of lens lipid membranes; (2) these properties are independent of phospholipid composition; and (3) the CBD ensures that the membrane is saturated with cholesterol.

This research is supported by grants EY015526, EB002052, and EB001980 from the National Institutes of Health.

EPR POSTER SESSION

Alexey A. Konovalov, Medical College of Wisconsin, Department of Biophysics, 8701 Watertown Plank Road, Milwaukee, WI, 53226, USA.
Ph: 414-456-4933, E-mail: akonovalov@mcw.edu

DOI: https://doi.org/10.56902/RMCMR.2011.53.1

167 **The EPR Characterization of the Oxygen Induced Radical Intermediates in Neuronal Nitric Oxide Synthase.**

Matthew D. Krzyaniak,[1] Vladimir Berk,[1,2] Ah-Lim Tsai,[2] Michael K. Bowman,[1]
1 The University of Alabama, Chemistry Department, Tuscaloosa, Alabama 35487-0336
2 University of Texas Health Science Center, Hematology Division, Department of Internal Medicine, Houston, Texas 77030

Nitric oxide(NO) is an important molecule in a number of physiological and pathophysiological processes. The biosynthesis of NO is catalyzed by three different nitric oxide synthase(NOS) isozymes: neuronal NOS(nNOS), endothelial NOS(eNOS) and inductible NOS(iNOS).[1] These isoforms of NOS share 50-60% sequence identity and have both a heme containing oxygenase domain and a flavin containing reductase domain.[2] Through a pair of coupled monooxygenase reactions NO and L-citrulline are formed from L-arginine. In addition to the substrate L-arg, NOS requires molecular oxygen, NADPH and a tetrahydrobiopterin(BH_4) cofactor in the oxygenase domain. Missing one of these elements(uncoupled conditions) could lead to the formation of superoxide, hydrogen peroxide or peroxynitrite.[3] In order to study the mechanism of NOS under uncoupled conditions rapid freeze quench was used to trap the oxygen induced paramagnetic intermediates formed in nNOS. These intermediates were studied utilizing echo detected field swept EPR, ENDOR and ESEEM spectroscopy. The individual components of the EPR spectrum were seperated based on their different T1 relaxation rates using a principal component analysis.

Supported by NIH.

1. Griffith, O. W.; Stuehr, D. *J., Annu Rev Physiol* **1995**, *57*, 707-736.
2. Alderton, W. K.; Cooper, C. E.; Knowles, R. G., *Biochem J* **2001**, *357*, 593-615.
3. Berka, V.; Wang, L. H.; Tsai, A. L., *Biochemistry-Us* **2008**, 47 (1), 405-420.

EPR POSTER SESSION

Matthew D Krzyaniak, The University of Alabama, Chemistry Department, Tuscaloosa, Alabama 35487-0336.
Ph: 205-348-8457, E-mail: mdkrzyaniak@bama.ua.edu

168 **ENDOR of Axial Centers of Nd^{3+} and Yb^{3+} in Lithium Niobate.**

Galina Malovichko, Valentin Grachev, Mark Munro, Physics Department, Montana State University, Bozeman, MT 59717; Edward Kokanyan, Institute of Physical Researches, Ashtarak, Armenia; Viktor Bratus, Sergey Okulov, Institute of Semiconductor Physics, Kiev, Ukraine.

Lithium Niobate (LN) doped with 4f-ions is of great interest for both fundamental science and applications including high efficiency lasers with frequency conversion, elements of all-optical telecommunication network and quantum cryptography. According to the Rutherford back scattering data, all trivalent ions substitute for Li and should create similar centers. Our EPR study has shown that 4f-ions create unexpected variety of completely different non-equivalent centers in both stoichiometric and lithium deficient congruent crystals. Four Nd^{3+}, two Er^{3+}, and nine Yb^{3+} centers were found and described. In order to clarify positions of rare-earth ions and compensation mechanism for their excess charges we carried out detailed study of ENDOR spectra of axial centers of Nd^{3+} and Yb^{3+}. We found that there are no other defects in the nearest surrounding of Nd^{3+} and Yb^{3+}. However, there is strong hyperfine interaction of Yb^{3+} electrons with Nb nucleus on the center axis, whereas dipole-dipole interactions with non-axial nuclei are dominant for Nd^{3+}. Different models, which can explain the obtained optical, EPR and ENDOR data, are discussed.

Supported by NSF 0805175.

EPR POSTER SESSION

Galina Malovichko, Montana State University, EPS 264, Physics Department, Bozeman, Montana 59717.
Ph: 406-994-3474, Fax: 406-994-4452, E-mail: malovichko@physics.montana.edu

169 **Investigations Into Cu^{2+}-Cu^{+} Redox Cycling in PrP Using CW X-band EPR.**

Alex J. McDonald, University of California Santa Cruz, Department of Chemistry, Santa Cruz, CA 95064; Glenn Millhauser, University of California Santa Cruz, Department of Chemistry, Santa Cruz, CA 95064

While the prion protein (PrP) is known to misfold and form neurotoxic amyloid plaques in the brains of mammals, its physiological role is not well understood. Cu^{2+} has been shown to coordinate to the largely unstructured n-terminus of PrP suggesting PrP is involved with copper homeostasis, signaling, or redox at neuronal synapses. Recent work has shown the n-terminus of PrP is capable of Cu^{2+}-Cu^{+} redox cycling. X-band EPR spectroscopy was used to investigate Cu^{2+}-Cu^{+} redox in peptides containing the n-terminal copper binding region of PrP, as well as full length recombinant PrP. Additionally, to confirm the generation the radical byproducts of copper redox cycling, X-band EPR spectroscopy with the nitrone spin trap

alpha-(4-pyridyl-1-oxide)-N-tert-butylnitrone (4-POBN) was performed.

EPR POSTER SESSION

Alex McDonald, University of California Santa Cruz, Department of Chemistry, Santa Cruz, CA 95064.
Ph: 609-933-6602, E-mail: alex.j.mcdonald@gmail.com

170 Hyperbolic-Cosine Waveguide Tapers and Oversize Rectangular Waveguide for Reduced Broadband Insertion Loss in W-Band EPR Spectroscopy.

Richard R. Mett,[1,2] Jason W. Sidabras,[1] and James S. Hyde[1]
1 Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI 53226-0509
2 Milwaukee School of Engineering, Department of Physics and Chemistry, Milwaukee, WI 53202-3109

The return loss of a 1 m length of waveguide was reduced by nearly 5 dB over a 4% bandwidth at W-band (94 GHz) for an electron paramagnetic resonance (EPR) spectrometer relative to WR10 waveguide. The waveguide has an oversize section of commercially available rectangular WR28 and a novel pair of tapers that vary in cross section with axial position according to a hyperbolic-cosine (HC) function. The tapers connect conventional rectangular WR10 waveguide to the WR28. For minimum loss, the main mode electric field is parallel to the long side of the WR28. Using mode coupling theory, the position of maximum flare (inflection point) in the taper was optimized with respect to the coupling to higher order modes and the reflection of the main mode. The optimum inflection point position is about one-tenth of the taper length from the small end of the taper. Reflection and coupling were reduced by about 20 dB relative to a linear taper of the same length. Comb-like dips in the transmission coefficient produced by resonances of the higher order modes in the oversize section were about 0.03 dB. Specially designed high-precision adjustable WR28 flanges with alignment to about 5 μm were required to keep higher order mode amplitudes arising from the flanges comparable to those from the HC tapers. A paper provides a foundation for further optimization if needed. Methods are not specific to EPR or the microwave frequency band. The observed degree of flat broadband performance is significantly better than the alternatives of circular and corrugated waveguide and is important for many types of EPR experiments including frequency swept EPR.[1]

The work is the subject of a forthcoming paper in Review of Scientific Instruments.

1. J. S. Hyde, R. A. Strangeway, T. G. Camenisch, J. J. Ratke, W. Froncisz, W-band frequency-swept EPR. *J. Magn. Reson.* 205, 93 (2010).

EPR POSTER SESSION

Richard R. Mett, Medical College of Wisconsin, Department of Biophysics, 8701 Watertown Plank Road, P.O. Box 26509, Milwaukee, WI 53226-0509.
Ph: 414-456-4024 or 414-277-7313, Fax: 414-456-6512, E-mail: rmett@mcw.edu

171 Resonator for Optimization of Liquid-Phase EPR Concentration-Sensitivity for Spin Labels at Q-Band: Practical Considerations.

Richard R. Mett,[1,2] James R. Anderson,[1] Jason W. Sidabras,[1] Timothy S. Thelaner,[1] James S. Hyde[1]
1 Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI 53226-0509
2. Milwaukee School of Engineering, Department of Physics and Chemistry, Milwaukee, WI 53202-3109

Progress on the fabrication of a previously reported resonator1 that optimizes liquid-phase concentration sensitivity at Q-band (35 GHz) is presented. The resonator has a coaxial TM_{020} mode, which is uniform in all but the radial direction. For maximum EPR signal, the DC magnetic field must be parallel to the resonator axis. The 50 ml sample volume in the form of a thin (0.09 mm) cylindrical shell of an 8 mm radius is predicted to give a saturable EPR signal 21 times the standard 0.5 ml sample in the cylindrical TE_{011}. With an aqueous sample, the device is predicted to have a loaded Q-value of about 1500 and a resonator efficiency parameter of 0.72 $G/W^{1/2}$. Sample access on one end of the cavity is provided by a circular cut on an rf current null. Design criteria and results of simulations are presented. Changes to the original design have been made as sample handling and resonator construction methodologies have developed. Fabrication of the resonator in two parts and the Rexolite sample holder, also in two parts, is underway. Measurements will be compared to predicted results.

1. R. R. Mett, J. R. Anderson, J. W. Sidabras, J. S. Hyde, *Resonator for Optimization of Liquid-Phase EPR Concentration-Sensitivity for Spin Labels at Q-band*, EPR symposium poster given at the 52nd Rocky Mountain Conference on Analytical Chemistry, Snowmass, CO, August 3, 2010.

EPR POSTER SESSION

Richard R. Mett, Medical College of Wisconsin, Department of Biophysics, 8701 Watertown Plank Road, P.O. Box 26509, Milwaukee, WI 53226-0509.
Ph: 414-456-4024 or 414-277-7313, Fax: 414-456-6512, E-mail: rmett@mcw.edu

172 **Characterization of the Relaxation Processes of DPPH.**

Virginia Meyer, Sandra S. Eaton, Gareth R. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, CO 80208

Optimization of the electron spin relaxation properties of organic radicals supports numerous chemical and analytical applications. DPPH (1:1 α,α-diphenyl-β-picryl-hydrazyl) is a solid stable radical that is used in EPR as a standard for g-factor determination[1] and for spectrometer performance assessment.[2] In solution it is used to assess radical scavenging activity[3] and dynamic nuclear polarization experiments in NMR.[4] The processes that contribute to the relaxation of DPPH and other organic radicals in solid matrix can vary depending on a number of factors, including concentration and frequency. The T^2 and T^1 relaxation times for DPPH in polystyrene were analyzed using pulsed EPR techniques in the temperature range 20-295K. The concentration dependence of the T_1 relaxation of DPPH doped in polystyrene was examined at X- and Q-band. Previously, a linear dependence of $\log(T_1)$ on temperature was reported;[5] however, our work has shown deviation from linearity. As suggested,[6,7] DPPH relaxation in polystyrene appears to be concentration dependent.

2. Jang, Z.H.; Suh, B.J.; Corti, M.; Cattaneo, L.; Hajny, D.; Borsa, F.; Luban, M. *Rev. Sci. Instrum.* **2008**, *79*, 046101-1-3.
3. Smolyaninov, I.V.; Antonova, N.A.; Poddel'sky, A.I.; Smolyaninova, S.A.; Osipova, V.P.; Berberova, N.T. J. *Organomet. Chem.* **2011**, *696*, 2611-2620.
4. Schacher, G.E. *Phys. Rev.* **1964**, *135*, A185-A190.
5. Turkevich, J.; Soria, J.; Che, M. *J. Chem. Phys.* **1972**, *56*, 1463-1466.
6. Höcherl, G.; Wolf, H.C. *Z. Phys.* **1965**, *183*, 341-351.
7. Yoshida, H.; Hayashi, K.; Okamura, S. *Ark. Kemi.* **1964**, *23*, 177-189.

EPR POSTER SESSION

Virginia Meyer, University of Denver, Department of Chemistry and Biochemistry, 2101 E. Wesley Ave, Denver, CO 80208.
Ph: 303-871-2642, E-mail: Virginia.Meyer@du.edu

173 **Nonselective Excitation of Pulsed ELDOR Using Multi-Frequency Microwaves.**

Hiroyuki Mino,[1] Yuki Asada,[1] Risa Mutoha,[2] M. Ishiura,[1,2]
1 Graduate School of Science, Nagoya University, Furo, Chikusa, Nagoya, 464-8602, Japan
2 Center for Gene Research, Nagoya University, Furo, Chikusa, Nagoya, 464-8602, Japan

Multiple microwave frequencies in the region of 8.5 -10.5 GHz were applied to spin excitation for pulsed electron paramagnetic resonance (EPR). Five different microwave frequencies were fed to the pulse-forming unit in the EPR microwave bridge and used for spin excitation for multiple spin packets. The efficiency of the spin excitation was evaluated by PELDOR measurements of the interaction between tyrosine radical and the manganese cluster in the plant photosystem II. The signal-to-noise (S/N) ratio of the PELDOR spectrum irradiated by five different microwave frequencies was 2.0 times larger than the S/N from a single microwave frequency. By using multiple microwave frequencies, the PELDOR spectrum in site-directed spin-labeled KaiB protein complexes was examined. The use of mixed microwave frequencies irradiates the different spin packets in the wide EPR spectrum efficiently, thereby improving the S/N ratio of the PELDOR signal in the broad EPR spectrum.

EPR POSTER SESSION

Hiroyuki Mino, Graduate School of Science, Nagoya University, Furo, Chikusa, Nagoya, 464-8602, Japan.
Ph: +81-52-789-2882, Fax: +81-52-789-2882, E-mail: mino@bio.phys.nagoya-u.ac.jp

174 **X-Band Rapid-Scan EPR.**

Deborah G. Mitchell, Mark Tseytlin, Richard W. Quine, Virginia Meyer, Gareth R. Eaton, and Sandra S. Eaton, Department of Chemistry and Biochemistry, University of Denver

Rapid-scan EPR at X-Band (9.8 GHz) was investigated. The term "rapid" means that the magnetic field is scanned through resonance in a time that is short relative to relaxation times, which causes oscillations in the signal response.[1] Deconvolution of the rapid-scan signals results in the conventional slow scan absorption and dispersion signals.[2]

The goal of this project is to develop X-band rapid-scan EPR methods to monitor transient species, such as spin trapped radicals and fast biological reactions such as redox reactions, membrane insertion, and protein folding. Currently, we have investigated several samples—Lithium phthalocyanine (LiPc), irradiated fused quartz,[3] nitroxyl radicals, and α,γ-bisdiphenylene-β-phenylallyl (BDPA)[4]—to better understand the advantages and limitations of this technique. We have also begun using rapid-scan EPR to measure the spectra of spin-trapped superoxide.

LiPc was studied because of its simple Lorentzian line. Simulations of rapid-scan spectra of LiPc were used to determine the

T_2 relaxation time. Irradiated fused quartz is a sample with long spin-lattice relaxation, which is easily saturated with CW EPR. Because rapid-scan EPR can be run at higher powers without saturation, undistorted rapid-scan spectra of fused quartz were collected and deconvolved to obtain the conventional CW spectrum.[3] Rapid scans of nitroxyl radicals demonstrated that as the scan rate increased, the linear power range increased.

1. Joshi, J. P.; Eaton, G. R.; Eaton, S. S., *Appl Magn Reson* **2005**, *28*, 239-249.
2. Tseitlin, M.; Rinard, G.A.; Quine, R.W.; Eaton, S. S.; Eaton, G.R., *J. Magn Reson* **2011**, *208*, 279–283.
3. Mitchell, D. G.; Quine, R. W.; Tseitlin, M.; Meyer, V.; Eaton, S. S.; Eaton, G. R., accepted for publication in Radiation Measurements.
4. Mitchell, D.G.; Quine, R. W.; Tseitlin, M.; Meyer, V.; Avery, A. Eaton, S. S.; Eaton, G. R., *J Phys Chem B.* DOI : 10.1021.

EPR POSTER SESSION

Deborah G. Mitchell, Dept. of Chemistry and Biochemistry, University of Denver, 2101 E. Wesley Ave, Denver, CO 80208. Ph: 303-871-2642, E-mail: Debbie.Mitchell@du.edu

175 **Irradiated Quartz Standard Samples for Pulsed EPR.**

Deborah G. Mitchell, Richard W. Quine, Sandra S. Eaton, and Gareth R. Eaton, University of Denver, Denver, CO, USA 80208; Peter Höfer, Bruker BioSpin, Karlsruhe, Germany, and Ralph T. Weber, Bruker BioSpin, Billerica, MA, USA 01821

For continuous wave (CW) EPR, the weak pitch sample has long been the standard for spectrometer quality assurance.[1] Early in the development of pulsed EPR, an irradiated (24 MRad, 240 kGy) fused quartz sample was proposed as a standard.[2] Improvements in spectrometer sensitivity, and the continued use of 8-bit digitizers necessitate a replacement standard with a weaker signal to be able to define signal amplitude and noise for a single echo. One such sample[3] is a 2 mm diameter, 10 mm long fused quartz rod irradiated to 1 kGy. This small sample has utility for a variety of measurements. For resonators that use standard 4 mm o.d. sample tubes (at X-band or lower frequency), a long 4 mm o.d. rod of irradiated (261 Gy) fused quartz can be positioned reproducibly more easily than the small cylinder. With the increasing importance of Q-band pulsed EPR, a standard for Q-band is also needed. A 1.6 mm o.d. rod irradiated to 261 Gy was produced for this purpose. The pair of samples permits comparison of X-band and Q-band pulsed EPR performance, as well as interlaboratory comparisons. The 1.6 mm o.d. and 4 mm o.d. 261 Gy fused quartz rods will be commercially available from Wilmad.

1. Quality Assurance in EPR, S. S. Eaton and G. R. Eaton, *Bull. Magn. Reson.* **13**, 83-89 (1992).
2. Irradiated Fused Quartz Standard Sample for Time Domain EPR, S. S. Eaton and G. R. Eaton, *J. Magn. Reson.* **A102**, 354-356 (1993).
3. A Signal-to-Noise Standard for Pulsed EPR, G. R. Eaton, S. S. Eaton, R. W. Quine, D. Mitchell, V. Kathirvelu, and R. T. Weber, *J. Magn. Reson.* **205**, 109-113 (2010). PMC 2885565

EPR POSTER SESSION

Deborah G. Mitchell, University of Denver, Denver, CO, USA 80208

176 **Next Generation Software Solutions for EPR Spectroscopists.**

Reef Morse, Scientific Software Services, Northville, MI 48167; Boris Epel, University of Chicago, Department of Radiation and Cellular Oncology, Chicago, IL 60637

Data acquisition and manipulation software has become an indispensable part of EPR spectroscopy. Many laboratories invest considerable time and resources in development of custom software with unique features not available in hardware-software complexes provided by large vendors. Often, however, the people involved with the software development move on leaving the software as an "orphan" with little or no support. An alternative option is to purchase software packages developed by reputable suppliers who can offer a continuous support for their product. These software packages can solve both immediate and long-term laboratory needs, extending lifetime of older spectrometers and ensuring smooth transition between generations of home-built spectrometers.

Scientific Software Services is one such company and its product lines, developed over more than 20 years, offer flexible solutions for spectroscopists at affordable prices. EWWIN offers data acquisition for multiple CW spectrometers and advanced data manipulation features. SpecMan4EPR is a sophisticated and flexible front end for pulse spectrocopy.

EWWIN and SpecMan4EPR have undergone significant changes in the last several years. For example, EWWIN now allows communication with an external data acquisition computer through a USB transfer cable which eliminates the difficulties of TCPIP/IP communications in restricted environments such as medical and, increasingly, academic locales. EWWIN also now includes lineshape analysis algorithms derived from EWVOIGT but with greatly improved FFT and Marquart-Levenberg minimization routines. Both software packages run on Windows 7 and have improved user interfaces. Further

details including images of the graphical user interfaces and the opportunity to actually use the software will be available at the conference.

EPR POSTER SESSION

Reef Morse, Scientific Software Services, Northville, MI 48167.
E-mail: reefmorse@scientific-software.com

177 **Structural Change of Circadian Clock Protein KaiB.**

Risa Mutoh, Nagoya University, Center for Gene Research, Nagoya, Aichi 464-8602; Hiroyuki Mino, Nagoya University, Graduate School of Science, Nagoya, Aichi 464-8602; Yuki Asada, Nagoya University, Graduate School of Science, Nagoya Aichi 464-8602; Masahiro Ishiura, Nagoya University, Center for Gene Research, Nagoya, Aichi 464-8602

The cyanobacterial circadian clock machinery is composed of only three clock proteins, KaiA, KaiB and KaiC, and generates circadian oscillation in the presence of ATP in vitro. They interact each other to form various complexes among them during clock oscillation. Stoichiometric interaction between KaiA and KaiB occurs depending on temperature *via* KaiA C-terminal domain.[1] Conformational or structural changes in KaiA and/or KaiB may be required for the interaction. Then, we prepared five cystein (Cys) residue-substituted mutants of KaiB, labeled their Cys residues with maleimide spin label (MSL), measured their EPR spectra, and calculated the correlation times τ of MSL at the five sites in KaiB; two ($KaiB_{T64C}$, $KaiB_{K67C}$) are located on the second α-helix on the dimer-dimer interface of the KaiB molecule and three ($KaiB_{Y94C}$, $KaiB_{G98C}$, $KaiB_{A101C}$) on the loop on the negatively charged ridges. The MSLs located near the interface, but not those on the negatively charged ridges, showed mobility changes on incubation at 40 °C for 24 h. Notably, MSL-labeled $KaiB_{T64C}$ showed large spectral changes, while MSL-labeled $KaiB_{K67C}$ only a slight change. In the former, the τ value decreased from 79 to 1.9 ns, and the slow motion peak disappeared while the fast motion peak appeared. These changes can be explained by the structural relaxation of the KaiB molecule induced at 40 °C. Furthermore, to clarify conformational or structural changes in KaiB during clock oscillation, we measured the distance between the MSLs introduced into $KaiB_{T64C}$ by the PELDOR method. We detected magnetic interactions between the MSL in KaiB corresponding to a distance of 35 Å only when the MSL-labeled $KaiB_{T64C}$ was incubated with KaiA, KaiC and ATP at 40 °C. This suggests that the conformation or structure of KaiB changes on its interaction with KaiA and/or KaiC.

1. R. Mutoh et al., *Genes Cells*, **2010**, *15*, 269-280

EPR POSTER SESSION

Risa Mutoh, Nagoya University, Center for Gene Research, Nagoya, Aichi 464-8602.
Ph: +81-52-789-4527, Fax: +81-52-789-4526, E-mail: mutoh@gene.nagoya-u.ac.jp

178 **Photolysis Studies of CO-inhibited Nitrogenase.**

W.K. Myers, Department of Chemistry, University of California, Davis, CA 95616; Weibing Dong, Department of Applied Science, University of California, Davis, CA 95616; Lifen Yan, Department of Applied Science, University of California, Davis, CA 95616; R. David Britt, Department of Chemistry, University of California, Davis, CA 95616; Christine H. Dapper, Department of Biochemistry, Virginia Tech, Blacksburg, VA 24061; William E. Newton, Department of Biochemistry, Virginia Tech, Blacksburg, VA 24061; Stephen P. Cramer, Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, Department of Applied Science, University of California, Davis, CA 95616

The inhibition of nitrogenase by CO has long been studied. CO is known to bind in two conformations during turn-over Hi-CO and Lo-CO generating a S=1/2 spin state, and it has been shown that Hi-CO photolyzes to generate Lo-CO. A third species was later identified by EPR as Hi(5)-CO that is thought to be a S=3/2 signal. In the wild-type nitrogenase, Hi(5)-CO does not photolyze, however, in a H195Q mutant it does photolyze. Concurrent low-temperature photolysis experiments by FT-IR have been performed. Comparison of photolytic and annealing behaviors by FT-IR and EPR of the H195Q mutant leads to the assignment of 1932 cm^(-1) as Hi(5)-CO and 1969 cm^(-1) as Hi-CO. The bridging CO of the Lo-CO form is less clearly identifiable, though a peak at 1745 cm^(-1) is suggestive of Lo-CO.

EPR POSTER SESSION

W.K. Myers, UC Davis Chemistry Dept., One Shields Ave, Davis, CA 95616.
Ph: 530-752-2964, E-mail: wkmyers@ucdavis.edu

179 **EPR Investigation of Sucrose and L-Alanine radicals Produced by Various Irradiations.**

Kouichi Nakagawa, Department of Radiological Life Sciences, Graduate School of Health Sciences, Hirosaki University, 66-1 Hon-Cho, Hirosaki 036-8564, Japan

We investigated stable radical-production cross sections (s) of sucrose and L-alanine radicals produced by heavy ions. The heavy-ion results were compared with X-ray irradiation at the same dose. The EPR (Electron Paramagnetic Resonance) spectral areas for the two compounds showed a linear relation with the absorbed dose, as well as a logarithmic correlation with the LET (Linear Energy Transfers).[1, 2] Further analysis was carried out for the radical-production cross section, which showed that stable radicals of the two compounds were produced through collisions of several particles with a single molecule. The relative σ–value of sucrose for C-ions was $1.29 \times 10^{-12} \pm 0.64 \times 10^{-12}$ [mm^2]. The value of alanine for C-ions was $6.83 \times 10^{-13} \pm 0.42 \times 10^{-13}$ [mm^2]. Considering the structural molecular sizes of sucrose and alanine, the σ 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 13.1 and X-rays were similar unlike alanine. Thus, the EPR results with X-ray and heavy-ion irradiations imply that sucrose can be useful as a radiation indicator.[3]

Supported by Research Project with Heavy Ions at NIRS-HIMAC and a Grant-in-Aid for Scientific Research (C) (21500410) from JSPS (K.N.).

1. K. Nakagawa, et al., Spectrochim. Acta Part A, *Molecular & Biomolecular Spectroscopy*, **69**, 1384-1387 (2008).
2. Y. Karakirova, K. Nakagawa, and N. D. Yordanov, *Radiat. Meas.*, **45**, 10-14 (2010).
3. K. Nakagawa and K. Anzai, *Appl. Magn. Reson.*, **39**(3), 285-293 (2010).

EPR POSTER SESSION

Kouichi NAKAGAWA, Department of Radiological Life Sciences, Graduate School of Health Sciences, Hirosaki University, 66-1 Hon-Cho, Hirosaki, 036-8564 Japan.
Ph. & Fax: 0172-39-5921, E-mail: nakagawa@cc.hirosaki-u.ac.jp

180 **Nucleotide Coordination to Mn^{2+} at the Myosin Active Site as Detected by Pulsed EPR.**

Andrei V. Astashkin, Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721;
Yuri E. Nesmelov, Department of Physics and Optical Science, University of North Carolina, Charlotte, NC 28223

ATP is an important cofactor for motor proteins, including myosin. ATP binding is required for myosin conformation change (recovery stroke), priming it for force generation. In the presence of a divalent cation (usually Mg^{2+}), myosin hydrolyzes ATP to ADP and phosphate, and their subsequent release presumably triggers the power stroke in myosin. According to crystal structures, Mg^{2+} at the myosin active site coordinates two (ATP analog) or one (ADP) phosphate(s) of the nucleotide. Apparently, if the number of coordinated phosphates could be determined, the kinetics of ATP hydrolysis might be studied. EPR is one of the powerful methods to study metal-bound proteins. To enable EPR investigations, Mn^{2+} can be used instead of Mg^{2+} without interruption of the myosin ATPase activity. In this work we used K_a-band pulsed EPR to address a problem whether Mn^{2+} at the myosin active site can distinguish between bound ATP and ADP. We studied myosin.Mn complexes with non-hydrolyzable nucleotide analogs, AMPPNP (triphosphate) and ADP.AlF_4 (diphosphate), as well as Mn.nucleotide complexes without myosin. Mn^{2+} binding was monitored by a pulsed ELDOR detection of the magnetic dipole interaction between Mn^{2+} and a nitroxide spin probe attached to A639C myosin mutant. The number of coordinated phosphates in myosin.Mn.AMPPNP complex determined by ^{31}P pulsed ENDOR was twice that detected for myosin.Mn.ADP.AlF_4 complex. We conclude that Mn^{2+} complexed with a nucleotide at the myosin active site is sensitive to the number of coordinated phosphates and can be used to distinguish between myosin.ATP and myosin.ADP biochemical states.

EPR POSTER SESSION

Yuri E. Nesmelov, Department of Physics and Optical Science, University of North Carolina at Charlotte, 9201 University City Blvd, Charlotte, NC, 28223.
Ph: 704-687-5886, E-mail: yuri.nesmelov@uncc.edu

181 **Light-Induced Charge Separation in Polymer-Fullerene Bulk-Heterojunctions: A Multi-Frequency EPR Study of Cations, Anions, and Radical Pairs.**

Jens Niklas and Oleg G. Poluektov, Argonne National Laboratory, Argonne, IL 60439

The ongoing depletion of fossil fuels, which currently cover majority of energy demands, has lead to an intensive search for new renewable energy sources. Solar-based technologies could provide a sufficient amount of energy to satisfy the global economic demands in the near future. Photovoltaic (PV) cells are the most promising man-made devices for direct solar energy utilization. In spite of the fact that organic based PVs did not demonstrate competitively high conversion efficiency so far, they are considered as a high potential option with many attractive features like low-cost fabrication and tunability of electronic properties. Recently, a considerable improvement of the efficiency to more than 8% has been demonstrated for PVs based on conjugated polymer-fullerene composites.

Advanced electron paramagnetic resonance (EPR) spectroscopy, such as light-induced time-resolved EPR, is a method of choice to study elementary steps of ET processes and to characterize the radical intermediates generated. In natural photosynthesis, EPR has been essential for understanding the mechanisms of the light-induced generation, separation, and recombination of the charge carriers. Here, we use light-induced EPR spectroscopy to study the structure of the charges in composites of multiple polymers and derivatives of C_{60} and C_{70}. Under illumination of the sample, two paramagnetic species are formed due to photo-induced electron transfer between conjugated polymer and fullerene. They are the positive, P^+, and the negative, P^-, polarons on the polymer backbone and fullerene cage, respectively. Using the high spectral resolution of high-frequency EPR (130 GHz), the EPR spectra of these species were completely resolved and characterized. The results obtained for the different polymers and fullerene derivatives are compared.

EPR POSTER SESSION

Jens Niklas, Argonne National Laboratory, Chemical Sciences and Engineering, Argonne, IL 60439.
Ph: 630-252-3547, E-mail: jniklas@anl.gov

182 **A Multi-Frequency EPR Spectroscopy Investigation of Conformational Changes in the Intrinsically Disordered Protein, IA_3.**

Natasha L. Pirman, Eugene Milshteyn, Matthew B. Chandler, Gail E. Fanucci, Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32611

Intrinsically disordered proteins (IDPs) contain little to no secondary or tertiary structure and are often essential in biological systems. Many IDPs undergo a conformational change, where structure is induced upon binding to a target protein. Due to their very nature, structural studies of IDPs are often challenging. Here, we show how site-directed spin-labeling (SDSL) electron paramagnetic resonance (EPR) spectroscopy can be utilized as a viable means to characterize the mobility and conformational changes of IDPs. We have applied this method to IA_3, which is a 68 residue IDP whose unstructured-to-α-helical conformational transition has been extensively characterized by various biophysical techniques. We monitored the chemically induced conformational change in the presence of the secondary structural stabilizer 2,2,2-trifluoroethanol (TFE), at both X-, and W-band frequencies. Analyses of the X-band EPR spectral line shapes reveal that the data report on global correlation time changes consistent with a two-state model of an unstructured system and the tumbling of a rigid helix; more detailed analyses of the X-band spectral line shapes can provide site-specific information on the residue level. Analysis of the W-band EPR spectral line shapes, however, more directly reveal site-specific structural changes. Line shape simulations of the data at both frequencies provide further information on the site-specific conformational changes occurring in the presence of TFE and are currently underway. Using IA_3 as a model system, we show multi-frequency EPR can provide insight into structural changes occurring in IDP systems that are otherwise difficult to characterize.

EPR POSTER SESSION

Gail E. Fanucci, University of Florida, Department of Chemistry, Gainesville, FL 32611.
Ph: 352-392-2345, Fax: 352- 392-0872. E-mail: fanucci@chem.ufl.edu

183 **Microwave Surface Resonator Array for In Vivo Electron Paramagnetic Resonance Spectroscopy.**

Jason W. Sidabras,[1] Richard R. Mett,[1,2] Shiv K. Varanasi,[1] Harold M. Swartz,[1] James S. Hyde[1]
1 Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI 5322, USA
2 Milwaukee School of Engineering, Department of Physics and Chemistry, Milwaukee, Wisconsin 53202, USA
3 Department of Radiology, Dartmouth Medical School, Hanover, Hew Hampshire, 03755, USA

A novel Surface Resonator Array (SRA) structure is described for the use of Electron Paramagnetic Resonance (EPR) in vivo spectroscopy of human finger-nails at X-band (9.5 GHz) to measure ionizing radiation dosages in a mass triage environment. When the sample is exposed to ionizing radiation, chemical bonds are broken in keratin and a stable free-radical is formed that can be detected by an EPR spectrometer. In order to reduce losses associated with tissues beneath the nail that yield no EPR signal, the SRA structure is designed to reduce depth sensitivity by creating an array of anti-parallel transmission line modes. Modeling, design, and simulations were performed using Wolfram Mathematica (Champaign, IL; v.7.0) and Ansoft High Frequency Structure Simulator (HFSS; Pittsburgh, PA; v.12.0). EPR signal intensities are comparable in experiments using a Bruker High Q cavity with a coal sample and the SRA structure with a coal sample and tissue equivalent material. Excellent agreements between simulated and experimental results are shown.

EPR POSTER SESSION

Jason W. Sidabras, Medical College of Wisconsin, Dept. of Biophysics, 8701 Watertown Plank Road, Milwaukee, WI 53226. Ph: 414-456-7355, E-mail: jsidabra@mcw.edu

184 **Resonator Advances for W-band Pulse Spectroscopy.**

Jason W. Sidabras,[1] Richard R. Mett,[1,2] James R. Anderson,[1] James S. Hyde[1]
1 Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI 5322, USA
2 Milwaukee School of Engineering, Department of Physics and Chemistry, Milwaukee, Wisconsin 53202, USA

In this work, two novel W-band resonators are described for use in Electron Paramagnetic Resonator (EPR) pulse experiments. In Saturation Recovery and Electron Electron Double Resonance (ELDOR) experiments, either a biomodal resonator configuration or microwave trap circuit is typically employed to remove the pump pulse.[1,2] At higher frequencies, a microwave trap becomes more problematic to maintain high-Q values while being able to change the frequency for frequency-swept pulse ELDOR. Here two W-band Loop-gap Resonators[3,4] are placed together to share a sample with a single cutoff septum between them, shown in Fig 1. A Hughes 180 degree hybrid combiner is used to "filter" out the pump pulse.

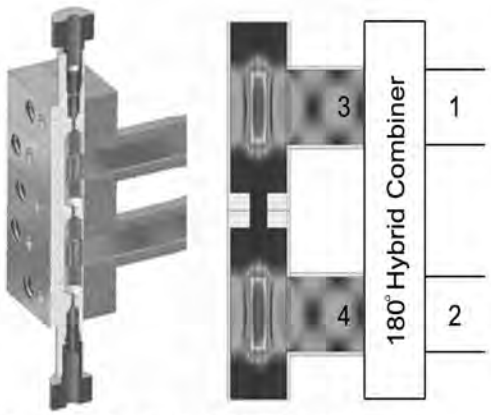


Figure 1. Partitioned bimodal resonator.

Also presented here is the first TE_{U02} uniform field rectangular cavity with access slots configured for in situ sample irradiation by light. Light slots beyond microwave cutoff allow up to 86% light access to a positioned flat-cell sample.

Both resonators utilize "long" iris technology, which minimizes frequency pulling by reducing magnetic stored energy in the iris,[5] important for long term experiment stability. Utra-precision electric discharge machining (EDM) technology was used to fabricate the resonators. Characteristics and performance are reported here.

1. J.S. Hyde, R.C. Sneed, Jr., and G.H. Rist, Frequency-swept electron-electron double resonance: DPPH in liquid and frozen solution. *J. Chem. Phys*. 51 (1969) 1404-1416.
2. J.S. Hyde, and W.K. Subczynski, Simulation of ESR spectra of the oxygen-sensitive spin-label probe CTPO. *J. Magn. Reson*. 56 (1984) 125-130.
3. W. Froncisz, and J.S. Hyde, The loop-gap resonator: A new microwave lumped circuit ESR sample structure. *J. Magn. Reson.* 47 (1982) 515-521.
4. J.W. Sidabras, R.R. Mett, W. Froncisz, T.G. Camenisch, J.R. Anderson, and J.S. Hyde, Multipurpose EPR loop-gap resonator and cylindrical TE011 cavity for aqueous samples at 94 GHz. Review of Scientific Instruments 78 (2007) 034701.
5. R.R. Mett, J.W. Sidabras, and J.S. Hyde Coupling of Waveguide and Resonator by Inductive and Capacitive Irises for EPR Spectroscopy. *Appl. Magn. Resona*. 2009,35(2): 285-318

EPR POSTER SESSION

Jason W. Sidabras, Medical College of Wisconsin, Dept. of Biophysics, 8701 Watertown Plank Road, Milwaukee, WI 53226. Ph: 414-456-7355, E-mail: jsidabra@mcw.edu

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

185 **Shifts in Conformational Populations of HIV-1PR Due to Primary and Secondary Mutations Measured by Double Electron-Electron Resonance Spectroscopy.**

Adam N. Smith, Ian Mitchelle S. De Vera; Gail E. Fanucci, University of Florida, Department of Chemistry, Gainesville, FL 32611-7200; Ben M. Dunn, University of Florida College of Medicine, Department of Biochemistry and Molecular Biology, Gainesville, FL 32610-0245

Human immunodeficiency virus (HIV) affects a large number of the world's population. One prominent treatment for HIV/AIDS is the inhibition of HIV-1 protease (HIV-1PR), which is an aspartic protease involved in viral maturation. HIV-1PR is a 99 residue homodimer that has a pair of flaps guarding inhibitor or substrate access to its active site. Molecular dynamics (MD) simulation studies reveal that the flaps can adopt the wide-open, semi-open, closed, and curled or tucked conformations. The current study employs a pulsed electron paramagnetic resonance (EPR) technique, double electron-electron resonance (DEER) in combination with side-directed spin labeling (SDSL). SDSL-DEER is used to measure distances between reporter sites on the flaps of HIV-1PR. Shifts in the conformational populations of the flaps were observed due to drug resistance-associated primary and secondary mutations in the protease. The population shifts due to the mutations were then statistically correlated to kinetics parameters previously measured for HIV-1PR.

EPR POSTER SESSION

Adam N. Smith, 214 Leigh Hall, University of Florida, Department of Chemistry, Gainesville, FL 32611-7200.
Ph: 239-595-0192, Fax: 352-392-8758, E-mail: adams@ufl.edu

186 **New Features in EasySpin.**

Stefan Stoll, R. David Britt, University of California Davis

EasySpin is a free software package for the simulation of cw and pulse EPR spectra. We illustrate features added in the last 12 months, which include absorption/dispersion admixture, field modulation, biquadratic exchange, correlated D-E strain, fast algorithms for oligometallic clusters and for systems with many magnetic nuclei, least-squares fitting of spectra containing multiple components, and reliable spin quantitation.

EPR POSTER SESSION

Stefan Stoll, Department of Chemistry, University of California Davis, One Shields Ave, Davis, CA 95616.
Ph: 530-752-2964, E-mail: sstoll@ucdavis.edu

187 **The Magnetic Structure of Tryptophan Radicals.**

Stefan Stoll,[1] Hannah S. Shafaat,[2] Jurek Krzystek,[3] Andrew Ozarowski,[3] Michael J. Tauber,[2] Judy E. Kim,[2] R. David Britt[1]
1 Department of Chemistry, University of California Davis, Davis, CA 95616
2 Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093
3 National High Magnetic Field Laboratory, Tallahassee, FL 32310

Tryptophan radicals serve as relays in multi-step electron transfer and as redox mediators in biotechnologically relevant enzymes that can oxidize high-reduction-potential organic substrates such as lignin. Little is known how proteins control these radicals. We use multi-technique EPR to elucidate the structure of two model tryptophan radicals, photogenerated in the electron-transfer protein azurin. One radical is located in a solvent-exposed region close to the protein surface, and the other in a hydrophobic pocket in the core of the protein. Q-band ^{1}H ENDOR gives spin density distributions and side chain conformations. ^{1}H/^{2}H exchange and ^{2}H ENDOR probe the presence of hydrogen bonds. CW EPR at uniquely high field and frequency (25 T, 700 GHz) is used to completely resolve the very narrow g tensors (g_{max}-g_{min} < 0.0015) and determine the g values using endohedral atomic hydrogen as a field standard. The g tensor anisotropy correlates with the presence/absence of a hydrogen bond to the tryptophan radical.

EPR POSTER SESSION

Stefan Stoll, Department of Chemistry, University of California Davis, One Shields Ave, Davis, CA 95616.
Ph: 530-752-2964, E-mail: sstoll@ucdavis.edu

188 **DEER Reveals Conformational Changes Upon Substrate Binding in Cytochrome P450cam.**

Stefan Stoll, Young-Tae Lee, David B. Goodin, R. David Britt, Department of Chemistry, University of California Davis, Davis, CA 95616

Cytochrome P450cam (CYP101A1) is a bacterial heme-thiolate enzyme that metabolizes camphor by selective hydroxylation using O2 and reducing equivalents via a well-known catalytic mechanism. However, despite decade-long research, the origin of substrate specificity and the exact mechanism of substrate binding are still unclear. Recent crystallographic studies[1] employing active-site probes reveal a significant range of protein conformations accessible during substrate binding and suggest a multi-step conformational selection mechanism, where the substrate-free enzyme starts in an open conformation with open substrate channel and transitions through an intermediate state to a closed conformation upon substrate binding. This hypothesis requires conformational studies in solution since there has been a long belief that P450cam stays mainly in the closed form even in the absence of substrate. We present DEER data obtained from a doubly spin-labelled mutant that provide direct evidence for the transition of the enzyme from an open to a closed conformation upon substrate binding in solution.

1. Y.-T. Lee, E. C. Glazer, R. F. Wilson, C. D. Stout, D. B. Goodin, *Biochemistry* **2011**, 50, 693

EPR POSTER SESSION

Stefan Stoll, Department of Chemistry, University of California Davis, One Shields Ave, Davis, CA 95616.
Ph: 530-752-2964, E-mail: sstoll@ucdavis.edu

190 **Tau Fibril Conformation Probed by Double Electron-Electron Resonance at Q-Band.**

Ayisha Siddiqua, Michael A. Swanson, Gareth R. Eaton, Sandra S. Eaton and Martin Margittai University of Denver, Department of Chemistry and Biochemistry

The deposition of tau protein into fibrillar inclusions is a characteristic hallmark of >20 neurodegenerative diseases including Alzheimer's disease, Pick's disease and progressive supranuclear palsy. In the adult human brain six tau isoforms are expressed that can be grouped into three-repeat (3R) tau and four-repeat (4R) tau, based on the absence or presence of the second of four microtubule binding repeats. Tau fibrils can be homogeneous (3R, 4R) or heterogeneous (3R/4R); and characteristic isoform depositions are observed in different tauopathies.[1] An asymmetric barrier in fibril growth exists where seeds of 3R and 3R/4R tau incorporate both 3R and 4R tau, but seeds of 4R tau only incorporate 4R tau.[2] X-ray crystallography and solution NMR spectroscopy, which are routinely used to study soluble proteins, have proven unsuccessful in providing structural information for tau fibrils. Double electron-electron resonance (DEER) is not limited by the size of the molecule and does not require crystals. Here, solid-state Q-band DEER measurements were performed on fibrils of 3R and 4R truncated tau constructs containing 2% doubly spin-labeled mutants. Differences between 3R and 4R tau fibrils were evident in the raw data as well as the time domain data supporting the hypothesis that the asymmetric barrier of fibril growth is caused by conformational differences. DEER data for 4R tau fibrils grown on 3R tau seeds more closely resembles data for homogeneous 3R tau fibrils than homogeneous 4R tau fibrils. This suggests that 4R tau isoforms adopt a conformation that is similar to the 3R tau isoforms. Importantly, the data demonstrate that DEER measurements are a promising new technique for identifying subtle conformational differences in fibril structure that may not be easily detectable by conventional biochemical means.

1. Siddiqua, A. and Margittai, M. (2010), *J. Biol. Chem.* 285, 37920-37926.
2. Dinkel, P. D., Siddiqua, A., Huynh, H., Shah, M. and Margittai, M. (2011) *Biochemisty 50*, 4330-4336.

EPR POSTER SESSION

Mike Swanson, University of Denver, Department of Chemistry & Biochemistry, 2101 E. Wesley Ave., Denver, CO 80208-2436.
Ph: 303-871-2978, Fax: 303-871-2254, E-mail: mswanso2@du.edu

191 **Power Saturation EPR on Both Surfactant Protein-B C- Terminus & Peptide Mimic KL4 Using Spin-labeled Peptide and Lipid in DPPC and POPC Enriched Vesicles.**

Austin L. Turner, Joanna Long, Gail E. Fanucci, Chemistry Department, University of Florida

KL_4 is a 21 amino acid peptide used to mimic the C-terminus of lung surfactant protein B, a protein known to lower the surface tension in the highly dynamic alveoli. Understanding how KL_4 interacts with lipid vesicles of varying composition will provide insight into potential treatment for diseases such as respiratory distress syndrome. Recent ^{31}P and ^{2}H NMR studies have shown that KL_4 binds differently to POPC:POPG and DPPC:POPG multilamellar vesicles, with the latter being found at elevated levels in lung surfactants. The current study uses electron paramagnetic resonance spectroscopy (EPR) and a technique called power saturation to study the effects of KL_4 binding to lipid bilayers. Power saturation can be used to determine a change in the accessibility of the spin label to molecular oxygen in the bilayer interior and to NiAA, an aqueous soluble nickel complex. In addition, recent studies are being performed on the SPB c-terminal end to see if similarities are seen between the two seemingly different peptides. Using information gathered from these experiments we will provide insights into the depth and orientation of the peptide within different bilayer systems. Future EPR experiments will include using pulsed EPR electron spin-echo envelope modulation (ESEEM) experiments to determine water concentration profiles in different membrane systems.

EPR POSTER SESSION

Austin L. Turner, Gail E. Fanucci Research Group, Leigh 352, Chemistry Department, University of Florida.
Ph: 847-910-5647, E-mail: austint@ufl.edu

192 **Formation of Free Radicals in Coffee During Roasting.**

Shreya Uppal, Reef Morse, Steppingstone MAgnetic Resonance Training Center, Farmington Hills, MI 48336

Free radicals are atoms, molecules, or ions with unpaired electrons. Free radicals are believed to be involved in degenerative diseases and cancers but are present in some common foods such as roasted coffee beans.[1] The formation of free radicals during roasting is controversial,[2-4] therefore we decided to study the effect of roasting coffee on free radical concentration.

Coffee beans were obtained from a local roaster who took samples every 30 seconds during the roasting process. The coffee samples were prepared by grinding them thoroughly in a coffee grinder. The samples were then placed in a quartz tube, with a diameter of 4mm. Each coffee sample was weighed and then the tube, itself, was weighed to determine the actual weight of the sample. The quartz tube with the sample was then centered in the EPR cavity. EPR studies were carried out on a Bruker300 using the program, EWWIN 2011 to gather data. Spectrometer settings were: magnet field center-3520g, field sweep 100g, modulation amplitude 1g and microwave power 15db. Each spectrum was taken over one minute with a time constant of 0.1 seconds. The integrated intensity of each sample was determined by simulating the spectum, calculating the double integral then dividingby the sample weight and the spectrometer amplitude. The integrated intensity was plotted as a function of roasting time.

At the very beginning of the roasting process, the signal was very faint. Between 2 to 5 minutes of roasting time, the integrated intensity increased exponentially, doubling every 30 seconds. After 5 minutes of roasting time, a second line, which was narrower than the first appeared at the same magnetic field. The second line grew from then on; it represented 10% of the integrated intensity. We believe that roasting coffee is a complex process which can be analyzed by EPR. The appearance of multiple lines of different line shapes may show the formation of different chemical regions as the roasting process progresses.

Supported in part by a Toyota Tapestry grant to R.M.. We gratefully acknowledge Chazzano Coffee (Birmingham, MI) for providing the coffee beans used in this study. Shreya Uppal acknowledges support by her parents.

1. J.P O'Meara, F.K. Truby, and T.M Shaw, *Food Science* 22:1, 96-101 (1957)
2. E. Nebesny and G. Budryn, *Deutche Lebensmittle-Rundschau* 102:11,526-530 (2006)
3. N.D. Yordanov and R. Mladenova, *International Journal of Food Science And Technology*, 42:12,1384-1389 (2007)
4. B.A. Goodman, E.C. Pascual and C. Yeretzian, *Food Chemistry* 125:1,248-254 (2011).

EPR POSTER SESSION

Shreya Uppal, Steppingstone MAgnetic Resonance Training Center, Farmington Hills, MI 48336.
E-mail: s_uppals@yahoo.com

193 **Determining the Binding Modes of Mtb CYP51B1 Inhibitors Using Pulsed EPR.**

Preethi R Vennam,[1] Matthew D. Krzyaniak,[1] Michael K Bowman,[1] Kip Conner,[2] William Atkins,[2] Kirsty J McLean,[3] Andrew W. Munro[3]

1 Department of Chemistry, The University of Alambama, Box 870336, Tuscaloosa, Al;
2 Department of Medicinal Chemistry, Box 357610, University of Washington, Seattle, WA 98195-7610;
3 Manchester Interdisciplinary Biocentre, Faculty of Life Sciences, University of Manchester, 131 Princess Street, Manchester, M1 7DN, UK

CYP51B1 from *Mycobacterium tuberculosis* belongs to the cytochrome P450 super family and catalyzes cleavage of the 14α-methyl group from steroid substrates. The emergence of drug-resistant *M. tuberculosis* makes CYP51B1 an attractive molecular target for next generation anti-TB drugs. 1H-1,2,3-triazole derivatives bind to and are competitive inhibitors of some P450s. Electron Paramagnetic Resonance (EPR) spectroscopy was used to examine the type II binding mode of the triazole group to CYP51B1 for a potential role in new anti-tuberculosis (TB) drugs targeting CYP51B1. Optical spectroscopy and continuous wave (CW) EPR were used to detect CYP51B1 binding triazole derivatives. A pulsed EPR technique HYSCORE was used, with frozen solutions, to measure the atomic positions of atoms in the axial ligands of the heme with and without the triazole inhibitor. The optical and CW EPR spectra of CYP51B1 show a typical low-spin heme with modest shifts upon binding of 17α-(1H-1,2,3-triazoyl)-estradiol (TAE) (K_D=23±2 μM). HYSCORE measurements on solutions in the absence of inhibitor located protons of axial water ligand at 2.6±0.1 Å from the heme Fe. However, the axial water protons were still present after binding of triazole inhibitors, indicating an unusual bridged type II binding mode with the triazole nitrogen hydrogen bonded to the axial water ligand. The optical and EPR spectra clearly indicate that the triazole inhibitors bind to CYP51B1 in a type-II mode. This result is in contrast to our earlier work where imidazole binding to CYP2C9 clearly caused disappearance of the axial water protons and appearance of protons at a distance of 3.3±0.1 Å from the axial imidazole. The pulsed EPR spectra provide a relatively quick means of characterizing the mode of binding of potential inhibitors to CYP51B1 and other P450s in solution without the need for either protein crystallization or isotopic labeling.

EPR POSTER SESSION

Preethi R Vennam, The University of Alabama, department of Chemistry, Tuscaloosa Al 35487-0336.
Ph: 205-348-8457, Email: prvennam@crimson.ua.edu

194 **Room Temperature Charge Carrier Spin Quantum Phase Coherence in Organic Semiconductors.**

W. J. Baker, D. R. McCamey, J. Wang, J. M. Lupton and C. Boehme, University of Utah, Dept of Physics and Astronomy

This work represents the first electrical room temperature spin-phase storage and recovery experiment demonstrated with an organic polymer device (OLED). Using pulsed electrically detected magnetic resonance,[1] we can observe how charge transport and recombination in poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) can be controlled by localized polaron (charge carrier) spin states. We have been able to electrically measure the polaron phase coherence time (T_2) by means of electrically detected Hahn-echo experiments. The results confirmed that hyperfine interaction with hydrogen in the organic network is the main coherence limiting effect.[2] Surprisingly, we observed a weak temperature dependence in intra-molecular hopping within the pairs of electron and hole polarons which is indicative of a slow tunneling transport mechanism and which questions the previously hypothesized thermally driven phonon-assisted hopping model.

1. C. Boehme et al. phys. stat. sol. (b), **246** (2009)
2. D. R. McCamey et al . *Phys. Rev. Lett.*, **104** (2010)

EPR POSTER SESSION

195 **Characterization of the Semiquinone Intermediate in Cytochrome bc_1 Complex.**

Preethi R Vennam,[1] Matthew D. Krzyaniak,[1] Savannah P. Whitted,[3] Alexander G. Maryasov,[4] Xu Quiang,[2] Jonathan L. Cape,[2] David M. Kramer,[2] Michael K. Bowman[1]

1 Department of Chemistry, The University of Alambama, Box 870336, Tuscaloosa, Al;
2 Institute of Biological Chemistry, Washington State University;
3 Department of Chemistry, Union University;
4 Institute of Chemical Kinetics & Combustion, Russian Academy of Science

The cytochrome bc_1 and related complexes are essential energy transduction components in the respiratory and photosynthetic electron transport chains of a wide range of organisms. The cyt bc_1 catalyzes the ubiquinol oxidation by forming a semiquinone (SQ) radical intermediate in close proximity to the hemes of the cyt *b* subunit and the Rieske FeS cluster. SQ radical has been trapped in cyt bc_1 by rapid freeze quench technique in 7 ms which is detected by CW and pulsed EPR measurements. Ubisemiquinone (USQ) radical anion and neutral USQ radical in cyclohexanol solution which is fairly hydrophobic, have been prepared and later characterized using pulsed EPR techniques. The slight difference in the g-tensor values of SQ trapped in cyt bc_1 and chemically prepared SQ is due to the difference in the SQ environment. Mims ENDOR

spectra of chemically prepared USQ radical anion have 3 sets of proton hyperfine couplings where as the neutral USQ radical have 4 sets. Mims ENDOR spectra of the SQ trapped in the enzyme have similar hyperfine coupling values as that of radical anion in solution. Lack of 4th set of hyperfine coupling values and lack of Nitrogen modulation in ESEEM and HYSCORE indicates that there is neither H-bonding nor strong interaction with amides or Histidine. The electron spin echo (ESE) decay rate has been used to probe the interactions of SQ and fast relaxing metal centers of heme and/or Reiske. ESE decay of the trapped semiquinone in cyt bc_1 is strongly enhanced relative to that of ubisemiquinone radical anion at X-band by a fast relaxing metal like Fe of heme. Measured dipolar interactions indicate distance of about 10 Å between SQ and Heme.

This work is supported by NIH GM 061904.

EPR POSTER SESSION

Preethi R Vennam, The University of Alabama, department of Chemistry, Tuscaloosa Al 35487-0336.
Ph: 205-348-8457, Email: prvennam@crimson.ua.edu

196 **Characterization of Phosphorus Donors in Silicon with Low Magnetic Field.** H. Morishita, School of Fundamental Science and Technology, Keio University, Yokohama 223-8522 and Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah 84112; K. M. Itoh, School of Fundamental Science and Technology, Keio University, Yokohama 223-8522

We report that an electron paramagnetic resonance (EPR) of ensembles of phosphorus donors in silicon has been detected electrically with externally applied magnetic fields lower than 200 G employing the home-built low-field electrically detected magnetic resonance (LFEDMR). An intensity of the LFEDMR signal is independent of the external magnetic field[1] and a sensitivity of the LFEDMR is about 10^5 times higher than that of the standard EPR.[2]

Because the hyperfine term dominates the phosphorus spin Hamiltonian at fields < 200 G, electron- and nuclear-spin levels of phosphorus mix. Therefore, the number of experimentally observed resonance peaks increased to five with respect to two that can be observed with the standard EPR. The results of LFEDMR mapping recorded by continuous tuning of magnetic fields between 0 and 200 G and resonance frequencies between 0 and 1 GHz agree very well with theoretical predictions for phosphorus donors in silicon.[3]

The work at Keio was supported in part by a Grant-in Aid for Scientific Research by MEXT, in part by Special Coordination Funds for Promoting Science and Technology, in part by the JST-DFT Strategic Cooperative Program on Nanoelectronics, in part by FIRST, and in part by a Grant-in-Aid for the Global Center of Excellence at Keio University.

1. A. V. Barabanov et al., *Phys. Rev. B* 1996, **54**, 2571.
2. V. Eremin et al., *J. Appl. Phys.* 2003, 93, 9659 & R. Laiho, et al., Phys. Rev. Lett. 1998, **80**, 1489.
3. H. Morishita et al., *Phys. Rev. B* 2009, **80**, 205206.

EPR POSTER SESSION

H. Morishita, Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah 84112.
E-mail: morishita@physics.utah.edu

INDEX OF PRESENTERS

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1

INDEX OF PRESENTERS

https://digitalcommons.du.edu/rockychem/vol53/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2011.53.1